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Sono-Fenton Chemistry Converts Phenol- and Phenyl-Derivatives into Polyphenols for Engineering Surface Coatings

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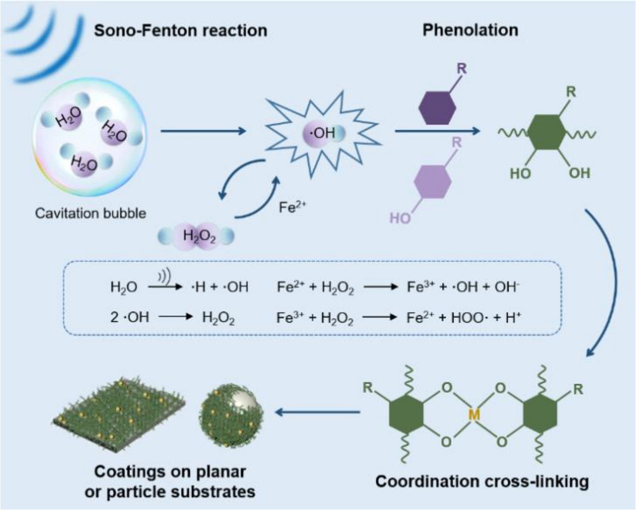
Abstract: Polyphenol-based supramolecular assembly has attracted interest for engineering a range of functional surface coatings. Herein, we report a sono-Fenton strategy to mediate the supramolecular assembly of metal–phenolic networks (MPNs) as substrate-independent coatings using phenol and phenyl derivatives as building blocks. The assembly process is initiated from the generation of hydroxyl radicals (•OH) using high-frequency ultrasound (412 kHz), while the metal ions synergistically participate in the production of additional •OH for hydroxylation/phenolation of phenol and phenyl derivatives via the Fenton reaction and also coordinate with the phenolic compounds for film formation. The coating strategy is applicable to various phenol and phenyl derivatives (from small molecules to biological macromolecules containing phenol groups) and different metal ions including Fe(II), Fe(III), Cu(II), and Co(II). In addition, the sono-Fenton strategy allows real-time control over the assembly process by turning the high-frequency ultrasound on or off. Importantly, the properties (e.g., radical scavenging and antibacterial activity) of the building blocks are maintained in the formed films. This work provides an environmentally friendly and controllable method to expand the application of phenolic coatings for the surface engineering of diverse materials.

Introduction

Supramolecular assembly of functional coatings provides a robust strategy for surface engineering in various fields ranging from materials science to biomedical engineering.[1] Polyphenols with catechol and/or pyrogallol groups are versatile components for forming functional coatings owing to their high adhesion on various surfaces.[2] To this end, the supramolecular assembly of metal–phenolic networks (MPNs) has been proven to be a modular approach to form robust coatings through the coordination of polyphenols and metal ions.[3] The facile and scalable MPN assembly process, along with the pH-responsiveness and high biocompatibility of MPN coatings makes them promising for applications in the environment,[4] catalysis,[5] and biomedicine.[6] In addition, various monophenols can be converted into corresponding catechols in the presence of enzymes (i.e., tyrosinase); the enzyme acts as a catalyst and facilitates subsequent coordination of the catechols with metal ions for the assembly of MPN films.[7] This enzyme-mediated approach expands the choice of phenolic compounds for supramolecular assembly; however, the requirement for enzymes and potential associated enzyme stability issues may limit their broad application. Therefore, exploring other approaches for the conversion of phenyl and monophenol compounds into polyphenols is of interest, as these will broaden the suite of MPN materials and their applications.

