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Improving the Photocatalytic H₂ Evolution Activities of TiO₂ by Modulating the Stabilizing Ligands of the Nanoscale Ti₈O₈-Cluster Precursors

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ABSTRACT

Titanium-oxo clusters (TOCs) are important model complexes and potential precise single-source precursors of TiO₂ materials. We report here a series of TiO₂ samples derived from TOCs with the same wheel-like Ti₈O₈ clustercore but different stabilizing ligands. Our results demonstrate that the ligands on TOCs not only influence the phase-transition during themolysis, but more importantly tune the photocatalytic H₂ evolution activities of the obtained TiO₂ materials. Through 500°C calcination, the nanosized Ti₈O₈ cluster stabilized by organic benzoate ligands gives rise to a TiO₂ sample with H₂ production rate of 611 μmol/h/g. When the stabilizing ligands are changed to inorganic SO₄²⁻, a significant improvement of H₂ evolution activity has been achieved, resulting in a 7-times higher value of 4527 μmol/h/g. This work provides a new strategy to produce TiO₂ with enhanced and tunable photocatalytic activities from titanium-oxo cluster precursors.

Keywords: H₂ generation, TiO₂, photocatalysis, titanium-oxo clusters, ligands effect

1. Introduction

Considering the severe crisis in global energy shortage and environment pollution, the development of clean and sustainable energy sources has attracted growing research interest.^[1-5] Water-splitting hydrogen production has been considered to be a promising solution.^[6-15] In 1972, Fujishima and Honda firstly discovered that titanium dioxide (TiO₂) could act as a catalyst for water splitting.^[16] Since then, TiO₂ has been regarded as one the most excellent catalysts and been widely studied, especially in photocatalytical hydrogen production.^[17-21] Thus the preparation of TiO₂ with high catalytic efficiency has always been an urgent mission for researchers. Although many synthetic methodologies have been developed, such as sol-gel method, micelle and inverse micelle method, chemical vapor deposition method, and electrodeposition method, the applied precursors are largely limited to small species like titanium alkoxides or TiCl₄.^[22-35] And due to the lack of structural information, the aggression process from single Ti ion *via* small polynuclear complex to TiO₂ is difficult to study. Therefore, it would be much helpful to use molecular Ti-O clusters with atomically defined structures as new kinds of precursors.

Although a great number of TOCs have been discovered, the influence of their molecular structures on the photocatalytic properties of targeted TiO₂ has been rarely studied. Crystalline titanium-oxo clusters have been regarded as the structure and reactivity model compounds of bulk TiO₂, and been intensively studied during the past decades.^[36-42] The precise structural information of these crystalline materials can

be well-examined by X-ray diffraction analysis.^[43] Therefore, they can act as structure-defined cluster precursors for the preparation of TiO₂, which will not only help understand the formation mechanisms but also provide molecular tool to tune the final photocatalytic behaviors. Wright group has recently utilized TOCs as precursors to prepare TiO₂/C composites with good electrochemical performances and lanthanide/TiO₂ composites with supercapacitor and dye photodegradation applications.^[44-47] Some other TiO₂ related nanomaterials have also been synthesized using TOCs as precursors.^[48-52] However, to the best of our knowledge, the ligand-effect in TOCs towards the photocatalytic H₂ evolution activities of the obtained TiO₂ materials has never been investigated.

Fig. 1. The wheel-like Ti₈O₈ core structures of compounds **1** (a) and **2** (b).

In this work, we studied the fabrication of TiO₂ using two structure-related TOCs as single-source molecular precursors, (C₄N₂H₁₂)₈·[TiO(SO₄)₂]₈·23H₂O (**1**) and [TiO(OOCC₆H₅)₂]₈·(CH₃CN)₂·H₂O (**2**). Although these two TOCs present the same wheel-like Ti₈O₈ cluster core of ~1.0 nm diameter (Fig. 1), their different stabilizing ligands show significant influence on the formation and property of the synthesized

TiO₂ materials. Temperature-dependent thermolysis investigations indicated that the presence of organic benzoate ligand produced rutile TiO₂ at lower temperature than inorganic sulfate ligand. The Brunauer–Emmett–Teller (BET) tests showed that the surface areas of samples synthesized from cluster **1** were always much larger than those prepared from cluster **2**. So did the photocatalytic H₂ evolution experiments. Finally, under the same synthetic and experimental condition, the sulfate-Ti₈O₈ derived TiO₂ gave the highest H₂ production rate of 4527 μmol/h/g, which is 7 times larger than that of the benzoate-Ti₈O₈ derived one.

