

Enhanced Photoelectrochemical Activity of a Hierarchical-Ordered TiO₂ Mesocrystal and Its Sensing Application on a Carbon Nanohorn Support Scaffold

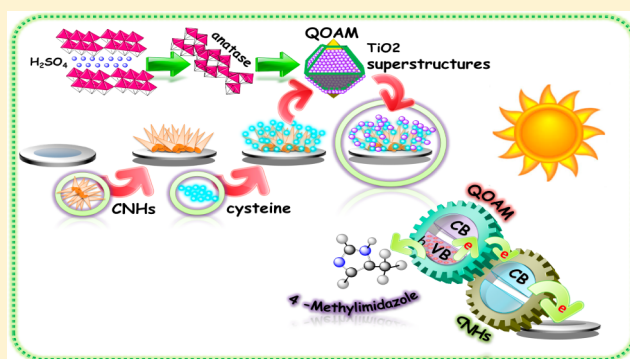
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S Supporting Information

ABSTRACT: A ternary hybrid was developed through interaction between a hierarchical-ordered TiO₂ and a thiol group that was obtained by in situ chemical polymerization of L-cysteine on the carbon nanohorn (CNH) superstructure modified electrode. Herein, unique-ordered TiO₂ superstructures with quasi-octahedral shape that possess high crystallinity, high porosity, oriented subunit alignment, very large specific surface area, and superior photocatalytic activity were first introduced as a photosensitizer element in the photoelectrochemical determination. Additionally, the assembly of hierarchical-structured CNHs was used to provide an excellent electron-transport matrix to capture and transport an electron from excited anatase to the electrode rapidly, hampering the electron–hole recombination effectively, resulting in improved photoelectrochemical response and higher photocatalytic activity in the visible light region. Owing to the dependence of the photocurrent signal on the concentration of electron donor, 4-methylimidazole, which can act as a photogenerated hole scavenger, an exquisite photoelectrochemical sensor was successfully fabricated with a wide linear range from 1×10^{-4} to 1×10^{-10} M, and the detection limit was down to 30 pM. The low applied potential of 0.2 V was beneficial to the elimination of interference from other reductive species that coexisted in the real samples. More importantly, the mesocrystal was first introduced in the fabricating of a biosensor, which not only opens up a new avenue for biosensors manufactured based on mesocrystal materials but also provides beneficial lessons in the research fields ranging from solar cells to photocatalysis.



Photoelectrochemical (PEC) sensing as a newly emerged yet dynamically developing analytical technique has drawn mounting interest in many research fields, such as cytosensing, immunoassay, and DNA analysis, which uses light to induce electron transfer among an analyte, a photoelectrochemical active species, and an electrode for generating the detectable signal.^{1–3} The PEC sensor possesses promising higher sensitivity than the conventional optical and electrochemical methods, attributing to the complete separation of the excitation source (light) and the detection signal (current), which results in the undesired background signal being greatly reduced.² To date, a series of PEC sensors have been proposed by using semiconductors, such as TiO₂, ZnO, WO₃, NaTaO₃, Fe₂O₃, CdS, and so on, which have exhibited excellent photocatalytic properties for PEC applications.^{4–6} Nonetheless, there are still many limits to meet the PEC processes before they become economically feasible, which include the reduction of the recombination of photogenerated electron–hole pairs

and the effective utilization of visible light. Accordingly, it is significant to delve new photosensitive materials to extend the applications of the PEC platform in analysis.