Sonochemistry, with the support of high-frequency ultrasound (>100 kHz), has been widely used for material synthesis,[8] food processing,[9] and environmental remediation,[10] where acoustic cavitation-induced free radicals (e.g., •OH) act as initiators to trigger chemical reactions including radical–radical coupling and radical-induced polymerization.[11] For example, sonochemistry can be used to initiate reversible addition–fragmentation chain transfer polymerization and for synthesizing polymer nanoparticles.[12] Our previous work has shown that free radicals generated by ultrasound promote the oxidative polymerization of dopamine even in acidic and anoxic conditions.[13] Furthermore, the Fenton reaction, an oxidation process that is activated by Fe(II) in the presence of H_2O_2, also generates radical species in solution and oxidizes a wide range of organic substrates with high activity,[14] and can be applied in a range of areas from polymer synthesis to cancer therapy.[15] The combination of sonochemistry and Fenton chemistry (resulting in sono-Fenton reactions) is expected to initiate cascade reactions and generate more radicals for materials engineering.[16] However, the application of the sono-



Scheme 1. Schematic illustration of sono-Fenton reaction-mediated phenolation process for engineering surface coatings, where Fe(II) ions promote the generation of further •OH for phenolation and coordinate with polyphenols for film formation.

Fenton reaction is currently limited to the degradation of organic contaminants and wastewater treatment,[17] where low-frequency ultrasound (20 kHz) is mostly used to increase mass transfer effects.[18] In most of these studies, the conventional Fenton reagent (H_2O_2/Fe ions) is used as a source of •OH and ultrasound is used to enhance the reaction rate through mass transfer effects generated by cavitation. Some studies have combined the use of high-frequency (>200 kHz) ultrasound and Fe ions in the absence of external H_2O_2.[19] As the application of high-frequency (>200 kHz) ultrasound can generate a relatively high amount of H_2O_2 through an acoustic cavitation process, the introduction of H_2O_2 into the reaction system is not required to achieve Fenton-type reactions.

Herein, we used 412 kHz ultrasound and metal ions to initiate the sono-Fenton reaction for the hydroxylation/phenolation of phenyl derivatives and the supramolecular assembly of MPNs for film and capsule formation (Scheme 1). Metal ions combined with ultrasound were used to increase the production of •OH via a Fenton-type reaction for the generation of phenolic compounds that subsequently coordinated with the metal ions to form coatings. Specifically, metal ions (i.e., Fe(II), Fe(III), Cu(II), and Co(II)) and molecules containing phenyl (e.g., L-phenylalanine, L-tryptophan, benzoic acid, and menadione sodium bisulfite) or phenol groups (e.g., phenol, hydroquinone, L-tyrosine, 2-(4-hydroxyphenyl)ethanol, 4-hydroxyphenylacetic acid, resveratrol (RES), and catalase) in the presence of high-frequency ultrasound (412 kHz) formed MPNs in aqueous solution. The engineering of MPN coatings based on the sono-Fenton strategy presents several advantages. First, the sono-Fenton reaction can continuously generate free radicals, unlike the conventional Fenton reaction, to modulate hydroxylation/phenolation for the conversion of phenolic compounds, thus avoiding the need for additional oxidants or enzymes during the assembly process. Second, the sono-Fenton reaction-mediated MPN coatings form on a range of substrates and the film thickness can be controlled from approximately 15 to 55 nm by varying the sonication time.

