Hemin is an iron-containing porphyrin, namely protoporphyrin IX Fe(III) complex, which is well-known as the active center of the hemoprotein family. Because of the reversible reaction of Fe(III)/Fe(II) redox couple, hemin has been extensively demonstrated as an efficient electrocatalyst for many small molecules such as hydrogen peroxide,1−3 oxygen,4−6 L-tyrosine,7 L-tryptophan,8 and artemisinin.9 Generally, hemin is loaded on some supporting materials to avoid the molecular aggregation of hemin molecules in aqueous solution and improve the stability and activity of catalyst.8 On the other hand, hemin is a structural analogue of chlorophyll, which can serve as a promising photosensitizer for TiO2 photocatalyst to harvest visible light.10 Moreover, the presence of Fe(III) porphyrin ring on the surface of TiO2 can reduce the electron–hole recombination rate and act as a mediator for continuous production of enriched concentration of hydroxyl radicals to enhance the photocatalytic activity of TiO2.11

TiO2 is the most intensively studied photocatalyst for degradation of various organic pollutants.12 In recent years, TiO2 nanoparticles have been widely utilized for fabrication of sensing devices because of their fascinating properties such as large surface area, good biocompatibility, high stability, and unique electronic and photocatalytic performances.13 When catalytic materials including metal nanoparticles, small molecules and biological macromolecules are immobilized on nanostructured TiO2, the obtained nanocomposites can act as bifunctional catalysts which not only possess the catalytic activity of introduced materials but also preserve the intrinsic photocatalytic capacity of TiO2.14 Recently, TiO2 nanomaterials coupled with hemin have been investigated for photocatalytic degradation of organic pollutants.9,15 and photoelectrochemical detection of glutathione.15 However, these previous reports have only focused on the photocatalytic activity of hemin-TiO2 composites.

In the present work, TiO2 nanoparticles coupled with hemin were prepared and utilized as bifunctional sensing materials to fabricate high-performance electrochemical/photoelectrochemical sensors. In as-prepared hemin-TiO2 film, hemin preserved its catalytic activity while mesoporous TiO2 film provided a solid support for the loading of hemin. The composite film showed high electrocatalytic activity toward H2O2. The current was linearly proportional to the concentration of H2O2 in the range of 3.0 × 10−7 to 4.7 × 10−4 mol · L−1. Moreover, hemin molecule with the structure of Fe-porphyrin ring could effectively enhance the absorption of TiO2 film to visible light. The hemin-TiO2 film exhibited high photoelectrocatalytic activity which was applied to photoelectrochemical sensing of hydroquinone (HQ) in the concentration range from 4.0 × 10−7 to 3.0 × 10−5 mol · L−1.

Materials and Methods

Chemicals.—Hydrogen peroxide (30%, w/v) was obtained from Shanghai Experimental Reagent Co., China. Titanium (IV) chloride, hemin, HQ and other reagents of analytical grade were obtained from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Poly(diallyldimethylammonium chloride) solution (PDDA) was obtained from Shanghai Experimental Reagent Co., Ltd. (Shanghai, China). Phosphate buffer solution (PBS) was prepared by mixing certain amount of Na2HPO4 and NaH2PO4. Double distilled water was used throughout the experiment.

