Synthesis of Nanoparticles and Degradation of Organic Pollutants

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Sonochemistry and Advanced Oxidation Processes: Synthesis of Nanoparticles and Degradation of Organic Pollutants

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Abstract

This century has seen a phenomenal growth in energy demands and environmental pollution, which has given rise to a worldwide awareness for the need to address these issues immediately.

This thesis focuses on the fabrication of high performance electrocatalysts applied in fuel cells and developing appropriate advanced oxidation processes for environmental remediation. It has been shown that ultrasonic irradiation is a promising method of synthesizing nanometer sized metal colloids with specific properties. Sonophotocatalysis has proved to be an effective process for the degradation of organic pollutants.

The synthesis of platinum monometallic and platinum-ruthenium bimetallic nanoparticles was successfully achieved by using sonochemical irradiation. A chemical method and a hybrid method were used to reveal and understand the process of Ru(III) reduction by sonochemistry. TEM images of the Pt and PtRu monometallic/bimetallic particles indicate typical diameters of less than 10 nm. An effort was made to investigate the influence of two different methods, namely simultaneous and sequential sonochemical reduction, on the structure and formation of PtRu bimetallic nanoparticles. It has been shown that the sequential reduction method produces a relatively higher yield of core-shell nanoparticles than the simultaneous reduction method. It has been concluded that Pt nanoparticles, which are formed first, play an important role in catalyzing the formation of Ru nanoparticles.

A number of methods including chemical, sonochemical and radiolytic synthesis were used to fabricate platinum and platinum-ruthenium monometallic/bimetallic nanoparticles. Furthermore, the evaluation of the electrocatalytic performance of these particles was performed by using cyclic voltammetry. Simultaneous and sequential methods for the synthesis of PtRu were adopted to investigate their influence on the electrocatalytic performance
of these bimetallic nanoparticles. It has been shown that simultaneous reduction is an effective means of fabricating high performance electrocatalytic PtRu catalysts. A number of experiments with different ratios of platinum to ruthenium ions in precursor solution were carried out to study the effect of the ruthenium composition in platinum-ruthenium electrodes. It has been found that the methanol oxidation ability of platinum-ruthenium bimetallic nanoparticles can change with the alternation of ratio of Pt(II) to Ru(III) in the precursor solution. Simultaneous radiolytic reduction has the potential to fabricate higher performance electrocatalytic bimetallic nanoparticles.

Although both photo-oxidation and sono-oxidation techniques are fascinating solutions to the environmental problems at hand, the critical limit of these individual processes is their low efficiency of environmental remediation. In my project, sonolysis and photocatalysis (sonophotocatalysis) have been simultaneously employed to degrade selective organic pollutants in aqueous environments, such as methyl orange, \textit{p}-chlorobenzoic acid, \textit{p}-aminobenzoic acid and \textit{p}-hydroxybenzoic acid. Experiments have been carried out in order to improve the efficiency of sonophotocatalytic reactions to ensure that a substantial amount of the electrical energy is utilized in degrading the organic pollutants.

Methyl orange, an azo dye, was selected as the degradation target for sonophotocatalysis. An orthogonal array analysis method was employed to clarify the correlation between the efficiencies of sonolysis, photocatalysis and sonophotocatalysis and the various operation conditions studied. Emphasis was placed on investigating the influence of pH and the ultrasound parameters on these three advanced oxidation processes. It was of interest to find that the degradation of methyl orange originates from hydroxylation and demethylation processes preceding aromatic ring-opening.

Sonophotocatalysis was also applied in the degradation of three aromatic carboxylic acids, \textit{p}-chlorobenzoic acid, \textit{p}-hydroxybenzoic acid and \textit{p}-aminobenzoic acid. Experiments were carried out in order to get a thorough understanding of the synergy effects produced by combining the two oxidation techniques. A number of advanced analytical techniques, such as HPLC and Q-TOF MS/LC, were employed to comprehensively monitor and analyze the sonophotocatalytic degradation process. It has been found that synergistic effects of the combined system have been identified with respect to the parent organic pollutant as well as its degradation products. Additionally, products were quantitatively analyzed by a kinetic simulation method in order to understand the reaction mechanism. This method also allowed us to quantify the synergy effects. It was observed that the solution pH played
a key role in determining the degradation rate and controlling the direction of the degradation reaction. Based on the analytical data gathered, the sonophotocatalytic degradation pathway of the aromatic carboxylic acids was established. The experimental results suggest that the sonophotocatalytic technique is likely to lead to a complete mineralization of organic pollutants in aqueous solutions.
Declaration

This is to certify that:

the thesis comprises only my original work towards the PhD except where indicated,

due acknowledgement has been made in the text to all other material used,

the thesis is less than 100,000 words in length, exclusive of tables, maps, bibliographies and appendices.
Frankly speaking, I do not think that English is the right language I can use to express exactly my heartfelt thanks, but I have tried my best to do.

Confucius said:” Everybody is worthy of learning from.” There are many people who helped me, whom I learned much from, during my first year study, in many different ways.

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<tr>
<td>CV</td>
<td>Cyclic Voltammetry</td>
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<td>DMFC</td>
<td>Direct Methanol Fuel Cell</td>
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<tr>
<td>ECSA</td>
<td>Electrochemical Active Surface Area</td>
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<tr>
<td>EDX</td>
<td>Energy Dispersive X-ray</td>
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<td>MS</td>
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<tr>
<td>min</td>
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<td>PABA</td>
<td>para-Amonobenzoic acid</td>
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<td>PCBA</td>
<td>para-Chlorobenzoic acid</td>
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<td>PHBA</td>
<td>para-Hydroxybenzoic acid</td>
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<td>PMT</td>
<td>Photomultiplier Tube</td>
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<tr>
<td>PSS</td>
<td>Poly(Sodium 4-Styrenesulfonate)</td>
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<td>PVP</td>
<td>polyvinyl-2-pyrrolidone</td>
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<td>Q-TOF</td>
<td>Quadrapole Time-of-Flight</td>
<td></td>
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<tr>
<td>rpm</td>
<td>revolution per minute</td>
<td></td>
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<td>S</td>
<td>Sonolysis</td>
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<td>SCE</td>
<td>Standard Saturated Calomel Electrode</td>
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<td>SDS</td>
<td>Sodium Dodecyl Sulphate</td>
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<td>SEM</td>
<td>Scanning Electron Microscopy</td>
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<td>SHE</td>
<td>Standard Hydrogen Electrode</td>
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<td>SPC</td>
<td>Sonophotocatalysis</td>
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<td>STEM</td>
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<td>TEM</td>
<td>Transmission Electron Microscopy</td>
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<td>TOC</td>
<td>Total Organic Carbon</td>
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<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
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Preface

Section 0.1
Publications


0.2. Presentations


- **Yuanhua HE**, Kizhanipuram Vinodgopal, Muthupandian Ashokkumar and Franz Grieser, *PFPC Advisory*

*Supported by University of Melbourne Postgraduate Overseas Research Experience Scholarship (PORES).*
0.3. Other Activities

Board Meeting–Poster Presentations, Poster Presentation, August 16, 2006, University of Melbourne, Victoria, Australian, Sonochemical Synthesis of Platinum-Ruthenium Composite Nanoparticles;

Yuanhua HE, Kizhanipuram Vinodgopal, Muthupandian Ashokkumar and Franz Grieser, RADIATION 2006 of Australian Institute of Nuclear Science & Engineering, Oral Presentation, April 20-21, 2006, the University of Sydney, NSW, Australian, Sonochemical Synthesis of Pt-Ru Composite Nanoparticles;


Yuanhua HE, Kizhanipuram Vinodgopal, Muthupandian Ashokkumar and Franz Grieser, 8th Japan-Australia Colloid and Interface Science Gakkai, November 27-30, 2005, Crowne Plaza Hotel, Terrigal, NSW, Australia, Sonochemical Synthesis of Metal Nano-colloids for Fuel Cell Catalysts;

Overseas Research in Radiation Laboratory*, the University of Notre Dame, April 28-July 28, 2007.
Life was like a box of chocolates you never know what you’re gonna get.

Forrest Gump

Life was like a tiny bubble you never know what you’re gonna get. Is stable or transient cavitation when you switch on the sonicator?

XH

Introduction

Ultrasound is simply defined as sound pitched above the upper threshold of human hearing and the field of sonochemistry embodies the diverse and ever growing range of ultrasonic applications in various industries and research disciplines. Much of the usefulness of ultrasound stems from its chemical effects, such as formation of free radicals to accelerate or alter chemical reactions. Cavitation is the origin of the sonochemical effect and therefore acts as an essential bridge between ultrasound and chemistry or a bridge between the physical pressure variation of the sound wave and the chemical effects. However, aside from the chemical effects, cavitation can also induce physical effects, such as micro-streaming, micro-jetting, turbulence, etc.
Acoustic cavitation occurs when sound waves pass through a liquid medium containing micrometer or submicrometer sized gas nuclei. This energy propagation introduces a vibrational motion to the molecular structure of the medium and consequently to the existing gas nuclei. These gas bubbles will alternately expand and compress under the mechanical influence of the sound wave. As the amount of material entering the bubble during the expansion half cycle is more than that expelled during the compression cycle, these microbubbles grow over many acoustic cycles and finally reach a critical size at which a resonance condition is met. These critical sized bubbles become extremely unstable and grow to a maximum size, where they finally violently collapse. A summary of these stages is depicted in Figure 1.1.

When the bubble collapse occurs, extremely high pressures and temperatures are generated inside the bubble leading to the formation of highly active H• and OH• radicals, which play critical roles in the chemical effects of ultrasound. At the same time, the physical effects of cavitation (e.g., micro-streaming, micro-jetting shockwave, and turbulence) may also contribute to the enhancement of the chemical efficiency.

Due to its unique chemical and physical effects, acoustic cavitation has been applied to a number of areas, including: therapeutic applications, contrast imaging, electrochemistry, the production of nanoemulsions, food technology, nanomaterials synthesis, materials extraction, phase separation, surface cleaning and waste-water treatment. Mason summarized three strands in ultrasonics research [1]:

- Sonochemistry with its origins in chemistry and physics: this includes synthesis, catalysis and fundamental studies of cavitation involving mainly academia;

- Power ultrasound with its origins in engineering and processing: this includes cleaning, welding and materials processing involving mainly industry;

- Diagnostic ultrasound involving non-destructive testing and medical scanning: this attracts major interest in both academia and industry.
1.1. Introduction

There is little doubt that the future for sonochemistry is promising, either from the point of view of greater interest in the fundamental principles of its action, or in the potential industrial and technological applications.

Figure 1.1: Formation, growth and collapse of cavitation bubbles.
1.2. Objectives

Striding into this new era of science and technology, we have to confront the difficulties of the growing energy crisis and environmental pollution. The objectives of this thesis are: to fabricate high performance electrocatalysts for applications in fuel cells and to develop appropriate advanced oxidation processes for environmental remediation.

Direct methanol fuel cells (DMFCs) can be potentially used as a power source in cameras, notebook computers, and other portable electronic devices. The efficiency of the DMFC is significantly affected by the metal catalytic particles used in the electrodes. The use of platinum/ruthenium bimetallic alloy particles has been found to produce maximum cell efficiencies. The use of conventional preparation techniques for Pt/Ru alloys often does not provide adequate and effective control of particle size and usually involves the use undesirable chemicals. Ultrasonic irradiation of aqueous solutions containing precious metal ions is an effective method for the preparation of nanometer sized metal colloids.

The first aim of this work is to systematically study the sonochemical synthesis of bimetallic nanoparticles. These particles are expected to possess a higher electrocatalytic activity in the application of fuel cells. In addition, the fundamental mechanism of acoustic cavitation and its associated physical and chemical effects are explained.

Because of the low efficiency of photo-oxidation or sono-oxidation techniques when used individually, many researchers have shown interest in exploring the synergistic effects of combining the photo- and sono-processes. However, the combined use of photocatalysis and ultrasonics for the treatment of pollutants is rather limited, mostly due to the lack of a detailed mechanism for this process. Most publications in this field deal with the kinetics of the degradation of a limited range of pollutants as a function of operating conditions. In addition, relatively little is known about the reaction by-products and pathways associated sonophotocatalytic treatments.

The second aim of this work is to develop an appropriate method for combining heterogeneous photocatalysis using different frequencies ultrasound in order to oxidize various organic pollutants in aqueous solutions. This new methodology (sonophotocatalysis) is expected to produce a better oxidation process and improve the efficiency of environmental remediation processes when compared to the component methods. In addition, heterogeneous
1.3. Scope of This Work

Sonophotocatalysis at the nano-scale is a novel and multi-disciplinary research field involving physical chemistry, photochemistry, sonochemistry, catalytic chemistry, biochemistry, material science and other associated subjects and techniques. Emphasis given to sonophotocatalytic reactions will contribute to the progress of this technique to these other disciplines. At the same time, the results will allow us to establish a research framework to evaluate the specific system of advanced oxidation process.

Above all, sonophotocatalysis might have potential in large-scale practical applications, resulting in improving living conditions through the minimization of environmental impact from waste which poses a serious risk to human health.

Like the water molecule itself under the influence of ultrasonic irradiation, this research can be divided into two major parts involving the two types of highly reactive radicals, i.e., reducing H• and oxidizing OH•.

This work is intended to introduce two new and important applications of ultrasound. The first is the sonochemical synthesis of nanoparticles and the second is environmental remediation using advanced oxidation processes.

This thesis continues, in Chapter 2, with an overview of the fundamentals of sonochemistry and its various applications. A mathematical model based on the Rayleigh-Plesset Equation was used to describe the behavior of a single bubble in an acoustic field and explain the fundamentals of the chemical and physical effects of sonochemistry. The second half of this chapter concentrates on the two most important practical applications of ultrasound: (i)fabrication of nanoparticles and (ii)sonophotocatalysis for environmental remediation.
1.3. **Scope of This Work**

In Chapter 3, the experimental procedure followed have been summarized. A number of advanced analytical techniques, such as: transmission electron microscopy, X-ray photoelectron spectroscopy and high performance liquid chromatography, were employed to monitor the sonochemical reaction processes and to characterize the products generated from these processes.

Chapter 4 describes the sonochemical synthesis of monometallic and bimetallic nanoparticles. The formation of bimetallic nanoparticles with different structures was achieved by using various methods. The formation of core-shell structured platinum-ruthenium nanoparticles demonstrates that Pt(0) nanoparticles act as a catalyst to accelerate the reduction of Ru(III) to Ru(0) particles.

Chapter 5 describes the promising ability of platinum-ruthenium bimetallic nanoparticles and their electrocatalytic properties, when synthesized by chemical, radiolytic and sonochemical methods. Despite a considerable amount of research, the nature of the active surface sites for the methanol electro-oxidation reaction is still an outstanding issue that needs to be addressed. Electro-oxidation of methanol on the surface of PtRu electrodes with various degrees of Ru coverage, and different preparation methods have been carried out in an attempt to establish how the synthetic method influences the electro-oxidation current.

Chapter 6 introduces ultrasound to assist in the photocatalytic degradation of methyl orange. The orthogonal array method was adopted to establish the correlation between operation parameters and the performance of sonolysis, photocatalysis and sonophotocatalysis, focusing on the synergistic effects in the combined system. The results of the products analysis demonstrate that sonophotocatalysis is a superior oxidation process for environmental remediation compared to either of the component.

Chapter 7 describes the sonophotocatalytic degradation processes of three aromatic carboxylic acids. A mathematical model was set up to evaluate the synergistic effects during the sonophotocatalytic degradation. A key observation has been the discovery of synergistic effects of the combined oxidation system on the reduction of the degradation products. The analysis of oxidation products produced during the sonophotocatalysis of parent organic pollutants demonstrates that the control of pH and the selection of oxidation process are able to control the direction of the whole degradation process.

The thesis finishes in Chapter 8 with conclusions in fulfilment of the objectives.
I have been but as a child playing on the seashore, now finding some prettier pebble or more beautiful shell than my companions, while the unbounded ocean of truth lay undiscovered before me.

Sir Isaac Newton

Theory and Literature Review

Sound, a form of energy propagation in elastic media, has been employed as a tool for decades with varied success. This surprising simple mechanical disturbance in a state of equilibrium is able to bring several disciplines to the science world: acoustics for sound generation, propagation and detection; mechanics for vibration and wave motion; phonetics for mechanisms of sound production and reception; music for musical sounds . . . . .

Bruce Lindsay presented a chart in his benchmark book [2] which summarized the diversified character of acoustic science. Acoustics is not simply a vibrating motion, but a wide-ranging discipline sharing frontiers with other subjects from science, technology and arts. Based on the center of fundamental physical acoustics, this discipline covers almost all branches of science and technology, and even arts (shown in Figure 2.1).
The contents provided here are concerned with a fundamental understanding of acoustic cavitation and its associated physical and chemical effects. Among the significant and useful applications of ultrasound, the majority of the discussion is focused on two prominent research areas: synthesis of nanoparticles and environmental remediation.

Figure 2.1: The Science of Acoustics: the cross and derivative branches of acoustics. (Adapted from reference [2].)
2.1. Sonochemistry

Section 2.1

Sonochemistry

2.1.1. Wave Structure and Ultrasound

The term *ultrasound* is generally used to refer to the sound waves above the frequency that can be detected by the human ear, which in reality terms is above a frequency of about 18 kHz.

There are two basic types of waves, transverse and longitudinal, differentiated by the way in which the wave is propagated. Sound propagates through air or other mediums as a longitudinal wave, in which the mechanical vibration constituting the wave occurs along the direction of propagation of the wave. Sound moving through the medium also compresses and rarefies the medium in the direction of travel of the sound wave as it vibrates back and forth. Normally, the wave structure is characterized by its wavelength, period, amplitude and wave velocity. The following equations (Equation 2.1 and 2.2) demonstrate the relationships between them.

\[ c = \lambda \nu \]  
\[ \nu = \frac{1}{T} \]  

Here, \( c \) is the speed of a wave in m/s; \( \lambda \) represents the wavelength of the sound and it is usually measured in metres; **Period**, a certain time which one full wavelength takes to pass a specific point in space, is represented by \( T \), measured in fractions of a second. The frequency (\( \nu \)) of the sound wave is the number of wavelengths passing per second which is traditionally measured in hertz and it has an inverse relationship with the period.

A *standing wave* is the combination of two waves moving in opposite directions, each having the same amplitude and frequency. When waves are superimposed, their energies are either added together or canceled out. The points having the greatest amplitude are signified as *antinodes* and the points at zero energy are called *nodes*. The standing wave is the critical condition of the phenomenon of *acoustic levitation* [3], which is the popular observation platform of a single bubble. Under appropriate conditions, the buoyancy force of a bubble can be canceled by the acoustic force. This permits examination of the dynamic characteristics of the bubble in considerable detail.
2.1. SONOCHEMISTRY

2.1.2. Acoustic Cavitation

The origin of sonochemical effects in liquids is the phenomenon of acoustic cavitation. The term cavitation (Figure 1.1) refers to the growth and violent collapse of pre-existing microbubbles in a liquid medium and the consequences of these physical perturbations. The first report on cavitation was published in 1895 by Thornycroft and Barnaby when they found that this was the reason why the propeller blades of a submarine were easily pitted and eroded. In 1917, Lord Rayleigh described a mathematical model of cavitation in an incompressible fluid in his great book *The Theory of Sound*. After the discovery of the chemical and biological effects of ultrasound [4–6], the key activity, cavitation, draws a number of considerable scientific interest [7–9].

Ultrasound passes through a liquid medium by inducing vibrational motion of the molecular structure of the medium due to the varying pressure. If the intensity of ultrasound is sufficient to overcome the tensile strength of the medium, a point is reached at which the intramolecular forces are not able to hold the molecular structure intact. This breaking point at weak spots leads to the formation of a cavity. The energy required to create a cavity or void is enormous. However, due to the fact that gas bubbles, solid impurities are inherently present in liquids and become the adventitious nuclei for cavitation, practical acoustic cavitation occurs at far lower sound pressures than that is required for void creation [3, 10].

Due to the different origins of cavitation bubbles, several types may be present at the same time in the sound field: empty cavities, gas-filled cavities, vapor-filled cavities or mixtures of gas and vapor. The relative proportions depend on the applied sound pressure, static pressure, temperature, the property of the liquid medium and so on. Figure 2.2* is a summary of the possible fates of bubbles in an aqueous solution under ultrasound irradiation. The processes can be distinguished into four main basic types: stable cavitation, rectified diffusion/coalescence, bubble dissolving and transient cavitation. Normally, the bubbles whose sizes are under a certain pressure threshold radius dissolve in the medium and disappear. In the absence of the acoustic field, a bubble in water will gradually dissolve due to the surface tension pressure. On exposure to the applied ultrasonic driving sound, the existing bubbles will undergo different fates. The very small bubbles will still dissolve, but some larger bubbles, whose size is beyond a

*Note: The spatial distribution of bubbles here is not a representation of that in an ultrasonic field but just a simply illustration of the fate of bubbles.
2.1. Sonochemistry

Figure 2.2: Bubble fate: possible processes that individual bubbles undergo in an ultrasonic field (modified from reference [11, 12]).

certain threshold radius will exist stably in the sound field. Apfel [13] adopted the threshold formulations to plot a diagrammatic representations of cavitation regimes. For each independent frequency, the thresholds are coherently related to the equilibrium bubble radius and the acoustic pressure amplitudes. In 1988, Church [14] examined the thresholds for these various processes by time-average numerical calculations. All their results indicate that the fate of a bubble in liquid is different depending on its radius and the driven time-varying pressure. It is the active bubbles which take part in collapse that will be the focus of the following paragraphs.
2.1. Sonochemistry

2.1.2.1. Bubble Dynamics

The oscillations of a gas bubble driven in an acoustic field are generally described by the Rayleigh-Plesset Equation [15–17], which is expressed by a second-order nonlinear differential equation:

\[
R \ddot{R} + \frac{3}{2} \dot{R}^2 = \frac{1}{\rho} \left[ (P_0 + \frac{2\sigma}{R_0} - P_v)(\frac{R_0}{R})^{3 \kappa} + P_v - \frac{2\sigma}{R} - \frac{4\eta\dot{R}}{R} - P_0 - P(t) \right]
\]  

(2.3)

where \(R\) is the velocity of the cavity wall; \(\dot{R}\) is the acceleration of the cavity wall; \(\rho\) is the mass density of the liquid which is assumed to be incompressible; \(P_0\) is the static pressure in the liquid outside the bubble; \(R_0\) is the radius of the bubble at its equilibrium position; \(\sigma\) is the surface tension of the liquid; \(\eta\) is the viscosity of the liquid; \(P_v\) is the vapor pressure; \(P(t)\) is the applied acoustic pressure and \(\kappa\) is the so-called polytropic index of the gas. This term is not a fundamental quantity, but takes an intermediate value between \(\gamma\) (the ratio of the specific heat of the gas at constant pressure to that at constant volume) and unity. The Rayleigh-Plesset Equation describes the response of a spherical bubble to a time-varying pressure field in an incompressible liquid. It also indicates that the motion of the bubble under an acoustic field is nonlinear. Obviously, the damping of the bubble dynamics by the sound field is not considered in this famous equation.

A simple damping model of uniform van der Waals gas without heat and mass exchange gives Rayleigh-Plesset Equation another form [18–22]:

\[
R \ddot{R} + \frac{3}{2} \dot{R}^2 = \frac{1}{\rho} \left[ (P_g - P_0 - P(t)) - \frac{2\sigma}{R_0} - \frac{4\eta\dot{R}}{c_0} + \frac{R}{c_0} (P_g + P_a) \right]
\]  

(2.4)

where,

\[
P_g = (P_0 + \frac{2\sigma}{R_0})(\frac{R_0^3 - a^3}{(R^3 - a^3)^\kappa})
\]  

(2.5)

the corresponding temperature

\[
T = \frac{T_0(R_0^3 - a^3)^{\kappa-1}}{(R^3 - a^3)^{\kappa-1}}
\]  

(2.6)

The left side of the Equation 2.4 indicates the inertia of the accelerating bubble in response to the different pressures inside and outside the bubble. The right side represents this net force on the bubble. Here, \(P_g\) is the pressure
of the gas inside the bubble. The collapse is stopped when the gas inside the bubble is compressed to its van der Waals hard-core radius $a$. Although this special form of Rayleigh-Plesset Equation (Equation 2.4) has been practically validated by a number of light scattering experiments [18, 19, 23–25], one obvious problem is that an adiabatic bubble motion is assumed with no heat exchanged between the bubble and exterior.

The characteristic form of the forcing pressure, bubble radius and bubble wall velocity is clearly shown in Figure 2.3*. A 5 µm air bubble gradually grows under the periodic driving pressure of 20 kHz and 1.3 atm to approach its maximum size about 45 µm. Sequentially, the bubble rapidly collapses to its van der Waals hard-core in very short time. The velocity of the interface of the bubble during the collapse is about 2880 m/s, which is beyond the speed of sound in water (1497.4 m/s [26]).

Appendix A contains a numerical simulation to the Rayleigh-Plesset Equation with consideration of the damping effect (i.e., Equation 2.4). This programme has the capacity to plot bubble radius-time curves for various values of the driving pressure and initial bubble size under different ultrasound frequencies.

### 2.1.2.2. Rectified Diffusion

When ultrasound passes through a liquid medium, the existing gas nuclei will alternately expand and compress under the mechanical influence of sound wave. The dominant and important pathway for the adventitious bubbles growth is a process called *rectified diffusion*. This process was first discovered in 1944 [27]. Rectified diffusion provides bubbles in gassy liquids a bridge to achieve the critical collapse condition which plays a key role in cavitation.

Figure 2.4 shows a theoretical model solution to Equation 2.4, indicating the radius of a typical air bubble as a function of time during the rectified diffusion process. Although the adventitious bubble goes through alternative expansion and compression, it generally increases after each cycle of the ultrasonic pressure force or sound wave.

The reason for the bubble growth during the rectified diffusion process is a result of unequal mass transfer

---

*See the gas pressure, gas temperature and radiation spectrum for the same values of the parameters in Figure 2.8, Figure 2.9 and Figure 2.12.
2.1. **Sonochemistry**

![Graph of time-varying pressure](image1)

(a) The time-varying pressure.

![Graph of changing radius](image2)

(b) The changing radius of an air bubble during cavitation.

![Graph of velocity](image3)

(c) The velocity of the bubble wall during cavitation as a function of time.

**Figure 2.3:** Bubble in Cavitation: radius-time curves of a typical air bubble whose initial radius is 5µm under 20 kHz and 1.3 atm ultrasonic field during stable cavitation. The radius-time curve is a solution to the Rayleigh-Plesset Equation with damping effect.
Figure 2.4: Rectified Diffusion: the radius of a typical air bubble in water as a function of time for rectified diffusion cycles. The dotted line is the driving sound amplitude. The solid line is a solution to the Rayleigh-Plesset Equation for $P_a=1.4$ atm, $f=213$ kHz, $R_0=8.43 \, \mu m$. In respond to the rectified diffusion process, the bubble grows gradually under each cycle of driving pressure.

During the bubble oscillation. During the negative pressure half cycle as the bubble expands, the net force of the pressure inside and outside the bubble creates a relative vacuum which allows the dissolved gas, solvent molecules and other volatile solutes existing in the liquid medium to enter into the bubble (see Figure 2.5a). During the following positive pressure half cycle of the sound wave, the bubble is compressed and its contents forced to expel into the surrounding liquid media (see Figure 2.5b). The diffusion of the gas out of the bubble is restricted by the smaller exchange surface. The amount of material that enters the bubble during the expansion half cycle
2.1. Sonochemistry

is greater than that expelled during the compression cycle. At the same time, due to the changing thickness of the liquid shell, concentration gradients during the rarefaction phase are higher than that during the compression phase. This shell-effect can enhance the area effect to accelerate the uneven mass transfer during the rarefaction and compression cycles [28, 29]. Over a few or hundreds or thousands of acoustic cycles [30, 31], a bubble will gradually grow to approach a critical size at the threshold of collapse or escape by buoyancy. Due to its ability to grow bubbles to resonance size, rectified diffusion is responsible for the liquid degassing off in an ultrasound field. The bubbles grow during the rectified diffusion process, trapping the dissolved gas, and finally collapse or rise to the surface of the liquid.

Figure 2.5: Cavitation Bubble: the behavior of a single bubble in aqueous solution under influence of an ultrasound irradiation.

Based on the mechanism of rectified diffusion, besides the initial bubble size and the driving pressure, the
2.1. Sonochemistry

effect of the bubble surface condition also contributes to this fundamental activity during cavitation. A number of information [28, 31–34] have focused on the influence of surfactants on rectified diffusion during the growth of a single bubble. The results suggested that the adsorption of the surfactants at the interface of the bubble can enhance the growth rate of the bubble by rectified diffusion.

2.1.2.3. Stable Cavitation

In stable cavitation, usually under moderate acoustic intensities, bubbles will oscillate around their equilibrium size and exist for many acoustic cycles. In this type of cavitation, the expansion rate during the rarefaction phase is equal to the rate of contraction during the compression phase. This requires that rectified diffusion, or the uneven mass transfer into the bubble during the acoustic wave cycle, does not occur.

Figure 2.6 shows the radius-time curve of two typical stable cavitations. Both of them display an important feature of stable cavitation: repetitive nature of the oscillation. The radii at the end of the acoustic cycle are equal to that of the initial cycle and the whole process then repeats itself in the next acoustic cycle. The stable cavitation of Figure 2.6b also exhibits these features, the amplitude of the bounces dies away completely before the beginning of the next cycle.

Figure 2.4 and Figure 2.6 show the single air bubbles behavior under the same ultrasonic field, namely, the same frequency* and same acoustic power. The different features they displays depend on their inherent conditions, such as the sizes of the initial bubble nuclei. Due to the relationship between the size and resonance frequency, the characteristic features of the bubble depends on its natural resonance frequency.

2.1.2.4. Transient Cavitation

In comparison to the stable cavitation, a transient cavity exists for only a few acoustic cycles in high intensity acoustic fields and undergoes explosive growth. The high energy collapse at the last cycle fragments the bubble into a few small ones which have potential to act as nuclei for further cavitation.

*213 kHz is the main ultrasonic frequency used in this research work and it will be discussed in the following chapters.
2.1. Sonochemistry

![Graph showing cavity radius-time curves](image)

(a) $P_a = 1.4$ atm, $f = 213$ kHz, $R_0 = 1.0 \mu m$.

(b) $P_a = 1.4$ atm, $f = 213$ kHz, $R_0 = 1.6 \mu m$.

Figure 2.6: Stable Cavitation: radius-time curves of a typical air bubble under 213 kHz and 1.4 atm ultrasonic field during stable cavitation. The dotted line represents the driving sound amplitude. The solid lines are solutions to the Rayleigh-Plesset Equation for different initial bubble radii.

When the resonance condition arises, these critical sized bubbles grow to a maximum size range, become extremely unstable and violently collapse during the following compression cycle. Usually before implosion, the bubbles grow several times larger than its initial size and then drastically collapses to create extreme temperatures and pressures within the cavity. The high pressure is responsible for some of erosion, dispersion and mechanical rupture, while the high temperature results in sonoluminescence and sonochemical effects.

It is not an easy task to practically distinguish these two different types of cavitation. For example, Figure 2.6b shows the so-called repetitive transient cavitation. With respect to its general effects, this kind of cavitation acts as stable cavitation. However, based on a selected period (Figure 2.7), it displays the transient characteristic...
2.1. SONOCHEMISTRY

properties. Strictly, it is important to know the threshold for transient cavitation. Apfel [13], Church [14] and Matula [24] tried to set up a theoretical threshold to differentiate these two types of cavitation.

![Graph showing transient cavitation](image)

**Figure 2.7:** Transient Cavitation: bubble radius as a function of time. The blue solid line is a simulation of the Rayleigh-Plesset Equation for $P_a=1.4$ atm, $f=213$ kHz, $R_0=1.6 \, \mu m$.

Figure 2.7 shows the radius as a function of time plot for a bubble of $R_0 = 1.6 \, \mu m$. For the first 2 $\mu$s, rapid oscillations occur and have a period of 0.26 $\mu$s, associating with frequency of 3.8 MHz, which is twice the resonance frequency of the bubble. After that, the bubble enters into the expansion stage. The negative half-cycle of driving pressure $P(t)$ causes the bubble to expand. This is sufficient to increase the bubble radius by as much as a factor of 2.2. When the applied pressure changes to positive, the expanded bubble collapses inertially over a very short time and generates an extremely high pressure and temperature. The collapse is followed by a series
of afterbounces with decreasing amplitude. The bubble oscillates at roughly its resonant frequency during the remaining half cycle, leading to the characteristic afterbounces.

### 2.1.3. Hot Spot

There were two competing theories existing to explain chemical cavitation: the *hot-spot theory* and the *electrical theory* [35–37]. The electrical theory has been completely discounted, due to experimented observation made from sonoluminescence and sonochemistry [38]. The hot-spot theory is now the generally accepted explanation for the origin of sonochemistry and sonoluminescence.

One of the core contents of the hot-spot theory is concerned with the extreme conditions (high temperature and high pressure) inside the bubble during the collapse procedure due to its importance of controlling the efficiency of sonochemical reactions. There are a number of research studies on direct and indirect methods of temperature measurement on bubble collapse [39–44]. A very simple way provided here is based on the famous *Planck’s law of radiation*. The temperature corresponding to the maximum radiation wavelength is given by:

$$ T = \frac{2.896 \times 10^6}{\lambda_{\text{max}}} $$

(2.7)

Here, the unit of $T$ is absolute temperature K and the unit of $\lambda_{\text{max}}$ is nm. In the sonoluminescence experiment, purple light was observed from the emission of collapsing bubbles, corresponding to a wavelength range from 400 nm to 450 nm. From Equation 2.7, the temperature of acoustic cavitation is approximately calculated around 6500-7000 K, which is consistent with the results from other experiments [45]. However, the black body radiation was a preliminary model during the earlier stage of investigation of sonoluminescence. Recent work [46, 47] has shown the light emission from cavitation is likely a mixture of plasma, molecule, electron-atom bremsstrahlung, radiative recombination and blackbody radiation.

Figure 2.8 and 2.9 are the time-varying pressure and temperature during the bubble collapse. It corresponds to the example (see Figure 2.3) mentioned earlier in this subsection. Here the pressure and temperature are expressed by Equation 2.5 and Equation 2.6, respectively. Both of these two equations originate from the *Rayleigh-Plesset*
2.1. **Sonochemistry**

*Equation*, considering damping effects (Equation 2.4).

\[
P_g = \left( P_0 + \frac{2\sigma}{R_0} \right) \frac{(R_0^3 - a^3)^\kappa}{(R^3 - a^3)^\kappa} \quad (2.5)
\]

\[
T = T_0 \frac{(R_0^3 - a^3)^{\kappa-1}}{(R^3 - a^3)^{\kappa-1}} \quad (2.6)
\]

The collapse or the implosion of bubbles leads to generation of extremely high pressure (more than 41,000 atm) and temperature (more than 6000 K) within the bubble. The lower curve in Figure 2.9a shows the detailed changes of temperature at the collapse point. It shows that the implosion of an air bubble happens in a very short time (approximately 2 ns). These studies have shown that extraordinary conditions, such as high temperature, high pressure and rapid heating and cooling rates, occur within a liquid at ambient temperature. All these extreme conditions definitely bring special effects to the liquid surround a bubble or the solute existing in the liquid media. The following subsections focus on these effects.

Experimentally, the determination of the temperature within a cavitation bubble can be achieved by a number of techniques. Roughly, these techniques can be divided into two categories: kinetic measurement and spectroscopic measurement. Due to the different products or different rate constants under different temperature during the sonochemical reactions, the temperature of these reactions can be deduced according to the already known conventional reactions. Because of the spatial distribution of bubbles and acoustic pressures, the kinetics measurement is unable to correctly reflect the conditions in each bubble in the cloud. Spectroscopic methods have become a relative reliable measurement. Based on the observation of emission lines from electronically excited atoms and molecules, the effective emission temperature can be determined by comparing their relative intensities. This method requires accurate measurement of discrete emission lines in the sonoluminescence spectra.
2.1. **Sonochemistry**

![Graph](image)

(a) The time-varying pressure (same as the curve in Figure 2.3a).

(b) The gas pressure inside the bubble with logarithmic vertical axis.

**Figure 2.8:** Effects of Bubble Collapse: pressure-time curves of a typical air bubble whose initial radius is 5 \( \mu m \) under 20 kHz and 1.3 atm ultrasonic field during stable cavitation. The solid lines are solutions to the Rayleigh-Plesset Equation for different initial bubble radii.
2.1. Sonochemistry

2.1.4. Physical Effects of Ultrasound

2.1.4.1. Sonoluminescence

As a result of the extremely high temperatures and pressures generated, a light is emitted from the collapsing bubble, a phenomenon known as sonoluminescence. There are two classes of sonoluminescence: multiple-bubble...
sonoluminescence and single-bubble sonoluminescence. Multiple-bubble sonoluminescence was first discovered by Frenzel and Schultes in the 1930s [48]. Single-bubble sonoluminescence, however, was first reported by Gaitan [23] in 1992. Whether multi- or single bubble sonoluminescence, since its discovery day, many researchers have investigated this special phenomenon both experimentally and theoretically [21, 25, 47, 49–53].

The typical emission spectrum during single-bubble sonoluminescence from water is characterized by a featureless continuum devoid of any lines or bands [25, 47, 54]. The presence of gas, the components of gas and the vapor inside the cavitation bubble is able to change the spectrum as chemiluminescence and atomic emission lines will contribute to the whole spectrum. At the same time, more energy will be spent on endothermic bond breaking and atom excitation in the presence of water vapor or other volatile solutes. Furthermore, quite a number of researchers believe that the light emission from the single bubble collapse is probably due to the combination of plasma processes, blackbody radiation and pressure-broadened discrete electronic transitions [55–60]. There are a number of experimental results [53, 61–67] demonstrating that in addition to the components inside the bubble, surfactant, molecular and ionic solutes around the bubble/solution interface also can take part in the overall sonoluminescence process. Understanding the exact mechanism of sonoluminescence is still a challenge that remains to be overcome.

2.1.4.2. Other Physical Effects

In addition to sonoluminescence, the mechanical effects of ultrasound have also attracted a considerable amount of interest in the field of science and engineering. These mechanical effects of ultrasonic irradiation are primarily responsible for the following effects [68]:

- Improvement of mass transport from turbulent mixing and acoustic streaming [9];
- The generation of surface damage at liquid-solid interfaces by shock waves and microjets [69];
- The generation of high-velocity interparticle collisions in slurries [70];
- The fragmentation of friable solids to increase their surface area [71].
2.1. Sonochemistry

Clearly, the physical effects of ultrasonic irradiation are mostly applied in heterogeneous systems. If solids are present in the liquid irradiated by ultrasound, due to the close position of cavitation bubbles to the solid surface, the resulting nonspherical cavity collapse leads to the formation of high speed (refer to Figure 2.3c) jets of liquid into the surface (see Figure 2.10a). These jets and associated shockwaves can cause substantial damage and expose highly heated surfaces [3, 7, 72]. Acoustic streaming (see Figure 2.10b) is another important nonlinear effect in which steady fluid flows are formed by acoustic waves. Acoustic streaming seems to be the result of radiation forces, diffraction and nonlinearities of acoustic field within the oscillatory boundary layer surrounding the bubble. The impingement of microjets, microstreaming and shockwaves on the solid surface creates the erosion responsible for many physical effects and applications of ultrasound in heterogeneous reactions.

![Figure 2.10: Microjet and Microstreaming: schematic diagrams showing the physical influence of cavitation bubble on a solid surface through the formation of microjet and microstreaming.](image_url)
2.1. Sonochemistry

2.1.5. Chemical Effects of Ultrasound

Ultrasound has proven to be a very useful tool in enhancing the reaction rates in a variety of chemical systems. Sonochemistry refers to the field of chemistry where chemical reactions are induced by sound [10]. The chemical and biological effects of ultrasound were first reported in 1927 [4]. The ultrasonic chemical effects of ultrasound are not attributed to a direct interaction of the sound field with molecular species. Instead, the source of the chemical effects is generation of the short lived, localized hot-spots [73].

When bubble collapse occurs in liquids, this transient activity results in an enormous concentration of energy from the conversion of the kinetic energy of liquid motion into heating of the content inside of bubbles. The extremely high local temperature and pressure generated inside the bubble leads to the formation of highly reactive radicals, which provides a unique driving force to initialize chemical reactions. It has been confirmed that during ultrasound driven cavitation, the water molecules inside the bubble can be cleaved into highly reactive H• and OH• radicals, which propel the subsequent chemical reactions (Reaction 2.8). H• and OH• radicals undergo a range of subsequent reactions including the generation of H₂O₂ [72].

\[
\text{H}_2\text{O} \rightarrow \text{H}• + \text{OH}•
\] (2.8)

It is well-known that radicals such as H• and OH• play a key role in most of aqueous sonochemical reactions. Makino et al. used spin trapping and electron spin resonance measurement to confirm the formation of H• and OH• radicals during the sonolysis of water [74].

Free hydrogen atoms have a highly reducing power in nature. With a reduction potential of -2.3 V [75], the hydrogen atom readily reduces inorganic ions having more positive reduction potentials. If oxygen is present, H• will react with it to form HO₂• radicals.

\[
\text{H}• + \text{H}• \rightarrow \text{H}_2
\] (2.9)

\[
\text{H}• + \text{O}_2 \rightarrow \text{HO}_2•
\] (2.10)

Contrary to hydrogen atoms, OH• radicals have a highly oxidizing power. OH• radicals exhibit a high oxidation potential of +2.7 V in acidic solution and +1.8 V in neutral solution [75]. OH• radicals produced from the
sonolysis of water are able to attack all organic compounds and form a series of organic products. Another source of OH• is the pyrolysis of molecular oxygen during bubble cavitation.

\[
\begin{align*}
\text{O}_2 \rightarrow & \text{O} + \text{O} & (2.11) \\
\text{O} + \text{O}_2 \rightarrow & \text{O}_3 & (2.12)
\end{align*}
\]

The reaction between HO2• radicals leads to the formation of hydrogen peroxide, which is utilized to quantify the amount of OH• radicals formed by the oxidation of iodide ions [10].

\[
\begin{align*}
\text{OH} + \text{OH} \rightarrow & \text{H}_2\text{O}_2 & (2.13) \\
\text{H} + \text{HO}_2 \rightarrow & \text{H}_2\text{O}_2 & (2.14) \\
\text{HO}_2 + \text{HO}_2 \rightarrow & \text{H}_2\text{O}_2 + \text{O}_2 & (2.15) \\
\text{H}_2\text{O} + \text{OH} \rightarrow & \text{H}_2\text{O}_2 + \text{H} & (2.16)
\end{align*}
\]

Under a nitrogen and oxygen atmosphere, other reactions can be expected to occur [10].

\[
\begin{align*}
\text{N}_2 + \text{O}_2 \rightarrow & 2\text{NO} & (2.17) \\
2\text{NO} + \text{O}_2 \rightarrow & 2\text{NO}_2 & (2.18)
\end{align*}
\]

The formation of nitrous and nitric acid resulting from the reaction of NO2 and H2O is the reason that the pH of water decreases during the sonication of air-saturated water [76, 77].