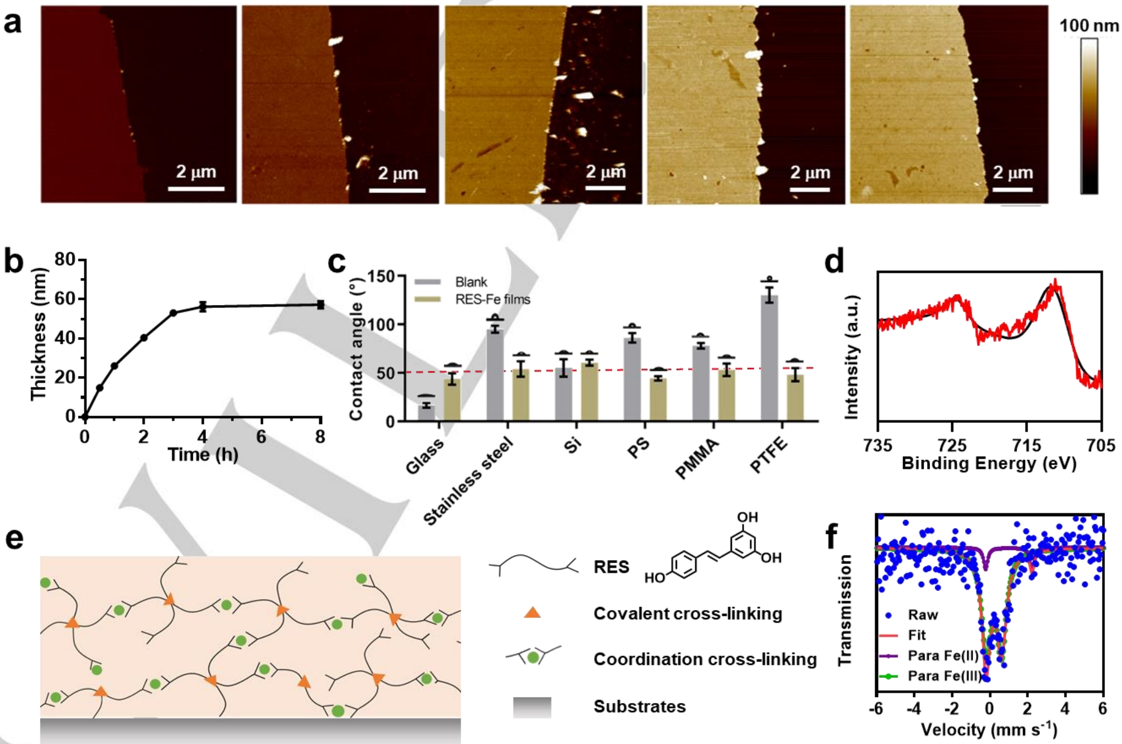


Figure 1. Formation of RES-Fe films on planar substrates mediated by the sono-Fenton reaction. (a) Atomic force microscopy (AFM) images of RES-Fe films formed at different sonication times (from left to right: 0.5, 1, 2, 3, and 4 h). (b) Thickness of the films as a function of sonication time. (c) Static contact angles of different substrates before and after coating with RES-Fe films. Si, silicon wafer; PS, polystyrene; PMMA, polymethyl methacrylate; PTFE, polytetrafluoroethylene. (d) XPS spectrum showing the presence of Fe ions in the films. (e) Schematic showing the formation of RES-Fe films. (f) Mössbauer spectrum of the RES-Fe complexes formed in solution.

Third, the MPN coatings maintain the inherent properties of the phenol derivatives (e.g., antioxidant and antimicrobial activities). This study provides a flexible and effective hydroxylation/phenolation strategy and expands the supramolecular assembly of functional phenolic coatings.

Results and Discussion

RES was used as the first example to investigate the sono-Fenton reaction-mediated film formation process (Figure 1). The sonication of RES in the presence Fe(II) resulted in the formation of thin films on glass with a controlled thickness of 15–55 nm by varying the sonication time (Figure 1a,b and S1). However, coatings were not obtained for the mixtures of RES and Fe ions in the absence of sonication, which indicates the requirement of ultrasound to form the coatings. When Fe(II) was replaced by Fe(III), the film growth was slower: the thickness of the Fe(III)-based MPN film was about one-third that of the Fe(II)-based MPN film after 4 h sonication (Figure S2), the difference being attributed to the lower sono-Fenton efficacy of Fe(III) compared to Fe(III).[14b] The influence of pH on film formation could be due to the formation of hydroxylation/phenolation of phenol and phenyl derivatives induced by the sono-Fenton reaction and the coordination between metal ions and polyphenols. The sono-Fenton reaction demonstrates higher efficiency at acidic pH below 4,[20] but low pH (below 3) is unfavorable for the formation of coordination (bis-complexes) between metal ions and polyphenols.[3a] AFM measurements confirmed that the maximum film thickness was obtained at pH 4 in our studies (Figure S3). The mechanistic details of the hydroxylation/phenolation of RES and other phenol-based molecules leading to film formation are discussed later.