2. Experimental

2.1. Materials

All reagents were purchased commercially and used without further purification. Titanium Tetraisopropanolate (Ti(OiPr)₄) and acetonitrile were bought from Energy Chemical, Piperazine, Tetrabutyl Titanate (Ti(O^tBu)₄) and sulfuric acid (H₂SO₄ 98%, AR) were bought from Sinopharm Chemical Reagent Co., Ltd. TiO₂ (P25, 20% rutile and 80% anatase) and benzoic acid were bought from Aladdin Chemical.

2.2. Synthesis of the TiO₂ samples

The two titanium-oxo clusters were synthesized according to the literature.^[53,54] The synthesized crystals of TOCs were then filtered, washed and dried. After that the crucible containing TOC crystals was placed in a muffle furnace for calcinations. The temperature was increased from room temperature to 200°C with a rate of 5°C min⁻¹, and after 200°C, the temperature was increased to terminal temperature

(500°C/600°C/700°C/800°C) with a rate of 2°C min⁻¹. And the specimens were kept at the terminal temperatures for 12h before being cooled down to room temperature.

2.3. Characterization

The thermogravimetric analyses (TGA) were performed on a Mettler Toledo TGA/SDTA 851e analyzer in air atmosphere with a heating rate of 10 °C/min from 30°C to 800 °C. Powder X-ray diffraction (PXRD) data was collected on a Rigaku Mini Flex II diffractometer using CuK α radiation ($\lambda = 1.54056 \text{ \AA}$) under ambient conditions. The morphologies of the obtained TiO₂ samples were observed by JEOL JSM6700F field-emission scanning electron microscope. The mapping and energy-dispersive X-ray (EDX)analysis of obtained TiO₂ samples were collected on JEOL JSM6700F field-emission scanning electron microscope equipped with a Oxford INCA system. The UV diffuse reflection data was recorded at room temperature using a powder sample with BaSO₄ as a standard (100% reflectance) on a Perkin Elmer Lamda-950 UV spectrophotometer and scanned at 200-800 nm. X-ray photoelectron spectra (XPS) of the TiO₂ powders were measured using ESCALAB 250Xi photoelectron spectrometer. Gas adsorption measurements were performed on the ASAP (Accelerated Surface Areaand Porosimetry) 2020 System.

2.4. Photocatalytic Activity Measurements

Photocatalytic hydrogen production tests were carried out in a pyrex reaction cell connected to a closed gas circulation and evacuation system (Perfect Light Company Labsolar-III (AG)). 40 mg of the obtained sample powder was dispersed in 100 mL

aqueous solution containing 10 vol% methanol and 33uL 1.0 wt% H_2PtCl_6 . The reaction temperature was maintained around 5°C. The 300W Xe lamp was used as the UV-vis light source. The gas in the system was analyzed by online-GC(FULI; TDX-01 column, TCD, Ar Carrier) to determine the amount of hydrogen generated with an interval of one hour.

Fig.2. The TGA curves of compounds **1** and **2**.

3. Results and Discussion

The two crystalline titanium–oxo cluster precursors $(\text{C}_4\text{N}_2\text{H}_{12})_8 \cdot [\text{TiO}(\text{SO}_4)_2]_8 \cdot 23\text{H}_2\text{O}$ (**1**) and $[\text{TiO}(\text{OOC}\text{C}_6\text{H}_5)_2]_8 \cdot (\text{CH}_3\text{CN})_2 \cdot \text{H}_2\text{O}$ (**2**) were synthesized according to the literature method.^[48,49] Fig. 1 shows the wheel-like Ti_8O_8 core motifs of the two clusters and their complete molecular structures are presented. The Ti_8O_8 wheel consists of eight vertex-sharing TiO_6 octahedra. The only difference between these two clusters is the bridging bidentate ligand. In compound **1**, 16 sulfate ligands stabilize the 8-member Ti_8 ring, with every two of them connecting the neighboring Ti atoms. The positions of all sulfates are replaced by benzoate ligands in compound **2**. The phase purity of these two complexes is confirmed by powder X-ray

diffraction (PXRD) analysis. Thermogravimetric analysis (TGA) has been carried out to analyze the thermal stability of compound **1** and **2** (Fig. 2). As shown in Fig. 2, both the cluster structures of **1** and **2** decompose from about 300°C, and the TiO₂ composites start to form after 500°C.

Fig.3. The XRD patterns of samples obtained by calcinations of cluster **1** and **2** at different temperatures. Pure anatase and rutile TiO₂ patterns are also presented for comparison.