TiO₂ has been demonstrated to be a potential candidate for widespread applications in environmental and energy areas ranging from photocatalysis and sensing to solar cells and lithium ion batteries.⁷ Up to date, many titania materials, for instance, anatase TiO₂, nanoparticle TiO₂, nanowire TiO₂ arrays, nanocrystal TiO₂, and mesoporous single-crystal rutile TiO₂, have been reported as excellent photocatalysts in PEC sensors. For these applications, the performance of TiO₂ mainly relies on its size, microstructure, surface condition, and crystalline phase. Recently, mesocrystals (crystallographically oriented assemblies of nanocrystals), especially, TiO₂ meso-

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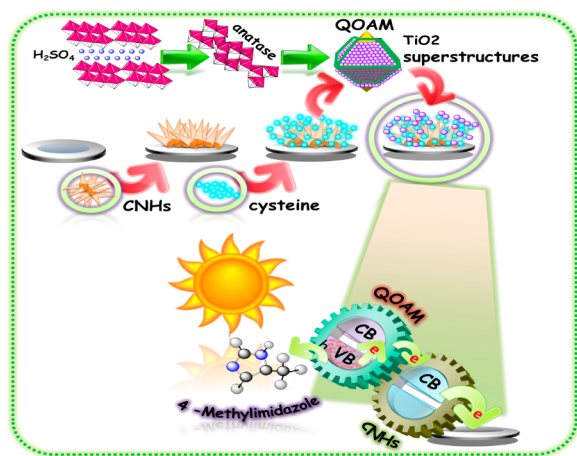
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crystals, have received increasing attention on the ground that their novel structure, property, and nonclassical crystallization process.^{8–12} Herein, we proposed a simple and favorable method for the additive-free preparation of quasi-octahedral anatase TiO₂ mesocrystals (QOAMs) by using hydrogen titanate as a precursor (Scheme 1). The resultant TiO₂

Scheme 1. Schematic Illustration of the Synthesis of QOAM and PEC Process for Oxidation of 4-MID at CNHs–PLC–QOAMs/GCE



mesocrystals with high-reactive facets possess better photocatalytic activity than other titania materials in the visible light region due to its unique properties such as the hierarchical structure, high crystallinity, high porosity, subunit alignment, and high specific area. However, the fast recombination of photogenerated electron–hole pairs is an impediment to its practical applications.

To improve the PEC performance of the TiO₂ anode, various electrode supported matrixes, such as metals,¹³ metal oxides,¹⁴ and carbonaceous materials,^{15,16} have been used as matrixes or conductive additives to enhance the conductivity of electrons and the photocatalytic activity of TiO₂ in PEC applications. Among these materials, the carbon nanohorns (CNHs) have been explored in many applications ranging from gas storage and nanoelectronics to biomedicine and biosensing, owing to the large theoretical specific area, variable porosity, unique electronic properties, and high electron mobility.^{17,18} As we all known, CNHs (the assembly of hierarchical structures) usually appear as spherical superstructures. They were assembled by many irregular conical subelements with particularly sharp apical angles composed of single-layer graphene sheets with lots of π -conjugated electrons, which lead to the distinctive electrical conductivity of CNHs. Additionally, the CNH superstructures and QOAM superstructures can form a good contact and further reduce the grain boundary of QOAMs that inhibit the recombination of the electrons. Therefore, the introduction of advanced nanocomposite that consisting of QOAMs and CNHs opens up a new way for the PEC application in the analysis field.

To evaluate the application of a novel nanocomposite in analysis detection, a classic foodborne contaminant, 4-methylimidazole (4-MID), was introduced into the determination as a research sample. 4-MID is a byproduct of the Maillard reaction during the manufacture of class III and class IV caramel color that serves to darken food products.^{19–22} It

has received mounting attention attributing to the fact that the National Toxicology Program has listed 4-MID as causing cancer and the International Agency for Research on Cancer plans to classify 4-MID as a group 2B compound.^{17,18} Therefore, accurate and rapid quantitative analysis of 4-MID can offer critical information on food products for both manufacturers and regulators. Hitherto, many protocols for the determination of 4-MID in foods have been proposed, such as gas chromatography, gas chromatography–mass spectrometry, high-performance liquid chromatography, and liquid chromatography tandem mass spectrometry.^{23–26} There is no doubt that the above methods can realize the 4-MID determination to some extent; nonetheless, each of these approaches suffers from at least one undesirable limitation, such as requiring very expensive instruments and operational complexity, lacking of portability and low sensitivity. Besides, these methods for the detection of 4-MID all involves significant sample preparation including extraction, and separation or derivatization, resulting in higher cost analysis with long cycle times. Meanwhile, the PEC methods possess many advantages such as simple equipment, facile pretreatment, and cost effectiveness, which can realize on-site and ultrasensitive detection and better meet the needs of practical application.