Preparation of hemin-TiO2 modified electrode.—The TiO2 nanoparticles were prepared by a flame synthesis technique as described in a previous work.16 The isoelectric point (IEP) of the obtained TiO2 nanoparticles was approximately 3.4 and lower than that of other phases (including anatase, mixture of anatase and rutile),17 which was pivotal to design novel devices for applications in sensing, catalysis and energy conversion. The resultant TiO2 powder was dispersed in 10.0 mL of NaOH solution to give a 5 mg · mL−1 TiO2 suspension by ultrasonic agitation. After the addition of 10 mg hemin, the mixture was ultrasonic for another 8 min to make small hemin molecules evenly dispersed in TiO2 suspension. The hemin-TiO2 mixed solution was utilized to modify a glass carbon electrode (GCE) (exposed geometric area of 0.096 cm2). Prior to modification, the GCE surface was polished to a mirror-like smoothness with emery papers and then cleaned successively with ethanol and deionized water. After dried with nitrogen gas, the GCE was immersed into 2% PDDA solution containing 0.5 mol · L−1 NaCl for 0.5 h, and then thoroughly rinsed with distilled water to remove the loosely adsorbed PDDA. After being dried with nitrogen gas, the GCE surface was immersed in hemin-TiO2 mixed solution (containing 5 mg · mL−1 TiO2 and 1 mg · mL−1 hemin) for 1 h. After thoroughly rinsed with distilled water to remove the loosely adsorbed hemin-TiO2, the modified electrode was dried with nitrogen gas. In this process, hemin and TiO2 were negatively charged in alkaline solution, and positively charged PDDA was beneficial to the immobilization of
nanocomposites on electrode surface through the electrostatic attraction. For comparison, TiO$_2$ or hemin modified electrode was prepared in the same procedure except that pure TiO$_2$ or hemin solution was used instead of hemin-TiO$_2$ mixed solution.

**Apparatus and procedure.**—The morphology of TiO$_2$ and hemin-TiO$_2$ modified electrodes were characterized with a field emission scanning electron microscope (FESEM) (FEI Sirion 200, Netherlands). The X-ray diffraction (XRD) pattern was measured using a X-ray diffractometer (PANalytical X’pert Pro, Netherlands) equipped with a Cu K$_\alpha$ ($\lambda = 1.54$ Å) radiation source. The accelerating voltage and applied current were 40 kV and 40 mA, respectively. UV-visible diffuse reflectance spectra (DRS) were recorded with a UV-2550 spectrophotometer (Shimadzu, Japan). The UV-visible absorption spectra were recorded using a TU-1900 UV-visible spectrometer (Beijing Purkinje General Instrument Company, China). Fourier transform infrared (FTIR) spectroscopic analysis was carried out with an Equinox 55 FTIR spectrometer (Bruker, Germany).

The electrochemical and photoelectrochemical experiments were performed on a CHI660A electrochemical working station (Shanghai Chenhua Instrument Co. Ltd., China) in a conventional three-electrode system. The fabricated hemin-TiO$_2$ modified electrode, a platinum wire, and a saturated calomel electrode (SCE) served as the working, auxiliary and reference electrodes, respectively. All voltammetric and amperometric experiments were carried out in deaerated solutions in an atmosphere of nitrogen. The photoelectrochemical measurements were performed in air-saturated solutions as described previously.$^{18}$ A xenon lamp (PLS-SXE300, Perfect Co., China) with an optical filter ($\lambda > 420$ nm) was used as the visible light irradiation source, and the distance between the lamp and working electrode surface was 15 cm.

The photodegradation experiments for HQ were carried out in a quartz beaker containing 100 mL of $2 \times 10^{-4}$ mol·L$^{-1}$ HQ aqueous solution. A 15-W UV lamp with a major emission wavelength at 254 nm was employed as the UV irradiation source. After irradiating for a certain time, 1 mL of sample was taken out of the photoreactor and mixed with 9 mL PBS, and then analyzed using the proposed photoelectrochemical sensor.

**Results and Discussion**

**Characterization of hemin-TiO$_2$ composite film.**—The surface morphology of pure TiO$_2$ and hemin-TiO$_2$ composite film modified electrode was characterized by FESEM. It was observed that for pure TiO$_2$ film, plenty of TiO$_2$ nanoparticles in the size of 10–50 nm were assembled on the electrode surface which formed a relatively rich and uniform mesoporous film structure (Fig. 1A). While hemin was coupled with TiO$_2$, the characteristic of TiO$_2$ nanoparticles and mesoporous film structure were not destroyed (Fig. 1B). Obviously, the mesoporous film structure of TiO$_2$ cannot only provide an excellent matrix for hemin incorporation but also offer many active adsorption sites for catalytic reactions.$^{19}$

The crystalline nature of the TiO$_2$ film was investigated by XRD. As shown in curve a in Fig. 2, the main diffraction peaks assigned to the rutile phase structure of TiO$_2$ (JCPDS 76-1940) were clearly observed, in accord with the previous report.$^{20}$ For comparison, the XRD pattern of hemin-TiO$_2$ film is depicted in curve b in Fig. 2. Consistent with SEM observation, the coupling of hemin did not change the crystal structure of TiO$_2$.