Based on the above TGA analysis, the calcination of these two TOCs towards TiO₂ materials has been studied from 500°C to 800°C. The TiO₂ samples synthesized from sulfate-stabilizing cluster **1** at different temperatures ($T = 500, 600, 700, 800^{\circ}\text{C}$) are denoted as TiO₂(S)- T and the corresponding ones obtained from benzoate-stabilizing cluster **2** are denoted as TiO₂(C)- T . PXRD patterns of the obtained TiO₂ samples are shown in Fig. 3. It is interesting to find that the phase structures of obtained TiO₂ depend not only on the heating temperature but also strongly on the stabilizing ligands

in TOC the precursors. When cluster **1** was used as precursor, pure anatase TiO_2 was obtained at 500°C and 600°C, and rutile TiO_2 began to form at 700°C to give a mixed TiO_2 phase. Pure rutile TiO_2 was achieved at 800°C. While in the case of using cluster **2** as precursor, pure anatase TiO_2 could only be prepared at 500°C. And the appearance of rutile TiO_2 was moved up to 600°C, giving rise to a mixed phase. At both 700°C and 800°C, only rutile TiO_2 was presented. Therefore, compared to benzoate ligands, the existence of sulfate ligands is more favorable for the formation of anatase TiO_2 which is widely believed to have better photocatalytic H_2 evolution activities. And the ligands of two cluster precursors play an important role in the transformation temperature from anatase to rutile and the phase structure of attained TiO_2 samples.

Scanning electron microscopy (SEM) studies have been conducted to observe the morphologies of the obtained TiO_2 materials, which were also significantly influenced by both calcinations temperature and the applied TOC precursors (Fig. 4). The results indicate that the crystallinity of the samples increases with the raise of calcinations temperature.

The observed morphologies depended significantly on the applied TOC precursors. As shown in Fig.4, $\text{TiO}_2(\text{S})$ -500 exhibits loose states while $\text{TiO}_2(\text{C})$ -500 is more compact. The Brunauer–Emmett–Teller (BET) tests also indicate that the surface area of $\text{TiO}_2(\text{S})$ -500 is much larger than that of $\text{TiO}_2(\text{C})$ -500 (Fig. 5, Table 1). Meanwhile, the pore sizes of $\text{TiO}_2(\text{S})$ -500 distribute more homogeneously and present higher values than those of $\text{TiO}_2(\text{C})$ -500. The same tendency can also be found for the other

calcination temperatures. These results might be attributed to the different gases produced during the calcination process. It can be expected that the decomposition of sulfate would release SO_2/SO_3 whilst the decomposition of benzoate would generate CO_2 . Considering the higher volume and corrosivity of SO_2/SO_3 than CO_2 , larger pores and higher porosity would form by the former gas. Moreover, the porosity of the obtained TiO_2 materials was also greatly influenced by the calcinations temperature. At the low calcination temperature (500°C and 600°C), the samples show loose hollows morphology. With the increase of calcination temperature, the TiO_2 grains aggregate dramatically, forming relatively compact surface. Therefore, higher calcinations temperature would produce higher crystallinity but lower surface areas.

Fig.4. The SEM images of $\text{TiO}_2(\text{S})$ -500 (a), $\text{TiO}_2(\text{C})$ -500 (b), $\text{TiO}_2(\text{S})$ -600 (c), $\text{TiO}_2(\text{C})$ -600 (d), $\text{TiO}_2(\text{S})$ -700 (e), $\text{TiO}_2(\text{C})$ -700 (f), $\text{TiO}_2(\text{S})$ -800 (g), and $\text{TiO}_2(\text{C})$ -800 (h).

The element distribution of crystalline TiO₂ samples was shown in Fig. S11-S18. It is of worth noting that, the Ti, O, S elements were distributed uniformly in TiO₂-S-500. The presence of S in TiO₂-S-500 was also detected by EDX analysis, which might be due to the existence of small amount of SO₄²⁻ ions adsorbed on the surface of TiO₂-S-500. The chemical states of obtained TiO₂ samples were further studied by XPS spectra. In the XPS survey spectrum of TiO₂-S-500, a weak signal corresponding to S was detected. Such a peak of S2/3p at 168.7eV can be attributed to S (+VI) in SO₄²⁻ ions.^[55]

Fig.5. Nitrogen adsorption–desorption isotherms of TiO₂(S)-500 (a), TiO₂(C)-500 (b) and corresponding pore size distribution curves of TiO₂(S)-500 (c),TiO₂(C)-500(d).

Table 1 Summary of the formation and characterization of obtained TiO₂ samples.

Sample	Calcination Temperature [°C]	S _{BET} [m ² g ⁻¹]	H ₂ Evolution Activity [μmol·h ⁻¹ ·g ⁻¹]	Particle Sizes [nm]
TiO ₂ (S)-500	500	99.0624	4527	10-30
TiO ₂ (C)-500	500	10.9719	611	100-200
TiO ₂ (S)-600	600	43.2079	3181	20-50
TiO ₂ (C)-600	600	5.1927	588	150-250
TiO ₂ (S)-700	700	8.9364	805	100-150
TiO ₂ (C)-700	700	2.3031	45.9	200-300
TiO ₂ (S)-800	800	3.6626	526	200-400
TiO ₂ (C)-800	800	2.1882	32	300-400

The obtained TiO₂ materials all show typical absorptions in the UV range (<420nm). The spectra of TiO₂(S)-T show the absorption edge at about 415 nm for TiO₂(S)-500 and TiO₂(S)-600. And a little red shift to 430 nm of absorption edge is observed for TiO₂(S)-700 and TiO₂(S)-800. Similar red shift of absorption edge with the increase of calcination temperature was also observed for TiO₂(C)-T samples.