Unfortunately, the recombination of highly reactive H• and OH• also occurs during cavitation. It has been theoretically estimated that about 80% of the primary radicals generated annihilate within the bubble (Reaction 2.19) and only about 20% are responsible for secondary chemical reactions in the solution phase [78]. Obviously, these “lost” radicals do not influence the chemical reactions in aqueous solution, which means they do not have positive effects on sonochemistry. Increasing the amount of effective radicals is the critical pivot to enhance the efficiency of sonochemistry.

\[
\begin{align*}
\text{H} + \text{OH} \rightarrow & \text{H}_2\text{O} & (2.19)
\end{align*}
\]
2.1. Sonochemistry

A number of measures have been adopted to inhibit the recombination of the primary radicals, such as addition of surfactants, polymers or alcohols to convert primary radicals to secondary radicals. Experimental evidence shows that some surfactants and alcohols have a strong influence on the efficiency of sonochemistry [33, 79–81].

2.1.6. Applications of Ultrasound

Sonochemistry shares, with sustainable chemistry, such aims as the use of less hazardous chemicals and solvents, a reduced energy consumption and an increased product selectivity. It is a new and rapidly growing research field with broad environmental applications, such as in waste water treatment, industrial waste treatment, etc.

The main task in sonochemical applications is the choice of the proper bubble behavior for the desired effect. Applications of ultrasound in processing and synthesis are ubiquitous, but two major beneficial effects contribute to its various applications: physical effects - mechanical effects for mixing and disintegration and chemical effects - high energy processes involving radical reactions.

2.1.6.1. Applications of the Physical Effects of Ultrasound

Ultrasonic cleaning and decontamination of surfaces are two of the most popular applications of ultrasound. In 1954, Elder et al. found that bubble-induced micro-streaming is one of the factors leading to the well-known ultrasonic cleaning effects [82, 83]. Specifically, the high flow velocities resulting from the bubble collapse lead to important drag and shear forces at the surface, responsible for cleaning and erosion effects. This concept is usually adopted to explain the pitting of solid surfaces observed under ultrasound fields and the overall particle dispersion in heterogeneous systems. The particular advantage of ultrasonic cleaning is that it can reach crevices or corners that are not easily accessible using conventional cleaning methods and also avoid involving other chemical contamination.

Ultrasonic nebulization provides an effective way to produce atomizer water sprays, which have many uses, such as dust suppression in industry, humidifiers, gel particle production and extraction [84]. One of the main advantages in using ultrasonic nebulization is that varying the ultrasonic power or the frequency can precisely control surface waves which determine the nebulized droplet sizes. In addition, alcohol and surfactant molecules
2.1. **SONOCHEMISTRY**

at the gas/liquid interface also contribute to the nebulization effect of ultrasound [85–87]. This is a great advantage in comparison with distillation operation, as ultrasonic nebulization rarely leads to phase changes.

*Ultrasonic extraction* is a powerful tool used to obtain natural products that usually require much longer time than conventional methods. The application of ultrasound-assisted extraction offers many advantages including the reduction of the quantity of solvent used, temperature and the time cost for extraction, specifically for the thermolabile and unstable compounds. Furthermore, ultrasonic extraction can be used for a broad number of compounds including dyes [88], elements [89], phenolic compounds [90–92], oils [93, 94], special compounds in plants [95–97], and so on.

*Ultrasonic dispersion* offers an attractive route for treating nanoparticles in aqueous environments with the possibility of de-aggregating and de-agglomerating particles in parallel to their homogeneous dispersion [98]. These processes are attributable to a combination of shockwaves, thermal gradients, micro-jets and other acoustic cavitation effects [99].

*Ultrasonic ultrafiltration* provides an effective method for membrane fouling control and cleaning. It is well-known that microsteaming, acoustic streaming, microjets and shock waves generated during cavitation are capable of removing portions of the foulant layers from membrane surfaces and preventing the deposition of particles which lead to membrane fouling. In other words, ultrasound influences effectively both the ultrafiltration production cycle and the cleaning cycle to enhance the efficiency of membrane ultrafiltration [100].

2.1.6.2. **Chemical Applications of Ultrasound**

Sonochemistry has been extensively used in materials synthesis, specifically for a broad range of inorganic materials. One of these sonochemical synthesis processes is the preparation of very narrow size distribution metal particles. The ultrasound-initiated formation of metal colloids in aqueous solution has been observed for a number of metals including Ag, Au, Pt and Pd. In addition to these metal nanoparticles, the synthesis of metal oxide has also attracted a special interest recently. The following section (Section 2.2) will discuss the synthesis of these metal and metal oxide nanoparticles by ultrasound irradiation.

A significant amount of work has been reported concerning the sonochemical effect on various systems in
2.1. Sonochemistry

Organic synthesis [10, 101]. Ultrasound has the ability to initiate or accelerate the synthesis of various organic compounds, by changing the reaction pathway. The sonochemical synthesis of organic materials is also extremely versatile [102].

In recent years, ultrasound chemistry has proved to be a novel technique to synthesize polymer latex particles without involving chemical initiator [103, 104]. Polymerization was thought to be the result of the primary radicals from cavitation attacking the monomer molecules to form monomeric radicals which could polymerize by a conventional mechanism [84, 105].

Another important application field of ultrasound is environmental remediation. The generation of highly reactive primary radicals during cavitation and the presence of extreme conditions inside the bubble provided the conditions to decompose almost all organic compounds around or inside the cavitation bubbles. This application will be discussed in Section 2.4.

2.1.6.3. Biological Applications of Ultrasound

Ultrasonic sterilization has been promoted as an alternative to other more conventional methods. The action of high intensity ultrasonics in liquid sterilization is perhaps attributable to cavitation and micro-streaming, which enhance the separation and dispersion of clusters of bacteria.

In addition to sterilization, ultrasound has been used successfully for many years for a range of applications including most notably the diagnosis, investigation and treatment of diseases. These extensive applications include cancer therapy [106], sonodynamic therapy [107], bone regeneration [108], tissue dissection and ablation [109], medical diagnosis [110], and many more. These critical developments have stimulated more research into the biophysical interactions of ultrasound with respect to health and safety and has further led to increasingly sophisticated medical and therapeutic techniques and equipment design.

Above all, ultrasound has great potential in a wide variety of processes in science, engineering, medical and a variety of industries, even replication of the prebiotic molecular evolution [111]. Timothy Mason summarized these potential trends of ultrasound in several reviews on ultrasound [1, 112–114], which are good reference resources for further reading.
Over the past few years, the synthesis of inorganic and bio-materials has developed as one of the most important applications of sonochemistry [68, 78, 115, 116]. With extremely high local temperatures and pressures accompanying drastically rapid cooling speeds, acoustic cavitation provides an unique preparation means for unusual materials with special properties from the precursor solution. At same time, due to its “green” preparation conditions, without any extra chemicals, sonochemical method has won more attractions compared with conventional preparation methods. Ultrasound has proved to be extremely useful in the synthesis of a wide range of nanometer-sized materials, including high-surface area metal, bimetal, alloys, carbides, oxides, sulfides, nitrides, chalcagonides, polymer composites, ceramic materials, dielectric materials and other colloids, These nanoparticles formed varied in size, shape, structure and crystal phase, but they were always in a narrow nanometer-sized distribution.

The following reactions describe the primary mechanism for the synthesis of metallic nanoparticles in aqueous solution. Obviously, the sonolysis of water to form highly oxidizing OH• and reducing H• (Reaction 2.8) is the fundamental base for the subsequent reactions.

\[
\begin{align*}
\text{H}_2\text{O} & \rightarrow \text{H}^\bullet + \text{OH}^\bullet \quad (2.8) \\
\text{ROH} & \rightarrow \text{H}^\bullet + \text{OH}^\bullet + \text{R}^\bullet + \text{RO}^\bullet + \text{O} \quad (2.20) \\
\text{ROH} + \text{OH}^\bullet & \rightarrow \text{RO}^\bullet + \text{H}_2\text{O} \quad (2.21) \\
n\text{H}^\bullet + \text{M}^{n^+} & \rightarrow \text{M} + n\text{H}^+ \quad (2.22) \\
n\text{RO}^\bullet + \text{M}^{n^+} & \rightarrow \text{M} + \text{R}^\prime + n\text{H}^+ \quad (2.23) \\
n\text{(M)} & \rightarrow \text{(M)}_n \quad (2.24)
\end{align*}
\]

Where, RO• denotes the alcohols or surfactants; M^{n^+} is a metal ion; (M)_n is a metal colloid with n atoms. Here, in addition to the primary radicals H• and OH•, there is another kind of radical RO•, which is called a secondary radical. If sonolysis occurs in pure water, only H• atom can be expected to be involved in synthesis of metal...
2.2. **Sonocatalytic Synthesis of Inorganic Nanoparticles**

Particulate [78]. The appearance of RO• greatly improves the efficiency of the sonocatalytic preparation metal colloids. These type of radicals play the key role in the synthesis of metal nanoparticles. Several studies have shown that the presence of aliphatic alcohols accelerates the reduction of metal ions [78, 117–119]. This enhancement is mainly attributed to the fact that the surface active solutes adsorbed at the bubble-solution interface are capable of scavenging the primary radicals to generate secondary radicals and inhibit the recombination of the primary radicals. There are two pathways for added alcohol to convert to secondary radicals. If the aliphatic alcohol is volatile, some of alcohol will evaporate into the cavitation bubbles. During the compression cycle which leads to high temperature, these molecules will convert into the alcohol radicals (Reaction 2.20 and Figure 2.5). The alcohol at the bubble/solution interface is likely to undergo the second pathway. Because of their advantageous position, they readily scavenge primary radicals (Reaction 2.8), thereby inhibiting the recombination of the primary species (Reaction 2.19). This activity of alcohols enables the highly oxidizing OH• radicals to convert to alcohol radicals possessing a reduction potential. These secondary radicals can reduce the metal ions in the bulk solution to form metal nanoparticles. Obviously, the presence of aliphatic alcohols has the capability of enhancing the formation of metal nanoparticles.

The addition of surfactants during the synthesis of nanoparticles by the sonocatalytic synthesis method has attracted much interest recently [119–121]. The surfactants influence the reaction in two ways: stabilizing the formed nanoparticles and influencing the behavior of cavitation. The former effect is similar to that of surfactant in the conventional preparation of nanoparticles. The charged surfactants are able to prevent the aggregation of nanoparticles by electrostatic forces. As shown in Figure 2.11, the stabilizing effects of the surfactant is due to the adherence of their long hydrocarbon chains to the surface of colloidal particles with the anionic head groups protruding out into the aqueous surroundings. The presence of surfactants affects the bubble growth process during both rectified diffusion [31] and coalescence [122–124].

In addition to the action of solutes such as alcohol and surfactant, the atmosphere during the reduction process also plays an important part in improving the efficiency of generating nanoparticles by ultrasonic irradiation. Based on the simple hydrodynamic model for a cavitation bubble, the theoretical temperature within the bubble can be expressed by Equation 2.6. According to this mathematic model, the temperature closely correlates with the polytropic index ($\kappa$) of the gas/vapor mixture and the van der Waals hard-core radius $a$, which strongly depends
2.2. Sonochemical Synthesis of Inorganic Nanoparticles

**Figure 2.11:** Stabilizing Function of Surfactants: potential energy of interaction $V$ between two colloidal particles as a function of interparticle distance $r$. $V_A$ is the attractive London-van der Waals interaction, $V_R$ is the repulsive interaction and $V$ is the total resulting interaction curve.

on the gas molecules originally dissolved in the fluid. Figure 2.12 shows the temperature changes with time during cavitation under an argon atmosphere.

Compared to the maximum temperature ($\sim 6000$ K) under an air (Figure 2.9a), the maximum temperature under argon atmosphere (Figure 2.12) reaches more than 16,000 K. This calculated result implies that monatomic gas can give rise to greater extent of heating during bubble collapse than a diatomic gas, thereby can be expected to increase the yield of highly reactive primary radicals. Although this number is calculated by a mathematically estimation, a large amount of experimental evidence [10, 119, 125, 126] has also demonstrated that monatomic gas atmosphere greatly enhances the reduction of metal ions to form metal nanoparticles. Another effect is that the
2.2. Sonochemical Synthesis of Inorganic Nanoparticles

Figure 2.12: Influence of gas atmosphere: the blue solid line is a simulation of temperature as a function of time for a initial 5 \( \mu \)m radius bubble sonicated at 20 kHz and 1.3 atm ultrasound under an argon atmosphere.

The acoustic power and frequency, the ambient temperature, pH, external pressure and the choice of solvent can be also expected to affect the efficiency of sonochemical reactions in different ways [10, 127]. Adjusting these factors to obtain the maximum efficiency is always a goal of the ultrasound application. Furthermore, some of these factors rather than being independent are interrelated and influence one another in a multitude of ways. For example, the addition of surfactant will not only alter the behavior of cavitation, but will also change the gas atmosphere has the thermal conductivity inside the bubble. Having the smallest thermal conductivity, Xe is the best candidate for the ambient gas for cavitation. At the same time, the inert atmosphere can form a protective ambient environment for the formed nanoparticles against oxygen, preventing oxidation back to metal ions.
2.2. Sonochemical Synthesis of Inorganic Nanoparticles

A special interest lies in the recent development of sonochemistry as a synthetic tool for the preparation of metal or bimetallic nanoparticles. These nanoparticles have attracted enormous interest because of their novel properties compared to bulk materials and unique phenomena occurring at the nanoscale regime. For example, they can serve as a model system to experimentally probe the effects of quantum confinement on electronic, magnetic, and other related properties. The fascinating properties of metal nanoparticles are mainly determined by their size, shape, composition, crystallinity and structure. Due to controllable reactions, inexpensive cost equipment and the ability to form particles with uniform shapes, narrow size distribution, ultrasonic irradiation of aqueous noble metal ion solutions is one important synthetic means to obtain nanometer-sized particles.

There are two possible pathways to synthesize inorganic nanoparticles sonochemically (shown in Figure 2.13). The first pathway is by radical reduction, which mainly happens in aqueous media. Normally the ultrasound-initiated formation of Au, Ag, Pt and Pd take place due to the role of radicals. The cavitation bubble is responsible for forming the highly active primary radicals and secondary radicals and the reduction process is same as conventional radical reaction. This pathway is the primary focus of the following. The second pathway is the pyrolysis of organometallic precursors in organic media, in which the extremely high temperature during collapse is playing the key role. The synthesis of Fe, Ni, Co is usually performed using this pathway. A brief summary is provided on this synthesis mechanism at the end of this section. During the early stage of nucleation, the metal salt is reduced to zerovalent metal atoms by either radical reduction or pyrolysis. Collision of these metal atoms or particles results in the formation of stable metal nuclei. The diameter of these nuclei is a few angstroms depending on the preparation conditions during the irradiation. At the same time, pre-existing metal atoms can act as catalysts to convert ions to atoms via absorption of radicals in the aqueous environment. This autocatalytic procedure also contributes to the formation of metal nuclei. Nanoparticle inter-collision [70] and autocatalytic reduction also
Figure 2.13: Metal Nanoparticle Synthesis Procedure: the sonochemical formation of metal nanoparticles in the presence of surfactant/alcohol.

plays a significant role in the growth process of metal nuclei.

Table 2.1 summarizes recent publications on sonochemically synthesized metal nanoparticle colloids in aqueous systems. There are four metallic ions which can be reduced by the active radicals of acoustic cavitation.

In some noble metals, such as gold, silver and copper, due to their nanometer size being below of an electron average free path (the distance between scattering collisions and the lattice centers), this gives rise to intensive

*Standard reduction potentials obtained from reference [26] are for bulk metal.
2.2. Sonochemical Synthesis of Inorganic Nanoparticles

Table 2.1: Recent reports on the sonochemical synthesis of metal nanoparticles in aqueous solution.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Reaction</th>
<th>$E^\circ/V^*$</th>
<th>Colloid Color</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gold</td>
<td>AuCl$_4^-$ + 3e$^-$ $\rightarrow$ Au + 4Cl$^-$</td>
<td>1.00</td>
<td>Reddish-violet</td>
<td>[117, 119, 121, 128–136]</td>
</tr>
<tr>
<td>Silver</td>
<td>Ag$^+$ + e$^-$ $\rightarrow$ Ag</td>
<td>0.80</td>
<td>Yellow</td>
<td>[129, 137–140]</td>
</tr>
<tr>
<td>Palladium</td>
<td>Pd$^{2+}$ + 2e$^-$ $\rightarrow$ Pd</td>
<td>0.95</td>
<td>Dark brown</td>
<td>[126, 129, 141–145]</td>
</tr>
<tr>
<td>Platinum</td>
<td>PtCl$_4^{2-}$ + 2e$^-$ $\rightarrow$ Pt + 4Cl$^-$</td>
<td>0.76</td>
<td>Dark brown</td>
<td>[118, 120, 126, 129, 134, 146, 147]</td>
</tr>
</tbody>
</table>

Absorbance of near UV-visible light. This results from the coherent oscillation of the free electrons within the particles, and is called surface plasmon absorption. The surface plasmon maximum absorption during the reduction is usually used to monitor the progress of the formation of the corresponding metal nanoparticles. Most recently, surface plasmon adsorption has received considerable attention for its potential in optical manipulation at the nanoscale.

2.2.1.1. Gold Nanoparticles

Gold nanoparticles have attracted considerable attention in the field of nanotechnology due to their unique optical properties, which depend on electronic properties rather than molecular structure, and the facile functionalization of this material with a variety of other molecules. Despite being known for many years, the application of this material continues to be actively studied showing the potential for major commercial use in the future.

Sonochemical synthesis of golds colloid usually starts with an aqueous solution of millimolar quantities of Au(III) ions. Without any surfactants or other alcohols, H• which has high reduction potential is the main reductant...
to reduce the Au(III) ions to produce gold nanoparticles. The color changes of the solution reflect the progress of the reduction. Normally, the color of the \( \text{AuCl}_4^- \) is yellow (220 nm) and the gold nanoparticle colloids are reddish-violet, corresponding to the plasmon absorption 530 nm (Shown in Figure 2.14).

\[
\text{AuCl}_4^- + 3\text{H}^+ \rightarrow \text{Au} + 3\text{H}^+ + 4\text{Cl}^- \tag{2.25}
\]

These absorption bands can be used to quantify the rate of the reduction of \( \text{AuCl}_4^- \) and the formation of zero-valent gold, respectively.

![UV-vis spectrum](image)

**Figure 2.14:** UV-vis spectrum observed after the sonochemical reduction of an aqueous solution of 1 mM \( \text{AuCl}_4^- \) containing 8 mM SDS and 0.2 M 1-propanol after 10 min sonication in an Ar atmosphere. The ultrasound frequency used was 213 kHz and the total power was 35 mW/mL.

The reduction rates of metal ions can be significantly enhanced in the presence of surface active solutes. Caruso *et al.* investigated the influence of different concentrations of different chain length alcohols [119]. They found
that longer chain alcohol and higher alcohol concentration can lead to the smaller size particles. Okitsu et al. concluded that the size of the Au nanoparticles produced was closely related to the rate of sonochemical reduction of the Au(III) ions [132]. Clearly, the alcohol concentration and the alcohol chain length have the potential to alter the reduction rate of the metal ions. Increasing the alcohol concentration gives rise to a greater amount of primary radical scavengers, which results in higher reduction rates. There are two possible reasons contributing to the influence of alcohol chain length. A longer carbon chain is associated with a greater hydrophobicity which enables the alcohol to be more readily concentrated on the interfaces of the gold/solution and bubble/solution. For the case of the alcohol at the gold/solution interface, it will stabilize the particle and inhibit further growth. In the latter case, the alcohol can collect more primary radicals during cavitation to enhance the yield of colloid gold. The TEM images of gold colloid prepared by the sonochemical method are shown in Figure 2.15.

During the sonochemical preparation of gold nanoparticles, there are a number of experimental parameters which can change the particle size, shape and other properties. For example, micro-gravity can affect the particle size distribution [131]; the concentration of stabilizer and ultrasonic irradiation power can influence the shape of gold nanoparticles [121, 136]; the subsequent aging after gold nanoparticles can induce the growth of nanoprisms [135].

If sonication occurs in the presence of another inorganic support or precursor, nanometer-sized cluster can be fixed on the surface of these supports, which can lead to the formation of very active supported heterogeneous catalysts [148]. Particular, this way provides an unique means of creating special gold nanoparticles which possess magnetic properties [149, 150].

2.2.1.2. Platinum Nanoparticle

Platinum nanoparticles are of special interest and are the subject of intense study as they exhibit special catalytic properties different from those of conventional platinum metal catalysts. The diameter of platinum nanoparticles synthesized by the sonochemical method is usually below 5 nm. The deviation in particle sizes is very small and essentially the particle size is homogeneous. This advantage provides high surface area catalysts, which are used in a range of applications.
2.2. Sonochemical Synthesis of Inorganic Nanoparticles

Figure 2.15: TEM images and crystal lattice of Au nanoparticles prepared by sonochemical reduction of an aqueous solution of 1 mM AuCl$_4^-$ containing 1 mg/mL PVP and 0.4 M 1-propanol under an Ar saturated atmosphere. The ultrasound frequency used was 355 kHz and the total power was 55 mW/mL.

Normally the preparation of platinum nanoparticles is by sonochemical reduction of PtCl$_2^-$ / PtCl$_6^{2-}$ ions, whose aqueous solution has a pale yellow color. Similar to the reduction of gold ions, the platinum ions may be reduced via two possible pathways, by radicals or via a thermal process, to form platinum nanoparticles. Mizukoshi *et al.* found that the Pt(IV) ion is reduced to zerovalent metal is via two steps: Pt(IV) to Pt(II) and then Pt(II) to Pt(0) [120]. While these two steps look simple, the mechanism involved is rather complex. Ciacchi *et al.* have theoretical investigated the initial nucleation of platinum nanoparticles by means of first principles molecular dynamics simulations. At equilibrium, a 1 mM K$_2$PtCl$_4$ solution consists of 5% PtCl$_4^{2-}$, 53% PtCl$_3$(H$_2$O)$^-$ and
2.2. Sonochemical Synthesis of Inorganic Nanoparticles

42% PtCl$_2$(H$_2$O)$_2$ [151].

\[
\begin{align*}
\text{PtCl}_4^{2-} + \text{H}_2\text{O} & \rightleftharpoons \text{PtCl}_3(\text{H}_2\text{O})^- + \text{Cl}^- \quad (2.26) \\
\text{PtCl}_3(\text{H}_2\text{O})^- + \text{H}_2\text{O} & \rightleftharpoons \text{PtCl}_2(\text{H}_2\text{O})_2 + \text{Cl}^- \quad (2.27)
\end{align*}
\]

Of the three Pt(II) complexes, only the neutral complex PtCl$_2$(H$_2$O)$_2$ binds an extra electron and reduction of this complex results in the formation of PtCl$_7^-$, which is reduced to PtCl$^-$ in the following step. After that, a platinum dimer is formed in aqueous solution. They emphasized that the formation of a Pt-Pt bond between the Pt(I) complex and an unreduced Pt(II) is the key step in the preparation of zerovalent nanoparticles. Obviously, the process of reduction from the platinum ions to platinum metal particles is much more complex than the simple chemical reaction from a stoichiometric point of view.

Not all metal particles show plasmon resonances. Metals such as iron, palladium and platinum do not show resonances because of lifetime broadening via strong plasmon decay channels. Strong conduction electron relaxation, radiation dumping, as well as transformation of the collective excitation into electron-hole pair excitation are other reasons for this behavior [152].

Caruso et al. found that the presence of aliphatic alcohols during the sonochemical synthesis of platinum nanoparticles had the same enhancement effect as that as gold ion reduction system [118]. Mizukoshi et al. have made similar observations [120, 146, 147].

2.2.1.3. Palladium Nanoparticle

Palladium nanoparticles are particularly noteworthy with respect to applications due to their potential use as catalysts, magnetic storage materials and hydrogen storage materials. A variety of techniques have been utilized to prepare palladium nanoparticles, such as photolytic decomposition, thermal decomposition and hydrogen reduction.

Similar to the process of gold and platinum, ultrasonic reduction of palladium salts in aqueous media was developed to generate palladium nanoparticles with a small size, high surface area, and narrow size distribution. The size of the particles depends on the initial concentration of surface active additives and alcohols, substantively
2.2. Sonochemical Synthesis of Inorganic Nanoparticles

hinge on the reduction rate. A typical synthesis experiment is to sonicate an aqueous solution containing palladium salts and stabilizer [polyvinyl-2-pyrrolidine (PVP)] in the presence of the radical scavenger, 1-propanol. The PVP is able to protect the palladium nanoparticles by adsorption to the particle surface via the coordination of the carbon-oxygen group with the palladium surface atoms [145].

Figure 2.16: TEM images and crystal lattice of Pd nanoparticles prepared by sonochemical reduction of an aqueous solution of 1 mM K₂PdCl₆ containing 1 mg/mL PVP and 0.4 M 1-propanol under an Ar saturated atmosphere. The ultrasound frequency used was 355 kHz and the total power was 55 mW/mL.

As mentioned before, the gas atmosphere during the reduction process plays an important role in controlling the temperature when bubbles collapse and thus affects the reduction rate. This influence of gas environment is reflected in the nanoparticle sizes [126]. As with gold nanoparticles, the palladium can be doped into the catalyst supports by addition of the precursor solutions of the support materials, such as activated carbon [142], porous silica [143], alumina [153] and Y-zeolite [144].
2.2. SONOCHEMICAL SYNTHESIS OF INORGANIC NANOPARTICLES

2.2.1.4. Silver Nanoparticles

Among the metals, silver nanoparticles have found interesting applications as optical polarizers, catalysts and photon crystals as well as for biomedical and chemical sensors.

The reduction of silver ions in aqueous solution by ultrasound is attributed to the reducing H• and R• radicals, as shown in the Reaction 2.28 and 2.29.

\[
\begin{align*}
\text{Ag}^+ + \text{H}• & \rightarrow \text{Ag} + \text{H}^+ \quad (2.28) \\
\text{Ag}^+ + \text{R}• & \rightarrow \text{Ag} + \text{R}′ + \text{H}^+ \quad (2.29)
\end{align*}
\]

By collision or by an autocatalytic process, the Ag atoms coagulate to form the metal nanoparticles. Considering the redox levels \(\text{(see Table 2.1)}\) involved in the reaction something about the mechanism is clearly incorrect \[78\]. The occurrence of these reactions requires that the redox potential of a few aggregated atoms should be lower than that of the bulk metal. By a thermodynamical cycle, Henglein concluded that the redox potential of silver atoms in aqueous solution was indeed \(E^{\ominus}(\text{Ag}^+/\text{Ag}^0) = -1.8\) V\text{NHE}, which is 2.6 V lower than that of the bulk material \[154\]. The size-dependent redox potentials of silver clusters were progressively determined to increase with cluster nuclearity.

Silver particles have the unique property that the excitation of the collective oscillation (plasmon absorption maximum at 380 nm) and the inter-band transitions (320 nm) occur in separate wavelength regimes. Usually the color of silver colloids, closely relating to these bands, depends on the metal particle size and shape. The difference in the particle size, shape and the properties of the surface results in different colors, and can range from yellow to green. However, colloid silver is a complex system and there are a number of parameters that play a role in determining their optical properties. For example, increasing the solvent polarity results in a blue-shift of the absorption band and increasing temperature leads to a red-shift. Figure 2.17 shows the TEM images of silver nanoparticles prepared by sonochemical reduction. The average particle size is less than 8 nm.
2.2. **Sonochemical Synthesis of Inorganic Nanoparticles**

Suslick and co-workers were the first to prepare amorphous metals in nonaqueous solvents [155]. They cleverly took advantage of the volatile properties of organometallic complexes and introduced them into the cavitation bubbles. The extremely high temperature of the bubble during the collapse leads to the decomposition of these complexes to form metal atoms. In order to accumulate an adequate amount of organic complexes in the bubble, it is necessary to dissolve them in organic liquids. Typically, sonochemical formation of iron starts with a solution of Fe(CO)$_5$ in octanol, decane or another organic solvents. Under the effects of ultrasound irradiation in an argon atmosphere, the volatile iron pentacarbonyl is decomposed inside the bubble and highly porous amorphous iron

---

**Figure 2.17:** TEM images and crystal lattice of Ag nanoparticles prepared by sonochemical reduction of an aqueous solution of 1 mM AgNO$_3$ containing 1 mg/mL PVP and 0.4 M 1-propanol under an Ar saturated atmosphere. The ultrasound frequency used was 355 kHz and the total power was 55 mW/mL.

2.2.1.5. **Synthesis of Metal Nanoparticles in Organic Media**
2.2. Sonochemical Synthesis of Inorganic Nanoparticles

Metal particles are formed.

\[ \text{Fe(CO)}_5 \\text{Fe(CO)}_n + n\text{CO} \]  \hspace{1cm} (2.30)

\[ \text{Fe(CO)}_3 + 2\text{Fe(CO)}_5 \rightarrow \text{Fe}_3\text{(CO)}_{12} + \text{CO} \]  \hspace{1cm} (2.31)

\[ \text{Fe(CO)}_n \rightarrow \text{Fe}_\text{(s)} + \text{CO} \]  \hspace{1cm} (2.32)

The amorphous nature of the iron prepared by ultrasound is attributed to the rapid cooling rates after the formation of iron metal. According to the Figure 2.12, it only takes less than 200 ns to cool from 16,000 K to ambient temperature. The cooling rate is more than \(10^{11}\) K/s. It is well-known that the faster cooling rate inhibits the organization and crystallization and finally leads to forming an amorphous structure.

In addition to iron particles, a number of nanometer-sized amorphous metal nanoparticles, such as cobalt, nickel, palladium, have been synthesized from their volatile organometallic complexes (see Table 2.2).

Table 2.2: Recent reports on sonochemical synthesis of metal nanoparticles in organic media.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Precursor</th>
<th>Solvent</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron</td>
<td>Fe(CO)_5,</td>
<td>Decane,</td>
<td>[155–157]</td>
</tr>
<tr>
<td>Cobalt</td>
<td>Co(CO)_3(NO)</td>
<td>Decane, Decalin</td>
<td>[157–160]</td>
</tr>
<tr>
<td>Nickel</td>
<td>Fe(CO)_4, Ni(C_8H_12)_2</td>
<td>Decane, Decalin, Toluene</td>
<td>[161–164]</td>
</tr>
<tr>
<td>Palladium</td>
<td>Pd(C_5O_2H_7)_2, Pd(O_2CCH_3)_2</td>
<td>Toluene, THF, Methanol</td>
<td>[165, 166]</td>
</tr>
</tbody>
</table>

2.2.2. Sonochemical Synthesis of Bimetallic Nanoparticles by Ultrasound

Bimetallic nanoparticles constitute a special class of nano-composite materials. They consist of two different particles which results in highly functional properties quite different from individual particles. Usually they exhibit modified and improved properties compared with their single component counterpart. By simply tuning the ratio...
of each component, the properties can be altered. With delicate control ability, it is possible to use ultrasound to synthesize these nano-structured bimetallic particles of desired shape, size and morphology.

The preparation method of binary nanoparticles can be divided into two categories: simultaneous and sequential. The simultaneous method is comparatively simple by means of varying the reaction speed to change the ratio of component. Sequential methods require more complicated procedures to control the formation of binary metal particles. Specifically in aqueous solution, the sequential method to form core-shell structure nanoparticles is by reduction of the core metallic ions following by the reduction of the shell metallic ions.

As with the monometallic nanoparticles, the bimetallic nanoparticles can be formed in either an aqueous environment or an organic medium. There are a number of literature reports concerning the synthesis of bimetallic nanoparticles in aqueous solution, such as AuPd [167–173], AuPt [134, 168, 170, 174], AuAg [175] and PtPd [174]. Normally by controlling the concentration of precursor ions or irradiation time via the simultaneous method, it is possible to form composite particles with different ratio of components.

The sonochemical preparation of bimetallic alloys from organic media has also been achieved by sonicating non-aqueous mixtures of organometallic complexes, such as FeCo [157, 176, 177], FeNi [178] and CoNi [179], even FeNiCo superparamagnetic nanoparticles [180]. The relative amount of each component could be controlled by changing the concentration ratio of the precursors in the solution under sonication.

### 2.2.3. Synthesis of Metal Compound Nanoparticles by Ultrasound

In addition to the metal and bimetallic nanoparticles, ultrasound also offers a very attractive means for the synthesis of various nanometer-sized metal oxides, sulfides and selenides. The reactions of the sonochemical preparation chalcogenide nanoparticles in aqueous solution are listed as follows [115, 181]:

\[
H_2O \longrightarrow H^+ + OH^- \quad (2.8)
\]

\[
RN + 2H^+ \longrightarrow R^- + H_2N \quad (2.33)
\]

\[
M^{2+} + yH_2N \longrightarrow M_xN_y + 2yH^+ \quad (2.34)
\]

\[
nM_xN_y \longrightarrow (M_xN_y)_n \quad (2.35)
\]
2.3. SYNTHESIS OF METAL NANOPARTICLES BY $\gamma$-RAY IRRADIATION

Where, N represents S or Se. In case of S, RN is CH$_3$CSNH$_2$, NH$_2$CSNH$_2$ or CH$_3$CH(SH)COOH; for Se, RN is NH$_2$CSeNH$_2$. Obviously, the strongly reducing radical H• is able to break up the carbon-sulfur or carbon-selenium bonds to form H$_2$S or H$_2$Se. This intermediate compound H$_2$S or H$_2$Se plays the critical role in forming the chalcogenide nanoparticles in aqueous solution.

These chalcogenide nanoparticles are extremely versatile as follows:

- **Oxides**: TiO$_2$, SiO$_2$, ZnO, ZrO$_2$, MnO$_x$, Fe$_2$O$_3$, Fe$_3$O$_4$, Eu$_2$O$_3$, Tb$_2$O$_3$, WO$_x$, Ti$_2$O,
  Cr$_2$O$_3$, Mo$_2$O$_5$, PdO, CeO$_2$, Cu$_2$O$_3$;
- **Sulfides**: ZnS, Sb$_2$S$_3$, SnS$_2$, CdS, CuS, PbS, Bi$_2$S$_3$, WS$_2$, ZnS, MoS$_2$, In$_2$S$_3$, Ag$_2$S;
- **Selenides**: PbSe, CdSe, HgSe;
- **Telluride**: PbTe, MoTe$_2$;

Ultrasound, a tool to create unique conditions for chemical reactions, has been used to synthesize a broad range of macrostructure materials. Some of these processes have been known for many years and continue to be used and more frequently. A number of excellent reviews exist concentrating on the synthesis of inorganic [68, 115, 116, 181–185] and organic nanoparticles [68, 102, 115], for further reading.

Section 2.3

Synthesis of Metal Nanoparticles by $\gamma$-Ray Irradiation

An array of exciting events in the growth of radiation chemistry was witnessed last century, due to the unique capability of radiation techniques to selectively generate free radicals and ions, with precise and measurable yields. The $\gamma$-ray irradiation technique has some special advantages: it is reproducible and can be applied at ambient temperature, no disturbing chemical impurities are introduced, and the reduction is initiated homogeneously. Therefore, this technique has been widely used to synthesize a broad range of nano-crystalline metals, alloys, metal oxides, metal sulfides, and nano-composites.
2.3. SYNTHESIS OF METAL NANOPARTICLES BY $\gamma$-RAY IRRADIATION

Radiolytic synthesis utilizes high energy rays to activate the water molecules of the solvent to generate highly reactive species including radicals and hydrated electrons, which play essential roles in the subsequent chemical reactions. Due to its high energy, $\gamma$-ray irradiation is a powerful technique for the formation growth of nanoparticles. Figure 2.18 illustrates the mechanism of synthesis of metal nanoparticle by the $\gamma$-ray irradiation technique.

**Figure 2.18:** The mechanism of metal ion reduction in aqueous solution by $\gamma$-ray irradiation (modified from reference [186]).

In the case of water, the initial act of radiolysis is given by the following Equation 2.36-2.39. Importantly, in the $\gamma$-ray irradiation process, in addition to OH• and H•, another important hydrated electrons are generated from...
2.3. Synthesis of Metal Nanoparticles by γ-Ray Irradiation

water.

\[
\begin{align*}
H_2O &\rightarrow H_2O^+ + e^- \\
H_2O^+ + H_2O &\rightarrow OH^- + H_3O^+ \\
e^- + H_2O &\rightarrow OH^- + H^- \rightarrow OH^- + H_2 + OH^- \\
e^- + H_2O &\rightarrow e_{aq}^- 
\end{align*}
\] (2.36)

\(e_{aq}^-\) is the hydrated electron, namely an electron solvated by water. By summarizing these three reactions as one, for the action of high energy radiation on water, the variety of early products typically formed is indicated by the Equation 2.40:

\[
H_2O \rightarrow e_{aq}^- (2.7), \quad H\bullet (0.55), \quad OH\bullet (2.7), \quad H_2(0.45), \quad H_2O_2(0.7) \quad (2.40)
\]

The numbers in parentheses represent the respective G values, which expresses the number of each species formed per 100 eV of energy absorbed by the water.

The hydrated electron, the most intriguing species formed during irradiation, is a strongly reducing agent with a redox potential estimated to be \(E^\circ (H_2O/e_{aq}^-) = -2.87 \text{ V}_\text{NHE}\) \([75]\). It is not surprising that it can react with most metal ions except the alkali and alkaline earth metal ions to obtain zerovalent metals. The hydrated electron may be visualized as an excess electron surrounded by a small number of oriented water molecules and behaves in some ways like a single charged anion of about the same size as the iodide ion. This solvated electron has an intense absorption band around 720 nm in the visible region of the electromagnetic spectrum \([75]\). It is possible to quantify this species by measuring this maximum absorption using spectrophotometry.

As with sonolysis (see Subsection 2.1.5), the γ-ray irradiation process of water also produces very strongly reducing \(H\bullet\) and oxidizing \(OH\bullet\) radicals. The hydrogen atoms have a slightly less powerful reducing potential than the hydrated electrons but usually it dominates the reduction in acidic solution. Due to the fact that its maximum absorption wavelength is less than 200 nm, it is difficult to directly measure the \(H\bullet\) radicals by spectrophotometry. The \(e_{aq}^-\) can convert to \(H\bullet\) radicals by reacting with acid (Reaction 2.41).

\[
e_{aq}^- + H_3O^+ \rightarrow H\bullet 
\] (2.41)
2.3. **Synthesis of Metal Nanoparticles by γ-Ray Irradiation**

H• radical has the ability to readily reduce most inorganic ions that have more positive reduction potentials than itself (See Reaction 2.22), but often at slower rates than the hydrated electrons.

The hydroxyl radical is a strong oxidizing agent and its maximum absorption wavelength is around 225 nm. Possessing such strongly oxidizing power, OH• radical is an undesirable species to have present in solution during the synthesis of metal nanoparticle by radiolytic reduction.

It is often desirable to modify the system to be totally oxidizing or totally reducing and this is achieved by adding solutes which convert specifically one of the primary products of the radiolytic reactions. For example, in order to obtain a totally oxidizing system, the reactions are usually performed under a nitrous oxide atmosphere that acts as a scavenger for the hydrated electrons. The presence of nitrous oxide improves the oxidizing condition by converting the e\textsubscript{aq} into OH•.

\[ \text{N}_2\text{O} + \text{e}\textsubscript{aq} + \text{H}_2\text{O} \rightarrow \text{OH}^- + \text{N}_2 + \text{OH}• \] (2.42)

On the other hand, it is desirable to convert OH• to alcohol radicals in order to enhance the capacity for reduction for metal particle synthesis. As OH• tends to oxidize the ions or the atoms into a higher oxidation state. It therefore hinders the formation of metal nanoparticles. For this reason, it is necessary to add an OH• radical scavenger, such as aliphatic alcohols and formic acids, to covert them to reducing species (Reaction 2.21 and 2.23). The RO• radicals, as oxidation product formed by OH• radical, is unable to oxidize the metal ions, but, in contrast, exhibit strong reducing power.

\[ \text{ROH} + \text{OH}• \rightarrow \text{RO}• + \text{H}_2\text{O} \] (2.21)
\[ n\text{RO}• + \text{M}^{n+} \rightarrow \text{M} + \text{R'} + n\text{H}^+ \] (2.23)

Secondary radicals formed from the reaction of primary radicals are much less reactive than the hydrated electron but can still lead to nanoparticle formation.

Direct absorption of radiation by the metal precursors can be neglected at concentrations less than 1 M [187]. The main reactions involve hydrated electrons, hydrogen atoms and hydroxyl radicals. When the metal ions are exposed to these highly active electrons and radicals, colloids of zerovalent metal atoms are indeed formed, which

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2.3. SYNTHESIS OF METAL NANOPARTICLES BY $\gamma$-RAY IRRADIATION

subsequently coalesce to form nanoparticles.

$$e_{aq}^- + M^{n+} \rightarrow M^{(n-1)+}$$  \hspace{1cm} (2.43)

$$e_{aq}^- + M^+ \rightarrow M^0$$  \hspace{1cm} (2.44)

$$mM^0 \rightarrow M_2 \rightarrow \ldots M_m \ldots \rightarrow M_{agg}$$  \hspace{1cm} (2.45)

$M^{n+}$ represents multivalent metal ions, possibly complexed by a ligand. Reaction 2.43 demonstrates that multivalent ions are reduced by multistep reactions. $m$ is the number of aggregation of a few units and $M_{agg}$ is the aggregate in the final stable state. When two transition metal atoms encounter each other, a very strong energy bond between these two atoms is developed to form a dimer. It is possible, however, that a dimer bond is formed between an atom and an excess ion:

$$M^0 + M^+ \rightarrow M_2^+$$  \hspace{1cm} (2.46)

After a multi-step process, these species may coalesce into a cluster $M_{m}^{x+}$ (see Figure 2.18).

Polymer or surfactant molecules present in the system act as cluster stabilizers by providing electrostatic repulsion and steric hindrance between nanoparticles (See Figure 2.11). Usually, these kind of molecules have a high affinity for metals which enables them to anchor to the cluster surface while the long chain prevents the cluster from coalescing with neighbors. Due to the presence of stabilizer, transfer of the electron from the solvent to the metal ion may involve a transition state. The stabilizer molecules on the metal ion may act as bridges for electron transfer.