Fig. 3 compares the FTIR spectra of TiO$_2$ and hemin-TiO$_2$ films. The pure TiO$_2$ film (curve a in Fig. 3) exhibited the characteristic absorption peaks at 3427 cm$^{-1}$, 1638 cm$^{-1}$ and 655 cm$^{-1}$ assigned to O-H and Ti-O bonds, respectively.$^{21}$ In comparison, the FTIR spectra of hemin-TiO$_2$ displayed the representative absorption peaks of hemin besides the absorption bands of TiO$_2$. As shown in curve b in Fig. 3, new absorption bands at 847 cm$^{-1}$ and 1000–1300 cm$^{-1}$ were assigned respectively to the C-H bending vibration and C-O stretching vibration in aromatic ring of hemin molecule. The bands at 1407 cm$^{-1}$ and 1466 cm$^{-1}$ were attributed to the contribution of C-H.
bending vibration, and the band 2923 cm\(^{-1}\) assigned to the C-H stretching vibration of methyl. The obvious absorption peaks at 1563 cm\(^{-1}\) might correspond to the C=C–H and amide band II. Moreover, the broad peak around 1652 cm\(^{-1}\) might be assigned to C=C–H and amide band I or -NH\(_2\) bending vibration and skeletal vibration of aromatic ring. Thus, the coupling of hemin with TiO\(_2\) in the composite film was successfully confirmed by FTIR spectroscopic analysis.

The incorporation of hemin obviously influenced the absorption of TiO\(_2\) in the visible light region. It was observed that pure TiO\(_2\) film mainly absorbed UV light at a wavelength less than 380 nm but exhibited weak absorption in the visible light region (curve a in Fig. 4). For hemin, the absorption curve was characterized by a Soret peak at ~388 nm along with a group of weak absorption bands between 500 and 600 nm attributed to Q-bands (curve b in Fig. 4). While hemin was coupled with TiO\(_2\), a redshift in the absorption onset value was observed and the absorption in the visible region was significantly improved (curve c in Fig. 4). The enhanced absorption of TiO\(_2\) film to visible light by hemin should be due to the structure of Fe-porphyrin ring in molecular structure.

**Electrochemical behavior of hemin-TiO\(_2\) composite film.**—The cyclic voltammograms (CVs) of TiO\(_2\), hemin and hemin-TiO\(_2\) modified electrodes were recorded in deaerated PBS at pH 7.0 (Fig. 5). The results indicated that no any reduction or oxidation peak was observed on either TiO\(_2\) (curve a in Fig. 5) or hemin (curve b in Fig. 5) modified electrode. By contrast, a couple of well-defined redox peaks were apparently observed at ca. –0.4 and –0.3 V on the hemin-TiO\(_2\) modified electrode (curve c in Fig. 5). The total formal potential estimated as the average value of the anodic and cathodic peak potential is ~0.33 V (vs. SCE), which is close to those obtained with hemin-adsorbed carbon felt and hemin-functionalized carbon nanotubes. Obviously, the redox peaks are attributed to the mono-electron transfer process concerning the Fe(II)/Fe(I) redox couple coordinated in the porphyrin ring of hemin. The mesoporous structure of TiO\(_2\) not only plays an important role for effective immobilization of hemin molecules on the electrode surface but also promotes the electron transfer between hemin and electrode.

The effects of scan rate and pH on the voltammetric behavior of hemin-TiO\(_2\) film were investigated. As shown in Fig. 6A, the cathodic peak potential of the hemin-TiO\(_2\) film shifted negatively with increasing the scan rate. Moreover, the cathodic peak current (\(i_{pc}\)) was linearly enhanced with the increase of the scan rate (\(\nu\)). The linear regression equation was expressed as \(i_{pc} (\mu A) = -0.0361v (mV \cdot s^{-1}) - 1.2573\) (correlation coefficient \(r = 0.996\)). This result indicates that the electrochemical reaction of hemin on hemin-TiO\(_2\) modified electrode is a surface-controlled process.