In this text, a facile and effective PEC sensing platform was first established on a glassy carbon electrode (GCE) for sensitive and specific determination of 4-MID based on a signal-on strategy at the relatively low potential. In the PEC detection, photoexcitation of semiconductor QOAMs lead to the transfer of electrons from the valence band (VB) to the conduction band (CB), yielding electron–hole pairs. Due to the lower CB of CNHs than that of QOAMs and the high electron mobility of CNH superstructure, the addition of CNHs suppressed the recombination of electron–hole pairs effectively, and a higher photocatalytic ability and photocurrent signal were achieved. Poly(L-cysteine) (PLC), as a link-agent, caused the improved absorption of QOAMs onto the matrix, resulting in the enhancement of photo-to-electric conversion. On the basis of the excellent PEC performance brought by the synergy of the ternary hybrid system, 4-MID was detected by the increasing of the photocurrent because it acted as an electron donor (Figure S-1, Supporting Information) who can transfer electrons to the holes located on the VB of QOAMs, reducing the recombination of electron–hole pairs (Scheme 1). The result showed that the proposed PEC sensor exhibited good performances such as facile fabrication, low cost, excellent selectivity, and superior sensitivity. It is especially noteworthy that the interface construed by hierarchical-structured TiO₂ can enhance the absorbance of visible light, which would be extremely beneficial to construct biosensors based on the PEC detection. Meanwhile, the research based on TiO₂ mesocrystals will also afford beneficial lessons in the research fields ranging from solar cells to photocatalysis.

■ EXPERIMENTAL SECTION

Materials and Reagents. 4-MID and L-cysteine were purchased from HWRK Chem Co. (Beijing, China) and Yuanhang Co. (Shanghai, China), respectively, and used without further purification. *N,N*-Dimethylformamide (DMF) and ethanol were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) and used as received. Coca Cola was purchased from a local market. CNHs (10 mg mL^{−1}) were prepared with DMF for the future use. Working solutions were freshly prepared before use by diluting the stock solution. A gift

sample of mixed-phase titania (P25, 80% anatase, 20% rutile with Brunauer–Emmett–Teller (BET) surface area of $56.63 \text{ m}^2 \text{ g}^{-1}$, and mean particle size of 28 nm) was bought from Degussa (Germany). It was used without further purification or treatment. The phosphate buffer solution (PBS) was prepared by mixing a stock solution of 0.1 M NaH_2PO_4 and 0.1 M Na_2HPO_4 and adjusting the pH. Other reagents were of analytical reagent grade. The water used for the preparation of the solution was purified using a water (China) purification system.

Apparatus. The crystal structure of the product was characterized by X-ray powder diffraction (XRD) (XRD-6000, Shimadzu Instrument, Japan) with $\text{Co K}\alpha$ radiation ($\lambda = 1.78897 \text{ \AA}$), and the data was changed to $\text{Cu K}\alpha$ data. Scanning electron microscopy (SEM, Hitachi S-4800) was used to observe the morphologies and sizes. Transmission electron microscopy (TEM, FEI F20 S-TWIN), high-resolution TEM (HRTEM), and the selected area electron diffraction (SAED) analysis were performed on a JEOL-2100 transmission electron microscope. Open circuit potential–time (OCP), linear sweep voltammetry (LSV), electrochemical impedance spectroscopy (EIS), chronocoulometry (CC), amperometric $i-t$ curve, and cyclic voltammetry (CV) were performed on a CHI 760 electrochemical workstation (Shanghai Chenhua Instrument Co., China) with a conventional three-electrode cell. An Ag/AgCl electrode (sat. KCl) was used as the reference electrode. A platinum wire and a modified GCE ($d = 3 \text{ mm}$) were used as the auxiliary electrode and the working electrode, respectively. The pH measurements were carried out on a PHS-3C exact digital pH meter (Shanghai Leici Co. Ltd., China), which was calibrated with standard pH buffer solutions. PEC measurements were performed with a homemade PEC system. A 300 W xenon lamp (LSH-X300, Zolix Instruments, Beijing, China) was utilized as the light source in the PEC detection.