The specificity of the radiation-induced synthesis of metal nanoparticles is due to its ability to generate radiolytic species of strongly reducing potential, more negative than that of any ion and any charged cluster. This fact requires that the redox potential of the reducing agent is so negative that the free metal ions are generally reduced at each encounter. In addition to the reducing power of the radiolytic products, the features of the nuclearity-dependent potential play a crucial role in the progressive nucleation, coalescence and growth of nanoparticles. The mechanism of the growth process leads to the final structure and size of the metal nanoparticles. Because of the ability to transfer electrons more readily than the corresponding bulk metals, the redox potential of these
2.3. SYNTHESIS OF METAL NANOPARTICLES BY $\gamma$-RAY IRRADIATION

Micro-aggregates is lower than that of the bulk metals. In other words, the redox potential of metal atoms or clusters is determined by their size and it increases with nuclearity. The reactions of ion association with atoms or clusters ($M_x^{m+}$) play an important role in the cluster growth by competing solvated electrons, hydrogen atoms and alcohol radicals with the free ions. This competition usually is controlled by the rate of reducing radical formation. At the same time, the growth process undergoes another competition with reverse oxidation by the solvent and radiolytic proton.

$$M^0 + H^+ \rightarrow M^+ + H\bullet$$  \hspace{1cm} (2.47)
$$H\bullet + H\bullet \rightarrow H_2$$  \hspace{1cm} (2.22)

This second competition may inhibit the overall reduction process and finally lead to failure to form stable particles. It is preferable to scavenge the protons by adding a base to the solution and to favor the coalescence [154, 188].

The radiolytic reduction method is perhaps most useful when enlarging colloidal metals or layering another metals over another to form core-shell type arrangements. The ratio of nucleation rate to growth rate determines the size and the number of nanoparticles. Usually, the redox potential of a free metal ion is much higher than that of a metal ion already adsorbed on a surface. Thus, the nanoparticles formed previously may act as catalysts for metal ion reduction by interaction with radicals and stored electrons. This pathway provides a possible method to form core-shell structured bimetallic nanoparticles (Reaction 2.48 and 2.49) [186].

$$M^0 + M^+ \rightarrow (MM')^+ \rightarrow M^0 + M'^+$$  \hspace{1cm} (2.48)
$$M_x^m + M_y^{m+} \rightarrow (M_{m+1}^{m-1} M_n^y)^{x+} \rightarrow (M_{m+1}^{m-1} M_n^y)^{x+} + M'^+$$  \hspace{1cm} (2.49)

In some cases, mixed coalescence and association of atoms can occur due to the control by the frequent encounters instead of the differences of redox potentials after the individual atoms are formed. In these cases, the pathway is
2.4. Application of Sonophotocatalysis in Environmental Remediation

likely to build alloyed clusters [186].

\[
\begin{align*}
M^0 + M^0 & \rightarrow (MM') \\
(MM') + M & \rightarrow (M_2M') \\
(M_mM'_n)^{x+} + M^+ & \rightarrow (M_{m+1}M'_n)^{(x+1)+} \\
(M_{m+1}M'_n)^{(x+1)+} + e_{aq}^{-}/R\cdot & \rightarrow (M_{m+1}M'_n)^{x+}/(M_{m+1}M'_n)^{x+} + R^+ 
\end{align*}
\]

Section 2.4

Application of Sonophotocatalysis in Environmental Remediation

No one questions the notion that this century has seen a phenomenal growth in industrial and agricultural activity which has given rise to a significant increase in atmospheric and water pollution. We know with confidence what has made disasters and health problems more serious than they had been before: the emission of waste chemicals and green house gases from human industrial activity. World-wide awareness of the global environmental crisis is growing intensely on a daily basis.

A great many scientists keep the long-lasting wish of hunting for simple but efficient methods to deal with the problems of a deteriorating human living environment, especially that of aqueous pollution. In line with this environmental issue, over the last few decades, the novel photocatalytic properties of nanometer-sized TiO\textsubscript{2}, especially its surface and interfacial effects, quantum size effect and quantum tunneling effect, has attracted many governments to spend significant funds to support researchers on photocatalytic oxidation processes. This is because of the following properties of semiconductors: (i) inexpensive, (ii) non-toxic, (iii) high surface area, (iv) broad absorption spectra with high absorption coefficients, (v) tunable properties which can be modified by size reduction, doping, sensitizers, etc., (vi) facility for multi-electron transfer processes and (vii) capable of extended use without substantial loss of photocatalytic activity [189].

Recently, the introduction of ultrasound to assist the photocatalytic degradation process has attracted considerable attention, as the photocatalytic oxidation was enhanced in the presence of the ultrasonic irradiation.
2.4. Application of Sonophotocatalysis in Environmental Remediation

*Sonophotocatalytic reaction* implies a sequential photocatalytic reaction and ultrasonic irradiation or the simultaneous irradiation of ultrasound and UV light with a photocatalyst in the presence of oxygen or other chemical oxidants. Power ultrasound induces chemical reactions and physical effects via highly active radicals which are produced during the collapse of bubbles.

2.4.1. Sonolysis

Ultrasound, an efficient mean of activation in chemistry and elsewhere, has been employed for decades with varied success. Sonochemistry shares with sustainable chemistry such aims as the use of less hazardous chemicals and solvents, a reduced energy consumption and an increased product selectivity. It is a new and rapidly growing research field with broad environmental applications, such as waste water treatment, industrial waste treatment, etc. Sonochemical treatment typically operates at ambient conditions and does not require the addition of extra chemicals. Sonochemistry has recently been classified as advanced oxidation process. The desirability of sonolysis for environmental remediation lies in its low maintenance requirements and the low energy efficiency of alternative methods.

Since the sonolysis of an organic liquid was first reported [190] in 1953, it has been recognized that powerful ultrasound has great potential for use in a wide variety of processes in environmental science and allied fields [72, 107, 191–193]. It is well known that the primary radicals produced during cavitation have the potential to decompose organic molecules or act as essential intermediates for the degradation of pollutants. Thus, sonolysis has been looked upon as potential treatment which is capable of degrading the potentially hazardous chemical compounds such as chlorinated hydrocarbons, aromatic compounds, textile dyes, phenolic compounds and esters into harmless substances, such as carbon dioxide and inorganic ions as final products.

There are a number of factors which are able to affect the sonochemical degradation in environmental remediation (shown in Figure 2.19). According to the mechanism of cavitation, there are a number of factors already mentioned that affect bubble cavitation (Section 2.1), such as ambient atmosphere, temperature, dissolved gases, pre-existing nuclei, frequency and intensity of ultrasound. All these factors can contribute to influencing the efficiency of sonochemical degradation for environmental remediation.
2.4. APPLICATION OF SONOPHOTOCATALYSIS IN ENVIRONMENTAL REMEDIATION

The nature of ultrasonic irradiation plays an significant role in chemical decontamination, but the mode of sonochemical degradation of organic compounds in aqueous solution is determined by these compounds’ physical and chemical properties. Similar to the synthesis of metal nanoparticles, there are two ways in which the cavitation bubble can bring two conditions for the organic pollutants. If the chemical is volatile, this property enables it to enter into the bubble and be destroyed through the extreme conditions generated on collapse. In the case of chemicals remaining in the aqueous phase, the cavitation bubble acts as a source of highly active radicals which enter the bulk solution and attack the pollutants [10, 194]. A typical example is the research work of Singla et al. [195, 196] on sonochemical degradation of benzoic acid. They investigated the influence of solution pH on the efficiency of sonolysis of benzoic acid in aqueous solutions and the results indicated that at two different

Figure 2.19: The influence of a number of factors on sonolysis of organic pollutants.
2.4. Application of Sonophotocatalysis in Environmental Remediation

pH values, the degradation of benzoic acid proceeded by different pathways. This is due to the fact that the neutral form of benzoic acid exhibits more volatile and surface active than its ionic form. The volatility property allows the compounds to evaporate into the cavitation bubble and decompose pyrolytically. The products under extremely high temperature are normally methane, ethane and acetylene. The surface active property enables the compounds to contrate at the interface of bubble and water. This advantageous position enhances the encounter probabilities with primary radicals, and consequently improves the rate of decomposition. With this pathway, the products are hydroxylated compounds, such as catechol and quinol.

In addition to the volatility and surface active properties, other properties of the organic pollutants can also contribute to the pathways of sonochemical decomposition by direct or indirect means, such as viscosity [197], molecular weight [198] and polarity, hydrophobicity [199]. These factors are capable of changing the molecular behaviors of cavitation bubble in some extent and consequently affect the degradation processes.

The presence of some ions or molecules or solid particles also plays important role in sonolytic degradation of organic pollutants. The addition of salt can be taken as an example. Addition of NaCl increases the ionic strength of the aqueous phase which pushes pollutant molecules from the bulk aqueous phase toward the bubble interface. This provides an organic compound a greater chance to capture primary radicals and so be decomposed. At same time, the presence of salt can decrease the vapor pressure and increases the surface tension [200–203]. According to recent reports from Ashokkumar and coworkers [11, 81, 204], another possible reason is that the addition of salt has the effect of reducing the strength of the electrostatic repulsion between the charged surfactant-like organic compounds and hence bring the bubbles closer, increasing the probability of coalescence which is likely to lead to enhanced degradation. In addition, the presence of Fe$^{2+}$ [205–207] results in a faster reduction of organic pollutants as these ions can function as Fenton reactions.

Another group of interesting additives are chlorinated compounds which are able to drastically enhance the ultrasonic degradation of organic pollutants [208–214]. This drastic enhancement is due to the formation of additional oxidizing species which is highly beneficial for the oxidation of non-volatile pollutant species. A popular additive, carbon tetrachloride, can be taken as an example. The possible reactions in the cavitation bubbles
2.4. Application of Sonophotocatalysis in Environmental Remediation

demonstrating the role of CCl$_4$ are shown below:

$$
\text{CCl}_4 \rightarrow \text{CCl}_3 + \text{Cl} \\
\text{CCl}_3 + \text{O}_2 \rightarrow \text{OOCCl}_3 \\
\text{H}_2\text{O} + \text{OOCCl}_3 \rightarrow \text{COCl}_2 + \text{HOCI} \\
\text{Cl} + \text{Cl} \rightarrow \text{Cl}_2 \\
\text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{HOCI} + \text{HCl}
$$

Under intensive ultrasonic irradiation, carbon tetrachloride is decomposed to release of Cl$\bullet$, which is capable of taking part in the desired reactions. In addition to being directly involved in an oxidation process, Cl$\bullet$ is likely to form additional oxidizing agents, such as Cl$_2$ and HOCI. These oxidizing intermediates are much more stable than the free radicals and hence accelerate the oxidation of organic pollutants.

The addition of solid particles, such as TiO$_2$ [215–221], ZnO [222], Al$_2$O$_3$ [223], exfoliated graphite [224, 225], coal ash [226] even sand [227], have also attracted considerable interest in the environmental application of sonochemical degradation [228]. The mechanism for intensification is still poorly understood, but there are several possible contributions of the existence of particle to ultrasonic cavitation. The presence of solid particles can supply crevices to provide additional nuclei; The rough wall of particles provides the sites for unsymmetrical collapse, which can lead to the formation of bubble nuclei from the fragmentation of large bubbles; the frequent collisions between the particles can enhance the mechanochemical activation of a particle surface; the existence of particles can redistribute the ultrasonic field to increase the cavitational active volume; the oxygen vacancies on the particle surface can also play an important role in producing cavitation bubbles, which lead to a greater OH$\bullet$ radicals formation and hence high decomposition efficiency.

2.4.2. Photocatalysis

Photocatalysis is mostly thought of in terms of the photodegradation of molecules initiated either by oxidative or by reductive processes. The big breakthrough, of course, came when Fujishima and Honda [229] showed how
TiO$_2$ would be used as photocatalyst for the decomposition of water in 1972. Soon after 1977 Frank and Bard examined the possibilities of using TiO$_2$ to decompose cyanide in water [230]. Since then, thousands of scientists have made use of electron and hole transitions in semiconductor colloids and explored complicated aspects of pollutant degradation on the surface of semiconductor particles. By recognizing how to degrade pollutants via sunlight, heterogeneous photocatalysis has proved to be of real interest as an efficient tool for degrading both aquatic and atmospheric organic contaminants.

Heterogeneous photocatalysis, an emerging treatment technology, focuses on the acceleration of a photoreaction in the presence of a semiconductor photocatalyst. Titanium dioxide is close to being an ideal photocatalyst due to its advantages including the operation at ambient conditions and the possible use of solar irradiation, while the catalyst itself is relatively inexpensive, readily available, non-toxic and chemically stable (see Appendix B for more details). The articles by Hoffmann et al. [231], Fujishima et al. [232, 233] and Carp et al. [234] provide a comprehensive overview of photocatalysis for environmental applications.

### 2.4.2.1. Mechanism of Photocatalysis

Compared to the mechanism of ultrasonic irradiation, the highly reactive hydroxyl radicals are generated by the light energy in the process of photocatalytic activity. Photocatalytic reaction is initiated when an electron excited by the photon energy is promoted from the valence band of the semiconductor photocatalyst to the empty conduction band and at same time leaves a hole in the valence band. This principle requires the energy of the photon is equal to or larger than the band gap of the semiconductor. It is well known that the minimum energy of the light required to make the material electrically conductive is equal to the band gap energy of the semiconductor. The threshold or ideal wavelength $\lambda_g$ corresponding to the bandgap energy $E_g$ of most semiconductor catalysts can be determined by Equation 2.59:

$$\lambda_g(\text{nm}) = \frac{1241}{E_g(\text{eV})}$$  \hfill (2.59)

As the bandgap of the anatase TiO$_2$ semiconductor catalyst is 3.2 eV, the threshold for the generation of electron-hole pairs can be calculated at 387 nm using the Equation 2.59. That means when TiO$_2$ is exposed to light of
2.4. Application of Sonophotocatalysis in Environmental Remediation

wavelength $\lambda \leq 387$ nm, the electrons from the valence band are promoted to the conduction band resulting in the simultaneous generation of positive (oxidant) holes in the valence band. These holes can react with water to produce highly reactive hydroxyl radicals (see Figure 2.20).

Figure 2.20: Schematic photocatalytic processes of photon activated TiO$_2$ semiconductor in environmental remediation.
2.4. APPLICATION OF SONOPHOTOCATALYSIS IN ENVIRONMENTAL REMEDIATION

The mechanism of photocatalysis involves the following reactions:

\[
\begin{align*}
\text{TiO}_2 + h\nu & \rightarrow h^+ + e^- \\
h^+ + \text{OH}^- & \rightarrow \text{OH}\cdot \\
h^+ + \text{H}_2\text{O} & \rightarrow \text{OH}\cdot + \text{H}^+ \\
\text{O}_2 + e^- & \rightarrow \text{O}_2\bullet^- \\
\text{O}_2\bullet^- + \text{H}^+ & \rightarrow \text{HO}_2\bullet \\
\text{HO}_2\bullet + \text{HO}_2\bullet & \rightarrow \text{H}_2\text{O}_2 + \text{O}_2
\end{align*}
\]

Both the holes and the hydroxyl radicals are very powerful oxidants, which can be used to oxidize most organic materials. The redox potential for photogenerated holes is +2.53 V relative to the standard hydrogen electrode (SHE) [235]. After reaction with water, these holes can produce hydroxyl radicals, whose redox potential is only slightly decreased, but still more positive than that for ozone. The redox potential for conduction band electrons is -0.52 V [235], which is in principle negative enough to evolve hydrogen from water. As mentioned before, the OH• radicals are very reactive and attack the pollutant molecule to degrade it into mineral acids including carbon dioxide and water.

2.4.2.2. Enhancements for Harvesting Light

Although photocatalytic degradation is one of the hot research areas in a variety of disciplines, almost all these researches have only one purpose: highly effective and efficient photocatalytic system [232]. Roughly all the effects can be divided into four prominent classes: to make an improvement of the photocatalysts intrinsic properties, modification of the photocatalyst, optimization of working conditions and combine with an other advanced oxide processes (shown in Figure 2.21 with different background colors). Among all these enhancements, the upper half of them in Figure 2.21 focus on the enhancement on the photocatalyst’s properties, such as maximization of light absorption and surface area enlargement and so on. It is worth noticing that all the enhancement in these four categories are not independent of each other. Once one factor changes, it is possible that another or several others will alter accordingly. It is therefore important to consider the relationship between these different parameters.
2.4. Application of Sonophotocatalysis in Environmental Remediation

Figure 2.21: Factors influencing photocatalytic activities of semiconductor photocatalyst in the application of environmental remediation can be classified into four categories, shown in four different background colors: (a) Cyan: natures of photocatalyst; (b) Red: modification of photocatalyst; (c) Green: conditions during photocatalytic degradation; (d) Yellow: combination with other advanced oxide processes.

The core part of photocatalytic reactions is the photocatalyst which plays an essential role in controlling the efficiency of the whole procedure. Consequently, the synthesis of prominent photocatalyst was always significantly highlighted in the whole internal improvement. Based on the mechanism of photocatalysis, the photocatalytic activity of the photocatalyst must be controlled by three basic factors: its light absorption property, the rates of re-
A broad range of research has been dedicated to investigating the influence of operation conditions (including reactors) on the efficiency of photocatalytic processes. These effects include the reactor design, adjustment of operation conditions, different organic compounds, the initial concentration of pollutants, and so on [231, 239–241].

The category of external enhancement is concentrated on combining photocatalysis with another advanced oxidation process in order to attain a high performance system [242–244]. These combinations tend to improve the photocatalytic degradation efficiency by shortening the reaction time in respect to the individual processes or cut the cost with respect of heterogeneous photocatalysis alone. These combined systems usually take one processes’ potential advantages and enhance another deficiencies. Generally, these coupling systems depend on the type of organic pollutants being decomposed. The most desired outcome is the synergistic effect which gives rise to an improvement of the efficiency of the photocatalytic process.
Among these oxidation techniques, the coupling system that combines photocatalysis with ultrasound irradiation is more attractive due to its effectiveness. The combination of photocatalysis with sonolysis is a recent advanced oxidation technique targeted at improving the photocatalytic process. A number of research groups have examined the combination of ultrasound and photocatalysis for environmental remediation [244–248]. The simultaneous use of both advanced oxide techniques for degradation of organic pollutants in aqueous solution can be more effective than their individual process.

According to the mechanism of sonolysis (see Reaction 2.8) and photocatalysis (see Reaction 2.60-2.62), both these advanced oxide processes are effective in the application of environmental remediation due to the formation of the same species, \( \text{OH}^- \) radicals. However, distinct mechanisms take effect in these two processes: photocatalytic reaction may occur through direct electron transfer from the organic compounds to the semiconductor oxide and sonochemical degradation may selectively degrade less hydrophilic compounds through pyrolytic degradation and radical reactions. The evidence from products analysis have further confirmed the different pathways the two oxide process undergo. The specificity of each process, such as temperature and pH in the cavitation bubbles in ultrasound irradiation and the presence of electron-hole pairs in photocatalysis, leads to the formation of different intermediate products and different pathways.

The results of most studies show that ultrasonic oxidation is effective in the treatment of most liquid-phase pollutants but it is highly energy intensive and not economical when used alone, in particular, for decomposing complex pollutants or mixtures of pollutants. As mentioned in the Subsection 2.4.1, the solid-phase photocatalyst nanoparticles may enhance the cavitation phenomenon by introducing additional nuclei and redistributing the sound field. In addition to the effect of photocatalyst particles, ultrasound also has the potential to form more oxidizing agents, \( \text{OH}^- \) radicals, from cavitation. When the two advanced oxidation processes are operated simultaneously, more free radicals are likely to be available for the reaction with the pollutants and the synergistic effect is to increase the rates of reaction.

On the side of photocatalysis, the acceleration of reaction is determined not only by chemical effects of ultrasound irradiation, but also by physical effects brought by the ultrasonic waves. The vibrating wave, the cleaning
2.4. APPLICATION OF SONOPHOTOCATALYSIS IN ENVIRONMENTAL REMEDIATION

effect of ultrasound and its surface activation play important roles in the enhancement of catalytic reactions. The effectiveness of sonophotocatalysis can be highlighted as follows:

- Ultrasound also provides an extra source of OH• from cavitation for the combined system;
- The partial blockage of the active sites of the photocatalyst by the degradation intermediates can be inhibited by the cleaning effect of ultrasound (acoustic cavitation generates a number of physical effects, such as shear forces, turbulence, micro-streaming, etc., which help regeneration the catalyst surface as the collapse of a cavitation bubble near a solid surface can result in a high velocity jet of fluid directed towards the surface);
- When the catalyst or the pollutant is in the form of a powder or an agglomerate, ultrasonic vibration is able to disperse the material uniformly, thereby increasing the available surface area for reaction.
- Ultrasound is able to enhance mass transfer towards the liquid-solid interface;
- Ultrasound is capable of accelerating the adsorption activity of reactant on the photocatalyst;
- Sonication is likely to decompose the hydrophobic part of the pollutant compound, which is unlikely to occur under photocatalysis.

For a given pollutant, normally it has hydrophobic and hydrophilic parts and both of them control the effectiveness of degradation. It is not easy for photocatalytic degradation to decompose the hydrophobic part of a molecule. As these hydrophobic parts tend to concentrate at the bubble surface, use of ultrasound is capable of degrading it easily during cavitation. On the another hand, the hydrophilic parts can adsorbed on the surface of photocatalyst and be decomposed by photocatalysis. As a result of these effects, ultrasound plays a profound role in the global rates of the sonophotocatalytic process. In summary, sonophotocatalytic oxidation results in the elimination of the main disadvantages of photocatalytic process by ultrasonic induced physical turbulence.
2.4. Application of Sonophotocatalysis in Environmental Remediation

2.4.3.1. Sonophotocatalytic Degradation of Azo Dyes

The term azo dye is applied to those synthetic organic colorants which have the chromophoric azo group (−N=N−). The presence of residual color, high levels of electrolytes, toxic substances and cancer-suspect agents in azo dye waste-water has drawn considerable attentions to mineralization of dyes which pose unacceptable environmental risks. Numerous investigations have examined the mineralization of azo dye pollutants by ultrasound and photocatalysis.

A number of different photocatalysts have been used in the sonophotocatalytic degradation of azo dyes in aqueous solution, including TiO$_2$ [249–251], Ag/TiO$_2$ [252], TiO$_2$-Na$_5$PV$_2$Mo$_{10}$O$_{40}$ [253], BiVO$_4$ [254], ZnO [255]. All of them contributed positive effects on the sonophotocatalytic degradation of organic pollutants in aqueous solutions. A review of Reddy et al. deals with TiO$_2$-loaded zeolites and mesoporous materials in the sonophotocatalytic decomposition of aqueous organic pollutants and emphasize the photocatalyst support plays an important role in governing the whole degradation efficiency [256].

Similar to sonolysis (Figure 2.19) and photocatalysis (Figure 2.21), the factors of each processes have been systematically investigated, such as initial concentration of organic pollutants, dosage of photocatalyst, pH, the existence of iron ions, gas atmosphere, ultrasonic intensity and frequency, UV transmission and so on. All the factors play the same role of individual process in the combined system. It is necessary to consider them carefully to arrive at an overview point.

2.4.3.2. Sonophotocatalytic Degradation of Aromatic Compounds

Due to their wide use and potential hazardous risks, aromatic compounds gained interest for applying advanced oxidation processes for their elimination.

Because of the molecular structure, usually the aromatic compounds posses bipolarity: hydrophobicity and hydrophilicity. The sonophotocatalytic degradation of bisphenol A (BPA) can be taken as a good example [257]. Under the ultrasonic irradiation or photocatalytic degradation, bisphenol A was decompose into hydrophobic and hydrophilic products. Thus, a combined system, consisting of sonolysis for hydrophobic and photocatalysis for hydrophilic, is a promising alternative for the complete elimination of the organic compound. Peller et al. arrived...
2.4. APPLICATION OF SONOPHOTOCATALYSIS IN ENVIRONMENTAL REMEDIATION

at the same conclusions during the degradation of chlorinated aromatic compounds [258].

The concentration of photocatalyst plays an important role in the synergistic effect. The synergistic effect may depend on the dosage of photocatalyst [257]. Because of its double function in photocatalysis and sonolysis, it is necessary to choose a certain concentration of photocatalyst in order to gain photocatalysis benefits from an ultrasonic action without generating a detrimental effect on cavitation activities.

An interesting studies on the influence of Cl\(^-\) anions on synergistic effects in a degradation process was carried out by Chen et al [259]. The addition of salt can increase the ionic strength of the aqueous phase, which drives the organic molecules close to the bubble surface, where the primary radical are concentrated. The surface tension is also able to affect the nucleation process and cavitation threshold. Consequently, the presence of Cl\(^-\) can enhance the overall sonochemical degradation rate. However, the existence of Cl\(^-\) anions introduced major negative effects on the photocatalytic process due to the undesirable Cl\(^-\) ions which adsorbed onto the positively charged TiO\(_2\) particle surface at low pH and hence decrease the efficiency of photocatalytic degradation.

Although advanced oxide processes were found to be effective in mineralizing many organic compounds reducing the potential toxicity and harm in many cases, they could also cause the formation of harmful by-products in the effluent [250, 260]. Therefore, it is necessary to optimize the efficiency of the degradation process to insure a clean pathway during degradation of organic compounds. This requires attention not only on the economics of the process but also on the final purpose of the whole advanced oxide procedure. The synergistic effects of acoustics and photocatalysis have not been adequately explored and exploited, and the mechanisms involved are still not completely resolved. In my doctoral research, the products analysis and the applications of ultrasound in environmental remediation focusing on the simultaneous or hybrid use of ultrasonic irradiation and photocatalysis in aqueous solutions, namely, sonophotocatalytic oxidation process, have been experimentally investigated.
When the gong sounds ten in the morning and I walk to school by our lane.

Every day I meet the hawker crying, "Bangles, crystal bangles!"

There is nothing to hurry him on, there is no road he must take, no place he must go to, no time when he must come home.

I wish I were a hawker, spending my day in the road, crying, "Bangles, crystal bangles!"

......

Vocation, Rabindranath Tagore

......

When I studied sonochemistry, I wish I were a hawker, spending my days in the Victoria Market, crying, "Bubble, bubble, single fresh bubble, one dollar each!".

......

Experimental Details

This experimental chapter is divided into three sections, synthesis of metallic/bimetallic nanoparticles, electrocatalytic performance test and sonophotocatalytic degradation. The specific conditions for each experiment are described in the discussion chapters or stated in the captions of the corresponding figures and tables.
3.1. SYNTHESIS OF METALLIC/BIMETALLIC NANOPARTICLES

The content of this section relate mainly to Chapter 4 and Chapter 5 that deal with the synthesis and characterization of metallic/bimetallic nanoparticles.

3.1.1. Materials

The metal precursor salts, ruthenium chloride (RuCl₃) and potassium tetrachloroplatinate (K₂PtCl₄), were purchased from Sigma-Aldrich and used without further purification.

The stabilizers used in the metallic nanoparticle synthesis, polyvinyl-2-pyrrolidone (PVP, MW = 55,000) and poly(sodium 4-styrenesulfonate) (PSS, MW = 70,000), were purchased from Sigma-Aldrich. Sodium dodecyl sulfate (SDS) was purchased from BDH Laboratory Supplies (Merck Pty. Ltd.).

1-propanol (> 99.5% purity) was supplied by Lancaster. Perchloric acid (AR grade, > 70% purity) was obtained from Sigma-Aldrich. Sodium borohydride (NaBH₄) (> 96% purity) was purchased from BDH Laboratory Supplies (Merck Pty. Ltd.).

All chemicals were used as received without further purification. Ultra pure water (> 18.6 MΩ/cm at 25 °C) provided by a Milli-Q system (Millipore) was used to make the respective aqueous solutions of required concentrations.

3.1.2. Synthesis of Metallic/Bimetallic Nanoparticles

3.1.2.1. Sonochemical Synthesis

Sonochemical preparation experiments were conducted using an ultrasound transducer (L-3 Communications, ELAC Nautik GmbH, diameter of oscillator: 54.5 mm) at a series frequencies of 213, 355, 647 and 1056 kHz and operated in continuous mode. Figure 3.1 displays the equipment for the preparation of nano-metallic particles. The sonication vessel used to house the solution (250 mL) allowed the solution to be cooled to a constant temperature.
3.1. **Synthesis of Metallic/Bimetallic Nanoparticles**

(23±3°C) by passing cold water through it continuously. Solutions were prepared to a total volume of 10 mL and placed in 15 mL vials fitted with rubber septa. Two vials were immersed together in the bulk liquid. In order to enhance the cavitation bubble temperature, argon gas was sparged through the solution for 15 min before sonication and maintained above the solution throughout the experiments.

![Equipment for the preparation of metallic nanoparticles](image)

**Figure 3.1:** Equipment for the preparation of metallic nanoparticles.

For work conducted at 20 kHz, a titanium horn with a stainless steel tip of length 5.5 cm and diameter of 2 cm was employed. The horn was coupled to a Branson Digital Sonifer (Model 450-D). A 250 mL sonication vessel
3.1. SYNTHESIS OF METALLIC/BIMETALLIC NANOPARTICLES

with water jacket was used to hold cold water. A 50 mL pyrex beaker was immersed in the bulk water.

For work conducted at 630 kHz, the sonochemical synthesis experiments were carried out using an Ultrasonic Energy Systems (Panama City, FL) setup. A specially designed glass vessel (approximately 700 mL) was attached to the transducer with silicon rubber. The actual solution (10 mL) was placed in a 15 mL vial which was dipped in a 700 mL ice-water mixture (0 °C). All the experiments were carried out in a saturated argon atmosphere in order to optimize the sonochemical reaction.

3.1.2.2. Chemical Synthesis

A fresh 5 mL aqueous solution of 150 mM sodium borohydride was made just before each synthetic experiment. A certain volume of this reducing agent NaBH₄ was added with 10 µL on each addition with stirring. UV-vis spectra were used to monitor the progress of synthesis after each addition of sodium borohydride. Slight heat treatment (80 °C) for 10 mins for each sample synthesized by the chemical method was carried out to remove any remaining sodium borohydride.

3.1.2.3. Radiolytic Synthesis

A γ-ray source (Co-60) was used to synthesize PtRu bimetallic nanoparticles. The absorbed dosage rate applied was 0.0144 Gy/min and the solutions were irradiated as soon as prepared. Nitrogen was bubbled through the solution for 30 min to remove oxygen, and the solution was irradiated under atmosphere pressure at ambient temperature. For simultaneous radiolytic synthesis, the irradiation time was 60 min. For sequential radiolytic synthesis, the Pt(II) precursor solution was first irradiated for 30 min and continued for another 30 min after addition of Ru(III) solution.
3.1. SYNTHESIS OF METALLIC/BIMETALLIC NANOPARTICLES

3.1.3. Methods

3.1.3.1. Power Calibration

A calorimetric method was adopted to estimate the applied ultrasound power for each sonication experiment. A 250 mL solution of Milli-Q water was sonicated for 1 min and the temperature changes recorded to calculate the power absorbed by the solution. With the assumption that an increase in temperature originates from the ultrasound and this is the only energy source, the ultrasound power and intensity can be approximated by considering the volume of the solution and the area of the transducer plate, using the heat capacity of water.

3.1.3.2. UV-vis spectrophotometry

The sonication was stopped at various times and absorption spectra (190-1100 nm) obtained using a 1 mm quartz cell on a Varian spectrophotometer (Cary Bio50) in order to check the progress of the particle synthesis.

3.1.3.3. Transmission Electron Microscopy and Energy Dispersive X-ray

Transmission electron microscope (TEM) images of the sonochemically prepared metal colloids were obtained on a Philips CM-10 transmission electron microscope at a voltage of 100 kV. To obtain the TEM images, a single drop of the colloidal solution was deposited on a 3 mm carbon supported Cu grid. Higher-resolution characterization of the structure and morphology of the metallic/bimetallic nanoparticles was achieved using FEI Tecnai TF20 (FEI Company) transmission electron microscope operated at 200 keV. Energy-dispersive X-ray (EDX) analysis was used to determine the elemental composition of the colloidal particles.

3.1.3.4. X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) was used to detect the presence or absence of oxides on the surface of bimetallic nanoparticles. XPS measurements were performed using an Axis Ultra spectrometer (Kratos Analytical...
3.2. Evaluation of Electrocatalytic Performance

This section focuses on the experimental details pertaining to Chapter 5, which concerns the electrocatalytic performance testing using cyclic voltammetry.

3.2.1. Material

Tetrahydrofuran (THF) and methanol (AR grade, > 99.9%) were purchased from Sigma-Aldrich. Sulfuric acid (H₂SO₄) was obtained from BDH Laboratory Supplies. Carbon fiber paper (Toray paper) and conducting glass were purchased from Fuelcellstore. Both were cut into 5 cm × 0.5 cm pieces.

3.2.2. Electrode Preparation

The metallic colloids were centrifuged at a speed of 10,000 r/min. The sample was subjected to repeated cycles of washing and centrifuging to removed excess ions. The metal nanoparticles were extracted by removal of the...
3.2. Evaluation of Electrocatalytic Performance

top aqueous solution and finally dispersed in tetrahydrofuran (THF) to obtain an approximate concentration of 50 µg/mL. An ultrasound bath was used to disperse the suspension for 10 min to obtain a uniform particle distribution.

Electrophoretic deposition was adopted to fabricate a fuel cell electrode assembly in order to prepare a uniform cover on the carbon Toray paper [261–263]. The electrophoretic deposition was operated in DC mode in a 100 V/cm electric field supply by a Fluke 415 power supplier. The Toray electrode was kept at a distance of 4 mm from a counter electrode (a conductive glass electrode). The deposition of the nanoparticles could be visibly observed as the metallic nanoparticles were driven to the Toray paper electrode and the solution became colorless. The deposition area of the catalyst nanoparticles was restricted to 1.5 cm × 0.5 cm (total area: 0.75 cm²).

The electrodes were either dried in a normal atmosphere or in an oven at 100 °C and reduced pressure for 1 hour prior to the electrocatalytic performance test.

3.2.3. Cyclic Voltammetry

Half cell reactions were carried out in a conventional three-electrode cell using Pt foil as the counter electrode and a standard calomel electrode (SCE) as the reference electrode (shown in Figure 3.2). An electrolyte solution containing 0.1 M H₂SO₄ was used to measure the electrochemical active surface area of the corresponding catalyst. During the methanol oxidation experiment, a mixture of 1 M methanol and 0.1 M H₂SO₄ was used as the electrolyte solution. Both of these solutions were sparged with nitrogen gas for 15 min to remove dissolved oxygen from the solution.

Five consecutive linear potential sweep cycles at 50 mV/s for electrochemical active surface area determination and 20 mV/s for methanol oxidation from -0.1 to 1 V_{SCE} (relative to a saturated calomel reference electrode) were used to stabilize the cyclic voltammetry curves.
3.2. Evaluation of Electrocatalytic Performance

![Three-electrode cell test device.](image)

**Figure 3.2**: Three-electrode cell test device.
3.3. ADVANCED OXIDATION PROCESS OF ORGANIC POLLUTANTS

Section 3.3
Advanced Oxidation Process of Organic Pollutants

This section concerns the sonolytic, photocatalytic and sonophotocatalytic degradation of organic pollutants, corresponding to Chapter 6 and Chapter 7.

3.3.1. Materials

Methyl orange (MO, GR) was purchased from Tokyo Chemical Industry Co., Ltd. p-Chlorobenzoic acid (PCBA, > 97%) and p-aminobenzoic acid (PABA, > 99%) were obtain from Sigma-Aldrich. p-hydroxybenzoic acid (PHBA, > 99%) was purchased from BDH Laboratory Supplies (Merck Pty. Ltd.).

All chemicals were of analytical reagent grade and used without further purification. Selected physical and chemical properties of the compounds are listed in Table 3.1. For each degradation experiment, a 250 mL solu-

Table 3.1: Four organic pollutants using in advanced oxidation processes and their physical and chemical properties.

<table>
<thead>
<tr>
<th>Name</th>
<th>MO</th>
<th>PCBA</th>
<th>PABA</th>
<th>PHBA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C_{14}H_{14}N_{3}NaO_{3}S</td>
<td>C_{7}H_{5}ClO_{2}</td>
<td>C_{7}H_{7}NO_{2}</td>
<td>C_{7}H_{6}O_{3}</td>
</tr>
<tr>
<td>Structure</td>
<td><img src="image1" alt="MO Structure" /></td>
<td><img src="image2" alt="PCBA Structure" /></td>
<td><img src="image3" alt="PABA Structure" /></td>
<td><img src="image4" alt="PHBA Structure" /></td>
</tr>
<tr>
<td>Molecular Weight</td>
<td>327.33</td>
<td>156.57</td>
<td>137.14</td>
<td>138.12</td>
</tr>
<tr>
<td>Solubility</td>
<td>soluble</td>
<td>very slightly</td>
<td>slightly</td>
<td>slightly</td>
</tr>
<tr>
<td>pK_{a1}</td>
<td>3.2-4.4</td>
<td>3.98</td>
<td>2.42</td>
<td>4.58</td>
</tr>
<tr>
<td>pK_{a2}</td>
<td>-</td>
<td>-</td>
<td>4.85</td>
<td>9.23</td>
</tr>
</tbody>
</table>
3.3. Advanced Oxidation Process of Organic Pollutants

A solution containing 100 µM organic pollutant was used as the initial solution for the sequential advanced oxidation processes.

Degussa (P25) TiO₂ was used as a photocatalyst and without further treatment. The loading of photocatalyst was based on the degradation requirements of each experiment.

The methanol (HPLC grade) used for mobile phase of high performance liquid chromatography was obtained from Ajax FineChem. Trifluoroacetic acid (TFA, > 99%) was purchased from Sigma-Aldrich. Ammonium acetate (AR, > 98%) was obtained from BDH Laboratory Supplies (Merck Pty. Limited, Kilsyth, Australia).

Sodium hydroxide (NaOH) and perchloric acid (HClO₄), used to adjust the solution pH value, were purchased from Ajax Chemicals. A series of different concentration acid and alkali solutions were made to change the reaction solution pH in appropriate sized steps.

The reagents for determining the standard total carbon and inorganic carbon, potassium hydrogen phthalate (HOOCC₆H₄COOK) and sodium hydrogen carbonate (NaHCO₃), came with the Total Organic Carbon Analyzer (Shimadzu).

For H₂O₂ yield measurement, ammonium molybdate tetrahydrate ((NH₄)₆Mo₇O₂₄·4H₂O), sodium hydroxide and potassium hydrogen phthalate (KC₈H₅O₄) were purchased from Ajax Chemicals. Potassium iodide (KI) was obtained from Chem-Supply.

Commercial reagents used for HPLC confirmation experiments, aniline, phenol, quinol, catechol, fumaric acid, chlorobenzene and 4-chlorophenol, were purchased from BDH Laboratory Supplies (Merck Pty. Ltd.). 3-Chloro-4-hydroxybenzoic acid, 4-chlorosalicylic acid, benzoic acid, 3,4-dihydroxybenzoic acid, 3-hydroxybenzoic acid, 2,5-dihydroxybenzoic acid, 3,5-dihydroxybenzoic acid, 3-chloro-4-hydroxybenzoic acid, 4-chlorosalicylic acid, and 4-aminosalicylic acid were obtained from Sigma-Aldrich.

3.3.2. Degradation

Sonophotocatalytic experiments were conducted in a 250 mL cylindrical pyrex vessel one side of which has a quartz plate. The equipment is shown in Figure 3.3. The sonication vessel used to house the solution (250 mL) was jacketed, allowing the solution to be cooled (23±3 °C) by passing cold water continuously through the jacket.
3.3. ADVANCED OXIDATION PROCESS OF ORGANIC POLLUTANTS

An ultrasound transducer was placed on the bottom of the vessel and was powered by an amplifier set at the appropriate frequencies and acoustic powers.

Photocatalysis experiments were performed in the same vessel as described above. A 450 W Oriel Model 66021 xenon-arc lamp was placed next to the reaction vessel. The optical filter (cut-off wavelength 320 nm) which can transmit light from the light source was installed between the vessel and the lamp. During photocatalysis, the sonicator was switched off. Sonolysis experiments were carried out without light irradiation, but in the presence of the TiO$_2$ photocatalyst. During sonophotocatalysis, the solution was irradiated with both light and ultrasound.

Before each oxidation experiment, the solution was stirred with an overhead stirrer for 30 min to uniformly disperse the photocatalyst in the aqueous mixture. During the whole degradation experiment, the stirring speed was kept constant at 400 r/min. An benchtop pH meter (Extech Equipment Pty. Ltd.) was used to monitor the solution pH for the whole experiment. NaOH and HClO$_4$ were used to adjust the pH values.

Prior to analysis, the solution pH of each sample were adjusted to above 12 in order to minimize the adsorbed...
3.3. ADVANCED OXIDATION PROCESS OF ORGANIC POLLUTANTS

amount of organic pollutants on the surface of TiO$_2$. All samples were filtered through a 0.45 µm PTFE membrane syringe filter (Gelman Science) to remove the suspended TiO$_2$ catalyst particles.

3.3.3. Analytical Determinations

3.3.3.1. Sonoluminescence Intensity

A similar procedure to that of Ashokkumar and coworkers [11, 12, 196] was adopted to measure the sonoluminescence intensity. The same vessel and ultrasonic unit were used. A photomultiplier tube (PMT, Hamamatsu, detection range 350-600 nm) was mounted directly facing the quartz window of the reactor. 800 volts was applied across the PMT with a high voltage power supply. The sonication set and photomultiplier tube were housed in a light-proof enclosure to minimize background light. During the whole measurement, the temperature was kept at 23±3 °C. The volume of the solution sonicated was 250 mL. The same volume as used in the advanced oxidation processes. Five experimental runs were carried out to obtain the average sonoluminescence intensity.

3.3.3.2. UV-vis spectrophotometry

A Varian spectrophotometer (Cary Bio50) was used to obtain the absorption spectra of various solutions in order to monitor the progress of the sonolytic, photocatalytic and sonophotocatalytic degradation. The linearity between absorption and concentration was tested using external standards of organic pollutants at various concentrations between 10 and 100 µM. The response was found to be linear (with a correlation coefficient $r^2 > 0.99$) over the whole range of concentrations under consideration.

3.3.3.3. High Performance Liquid Chromatography

A computer controlled HPLC system (Shimadzu LC-10 AT VP system) comprising a solvent delivery pump, diode array, Shimadzu SPD-10 AVP UV-visible absorbance detector and an autosampler was used to record the organic pollutants and their product concentration-time profiles. An Alltech Econosphere C18 5 u, 150 mm ×
3.3. ADVANCED OXIDATION PROCESS OF ORGANIC POLLUTANTS

4.6 mm HPLC column was used to separate the degradation solution components. The whole HPLC system was operated in an isocratic mobile phase at 0.8 mL/min and temperature of 40 °C. For each compound, separation was obtained under isocratic conditions using a set of parameters listed in Table 3.2. The injection volumes were 20 µL and the detection was achieved with the diode array detector set at a certain wavelength range for each sample. Quantification was based on the chromatograms taken using the Shimadzu Class-VP chromatography data handling software. The linearity between absorbance and concentration was obtained by using calibration standards at various concentrations and the response was found to be linear over the whole range of concentrations. Blank samples were run between samples to ensure that no residues from the previous run were carried over to the next run.