On the other hand, the cathodic peak potential of hemin-TiO\(_2\) film shifted negatively with increasing the solution pH from 6.0 to 8.0 (Fig. 6B). A linear relationship was found between the cathodic peak potential (\(E_{pc}\)) and pH, which could be expressed by \(E_{pc} (V) = -0.0421pH-0.100\) (correlation coefficient \(r = 0.993\)). The slope of 0.042 V/pH is lower than the theoretical value of 0.059 V/pH for a reversible one proton coupled single-electron transfer, implying that protons are not only involved in the interfacial charge compensation associated with the electron transfer process. The solution pH can cause changes in protonation state of the propionate side chains attached to the protoporphyrin macro-cycle and the ligation state of the iron center of hemin.

**Electrocatalytic activity of hemin-TiO\(_2\) and amperometric sensing of H\(_2\)O\(_2\).**—Fig. 7 displays the CVs of various modified electrodes recorded in deaerated PBS without and with 0.1 mmol⋅L\(^{-1}\) H\(_2\)O\(_2\). On pure TiO\(_2\) modified electrode (Fig. 7A), the CV curve did not show obvious change after H\(_2\)O\(_2\) was added. When hemin modified electrode was applied (Fig. 7B), the presence of H\(_2\)O\(_2\) led to a slight enhancement in cathodic current. In comparison, when H\(_2\)O\(_2\) was added into the solution, the reduction peak current of hemin-TiO\(_2\) modified electrode was dramatically enhanced, accompanied by disappearance of oxidation peak current (Fig. 7C). This result is similar to our previous observation on a graphene-hemin modified graphite electrode.
Figure 6. (A) CVs of hemin-TiO2 modified electrode in deaerated PBS (0.1 mol·L⁻¹, pH 7.0) at different scan rates (mV/s): (a) 10, (b) 20, (c) 30, (d) 40, (e) 50, (f) 75, (g) 100, (h) 125, (i) 150, (j) 200. Inset: linear relationship between cathodic peak current and scan rate. (B) CVs of hemin-TiO2 modified electrode at 0.05 V/s in deaerated PBS (0.1 mol·L⁻¹) at different pH values: (a) 6.0, (b) 6.5, (c) 7.0, (d) 7.5, (e) 8.0. Scan rate: 0.05 V/s. Inset: linear relationship between cathodic peak potential and pH.

demonstrating the high electrocatalytic activity of hemin-TiO2 toward the reduction of H₂O₂.

The hemin-TiO2 modified electrode was explored as an electrochemical sensor for quantitation of H₂O₂ concentration by chronoamperometry. Although the reduction peak potential for H₂O₂ displayed in CV was around −0.32 V (curve b in Fig. 7C), the applied potential for amperometric sensing of H₂O₂ should be more positive to decrease the background current and minimize the response of common interference species.²⁶,²⁷ We studied the influence of the applied potential on the amperometric response of the sensor to H₂O₂. As shown in Fig. 8A, the current response toward H₂O₂ was obviously enhanced when the applied potential was shifted from −0.10 to −0.15 V. When the applied potential was further negatively shifted from −0.15 to −0.35 V, the background current was markedly increased whereas the current response toward H₂O₂ decreased. Therefore, we selected −0.15 V as the working potential for amperometric sensing of H₂O₂ in the following experiments.