The versatility of the sono-Fenton reaction-mediated film formation was examined on different substrates, including glass, stainless steel, silicon wafer, polystyrene (PS), polymethyl methacrylate, and polytetrafluoroethylene. After formation of the coatings, the contact angles of these substrates were between 45–60° (Figure 1c). To examine the composition of the coatings, X-ray photoelectron spectroscopy (XPS) was used to examine the films. The peaks at 712 and 725 eV (Fe 2p) indicated the presence of Fe ions in the films (Figures 1d and S4),[1e,7] which was attributed to the coordination of the metal ions with phenolated RES, as shown in Figure 1e. As an approximation of the Fe content and the ratio of Fe(II)/Fe(III) in the MPN films, we formed the MPN complexes in solution and analyzed the complexes by inductively coupled plasma mass spectrometry (ICP-MS) and Mössbauer spectroscopy. The Fe content in the MPN complexes was 63.9 µg mg^{-1} from ICP-MS analysis and the ratio of Fe(II)/Fe(III) was 1:11 from Mössbauer spectroscopy analysis (Figure 1f).

Capsule Formation and Characterization

In addition to planar substrates, PS microspheres were used as templates to investigate the sono-Fenton reaction-mediated film formation process. In the presence of RES, Fe(II), and ultrasound, coatings were formed on the surface of the PS particles, which appeared rough (Figure 2a) in contrast to the relatively smooth surface of the bare PS particles (Figure S5). Following removal of the PS template, intact capsules, which were well dispersed in water, were obtained (Figure 2b–d). Creases and folds typical of air-dried capsules, owing to the loss of water, were observed (Figure 2c,d).[21] Scanning transmission electron microscopy (STEM) coupled with energy-dispersive X-ray spectroscopy (EDX) confirmed the presence of Fe in the capsules (Figure 2e). The representative high-angle annular dark-field (HAADF)-STEM image is in accordance with the element mapping images of C, O, and Fe (Figure 2e), which indicates the uniform distribution of these elements in the capsules.

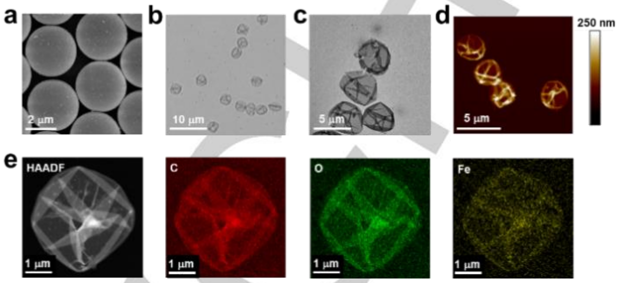


Figure 2. Formation of RES-Fe films on particle substrates mediated by the sono-Fenton reaction. (a) SEM image of PS particles coated with RES-Fe film. (b) Optical microscopy, (c) TEM, and (d) AFM images of RES-Fe capsules. (e) HAADF-STEM and EDX elemental mapping images of RES-Fe capsules.

Different phenol derivatives, ranging from phenol, L-tyrosine, 2-(4-hydroxyphenyl)ethanol, 4-hydroxyphenylacetic acid, hydroquinone to catalase (biomacromolecule) containing phenol groups were used as building blocks for the sono-Fenton reaction-mediated assembly (Figure 3a). Incubation of PS particles with phenol-based molecules and Fe(II) in the presence of ultrasound for 2 h resulted in color changes of the PS suspensions, which indicated the occurrence of the sono-Fenton reaction (Figure S6). The surface of the PS particles became rough after sonication, which indicated the formation of coatings (Figure S7). After removing the PS templates, intact capsules were obtained (Figure 3b), which further supported the formation of films on the PS particles. These results indicate that the sono-Fenton reaction-mediated coating strategy developed herein is applicable not only to small molecules but also to biological macromolecules containing phenol groups, which expands the range of phenolic coatings that can be applied for surface engineering.