Table 3.2: The parameters of high performance liquid chromatography used during analysis of organic pollutant degradation.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Mobile Phase</th>
<th>Flow Rate</th>
<th>Detection Wavelength</th>
</tr>
</thead>
<tbody>
<tr>
<td>MO</td>
<td>MeOH:10 mM Ammonium acetate 30:70 (v/v)</td>
<td>1.0 mL/min</td>
<td>190-640 nm</td>
</tr>
<tr>
<td>PCBA</td>
<td>MeOH:0.1% TFA 47:53 (v/v)</td>
<td>0.8 mL/min</td>
<td>190-370 nm</td>
</tr>
<tr>
<td>PABA</td>
<td>MeOH:0.1% TFA 5:95 (v/v)</td>
<td>0.8 mL/min</td>
<td>190-370 nm</td>
</tr>
<tr>
<td>PHBA</td>
<td>MeOH:0.1% TFA 55:45 (v/v)</td>
<td>0.8 mL/min</td>
<td>190-370 nm</td>
</tr>
</tbody>
</table>
3.3. ADVANCED OXIDATION PROCESS OF ORGANIC POLLUTANTS

3.3.3.4. H$_2$O$_2$ Measurement

There is no better description of H$_2$O$_2$ determination than that from the laboratory record of Devi Sunartio [12] (see Figure 3.4*).

Figure 3.4: The procedure of H$_2$O$_2$ yield determination by absorption spectroscopy.

The mechanism is based on the assumption that all the OH• radicals generated during cavitation are able to oxidize the iodide ions into tri-iodide ions through consecutive multistep reactions.

\[
\begin{align*}
\text{H}_2\text{O} & \rightarrow \text{H}^+ + \text{OH}^- \\
\text{OH}^- + \text{OH}^- & \rightarrow \text{H}_2\text{O}_2 \\
\text{H}_2\text{O}_2 + 2\Gamma^- & \rightarrow \text{I}_2 + 2\text{OH}^- \\
\text{I}_2 + \text{OH}^- & \rightarrow \text{I}_3^-
\end{align*}
\]

*Adapted from the laboratory record of Devi Sunartio.
3.3. ADVANCED OXIDATION PROCESS OF ORGANIC POLLUTANTS

The tri-iodide ions have a molar absorption coefficient of $2.64 \times 10^4$ L mol$^{-1}$ cm$^{-1}$ at 353 nm (25°C). The actual concentration of H$_2$O$_2$ assumed to be equal to the tri-iodide ion concentration can be spectrophotometrically determined by using the Beer-Lambert Law.

It is worth noting that the iodide reagent made by mixing solution A and B (see Figure 3.4) should be used immediately once mixed due to the fact that it is subject to oxidizing by dissolved oxygen.

3.3.3.5. Q-TOF LC/MS Analysis

Mass spectrometry was performed on an Agilent Technologies 6510 Accurate-Mass Q-TOF coupled with an Agilent 1100 Series HPLC system. This system is a LC/MS combined system.

Chromatographic separation of the degradation products was performed using an Eclipse Plus C18 column (Agilent Technologies, 4.6 × 50 mm). A gradient method was selected to separate the compounds (Solution A: 0.1% TFA aqueous solution; Solution B: 95% acetonitrile containing 0.1% TFA). A time program was developed to linearly increase 5% to 100% of solution B for 6 min at a flow rate of 0.5 mL/min.

For the Q-TOF component, region scan mass spectra were recorded between $m/z$ 25 and 1000 with a scan rate of 1.02 spectra/s in Auto MS/MS mode. The gas temperature was set at 325 °C. The collision energy was set to increase linearly with a 2 V/100 Da and 10 V offset.

Data were acquired by Agilent MassHunter Workstation Software Acquisition and processed by Agilent MassHunter Workstation Software Qualitative Analysis.

3.3.3.6. Total Organic Carbon Analysis

A TOC-V$_{CSH}$ (Shimadzu) coupled with a TOC analyzer V (Shimadzu) software was used to determine the total organic carbon during each degradation process. An auto-sampler (ASI-V) was mounted to the TOC analyzer. Zero-degree compressed air was used to support the gas flow for analysis. The value of the TOC was deduced from the difference between total carbon (TC) and inorganic carbon (IC). The analyzer was calibrated for both TC and IC prior to each measurement.
Section 4.1
Introduction

Among the various applications of ultrasound, one significant application is the synthesis of precious metal nanoparticles as they play an important role in scientific research. Ultrasonic irradiation of aqueous solutions containing precious metal ions is an effective method for the preparation of nanometer-sized metal colloids [118, 119, 182]. The sonochemical synthetic method has an advantage over other...
4.1. INTRODUCTION

methods in generating nanoparticles of uniform shape and size [10, 72, 115]. Conventional preparation techniques often do not provide adequate and effective control of particle size and usually involve undesirable stabilizers for further applications. It is well known that ultrasonic irradiation of aqueous noble metal ion solutions results in nanometer sized metal colloids [167, 179, 264, 265] with a relative narrow size distribution.

Bimetallic nanoparticles have attracted considerable attention in the field of nanotechnology as candidates for optical, electronic and catalytic applications, owing to the fact that one of the metal determines the surface properties of the nanoparticles while the other may be responsible for specific functions. Composite Pt-Ru catalyst particles have attracted a considerable amount of attention in recent years as ruthenium helps to protect platinum catalyst from CO poisoning [266–268] in fuel cells.

Currently, the processes responsible for the generation of noble metal nanoparticles by using ultrasound have not been fully understood, mostly due to the lack of a detailed mechanism for this process. The aim of this chapter is to systematically investigate and clarify the formation mechanism of precious metallic or bimetallic nanoparticles during reduction using ultrasound. In order to gain a better understanding of the effective contribution of the solutes during acoustic cavitation, a number of experimental parameters were varied to identify the role that each component plays in the reduction procedure.

Although the synthetic methods are quite similar, this chapter is divided into two parts. The first part includes Section 4.2 and Section 4.3 which focus on the synthesis of metallic colloids by ultrasound. A number of experimental runs with variations in conditions were carried out in order to investigate the correlation between the efficiency of particle formation and morphology of the nanoparticles as a function of aqueous solution components and the influence of the preparation methods. Platinum and ruthenium preparation systems are addressed in these two sections. It is well known that platinum nanoparticles are easily synthesized by sonochemical methods and this field has attracted considerable attention [118, 120]. Thus, in this chapter the main emphasis will be paid to the reduction of ruthenium. The synthesis of platinum is not the primary focus of this research and considered as a reference for the following part dealing with the bimetallic system. As the whole procedure of the ruthenium synthesis is more complex than that of other noble metal particles, both chemical and hybrid methods were selected to clarify the perplexing problems met in the sonochemical reduction of ruthenium(III) solutions. UV-vis spectrometry was used to monitor the whole sonication reduction process and transmission electron microscopy (TEM) was
4.2. SYNTHESIS OF PLATINUM NANOPARTICLES

employed to observe the micromorphology of the sonicated compounds. X-ray photoelectron spectrometry (XPS) was used to investigate changes of the ruthenium oxide states.

The main content of the second part, consisting of the Section 4.4 is an investigation of the procedure of the synthesis of bimetallic nanoparticles through sonochemical reduction. Two different procedures, namely, simultaneous and sequential reductions, were followed during the sonochemical synthesis of these bimetallic nanoparticles. TEM images clearly show evidence of a bimetallic core-shell structure with a platinum core surrounded by a ruthenium shell. The sequential reduction method produces relatively higher yields of core-shell nanoparticles than the simultaneous reduction method. Additionally, the roles of alcohol and stabilizers acting in the synthesis of precious metallic or bimetallic nanoparticles were investigated in this part.

Section 4.2
Synthesis of Platinum Nanoparticles

A similar procedure to that reported by Caruso et al. [118, 120] was followed for the synthesis of platinum nanoparticles. The color of the aqueous solution containing K₂PtCl₄ and surfactant turned from pale yellow, originating from the PtCl₂⁻ complex, to dark brown during sonication. The absorption spectra of an aqueous solution of 1 mM K₂PtCl₄, 0.1 M HClO₄, 8 mM SDS and 0.2 M 1-propanol over the wavelength range 200-800 nm are shown in Figure 4.1. In the early stages of sonication, the absorbance in the UV region gradually decreased due to a decrease in Pt(II) ion concentration as a result of sonication. Concurrently the absorption in the longer wavelength region increased, indicating the formation of platinum nanoparticles. The increase in the slope of absorbance with irradiation time were attributed to two reasons. One is the formation of platinum which is able to disperse the light. Another is the increase of the sizes of existing platinum nanoparticles as bigger particles have capacity of dispersing the longer wavelength light.

Figure 4.2a shows the TEM image of platinum nanoparticles prepared by ultrasound irradiation for 2 hours. The sonochemically synthesized platinum particles were found to be spherically shaped and well separated. Figure 4.2b shows the particle size distribution of platinum nanoparticles synthesized by ultrasonication. Average diameters of the particles prepared in the presence of PVP stabilizer and propanol were less than 5 nm. The sta-
4.2. SYNTHESIS OF PLATINUM NANO PARTICLES

Figure 4.1: UV-vis spectra observed during the sonochemical reduction of an aqueous solution of 1 mM K₂PtCl₄ containing 0.1 M HClO₄, 8 mM SDS and 0.2 M 1-propanol under an Ar saturated atmosphere. The ultrasound frequency used was 213 kHz and the total power was 35 mW/mL.

bilizer here can inhibit the aggregation of platinum nanoparticles and also act a source of scavenging of primary radicals to form secondary radicals which accelerates the reduction of metallic ions. The propanol has the same function of scavenging the primary radicals. This function can prevent the recombination of hydrogen atoms and hydroxide radicals and improve the efficiency of metal nanoparticle synthesis.

With the high resolution of TEM image shown in Figure 4.3, it is easy to observe the crystal faces [111] and [200] of platinum nanoparticles. The lattice interfaces further confirm the formation of platinum nanoparticles by ultrasound irradiation.
4.2. Synthesis of Platinum Nanoparticles

(a) TEM micrograph of Pt nanoparticles.

(b) Histogram for the size distribution of Pt nanoparticles.

**Figure 4.2:** TEM image of Pt colloids prepared by sonication of an aqueous solution of 1 mM K$_2$PtCl$_4$ containing 1 mg/mL PVP + 0.4 M 1-propanol under an Ar saturated atmosphere. The ultrasound frequency used was 213 kHz and the total power was 55 mW/mL.
4.3. Synthesis of Ruthenium Nanoparticles

The second metal nanoparticle synthesized by ultrasound irradiation was ruthenium. Compared to the synthesis of platinum particles, the preparation process for ruthenium particles is more complex than that of platinum. In order to...

**Figure 4.3:** TEM image and crystal lattice of Pt nanoparticles prepared by sonochemical reduction of an aqueous solution of 1 mM $\text{K}_2\text{PtCl}_4$ containing 1 mg/mL PVP and 0.4 M 1-propanol under an Ar saturated atmosphere. The ultrasound frequency used was 213 kHz and the total power was 55 mW/mL.
to understand the mechanism of the reduction process, in addition to the sonochemical preparation, both chemical reduction of Ru(III) by sodium borohydride and a combination of sonochemical and chemical driven reduction were also carried out under the same experimental conditions.

The following three sections focus on the synthesis of ruthenium nanoparticles by three separate processes. UV-vis spectrometry, transmission electron microscopy and X-ray photoelectron spectrometry were adopted to characterize the ruthenium nanoparticles prepared by these three methods.

### 4.3.1. Sonochemical Method

Sonochemical reduction of Ru(III) was conducted in an aqueous solution of 1 mM RuCl$_3$, 0.1 M HClO$_4$, 8 mM SDS and 0.2 M 1-propanol. As it is well-known that the rate of reduction of Ru(III) is sensitive to the ambient temperature, the temperature of the sonicated solution was kept at 20±5°C. The initial absorption of Ru(III) has three characteristic peaks which corresponding to different hydrolyzed forms of ruthenium(III) chloride. The whole absorption spectra of Ru(III) is shown in Figure 4.4a. The peak with a maximum absorbance at 380 nm is related to [RuCl$_4$(H$_2$O)$_2$]$^-$, one of hydrolyzed forms of ruthenium(III) chloride. The 560 nm absorption peak corresponds to the [RuCl(H$_2$O)$_5$]$^{2+}$. The absorption band around 450 nm is attributed to two of the hydrolyzed forms, [RuCl$_3$(H$_2$O)$_3$] and [RuCl$_2$(H$_2$O)$_4$]$^+$ [269–271].

\[
[RuCl_4(H_2O)_2]^- \rightarrow [RuCl_3(H_2O)_3] \rightarrow [RuCl_2(H_2O)_4]^+ \rightarrow [RuCl(H_2O)_5]^{2+}
\] (4.1)

After 13 hours, the three Ru(III) characteristic peaks at 560, 450 and 380 nm, slowly disappeared due to the reduction of Ru(III) (Figure 4.4a). The dark red solution of Ru(III) gradually changed into yellow in a matter of hours. In addition to the disappearance of the three peaks mentioned above, a small "hump" around 300 nm appeared after 13 hours irradiation and persisted after even longer sonication times. The following Subsections 4.3.3 and 4.4.2, will discuss this perplexing phenomenon during the reduction of ruthenium(III) chloride.

It is well known that the frequency of ultrasonic irradiation is one of the most significant factors that has great impact on the cavitation activity and on metal ion reduction [132]. The reduction of ruthenium at different frequencies was carried out to determine if any frequency affects the reduction rate. A plot of the changes in the
4.3. SYNTHESIS OF RUTHENIUM NANOPARTICLES

(a) Absorption spectra changes of Ru(III) ions during the 213 kHz ultrasound irradiation.

(b) Rate of Ru(III) reduction as a function of ultrasound frequency.

Figure 4.4: UV-vis spectra and Ru(III) reduction rates observed during the sonochemical reduction of an aqueous solution of 1 mM RuCl₃ containing 0.1 M HClO₄, 8 mM SDS and 0.2 M 1-propanol under an Ar saturated atmosphere. The ultrasound frequencies used were 20 kHz, 213 kHz, 355 kHz, 647 kHz and 1056 kHz. The total power of all frequencies was 35 mW/mL.

absorbance of the 450 nm band as a function of sonication time at different frequencies is plotted in Figure 4.4b. With an extinction coefficient value of 3068 L/mol cm for the 450 nm absorption band, the different rates of reduction of the Ru(III) at 20 kHz, 213 kHz, 355 kHz, 647 kHz and 1056 kHz were compared in Figure 4.4b. The optimum frequencies for sonication are 213 kHz and 355 kHz, consistent with experimental investigation on the effects of ultrasound frequency on sonoluminescence, yield of H₂O₂ and ultrasonic synthesis of gold nanoparticles [132]. Kanthale et al. [272] conducted a numerical study on the influence of ultrasound on the H₂O₂ yield.
4.3. SYNTHESIS OF RUTHENIUM NANOPARTICLES

The average bubble temperature and the number of active bubbles play a key role in determining the extent of the sonochemical reactions. At the same acoustic power, the number of active bubbles increases significantly as the irradiation frequency increases. However, the average size of the collapsing bubbles, which determine the maximum temperature $T_{\text{max}}$ (see Equation 2.6), follows the opposite trend. It is important to balance these two factors to achieve the maximum sonochemical efficiency. An intermediate number of active bubble and not too low a $T_{\text{max}}$ for collapsing bubbles contribute to the outcome that 214 kHz and 355 kHz are the optimal frequencies.

Transmission electron microscopy was adopted to characterize the nanoparticles prepared by the sonochemical method. Figure 4.5a is the TEM image of the colloids after 5 hours of sonication of a Ru(III) ion solution and the Figure 4.5b shows the particle size distribution obtained. The image reveals that the diameters of the nanoparticles are uniform and the size ranges from 2 to 3 nm.

In order to follow the changes to the ruthenium oxidation states, X-ray photoelectron spectroscopy was used to observe the shifts of binding energy after ultrasound irradiation. It is well known that XPS of Ru compounds is not an easy task as the Ru $3d$ signals share the same energy range as that of the C $1s$ peak, while the Ru $3p$ levels are typically broad and insensitive to changes in the ruthenium chemical environment. Throughout this work, both $3d$ and $3p$ regions of ruthenium were collected for each specimen because an estimation of the overall Ru $3p$ and $3d$ is useful in verifying the accuracy of each other in the curve fitting of the (Ru $3d + C 1s$) envelope and Ru $3p$.

As it is known that the $3d$ of ruthenium and $1s$ of carbon overlap at the same energy bond range from 279 eV to 292 eV, the ruthenium(III) ion solution was irradiated by ultrasound without the stabilizer PVP which contributes the enhancement of the C $1s$ peak intensity. Figure 4.6 shows the overlapped corresponding peak marked by C $1s$. The intensity of C $1s$ peak still has a strong impact on the analysis of Ru $3d$ due to the progressive coverage by adventitious carbon and the remains of hydrocarbon compounds of initial precursor.

The main peaks observed in the XPS spectrum of the sonochemically irradiated sample are C $1s$, Ru $3d$ and Ru $3p$ peaks, centered at 285, 279-292 and 458-492 eV, respectively. After a fitting treatment of these curves, several conclusions can be drawn from the XPS spectrum. It can be seen from Figure 4.6b that the irradiated ruthenium compound contains a characteristic peak at 286.2 eV corresponding to Ru(III) $3d_{3/2}$ [273, 274]*, which suggests

*To investigate the influence of ultrasonication on the oxide states changes of ruthenium, a XPS analysis of standard Ru(III) chloride was done as a reference spectrum.
4.3. Synthesis of Ruthenium Nanoparticles

Figure 4.5: TEM image of Ru colloids prepared by sonochemical sonication of an aqueous solution of 1 mM RuCl$_3$ containing 1 mg/mL PVP + 0.4 M 1-propanol under an Ar saturated atmosphere. The ultrasound frequency used was 213 kHz and the total power was 55 mW/mL.

that the coordination surroundings of the Ru atom remain almost in the same state as that before ultrasonication. However, compared to the peak of Ru(III) $3d_{3/2}$, the shoulder of the peak at 286.2 eV is broader, which indicates the presence of Ru(IV) $3d_{3/2}$. The binding energy of Ru(IV) $3d_{5/2}$ is 282.6 eV [274, 275] slightly shifting from Ru(III) $3d_{3/2}$. The same thing happens with Ru $3p$ (shown in Figure 4.6c). The fact that the main peaks of Ru $3d$
4.3. Synthesis of Ruthenium Nanoparticles

(a) The full X-ray photoelectron spectrometry spectrum of the ruthenium(III) chloride after ultrasonic irradiation.

(b) The Ru 3d + C 1s X-ray photoelectron spectrum of the ruthenium(III) chloride after ultrasonic irradiation.

(c) The Ru 3p X-ray photoelectron of the ruthenium(III) chloride after ultrasonic irradiation.

Figure 4.6: X-ray photoelectron spectrometry survey scan of the ruthenium compound nanoparticles: XPS spectrum observed after 7 hours sonochemical reduction of an aqueous solution of 1 mM RuCl$_3$ containing 0.4 M 1-propanol under an Ar saturated atmosphere. The ultrasound frequency used was 213 kHz and the total power was 55 mW/mL.

and 3p appear at the same position of Ru(III) reveals that main oxides of the sample after ultrasonic irradiation is the +3 state. According to the XPS binding energy peaks, no signal for the metallic ruthenium could been seen. This indicates that ultrasound is unable to change Ru oxide states from Ru(III). There is a minor portion of Ru(IV) compounds, in agreement with the literature [273, 276] that commercial RuCl$_3$ contains a variety of oxochloro and hydroxochloro species of variable oxidation states. Another reason of the presence high oxide state is most probably due to exposure to the air during transfer [277].
4.3. SYNTHESIS OF RUTHENIUM NANOPARTICLES

| Standard Reduction Potentials (E^0/V) |
| --- | --- | --- | --- | --- | --- |
| +8 | +7 | +6 | +4 | +3 | +2 | 0 |
| RuO_4 | RuO_4^2- | RuO_4^{2-} | RuCl_5OH^2- | RuCl_5^2- | Ru^2+ | Ru | 0.9 | 1.6 | 1.75 | 1.3 | 0.3 | 0.45 | 1.5 | 0.6 |

These XPS spectrum proved that the nanoparticles we reported in the paper [278] were ruthenium oxochloro and hydroxochloro species instead of ruthenium nanoparticles. The reason for the slow reduction of Ru(III) ions by ultrasound is perhaps due to the higher reduction potentials of the metallic ions in its hydrolyzed forms. Reaction 4.2 [279] shows the reduction potentials of each step from the +8 oxide state to the metallic state. However, the observations from XPS spectra indicate that Ru(III) intends to form more stable RuCl_xO_y compound in an aqueous environment. Although it is well-known that during bubble collapse, extremely high pressure and temperature inside the bubble lead to the formation of active H• and OH• radicals (see Equation 2.8) and consequent secondary radicals, which play a key role in initializing the reduction of metal ions in aqueous solution. The ruthenium ion in aqueous solution seems beyond the capacity of these active radicals. In order to form the ruthenium zero-state nanoparticles, it is necessary to go through an alternative pathway under the ultrasound irradiation.

4.3.2. Chemical Method

In order to reveal and understand the process of Ru(III) reduction by ultrasound irradiation, sodium borohydride was used as a reductant to covert Ru(III) ion to Ru(0) nanoparticles. The same solution mentioned in the subsection 4.3.1 was mixed dropwise with 150 mM sodium borohydride until the three characteristic peaks of Ru(III) totally disappeared indicating the completion of ruthenium colloid formation. Figure 4.7 shows the ruthenium colloids reduced by chemical synthesis. The particle size of ruthenium obtained by the chemical method is less than 4 nm, which is slightly larger than the particles synthesized by the sonochemical process.
4.3. Synthesis of Ruthenium Nanoparticles

(a) TEM micrograph of Ru nanoparticles reduced by sodium borohydride.

(b) Histogram for the size distribution of Ru nanoparticles.

Figure 4.7: TEM image of Ru colloid deoxidized by chemical methods: a 10 mL aqueous solution of 1 mM RuCl$_3$ containing 1 mg/mL PVP + 0.4 M 1-propanol was reacted with 120 $\mu$L of 150 mM sodium borohydride.

In comparison with the XPS spectrum of the ultrasonicated sample (Figure 4.6a), the signal of ruthenium $3p$ reduced by sodium borohydride 4.8a is much stronger. After the curve fitting process, the signal of Ru $3d_{5/2}$ appeared at 282.1 eV (shown in Figure 4.8b), which corresponds to Ru(III). It is obvious that there is only a small amount of Ru(III) species on the surface of the chemically reduced sample, perhaps attributable to oxidation on the surface. A larger and new signal appeared at 280.6 eV that can be ascribed to ruthenium oxychloride.
4.3. Synthesis of Ruthenium Nanoparticles

RuCl$_3$O$_y$ [277, 280]. The above results demonstrate that a fraction of the initial ruthenium is forming ruthenium oxychlorides, which is sufficiently stable not to react with the stronger reductant, sodium borohydride.

The interesting point is that stronger Ru $3d_{3/2}$ and $3d_{5/2}$ signals appear at 280.1 and 283.7 eV respectively, which can be assigned to Ru(0) [275, 277, 281]. It is obvious that among the three ruthenium species, the Ru(0) dominates the whole spectrum of $3d$. The same conclusion can be deduced from the deconvoluted spectra of Ru $3p$ (Figure 4.8c). Both Ru $3p_{3/2}$ and Ru $3p_{5/2}$ peaks consist of the corresponding contributions from metallic
ruthenium and oxychloridic ruthenium. The reduction potential of sodium borohydride is insufficient to transform ruthenium oxychloridic ions into the metallic form as this compound seems to interact strongly with the material support.

The chemical reaction steps involved in the reduction of ruthenium metallic ions have not been completely resolved. Further study of the formation of ruthenium oxychlorides is needed in the future.

4.3.3. Hybrid Method

An attempt to clarify the changes of ruthenium oxide state was carried out by ultrasonic irradiation then followed by chemical reduction. As mentioned in Subsection 4.3.1, the UV-vis spectra of 13 hours sonicating Ru(III) ion aqueous solution show the presence of a band around 320 nm, which remains even after prolonged irradiation.

After adding the sodium borohydride solution, the band disappeared indicating the transformation of the oxide states of ruthenium. The TEM image in Figure 4.9 shows there is no significant particle size change before (see Figure 4.5a) and after (see Figure 4.9a) chemical reduction.

Figure 4.10a and 4.10b present the Ru 3d and 3p XPS profiles respectively for the sonicated sample after further reduction by sodium borohydride. It is obvious that owing to the addition of the stronger reductant, the Ru 3d and 3p doublets shift a small distance toward lower binding energy due to the reduction of ruthenium. The disappearance of the peak at 282.6 eV indicates that the +4 oxide states has been completely reduced. Although the ruthenium(III) species at 282.1 eV for 3d_{5/2} and 286.2 eV for 3d_{3/2} are also present, the fraction of this ruthenium oxide is dramatically reduced compared to the sonicated sample (see Figure 4.6b). The small shift, attributed to a reduction effect, is confirmed to be the Ru zero-state species. After reduction with sodium borohydride, the XPS spectra of the ultrasonic prepared compound reveal a new Ru 3d doublet at a binding energy of 283.7 eV for 3d_{3/2} and 280.1 eV for 3d_{5/2} corresponding to metallic ruthenium nanoparticles. It is remarkable that the peak of ruthenium oxychloride at 280.6 eV which appears in the chemically prepared sample is still present with the hybrid reduced sample. The ruthenium oxychloridic forms are not reduced in the presence of excess sodium borohydride due to this compound interacting strongly with the material support.
4.3. SYNTHESIS OF RUTHENIUM NANOPARTICLES

(a) TEM micrograph of Ru nanoparticles prepared by the hybrid method.

(b) Histogram for the size distribution of Ru nanoparticles prepared by the hybrid method.

Figure 4.9: TEM image of Ru colloid prepared by sonochemical sonication of a 10 mL aqueous solution of 1 mM RuCl₃ containing 1 mg/mL PVP + 0.4 M 1-propanol under an Ar saturated atmosphere following reaction with 80 µL of 150 mM sodium borohydride. The ultrasound frequency used was 213 kHz and the total power was 55 mW/mL.
4.3. SYNTHESIS OF RUTHENIUM NANOPARTICLES

Figure 4.10: X-ray photoelectron spectrometry survey scan of the ruthenium compound nanoparticles: XPS spectrum observed after 7 hours sonochemical reduction of a 10 mL aqueous solution of 1 mM RuCl₃ containing 0.4 M 1-propanol under an Ar saturated atmosphere followed by a sequential reduction with 80 µL of 150 mM sodium borohydride. The ultrasound frequency used was 213 kHz and the total power was 55 mW/mL.
4.4. Sonochemical Synthesis of Platinum-Ruthenium Bimetallic Nanoparticles

Composite Pt-Ru catalyst nanoparticles have attracted a considerable amount of attention in recent years as a catalyst in direct methanol fuel cells (DMFC) (see Chapter 5) and other optoelectronic and catalytic applications. In the realm of optoelectronic applications, metal nanoparticles have interesting size and shape dependent optical and electronic properties that can be suitably modulated by the addition of another metal. For catalytic applications, the expectation is that they will have better catalytic properties than the component metals alone or even have new properties.

Furthermore, it is well known that the catalytic performance of direct methanol fuel cells strongly depends on the size of the precious metal catalyst particles. It is well established that ultrasonic irradiation of aqueous noble metal solutions results in nanometer sized metal colloids.

In this section, two methods were adopted to prepare platinum-ruthenium bimetallic nanoparticles: (i) simultaneous reduction of the precursor metal ions and (ii) sequential reduction of the precursor ions. The latter usually gives rise to core-shell structures.

4.4.1. Simultaneous Method

Figure 4.11 shows the UV absorption spectra of platinum-ruthenium bimetallic colloid prepared by simultaneous sonochemical irradiation. An aqueous solution of 1 mM K₂PtCl₄, 1 mM RuCl₃, 0.1 M HClO₄, 8 mM SDS and 0.2 M 1-propanol was used to prepare the platinum-ruthenium bimetallic nanoparticles. The presence of alcohols here can enhance the metal ion reduction process, as the reaction of alcohols with the primary radicals generates secondary reducing radicals. There are two explanations to demonstrate the catalytic function of alcohols. First, it is well known that acoustic cavitation leads to the formation of highly reactive H• and OH• (see Equation 2.8) radical species in aqueous solution. The presence of alcohols around cavitation bubbles is able to inhibit the recombination of these two active primary radicals. The hydrogen radical may react directly with metal ions in bulk solution to reduce to metallic particles (see Equation 2.20) and a proportion of
4.4. **Sonochemical Synthesis of Platinum-Ruthenium Bimetallic Nanoparticles**

(a) UV-vis spectra observed during the simultaneous sonochemical reduction.

**Figure 4.11:** UV-vis spectra observed during simultaneous sonochemical reduction of an aqueous solution of 1 mM K$_2$PtCl$_4$ and 1 mM RuCl$_3$ containing 0.1 M HClO$_4$, 8 mM SDS and 0.2 M 1-propanol under an Ar saturated atmosphere. The ultrasound frequency used was 213 kHz and the total power was 35 mW/mL.

The hydroxyl radicals may be scavenged by added organic solutes, such as surfactants and alcohols, to generate the secondary radicals (see Equation 2.21). In the latter case, the alcohol converts OH•, which has no potential to reduce the metallic ions, to the highly reductive alcohol radicals. Thus, it is necessary to add alcohol to accelerate and enhance the reduction process of the metallic ions.
Based on the UV-vis spectrum, the same three characteristic peaks at 560, 450 and 380 nm mentioned in Subsection 4.3.1 in the visible region of the spectrum arising from RuCl$_3$, appeared in the initial absorption spectrum. After sonicating for 7 hours, the solution turned dark brown and the three peaks gradually disappeared implying that Pt(III) and Ru(III) had been reduced to Pt(0) and Ru(0) respectively. Obviously, the reduction rate for Ru(III) in the presence of Pt(0) is much faster than that of the reduction of Ru(III) alone. Within four hours, nearly all of the above mentioned absorption bands had disappeared, and a clear brown solution was obtained.

It has been concluded that Pt nanoparticles, which are formed first, play an important role in catalyzing the formation of Ru nanoparticles \cite{265}. Precious metal nanoparticle colloids act as a sink for excess electrons, and these electrons can initiate reduction of other solutes. The platinum colloids can act as nanoelectrodes, and electrons are transferred to the platinum surface from the reducing radicals produced by the propanol and surfactant during sonication. The overall accelerated reduction rate of Ru(III) can be attributed to the existence of excess electrons on the surface of the Pt nanoparticles donated by the reducing alcohol radicals produced by sonolysis. The changes in the absorption spectrum also indicate that the reduction of the Ru(II) occurs simultaneously with the reduction of Pt(II). The faster reduction rate for Pt(II) relative to Ru(III) means that colloidal platinum nanoparticles are preferentially produced which eventually accelerate the formation of zerovalent ruthenium.

Figure 4.12a shows the TEM image of the bimetallic nanoparticles obtained from simultaneous sonication. According to the TEM image of the particles, the bimetallic colloids seem to be a mixture of 3-15 nm diameter nanoparticles (shown in Figure 4.12b). The larger particles are most likely ruthenium particles and the smaller ones are platinum particles. This is consistent with our experimental observations that the sonochemical reduction of platinum(II) to produce platinum colloids is substantially faster than the similar reduction of ruthenium(III) and that faster reduction rates results in smaller particle sizes. It is known that the nucleation process plays a key role
in determining the particle size. Okitsu et al. has used the formation of gold nanoparticles to demonstrate the dependence of particles size distribution on the rate of sonochemical reduction [132, 133].

Figure 4.12: TEM image of PtRu bimetallic nanoparticles prepared by simultaneous sonochemical reduction of an aqueous solution of 1 mM K₂PtCl₄ and 1 mM RuCl₃ containing 0.1 M HClO₄, 8 mM SDS and 0.2 M 1-propanol under an Ar saturated atmosphere. The ultrasound frequency used was 213 kHz and the total power was 35 mW/mL.
4.4. SONOCHEMICAL SYNTHESIS OF PLATINUM-RUTHENIUM BIMETALLIC NANOPARTICLES

4.4.2. Sequential Method

The sequential sonolysis was carried out in order to elucidate the catalytic role of the presence of platinum nanoparticles during the reduction of ruthenium(III) ions. 213 kHz ultrasound initially was applied to the tetrachloroplatinate solution containing 1 mg/mL PVP, 0.2 M propanol and 0.1 M HClO₄ to produce colloidal platinum. From the start to 1 hour, when all of K₂PtCl₄ had been completely reduced, the pale yellow color of Pt(II) solution changed to brown as observed in the reduction of platinum alone. Then, a solution of 1 mM RuCl₃ in 0.1 M HClO₄ was added to the Pt colloid solution. After continuous ultrasonic irradiation for an additional 3 hours, the color of the solution turned to dark brown.

Figure 4.13 shows the absorption spectra of the colloidal solution beginning with the K₂PtCl₄ solution at the start and continuing through the addition of RuCl₃ and its subsequent reduction. The absorption spectrum immediately upon addition of the ruthenium chloride solution is quite different from that of ruthenium ion solution alone. The interesting point is that when the RuCl₃ solution was added to the Pt colloid solution, only one prominent feature at 380 nm existed while the other two disappeared indicating an instantaneous partial reduction of Ru(III) upon addition to the colloidal platinum solution. Compared to the UV-vis spectra of simultaneous reduction, it takes only 3 hours to completely reduce Ru(III) by using the sequential method. This is more likely to be due to the catalytic activity of the pre-existing platinum nanoparticles. Reduction to metallic ruthenium is complete at the end of 3 hours. Obviously, the perplexing peak around 300 nm of ultrasonicated ruthenium(III) sample reappears again. This peak indicates the ruthenium(III) ions are not reduced completely by ultrasound.

In order to confirm the formation of ruthenium metallic nanoparticles, XPS was employed to survey scan the ruthenium compound reduced by sequential sonochemical irradiation. Figure 4.14 shows the XPS spectra of the ruthenium(III) chloride after 7 hours ultrasonic irradiation. It is clear that two new peaks appear before the (Ru 3d + C 1s) envelope corresponding to K 2p₁/₂ and 2p₃/₂. The presence of potassium is due to the initial solution containing K₂PtCl₄. Similar to the chemical reduction of ruthenium(III) ion, the Ru 3d and 3p were deconvoluted into three ruthenium species. The doublet at 283.7 and 280.1 eV presents the existence of zero-valent ruthenium. Clearly, the presence of Pt metallic nanoparticles speeds up the formation of ruthenium nanoparticles by providing an alternative pathway from ruthenium ions to metallic particles. This new pathway has...
4.4. **Sonochemical Synthesis of Platinum-Ruthenium Bimetallic Nanoparticles**

![Absorption spectra of PtRu colloids](image)

**Figure 4.13:** Absorption spectra of PtRu colloids: UV-vis spectra observed during the sequential sonochemical reduction of an aqueous solution of 1 mM K$_2$PtCl$_4$ containing 1 mg/mL PVP + 0.4 M 1-propanol followed by the reduction of 1 mM RuCl$_3$ under an Ar saturated atmosphere. The ultrasound frequency used was 213 kHz and the total power was 35 mW/mL.

A higher reduction potential than that of the original pathway. In the same chemical environment, a large fraction of ruthenium ion can cross the activation barrier and be reduced to Ru(0). Details of these catalytic activities of platinum are discussed at the end of this subsection.

At the same time, the doublet peaks corresponding to Ru(III) and RuCl$_x$O$_y$ appear with Ru(0) at Ru 3$d$ and 3$p$. It is noticeable that the portion of RuCl$_x$O$_y$ species is almost equal to that of Ru(0) indicating that a large fraction of ruthenium oxychloride was produced during the sequential sonication of ruthenium and platinum ions. Also,
4.4. **Sonochemical Synthesis of Platinum-Ruthenium Bimetallic Nanoparticles**

(a) The full X-ray photoelectron spectrometry spectrum of the platinum-ruthenium bimetallic nanoparticles prepared by a sequential sonochemical method.

(b) The Ru 3d + Cl 1s X-ray photoelectron spectrum of the platinum-ruthenium bimetallic nanoparticles prepared by a sequential sonochemical method.

(c) The Ru 3p X-ray photoelectron of the platinum-ruthenium bimetallic nanoparticles prepared by a sequential sonochemical method.

**Figure 4.14:** X-ray photoelectron spectrometry survey scan of the platinum-ruthenium bimetallic nanoparticles: XPS spectrum observed after 7 hours sonochemical sequential reduction of an aqueous solution of 1 mM K$_2$PtCl$_4$ containing 0.4 M 1-propanol under an Ar saturated atmosphere followed by the reduction of 1 mM RuCl$_3$ under an Ar saturated atmosphere. The ultrasound frequency used was 213 kHz and the total power was 55 mW/mL.

A comparison with the peak area of Ru(III) in chemical reduced sample shows that the signal of Ru(III) in the sequential reduction process is much stronger, indicating that the reduction by ultrasound process is less efficient. The same conclusions can be deduced from the XPS spectrum of ruthenium 3p.
According to the above observations, the peak appearing at 300 nm in the UV-vis spectrum of the final reduction is more likely to be one or more hydrolyzed forms of ruthenium(III) chloride. Although Ru(III) exists in the samples treated by chemical reduction or the hybrid method, the fraction of the +3 oxide state species is too small to be detected by spectrophotometry. In the samples only irradiated by ultrasound, the Ru(III) chlorides is in a greater proportion resulting in an obvious change in the UV-vis spectra.

Figure 4.15a shows the TEM image of platinum-ruthenium bimetallic nanoparticles prepared using PVP as a stabilizer. The observation that the particles size is much smaller than 2 nm in the PVP system as compared to the SDS system (see Figure 4.17) is consistent with the observation that faster reduction rates result in smaller particle sizes [132]. However, the images do not conclusively indicate that the structure of particles is core-shell. This requires higher resolution TEM images.

To confirm the presence of these core-shell structures, we have examined the sample prepared by sequential reduction using SDS surfactant on a copper grid at higher resolution at 200 kV, and the resulting TEM image shown in Figure 4.16a and Figure 4.16b. The larger particle whose diameter is around 20 nm does indeed show clearly defined core-shell bimetallic structures with the ruthenium forming a layer around the platinum particles. We have chosen one representative particle to illustrate this geometry in Figure 4.16c. The composite nanoparticles clearly seem to have core-shell structure that a layer of ruthenium was formed around the platinum particles. The diameters of the platinum particles core ranges approximately from 15 nm to 20 nm and the thickness of ruthenium shell is between 3 nm and 4 nm. The crystal lattices of the platinum core and the ruthenium shell are observed clearly in the high resolution TEM image. The lattice interfaces further confirm the formation of platinum-ruthenium core-shell nanoparticles by sonochemical reduction.

As mentioned before, the accelerating function of platinum on the reduction rate of Ru(III) is most likely due to the presence of platinum, holding the electrons donated by the reducing radicals produced by sonolysis. The platinum-ruthenium core-shell structure in the TEM image (Figure 4.16a-4.16c) further confirms the experimental observation that the platinum plays a significant role in the reduction of Ru(III). The formation of the core-shell structure of PtRu bimetallic nanoparticles is shown in Figure 4.16d. The highly active primary $\text{H}^\bullet$ and $\text{OH}^\bullet$ generated in the cavitation bubble readily react with the alcohol molecules around them to produce the alcohol radical (referred to propanol radical in this case). Due to the capacity of electron storage, the surface of the
4.4. Sonochemical Synthesis of Platinum-Ruthenium Bimetallic Nanoparticles

(a) TEM micrograph of PtRu bimetallic nanoparticles obtained by sequential sonochemical reduction.

(b) Histogram for the size distribution of PtRu nanoparticles.

Figure 4.15: Sequential sonochemical reduction of an aqueous solution of 1 mM K$_2$PtCl$_4$ containing 1 mg/mL PVP + 0.4 M 1-propanol followed by the reduction of 1 mM RuCl$_3$ under an Ar saturated atmosphere. The ultrasound frequency used was 213 kHz and the total power was 55 mW/mL.

Platinum existing in the solution collects the electrons after the alcohol radicals shift to a more stable energy state. Once the electron is captured by the platinum, the surface of platinum particles will be negative charged. Obviously, the positively charged ruthenium ions are easily attracted by the platinum particles by the electrostatic force. The positive ruthenium ions continuously accumulate on the platinum surface to form a shell layer. In this
4.4. Sonochemical Synthesis of Platinum-Ruthenium Bimetallic Nanoparticles

(a) TEM images of core-shell PtRu bimetallic nanoparticles prepared by sequential sonochemical reduction.

(b) TEM images of core-shell PtRu bimetallic nanoparticles prepared by sequential sonochemical reduction.

(c) TEM images of PtRu colloids prepared by sequential sonochemical reduction.

(d) The mechanism of core-shell structure forming during the sequential sonication.

Figure 4.16: TEM images and mechanism of sequential sonochemical reduction of an aqueous solution of 1 mM K$_2$PtCl$_4$ containing 0.1 M HClO$_4$, 8 mM SDS and 0.2 M 1-propanol followed by the reduction of 1 mM RuCl$_3$ under an Ar saturated atmosphere. The ultrasound frequency used was 213 kHz and the total power was 35 mW/mL.

The whole procedure of ruthenium reduction, platinum particles act as catalysts to provide a new pathway to reduce the ruthenium ion by offering electrons instead of the normal radicals, which is likely to have a more powerful potential to reduce metallic ions [265].

4.4.3. Stabilizer Dependence

The influence of the stabilizer on the synthesis of bimetallic nanoparticles was also investigated using both SDS and polyvinyl-2-pyrrolidine (PVP). According to the changes in the observed spectra, the reduction rate with the
PVP system is clearly faster than that with the SDS system. The formation of Pt particles with the PVP system was accelerated dramatically and the sonication time was reduced from 4 hours in the SDS system to 1 hour.

The observation that compared to the SDS system (Shown in Figure 4.17b), the particles size is much smaller in the PVP system (shown in Figure 4.15b) further confirms that the reduction rate is faster than that with the SDS system. As mentioned before, faster reduction leads to smaller particles [132].

It is difficult to adequately explain the difference in the rate of reduction observed with the two different stabilizers. The primary function of both PVP and SDS is to stabilize the metal particles. They do not influence the sound field and do not affect the bubble dynamics. On the basis of these facts, we are confident that both SDS and PVP do not affect the cavitation bubbles or the bubble field or the sound field.

However, there are two possible reasons for the different reduction rate with two surfactants: SDS, being surface active, is more likely to scavenge some of active primary radicals at the bubble solution interface. The advantageous position of surfactant enables them to easily accept the primary radicals generated from the cavitation process. This should enhance the rate of metal ion reduction as the surfactant radicals, like alcohol radical discussed previously, can be expected to lead to metal ion reduction and therefore metallic nanoparticles. However, it must also be remembered that SDS is a negatively charged solute and can complex with some of the positive metal ion complexes in solution and conversely repel the negatively charged species, which is particularly relevant when considering reactions on the surface of the colloid particles in the system. Finally, the degree of adsorption of the stabilizer on the colloid particles can be expected to be quite different, and this also will affect the size of the colloid particles formed. How all these effects contribute to the rate of reduction in the complex system remains to be clearly understood.