Fig. 8B illustrates the chronoamperometric response of the hemin-TiO2 modified electrode to the successive injection of H₂O₂ into PBS under constant passage of high purity nitrogen gas. It was seen that upon each addition of H₂O₂, the amperometric current was increased sharply and then reached to a steady value within a response time less than 5 s. With increasing the concentration of H₂O₂ from 3.0 × 10⁻⁷ to 4.7 × 10⁻⁴ mol·L⁻¹, a linearly enhanced amperometric response was obtained (Fig. 8C). The linear regression equation was expressed as I (µA) = −0.036 [H₂O₂] (µmol·L⁻¹)−0.226 (correlation coefficient r = 0.999). The limit of detection (3S/N) was estimated to be 7.2 × 10⁻⁸ mol·L⁻¹, which was lower than previously reported results.¹,²⁷-²⁹

For comparison, the amperometric responses of pure TiO₂ and hemin modified electrodes to H₂O₂ were also studied under the same experimental conditions. As shown in Fig. 8D, the TiO₂ modified electrode did not show any response to the addition of H₂O₂ while hemin modified electrode responded to H₂O₂. The amperometric current on hemin modified electrode was found to be increased linearly.
with increasing the concentration of H$_2$O$_2$ from $5.0 \times 10^{-6}$ and $2.8 \times 10^{-4}$ mol·L$^{-1}$ (inset of Fig. 8D). The linear relationship could be expressed as $I$ (μA) = $-0.026$ [H$_2$O$_2$] (μmol·L$^{-1}$)$-0.003$ (correlation coefficient $r = 0.998$), and the detection limit (3S/N) was estimated to be $1.9 \times 10^{-4}$ mol·L$^{-1}$. Obviously, hemin-TiO$_2$ modified electrode exhibited higher sensitivity and lower limit of detection for H$_2$O$_2$ determination than hemin modified electrode, suggesting the high performance of the proposed sensor based on TiO$_2$-supported hemin.

The reproducibility of such an electrochemical sensor was investigated by recording the current responses of ten independently prepared hemin-TiO$_2$ modified electrodes in deaerated PBS containing $1.0 \times 10^{-5}$ mol·L$^{-1}$ H$_2$O$_2$. The relative standard deviation (RSD) was 2.1%, showing a good reproducibility. The RSD of the sensor for 10 successive measurements was 2.8%, indicating a good repeatability. The stability of the developed sensor was investigated by recording the current response every four days. When not in use, the sensor was stored in 4°C. The result indicated that the response did not show obvious change after sixteen days, demonstrating that the sensor owned a high stability.

Moreover, the applicability of the developed sensor was evaluated for the determination of H$_2$O$_2$ concentration in practical honey samples purchased from a supermarket in Wuhan City. Prior to the electrochemical measurement, the diluted honey solution was obtained by dissolving 2.0 g of the honey sample into 10.0 mL distilled water. Then 1.0 mL of the sample solution was transferred to 9.0 mL PBS (pH 7.0) to record the amperometric current on hemin-TiO$_2$ modified electrode. Because no H$_2$O$_2$ was detected in the original honey sample, we carried out the electrochemical determination using the standard addition method by spiking different amounts of standard H$_2$O$_2$ into the sample. As can be seen from Table I, the recovery values of the proposed method were in the range from 98.6% to 102.4%, indicating the feasibility of the hemin-TiO$_2$ based electrochemical sensor for the determination of H$_2$O$_2$ in real samples.

**Photoelectrochemical sensing of hydroquinone.**—Considering that the photoelectrocatalytic activity of semiconducting materials could be evaluated by photocurrent, we measured the photocurrent response of hemin-TiO$_2$ modified electrode in 0.1 mol·L$^{-1}$ PBS (pH 7.0) under visible light illumination. As shown in curve a in Fig. 9A, the hemin-TiO$_2$ modified electrode responded sensitively to the visible light irradiation. When the lamp was switched on, the current was rapidly increased until a nearly steady-state photocurrent value was measured.