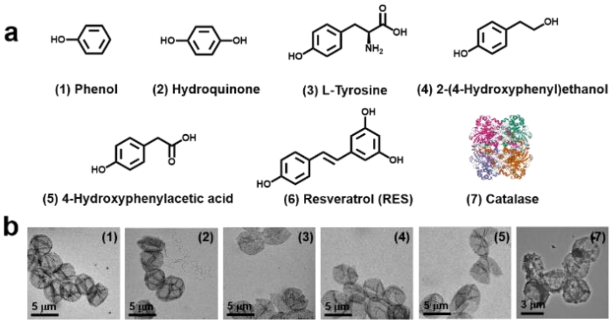


Figure 3. Phenol-based molecules used in the sono-Fenton-mediated assembly of MPNs on PS microspheres. (a) Molecular structures of phenol (**1**), hydroquinone (**2**), L-tyrosine (**3**), 2-(4-hydroxyphenyl)ethanol (**4**), 4-hydroxyphenylacetic acid (**5**), RES (**6**), and catalase (**7**). (b) TEM images of the capsules formed from the phenol derivatives shown in (a); the numbers in the TEM images correspond to the phenol derivatives used in (a) for the formation of the capsules.

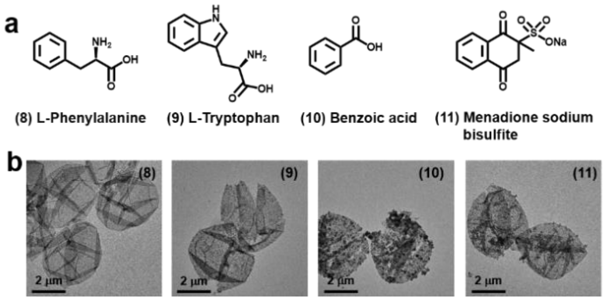


Figure 4. Phenyl-based molecules used in the sono-Fenton-mediated assembly of MPNs on PS microspheres. (a) Molecular structures of L-phenylalanine (**8**), L-tryptophan (**9**), benzoic acid (**10**), and menadione sodium bisulfite (**11**). (b) TEM images of the capsules formed from the phenyl-based derivatives shown in (a); the numbers in the TEM images correspond to the phenyl derivatives used in (a) for the formation of the capsules.

The current coating strategy is also applicable to phenyl-based molecules, including L-phenylalanine, L-tryptophan, benzoic acid, and menadione sodium bisulfite (Figure 4a). The color changes of the PS suspensions (Figure S8) and the rough surface morphology (Figure S9) of the PS microspheres indicate the formation of coatings after incubation with different phenyl-based molecules and Fe(II) in the presence of ultrasound. TEM images revealed that the coatings resulted in the formation of capsules after template removal (Figure 4b). To the best of our knowledge, this is the first report that demonstrates the assembly of films and capsules using phenyl derivatives as building blocks using the sono-Fenton reaction.

Mechanism of the Assembly Process

To investigate the mechanism of the MPN assembly process, phenol as the simplest monophenol was chosen and subjected to a sonication process in the absence of metal ions, and changes in its mass spectral profile were monitored. Electron paramagnetic resonance spectroscopy proved the production of •OH by high-frequency ultrasound (Figure S10). The production rate of •OH was about 100–120 µM min^{-1} as reported in our previous work.[12b] Time-dependent degradation experiments of methylene blue and rhodamine B were also performed to confirm the generation of •OH during sonication (Figure S11). The generation of •OH using high-frequency ultrasound is due to acoustic cavitation,[18,22] which could induce the hydroxylation/phenolation of phenol to form catechol or pyrogallol groups as well as their oligomers. As shown in Figure S12, phenolated phenol as well as dimers, trimers, and oligomers of phenol were obtained after sonication for 2 h. Table S1 summarizes the possible products formed, including catechol, hydroquinone, pyrogallol, and their dimers. The proposed hydroxylation/phenolation and polymerization mechanism is shown in Figure 5a. The sonication-induced hydroxylation/phenolation was further confirmed by the mass spectrometry results of RES, which was subjected to the same sonication process in the absence of metal ions (Figure S13).