Synthesis of QOAMs. In a typical synthesis for a titanate nanowire sample, 0.6 g of anatase TiO_2 was dissolved in a 30 mL of 15 M KOH solution. After being stirred for 10 min, the solution was transferred to a 45 mL Teflon-lined autoclave. The reactor was sealed, kept at 170°C for 72 h in an oven, and then cooled down naturally to room temperature. After that, the resulting precipitate was washed several times with 0.1 M H_2SO_4 solution to the pH of the resulting precipitate reached 2. Then, the titanate nanowires were collected by centrifugation and dried at 70°C for 12 h in air. Successively, 75 mg of titanate nanowires were dispersed in 25 mL of 1 M H_2SO_4 solution under stirring at 70°C for 7 days, and the final product was attained by centrifugation, washed thoroughly with distilled water, and dried at 70°C for 12 h in air. Then, 10 mg mL^{-1} TiO_2 solution was prepared with anhydrous ethanol for the future use.

Preparation of a Modified GCE. Prior to modification, the bare GCE ($\phi = 3 \text{ mm}$) was polished with 0.3 and $0.05 \mu\text{m}$ alumina slurry on chamois leather to produce a mirrorlike surface, then washed successively with anhydrous alcohol and doubly distilled water in an ultrasonic bath, and dried in air before use. For preparation of modified electrodes, 1 mg mL^{-1} CNH, 3 mg mL^{-1} QOAM, and 3 mg mL^{-1} P25 solutions were prepared.

For the contrast experiment of the PEC performance of QOAMs and P25, with a micropipet, $4 \mu\text{L}$ each of QOAM and P25 solutions (3 mg mL^{-1}) was deposited on freshly prepared GCE surfaces, respectively, which were then placed under an IR lamp until the solvents were evaporated. After the electrodes

were cooled to room temperature, the QOAMs/GCE and P25/GCE were successfully prepared.

For the treatments of modified electrodes in the PEC detection, with a micropipet, $4 \mu\text{L}$ of CNH solution was deposited on the freshly prepared GCE surface, and it was placed under an IR lamp until the solvent was evaporated; then, the CNHs/GCE was obtained after the electrode was cooled to room temperature. Afterward, PLC was deposited on the CNH-modified electrode by in situ electrochemical polymerization in 0.1 M PBS, pH 7.0, containing 0.01 M L-cysteine between -0.2 and 2.0 V . Then, the CNHs–PLC/GCE was thoroughly washed with redistilled water to remove any physically absorbed material and dried in air. Finally, the CNHs–PLC/GCE was immersed into a centrifuge tube containing $500 \mu\text{L}$ of 3 mg mL^{-1} QOAM solution for 10 min at room temperature. Then, the CNHs–PLC–QOAMs as a ternary hybrid was successfully developed through the above stepwise self-assembly process (Scheme 1). Similarly, the CNHs–PLC/GCE and CNHs–QOAMs/GCE were fabricated by the above technique without the last step and the electropolymerization process, respectively.

RESULTS AND DISCUSSION

Characterizations of Anatase. Typical SEM, TEM, and HRTEM images provided insight into the morphologies and structures of the samples. As shown in Figure 1A, large-scale