**Table I. Determination of H$_2$O$_2$ in honey samples by the proposed sensor (n = 5).**

| Samples | Spiked (μmol·L$^{-1}$) | Found (μmol·L$^{-1}$) | RSD (%) | Recovery (%) |
|---------|-----------------------|-----------------------|---------|--------------|
| 1       | 0                     | 0                     | -       | -            |
| 2       | 10.00                 | 10.24                 | 1.5     | 102.4        |
| 3       | 20.00                 | 19.72                 | 1.8     | 98.6         |

Figure 8. (A) Amperometric responses of hemin-TiO$_2$ modified electrodes recorded in deaerated PBS (0.1 mol·L$^{-1}$, pH 7.0) for injection of 5 μmol·L$^{-1}$ H$_2$O$_2$ at different applied potentials (V): (a) −0.10, (b) −0.15, (c) −0.20, (d) −0.25, (e) −0.30, and (f) −0.35. (B) Chronoamperometric curve at an applied potential of −0.15 V recorded on hemin-TiO$_2$ modified electrode in deaerated PBS (0.1 mol·L$^{-1}$, pH 7.0) after successive injection of H$_2$O$_2$. (C) Linear relationship between chronoamperometric current and H$_2$O$_2$ concentration on hemin-TiO$_2$ modified electrode. (D) Chronoamperometric curve at an applied potential of −0.15 V recorded on (a) TiO$_2$ and (b) hemin coated electrodes in deaerated PBS (0.1 mol·L$^{-1}$, pH 7.0) after successive injection of H$_2$O$_2$. Inset: linear relationship between chronoamperometric current and H$_2$O$_2$ concentration on hemin modified electrode.
TiO2 film only displayed a low photoelectrocatalytic activity under UV irradiation.

(B) Photocurrent responses of hemin-TiO2 modified electrode in 0.1 mol PBS (pH 7.0) in the presence of (a) 0, (b) 0.4, (c) 1, (d) 5, (e) 10, (f) 20 and (g) 30 μmol·L⁻¹ HQ at a bias potential of 0.6 V. Inset: calibration curve for HQ on developed photoelectrochemical sensor. (C) Photocurrent responses of hemin-TiO2 modified electrode at a bias potential of +0.6 V toward HQ in PBS (pH 7.0) before (a) and after degraded for (b) 30 min and (c) 60 min under UV irradiation.

Figure 9. (A) Photocurrent responses of (a) hemin-TiO2 and (b) TiO2 modified electrodes in 0.1 mol·L⁻¹ PBS (pH 7.0) at a bias potential of +0.6 V. (B) Photocurrent responses of hemin-TiO2 modified electrode in 0.1 mol·L⁻¹ PBS (pH 7.0) in the presence of (a) 0, (b) 0.4, (c) 1, (d) 5, (e) 10, (f) 20 and (g) 30 μmol·L⁻¹ HQ at a bias potential of +0.6 V. Inset: calibration curve for HQ on developed photoelectrochemical sensor. (C) Photocurrent responses of hemin-TiO2 modified electrode at a bias potential of +0.6 V toward HQ in PBS (pH 7.0) before (a) and after degraded for (b) 30 min and (c) 60 min under UV irradiation.

reached. While the lamp was switched off, the current was quickly decreased to the original low dark-current value. This confirms the high sensitivity, good reproducibility and high stability. Meanwhile, the sensitization of TiO2 by hemin remarkably promoted the photoelectrocatalytic activity of TiO2 to visible light. Based on the high photoelectrocatalytic activity of hemin-TiO2, a photoelectrochemical sensor for the determination of HQ was developed. Thus, hemin-TiO2 composites were successfully demonstrated in developing electrochemical and photoelectrochemical sensing devices.

Conclusions

In this work, hemin-functionalized TiO2 nanoparticles were found to simultaneously possess both the catalytic properties of hemin and TiO2. Due to the electrocatalytic activity of hemin toward H₂O₂ and mesoporous structure of TiO2 for hemin loading, the hemin-TiO2 modified electrodes could be utilized as a H₂O₂ sensor, which displayed a high sensitivity, good reproducibility and high stability. Meanwhile, the sensitization of TiO2 by hemin remarkably promoted the photoelectrocatalytic activity of TiO2 to visible light. Based on the high photoelectrocatalytic activity of hemin-TiO2, a photoelectrochemical sensor for the determination of HQ was developed. Thus, hemin-TiO2 composites were successfully demonstrated in developing electrochemical and photoelectrochemical sensing devices.

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