To experimentally confirm the role of metal ions in the

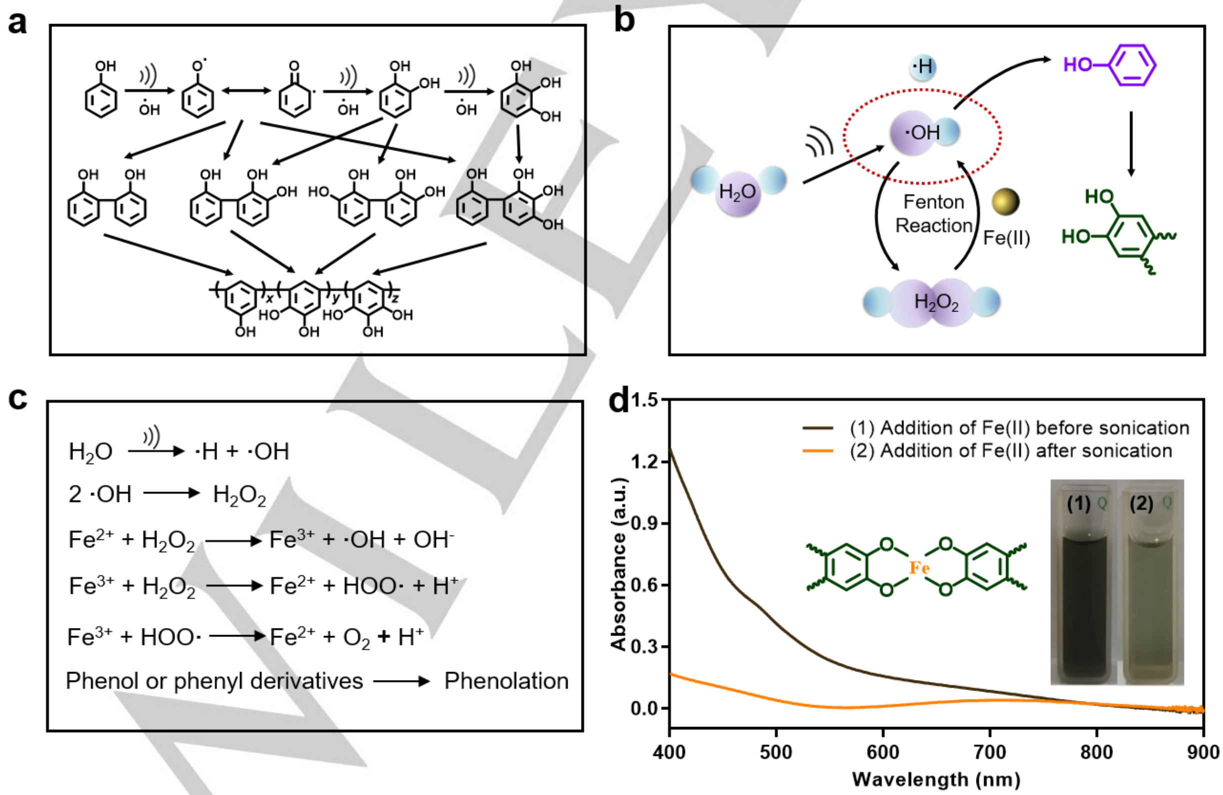


Figure 5. (a) Scheme of potential pathways to the conversion of phenol into phenol derivatives using high-frequency ultrasound. (b) Scheme of the sono-Fenton reaction for the conversion of phenol into polyphenols. (c) Proposed mechanism of the sono-Fenton reaction for phenolation. (d) UV–vis absorption spectra showing the LMCT band of catechol-Fe complexes. The inset are photographs of the MPN complexes in solution. Fe(II) ions are added either before (1) or after (2) sonication.