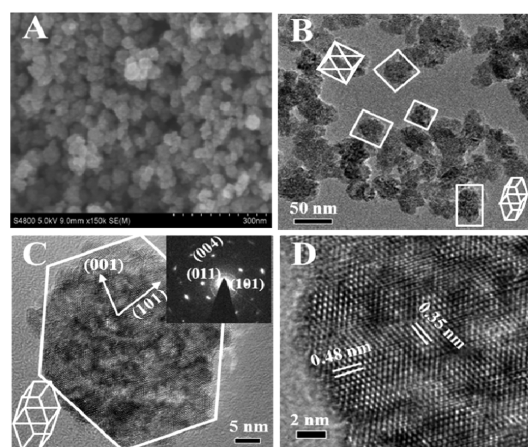


Figure 1. (A) SEM, (B, C) TEM, and (D) HRTEM images of the TiO_2 mesocrystals, respectively. The insets in (B) are the truncated-octahedral and octahedral models, and those in (C) are the SAED pattern and a truncated-octahedral model.

monodisperse crystallites with not only rough surfaces but also size in the range 25–50 nm can be observed, which amounts to the octahedral was constructed by nanoparticle subunits. Further investigation was carried out by TEM to reveal the organization of such anatase TiO_2 nanoparticles. Figure 1B exhibited the anatase TiO_2 nanoparticles with truncated-octahedral or quasi-octahedral shapes were built from very tiny nanoparticles. The magnified TEM image of an individual nanoparticle was depicted in Figure 1C, which confirms the hierarchical-structured anatase TiO_2 nanoparticle with a truncated-octahedral shape was constructed from tiny nanoparticle subunits. As exhibited in the inset of Figure 1C, the SAED pattern taken from the whole nanoparticle shown single-crystal-like diffraction, which indicated that the tiny nanoparticle subunits were highly oriented and resulted in the

formation of truncated-octahedral nanoparticles elongated along the (001) direction and oriented along the (101) direction. The diffraction spots were slightly elongated, which are neither typical ringlike spots nor standard diffraction spots, amounting to the aligned nanoparticle subunits were ordered locally in the whole octahedral or that there was a relatively large mismatch between the boundaries of the nanoparticles when they were assembled into the loosely packed octahedral. Figure 1D clearly represented the HRTEM image taken from a part of the single nanoparticle, which offered further insight into the fine structure of the TiO_2 products and indicated crystallographically oriented assemblies of nanocrystals in the mesocrystal. Additionally, it showed two sets of lattices, and the interplanar distances were 0.35 and 0.48 nm due to the spacing of the (101) and (002) planes of anatase, respectively. Combining the typical shape of the nanocrystal, we can deduce that the TiO_2 superstructure was exposed with the high-reactive (001) facets. This crystal structure will enhance the photocatalytic activity compared to the nanocrystals dominated by the thermodynamic stable (101) facets.

The crystallite size obtained by SEM and XRD (Figure S-2, Supporting Information) all indicated that the prepared QOAMs possess the classical characteristics of the mesocrystal, which is consistent with the result of a N_2 adsorption–desorption isotherm. The sharp uptake at relative pressures $P/P_0 < 0.05$ confirmed the presence of micropores, and an H_1 hysteresis loop at $P/P_0 > 0.7$ indicated the presence of mesopores. The BET surface areas are $211.07 \text{ m}^2 \text{ g}^{-1}$ and $0.43 \text{ cm}^3 \text{ g}^{-1}$, respectively, which are much larger than that of P25 and those of TiO_2 mesocrystals reported in the literature.^{27–29} More interestingly, a single peak in Barrett–Joyner–Halenda pore distribution at 19 nm was observed, indicating that very uniform mesopores can be obtained with the simple method.

PEC Investigation of Anatase. Figure 2A compared the open-circuit potential (OCP) responses of QOAM and P25

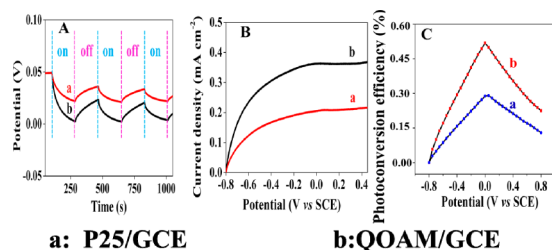


Figure 2. (A) Open-circuit voltage response, (B) photocurrent density versus bias potential, and (C) corresponding photoconversion efficiency as a function of the applied potential of (a) P25 and (b) QOAMs.