Section 4.5 Supplemental Measurements

Besides the UV-vis spectrometry, transmission electron microscopy and X-ray photoelectron spectrometry, X-ray diffraction (XRD), Scanning Transmission Electron Microscope (STEM), energy-dispersive X-ray (EDX) spectrometry were used to characterize the colloids of ruthenium, platinum and platinum-ruthenium colloids.
4.5. Supplemental Measurements

(a) TEM micrograph of PtRu bimetallic nanoparticles by sequential sonochemical reduction using SDS surfactant.

(b) Histogram for the size distribution of PtRu nanoparticles.

Figure 4.17: Sequential sonochemical reduction of an aqueous solution of 1 mM K$_2$PtCl$_4$ containing 0.1 M HClO$_4$, 8 mM SDS and 0.2 M 1-propanol followed by the reduction of 1 mM RuCl$_3$ under an Ar saturated atmosphere. The ultrasound frequency used was 213 kHz and the total power was 55 mW/mL.

Due to the limited amount of the metal colloids prepared, it was difficult to get a clear corresponding XRD pattern. In comparison to EDX, XPS spectra are able to provide not only the elements information with the samples as well as the oxide states of corresponding elements. Here only XPS data were selected to show the
4.5. Supplemental Measurements

ruthenium oxide states. Because of the smaller sizes of the prepared nanoparticles, the images of STEM could not show clearly the micromorphology of the metal or bimetallic particles.
The main purpose of this chapter is to let you understand why Aladdin Lamp has magic function and the manufacture procedure was presented in details. The potential materials for this lamp were also explored by comparing their magic performance.

XH

5

Application of PtRu Bimetallic Nanoparticles For A Fuel Cell*

B eing recognized as a promising catalyst, PtRu bimetallic nanoparticles have attracted a considerable level of attention for their electronic and catalytic properties. In this chapter, PtRu particles are considered with respect to possible applications in fuel cells, one of various applications, of bimetallic nanoparticle synthesized by chemical, sonochemical and radiolytic reduction. Cyclic voltammetry was

*In the previous chapter, the sonochemical synthesis of Pt-Ru was described. This chapter also deals with the synthesis of bimetallic particles. However, this work was done with a different system at the University of Notre Dame. In addition to the sonochemical method, chemical and radiolytic synthesis of Ru-Pt bimetallic particles and their electrocatalytic properties were carried out.
5.1. **Introduction**

Fuel cells are electrochemical devices that convert the chemical energy in fuels into electrical energy directly, promising power generation with high efficiency and low environmental impact. There are a number of different types of fuel cells, such as solid oxide, molten carbonate, proton-exchange membrane, and direct methanol fuel cells (DMFCs).

Implementation of direct methanol fuel cells allows the direct use of methanol without a fuel processor; the liquid fuel, i.e., methanol, needs no other external reforming, is easy to store and has a high energy density. The DMFC is seen as the leading candidate technology for the application of fuel cells in cameras, notebook computers, and other portable electronic applications. Figure 5.1 shows the basic structure of a typical direct methanol fuel cell. It can be seen in this figure that electrons flow from the anode to the cathode, and at the same time, carbon dioxide forms at the anode and water at the cathode. It should be noted that the electrocatalyst plays a leading role in creating an electric current by separating electrons from methanol. The presence of an acidic electrolyte is necessary as it provides conductivity between the electrodes to complete the chemistry of the whole system.

Although the DMFC is a fascinating candidate in the future of power supplies, the vital bottleneck of this technology is the low efficiency of the anode catalyst which yields a slow kinetics of methanol electro-oxidation. Often, high catalyst loadings are required in order to obtain a useful power output in DMFCs. This results in increasing the cost of fuel cells in practical applications. Research has focused on finding more active electrocatalytic anode materials to promote methanol oxidation. In this chapter, bimetallic platinum-ruthenium nanoparticles synthesized by chemical, sonochemical and radiolytic methods are compared on the basis of their electrocatalytic performance in this chapter.

**Section 5.1**

**Introduction**
5.1. **Introduction**

![Schematic structure of a typical direct methanol fuel cell.](image)

**Figure 5.1**: Schematic structure of a typical direct methanol fuel cell.

### 5.1.1. Platinum Electro catalyst

Normally, the catalyst for both the anode and cathode in DMFCs is platinum-based. The electrochemical oxidation of methanol is much more complicated than the anodic oxidation of hydrogen. To promote methanol oxidation, the anode uses either a pure platinum metal catalyst or a supported platinum catalyst, typically on carbon or graphite for pure hydrogen feed streams. Oxygen reduction at the cathode may use either platinum metal or the supported catalyst. However, the cathodic oxygen reduction process is much slower, and therefore can be assumed to be the rate determining step under most conditions. Normally, sulfuric acid is used as the electrolyte. Due to the fact that electrolyte is circulated through the fuel cell, the fuel is delivered with the electrolyte.

The reactions during methanol electro-oxidation process of platinum nanoparticles are shown in Figure 5.2.
5.1. **Introduction**

(Reactions I - VIII). The oxidation process takes place at the anode where methanol adsorbs on the platinum surface and undergoes sequential oxidation [266, 267, 282]. Figure 5.2 shows that platinum plays a significant role in the sequential stripping of protons and electrons from methanol adsorbed on its surface. As a result, carbon-containing intermediates are like to be produced during the sequential oxidation.

![Diagram of methanol oxidation process](image)

**Figure 5.2:** The scheme of the methanol oxidation process at the platinum anode of a direct methanol fuel cell (modified from reference [283]).
5.1. INTRODUCTION

The main reactions occurring at the anode and cathode are summarized in Reaction 5.1-5.3:

Anode reaction: \( \text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 6\text{H}^+ + 6\text{e}^- \) (5.1)

Cathode reaction: \( \frac{3}{2}\text{O}_2 + 6\text{H}^+ + 6\text{e}^- \rightarrow 3\text{H}_2\text{O} \) (5.2)

Overall reaction: \( \text{CH}_3\text{OH} + \frac{3}{2}\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \) (5.3)

For the oxidation taking place at the anode, the thermodynamic voltage is 0.046 \( V_{\text{SHE}}^* \) at 25 °C [283, 284]. Methanol is finally oxidized to carbon dioxide, protons and electrons. In the reduction process, the protons react with oxygen to form water and the electrons are transferred to produce the electrical power. The corresponding thermodynamic voltage is 1.23 \( V_{\text{SHE}} \) [283, 284]. Thus the maximum thermodynamic voltage of the whole DMFC reaction is 1.18 \( V_{\text{SHE}} \) [283, 284]. However, the cell voltage is much less than this because of losses from poor cathode activity, catalyst loading and impedance sources within the cell.

5.1.2. Role of Ruthenium Particles

Normally, the clean surfaces of Pt catalysts show very high activity for methanol oxidation, but these very rapidly decrease in current upon the formation of strongly bound intermediates (see Reactions 5.4-5.7 and Figure 5.2). CO is the most widely found residue from methanol. This intermediate species is irreversibly adsorbed on the surface of the electrocatalyst and severely poisons the Pt, slowing down the overall reaction. This poisoning has the effect of significantly reducing the fuel consumption efficiency and the power density of the fuel cell. It is only

\* \( V_{\text{SHE}} \) refers to the voltage relative to the standard hydrogen electrode.
at high overpotentials that these intermediates can be oxidized.

\[
\begin{align*}
\text{CH}_3\text{OH} + \text{Pt} & \rightarrow \text{Pt-CH}_2\text{OH} + \text{H}^+ + \text{e}^- \\
\text{Pt-CH}_2\text{OH} + \text{Pt} & \rightarrow \text{Pt-CHOH} + \text{H}^+ + \text{e}^- \\
\text{Pt-CHOH} + \text{Pt} & \rightarrow \text{PtCHO} + \text{H}^+ + \text{e}^- \\
\text{PtCHO} & \rightarrow \text{Pt-CO} + \text{H}^+ + \text{e}^-
\end{align*}
\]

(5.4) \hspace{2cm} (5.5) \hspace{2cm} (5.6) \hspace{2cm} (5.7)

The development of platinum based catalysts has focused on the introduction of a secondary component, for example ruthenium, that is able to provide an adsorption site capable of forming OH species at low potentials adjacent to poisoned Pt sites. The presence of the ruthenium in the catalyst alloy serves to reduce the poisoning of the Pt surface by carbon monoxide.

A number of studies have put forth the primary theories of the enhancement due to the presence of Ru [266, 267, 284, 285]. The enhanced behavior of PtRu over Pt has been attributed to a ligand (electronic) effect of Ru and a bifunctional effect [286, 287], in which the role of Ru is to offer adsorbed oxygen-containing species to oxidize carbonaceous adsorbates on Pt sites.

## Section 5.2

### Fuel Cell Performance of Platinum Nanoparticles

A key parameter, the electrochemical active surface area (ECSA), determines the electrocatalytic performance of these Pt particles deposited on carbon Toray paper. The cyclic voltammetry technique is finding wide use in measuring catalytic surface areas for electrically conductive catalysts.

Figure 5.3 shows the cyclic voltammogram of a Pt electrocatalyst synthesized by the sonochemical reduction of a solution containing 1 mM K₂PtCl₄, 1 mg/mL poly(sodium 4-styrenesulfonate)(PSS) and 0.4 M 1-propanol. It exhibits the typical features of a Pt electrode in 0.1 M H₂SO₄ solution. Hydrogen adsorption and desorption regions between 0.0 Vₘₛₖₑ and -2.7 Vₘₛₖₑ indicate the success of Pt particles’ electro-deposition on the carbon

*Vₘₛₖₑ refers to the voltage relative to the standard saturated calomel electrode.
Figure 5.3: Cyclic voltammogram for Pt nanoparticles synthesized by the sonochemical reduction of a 10 mL aqueous solution containing 1 mM K$_2$PtCl$_4$, 1 mg/mL PSS and 0.4 M 1-propanol under an Ar saturated atmosphere. The ultrasound frequency used was 630 kHz and the total power was 20 W. The acidic electrolyte used was 0.1 M H$_2$SO$_4$ solution and the scan rate was 50 mV/s. The area of the electrode was 0.75 cm$^2$.

Toray paper. A shoulder at 0.7 V$_{SCE}$ is due to the oxidation of Pt (Reaction 5.8). The oxidation stripping was
5.2. Fuel Cell Performance of Platinum Nanoparticles

found on the negative returning sweep near 0.5 \( V_{SCE} \) (Reaction 5.9).

\[
\begin{align*}
\text{Pt} + \text{H}_2\text{O} & \rightarrow \text{PtOH} + \text{H}^+ + e^- \quad (5.8) \\
\text{PtOH} + \text{H}^+ + e^- & \rightarrow \text{Pt} + \text{H}_2\text{O} \quad (5.9)
\end{align*}
\]

The ECSA of an electrocatalyst is a measure of the number of electrochemically active sites per gram of the catalyst and is determined by integrating the area under the potential window for the hydrogen adsorption/desorption peaks after subtracting the charge from the double layer region [263, 288–291]. For this estimation, the hydrogen underpotential deposition charge density was taken as 210 \( \mu \text{C/cm}^2 \) [263, 290, 291].

\[
\text{ECSA}[\text{cm}^2/\text{g}] = \frac{\text{Charge}[Q_H, \mu \text{C/cm}^2]}{210[\mu \text{C/cm}^2] \times \text{Catalyst Loading}[\text{g}_\text{Pt}/\text{cm}^2]} \quad (5.10)
\]

Using Equation 5.10 and integration of the current from 0.4 V to 0 \( V_{SCE} \), the ECSA was calculated to be 10.9 m\(^2\)/g. It is interesting to note that this ESCA value of the Pt nanoparticles synthesized by sonochemical reduction is significantly higher than bare platinum (2.8 m\(^2\)/g), reinforcing the advantages of the sonochemical synthesis method (discussed in Chapter 4).

Figure 5.4 shows the cyclic voltammograms recorded with ultrasound-prepared platinum on carbon Toray paper in N\(_2\)-sparged 0.1 M H\(_2\)SO\(_4\) containing 1 M methanol at 20°C. Five repetitive scans were carried out in order to acquire a reproducible cyclic voltammograms without noticing any deviations in the current values. Figure 5.4 is of the fifth scan, which is stable after four repetitive scans. This voltammogram exhibits the characteristic features of methanol oxidation on platinum in aqueous acid solutions. Methanol oxidation is represented by the anodic peak around 630 mV. On the reverse scan, the adsorbed intermediates produce a second oxidation peak at 490 mV. The magnitude of the first peak at 630 mV is directly proportional to the amount of methanol oxidized at the electrode. The anodic peak of 490 mV is known to be related to the removal of incompletely oxidized carbonaceous species formed in the forward scan. These two peaks are explained below in detail [263, 291].

On the forward scan, the adsorption and continuous oxidation of methanol leads to an increase of current. At the same time, Pt-CO bonds at the surface of the Pt nanoparticles develop after multistep reactions with methanol.
Figure 5.4: Cyclic voltammogram for Pt nanoparticles synthesized by the sonochemical reduction of a 10 mL aqueous solution containing 1 mM K$_2$PtCl$_4$, 1 mg/mL PSS and 0.4 M 1-propanol under an Ar saturated atmosphere. The ultrasound frequency used was 630 kHz and the total power was 20 W. The acidic electrolyte used was 1 M methanol and 0.1 M H$_2$SO$_4$ solution and the scan rate was 20 mV/s. The area of the electrode was 0.75 cm$^2$.

(see Reactions 5.4-5.7). Furthermore, the adsorbed water might react with this Pt-CO species to form hydroxide...
(Pt-OH) at higher voltages. The substantial amount of OH species absorbed on the surface leads to a decrease in the number of active sites on the electrode surface. Consequently, the oxidation current decreases after the peak current.

On the reverse scan, the desorption of Pt-OH is capable of reacting with poisoned Pt sites and leads to an increase in current (Reaction 5.9). Thus, the cleaning process of the Pt surface results in the second oxidation current peak.

\[
\text{Pt-CO + Pt-OH} \rightarrow 2\text{Pt + CO}_2 + \text{H}^+ + e^-
\]  

(5.11)

Although Reactions 5.1-5.3 look simple from a stoichiometry point of view, the chemisorption and electrochemical oxidation of methanol on a platinum catalyst is quite a complicated multistep process. Chemisorption of methanol on platinum takes place very rapidly on the bare catalyst surface. The process of methanol oxidation involves the formation of chemisorbed fragments, predominantly CO, and probably COH [267] (see Reaction 5.4-5.7 and Figure 5.2). The formation of these strongly adsorbed reaction intermediates is the major reason for the sluggish electro-oxidation. An approach for enhancing the oxidation activity of Pt for methanol oxidation is through the utilization of alloys. The second metal forms a surface oxide in the potential range appropriate for methanol dehydration. A number of studies [266, 267, 286, 287] have proved that ruthenium is the best candidate for this second metal. The following sections focus on the electrocatalytic performance of PtRu bimetallic nanoparticles synthesized by chemical, sonochemical and radiolytic methods.

**Section 5.3**

**Chemical Synthesis Methods**

As described in Subsection 4.3.2 of Chapter 4, a solution of sodium borohydride was used as a reductant to convert Ru(III) and Pt(II) ions to PtRu bimetallic nanoparticles. Two different methods, sequential and simultaneous reduction, were used to synthesize the PtRu bimetallic nanoparticles.
5.3. CHEMICAL SYNTHESIS METHODS

5.3.1. Sequential Reduction

The electrocatalysts in Figure 5.5 were prepared using sequential chemical reduction. 10 mL solution containing Pt(II) and Ru(III) ions were added dropwise to 120 µL of 150 mM sodium borohydride aqueous solution. The reduction of a solution containing 1 mM K₂PtCl₄, 1 mg/mL PSS and 0.4 M 1-propanol was followed by sequential reduction of 1 mM RuCl₃. The ratios of Pt(II) to Ru(III) in precursor solutions were 5:1, 2:1, 1:1 and 1:2 (shown in Figures 5.5a-5.5d, respectively.).

According to the cyclic voltammograms in Figure 5.5, all the sequential chemical reduction samples show similar features to Pt in Figure 5.4. In the anodic sweep, the peaks indicating the oxidation of methanol are located at around 620 mV when the ratios of Pt(II) and Ru(III) in precursor solution are 5:1, 2:1 and 1:1. For the case of 1:2 (Pt(II):Ru(III)), it can be seen that the methanol oxidation peak shifts slightly negatively to 570 mV. This slight shift shows that small amounts of Ru(0) were incorporated with Pt(0) formed earlier. A detailed discussion of the function of Ru in the Pt electrode will be presented in the following subsection. It is evident that PtRu electrocatalysts synthesized by the sequential chemical method only show the basic features of a Pt catalyst in methanol oxidation. The PtRu bimetallic nanoparticles prepared by using sequential chemical reduction seem to be a simple mixture of platinum and ruthenium nanoparticles. This may be the main reason for the low electrocatalytic performance.

A number of studies [266, 287, 292] show that the ratios of Pt and Ru in the electrocatalyst play a significant role in influencing current during the oxidation of methanol. In our case, an accurate quantitative technique (e.g., inductively coupled plasma) to determine the actual Pt and Ru ratio, was unavailable. Thus, the influence of the component ratio in electrocatalysts on the current of cyclic voltammograms will not be discussed in this work.

5.3.2. Simultaneous Reduction

Figure 5.6 shows the cyclic voltammograms of platinum-ruthenium bimetallic electrocatalysts prepared by simultaneous chemical reduction of Pt(II) and Ru(III) ions in aqueous solution. A 120 µL aqueous solution of 150 mM sodium borohydride was added dropwise to a 10 mL mixture of K₂PtCl₄ and RuCl₃ solution. 1 mg/mL PSS was used to control the nanoparticle size and act as a stabilizer of the bimetallic colloids (see Chapter 2). It should be
5.3. Chemical Synthesis Methods

Figure 5.5: Cyclic voltammogram of PtRu nanoparticles synthesized by chemical sequential reduction of a 10 mL aqueous solution containing 1 mM K$_2$PtCl$_4$, 1 mg/mL PSS and 0.4 M 1-propanol followed by the reduction of 1 mM RuCl$_3$. The added reductant was 120 µL aqueous solution of 150 mM sodium borohydride. The acidic electrolyte used was 1 M methanol and 0.1 M H$_2$SO$_4$ solution and the scan rate was 20 mV/s. The area of the electrode was 0.75 cm$^2$ in each case.
5.3. Chemical Synthesis Methods

noted that the stabilizer used here is PSS instead of PVP or SDS which were previously used in Chapter 4. The results of separate experiments show that PVP or SDS can influence the conductivity of electrodes and consequently significantly impede the performance of PtRu-based electrocatalysts. Thus, PSS was selected to stabilize the metallic or bimetallic colloids in evaluating the performance of the fuel cell. The presence of alcohol, 1-propanol, was to make a reference system to the sonochemical and radiolytic systems in which alcohol is involved in the reaction (see Chapter 2).

The cyclic voltammograms of the PtRu bimetallic catalyst, simultaneously chemically prepared in four different molar ratios, 5:1, 2:1, 1:1 and 1:2, of Pt(II) and Ru(III) metallic ions in precursor solution are shown in Figures 5.6a-5.6d, respectively. It can be seen that the characteristics of these four cyclic voltammograms are quite different from those of PtRu synthesized by sequential chemical reduction. The second oxidation current peak on the cathodic scan clearly decreases, especially that of the 1:2 molar ratio sample almost completely disappeared. The decreases in the reverse oxidation peaks indicate that the ruthenium was successfully incorporated into the platinum nanoparticles. The introduction of ruthenium suppresses the CO poisoning on the surface of platinum. At the same time, it also can be observed that the methanol oxidation peaks on forward scans clearly shift negatively (around 0.48 V<sub>SCE</sub>). Furthermore, compared to the samples from the sequential chemical method, the simultaneously synthesized PtRu bimetallic electrocatalysts have lower onset potentials for methanol oxidation in the voltammogram. For example, in the case of the 1:1 molar ratio, the methanol oxidation onset potential of PtRu bimetallic nanoparticles synthesized by sequential reduction (Figure 5.5c) is 0.3 V<sub>SCE</sub>, but that of the simultaneously chemically reduced PtRu (Figure 5.6c) is 0.1 V<sub>SCE</sub>.

It can also be seen that the onset potential for methanol oxidation shifts from 0.3 V<sub>SCE</sub> for the 5:1 molar ratio sample (Figure 5.6a) to 0.1 V<sub>SCE</sub> for the 1:2 molar ratio sample (Figure 5.6d). This observation demonstrates that an increase in the molar proportion of ruthenium ions in precursor solution is likely to lowering the onset potential for the methanol oxidation. The ruthenium component of PtRu synthesized by the simultaneous chemical method is likely to play a significant role in improving the efficiency of the overall electrocatalytic activities.

All the above observed phenomena demonstrate that the simultaneous chemical reduction method has ability to synthesize better performance electrocatalyst than the sequential chemical reduction method. In addition, the results suggest that the introduction of ruthenium to platinum-based electrocatalysts, as the second component,
5.3. Chemical Synthesis Methods

Figure 5.6: Cyclic voltammograms of PtRu nanoparticles synthesized by chemical simultaneous reduction of 1 mM K₂PtCl₄, 1 mM RuCl₃, 1 mg/mL PSS and 0.4 M 1-propanol. The reductant added was 120 µL aqueous solution of 150 mM sodium borohydride. The acidic electrolyte used was 1 M methanol and 0.1 M H₂SO₄ solution and the scan rate was 20 mV/s. The area of the electrode was 0.75 cm² in each case.

(a) 1 mM K₂PtCl₄ + 0.2 mM RuCl₃
(b) 1 mM K₂PtCl₄ + 0.5 mM RuCl₃
(c) 1 mM K₂PtCl₄ + 1 mM RuCl₃
(d) 0.5 mM K₂PtCl₄ + 1 mM RuCl₃
results in an increase in the performance of electrocatalytic properties of the electrode. The contribution of the presence of ruthenium in platinum-based catalysts is mainly due to the bifunctional mechanism, ligand effects and lower CO oxidation potential on the Ru surface.

A number of studies [266–268, 285, 286] show that Pt promotion by Ru for methanol oxidation is mainly attributable to the bifunctional mechanism, in which the formation of surface hydroxide on ruthenium is able to increase the tolerance to CO poisoning. Normally, at 298 K, the onset potential of the adsorption of OH species to ruthenium (0.2 V_{SHE}) is lower than that of platinum (0.7 V_{SHE}) [266, 293]. Consequently, at the lower electrode potential, water discharging can occur on the ruthenium surface with formation of RuOH species on the PtRu bimetallic catalyst.

\[
\text{Ru} + \text{H}_2\text{O} \rightarrow \text{RuOH} + \text{H}^+ + \text{e}^- \quad (5.12)
\]

The surface-bound OH-groups forms on the ruthenium are able to convert these carbon monoxide intermediates to carbon dioxide. This CO stripping ability of ruthenium can reactivate the blocked platinum electrode sites for further methanol oxidation.

\[
\text{RuOH} + \text{Pt-CO} \rightarrow \text{Pt} + \text{Ru} + \text{CO}_2 + \text{H}^+ + \text{e}^- \quad (5.13)
\]

A number of studies [266, 284, 287, 293] suggests that the synergistic promotion exerted by PtRu bimetallic catalysts is not only due to the bifunctional mechanism, but also to the ligand effect occurring on account of the interaction between Pt and Ru. It is known that the formation of Pt-CO involves the $\sigma^*$ anti-bonding orbitals of CO donating an electron pair to the $5d$ orbitals of Pt. This band is stabilized by back donation of electron density from platinum to the unfilled $\pi^*$ orbitals of CO. The presence of ruthenium alters the electronic properties of adjacent platinum atoms, which is likely to decrease the bond energy of Pt-C [266, 293]. The presence of ruthenium leads to increasing the electron density around Pt sites, which consequently results in a weaker chemisorption of methanolic residues on Pt.

Apart from the bifunctional mechanism and ligand effects, the presence of ruthenium is likely to introduce the reaction toward producing proportionately more carbon dioxide and less formic acid and formaldehyde than pure platinum catalysts [287]. In short, the ruthenium is able to alter the methanol oxidation selectivity to the products.
According to the bifunctional mechanisms of ligand effects, the presence of ruthenium has significant positive effects on the electrocatalytic ability of PtRu bimetallic nanoparticles. However, the extent of these effects is effectively determined by the atomic Pt:Ru ratios and ruthenium distribution in platinum atoms. It is known that the rate of electro-oxidation of methanol is strongly dependent on platinum content, as the current density is proportional to the methanol adsorption on Pt (see Reactions 5.4-5.7). Therefore, large quantities of platinum in PtRu catalyst accounts for the higher methanol adsorption rate, consequently the higher current density. At the same time, the adsorption of methanol on the surface of ruthenium only occurs at high temperature \([294]\). Furthermore, even at high temperature, platinum is the leading component in adsorbing methanol.

However, the bifunctional mechanism described above suggests that the presence of ruthenium has potential to oxidize the adsorbed methanol oxidation residues at low potentials. Furthermore, the in-situ CO stripping voltammetry provides clear evidence that the overall rate of methanol electro-oxidation process is determined by CO removal \([266, 293]\). The bifunctional mechanism demonstrates that Pt is a good catalyst for methanol adsorption and dehydrogenation, but not for water dissociation. Ruthenium is capable of effective water dissociation and CO oxidation to recover the poisoned Pt, but it cannot adsorb methanol. At higher temperature (above 90 °C), ruthenium is able to participate in the methanol chemisorption process at low potentials, but the chemisorption energy of oxygen on Ru surface is too high to inhibit the reactivating function of ruthenium for the methanolic residues. Thus, incorporation with ruthenium is necessary for a platinum-based electrocatalyst. In addition, the introduction of ruthenium is likely to modify the electronic properties of platinum to favor the adsorption of methanol \([295]\).

Therefore, there is an optimal ratio of platinum to ruthenium content in order to attain the highest electrocatalytic performance in a fuel cell application.

As both the adsorption of methanol on the surface of platinum and water discharging behavior on ruthenium are related to the ambient temperature, this optimal ratio of platinum and ruthenium will change with the environmental temperature. In addition to the elemental composition and ambient temperature, the electrode potential, the spatial arrangement and the reactant concentration in solution also have impact on the rate of methanol oxidation. Therefore, the methanol oxidation on PtRu electrode is a complicated process involving a number of factors. The following paragraph focus on the effect of the spatial arrangement of platinum and ruthenium.

Based on the bifunctional mechanism and ligand effects, the blending together of platinum and ruthenium also
plays an important role in improving the electrocatalytic performance. As described for the bifunctional effect, Ru-OH can only access the neighboring Pt-CO species to reactivate the blocked Pt sites. For the ligand effect, only adjacent ruthenium atoms have influence on the electronic structures of platinum. Therefore, the prerequisite for achieving this effect by introducing ruthenium into the platinum-based catalyst is that the ruthenium is strongly blended with the platinum.

For PtRu synthesized by sequential chemical reduction, the platinum and ruthenium seem to be independently formed without any association between these individual components. However, during synthesis in the simultaneous chemical method, Pt(II) and Ru(III) ions are reduced by sodium borohydride at the same time. This kind of formation is likely to produce PtRu alloys or the mixture of small island particles of platinum and ruthenium. Due to the greater number of adjacent PtRu sites and boundaries between the domains of Pt and Ru surface atoms, the simultaneous chemical reduction seems to be an effective synthesis method to prepare high performance PtRu electrocatalysts.

**Section 5.4**

**Sonochemical Synthesis Methods**

As described in Chapter 2, sonochemical reduction of noble metallic ions in precursor solutions is likely to be an effective method to form small size nanoparticles with uniform shapes and narrow size distribution. In Chapter 4, two different methods, sequential and simultaneous reduction, were used to prepare PtRu bimetallic nanoparticles. The point of interest is that the sequential sonochemical reduction seems to form core-shell structure PtRu bimetallic nanoparticles. The main attention of this section is focused on the evaluation of the electrocatalytic performance of these noble bimetallic materials.

**5.4.1. Simultaneous Reduction**

A frequency of 630 kHz ultrasound was applied to irradiate a 10 mL solution containing K$_2$PtCl$_4$, RuCl$_3$, 1 mg/mL PSS and 0.4 M 1-propanol. Various concentration ratios of K$_2$PtCl$_4$ and RuCl$_3$ in precursor solutions were used
to alter the ratios of Pt(II) to Ru(III) to 5:1, 2:1, 1:1 and 1:2.

Due to the particle sizes of these four different molar ratios being too small, the high speed centrifugation process (speed: 10,000 rpm) was unable to extract these metallic nanoparticles from the aqueous solution. The failure of this crucial step led to unsuccessful deposition of PtRu on the Toray paper. Several methods were used to attempt to extract the PtRu metallic nanoparticles, but all of them failed. For example, normal filtering was unable to separate such small bimetallic nanoparticles. Drying the solution in an oven or under normal conditions is likely to incorporate ionic and hydrolyzed species (see Chapter 4) with the final electrocatalyst and undesirable. Even through this method was tried, it was not successful. Furthermore, it is a tedious and time-consuming process to dry PtRu bimetallic nanoparticles and not practically worth undertaking.

Therefore, in the future, it is necessary to develop a novel but convenient method to extract the PtRu nanoparticles synthesized by simultaneous sonochemical reduction in order to evaluate their electrocatalytic performance.

5.4.2. Sequential Reduction

As described in Chapter 4, a tetrachloroplatinate solution containing 1 mg/mL PSS and 0.4 M 1-propanol was initially ultrasonicated to produce platinum colloids. A solution of RuCl$_3$ and 0.4 M 1-propanol was mixed with the Pt colloids. The final molar ratios of Pt(II) to Ru(III) were 5:1, 2:1, 1:1 and 1:2. The mixed solutions were sonicated until there were no further changes taking place in the UV-vis absorption spectra.

Figure 5.7 shows two cyclic voltammograms of PtRu prepared by sequential sonochemical reduction of the metallic ion precursor solutions, whose Pt(II) to Ru(III) molar ratios are 1:1 and 1:2, respectively. Due to the same reason as for the simultaneous sonochemical reduction samples mentioned in the previous subsection, high speed centrifugation could not successfully extract the PtRu bimetallic nanoparticles from the 5:1 and 2:1 molar ratio samples.

Both the 1:1 and 1:2 molar ratio samples exhibit similar basic features to a pure platinum electrocatalyst. The methanol oxidation onset potentials of the PtRu bimetallic electrocatalyst in the 1:1 and 1:2 molar ratio samples are around 0.3 V$_{SCE}$ and 0.4 V$_{SCE}$, respectively. The same onset potential as the pure platinum catalyst indicates that the ruthenium atoms seem not to have been incorporated well among the platinum atoms in the PtRu nanoparticles.
5.4. Sonochemical Synthesis Methods

Figure 5.7: Cyclic voltammograms of PtRu nanoparticles synthesized by the sequential sonochemical method: cyclic voltammogram of PtRu observed after 5 hours sequentially sonochemical reduction of an aqueous solution of 1 mM K$_2$PtCl$_4$ containing 1 mg/mL PSS and 0.4 M 1-propanol followed by the reduction of 1 mM RuCl$_3$ under an Ar saturated atmosphere. The ultrasound frequency used was 630 kHz and the total power was 20 W. The acidic electrolyte used was 1 M methanol and 0.1 M H$_2$SO$_4$ solution and the scan rate was 20 mV/s. The area of the electrode was 0.75 cm$^2$ in each case.

(a) 1 mM K$_2$PtCl$_4$ + 1 mM RuCl$_3$

(b) 0.5 mM K$_2$PtCl$_4$ + 1 mM RuCl$_3$

formed by sequential sonochemical irradiation.

As showed in Chapter 4, the composite PtRu nanoparticles prepared by sequential sonochemical reduction clearly have a core-shell structure (see Figure 4.16). A layer of ruthenium was formed around the platinum particles. According to the mechanism of the bifunctional effect, platinum is responsible for chemisorption and
5.5. Hybrid Synthesis Method

The hybrid synthesis method, namely ultrasonic irradiation followed by chemical reduction, was carried out to investigate the changes of electrocatalytic performance of sequentially ultrasonicated PtRu nanoparticles. 60 µL quantities of 150 mM sodium borohydride solution were added dropwise into the two sequential sonochemically irradiated PtRu solutions (Subsection 5.4.2).

Figure 5.8 shows two cyclic voltammograms of PtRu prepared by sequential sonochemical reduction of the Pt and Ru metallic ion precursor solutions followed by sodium borohydride reduction. It can be seen that the methanol oxidation onset potentials of these two PtRu bimetallic electrocatalysts prepared by the hybrid reduction method is slightly shifted to about 0.2 V<sub>SCE</sub>. The negative shift of onset potentials shows that subsequent to chemical reduction the incorporation of platinum and ruthenium is strengthened. The strong reducing conditions enable the ruthenium oxide and hydrolyzed species, which are not completely reduced during ultrasonic irradiation, to convert into Ru(0). Therefore, a small amount of the subsequently formed ruthenium particles are possibly incorporated with pre-existing platinum nanoparticles to form PtRu composite catalysts. This incorporation may
5.5. Hybrid Synthesis Method

Figure 5.8: Cyclic voltammograms of PtRu observed after 5 hours of sequential sonochemical reduction of an aqueous solution of 1 mM $\text{K}_2\text{PtCl}_4$ containing 1 mg/mL PSS and 0.4 M 1-propanol followed by the reduction of 1 mM $\text{RuCl}_3$ under an Ar saturated atmosphere and sequentially followed by reaction with 80 µL of 150 mM sodium borohydride. The ultrasound frequency used was 630 kHz and the total power was 20 W. The acidic electrolyte used was 1 M methanol and 0.1 M $\text{H}_2\text{SO}_4$ solution and the scan rate was 20 mV/s. The area of the electrode was 0.75 cm$^2$ in each case.

(a) 10 mL of a mixture of 1 mM $\text{K}_2\text{PtCl}_4$ and 1 mM $\text{RuCl}_3$ + 80 µL of 150 mM NaBH$_4$

(b) 10 mL of a mixture of 0.5 mM $\text{K}_2\text{PtCl}_4$ and 1 mM $\text{RuCl}_3$ + 80 µL of 150 mM NaBH$_4$

lead to the negative shift of the methanol oxidation onset potential.

In addition, it can be observed that there was no significant effect of element component ratio on the onset potential in cyclic voltammograms. However, compared to the cyclic voltammograms of the sequential sonochemical reduced samples, the methanol oxidation onset potential of the 1:1 molar ratio sample shifted from 0.3
5.6. Radiolytic Synthesis Method

The $\gamma$-radiolysis technique is widely used to synthesize a broad range of nanometer size materials, due to its high energy rays. The detailed mechanism and reactions are discussed in the Section 2.3 of Chapter 2. It is well-known that due to its high energy, $\gamma$-rays are able to disassociate water molecules of the solvent into highly reactive species, such as H•, OH• and e$_{aq}^-$. The strongly reducing H• and e$_{aq}^-$ species have the ability to convert almost all metal ions into zerovalent metals [154, 186, 188].

Similar to the chemical and sonochemical methods, the sequential and simultaneous methods are used in this section to investigate the effects of different processes on the catalytic performance of the PtRu bimetallic nanoparticles formed.
5.6. **Radiolytic Synthesis Method**

### 5.6.1. Sequential Reduction

An absorbed dosage rate of 0.0144 Gy/min of \(\gamma\)-rays was used to irradiate an 30 mL aqueous solution containing \(K_2PtCl_4\), 1 mg/mL PSS and 0.4 M 1-propanol for 30 min. After the platinum ions were completely reduced, a RuCl\(_3\) solution at a certain concentration was added to the reduced platinum colloids. The \(\gamma\)-irradiation was continued of the solution mixture until there were no significant changes in the UV-vis spectra (30 min). By adjusting the concentration ratios of \(K_2PtCl_4\) to RuCl\(_3\), the ratios of Pt(II) to Ru(III) in the precursor solution were set to 5:1, 2:1, 1:1 and 1:2.

Figures 5.9a-5.9d show the cyclic voltammograms of PtRu synthesized by sequential radiolytic reduction of precursor solutions whose Pt(II) to Ru(III) molar ratios were 5:1, 2:1, 1:1 and 1:2. The 5:1, 2:1 and 1:1 molar ratios show the basic characteristics of pure platinum cyclic voltammograms whose methanol oxidation onset potential is around 0.3 V\(_{SCE}\). However, the onset potential of the 1:2 molar ratio PtRu shifts to 0.2 V\(_{SCE}\). This negative shift indicates that the high proportion of ruthenium ions in the precursor solution is likely to lead to comparatively stronger incorporation between platinum and ruthenium during the radiolytic irradiation. This observation was also reflected in the shifts of the methanol oxidation peaks. As a general trend, the shift of the methanol oxidation peak to negative voltage increases with an increase of the ruthenium component in the initial solutions during \(\gamma\)-ray irradiation.

It is worthwhile to point out that the platinum-ruthenium bimetallic nano-electrocatalysts prepared by the sequential method applied during the chemical, sonochemical and radiolytic synthesis do not possess high electrocatalytic properties. According to the mechanism of bifunctional mechanism and ligand effect, the PtRu composite nanoparticles with more adjacent sites and boundaries between these two components have the potential to demonstrate better methanol oxidation ability and more synergistic promotions. The sequential reduction process requires that one component (normally platinum particles) is produced first and followed by reduction of the second type precursor ions (normally ruthenium). This particle synthesis method is likely to lead to the formation of core-shell structure bimetallic nanoparticles and independent, dispersed platinum and ruthenium metallic nanoparticles. As discussed before, the core-shell structure inhibits the influence of bifunctional mechanism and ligand effect and consequently retards the methanol oxidation process. For the independently formed platinum
5.6. Radiolytic Synthesis Method

![Cyclic voltammograms](a) 1 mM K\textsubscript{2}PtCl\textsubscript{4} + 0.2 mM RuCl\textsubscript{3}  

![Cyclic voltammograms](b) 1 mM K\textsubscript{2}PtCl\textsubscript{4} + 0.5 mM RuCl\textsubscript{3}  

![Cyclic voltammograms](c) 1 mM K\textsubscript{2}PtCl\textsubscript{4} + 1 mM RuCl\textsubscript{3}  

![Cyclic voltammograms](d) 0.5 mM K\textsubscript{2}PtCl\textsubscript{4} + 1 mM RuCl\textsubscript{3}

**Figure 5.9:** Cyclic voltammograms of PtRu observed after 3 hours sequential radiolytic reduction of an aqueous solution of 1 mM K\textsubscript{2}PtCl\textsubscript{4} containing 1 mg/mL PSS and 0.4 M 1-propanol followed by the reduction of 1 mM RuCl\textsubscript{3} under an nitrogen saturated atmosphere. The absorbed dosage rate of γ-ray was 0.0144 Gy/min. The acidic electrolyte used was 1 M methanol and 0.1 M H\textsubscript{2}SO\textsubscript{4} solution and the scan rate was 20 mV/s. The area of the electrode was 0.75 cm\textsuperscript{2} in each case.
and ruthenium nanoparticles, it is difficult, especially in the presence of surfactant, to create a proper environment which can produce a synergistic promotion through a bifunctional mechanism and ligand effect.

### 5.6.2. Simultaneous Reduction

Four 30 mL aqueous solutions of various K$_2$PtCl$_4$ RuCl$_3$ concentrations including 1 mg/mL PSS and 0.4 M 1-propanol were irradiated by a $\gamma$-radiolysis at absorbed dosage rate of 0.0144 Gy/min. In these cases, the Pt(II) and Ru(III) were reduced by radiolysis simultaneously.

Figure 5.10 shows the cyclic voltammograms of the PtRu catalysts prepared by simultaneous radiolytic reduction. The platinum to ruthenium salt ratios in the precursor solutions of Figures 5.10a-5.10c are 5:1, 2:1, 1:1 and 1:2, respectively.

The peaks, corresponding to methanol oxidation, of the 5:1, 2:1 and 1:2 platinum and ruthenium molar ratios, are located at around 610 mV, while that of the 1:1 molar ratio sample is at 480 mV. Furthermore, the methanol oxidation onset potentials of these four different ratios sample are 0.3, 0.3, 0.1 and 0.2 V$_{SCE}$, respectively. In addition, the oxidation peak of the 1:1 molar ratio PtRu during the reverse scan almost completely disappears, which is similar to the basic features of the PtRu alloy electrocatalyst [296]. Due to the successful incorporation of platinum and ruthenium, the presence of ruthenium suppresses the CO poisoning process on the surface of platinum and completely removes the carbonaceous residues. All these observations prove that the PtRu synthesized by simultaneous radiolytic reduction of the 1:1 Pt(II) to Ru(III) molar ratio precursor solution exhibits better electrocatalytic performance during methanol oxidation.

As discussed before, the PtRu catalysts ability to oxidize methanol is determined by the ambient temperature, ruthenium composition, the number of adjacent sites and boundaries of ruthenium and platinum, the surface status of the catalyst, the nature of the catalyst supports, and so on. Furthermore, the electro-oxidation of methanol is a complicated process. As a result, the optimum Ru content in PtRu catalysts is quite different to achieve for different systems. Based on the bifunctional mechanism of the surface Reaction 5.13 between Pt-CO and Ru-OH, 50% of ruthenium surface composition is likely to maximize the bifunctionality and ligand effects, due to the maximization of the number of PtRu neighbors and boundaries. However, this 50% ruthenium atomic coverage works
Figure 5.10: Cyclic voltammograms of PtRu observed after 3 hours simultaneous radiolytic reduction of an aqueous solution of 1 mM K$_2$PtCl$_4$ and 1 mM RuCl$_3$ containing 1 mg/mL PSS and 0.4 M 1-propanol under a nitrogen saturated atmosphere. The absorbed dosage rate of $\gamma$-ray was 0.0144 Gy/min. The extraction method was centrifugation. The acidic electrolyte used was 1 M methanol and 0.1 M H$_2$SO$_4$ solution and the scan rate was 20 mV/s. The area of the electrode was 0.75 cm$^2$ in each case.
only at high temperature, as the methanol adsorption, dehydrogenation and water disassociation arrive at an equilibrium. When the temperature drops down to room temperature, the dehydrogenation of methanol on the surface of platinum becomes the rate-determining step of the overall reaction. According to the Reactions 5.4-5.7 and Figure 5.2, the dissociation of an adsorbed methanol molecule needs three neighboring platinum sites [266, 293]. As a result, the PtRu catalysts with a good portion of an arrangement of three adjacent Pt sites may provide greater electrocatalytic activity. Due to the complicated condition for methanol oxidation, various optimal ruthenium contents have been reported [266, 293] for different systems.

During the simultaneous radiolytic reduction of platinum and ruthenium ion mixtures, the rate of each composition formation is determined by the reduction potentials of Pt(0) and Ru(0), and also the chance of encountering \( \text{H}^\bullet, \text{R}^\bullet \text{ and } e^-_{\text{aq}} \) generated by \( \gamma \)-ray irradiation (see Figure 2.18). The formed atoms may aggregate and grow through coalescence and an autocatalytic process. Due to the presence of mixing various atoms, it is possible that heterogeneous aggregation takes place to form alloys or island composite nanoparticles. Consequently, this heterogeneous distribution of Pt and Ru in the bimetallic nanoparticles provides more adjacent and neighboring domains, in which the electocatalytic ability of platinum is significantly promoted by the presence of ruthenium atoms. Consequently, the ratio of platinum to ruthenium ions in the precursor solution plays an important role in determining the actual composition and distribution of each metal in the PtRu catalyst.