To assess their photocatalytic activities, water-splitting H₂ evolution studies were carried out using these samples as photocatalysts. Typically, the catalysts (40 mg) were placed into an aqueous solution (100 mL) in a closed-gas circulation system, using 10% methanol as sacrificial reagent and 33 μL H₂PtCl₆ (1g/100mL) as co-catalyst. The testing system was irradiated by UV-*vis* light Xe lamp (300 W) with continuously stirring. For comparison, the H₂ generation by commercial TiO₂, P25,

has also been examined under the same condition. The obtained time courses of H_2 evolution have been shown in Fig. 6. It can be clearly seen that the higher calcination temperature the lower H_2 evolution activity. For TiO_2 samples derived from Ti_8O_8 -sulfate, the H_2 production rate reaches $4527 \mu\text{mol/h/g}$ with $TiO_2(\text{S})$ -500, following by $3181 \mu\text{mol/h/g}$ with $TiO_2(\text{S})$ -600. The values greatly decrease to 805 and $526 \mu\text{mol/h/g}$ with $TiO_2(\text{S})$ -700 and $TiO_2(\text{S})$ -800, respectively. As for TiO_2 samples derived from Ti_8O_8 -benzoate, 611 and $588 \mu\text{mol/h/g}$ H_2 evolution are obtained with $TiO_2(\text{C})$ -500 and $TiO_2(\text{C})$ -600. Whist the activities become more than 10 times lower to give only 45.9 and $32 \mu\text{mol/h/g}$ H_2 production with $TiO_2(\text{C})$ -700 and $TiO_2(\text{C})$ -800. Cyclic tests on $TiO_2(\text{S})$ -500 and $TiO_2(\text{C})$ -500 have been implemented, which demonstrated the photocatalytic stability of the samples under the test.

Fig.6. (a) Time course of H_2 evolution by $TiO_2(\text{S})$ -T. (b) Time course of H_2 evolution by $TiO_2(\text{C})$ -T. (c) Comparison of H_2 evolution by $TiO_2(\text{S})$, $TiO_2(\text{C})$ and P25. (d) H_2 production rates by $TiO_2(\text{S})$, $TiO_2(\text{C})$ and P25.

The above calcination temperature dependent H₂ evolution activities are in accordance with the BET values of the obtained TiO₂ samples, indicating that higher porosity could benefit the photocatalytic behaviors. More interestingly, the TiO₂(S)-T samples show significantly better H₂ evolution activities than TiO₂(C)-T. The H₂ production rate of TiO₂(S)-500 is 7-times higher than TiO₂(C)-500, and is even 1.7 times larger than P25. Although TiO₂(S)-700 displays lower BET value than TiO₂(C)-500, it still presents much higher H₂ production rate. Meanwhile, as the worst catalyst in the TiO₂(S) family, TiO₂(S)-800 also produces >10 times more H₂ than TiO₂(C)-700 and TiO₂(C)-800. Therefore, it can be concluded that although the porosity of TiO₂ samples greatly affects their photocatalytic activities, the applied cluster precursors show more significant influences.

4. Conclusion

In summary, two crystalline wheel-like Ti₈O₈ clusters have been applied as single-source precursors for the fabrication of TiO₂ materials. The phase structures and porous properties of the obtained TiO₂ samples are not only determined by the calcination temperature, but also greatly influenced by the stabilizing ligands on the Ti₈O₈ clusters. The ligands of two cluster precursors greatly influence the transformation temperatures from anatase to rutile. The presence of sulfate ligand produces anatase at broader calcination temperature range and gives rise to larger surface areas than benzoate ligand. Moreover, the ligands on the clusterprecursors

significantly affect the photocatalytic activities of the obtained TiO_2 materials, with Ti_8O_8 -sulfate derived ones presenting much higher H_2 evolution rates than the Ti_8O_8 -benzoate derived ones. Therefore, $\text{TiO}_2(\text{S})$ -500 gives the best H_2 production performance of $4527 \mu\text{mol/h/g}$ which is 7-times higher than $\text{TiO}_2(\text{C})$ -500 and even 1.7 times higher than commercial P25. Our work clearly demonstrates the strong capacity of crystalline titanium-oxo clusters as precursors to produce excellent TiO_2 materials and improve their photocatalytic activities.

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