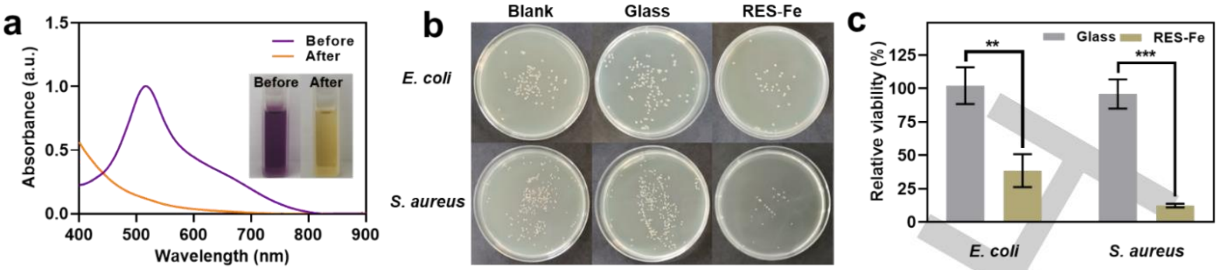


Figure 6. (a) UV–vis absorption spectra and photographs (inset) of DPPH solutions before and after incubation with PS particles coated with RES-Fe films. (b) Photographs and (c) bar graphs to show the antimicrobial activities of RES-Fe films against *E. coli* and *S. aureus*. In (b), the blank represents the group without any treatment. Data in (c) are represented as the mean ± SD (n = 3). ***P* < 0.01; ****P* < 0.001.

assembly process, UV–vis absorption spectroscopy measurements were performed. In the absence of ultrasound, no related absorption characteristics of the phenol derivatives were observed at 400–900 nm regardless of the addition of Fe(II) (Figure S14). In contrast, following the application of sonication, absorption features at 400–900 nm were observed, though minor, with or without the addition of Fe(II) (Figure S15a,b). In addition, a ligand-to-metal charge transfer (LMCT) band was observed in the solution containing phenol and Fe(II) after sonication (Figures 5d and S15c), which indicates the formation of catechol–Fe complexes.[23] The order of Fe(II) addition before and after the application of sonication resulted in different colors and UV–vis absorbance of the formed MPN solution. The ultrasound and Fenton reaction generated higher absorbance when phenol was mixed with Fe(II) before sonication. These results demonstrate the importance of the order in which Fe(II) ions are added for the assembly of MPNs in solution and coatings, where the presence of Fe(II) during sonication is vital to convert phenol derivatives into polyphenols for subsequent coordination with Fe ions. Similar observations were made for the coatings prepared using phenyl derivatives, where mixing of the phenyl derivatives and Fe(II) before sonication resulted in the formation of metal–phenolic complexes (Figures S16 and S17).

It has been reported that the sono-Fenton reaction can generate more •OH compared with either ultrasound or the Fenton reaction for the oxidation of organic molecules.[16,17] We speculate that the metal ions not only contribute to the generation of •OH for the hydroxylation/phenolation of phenol and phenyl derivatives but also are involved in coordination for the assembly of the MPN films. The sonication-induced •OH can react to form H_2O_2,[12b] which subsequently participates in the Fenton reaction in the presence of Fe(II) and therefore promotes the generation of more •OH (Figure 5b, c). The cascade reaction for the formation of •OH is favorable for the hydroxylation/phenolation of phenol and phenyl derivatives, which can subsequently coordinate with metal ions to form MPN films on various substrates (Figures 1 and 2).

Although sonication and the addition of metal ions synergistically promote hydroxylation/phenolation and the assembly of MPN coatings as indicated from the UV–vis absorbance in Figures 5d and S14–S17, sonication is essential for initiating the sono-Fenton reaction. As a result, the formation of metal–phenolic complexes initiated by the sono-Fenton reaction could be manipulated simply by turning the ultrasound on and off, where the absorbance of the mixture increased when sonication was applied and remained relatively constant for the duration that the ultrasound was switched off (Figure S18). The advantage of the sono-Fenton reaction lies in the controllable generation of •OH and therefore control over the formation of the coatings.[19] In addition, along with the increase in sonication time, the absorbance of the mixture increased, which indicates the formation of more complexes, and thereby leading to the formation of thicker films (Figures 1 and S18).