Rather than using the centrifuging process, a 100°C, low pressure oven was used to heat-treat and dry the PtRu catalyst synthesized by simultaneous radiolytic reduction in a nitrogen atmosphere. Figure 5.11 shows the cyclic voltammograms of these heat-treated PtRu bimetallic nanoparticles. Compared to the PtRu catalyst with centrifuging extraction (see Figure 5.10), the heat treatment does not exert any remarkable influence on the electocatalytic performance of the PtRu particles. This negligible influence may be due to the fact that the low temperature heat-treatment is unable to strengthen the alloying effect between platinum and ruthenium.
5.6. Radiolytic Synthesis Method

Figure 5.11: Cyclic voltammograms of PtRu observed after 3 hours simultaneous radiolytic reduction of an aqueous solution of 1 mM K$_2$PtCl$_4$ and 1 mM RuCl$_3$ containing 1 mg/mL PSS and 0.4 M 1-propanol under an nitrogen saturated atmosphere. The absorbed dosage rate of $\gamma$-ray was 0.0144 Gy/min. The extraction method was oven drying at 100°C. The acidic electrolyte used was 1 M methanol and 0.1 M H$_2$SO$_4$ solution and the scan rate was 20 mV/s. The area of the electrode was 0.75 cm$^2$ in each case.
5.7. Comparison of Onset Potentials

Section 5.7
Comparison of Onset Potentials

Table 5.1 lists all the methanol oxidation onset potentials of different PtRu molar ratios catalysts synthesized by various methods and different processes. It can be seen that all the PtRu bimetallic particles formed with chemical, sonochemical and radiolytic method are all of nanometer size range. As a result, the high surface area of the PtRu in all case has sufficient coordination sites to oxidize methanol.

According to Table 5.1, the PtRu synthesized by the simultaneous reduction method generally is more active than that prepared by sequential method. As discussed before, simultaneous synthesis is likely to strengthen the alloying structure of platinum and ruthenium.

Table 5.1: The influence of synthesis methods, the initial concentration ratios of platinum to ruthenium ions and the extraction methods on the methanol oxidation onset potentials of PtRu bimetallic nanoparticles.

<table>
<thead>
<tr>
<th>Synthesis Method</th>
<th>Reduction Method</th>
<th>Extraction Method</th>
<th>Onset Potential (V_{SCE})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>5:1</td>
</tr>
<tr>
<td>Chemical</td>
<td>Sequential</td>
<td>Centrifuging</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>Simultaneous</td>
<td>Centrifuging</td>
<td>0.3</td>
</tr>
<tr>
<td>Sonochemical</td>
<td>Sequential</td>
<td>Centrifuging</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Simultaneous</td>
<td>Centrifuging</td>
<td>-</td>
</tr>
<tr>
<td>Radiolytic</td>
<td>Sequential</td>
<td>Centrifuging</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>Simultaneous</td>
<td>Centrifuging</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>Simultaneous</td>
<td>Oven drying</td>
<td>0.3</td>
</tr>
</tbody>
</table>

In addition, the onset potential of PtRu electrocatalyst generally decreases with an increase of ruthenium ions in the precursor solution. Due to the higher reduction potential of ruthenium compared to that of platinum, an
5.7. Comparison of Onset Potentials

An increase in concentration of ruthenium is able to increase the possibility of encountering reducing agents.

The synergistic performance of a second element addition in methanol oxidation at the Pt catalysts is determined by how efficiently and effectively the second element lowers the potential of water dissociation, weakens the CO chemisorption, and enhances the electro-oxidation of methanol residues on platinum. As described above, none of the binary alloy catalysts, even the PtRu catalyst, possess all of these promoting effects together. Consequently, introduction of a third or fourth component is expected to give rise to all the enhancing promotions into one alloy system [266, 268, 293].

Radiolytic reduction seems to be an effective synthetic method to produce high electrocatalytic performance catalysts. When the ion ratio of platinum to ruthenium is 1:1, the prepared PtRu bimetallic nanoparticles exhibit optimal electrocatalytic activities. The simultaneous sonochemical irradiation has potential to achieve synthesis of high performance electrocatalyst.
In the beginning, God said, Let there be light: and there was light.

......

In the beginning, XiaoHe said, Let there be synergism, and there was NO synergism.

XH

6

Sonophotocatalytic Degradation of Methyl Orange

As indicated earlier, the OH• radicals formed during the sonolysis of water have a high oxidation potential (refer Chapter 2). In this chapter, the optimization for utilizing this oxidizing species for the degradation of methyl orange is systematically described. A number of experimental runs were carried out to evaluate the correlation between the efficiencies of individual systems (sonolysis or photocatalysis) and for the combined process of sonophotocatalysis, and the operation conditions. An orthogonal array of experimental design was adapted to establish the correlation between operation parameters and the performances of sonolysis, photocatalysis and sonophotocatalysis, especially the synergism of the combined system.
Azo dyes are used in a wide range of processes in textile, paper, food, cosmetics and pharmaceutical industries [297]. More than half the commercial dyes belong to azo dye group, which contain the azo group $-\text{N}=\text{N}-$ as part of their molecular structure. Usually the azo group is directly attached to benzene or naphthalene derivatives, possessing electron-accepting and electron-donating groups.

Methyl orange is a typical azo dye and a well-known pH indicator (pH 3.2 - 4.4 [26]). Figure 6.1a shows the speciation associated with the color changes of methyl orange, as the pH is changed.

![Mechanism of methyl orange as a pH indicator.](image1)

![Influence of pH on UV-vis spectra of methyl orange aqueous solution.](image2)

**Figure 6.1:** pH Indicator: the mechanism of pH indicating ability of methyl orange and changes of UV-vis spectra with pH.
Figure 6.1b shows the changes of absorption spectra of methyl orange with varying pH values. Above pH 4.4 in aqueous solution, methyl orange exists as the azo form (yellow color). This form has a maximum absorption wavelength of 504 nm and the molar absorption coefficient at this wavelength is $3.89 \times 10^4$ L mol$^{-1}$ cm$^{-1}$. When the pH shifts to strongly acidic, the protonation of methyl orange occurs and methyl orange exists as the azonium tautomer. The maximum absorption wavelength shifts to 465 nm, giving a red colored adsorption and the molar absorption coefficient at this wavelength is $2.61 \times 10^4$ L mol$^{-1}$ cm$^{-1}$. Due to the different forms of methyl orange and consequently different properties at different pH, it is necessary to consider the effect of pH during the degradation of methyl orange by different oxidation processes.

### Section 6.2

**Orthogonal Array Experimental Design**

Orthogonal design is an effective method of designing experiments which usually requires only a fraction of the full factorial combinations. An orthogonal array means the design is balanced so that factor levels are weighted equally and the primary goal is to find a factor set that can be adjusted to maximize the output. Consequently, orthogonal array design can evaluate each factor independently of all the other factors [298].

#### 6.2.1. Experimental Design

A four level of four factors orthogonal array $L_{16}(4^4)$ was applied to optimize the degradation efficiency of sonolytic, photocatalytic and sonophotocatalytic processes and also to understand the synergistic effect between sonolysis and photocatalysis.

The chosen levels of the four factors and their values are shown in Table 6.1. Ultrasonic frequency and power are the main parameters of the sonolytic degradation. The pH values play an important role in controlling the molecular forms of the dye and the adsorption affinity between the dye and photocatalyst. From pH 2 to pH 7, the selected pH values include below, around and above the $pK_a$ (pH 3.2 - 4.4) of methyl orange and the isoelectric point of TiO$_2$ (pH 6.2). The dosage of the photocatalyst not only exerts influence on photocatalysis efficiency,
but also affects sonolysis. Each level for each variable was chosen according to the preliminary experiments and practical experimental conditions.

**Table 6.1**: The factors and levels of the $L_{16}(4^4)$ orthogonal array during sonolysis, photocatalysis and sonophotocatalysis of methyl orange.

<table>
<thead>
<tr>
<th>Factors / Levels</th>
<th>Level I</th>
<th>Level II</th>
<th>Level III</th>
<th>Level IV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Frequency (kHz)</td>
<td>213</td>
<td>355</td>
<td>647</td>
<td>1056</td>
</tr>
<tr>
<td>Power (mW/mL)</td>
<td>16</td>
<td>88</td>
<td>55</td>
<td>35</td>
</tr>
<tr>
<td>pH</td>
<td>7</td>
<td>4</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>Dosage of TiO$_2$ (mg/mL)</td>
<td>1.0</td>
<td>2.0</td>
<td>5.0</td>
<td>0.5</td>
</tr>
</tbody>
</table>

The $L_{16}(4^4)$ factorial experimental matrix is shown in Table 6.2. Sixteen experiments in a sequential order were carried out to fulfil the factorial design. During the present orthogonal array design of experiments, the degradation efficiencies (degradation rate constants) during first 60 minutes were calculated from the changes in methyl orange concentration. The kinetics and mechanism for the advanced oxidation processes of sonolysis and photocatalysis are still unclear, although a number of individual sonochemical and photocatalytic reaction steps have been reported. In most reports a simple semilogarithmic plot of $\ln(C_0/C_t)$ as a function of time is used to discuss and compare the results. The obtained data were found to roughly obey first order kinetics from which the rate constants could be determined. The rate constants were compared to find the optimal combination conditions for sonolysis, photocatalysis and sonophotocatalysis. The detailed results analysis of orthogonal array experimental design were discussed in Appendix C.

### 6.2.2. Photocatalysis

The influence of the four selected condition factors on the photocatalysis of methyl orange is shown in Figure 6.2 and Table C.3. By comparing the differences between the maxima and minima mean values of the rate constants
6.2. ORTHOGONAL ARRAY EXPERIMENTAL DESIGN

Table 6.2: Experimental matrix: the $L_{16}(4^4)$ orthogonal array design.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
<th>Run No.</th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
</tr>
</thead>
<tbody>
<tr>
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<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>9</td>
<td>3</td>
<td>1</td>
<td>3</td>
<td>4</td>
</tr>
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<td>11</td>
<td>3</td>
<td>3</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
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<td>1</td>
<td>4</td>
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<td>4</td>
<td>12</td>
<td>3</td>
<td>4</td>
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<td>2</td>
<td>3</td>
<td>13</td>
<td>4</td>
<td>1</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>6</td>
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<td>2</td>
<td>1</td>
<td>4</td>
<td>14</td>
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<td>1</td>
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<td>4</td>
<td>1</td>
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</tr>
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<td>8</td>
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<td>2</td>
<td>16</td>
<td>4</td>
<td>4</td>
<td>1</td>
<td>3</td>
</tr>
</tbody>
</table>

for each factor group, it can be seen that pH and dosage of TiO$_2$ have a relatively stronger influence on the efficiency of photocatalysis than ultrasonic frequency and power*. This result is in good agreement with the experimental outcomes that the two main parameters of ultrasound did not exert any influence on photocatalytic degradation as ultrasound was not applied during photocatalysis. Thus, emphasis was directed at investigating the influence of pH values and dosage of TiO$_2$ on the efficiency of photocatalytic degradation of methyl orange.

6.2.2.1. Dependence on pH

Based on the observation from Figure 6.2, the solution pH is one of the factors that control the reaction rate of photocatalytic degradation process. According to the mechanism of photocatalysis (Figure 2.20), the overall degrada-

*It should be pointed out that in Table C.3, there exist some deviations with different ultrasonic frequency and power during photocatalysis. The reason of these deviations is due to the different combination of pH and TiO$_2$ loading. It can be seen from Table 6.2, there is no duplicate factorial combination, even when only pH and TiO$_2$ loading are taken into account. An orthogonal array requires that all the factorial levels involved are weighted equally. Thus, any set of factor combinations, or a part of this set, is unique within the whole array.
Figure 6.2: Photocatalytic degradation process optimization during oxidation of 100 µM methyl orange in aqueous solution.

...
According to Figure 6.2, the photocatalytic degradation of methyl orange is slower at pH 4 and is markedly faster at both pH 2 and pH 7. As mentioned before, the pH has the ability to influence the adsorption of dye onto the surface of the semiconductor particles. In addition, it also affects the formation of reactive OH• radicals, that play an essential role in the degradation process. A neutral environment (pH 7) is beneficial in forming active OH• radicals due to an improved transfer of holes to the adsorbed OH− ions on the semiconductor surface [299]. However, the adsorption process on the semiconductor surface is inhibited by the repulsive forces between the negatively charged TiO₂ nanoparticles and the anionic dye. At pH 2, due to the electrostatic attraction of positively charged TiO₂ nanoparticles and the anionic dye, a strongly acidic environment facilitates the adsorption of the dye at the semiconductor/solution interface. Thus, the photocatalytic degradation of methyl orange is faster at pH 2 and pH 7. At pH 4, the results of separate dye adsorption experiment show that there is negligible dye adsorption on the surface of photocatalyst particles. Furthermore, a moderate production of active surface radicals is likely to lead to the lowest decomposition rate. Based on the observed results, the adsorption effect seems to dominate the photocatalysis process at pH 2 and the formation of more reactive radicals predominates over the adsorption process at pH 7.

6.2.2.2. Dependence on Dosage of TiO₂

In the photocatalytic process, the dosage of TiO₂ is another important parameter that can affect the degradation efficiency. As indicated in Figure 6.2, the relationship between the degradation rate constant of methyl orange and the amount of TiO₂ is complex. An increase in the dosage of TiO₂ from 0.5 mg/mL to 2.0 mg/mL leads to an enhancement in the degradation of methyl orange. It can be seen that the optimal amount of TiO₂ in photocatalytic degradation of methyl orange is 2.0 mg/mL. It is well known that the addition of more photocatalysts into the solution provides more reaction sites for producing OH• and leads to the adsorption of more organic pollutants onto the surface of TiO₂ nanoparticles [232, 300]. The adsorption activity of the photocatalyst can enhance the reaction between the photo-generated charged carriers and the pollutant molecules. In addition, the presence of more TiO₂ photocatalyst is likely to result in better absorption of UV light leading to the formation of more reactive species.
Above 2.0 mg/mL, the degradation efficiency decreased. This is most likely the result of the UV light penetration into the bulk suspension being reduced by excess TiO$_2$ particles, and therefore a reduction in the excitation of TiO$_2$ and the amount of reactive charge-carriers. Furthermore, a relatively high catalyst loading may enhance the aggregation of TiO$_2$ particles which leads to a decrease in the efficiency of photocatalysis.

### 6.2.3. Sonolysis

As shown in Figure 6.3 and Table C.2, the influence of the four factors on the sonochemical degradation of methyl orange is significantly different compared to their influence on the photocatalytic decomposition. Comparing the differences between the maxima and minima of the average rate constants of each group, ultrasonic frequency and power have a more pronounced effect on the efficiency of sonolysis than pH and TiO$_2$ loading. These results indicate that the cavitation activity as would be expected, plays a key role in the sonochemical degradation of organic pollutants.

#### 6.2.3.1. Dependence on Ultrasonic Power

Figure 6.3 indicates that the ultrasonic power is the most important parameter for the sonolysis of methyl orange. An increase in ultrasonic power can dramatically increase the methyl orange degradation process. This is most probably due to a greater number of bubbles being created and more violent cavitation taking place at higher power levels.

Figure 6.4 shows the radius ratio* and temperature-time curves of a 5 µm air bubble under different ultrasonic powers. These curves were generated by numeric solutions using the Rayleigh-Plesset Equation (see Equation 2.4) at a frequency of 213 kHz. The power of ultrasound greatly changes the behavior of bubble cavitation. Enhancing the bubble growth by rectified diffusion leads to increasing the average bubble size and hence the collapse temperature. When the power density is 16 mW/mL, the maximum radius of the bubble is just slightly larger (1.4 times)

*The radius ratio refers to the ratio between $R(t)$ and $R_0$, i.e. $R(t)/R_0$. R(t) is the cavitation bubble radius as function of time under the time-varying acoustic pressure. See Chapter 2 for more details.
than the original radius, while it can reach 4 times the original radius at 88 mW/mL. The same trend occurs with maximum temperatures ($T_{\text{max}}$) reached within the bubbles. The $T_{\text{max}}$ rises from 450 K to 4500 K, almost 10 times, when the power increases from 16 mW/mL to 88 mW/mL. The increase in radius and temperature demonstrates

**Figure 6.3:** Sonochemical degradation process optimization during oxidation of 100 µM methyl orange in aqueous solution.
that higher applied acoustic power gives rise to more violent collapses. The increase of collapse intensity leads to a corresponding increase in sonoluminescence intensity and yield of primary radicals which consequently improve the degradation reactions.

In addition, increasing acoustic power has a significant effect on increasing the population of active bubbles, rate of rectified diffusion and bubble clustering [11, 53, 301]. The increase of the bubble population results in enhancing the chemical effects of ultrasound. Thus, the influence of applied ultrasonic power is a mixture of various effects brought by the applied power and they affect the whole system together.

### 6.2.3.2. Dependence on Ultrasonic Frequency

The frequency of the ultrasound is the second important parameter in the sonochemical degradation of methyl orange as shown in Figure 6.3. The influence of the applied ultrasound frequency on the rate of the degradation reaction is attributed to the effect on the cavitation activities of bubbles, as it brings the changes to the critical size of the cavitation bubbles and the active bubble population. When the ultrasound frequency is varied whilst keeping the power constant, it can give rise to changes in one or both of these two factors. However, the influence of ultrasonic frequency is unclear and complicated. A number of studies [44, 302] on cavitation bubble temperature determination showed that ultrasonic frequency has negligible effect on the average temperature of the whole ultrasonic irradiation, taking into account the level of water content entering the bubble. From this point of view, the effect of ultrasonic frequency on chemical reaction is attributable to its influence on bubble population.

As mentioned in Chapter 4, the frequency of ultrasonic irradiation has a great impact on the ruthenium ion reduction (see Figure 4.4b). The optimum frequencies for the reduction of ruthenium ions are 213 kHz and 355 kHz due to a moderate active bubble population and average size of the collapsing bubbles. This result is in agreement with the observation in Figure 6.3. 213 kHz and 355 kHz are also the optimum frequencies for sonochemical degradation of methyl orange due to the highest yield of primary radicals at these two frequencies.
Figure 6.4: Influence of Ultrasonic Power: radius ratio and temperature of a typical air bubble as a function of time under the influence of different ultrasound powers. The initial radius is 5 µm at 213 kHz. The radius ratio-time curve (blue solid line) is generated using the Rayleigh-Plesset Equation taking into account damping. The green solid lines are the corresponding temperature curves.
6.2. ORTHOGONAL ARRAY EXPERIMENTAL DESIGN

6.2.3.3. Dependence on pH

The solution pH plays a key role in determining the molecular structure of the dye and the affinity between dye and photocatalyst. For more details, see the discussion of pH influence in Section 6.1 and Subsection 6.2.2.1. In order to clarify the influence of pH on sonolysis, an separate sonochemical degradation of methyl orange at two different pH was carried out as shown in Figure 6.5. Furthermore, there was no TiO$_2$ present in these experiments. The observed results in Figure 6.5 illustrate that there is a slight influence of pH, implying there is not a large difference between the surface activity and volatility of the two different methyl orange molecular forms. Both tautomers behave similarly in solution and have a similar degradation rates.

6.2.3.4. Dependence on Dosage of TiO$_2$

A number of studies [215, 216, 218, 219, 221, 228] have shown the sonochemical degradation of an organic solute may be intensified in the presence of solid particles in the solution. The existence of particles seems to provide additional nuclei for cavitation. However, in our case, the effect of TiO$_2$ nanoparticles was not observed in the sonolysis of methyl orange (see Figure 6.3).

An independent experiment was carried out to systematically investigate the effect of photocatalyst particles on the sonolysis of methyl orange. It is evident that the presence of TiO$_2$ nanoparticles has a negligible effect on the degradation rate, as shown in Figure 6.6.

6.2.4. Sonophotocatalysis

As described in Subsection 2.4.3, each factor in the combined system, sonophotocatalysis, inherits a similar influence from an individual application. For example, ultrasonic power and frequency can influence a sonophotocatalytic system in the same way as in a sonolysis process. However, in a sonophotocatalytic degradation system, there are more factors in need of consideration, resulting from the interaction of the two processes.

Figure 6.7 and Table C.4 demonstrate the influence of each factor on the sonophotocatalytic degradation of methyl orange. Ultrasonic power and frequency are still the predominate factors, while pH is a less important fac-
6.2. Orthogonal Array Experimental Design

Figure 6.5: The influence of pH on the sonochemical degradation of methyl orange. The ultrasound frequency used was 213 kHz and the total power was 35 mW/mL.

Compared to these three factors, dosage of TiO$_2$ is the least important factor affecting the sonophotocatalytic degradation of methyl orange.
The same power of applied ultrasound has the same functions as in sonolysis. The rate constant during sonophotocatalytic degradation of methyl orange increases with an increase in the applied ultrasonic power. At the lowest power level, 16 mW/mL, the sonophotocatalytic degradation reaction appears to be faster than that of sonolysis.
Figure 6.7: Sonophotocatalytic degradation process optimization during oxidation of 100 µM methyl orange. 

process alone as the photocatalytic process contributes to the whole degradation in the combined system. There are a number of reasons behind the influence of applied ultrasonic power.

Varying ultrasonic power leads to a change in the bubble population, average bubble size, the growth process of a bubble, clustering structure of a bubble cloud and as well as the variety of chemical effects induced by
6.2. ORTHOGONAL ARRAY EXPERIMENTAL DESIGN

ultrasound. These chemical effects of ultrasound can provide an extra source of the highly reactive OH• to contribute to a faster degradation.

In a sonophotocatalysis system, the intensification of ultrasound affects the process of photocatalysis by its chemical effects as well as by physical effects. Higher power ultrasound is able to provide a much stronger cleaning effect, which reactivates the blocked active sites of the TiO₂ photocatalyst. Higher power ultrasound also deaggregates clustered TiO₂ nanoparticles and consequently increases the available active sites for photocatalytic reactions.

Obviously, the influence of ultrasonic power on a sonophotocatalytic system results from not only the effects through sonochemical degradation, but also the coupling interaction between sonolysis and photocatalysis.

6.2.4.2. Dependence on Ultrasonic Frequency

Similar to the sonolysis, applied acoustic frequency is a significant parameter involved in determining the optimal reaction conditions in sonophotocatalysis. As depicted in Figure 6.7, the methyl orange sonophotocatalytic degradation efficiency decreases with an increase of applied frequency in the order 355 > 213 ≈ 647 > 1056 kHz. This result is almost the similar as obtained in sonolysis. The similar influence on the average first-order rate constants of ultrasonic frequency in sonolysis and sonophotocatalysis implies the effect of frequencies is independent of the process of the photocatalysis. On the other hand it can be suggested that the influence of ultrasonic frequency on the interaction between sonolysis and photocatalysis is insignificant compared to its effect on the sonolytic process alone.

Figure 6.8 shows the sonoluminescence intensity as a function of ultrasonic frequency. At the same acoustic power, the sonoluminescence intensity decreases significantly as the irradiation frequency increases. This phenomenon may be a consequence of a number of factors. It is well-known that the maximum temperatures ($T_{\text{max}}$) of collapse cavitation bubble is mainly contributing to the sonoluminescence intensity [11, 12, 50, 272]. Lower frequency allows the bubble to undergo a relatively longer expansion cycle and thus increase the maximum size of the bubble at the point of collapse. It is acknowledged that the bigger bubble produce higher temperature when the bubble collapses (see Equation 2.6). As mentioned before, in practical experiments [44, 302], water content
6.2. **ORTHOGONAL ARRAY EXPERIMENTAL DESIGN**

insider bubble is able to quench the temperature generated during cavitation, ultrasonic frequency does not exhibit significant effects on the average temperature of each bubble. Consequently, the influence of ultrasonic frequency on bubble population is the main factor leading to the chemical effect of frequency.

The number of active bubbles contributes to the sonoluminescence intensity, but it goes the opposite direction with frequency. An increase in the number of bubbles may be the reason why 315 kHz are the optimum frequencies for sonoluminescence intensity.

The most effective influence of ultrasonic frequency on the efficiency of sonophotocatalysis is due to the changes in the amount of OH• radicals generated under different frequency ultrasound irradiation. It is known that the overall yield of OH• radicals is determined by the bubble population, bubble size and bubble lifetime. Although ultrasound is unable to change the number of pre-existing gas nuclei of the solution, it can alter the amount of offspring nuclei after the earlier collapse by exerting an effect on the bubble collapse behavior leading to fragmentation of large bubbles. Altering the frequency of ultrasound can lead to changes to the minimum size on bubble collapse which results in changes in the average temperature formed during cavitation and as well as the level of water content inside the bubble. Both the average bubble size and the amount of water vapor inside the bubble determine the yield of OH• per bubble collapse. The frequency of ultrasound also contributes to the threshold of bubble collapse which determines the population of active bubbles. The measurement of OH• radical yield [12, 272] also proved that the frequency of 355 kHz are the optimum frequencies. Normally, the yield of OH• per bubble oscillation increases with decreasing frequency as low frequency allows more water molecules to evaporate into the bubbles during the expansion phase of a bubble oscillation leading to a higher yield of OH• per bubble collapse. However, the population of active cavitation bubbles at lower frequency is much smaller than that in a higher frequency field. Thus 355 kHz have been found to be the optimum frequencies for the sonophotocatalytic degradation of methyl orange.

6.2.4.3. **Dependence on pH**

The solution pH has a complex effect on the degradation rates of the combined system. The effect of pH on the sonophotocatalytic processes is related to the changing forms of the dye, alteration of the surface charge
6.2. Orthogonal Array Experimental Design

![Graph](image)

**Figure 6.8**: Influence of Ultrasonic Frequency: the relative sonoluminescence intensity to pure water of 100 μM methyl orange aqueous solution under the influence of different ultrasound frequencies. All ultrasonic power under different frequencies was 55 mW/mL.

...on the photocatalyst and the redox levels of the valence and conduction bands of the semiconductor [231, 232, 234]. On the sonochemical side, pH has a significant effect on the hydrophobic/hydrophilic properties of the dye molecules. Furthermore, to some extent, the degradation pathway is also influenced by pH. In the case of methyl orange, pH 4 is unfavored for both photocatalytic and sonochemical degradation. In the environment of
higher hydrogen ion concentration, both sonolysis and photocatalysis show higher degradation rate constants, but the mechanism behind these observation is different. Faster degradation in sonolysis is due to an increase in the surface active properties of the dye molecule and in photocatalysis it is due to an increase in adsorption extent. In a sonophotocatalytic system, the combined effect of all that effects can be expected.

6.2.4.4. Dependence on Dosage of TiO$_2$

In the degradation process using sonophotocatalysis, although the influence is not as strong as the other three factors. The loading of TiO$_2$ plays some role in influencing the whole degradation process. The average rate constants decrease at 5.0 mg/mL loading. This may be due to the same reason as has been proposed in the discussion of photocatalytic degradation, namely, that excess TiO$_2$ nanoparticles are likely to scatter light and hence affect the activity of photocatalyst.

The lowest dosage of TiO$_2$, 0.5 mg/mL, has a similar influence as at higher photocatalyst loading. This result implies that the combination treatment requires less catalyst loading in comparison with photocatalysis. TiO$_2$ loadings as small as 0.5 mg/mL or less are sufficient to maintain an effective degradation rate in the sonophotocatalytic degradation system. It also demonstrates that the presence of an ultrasonic field has a positive effect in assisting the degradation process of photocatalysis. Peller et al. arrived at a similar conclusion in their study on the degradation of chlorinated aromatic compounds [258].

6.2.5. Synergistic Effects

The beneficial effects of two different separate processes always attract a considerable interest for evaluating the efficiency of a combined system. The Subsection 2.4.3 of Chapter 2 lists a number of reasons for the synergistic effect in the combination of sonolysis and photocatalysis. However, it is difficult to isolate each factor and to compare their influence on the synergistic effect as this beneficial effect is attributable to the overall consequence of several factors.

The ratio of sonophotocatalytic rate constant and the summed rate constants of the individual processes was
used to evaluate the synergistic effect of a combined system as shown in Equation 6.1.

\[
S = \frac{k_{\text{sonophotocatalysis}}}{k_{\text{sonolysis}} + k_{\text{photocatalysis}}}
\]  

(6.1)

where, \(k_{\text{sonophotocatalysis}}\), \(k_{\text{sonolysis}}\) and \(k_{\text{photocatalysis}}\) are the rate constants of sonophotocatalysis, sonolysis and photocatalysis, respectively. If \(S > 1\), the combined system exhibits a synergistic effect; If \(S < 1\), there is an inhibition effect between the two processes in in the coupled system; If \(S = 1\), there is only an additive effect between sonolysis and photocatalysis.

It is clearly seen from Table 6.3 that there is no apparent synergistic effect over the 16 experimental runs conducted. The combined system shows an additive effect or negative influence under the various experimental conditions selected. It is easy to understand the additive effect, as heterogeneous photocatalysis and ultrasonic irradiation cause degradation of organic pollutants by reaction with \(\text{OH}^\bullet\) radicals. The cumulative effect of \(\text{OH}^\bullet\) radicals can lead to an additive effect.

**Table 6.3:** Synergism on orthogonal array design during the sonophotocatalytic degradation of 100 µM methyl orange.

<table>
<thead>
<tr>
<th>Experimental No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synergism</td>
<td>1.1</td>
<td>0.6</td>
<td>0.5</td>
<td>0.9</td>
<td>0.7</td>
<td>0.7</td>
<td>0.9</td>
<td>0.6</td>
</tr>
<tr>
<td>Experimental No.</td>
<td>9</td>
<td>10</td>
<td>11</td>
<td>12</td>
<td>13</td>
<td>14</td>
<td>15</td>
<td>16</td>
</tr>
<tr>
<td>Synergism</td>
<td>0.9</td>
<td>1.0</td>
<td>0.8</td>
<td>0.8</td>
<td>0.9</td>
<td>0.8</td>
<td>0.9</td>
<td>0.7</td>
</tr>
</tbody>
</table>

It is known that a synergistic effect is a consequence of a number of factors, ranging from the micro-bubble oscillation to the distribution of the ultrasonic field in the reaction, from the molecular structure of the pollutants to the geometry of the reactor, and so on.
A synergistic effect may favor certain classes of molecules whose structure contains both hydrophilic and hydrophobic components. Whereas, the photocatalytic process degrades the hydrophilic part and sonolysis acts on the hydrophobic components. If one of the intermediate products from one process is degradable by the other process, the degradation of the organic compound in the combined system is likely to show a synergistic effect.

Ultrasonic power and frequency are also essential factors that may contribute to the synergistic effect in a combined system, since they are the key factors in the sonochemical degradation process (see Figures 6.3 and 6.7). The ultrasonic acceleration of photocatalytic degradation is determined not only by the chemical effects of ultrasound irradiation, but also by the mechanical effects caused by the microstreaming of fluid surrounding a collapsing bubble, leading to particle de-agglomeration, mass transfer and surface cleaning.

Based on the investigation of synergism by orthogonal array experimental design, there is no clear influence of solution pH. However, as mentioned before, pH plays an essential role in both photocatalytic and sonochemical degradation. The loading of TiO$_2$ is also an important factor in a synergistic effect. The TiO$_2$ not only acts as photocatalyst in heterogenous photocatalysis, but may also be an extra source for bubble nuclei. As a result, the dosage of photocatalyst nanoparticles is an important influence on synergism in sonophotocatalytic degradation of methyl orange.

### Section 6.3
#### Products Analysis

#### 6.3.1. UV-vis Spectral Analysis

UV-visible spectroscopy is a widely used as a convenient analytical means of studying degradation pathways. Figure 6.9 shows the absorption spectra observed during the photolytic, sonolytic, photocatalytic and sonophotocatalytic degradation of methyl orange at pH 7.

Figure 6.9a shows that degradation of methyl orange due to photolysis during photocatalysis or sonophotocatalysis can be neglected as it did not contribute significantly in the decomposition of methyl orange (less than 3%). As shown in Figure 6.9b and Figure 6.9c, both sonolysis and photocatalysis degraded methyl orange effec-
6.3. Products Analysis

Figure 6.9: UV-vis spectra observed during the photolytic, sonochemical, photocatalytic and sonophotocatalytic degradation of 96 µM methyl orange at pH 7.
tively. The absorption maximum at 504 nm gradually decreases under ultrasound or photocatalytic irradiation. An interesting point to note is that the spectra observed in these two processes are similar. This observation indicates that the degradation of methyl orange undergoes a similar pathway. Thus the products from these two different oxidation processes are the same and consequently result in the similar absorption band. However, the absorption band at 250-370 nm shows some different features in both advanced oxidation processes. During the sonolysis, the absorption band of 250-370 nm gradually increases at the early stages of sonolysis. After 1 hour irradiation, this band starts to decrease, showing the involvement of some products. Even after 2 hours of sonolysis, the absorption band around 250-370 nm did not disappear, indicating that these products from degradation of methyl orange still remain. However, for photocatalysis process, the band in this range decreases with an increase in photocatalytic degradation time. After two hours, this band has almost disappeared. As the bands at 276 and 319 nm are attributed to the $\pi \rightarrow \pi^*$ transition located in the aromatic rings of methyl orange, the decrease of the band around 250-370 nm suggests the photocatalytic process has a greater ability to break down the aromatic rings than does sonochemical degradation. It implies that photocatalysis is more effective than sonolysis in achieving mineralization. The similar observation was also made in the study conducted by Kamat and coworkers [250].

As shown in Figure 6.9d, in the combination of photocatalysis and sonolysis, the degradation of methyl orange is faster than the individual oxidation process. At the same time, sonophotocatalysis had a pronounced effect on the mineralization of the azo dye. The absorption peak corresponding to methyl orange, as well as the band of the products, completely disappeared after two hours of sonophotocatalytic treatment.

### 6.3.2. Total Organic Carbon Analysis

Figure 6.10 shows the TOC elimination of methyl orange by first-order kinetics during the sonochemical, photocatalytic and sonophotocatalytic degradation of methyl orange at pH 2. It is obvious that the total organic carbon of all system gradually decreases with an increase in irradiation time, showing that the photocatalytic and sonochemical oxidation processes can effectively decompose the azo dye. The combined system seems to have a higher efficiency. Compared to the sonolysis process, photocatalytic mineralization of the azo dye is likely to be a much cleaner advanced oxidation technique. These results are in agreement with the observations made of UV-vis
spectral changes.

Figure 6.10: Total Organic Carbon Analysis: changes of TOC observed as a function of irradiation time during the sonochemical, photocatalytic and sonophotocatalytic degradation of 96 µM methyl orange at pH 2 in aqueous solution. The dosage of TiO$_2$ in photocatalytic and sonophotocatalytic processes was 1 mg/mL. Ultrasonic frequency was 213 kHz and power was 55 mW/mL.
6.3. PRODUCTS ANALYSIS

6.3.3. High Performance Liquid Chromatographic Analysis

High performance liquid chromatography is an effective method with which to identify the products generated during sonochemical and photocatalytic degradation reactions. Figure 6.11 depicts the chromatograms of methyl orange after 60 mins sonolysis, photocatalysis and sonophotocatalysis. The chromatograms show clearly the peaks corresponding to the products generated from the degradation of methyl orange.

After 60 minutes degradation, nearly 50% of the methyl orange was removed by sonolysis, 70% by photocatalysis and 80% by sonophotocatalysis. However, according to Figure 6.11, many peaks of intermediates are still present in the solution. There are seven main products (A-G) observed from the chromatographs from the three advanced oxidation processes. The remaining peak corresponding to methyl orange decreases in the order sonophotocatalysis < photocatalysis < sonolysis. These observations indicate that photocatalytic and sonophotocatalytic degradation processes are efficient in decomposing the parent azo dye. This observation is in agreement with UV-vis spectra and TOC analysis. In addition, the products contain hydrophobic products as well as hydrophilic intermediate compounds. As mentioned previously, this molecular property favors different processes during the sonophotocatalytic degradation. The hydrophobic products normally tend to be surface active and therefore are easily degraded by acoustic cavitation. However, photocatalysis is capable of decomposing the hydrophilic products.

By analyzing the samples by means of mass spectrometry and comparing the results from the literature [300, 303–305] under similar chromatographic conditions, the molecular structures of the products are deducible. Figure 6.12 illustrates the UV-vis spectra and the molecular structures of the intermediate products during the sono-lytic and photocatalytic degradation of methyl orange in aqueous solutions. The parent molecule, methyl orange (retention time: 8.4 min), exhibits a clear MS signal corresponding to a negative ion m/z 304. It is worth noting that one intermediate among these seven products, product G, exhibits a longer retention time (m/z 320, retention time: 12.8 min) indicating more hydrophobicity. Normally, hydroxylated products show a more hydrophillic character. In this case, it was confirmed that product to be a monohydroxylated product of methyl orange. The same hydrophobic hydroxylated product has been observed by a number of research groups [303–305].
6.3. Products Analysis

(a) Photocatalysis

(b) Sonolysis

(c) Sonophotocatalysis

(d) Photocatalysis (at 464 nm)

(e) Sonolysis (at 464 nm)

(f) Sonophotocatalysis (at 464 nm)

Figure 6.11: HPLC: High performance liquid chromatographs observed after 60 mins of sonolytic, photocatalytic and sonophotocatalytic degradation of 96 µM methyl orange at pH 2. The TiO$_2$ loading in all three oxidation system was 1 mg/mL. In sonolysis and sonophotocatalysis, the ultrasonic frequency was 213 kHz and the power was 55 mW/mL.

Product D is a demethylated intermediate formed by cleaving a methyl- group from methyl orange molecule ($m/z$ 290, retention time: 3.6 min). The remaining intermediate compounds are products formed by the introduc-
6.3. Products Analysis

The degradation of methyl orange results in the formation of one or two hydroxyl groups or cleavage of a methyl or two methylic groups. For example, Product B ($m/z$ 292, retention time: 2.4 min) is a derivative formed by adding a hydroxyl group and remains two methyl groups from a methyl orange molecule. All the molecular structures and the corresponding UV spectra are shown in Figure 6.12.

Based on the structures of the products formed during the degradation of methyl orange, all the identified intermediates contain the azo group and the sulfonic group. These individual structures were further confirmed by UV-vis spectra. Due to very low concentrations generated, it was difficult to extract the UV spectra of Product A and B. However, other products did yield UV-vis absorption bands, illustrating that all these products are colored intermediates. These observations demonstrate that the chromophores are still present in these products. The degradation pathway is discussed in the following subsection.

6.3.4. Proposed Sonophotocatalytic Degradation Pathway

As demonstrated in the list of products (see Figure 6.12), the products formed during the sonolytic, photocatalytic and sonophotocatalytic degradation of methyl orange originate from the hydroxylation and/or demethylation of methyl orange. Figure 6.13 is a proposed sonophotocatalytic degradation pathway scheme. It mainly focuses on the transformation of intermediate species, which precede the aromatic ring-opening.

According to Figure 6.13, Product D and G are the intermediate compounds by demethylation and hydroxylation of methyl orange, respectively. The demethylation of methyl orange is a process which involves the homolytic rupture of the nitrogen-carbon bond of the amine group leading to the substitution of a methyl group with a hydrogen atom. Consecutive demethylation is likely to lead to the formation of Product E and B. Whatever the decomposition process methyl orange molecules undergo, sonolysis or photocatalysis, OH• radical attack is the main mechanism of degradation. Product A, B, E and G are the products formed by multiple substitution of hydroxyl groups. Evidently, due to simultaneous and independent occurrences, both demethylation and hydroxylation can be expected to couple with each other or take effect alternatively. Consequently, the products of methyl orange degradation are determined by the individual demethylation, hydroxylation and their combinations.
6.3. PRODUCTS ANALYSIS

Figure 6.12: UV-vis spectra of the products generated during the sonolytic, photocatalytic and sonophotocatalytic degradation of 96 µM methyl orange at pH 2. The TiO₂ loading in all three oxidation systems was 1 mg/mL. In sonolysis and sonophotocatalysis processes, the ultrasonic frequency was 213 kHz and the power was 55 mW/mL.
6.3. Products Analysis

Figure 6.13: Proposed Degradation Pathway: schematic illustration of the sonophotocatalytic events may take place during the degradation of methyl orange.

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6.3. PRODUCTS ANALYSIS

6.3.5. Degradation of Products

Two intermediate products, Product D (a demethylated product) and Product G (a monohydroxylated product), primary intermediates, were selected in order to investigate the influence of sonochemical, photocatalytic and sonophotocatalytic degradation on the derivative products. The peak areas recorded in the HPLC profiles for these two detected intermediates against the irradiation time are shown in Figure 6.14. Both products at different pH at first increase and subsequently decrease, demonstrating that these products undergo two processes: formation and subsequent decomposition.

Figure 6.14a shows the formation trend of Product D as a function of irradiation time during sonolysis, photocatalysis and sonophotocatalysis. The area changes in both photocatalysis and sonophotocatalysis show a "bell" shape trend with irradiation time, with 30 minutes being the time of maximum amount formed. However, the amount of Product D existing in the aqueous solution gradually increases over the whole sonochemical degradation process. This observation demonstrates that the decomposition is faster than the formation during photocatalytic and sonophotocatalytic degradation, and the hybrid technique is better for decomposing the intermediate product D. The destruction of the intermediate by ultrasound seems to be the slowest among these three advanced oxidation processes.

Compared to pH 2, the amount of Product D formed at pH 10 is much larger (shown in Figure 6.14b), indicating that in spite of the formation of the same main active species, the pH environment is capable of changing the proportion of the products. At pH 10, the amount of Product D during sonophotocatalytic process reaches a maximum at 30 minutes, but in photocatalysis it is at 90 minutes. The trend of peak area as a function of time of sonolysis forms a "bell" shape in this case. At pH 10, the hybrid system exhibits a greater synergistic effect than that at pH 2.

Figure 6.14c and 6.14d show the change in amount of Product G with irradiation time under three advanced oxidation processes at pH 2 and pH 10, respectively. At these two pH levels, sonophotocatalysis is the most effective. The hydroxylation of methyl orange in photocatalytic and sonophotocatalytic processes is faster than under sonolysis. During the first 30 minutes at pH 2, methyl orange was hydroxylated by photocatalysis at the same speed as sonophotocatalysis. However, after 30 min, the amount of monohydroxylated product in sonophotocatal-
6.3. Products Analysis

Figure 6.14: Product Degradation: The concentration changes of Product D and Product G during 120 minutes sonophotocatalytic degradation of 96 µM methyl orange at pH 2 and pH 10. The loading TiO$_2$ was 1 mg/mL. In sonolysis and sonophotocatalysis processes, the frequency of ultrasound was 213 kHz and the power was 55 mW/mL.
6.3. Products Analysis

Analysis decreases while that in photocatalysis increases until 60 min. The reason for the faster sonophotocatalytic decomposition of Product G may lie in the sonochemical process. Compared to Product D, Product G exhibits relatively more hydrophobicities (HPLC chromatograph in Figure 6.11), leading to a higher surface active. This property allows these molecules to accumulate at the liquid/bubble interface, and thus enables them to readily react with the primary radicals generated within the cavitation bubbles. In other word, sonolysis is more effective in decomposing hydrophobic products.