Sono-Fenton-Like Reaction for MPN Assembly

In addition to Fe(II), metal ions including Fe(III), Cu(II), and Co(II) can coordinate with catechol groups[3b,24] and trigger Fenton or Fenton-like reactions in the presence of H_2O_2.[25] As observed from the UV–vis absorption spectroscopy studies, greater absorption was observed for the RES/metal ion mixtures subjected to sonication for 2 h when compared with that obtained for RES subjected to sonication or RES subjected to sonication prior to the addition of metal ions (Figure S19). Importantly, Fe(III), Cu(II), and Co(II) also triggered the sono-Fenton-like reaction for the preparation of capsules using the same method (Figure S20). It is well known that Fe(II) is readily oxidized to Fe(III) by oxygen in solution, which could decrease the rate constant of Fenton reaction.[14b] However, when RES was used as the building block, the Fe(II) content remained relatively high, >67%, after the reaction, regardless of using Fe(II) or Fe(III) as metal ions. This could be due to the strong antioxidant properties of RES, which could reduce Fe(III) to Fe(II) after the reaction (Figure S21, Table S2).

Antibacterial Performance

As a naturally active molecule, RES has both strong antioxidant properties and effective antibacterial and anti-inflammatory capabilities.[26] As the RES derivatives can reduce Fe(III), the sono-Fenton reaction-mediated films formed using RES as building blocks are expected to have antioxidant properties. To demonstrate this, PS particles coated with RES-Fe films were examined by the 2,2′-diphenyl-picrylhydrazyl (DPPH) assay. After incubation of the RES-Fe-coated PS particles with DPPH solution for 30 min, the color of the solution changed from purple to yellow (Figure 6a). The UV–vis absorbance at 515 nm disappeared following incubation, which indicated that the film could scavenge DPPH radicals. In addition, the antibacterial ability of the films was evaluated in vitro against gram-negative *Escherichia coli* (*E. coli*) and gram-positive *Staphylococcus aureus* (*S. aureus*). As shown in Figure 6b, the glass substrates (with no coating) did not inhibit bacterial growth. In contrast, after coating with RES-Fe films, the viability of *E. coli* and *S. aureus* reduced to 39 and 13%, respectively (Figure 6c). Overall, the sono-Fenton reaction not only mediates hydroxylation/phenolation of phenol and phenyl derivatives but also facilitates the assembly of functional coatings while maintaining the inherent functionality of the original building blocks.

Conclusion

High-frequency ultrasound and the Fenton reaction were employed as a combined strategy to convert phenol and phenyl derivatives for the assembly of MPN films and capsules. The sono-Fenton-based coating strategy was applicable not only to small molecules but also to biological macromolecules containing phenol groups. The addition of metal ions triggered the Fenton or Fenton-like reaction to generate hydroxyl radicals for the hydroxylation/phenolation of phenol and phenyl derivatives. Concurrently, the metal ions participated in coordination reactions with catechol groups for the formation of MPN films and capsules. The formation of metal–phenolic complexes was controlled by turning the ultrasound on or off, and the film thickness was tuned by adjusting the sonication time; thicker films were obtained by prolonging the sonication process. We also showed the applicability of the present coating strategy to other metal ions such as Fe(III), Cu(II), and Co(II). Notably, the resulting films maintained the functions inherent to the original building blocks (e.g., RES), including free radical scavenging and antibacterial properties. Considering the broad availability, diversity, and functionality of phenol and phenyl derivatives, the reported sono-Fenton reaction-mediated assembly strategy provides a promising avenue for the engineering of functional coatings.

Acknowledgements

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Keywords: polyphenol • sonochemistry • sono-Fenton reaction • surface chemistry • thin films

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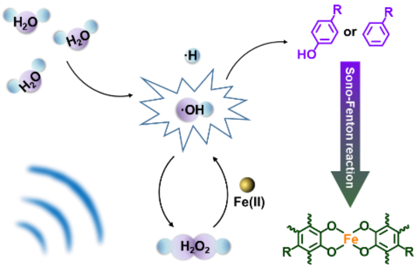

Sono-Fenton chemistry is used to generate polyphenols from small molecules and biological macromolecules containing phenolic groups, enabling the subsequent coordination of the polyphenols with metal ions to engineer coatings on a variety of substrates.