The maximum amount of Product D and G is higher at pH 10 than that at pH 2. One possible reason is that the alkaline environment favors formation of OH• radicals and consequently facilitates the hydroxylation process.
Every morning, the stepmother of Snow-White stood before her magic mirror, looked at herself, and said:
Mirror, mirror, on the wall,
Who in this land is fairest of all?

Little Snow-White

Every morning, I stood before the sonicator, looked at the bubbles, and said:
Bubble, bubble, in the water,
Where is my synergistic effect?

Sonophotocatalytic Degradation of Aromatic Carboxylic Acids

Application of ultrasound in environmental remediation recently attracted considerable attention. The main purpose of the work described in this chapter is to assess the possibility of employing a hybrid method which combines ultrasonic irradiation and photocatalytic oxidation for the degradation of three aromatic carboxylic acids. The overall oxidation performance of the combined system on the degradation of organic pollutants in aqueous solution was evaluated by kinetic analysis. Several analytical techniques were used to monitor the degradation process and identify the reaction products formed during the sonophotocatalytic degradation process.
Aromatic carboxylic acids are pollutants of high environmental impact because of their widespread use and potential to form toxic products. Aromatic carboxylic acids are introduced into the environment as a result of many man-made activities. These compounds constitute a substantial fraction of preservative agents for wood, paints, vegetable fibers and leather pesticides and herbicides due to their bactericidal activities. In addition, they have been widely used in a number of industrial processes, e.g., raw materials in the manufacture of herbicides, pesticides, pharmaceuticals and dyes. Aromatic carboxylic acids may also be the end products formed during the natural biodegradation of industrial aromatic pollutants.

*para*-Chlorobenzoic acid (PCBA), *para*-aminobenzoic acid (PABA) and *para*-hydroxybenzoic acid (PHBA) are three typical aromatic carboxylic acids. At room temperature, they are weak acids, due to the presence of the carboxyl group. All of them have a $pK_a$ around 4.5 (*p*-chlorobenzoic acid: 3.98 [26]; *p*-aminobenzoic acid: 4.85 [26]; *p*-hydroxybenzoic acid: 4.58 [26]) in aqueous solution. In addition, both *p*-aminobenzoic acid and *p*-hydroxybenzoic acid have a second $pK_a$ because they also possess a second pH responsive functional group. As a result, there are two different forms that exist at different pH values: acid form and conjugate base form. The different forms have a potential impact on the degradation mechanism involved during photocatalysis and sonolysis processes.

Due to the different forms of the solutes, all of these aromatic carboxylic acids display different absorption characteristics at different pH. The changes in the UV spectra of *p*-chlorobenzoic acid, *p*-aminobenzoic acid and *p*-hydroxybenzoic acid at various pH values are presented in Figure 7.1, Figure 7.2 and Figure 7.3, respectively. It is evident that these compounds exhibit absorption maximum at different wavelength with different pH values.
7.2. *p*-Chlorobenzoic Acid

![Absorbance vs Wavelength Graph]

**Figure 7.1:** Influence of pH on UV-vis spectra: UV-vis spectra of 100 μM *p*-chlorobenzoic acid observed with varying pH values in aqueous solution.

Although the oxidation process of different organic pollutants are quite similar, this section focuses on the sonophotocatalytic degradation of *p*-chlorobenzoic acid. A number of analytical techniques, such as spectrophotometry, HPLC and MS/MS, were used to investigate the photocatalysis, sonolysis and sonophotocatalysis of *p*-chlorobenzoic acid. A quantitative simulation of the concentration changes of the products during the hybrid process was used to evaluate the synergistic effects produced by combining the two advanced oxidation techniques.

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**Section 7.2**

*p*-Chlorobenzoic Acid
7.2. *p*-CHLOROBENZOIC ACID

![UV-vis Spectra Analysis](image)

**Figure 7.2:** Influence of pH on UV-vis spectra: UV-vis spectra of 100 µM *p*-aminobenzoic acid observed with varying pH values in aqueous solution.

### 7.2.1. UV-vis Spectra Analysis

Figure 7.4 displays the UV-vis spectral changes observed during the sonophotocatalytic degradation of 100 µM *p*-chlorobenzoic acid at two different pH values. At both pH values, the band around 234 nm*, corresponding to the concentration of *p*-chlorobenzoic acid, was markedly reduced with an increase in the sonophotocatalytic degradation time. These observations indicate that the sonophotocatalytic process is an effective technique for the...

*It should be pointed out that in order to minimize the influence of *p*-chlorobenzoic acid adsorption on the surface of TiO₂, the pH value of all the sample solutions were first converted to pH 10 before analysis. This is the reason for the maximum absorption wavelength being 234 nm for the degradation of *p*-chlorobenzoic acid at pH 2.
7.2. p-Chlorobenzoic Acid

Figure 7.3: Influence of pH on UV-vis spectra: UV-vis spectra of 100 µM p-hydroxybenzoic acid observed with varying pH values in aqueous solution.

degradation of p-chlorobenzoic acid.

Clearly, the sonophotocatalytic decomposition of p-chlorobenzoic acid at pH 2 is much faster than that at pH 10, mainly due to the adsorption activity on TiO$_2$ at pH 2. As explained in Chapter 6, at pH 10, the negatively charged TiO$_2$ surface is likely to repel the p-chlorobenzoic acid anions, resulting in weaker adsorption activity of TiO$_2$ and hence a decrease the oxidation rate. In addition, the surface active property enables the organic molecules to readily capture the primary radicals from the cavitation bubbles [195, 306].

It is interesting to note that the changes to the absorption spectra are quite different at different pH values. At pH 10, there is still an absorption band from 215 to 240 nm after 1 hour of sonophotocatalytic degradation, showing that there are more products formed during the degradation of p-chlorobenzoic acid compared to the
7.2. $p$-CHLOROBENZOIC ACID

Figure 7.4: UV-vis spectra analysis: changes of the absorption spectra observed during sonophotocatalytic degradation of 100 µM $p$-chlorobenzoic acid at pH 2 and pH 10. The irradiation frequency of ultrasound was 213 kHz and the power was 55 mW/mL. The loading of TiO$_2$ in the sonophotocatalytic degradation experiment was 1 mg/mL.

degradation at pH 2. The sonophotocatalytic degradation at pH 2 is therefore likely to lead to mineralization of $p$-chlorobenzoic acid.

7.2.2. High Performance Liquid Chromatographic Analysis

It is difficult to quantitatively analyze products generated using UV-vis spectra during the sonophotocatalytic degradation of $p$-chlorobenzoic acid, since the products absorb at the same wavelength region as that of the reactant. High performance liquid chromatography is able to separate the parent compound and individual products.
7.2. \textit{p}-CHLOROBENZOIC ACID

effectively.

Figure 7.5 and 7.6 shows the high performance liquid chromatograms observed during sonophotocatalytic degradation of 100 µM \textit{p}-chlorobenzoic acid at two different solution pH values. It is evident that the peak (retention time: 10.2 min\(^*\)) that corresponds to \textit{p}-chlorobenzoic acid gradually decreases with the irradiation time, indicating that \textit{p}-chlorobenzoic acid was effectively decomposed by sonophotocatalytic oxidation. After 30 min sonophotocatalytic irradiation, more than half of the \textit{p}-chlorobenzoic acid was degraded in both pH environments. A full comparison of rate constants and the synergistic effect is discussed in Subsection 7.2.5.

It is interesting to note that the amount of the same product generated at different pH is quite different. This means that the solution pH affects the degradation pathway during the sonophotocatalysis of \textit{p}-chlorobenzoic acid. The major products (marked in Figure 7.5 and 7.6) of sonophotocatalysis, \textbf{A} and \textbf{B}, are formed in different amounts at different pH. The conditions at pH 10 facilitate the degradation process which produces product \textbf{A}. Only a small amount of product \textbf{A} was produced at pH 2. The independent sonolysis and photocatalysis experiments of \textit{p}-chlorobenzoic acid degradation demonstrated that the small amount of product \textbf{A} is only derived from the sonochemical degradation of \textit{p}-chlorobenzoic acid at pH 2, while no product \textbf{A} was detected by photocatalytic degradation. This suggests that the pH of aqueous solution influences the sonochemical degradation pathway. A larger amount of product \textbf{A} at pH 10 may be the reason there is still a substantial absorption band in UV-vis spectra (see Figure 7.4) after 60 min sonophotocatalysis at pH 10.

Another interesting point to note is the degradation of the products generated from the sonophotocatalytic degradation of \textit{p}-chlorobenzoic acid. As discussed for the sonophotocatalytic degradation of methyl orange in Chapter 6, sonophotocatalysis can decompose the parent organic pollutants as well as the products. The peak area that corresponds to product \textbf{A} does not decrease, but it is evident that product \textbf{B} first increases and subsequently decreases at both pH values. Thus, sonophotocatalysis is able to decompose the products produced from the degradation of \textit{p}-chlorobenzoic acid. In addition, the amount of product \textbf{B} reaches a maximum after 20 min sonophotocatalytic degradation at pH 2, while it was 30 min at pH 10.

\(^*\)Due to the fluctuation in temperature, there is a slight time shift (approximately 0.06 min) between the corresponding chromatograph peaks in Figure 7.5b and Figure 7.6b.
4.3. HPLC Analysis

HPLC Analysis: the high performance liquid chromatographs observed during the sonophotocatalytic degradation of an aqueous solution of 100 µM p-chlorobenzoic acid at pH 2. The TiO$_2$ loading in the oxidation system was 1 mg/mL. The applied ultrasonic frequency was 213 kHz and the power was 55 mW/mL.

Mass Spectrometry Analysis

Mass spectral analysis was conducted to identify the products formed during the degradation of p-chlorobenzoic acid. Figure 7.7 shows the mass spectra in negative mode before and after sonophotocatalytic degradation at pH 2. In the initial solution, there are two strong signals that appear in the mass spectra of 100 µM p-chlorobenzoic acid. The peak at m/z 98.9 represents the loss of hydrogen from perchloric acid molecule, which was used to maintain the whole aqueous solution at pH 2 for the overall sonophotocatalytic degradation and its chlorine-37

Figure 7.5: HPLC Analysis: the high performance liquid chromatographs observed during the sonophotocatalytic degradation of an aqueous solution of 100 µM p-chlorobenzoic acid at pH 2. The TiO$_2$ loading in the oxidation system was 1 mg/mL. The applied ultrasonic frequency was 213 kHz and the power was 55 mW/mL.

5.5. $5.6. 5.7. 5.8. 5.9. 6^{-1}$

0
1
2
3
4
5
6
7
Time (min)

mAu

(a) The 3D chromatogram observed after 30 min sonophotocatalysis at pH 2.
(b) The changes in chromatographs during sonophotocatalysis at pH 2. The detection wavelength used in the HPLC was 245 nm.
7.2. $p$-CHLOROBENZOIC ACID

(a) The 3D chromatographs observed after 30 min sonophotocatalysis at pH 10.

(b) The changes in chromatographs during sonophotocatalysis at pH 10. The detection wavelength used in the HPLC was 245 nm.

Figure 7.6: HPLC Analysis: the high performance liquid chromatographs observed during the sonophotocatalytic degradation of an aqueous solution of 100 $\mu$M $p$-chlorobenzoic acid at pH 10. The TiO$_2$ loading in the oxidation system was 1 mg/mL. The applied ultrasonic frequency was 213 kHz and the power was 55 mW/mL.

The chlorine-37 isotope is observed at $m/z$ 100.9. The $p$-chlorobenzoic acid precursor ions were found at $m/z$ 154.9 in the negative ion mode. Due to the presence of the chlorine-37 isotope, the second peak of $p$-chlorobenzoic acid precursor ions also appears at $m/z$ 156.9.

The peaks corresponding to perchloric acid still existed in the mass spectra after sonophotocatalytic treatment (see Figure 7.7b). There are a few product ions observed in the same mass spectra. The peak at $m/z$ 34.9 is due to the formation of a chloride ion fragment. The three product ions at $m/z$ 110.9, 126.9 and 170.9 show the corresponding chlorine-37 isotope pattern indicating they retain the chlorine atom. According to the charge-to-
7.2. *p*-CHLOROBENZOIC ACID

Figure 7.7: Mass spectrometry analysis (the background signals were subtracted.): mass spectra of 100 μM *p*-chlorobenzoic acid before and after 60 min sonophotocatalytic degradation. The applied ultrasonic frequency was 213 kHz and power was 55 mW/mL. The loading of TiO$_2$ nanoparticles was 1 mg/mL.
mass data, the complete molecular form of chlorobenzene was evident as well as the loss of a carboxyl group from \( p \)-chlorobenzoic acid molecule \((m/z \ 154.9 \rightarrow 110.9)\). \(m/z \ 126.9\) was identified as chlorophenol, a derivative of \( p \)-chlorobenzoic acid by substitution of the carboxyl group with a hydroxyl group. A monohydroxylated product of \( p \)-chlorobenzoic acid \((m/z \ 170.9)\) was also found during sonophotocatalytic degradation.

The peak at \( m/z \ 68.9\) remains unidentified. Although the mass of \( C_3H_2O_2 \) matches the value of \( m/z \ 68.9\), there is no evidence and mechanism supporting that \( C_3H_2O_2 \) is formed during sonophotocatalytic process. But it is confirmed that it does not contain any chlorine atom as there is no chlorine isotope pattern. This compound may be produced after the opening benzene ring. High performance liquid chromatographic analysis of standard commercial samples including chlorobenzene, 4-chlorophenol, 3-chloro-4-hydroxybenzoic acid and 4-chlorosalicylic acid was conducted to confirm the peaks in the chromatograms (Figure 7.5 and 7.6). The observation confirms that the product B (retention time: 5.8 min) is 4-chlorophenol. A special effort was paid to identify the product A by a number of HPLC experimental runs with possible commercial chemicals, such as phenol, 3-chloro-4-hydroxybenzoic acid, 4-chlorosalicylic acid, benzoic acid, \( p \)-hydroxybenzoic acid, 3,4-dihydroxybenzoic acid, quinol, catechol, 3-hydroxybenzoic acid, 2,5-dihydroxybenzoic acid, 3,5-dihydroxybenzoic acid and fumaric acid. However, the product A could not be identified despite the expectation that its hydrophilicity is quite close to that of 4-chlorophenol.

Table 7.1 summarizes the identification of high performance liquid chromatographic products during sonophotocatalytic degradation of \( p \)-chlorobenzoic acid.

### 7.2.4. Proposed Sonophotocatalytic Degradation Pathway

The sonophotocatalytic degradation reactions shown in Figure 7.8 were based on previous reports [195, 196, 307]. As sonolysis and photocatalysis mainly involve the attack of \( OH^- \) radicals on the organic pollutants, it can be expected that the first intermediate compounds produced would be hydroxylated products. When the aromatic ring of a \( p \)-chlorobenzoic acid molecule is attacked by an \( OH^- \) radical, the hydroxyl group is likely to undergo substitution with a hydrogen atom or the carboxyl group of the aromatic ring. According to the high performance liquid chromatograph observation that 4-chlorophenol constitutes the main product, the replacement of carboxyl
Table 7.1: Identification of high performance liquid chromatographic products during sonophotocatalytic degradation of \( p \)-chlorobenzoic acid.

<table>
<thead>
<tr>
<th>Name</th>
<th>Structure</th>
<th>MS (m/z)</th>
<th>Retention Time (min)</th>
<th>Symbol in Reaction 7.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>HCl</td>
<td>34.9</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>?</td>
<td>?</td>
<td>68.9</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Perchloride Acid</td>
<td>HClO(_4)</td>
<td>98.9</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td><img src="structure_chlorobenzene.png" alt="Structure" /></td>
<td>110.9</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4-Chlorophenol</td>
<td><img src="structure_4-chlorophenol.png" alt="Structure" /></td>
<td>126.9</td>
<td>5.8</td>
<td>B</td>
</tr>
<tr>
<td>( p )-Chlorobenzoic Acid</td>
<td><img src="structure_p-chlorobenzoic_acid.png" alt="Structure" /></td>
<td>154.9</td>
<td>10.2</td>
<td>A</td>
</tr>
<tr>
<td>4-Chlorosalicylic Acid or its isomers</td>
<td><img src="structure_4-chlorosalicylic_acid.png" alt="Structure" /></td>
<td>170.9</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

The decrease in the 4-chlorophenol concentration with an increase in the oxidation time indicates that this product was converted into other products by undergoing further reaction with OH• radicals, or by substitution of chlorine with a hydrogen atom, or by pyrolysis inside cavitation bubbles. Through the introduction of a hydroxyl group or the replacement of a chlorine atom, hydroquinone, benzoquinone and trihydroxybenzene were formed by OH• radical attack. These aromatic intermediate products are very unstable under intensive attack by OH• radicals, and degraded simultaneously along with the parent compound. They are suspected as precursors to ring opening. It is known that continuous attack of the OH• radicals on the aromatic ring of benzene derivatives can lead to ring cleavage and further degradation into small carboxylic acid molecules [308]. Further sonication of these molecules eventually results in complete mineralization and formation of H\(_2\)O, CO\(_2\) and HCl.
Figure 7.8: Proposed degradation pathway: schematic illustration of the sonophotocatalytic events that may take place during the degradation of p-chlorobenzoic acid.
7.2.5. Degradation Kinetics and Synergistic Effects

7.2.5.1. Kinetics and Synergistic Effects of Degradation of \( p \)-Chlorobenzoic Acid

The comparison of the degradation rates of \( p \)-chlorobenzoic acid observed for different advanced oxidation processes is shown in Figure 7.9. A pseudo-first order kinetics model (Equation 7.1) was applied to compare the degradation performance of the three advanced oxidation processes.

\[
\ln \frac{C_0}{C_t} = kt
\]  

(7.1)

Here, \( C_0 \) is the initial concentration of the degradation reactant; \( C_t \) is the concentration corresponding to the time \( t \); \( k \) is the rate constant and its unit is \( \text{min}^{-1} \). The pseudo-first order model is based on the assumption that during the whole degradation process, the production of \( \text{OH} \) radicals is expected to remain constant and react only with the organic pollutant. However, the amount of products generated from degradation of the parent pollutant increases with an increase in degradation time. These products are likely to compete with parent pollutant for \( \text{OH} \) radicals, which is not expected in the pseudo-first order model. In our case, the data of the first 30 min were plotted according to pseudo-first order kinetics as shown in Figure 7.9. It is evident that for the first 30 min, the experimental results seem to fit well with the pseudo-first order kinetics plot due to low concentration of the products.

At both pH 2 and pH 10, it is obvious that the sonophotocatalytic process is the fastest degradation process among the three advanced oxidation processes. It is also noted that for all three processes, the degradation at pH 2 is faster than that at pH 10. As mentioned in Chapter 6, lower pH increases the proportion of the neutral form of the organic pollutant. This leads to an increase in the adsorption of the \( p \)-chlorobenzoic acid on TiO\(_2\) surface and bubble/solution interface, and this is what is behind for the enhancement in the reaction rate.

It is interesting that at pH 10, sonophotocatalysis has almost the same rate constant as photocatalysis during the degradation of \( p \)-chlorobenzoic acid. This observation implies that at pH 10, photocatalysis is the leading degradation process in the combined system. In other words, the degradation performance of sonolysis is negligible.
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Figure 7.9: Kinetics: the pseudo-first order kinetics curves observed during the sonophotocatalytic degradation of an aqueous solution containing 100 µM *p*-chlorobenzoic acid at pH 2 and pH 10. The TiO$_2$ loading was 1 mg/mL. The applied ultrasonic power was 55 mW/mL and frequency was 213 kHz. The detection wavelength used in the HPLC was 238 nm.

Table 7.2 lists the theoretically fitted results* based on a pseudo-first order model. The index $S$ (named by $S_1$ in Table 7.2 and Table 7.3) mentioned in Chapter 6 was used to evaluate the synergistic effect of the

*Note that the rate constants $k_1$ calculated here are not based on Figure 7.9. Figure 7.9 was plotted from the average of three data sets with standard deviation. Due to further application of these rate constants in the simulation of products later in this subsection, one of three data sets was selected to calculate the rate constants as listed in Table 7.2.
sonophotocatalytic degradation of \( p \)-chlorobenzoic acid (Equation 6.1).

\[
S = \frac{k_{\text{sonophotocatalysis}}}{k_{\text{sonolysis}} + k_{\text{photocatalysis}}}
\]  

(6.1)

The value 1.24 of synergistic effect index at pH 2 (Table 7.2) suggests that there is a slight synergistic effect between sonolysis and photocatalysis process. However, the sonophotocatalytic degradation of \( p \)-chlorobenzoic acid at pH 10 is an additive effect.

### Table 7.2: The pseudo first-order rate constants of sonolysis, photocatalysis and sonophotocatalysis of 100 \( \mu \text{M} \) \( p \)-chlorobenzoic acid in aqueous solution at pH 2 and pH 10.

<table>
<thead>
<tr>
<th>pH</th>
<th>Process</th>
<th>( k ) (( \times 10^{-2} \text{min}^{-1} ))</th>
<th>( S_1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 2</td>
<td>Sonolysis</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Photocatalysis</td>
<td>3.0</td>
<td>1.24</td>
</tr>
<tr>
<td></td>
<td>Sonophotocatalysis</td>
<td>5.6</td>
<td></td>
</tr>
<tr>
<td>pH 10</td>
<td>Sonolysis</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Photocatalysis</td>
<td>3.4</td>
<td>0.97</td>
</tr>
<tr>
<td></td>
<td>Sonophotocatalysis</td>
<td>3.8</td>
<td></td>
</tr>
</tbody>
</table>

In the evaluation of the synergistic effect of the combined system, it is also necessary to consider the influence of the combined techniques on the products of degradation, which may lead to reducing the decomposition efficiency of \( p \)-chlorobenzoic acid. Thus, the process of product degradation is discussed in the following subsection in order to achieve an overall evaluation of sonophotocatalysis.
7.2.5.2. Kinetics and Synergistic Effects of Degradation of Products

The high performance liquid chromatograms observed during sonophotocatalytic degradation of 100 µM \( p \)-chlorobenzoic acid are shown in Figure 7.5 and 7.6. It is clear that 4-chlorophenol is the major product\(^*\) formed during sonolytic, photocatalytic and sonophotocatalytic degradation of \( p \)-chlorobenzoic acid. As a result, the whole degradation process can be expressed as a chain reaction as shown in Reaction 7.2.

\[
\text{(7.2)}
\]

\[
\begin{align*}
\text{A} & \xrightarrow{k_1} \text{B} \xrightarrow{k_2} \text{D} \\
\text{A} & \xrightarrow{k_3} \text{C}
\end{align*}
\]

\[
\begin{align*}
k & = k_1 + k_3
\end{align*}
\]  

(7.3)

where, \( \text{A} \) represents \( p \)-chlorobenzoic acid; \( \text{B} \) is 4-chlorophenol; \( \text{D} \) is the only product from the oxidation of 4-chlorophenol, or a representative of the whole product whose stoichiometric molar ratio to the corresponding 4-chlorophenol is 1:1; \( \text{C} \) represents all the products except 4-chlorophenol formed during the degradation of \( p \)-chlorobenzoic acid and its stoichiometric molar ratio to \( p \)-chlorobenzoic acid is 1:1\(^\dagger\). It is assumed that the single reactant \( \text{A} \) undergoes independent, concurrent reactions to yield two different products: \( \text{B} \) and \( \text{C} \). \( k_1 \) and \( k_3 \) are the rate constants for the formation of compound \( \text{B} \) and \( \text{C} \), respectively; \( k \) and \( k_2 \) are the rate constants for the degradation of \( p \)-chlorobenzoic acid (\( \text{A} \)) and 4-chlorophenol (\( \text{B} \)), respectively.

\(^*\)In fact, there are a number of products that appear during the \( p \)-chlorobenzoic acid oxidation. These intermediate compounds include identified and unidentified compounds analyzed by high performance liquid chromatograph and gas chromatograph in the case of gaseous products. For mathematical simplicity, the kinetics simulation here did not consider the other products except 4-chlorophenol.

\(^\dagger\)In fact, there are a number of products accompanying the formation of 4-chlorophenol. For the following simulation simplification, compound \( \text{C} \) was used to represent all of the products except 4-chlorophenol during the degradation of \( p \)-chlorobenzoic acid.
By assuming that all the reactions involved in Scheme 7.2 obey pseudo-first order kinetics, the concentration of each compound in the aqueous solution can be expressed as a function of the following equations*:

\[
C_A = C_A^0 e^{-kt} \tag{7.4}
\]

\[
C_B = \frac{C_A^0 k_1}{k_2 - k} \left[ e^{-kt} - e^{-k_2 t} \right] \tag{7.5}
\]

\[
C_C = \frac{C_A^0 (k - k_1)}{k} \left[ 1 - e^{-kt} \right] \tag{7.6}
\]

\[
C_D = \frac{C_A^0 k_1}{k(k - k_2)} \left[ k(1 - e^{-k_2 t}) - k_2(1 - e^{-kt}) \right] \tag{7.7}
\]

Here, the concentration of compound A, namely \( p \)-chlorobenzoic acid, as a function of irradiation time is expressed in Equation 7.4 which was deduced from Equation 7.1; \( C_A^0 \) is the initial concentration of compound A; \( C_B, C_C \) are the concentrations of compound B and C, respectively. The concentration of 4-chlorophenol (B) expressed in Equation 7.5 indicates that it undergoes two processes during the whole degradation of the parent pollutant: formation and degradation. Due to the observation that the chromatograph peaks that correspond to 4-chlorophenol first increase and subsequently decrease in all three advanced oxidation processes, this theoretical model requires that the degradation is much faster than the formation of 4-chlorophenol, i.e., \( k_2 > k_1 \). In fact, compound C and compound D also follow a similar trend since the oxidation processes decompose them after they are formed. Here, the theoretical model does not account for the subsequent degradation of compound C and D.

The experimental data and the simulated data of the degradation of 100 µM \( p \)-chlorobenzoic acid at pH 2 and pH 10 are presented in Figure 7.10. The corresponding \( k_1 \) and \( k_2 \) values in each process can be calculated by fitting the experimental data using Equation 7.5, as the value of \( k \) is known for the degradation of \( p \)-chlorobenzoic acid (see Table 7.2). With the calculated \( k_1 \) and \( k_2 \) values, it is possible to deduce the concentration of each compound as a function of irradiation time (Equation 7.4-7.7).

*The equations used here are the combination of parallel and consecutive reactions. The theoretical concentration equation of each
7.2. \textit{p}-CHLOROBENZOIC ACID

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure7_10}
\caption{Figure 7.10: Kinetics analysis of product degradation: the analytical data and simulated concentration curves of each component during the degradation of 100 \(\mu\text{M}\) \textit{p}-chlorobenzoic acid in aqueous solution at pH 2 and pH 10. For the analytical data of \textit{p}-chlorobenzoic acid, the detection wavelength used in the HPLC was 238 nm. For the analytical data of 4-chlorophenol, the detection wavelength used in the HPLC was 245 nm.}
\end{figure}

For consecutive reactions \(A \rightarrow B \rightarrow C\) and parallel reactions are separately provided in reference [309].
It is obvious that the simulation results fit well with the experimental data and exhibit the characteristic behavior of each compound during the whole oxidation process. For example, the simulation curve effectively reflects the special bell-shaped behavior of 4-chlorophenol concentration under the six different experimental sets. Figure 7.10a and 7.10d show the concentration changes of these four compounds (A-D) involved in sonolysis at pH 2 and pH 10. The concentration of parent organic compound, p-chlorobenzoic acid, was exponentially reduced with an increase of ultrasonic irradiation time. It is clear that the process at pH 2 is faster than that at pH 10. The pH 2 curve of the product pollutant (4-chlorophenol) exhibits a bell shape with the degradation time, indicating the decomposing activity competes effectively with the formation process. However, at pH 10, the concentration of 4-chlorophenol did not show any decrease during the whole 120 min degradation, which indicates that the sonochemical degradation of 4-chlorophenol at pH 10 is comparatively slower than that at pH 2. Hence, pH 2 is a better condition for sonochemical degradation of p-chlorobenzoic acid as well as its organic product, 4-chlorophenol.

Both photocatalysis and sonophotocatalysis at the two pH values show similar results to that observed for the sonolysis process, as shown in Figures 7.10b-7.10f. Furthermore, the products generated during the degradation of p-chlorobenzoic acid are also decomposed in all the three advanced oxidation processes. In addition, it is evident that the sonophotocatalytic degradation of the parent organic pollutant as well as the derivative products is much faster than the individual oxidation processes. It is also observed that the formation of product D is favored during the sonophotocatalysis.

The numeric simulation results are listed in Table 7.3. \( k \) is the rate constant of degradation of p-chlorobenzoic acid which includes the formation rate constants of compound B as well as compound C (Equation 7.3). \( S_1 \) represents the synergistic effect, defined by Equation 6.1, during the sonophotocatalytic degradation of p-chlorobenzoic acid. As discussed earlier, there is a slight synergistic effect observed during the conversion of p-chlorobenzoic acid to 4-chlorophenol at pH 2. \( k_2 \) is the rate constant of 4-chlorophenol degradation and also the compound D formation. \( S_2 \) is the synergistic effect index during the sonophotocatalytic degradation of 4-chlorophenol, the main product during the degradation of p-chlorobenzoic acid. As shown in Table 7.3, the interaction between sonolysis and photocatalysis at pH 2 for the degradation of p-chlorobenzoic acid in the combined system is additive.

As mentioned previously, at pH 10, the oxidation of p-chlorobenzoic acid by the hybrid technique seems to show additive effects. However, the product degradation seems to lower the degradation efficiency. This hin-
### Table 7.3: The calculated rate constants for each reaction and synergistic effect indices of the combined system during sonolytic, photocatalytic and sonophotocatalytic degradation of 100 µM \(p\)-chlorobenzoic acid in aqueous solution at pH 2 and pH 10.

<table>
<thead>
<tr>
<th>pH</th>
<th>Process</th>
<th>(k_1(10^{-2}\text{min}^{-1}))</th>
<th>(S_1)</th>
<th>(k_2(10^{-2}\text{min}^{-1}))</th>
<th>(S_2)</th>
<th>(k_3(10^{-2}\text{min}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 2</td>
<td>Sono</td>
<td>1.5</td>
<td>0.8</td>
<td>2.7</td>
<td>0.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Photo</td>
<td>3.0</td>
<td>1.24</td>
<td>2.2</td>
<td>0.99</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>Sonophoto</td>
<td>5.6</td>
<td>2.9</td>
<td>7.9</td>
<td>2.7</td>
<td></td>
</tr>
<tr>
<td>pH 10</td>
<td>Sono</td>
<td>0.5</td>
<td>0.4</td>
<td>0.8</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Photo</td>
<td>3.4</td>
<td>0.97</td>
<td>1.5</td>
<td>0.55</td>
<td>1.9</td>
</tr>
<tr>
<td></td>
<td>Sonophoto</td>
<td>3.8</td>
<td>1.5</td>
<td>2.2</td>
<td>2.3</td>
<td></td>
</tr>
</tbody>
</table>

The synergistic effect is mainly due to the competition from other products during the degradation of \(p\)-chlorobenzoic acid. The high performance liquid chromatographs clearly show one more main product formed at pH 10 (Figure 7.5 and 7.6). It is possible that this main product competes for the highly reactive OH• causing the lower degradation rate.

The evaluation of the synergistic effect in the combined system requires consideration of the overall influence of the hybrid technique. Thus, it is better to take into account the degradation performance of each compound including the parent organic pollutants and its derivative products.

### 7.2.6. Changes of Synergistic Effect with Irradiation Time

Figure 7.11 is a plot of the synergistic effect index as a function of irradiation time during the sonophotocatalytic degradation of \(p\)-chlorobenzoic acid. Each data point was based on the assumption that the sonolysis, photocatalysis and sonophotocatalysis of \(p\)-chlorobenzoic acid obey pseudo-first order kinetics.

It can be observed that there is a slight synergistic effect during the whole 60 min sonophotocatalytic degradation.
7.2. \textit{p}-CHLOROBENZOIC ACID

Figure 7.11: Synergistic effect index as a function of degradation time: the synergistic effect index of sonophotocatalytic degradation of 100 \( \mu \text{M} \) \( p \)-chlorobenzoic acid in aqueous solution at pH 2 and pH 10 as a function of degradation time.

The synergistic effect index gradually increases during the first 40 min and reaches a maximum after 40 min degradation at pH 2. The mechanism of interaction between sonolysis and photocatalysis is not clear. One possible reason is that the interaction between these two systems involves chemical effects as well as physical effects, which need time to adjust to each other to deliver the maximum performance.
After 40 min, the index decreases with further increase of irradiation time. It is possible that large amounts of products from the degradation of \( p \)-chlorobenzoic acid may compete for \( \text{OH}^\bullet \) radicals generated from sonolysis or photocatalysis, leading to an inhibition effect on the degradation of the parent organic compounds. As a result, the degradation of \( p \)-chlorobenzoic acid can be expected to gradually slow down when the product pollutant molecules takes the position of their parents, such as at the surface of \( \text{TiO}_2 \) nanoparticles in photocatalysis or at the interface of the cavitation bubbles in sonolysis.

Above all, during the evaluation of the degradation performance, the early irradiation period reflects the actual degradation efficiency of the advanced oxidation technique for the parent organic pollutant. For the overall evaluation of the whole system, it is better to take into account the degradation of parent organic pollutants as well as their products.

Section 7.3
\( p \)-Aminobenzoic Acid

7.3.1. The Influence of pH on Degradation Rate

Pseudo-first order plots of each oxidation process at pH 2 and pH 12 are used to evaluate the sonophotocatalytic degradation of \( p \)-aminobenzoic acid (shown in Figure 7.12). Similar to the degradation of \( p \)-chlorobenzoic acid, the first 30 min data for \( p \)-aminobenzoic acid were used to calculate the degradation rate constants.

It can be seen that at pH 2, there is no significant difference between sonolysis, photocatalysis and sonophotocatalysis for the degradation of \( p \)-aminobenzoic acid. The combined system actually shows some inhibiting effects instead of an enhancing effect. The \( p \)-aminobenzoic acid degradation performance of the photocatalysis and sonophotocatalysis processes were enhanced when the pH of the aqueous solution was increased to 12, while the sonolysis degradation became slower than that at pH 2.
7.3. p-AMINOBENZOIC ACID

Figure 7.12: Kinetics: the pseudo-first order kinetics curves observed during the sonolytic, photocatalytic and sonophotocatalytic degradation of an aqueous solution containing 100 µM p-aminobenzoic acid at pH 2 and pH 12. The TiO$_2$ loading in the oxidation system was 1 mg/mL. The applied ultrasonic frequency was 213 kHz and the power was 55 mW/mL. The detection wavelength used in the HPLC was 277 nm.

7.3.2. The Influence of pH on Product Selection

Figure 7.13 is a mass spectra in positive ion mode observed after 70 min sonophotocatalytic degradation of 100 µM p-aminobenzoic acid at pH 12. The mass-charge ratio 138.1 m/z corresponds to the positively charged parent organic compound p-aminobenzoic acid ion.

Due to the strong background signal, only three products were successfully identified by mass spectrometry. The peak at m/z 139.1 is due to the substitution of the amino group with a hydroxyl group. The product ion
7.3. *p*-AMINOBENZOIC ACID

Figure 7.13: Mass spectrometry analysis (the background signal was subtracted): mass spectra of 100 µM *p*-aminobenzoic acid before and after 70 min sonophotocatalytic degradation. The applied ultrasonic frequency was 213 kHz and power was 55 mW/mL. The loading of TiO$_2$ nanoparticles was 1 mg/mL.

Of *m/z* 154.0 is the hydroxylated *p*-aminobenzoic acid compound. There are a few isomeric compounds for *m/z* 154.0. Through HPLC analysis using commercial standard samples, it was confirmed that *p*-hydroxybenzoic acid and 4-amino-3-hydroxybenzoic acid were the products during sonophotocatalytic degradation of *p*-aminobenzoic acid. Figure 7.14 shows the peaks that correspond to these two identified products in the HPLC traces.
Two high performance liquid chromatograms observed after 70 min sonophotocatalytic degradation of 100 μM p-aminobenzoic acid at pH 2 and pH 12 are shown in Figure 7.14. It is obvious that at different pH values, the products from the same oxidation process are different. In other words, the pH environment appears to control the reaction direction of the sonophotocatalytic degradation of p-aminobenzoic acid.

Table 7.4 lists a series of products generated during sonolytic, photocatalytic and sonophotocatalytic degradation of p-aminobenzoic acid at different pH values. Although most of these products are the same, it is evident that the pH or the selection of different oxidation processes control the direction of the degradation. Consequently, it is possible to adopt the right process and pH value to select the products which may be less harmful to the environment or to reduce the amount of comparatively more hazardous products. In addition, it should be noted that sonophotocatalysis is likely to lead to a more efficient mineralization of organic pollutants due to its faster degradation of the parent as well as the product compounds.

Table 7.4: Influence of pH and advanced oxidation process on product selection during sonolytic, photocatalytic and sonophotocatalytic degradation of 100 μM p-aminobenzoic acid in aqueous solution. (−: there is no corresponding product produced; √: There is a significant amount of corresponding product produced; small: There is a very small amount of corresponding product produced.)

<table>
<thead>
<tr>
<th>pH</th>
<th>Process</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 2</td>
<td>Sonolysis</td>
<td>√</td>
<td>√</td>
<td>small</td>
<td>small</td>
<td>√</td>
<td>√</td>
</tr>
<tr>
<td></td>
<td>Photocatalysis</td>
<td>-</td>
<td>√</td>
<td>√</td>
<td>-</td>
<td>-</td>
<td>√</td>
</tr>
<tr>
<td></td>
<td>Sonophotocatalysis</td>
<td>√</td>
<td>√</td>
<td>√</td>
<td>-</td>
<td>small</td>
<td></td>
</tr>
<tr>
<td>pH 12</td>
<td>Sonolysis</td>
<td>√</td>
<td>-</td>
<td>√</td>
<td>√</td>
<td>√</td>
<td>√</td>
</tr>
<tr>
<td></td>
<td>Photocatalysis</td>
<td>√</td>
<td>-</td>
<td>√</td>
<td>√</td>
<td>√</td>
<td>√</td>
</tr>
<tr>
<td></td>
<td>Sonophotocatalysis</td>
<td>√</td>
<td>-</td>
<td>√</td>
<td>√</td>
<td>√</td>
<td>small</td>
</tr>
</tbody>
</table>

Table 7.5 summarizes the identification of products by using high performance liquid chromatographic and mass spectrometric analysis. In addition, a number of HPLC runs were taken with the commercially available...
7.3. *p*-AMINOBENZOIC ACID

**Figure 7.14**: HPLC analysis: the high performance liquid chromatograms observed during the sonophotocatalytic degradation of an aqueous solution of 100 µM *p*-aminobenzoic acid at pH 2 and pH 12. The TiO$_2$ loading in the oxidation system was 1 mg/mL. The applied ultrasonic frequency was 213 kHz and the power was 55 mW/mL. The detection wavelength used in the HPLC was 230 nm which is the maximum absorbance wavelength of product D.

chemicals, such as phenol, aniline, 4-aminosalicylic acid, benzoic acid, *p*-hydroxybenzoic acid, 3,4-dihydroxybenzoic acid, quinol, catechol, 3-hydroxybenzoic acid, 2,5-dihydroxybenzoic acid, 3,5-dihydroxybenzoic acid and fu-
maric acid in order to identify products A, B, C and E. However, there were no exact matches. Further analysis is required to identify these products.

**Table 7.5:** Identification of high performance liquid chromatographic products during sonophotocatalytic degradation of *p*-aminobenzoic acid.

<table>
<thead>
<tr>
<th>Product</th>
<th>Name Structure</th>
<th>Retention Time (min)</th>
<th>MS (m/z)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>-</td>
<td>3.2</td>
<td>-</td>
</tr>
<tr>
<td>B</td>
<td>-</td>
<td>3.7</td>
<td>-</td>
</tr>
<tr>
<td>C</td>
<td>-</td>
<td>5.0</td>
<td>-</td>
</tr>
<tr>
<td>D</td>
<td>4-Amino-3-hydroxybenzoic Acid</td>
<td>5.9</td>
<td>154.0</td>
</tr>
<tr>
<td>E</td>
<td>-</td>
<td>7.8</td>
<td>-</td>
</tr>
<tr>
<td>F</td>
<td><em>p</em>-hydroxybenzoic acid</td>
<td>-</td>
<td>139.1</td>
</tr>
</tbody>
</table>

### 7.3.3. Synergistic Effect

A similar mathematical simulation model to that used in the analysis of *p*-chlorobenzoic acid was applied for evaluating the synergistic effect during the sonophotocatalytic degradation of 100 µM *p*-aminobenzoic acid. Furthermore, the reaction scheme 7.2 is also valid for the sonophotocatalytic degradation of *p*-aminobenzoic acid. Thus Equations 7.4-7.7 can be applied to analyze the kinetics of the degradation reaction of *p*-aminobenzoic acid.

The decomposition rate constant *k* of *p*-aminobenzoic acid was obtained by pseudo-first order kinetics (Figure 7.12). It is evident that there is no synergistic effect at either pH value (see Table 7.6). As discussed for the methyl orange degradation process, the interaction between sonolysis and photocatalysis involves chemical reactions as well as physical influences. The synergistic effect of sonophotocatalysis has a number of critical reaction
conditions. In addition, it is necessary to consider the products’ degradation performance during the evaluation of the synergistic effect of the whole system.

Equation 7.5 was used to simulate the formation \( (k_1) \) and degradation \( (k_2) \) rate constants of 4-amino-3-hydroxybenzoic acid, which was one of intermediate products formed during the sonophotocatalytic degradation of \( p \)-aminobenzoic acid. The concentration changes of 4-amino-3-hydroxybenzoic acid observed for 120 min were used to fit this equation.

The simulated curves are shown in Figure 7.15 and the numeric results are listed in Table 7.6. Due to the small amount of 4-amino-3-hydroxybenzoic acid produced during the sonophotocatalytic degradation of \( p \)-aminobenzoic acid, the changes of 4-amino-3-hydroxybenzoic acid and its product (compound D) are not as clear as in the 4-chlorophenol in \( p \)-chlorobenzoic acid system. However, it can be seen that sonolysis, photocatalysis and sonophotocatalysis have a strong capability in degrading \( p \)-chlorobenzoic acid and its product, 4-amino-3-hydroxybenzoic acid. It is evident that the formation of 4-amino-3-hydroxybenzoic acid was boosted at pH 12. The concentration curves of 4-amino-3-hydroxybenzoic acid show a bell shape, indicating two simultaneous processes take place, formation and degradation.

The calculated rate constants for each component are listed in Table 7.6. \( S_1 \) and \( S_2 \) are the synergistic effect indices during the sonophotocatalytic degradation of \( p \)-aminobenzoic acid and its product, respectively. It is evident that the sonophotocatalytic degradation of the parent compound, \( p \)-aminobenzoic acid, displays some inhibition instead of a synergistic effect at both pH values. However, the synergistic index of destruction of its intermediate product, 4-amino-3-hydroxybenzoic acid, indicates that there is a strong synergistic effect in the combination of sonolysis and photocatalysis at pH 2 and pH 12. At pH 2, the sonochemical irradiation appears not to produce 4-amino-3-hydroxybenzoic acid from the degradation of \( p \)-aminobenzoic acid. However, this ultrasonic oxidation technique is likely to degrade the 4-amino-3-hydroxybenzoic acid molecule which was formed from the photocatalytic oxidation process. The same process occurred with the product E marked in Figure 7.14. According to Table 7.4, product E only appears during the sonochemical degradation at pH 2 and a very slight amount appears in the sonophotocatalytic process. In the combined system, photocatalysis accelerated the degradation of product E formed in sonolysis. In other words, sonophotocatalysis is likely to apply both the oxidation capacities of sonolysis and photocatalysis in the destruction of each product formed from either of the two individual oxidation
Figure 7.15: Kinetics analysis of product degradation: the analytical data and simulated concentration curves of each component during the degradation of 100 µM p-aminobenzoic acid in aqueous solution at pH 2 and pH 12. For the analytical data of p-aminobenzoic acid, the detection wavelength used in the HPLC was 277 nm. For the analytical data of 4-amino-3-hydroxybenzoic acid, the detection wavelength used in the HPLC was 230 nm.
processes. Specifically, the combined system is most effective in the degradation of products that are formed exclusively by either sonolysis or photocatalysis alone. As a result, the sonophotocatalytic technique is likely to be a cleaner oxidation process.

Table 7.6: The pseudo first-order rate constants of sonolysis, photocatalysis and sonophotocatalysis of 100 μM p-aminobenzoic acid in aqueous solution at pH 2 and pH 12.

<table>
<thead>
<tr>
<th>pH</th>
<th>Process</th>
<th>( k_1(10^{-2}\text{ min}^{-1}) )</th>
<th>( S_1 )</th>
<th>( k_2(10^{-2}\text{ min}^{-1}) )</th>
<th>( S_2 )</th>
<th>( k_3(10^{-2}\text{ min}^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 2</td>
<td>Sono</td>
<td>1.8</td>
<td>≈0</td>
<td>1.5</td>
<td>2.80</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td>Photo</td>
<td>2.0</td>
<td>0.58</td>
<td>0.1</td>
<td>4.2</td>
<td>1.9</td>
</tr>
<tr>
<td></td>
<td>Sonophoto</td>
<td>2.2</td>
<td>0.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH 12</td>
<td>Sono</td>
<td>0.7</td>
<td>0.1</td>
<td>0.9</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Photo</td>
<td>2.8</td>
<td>0.83</td>
<td>2.3</td>
<td>1.31</td>
<td>2.3</td>
</tr>
<tr>
<td></td>
<td>Sonophoto</td>
<td>2.9</td>
<td>0.7</td>
<td>4.2</td>
<td></td>
<td>2.2</td>
</tr>
</tbody>
</table>

Future work is required to consider the degradation of other products from p-aminobenzoic acid degradation in order to evaluate the overall synergistic effect. Due to the competition for oxidizing species provided by sonolysis and photocatalysis, each organic component is likely to be involved in the whole degradation process and contribute to the synergistic effect.

Section 7.4
p-Hydroxybenzoic Acid

7.4.1. Effect of pH on Degradation Kinetics

Figure 7.16 shows the pseudo-first order kinetic plots at four different pH values observed during sonolytic, photocatalytic and sonophotocatalytic degradation of 100 μM p-hydroxybenzoic acid aqueous solution. This fi-
ure clearly shows that sonophotocatalytic oxidation has a stronger degradation ability for the degradation of $p$-hydroxybenzoic acid than the individual process at all pH values.

![Kinetics Analysis: the pseudo-first order kinetics curves observed during the sonolytic, photocatalytic and sonophotocatalytic degradation of an aqueous solution containing 100 µM $p$-hydroxybenzoic acid at pH 2, pH 6, pH 9 and pH 12. The TiO$_2$ loading in the oxidation system was 1 mg/mL. The applied ultrasonic frequency was 213 kHz and the power was 55 mW/mL. The detection wavelength used in the HPLC was 253 nm.](image)

**Figure 7.16:** Kinetics Analysis: the pseudo-first order kinetics curves observed during the sonolytic, photocatalytic and sonophotocatalytic degradation of an aqueous solution containing 100 µM $p$-hydroxybenzoic acid at pH 2, pH 6, pH 9 and pH 12. The TiO$_2$ loading in the oxidation system was 1 mg/mL. The applied ultrasonic frequency was 213 kHz and the power was 55 mW/mL. The detection wavelength used in the HPLC was 253 nm.

In addition, the degradation performances of all three advanced oxidation processes decrease with an increase
of solution pH. At pH 2, all of them reach their highest performance, demonstrating the lower pH favors sonolysis, photocatalysis and sonophotocatalysis of p-hydroxybenzoic acid. There is a large decrease in the photocatalytic degradation from pH 2 (under pH 6) to pH 9 and pH 12 (above pH 6). As discussed before (Chapter 6), the isoelectric point of TiO$_2$ nanoparticles is 6.2 which is pivotal in determining the charge of TiO$_2$ nanoparticles. The positively charged surface at low pH readily attracts negative organic ions and consequently results in a faster decomposition of organic pollutants. The neutral form of p-hydroxybenzoic acid has a higher surface active character than its conjugate base form which enables it to concentrate at the surface of cavitation bubbles. This was discussed in detail in Chapter 6.

The calculated rate constants of each process in Figure 7.16 are listed in Table 7.7. At all pH values, the combined system, sonophotocatalysis, exhibits additive effects, perhaps even a slight retardation effect at pH 12. As mentioned with the p-chlorobenzoic acid system (Subsection 7.2.5), it is hard to judge the synergistic effect only by the index from Equation 6.1. When the rate constant of one process is negligible, the error level in practical measurements outweighs the real existing interaction. It is of interest that there is a big difference between the rate constants of sonolytic degradation of p-hydroxybenzoic acid at pH 2 and pH 6, whereas the difference is small at pH 6, pH 9 and pH 12. As mentioned the first pK$_a$ of p-hydroxybenzoic acid is 4.58, p-hydroxybenzoic acid exists in the neutral form when the pH value is under 4.58. This conjugate acid form has a higher surface active character resulting in it preferring the liquid/bubble interface where it can capture the active radicals directly from the bubble core.

### 7.4.2. High Performance Liquid Chromatographic Analysis

The high performance liquid chromatograms of the sonophotocatalytic degradation of 100 µM p-hydroxybenzoic acid at four pH values are shown in Figure 7.17. The detection wavelength was 216 nm, which corresponds to the maximum absorption wavelength of product E. The peaks corresponding to p-hydroxybenzoic acid and the products are marked as p-hydroxybenzoic acid, products A-F.

Noticeably, the number of products formed is quite different at different pH values. For example, only a very negligible amount of product E was produced at pH 2 and there is no signal from product B during the
7.4. *p*-HYDROXYBENZOIC ACID

**Table 7.7:** The calculated rate constants for each reaction and synergistic effect index of the combined system during sonolytic, photocatalytic and sonophotocatalytic degradation of 100 µM *p*-hydroxybenzoic acid in aqueous solution at pH 2, pH 6, pH 9 and pH 12.

<table>
<thead>
<tr>
<th>pH</th>
<th>Process</th>
<th>$k \times 10^{-2} \text{min}^{-1}$</th>
<th>$S$</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 2</td>
<td>Sonolysis</td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Photocatalysis</td>
<td>2.2</td>
<td>0.87</td>
</tr>
<tr>
<td></td>
<td>Sonophotocatalysis</td>
<td>3.3</td>
<td></td>
</tr>
<tr>
<td>pH 6</td>
<td>Sonolysis</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Photocatalysis</td>
<td>2.2</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>Sonophotocatalysis</td>
<td>3.0</td>
<td></td>
</tr>
<tr>
<td>pH 9</td>
<td>Sonolysis</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Photocatalysis</td>
<td>0.8</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>Sonophotocatalysis</td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td>pH 12</td>
<td>Sonolysis</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Photocatalysis</td>
<td>0.5</td>
<td>0.70</td>
</tr>
<tr>
<td></td>
<td>Sonophotocatalysis</td>
<td>0.7</td>
<td></td>
</tr>
</tbody>
</table>

degradation of *p*-hydroxybenzoic acid at pH 6, pH 9 and pH 12. This demonstrates that the solution pH plays an essential role in determining the degradation pathway of *p*-hydroxybenzoic acid. The observed results from independent sonolytic and photocatalytic degradation experiments suggests that these effects on the degradation pathway are mainly expressed in their influence via sonolysis. It is known that the neutral and ionized organic molecules undergo different degradation pathways due to the nature of cavitation [194–196]. The pyrolysis of volatile neutral molecules could be expected to occur within the cavitation bubbles. In addition, the electronic structure changes of organic molecules always accompanies the transformation between the molecular and ionized...
7.4. *p*-HYDROXYBENZOIC ACID

Figure 7.17: HPLC Analysis: the high performance liquid chromatographs observed during the sonophotocatalytic degradation of an aqueous solution of 100 μM *p*-hydroxybenzoic acid at pH 2, pH 6, pH 9 and pH 12. The TiO$_2$ loading was 1 mg/mL. The applied ultrasonic frequency was 213 kHz and the power was 55 mW/mL. The detection wavelength used in the HPLC was 216 nm which is the maximum absorbance wavelength of Product E.

forms. These changes are able to alter the rates at which radicals attack sites on a molecule, and also may lead to different products.
7.4. p-HYDROXYBENZOIC ACID

7.4.3. Degradation of Products

In order to understand the influence of pH on the sonophotocatalytic degradation of p-hydroxybenzoic acid, the graphical plots showing the concentration of six products against the degradation time are shown in Figure 7.18. Due to the fact the peaks of product A and B lie in the system peaks (retention time: 3.0-4.5 min), the height of respective peaks were used to compare the degradation of products. Because of the very small amounts of products C, D and F, the height of their peaks were also used to represent the concentration of each component.

As shown in Figure 7.18, the peak height of product A and B at pH 2 is far higher than that at pH 6, pH 9 and pH 12, indicating that low pH value favors the formation of the hydrophilic products. It is of interest to note that a large amount of product B was formed during the first 10 min of degradation at pH 2. After that, there is only a slight increase observed.

There is almost no effect of pH on the formation of product C. However, higher solution pH facilitates the formation of products D, E and F. All of these three products reach their maximum amount at pH 12 during sonophotocatalytic degradation, which is larger than the amount formed at pH 2. For these three products, the amount produced at pH 12 is far more than that at pH 2. According to the results from a separate series of experiments, these large differences appear to be mainly due to sonochemical degradation and only minimal amount changes take place at various pH values during photocatalysis. For example, there was no product F generated during photocatalytic degradation at all four pH values.

In summary, the aqueous solution pH has a strong influence on the pathway and direction of the sonophotocatalytic degradation of p-hydroxybenzoic acid. It is possible to adjust the solution pH in order to select certain degradation reactions that minimize the more harmful degradation products, and even convert them to useful materials for other reactions. In addition, for those products formed in one individual oxidation process, whereas not in the other, they are expected to undergo faster degradation in sonophotocatalysis compared to the individual techniques, as both sonolysis as well as photocatalysis can decompose these products simultaneously in the hybrid system.
7.4. *p*-HYDROXYBENZOIC ACID

Figure 7.18: Product Degradation: the high performance liquid chromatographic peaks (or areas) of each component as a function of degradation time observed during the degradation of 100 µM *p*-hydroxybenzoic acid in aqueous solution at pH 2, pH 6, pH 9 and pH 12. The TiO$_2$ loading in the oxidation system was 1 mg/mL. The applied ultrasonic frequency was 213 kHz and the power was 55 mW/mL.
Concluding Remarks

The primary goal of this thesis work was to focus on fabricating high performance electrocatalysts for application in fuel cells and developing an appropriate advanced oxidation process for environmental remediation, as well as to gain fundamental understanding of the mechanism of acoustic cavitation and any external influences acting on it. Substantial progress in studying and exploring the fundamental applications of ultrasound has been made in achieving the research objectives.
8.1. **PtRu Bimetallic Nanoparticles Synthesis and their Electrocatalytic Ability**

The aim of this research component was to develop an appropriate sonochemical synthetic method to fabricate monometallic/bimetallic nanoparticles with certain structure and properties for further applications. A comparative study of the electrocatalytic ability of PtRu nanoparticles synthesized by different methods was also of particular interest for the fabrication of high performance nanoparticles. The experimental results from this study suggest that ultrasound is very useful in synthesizing a wide range of nanometer-sized materials.

The synthesis and evaluation of monometallic/bimetallic nanoparticles led to the following conclusions:

- **Ultrasound irradiation of aqueous solutions containing precious metal ions is an effective method for the preparation of nanometer sized metal colloids.** It has been clearly shown that in the absence of ultrasound, the precursor solutions of Pt(II) or mixture of Pt(II) and Ru(III) ions were successfully converted into zerovalent metallic or bimetallic colloids. Furthermore, ultrasonic irradiation provided a controllable and inexpensive method to fabricate these particles with uniform shapes and narrow size distribution. The diameters of platinum and platinum-ruthenium particles synthesized at a frequency of 213 kHz ultrasound irradiation were less than 10 nm. In addition, the sonochemical synthesis was found to be a green technology and avoids the involvement of undesirable chemicals;

- **The high resolution transmission electron microscopic images do indeed show core-shell bimetallic structures with the ruthenium forming a layer around the platinum core particles.** The structural characterization proved that the sequential reduction method produces a relatively higher yield of core-shell nanoparticles than the simultaneous reduction method. The electron collection behavior of existing platinum particles was found to play a significant role in forming the core-shell structure.

- **The X-ray photoelectron spectra proved that the presence of Pt can provide a new pathway to assist the ultrasonic synthesis of ruthenium metal nanoparticles.** It was found that ultrasound irradiation is unable to convert ruthenium ions to zerovalent metal particles unless platinum metal particles are present in the
8.2. Degradation of Organic Pollutants Using Combined Oxidation Techniques

aqueous solution. The platinum nanoparticles act as a catalyst during sonochemical synthesis of ruthenium particles.

It has been found that the stabilizer has a significant influence on the sonochemical synthesis of nanoparticles. Monitoring of the absorption spectra has shown that the preparation of PtRu bimetallic nanoparticles with PVP is faster than that with SDS. Due to the fact that faster reduction leads to relatively smaller particles, the observation that smaller particles were prepared in PVP system has suggested that PVP is the more favorable stabilizer for sonochemical synthesis of nanoparticles.

It has also been observed that PSS is a better stabilizer than PVP and SDS during the sonochemical synthesis of PtRu nanoparticles for fuel cell application. It can provide better conductive environment and therefore enhance the electrocatalytic performance of these bimetallic nanoparticles.

The synthesis of platinum-ruthenium bimetallic nanoparticles, the most promising electrocatalyst candidate for fuel cells, can be successfully achieved by using either sonochemical or radiolytic irradiation.

The change of platinum to ruthenium ions ratio in the precursor solution is an effective method of altering the composition percentage of prepared PtRu bimetallic nanoparticles and consequently influencing their electrocatalytic performance.

PtRu nanoparticles synthesized by simultaneous reduction, especially simultaneous radiolytic irradiation, have potential use as catalysts in fuel cells.

Section 8.2

Degradation of Organic Pollutants Using Combined Oxidation Techniques

The aim of this aspect of the work was to obtain an in-depth understanding and conduct a comprehensive evaluation of the sonophotocatalytic degradation of organic pollutants in aqueous environments. The degradation efficiencies of sonolysis, photocatalysis and sonophotocatalysis were systematically studied and compared.
8.2. Degradation of Organic Pollutants Using Combined Oxidation Techniques

A number of findings of this study reveal the potential application for environmental remediation. The following is a summary of these findings:

- Sonophotocatalysis was systematically studied and applied to oxidize various organic pollutants in aqueous solutions. A key observation of this study was the discovery of synergistic effects of the combined oxidation system on the degradation of the subsequent products formed during the degradation of the parent compound. Specifically, the combined system is most effective in the degradation of products that are formed exclusively by either sonolysis or photocatalysis alone. It has been observed that sonolysis, photocatalysis and sonophotocatalysis can decompose the parent organic pollutants as well as their products. Therefore, in the overall evaluation of the synergistic effect of the combined system, it is necessary to consider the influence of the combined process on the degradation of the reaction products. The decomposition of these products was also found to reduce the degradation efficiency of the parent organic pollutants.

- The results of the orthogonal array experimental design suggest that the efficiency of sonophotocatalytic degradation is significantly controlled by the frequency and power of the applied acoustic field, the pH of the aqueous solution and the photocatalyst loading. The efficiency of degradation correlated with the rate of production of the highly reactive radicals, which in turn is influenced by the applied ultrasound irradiation.

- It been shown that photocatalysis combined with sonolysis is likely to require less photocatalyst loading in comparison with individual photocatalysis.

- It was observed that the solution pH and the nature of the solute played a key role in the sonophotocatalytic degradation. The pH and nature of the organic pollutants can alter the hydrophobic and surface active properties of the pollutants. These changes are likely to alter the overall sonophotocatalytic degradation rate.

- Analysis of the products formed during sonophotocatalytic degradation has demonstrated that the pH or the selection of oxidation process is able to control the direction of the whole degradation. The quantitative yield measurement of the products has shown that the solution pH or oxidation process can alter the
8.2. Degradation of Organic Pollutants Using Combined Oxidation Techniques

amount of each product generated during sonophotocatalytic degradation. This observation reveals the potential of sonophotocatalysis to guide the degradation reaction in a less harmful direction for environmental remediation.

Based on the analysis of the mathematical model, sonophotocatalytic degradation of the parent organic pollutants as well as the derivative products is much faster than the individual oxidation processes, namely sonolysis and photocatalysis. Therefore, the sonophotocatalytic technique is likely to lead to a more complete and faster mineralization of organic pollutants in aqueous solutions.

It has been shown that sonolysis is effective in decomposing hydrophobic organic compounds and photocatalysis is better for hydrophilic ones. The hydrophobic property leads to a higher surface activity, which results in increasing the organic molecules probabilities of encountering with highly reactive primary radicals at the liquid/bubble interface. Hydrophilic molecules are readily adsorbed on the surface of TiO$_2$ and decomposed by photocatalysis.

It has been hypothesized that by combining the photocatalytic technique with the sonochemical technique the efficiency of these photocatalysts will be enhanced for the degradation of the parent organic pollutants. However, the data obtained did not show any remarkable evidence that the photocatalytic oxidation may be improved by the introduction of sonolysis. The interaction between sonolysis and photocatalysis has been found to be more complicated, as it involves chemical reactions as well as physical influences. Thus, it is clear that understanding the mechanism of the interaction of a combined system is prerequisite to obtaining synergistic effects between sonolysis and photocatalysis of organic pollutants.

Although these results of the sonochemical synthesis of nanoparticles and sonophotocatalytic degradation of organic pollutants are still at a preliminary stage, some of these results are useful for understanding the fundamental role that sonochemistry plays in nano-material synthesis and environmental remediation and have potential to pave a road for further use in practical applications of ultrasound and advanced oxidation processes.
Appendices
Numerical Simulation of Bubble Motion

Section A.1
Introduction

The equation for the motion of a spherically oscillating gas bubble under harmonic irradiation is given by the Rayleigh-Plesset Equation. A particular form of this equation investigated here is one that has been frequently used in recent studies.

\[ R\ddot{R} + \frac{3}{2} \dot{R}^2 = \frac{1}{\rho} [(P_g - P_0 - P(t)) - \frac{2\sigma}{R} - \frac{4\eta}{c_0} \dot{P}_g + \dot{P}_a] \]  

(2.4)
A.2. REFERRED CONSTANTS

The constants used in simulation are listed in Table A.1.

<table>
<thead>
<tr>
<th>Name</th>
<th>Symbol</th>
<th>Value</th>
<th>Unit</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density of Water</td>
<td>$\rho$</td>
<td>997.0480</td>
<td>kg/m$^3$</td>
<td>[26]</td>
</tr>
<tr>
<td>Speed of Sound (air)</td>
<td>$c_0$</td>
<td>1497.4</td>
<td>m/s</td>
<td>[26]</td>
</tr>
<tr>
<td>Standard Atmosphere Pressure</td>
<td>$P_0$</td>
<td>$1.01325 \times 10^5$</td>
<td>Pa</td>
<td>[26]</td>
</tr>
<tr>
<td>Surface Tension of Water</td>
<td>$\sigma$</td>
<td>0.07199</td>
<td>N/m</td>
<td>[26]</td>
</tr>
<tr>
<td>Viscosity of Water</td>
<td>$\eta$</td>
<td>$0.89 \times 10^{-3}$</td>
<td>Pa s</td>
<td>[26]</td>
</tr>
<tr>
<td>Ratio of the Specific Heat</td>
<td>$\kappa$</td>
<td>1.401 for air, 5/3 for Ar</td>
<td>-</td>
<td>[18, 26]</td>
</tr>
<tr>
<td>van der Waals Hard-core</td>
<td>$a$</td>
<td>$R_0/8.54$ for air, $R_0/8.8$ for Ar</td>
<td>-</td>
<td>[18–21]</td>
</tr>
</tbody>
</table>

Section A.3

MatLab Code

The whole simulation code was implanted in a technical language MatLab. The functions used in are included in MatLab basic function library. For usage of each function, please refer to the specific help documents of MatLab.
The whole program is marked with comments in order to develop an easy way to understand each steps.

```matlab
function [Radius,time]=BubbleDynamics(Frequency,InitialRadius,USPower,Area,Time,Gas,Pa)

% Author : Yuanhua HE
% School of Chemistry, University of Melbourne, Australia
% Create: 01/11/2008 23:08:23

% Brief Introduction:
% BubbleDynamics - A numerical solution to Rayleigh-Plesset Equation
% considering the damping effect.
% Input: a series of initial conditions and ultrasonic parameters.
% Frequency: the frequency of the driving ultrasound, kHz;
% InitialRadius: the initial radius of a bubble, um;
% USPower: the total power of the driving ultrasound, W;
% Area: the affected area of the above power, cm2;
% Time: the investigated time period, s;
% Gas: ‘A’ for argon, the all rest for air atmosphere;
% Pa: pressure amplitude if the unit is atm. It has priority to the values of Power and Area for calculating the driving pressure.
% Output: the radius (um) changes of the bubble and the corresponding time (us);

% For Example:
% [Radius,time]=BubbleDynamics(20,5,0,80,80,'s',1.3);
% [Radius,time]=BubbleDynamics(213,1.6,100,-6,40,'x',1.4);
% [Radius,time]=BubbleDynamics(20,5,0.5894,1,80,'A');

% Convert to international units
```

YUANHUA HE

PhD THESIS
f=Frequency*1e3;
R0=InitialRadius*1e-6;
T=Time*1e-6;

% If the unit of pressure is atm
if nargin==7
    P=Pa*1.01325e5;
else
    I=USPower/(Area*1e-4);
    rho=997.0480;
    c0=1497.4;
    P=sqrt(2*I*rho*c0);
end;

% A numerical solution based on Runge-Kutta(4,5) formula
option = odeset('RelTol',1e-7);
sol = ode45(@BubbleSize,[0 T],[R0; 0],option,R0,f,P,Gas);
time = sol.x*1e6;
Radius = sol.y(1,:)*1e6;
Pt = P*sin(2*pi*f*sol.x)/1.01325e5;

% Plot the radius of bubble vs time
figure('Color','w');
[AX,H1,H2]=plotyy(time,Radius,time,Pt);
set(H1,'LineStyle','-','LineWidth',2);
set(H2,'LineStyle',':','LineWidth',2);
set(get(AX(1),'Ylabel'),'String','Bubble Radius ("mum")','FontWeight','bold','FontSize',20);
set(get(AX(2),'Ylabel'),'String','Pressure (atm)','FontWeight','bold','FontSize',20);
xlabel('Time ("mus")','FontWeight','bold','FontSize',20);
A.3. MatLab Code

function dRdt = BubbleSize(t,y,R0,f,P,Gas)

rho = 997.0480; % Density of Water:
c0 = 1497.4; % Speed of sound:
P0 = 1.01325e5;
sigma = 0.07199; % Surface Tension
eta = 0.89e-3; % Viscosity
if Gas == 'A' % Argon
    k = 5/3;
    a = R0/8.8;
else k = 1.401; % Air
    a=R0/8.54;
end;

Pt=P*sin(2*pi*f*t);
dPt=2*pi*f*P*cos(2*pi*f*t);

Pg=(P0+2*sigma/R0)*(R0^3-a^3)^(k/(y(1)^3-a^3))^k;
dPg=-3*k*(P0+2*sigma/R0)*(R0^3-a^3)^k*y(1)^2*y(2)/(y(1)^3-a^3)^(k+1);

Pl= Pg-P0-Pt-2*sigma/y(1);
Pvis=4*eta*y(2)/y(1);
Pd=y(1)/c0*(dPg-dPt);

dRdt = [y(2); ((Pl-Pvis+Pd)/rho-3/2*y(2)^2)/y(1)];
Section B.1

Crystal Types of TiO₂

There are three crystal structures of titanium dioxide: rutile, anatase and brookite. The last one is usually found only in minerals and has a orthorhombic crystal structure. The rutile and anatase have attracted a considerable attention in recent years, particularly in the field of photocatalysts. The lattice structures are shown in the following figures (Figures B.1 and B.1).

In the rutile and anatase forms, the TiO₆ binding octahedra are slightly distorted with two different Ti-O binding lengths and different O-Ti-O angles. The distortion in the anatase form is larger than in the rutile form.
Brookite is the most complicated structure with six different Ti-O binding lengths and 12 different O-Ti-O binding angles.

Anatase type titanium dioxide generally shows a higher photoactivity than the other types of titanium dioxide [232]. One of the reasons for this may lie in the differences in their semiconductor energy band structures. The bandgap of anatase-type titanium dioxide is 3.2 electron volts (eV) corresponding to UV light 388 nm, while the bandgap of the rutile-type is 3.0 eV corresponding to 413 nm. The valence bands for the anatase and rutile forms are similar, and the conduction band of anatase is higher in the energy diagram, this type of TiO$_2$ has a higher reducing power.

It is well known that the crystalline quality is a significant factor in the photocatalytic activity, and a high degree of crystallinity brings high photocatalytic activity. However, the mechanism of the influence of crystal phases on photocatalytic activity is still unclear. There are quite a number of publications studying the effects of rutile/anatase crystal types on photocatalytic ability but few relating to sonochemical degradation.

---

**Figure B.1:** Structure of anatase crystal.

---
B.2. The Influence of TiO$_2$ Particle Size on Its Bandgap

In the process of photocatalysis in the presence of TiO$_2$, it is well established that the size of the particles play a key role in improving the efficiency of degradation. Louis Brus mathematically described the size-dependent bandgap shifts in quantum-size semiconductors by using electronic wave functions [311].

$$\Delta E_g = E(R) - E(R \to \infty) = \frac{\hbar^2 \pi^2}{2\mu R^2} - \frac{1.786e^2}{\epsilon R} - 0.248E_{Ry}^*$$  \hspace{1cm} (B.1)

Figure B.2: Structure of rutile crystal.
B.2. The Influence of TiO$_2$ Particle Size on Its Bandgap

Table B.1: Crystal structure data of the three crystal modifications of TiO$_2$. [310]

<table>
<thead>
<tr>
<th>Properties</th>
<th>Rutile</th>
<th>Anatase</th>
<th>Brookite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal Structure:</td>
<td>Tetragonal</td>
<td>Tetragonal</td>
<td>Orthorombic</td>
</tr>
<tr>
<td>Lattice Constant a (Å):</td>
<td>4.5929</td>
<td>3.785</td>
<td>9.166</td>
</tr>
<tr>
<td>Lattice Constant b (Å):</td>
<td>4.5929</td>
<td>3.785</td>
<td>5.436</td>
</tr>
<tr>
<td>Lattice Constant c (Å):</td>
<td>2.9591</td>
<td>9.514</td>
<td>5.135</td>
</tr>
<tr>
<td>Space group:</td>
<td>$P4_2/mmm$</td>
<td>$I4_1/amd$</td>
<td>$Pbca$</td>
</tr>
<tr>
<td>Atoms per cell:</td>
<td>6</td>
<td>6</td>
<td>24</td>
</tr>
<tr>
<td>Basis coordinates in units:</td>
<td>Ti: 0.0 0.0 0.0</td>
<td>Ti: 0.0 0.0 0.0</td>
<td>Ti: 0.127 0.113 0.873</td>
</tr>
<tr>
<td>of the lattice constants:</td>
<td>O: 0.3056 0.3056 0.0</td>
<td>O: 0.0 0.0 0.2064</td>
<td>O$_1$: 0.010 0.155 0.180</td>
</tr>
<tr>
<td></td>
<td>O$_2$: 0.230 0.105 0.535</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti-O bond length (Å):</td>
<td>1.945 (4 ×)</td>
<td>1.937 (4 ×)</td>
<td>1.92 up to 1.98</td>
</tr>
<tr>
<td></td>
<td>1.985 (2 ×)</td>
<td>1.964 (2 ×)</td>
<td></td>
</tr>
<tr>
<td>O-Ti-O bond angle:</td>
<td>81.0°</td>
<td>77.6°</td>
<td>77° up to 100°</td>
</tr>
<tr>
<td></td>
<td>90.0°</td>
<td>92.6°</td>
<td></td>
</tr>
</tbody>
</table>

Here, $E(R)$ is the absorption bandgap of nano-semiconductor particles; $E(R \to \infty)$ is the bulk semiconductor bandgap energy; $R$ is the radius of the particles; $\mu$ is the exciton reduced mass of the exciton, i.e., $\mu = (1/m_e^* + 1/m_h^*)^{-1}$, where $m_e^*$ is the effective mass of the electron and $m_h^*$ is the effective mass of the holes; $\epsilon$ is the dielectric constant of the material; $E_{Ry}^*$ is the effective Rydberg energy of the bulk exciton, i.e., $E_{Ry}^* = \mu e^4/2\epsilon^2h^2$.

According to the Brus Equation B.1, the relationship (Figure B.3) between the bandgap shifts and the particle radius can be calculated in terms of $\epsilon = 184$, $\mu = 1.63m_e$ (where $m_e$ is the electron rest mass) [312].

The critical radius of the quantum size effect is mathematically deduced with a resultant value of 16 nm (as the inset of Figure B.3), which means for titanium dioxide, there is no bandgap shifts until the particle size is less than 32 nm.
Section B.3

MatLab Code for Solving the Brus Equation

The code is implanted by using the technical language, MatLab.

Figure B.3: The quantum size effect of nanometer sized titanium dioxide.
function y=Brusplot
% Author : Yuanhua HE
% School of Chemistry, University of Melbourne, Australia
% Create: 08/06/2005 09:35:13

x1=[0.5:0.01:1,1.1:0.1:3]';
x=x1/10ˆ9;
e=1.6021773349*10ˆ(-19);
me=9.109389754*10ˆ(-31);
h=6.626075540*10ˆ(-34);
epsilon=184*4*pi*8.854187817*10ˆ(-12);
mestar=9*me;
mhstar=2*me;
mu=1/(1/mestar+1/mhstar);
ERy=eˆ4/(2*epsilonˆ2*hˆ2*(1/mestar+1/mhstar));

First=((h/2/pi)ˆ2*piˆ2/2/mu.*x.ˆ(-2))/e;
Second=(1.786*eˆ2/epsilon.*x.ˆ(-1))/e;
Third=0.248*ERy/e;
F=First-Second-Third;

vpa([x1,3.2+F,F/3.2*100],6)

hold off;
plot(x1,F,'k-','LineWidth',1);
hold on;
plot(x1,First,'k:','LineWidth',1);
plot(x1,Second,'k--','LineWidth',1);
B.3. MatLab Code for Solving the Brus Equation

```matlab
plot(x1, Third*ones(size(x1)), 'k-.', 'LineWidth', 1);
legend('"DeltaEg', 'First', 'Second', 'Third');
set(gca, 'FontWeight', 'bold', 'FontSize', 11, 'LineWidth', 1);
xlabel('R (nm)', 'FontWeight', 'bold', 'FontSize', 16);
ylabel('"DeltaEg (eV)', 'FontWeight', 'bold', 'FontSize', 16);
```
Application of Orthogonal Array Design in Methyl Orange Degradation

This appendix provides the supplementary materials to support and explain the orthogonal array experiment design and analysis used in Chapter 6. A Design of Experiments (DOE) module of MINITAB statistical software was used to demonstrate the procedure of orthogonal array analysis.
Section C.1

Results of Orthogonal Array Experimental Design

An $L_{16}(4^4)$ orthogonal array was used to develop an effective method to reveal the correlation between the effi-

Table C.1: The first-order rate constants and synergism of 60 min sonolysis, photocatalysis and sonophotocatalysis of 100 $\mu$M methyl orange in 16 orthogonal array experimental runs.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Freq. (kHz)</th>
<th>Power (mW/mL)</th>
<th>pH</th>
<th>TiO$_2$ (mg/mL)</th>
<th>$k_S$ $(10^{-2}\text{min}^{-1})$</th>
<th>$k_{PC}$ $(10^{-2}\text{min}^{-1})$</th>
<th>$k_{SPC}$ $(10^{-2}\text{min}^{-1})$</th>
<th>$S$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>213</td>
<td>16</td>
<td>7</td>
<td>1.0</td>
<td>0.1</td>
<td>1.3</td>
<td>1.5</td>
<td>1.1</td>
</tr>
<tr>
<td>2</td>
<td>213</td>
<td>88</td>
<td>4</td>
<td>2.0</td>
<td>4.0</td>
<td>1.6</td>
<td>3.2</td>
<td>0.6</td>
</tr>
<tr>
<td>3</td>
<td>213</td>
<td>55</td>
<td>3</td>
<td>5.0</td>
<td>1.9</td>
<td>1.8</td>
<td>1.8</td>
<td>0.5</td>
</tr>
<tr>
<td>4</td>
<td>213</td>
<td>35</td>
<td>2</td>
<td>0.5</td>
<td>1.0</td>
<td>2.1</td>
<td>3.0</td>
<td>0.9</td>
</tr>
<tr>
<td>5</td>
<td>355</td>
<td>16</td>
<td>4</td>
<td>5.0</td>
<td>0.0</td>
<td>1.8</td>
<td>1.3</td>
<td>0.7</td>
</tr>
<tr>
<td>6</td>
<td>355</td>
<td>88</td>
<td>7</td>
<td>0.5</td>
<td>5.7</td>
<td>1.5</td>
<td>4.9</td>
<td>0.7</td>
</tr>
<tr>
<td>7</td>
<td>355</td>
<td>55</td>
<td>2</td>
<td>1.0</td>
<td>3.1</td>
<td>1.9</td>
<td>4.6</td>
<td>0.9</td>
</tr>
<tr>
<td>8</td>
<td>355</td>
<td>35</td>
<td>3</td>
<td>2.0</td>
<td>2.2</td>
<td>1.9</td>
<td>2.7</td>
<td>0.6</td>
</tr>
<tr>
<td>9</td>
<td>647</td>
<td>16</td>
<td>3</td>
<td>0.5</td>
<td>0.1</td>
<td>1.7</td>
<td>1.6</td>
<td>0.9</td>
</tr>
<tr>
<td>10</td>
<td>647</td>
<td>88</td>
<td>2</td>
<td>5.0</td>
<td>2.6</td>
<td>1.5</td>
<td>4.0</td>
<td>1.0</td>
</tr>
<tr>
<td>11</td>
<td>647</td>
<td>55</td>
<td>7</td>
<td>2.0</td>
<td>1.1</td>
<td>1.8</td>
<td>2.4</td>
<td>0.8</td>
</tr>
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<td>1.2</td>
<td>1.4</td>
<td>0.8</td>
</tr>
<tr>
<td>13</td>
<td>1056</td>
<td>16</td>
<td>2</td>
<td>2.0</td>
<td>0.0</td>
<td>2.1</td>
<td>1.9</td>
<td>0.9</td>
</tr>
<tr>
<td>14</td>
<td>1056</td>
<td>88</td>
<td>3</td>
<td>1.0</td>
<td>1.9</td>
<td>1.3</td>
<td>2.7</td>
<td>0.8</td>
</tr>
<tr>
<td>15</td>
<td>1056</td>
<td>55</td>
<td>4</td>
<td>0.5</td>
<td>0.5</td>
<td>1.0</td>
<td>1.3</td>
<td>0.9</td>
</tr>
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<td>16</td>
<td>1056</td>
<td>35</td>
<td>7</td>
<td>5.0</td>
<td>0.1</td>
<td>1.8</td>
<td>1.2</td>
<td>0.7</td>
</tr>
</tbody>
</table>
C.1. Results of Orthogonal Array Experimental Design

Efficiencies of the individual systems and the synergistic effect of sonophotocatalysis, and the operation conditions described in Chapter 6. The calculated first-order rate constants for each process and the synergistic effect index of combined system are listed in Table C.1. Here, \( k_S \) is the first-order rate constant for 60 min sonolysis of methyl orange, and \( k_{PC} \), for photocatalysis and \( k_{SPC} \) for sonophotocatalysis, respectively. As discussed in Chapter 6, the ratio \( (S) \) of the sonophotocatalytic rate constant and the summed rate constants of the individual processes was used to evaluate the synergistic effect of a combined system (refer to Equation 6.1).

\[
S = \frac{k_{SPC}}{k_S + k_{PC}}
\]  

(C.1)

C.1.1. Results of Sonolysis

The numerical results listed in Table C.2 are related to Figure 6.3. Table C.2 lists the analytical results of the orthogonal array design method for 60 min sonolysis of 100 µM methyl orange.

The average first-order constants \( (k_I - k_{IV}) \) correspond to their unique factor and level. For example, the third level of ultrasonic power (55 mW/mL) corresponds to Experiments 3, 7, 11 and 15. Therefore,

\[
k_{\text{Power}}^{\text{III}} = (1.9 + 3.1 + 1.1 + 0.5)/4 = 1.65(\times10^{-2}\text{min}^{-1})
\]

(C.1)

All the calculated average first-order constants for each level of each factor are shown in the middle of Figure C.2. \( \Delta k \) is the difference between the maximum and the minimum of the average first-order constant of each factor. Taking the rate constants for the pH factor as an example, the maximum average first-order rate constant is 1.73\( \times10^{-2}\text{min}^{-1} \) and the minimum is 1.28\( \times10^{-2}\text{min}^{-1} \). Consequently, \( \Delta k \), the difference between them, is 0.46\( \times10^{-2}\text{min}^{-1} \). \( \Delta k \) indicates the influence of the corresponding factor on the degradation efficiency of sonolysis. According to the calculated \( \Delta k \), the ultrasonic power has the greatest influence on the sonochemical degradation of methyl orange. In other words, the selection of ultrasonic power leads to greatest change of degradation efficiency.
C.2. Orthogonal Array Analysis with MINITAB Statistical Software

C.1.2. Results of Photocatalysis

The numerical results listed in Table C.3 relate to Figure 6.2. All the calculations followed the method described in Subsection C.1.1.

C.1.3. Results of Sonophotocatalysis

The numerical results listed in Table C.4 are related to Figure 6.7. The same calculation procedure in Subsection C.1.1 was used in the sonophotocatalysis of methyl orange.

Section C.2

Orthogonal Array Analysis with MINITAB Statistical Software

MINITAB, a statistical software package, provides a convenient way to create orthogonal array experimental runs and quantitatively analyze the obtained results. This Section takes the sonophotocatalytic degradation of methyl orange as a typical example to demonstrate MINITAB can be create and analyze an orthogonal array experiment design. The Manual of MINITAB, Help-to-Go [313], provides a detailed procedure for each operation, which is a good reference resource for further reading.

C.2.1. Creating An Orthogonal Array Design

Create a $L_{16}(4^4)$ orthogonal array: Menu Stat → DOE → Taguchi → Create Taguchi Design...

In the Taguchi Design window, select 4-Level Design (2 to 5 factors) and 4 (factors) in Number of factors roll list.

Arrange four factors and four levels;
C.2. **Orthogonal Array Analysis with MINITAB Statistical Software**

**Figure C.1:** Create a $L_{16}(4^4)$ orthogonal array.

Click the **Designs...** button and select $L_{16} 4**4$ in **Taguchi Design - Design** window, then click **Factors...** and input values as shown in Figure C.2.

Run 16 experiments and fill the results in the last column (shown in Figure C.3).

**C.2.2. Analyzing the Orthogonal Array Design**

MINITAB Statistical Software also integrates the analysis function. It is a convenient way to avoid tedious statistical calculations.

Start the function of the orthogonal array design analysis (*see* Figure C.4).
Figure C.2: Input four factors and their corresponding four levels.

- Set the calculated first-order rate constants as **Response data** (see Figure C.5).

- The results are shown in the **Session** window (see Figure C.6).
## C.2. Orthogonal Array Analysis with MINITAB Statistical Software

![Worksheet 2](image)

<table>
<thead>
<tr>
<th>C1 Frequency</th>
<th>C2 Power</th>
<th>C3 pH</th>
<th>C4 TiO2</th>
<th>C5 k_SPC</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>213</td>
<td>16</td>
<td>7</td>
<td>1.0</td>
</tr>
<tr>
<td>2</td>
<td>213</td>
<td>88</td>
<td>4</td>
<td>2.0</td>
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**Figure C.3:** Run 16 experiments and input first-order rate constants for each sonophotocatalysis experiment.
### C.2. Orthogonal Array Analysis with Minitab Statistical Software

Table C.2: The results of orthogonal array design analysis for 60 min sonolysis of 100 µM methyl orange.

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| $k_I$   | 1.77        | 0.06          | 1.67| 1.83           |
| $k_{II}$| 2.74        | 0.99          | 1.54| 1.41           |
| $k_{II}$| 1.09        | 1.65          | 1.28| 1.84           |
| $k_{IV}$| 0.63        | 3.53          | 1.73| 1.15           |

| $\Delta k$ | 2.11 | 3.47 | 0.45 | 0.68 |
| Rank        | 2    | 1    | 4    | 3    |
### C.2. Orthogonal Array Analysis with Minitab Statistical Software

**Table C.3:** The results of orthogonal array design analysis for 60 min photocatalysis of 100 µM methyl orange.

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### C.2. Orthogonal Array Analysis with Minitab Statistical Software

**Table C.4:** The results of orthogonal array design analysis for 60 min sonophotocatalysis of 100 μM methyl orange.

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### C.2. Orthogonal Array Analysis with MINITAB Statistical Software

**Figure C.4:** Analyze the results of $L_{16}(4^4)$ orthogonal array experiment design.

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C.2. Orthogonal Array Analysis with MINITAB Statistical Software

Figure C.5: Set the first-order rate constants of sonophotocatalysis as response data.
Figure C.6: Automatically calculate the results.
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