samples to illumination followed by termination of illumination. The OCP of the PEC cell represents the difference in Fermi level between the counter electrodes and TiO_2 . The excited photoelectrons transfer and accumulate within the TiO_2 films on account of the holes are scavenged by the electron donor species in the electrolyte following light irradiation, resulting in an apparent shift of the Fermi level to more negative potentials and an increase in OCP. Owing to the electron accumulation competing with the charge recombination, the OCP reaches a maximum and then attains a steady state. When the illumination was cut off, the accumulated electrons were slowly discharged because they were scavenged by the electron acceptor in the electrolyte simultaneously with undergoing

recombination with trapped holes.^{30–32} Thus, monitoring the decay of the voltage provides an insight into the paves by which loss of accumulated electrons occurs within the TiO_2 network. As exhibited in Figure 2A, the recorded OCP showed a slower decay for quasi-octahedral anatase TiO_2 than that for P25, that is to say, the electrons survive for a longer time in QOAMs, indicating more efficient charge separation and less recombination for QOAMs.

To further evaluate the PEC performance of both QOAMs and P25, typical linear sweep voltammograms of samples are shown in Figure 2B. In the dark, when the electrode potential was linearly swept from -0.8 to 0.4 V, there were no obvious current responses for all the film electrodes (data not shown). Under visible light illumination, a sharp increase in the photocurrent density throughout the potential window occurred, and it reached a saturated current at a specific potential, implying that the electric field led to photo-generated electron–hole pairs separation. A maximum photocurrent density of 0.36 mA cm^{-2} was attained for QOAMs, higher than that for P25 (0.2 mA cm^{-2}), owing to its better photoresponse and separation efficiency of electron–hole pairs. Additionally, the overt negative shift of saturation potential further confirmed that the charge separation and transportation in quasi-octahedral anatase TiO_2 (-0.08 V) are more efficient than those in P25 (0.1 V).

The photoconversion efficiency (η) of light energy to chemical energy in the presence of an external applied potential E_{app} was calculated using the following expression:^{33,34}

$$\eta(\%) = \frac{\text{TPO} - \text{EPI}}{\text{LPI}} * 100 = \frac{j_p * (E_{\text{rev}}^0 - |E_{\text{app}}|)}{I_0} * 100 \quad (1)$$

where TPO is the total power output, EPI is the electrical power input, LPI is the light power input j_p is the photocurrent density (mA cm^{-2}), E_{rev}^0 is the standard state-reversible potential (which is 1.23 V for the water-splitting reaction), $|E_{\text{app}}|$ is the absolute value of the applied potential E_{app} which is obtained as $E_{\text{app}} = E_{\text{meas}} - E_{\text{aoc}}$, where E_{meas} is the electrode potential (vs Ag/AgCl) of the working electrode at which the j_p was measured and E_{aoc} is the electrode potential of the same working electrode at open circuit, which is measured under the same illumination and in the same electrolyte solution at which j_p was measured, and I_0 is the power density of the incident light (86 mW cm^{-2}).

Figure 2C displayed the corresponding photoconversion efficiency as a function of the applied potential (vs Ag/AgCl) for QOAM- and P25-modified electrodes under simulative solar irradiation. A maximum photoconversion efficiency can be seen for P25 at an applied potential of 0.023 V around 29.0% , while it was 51.9% for the QOAMs at 0.002 V, an approximately 1.76 times enhancement, indicating the relative photocatalytic activity of QOAM is much better than that of P25, which agrees well with the OCP and LSV experiments. It is reasonable if we take into consideration the hierarchical structure, high crystallinity, and higher specific surface area of the QOAMs, which usually results that more photons could be absorbed and consequently much higher photoconversion efficiency can be obtained.

All above these results, strongly verified the QOAM shows a much higher PEC activity than the P25, which may be arisen from four reasons. First, the hierarchical structure of QOAMs can increase absorbance of the visible light, owing to the strong light-scattering effect caused by the tiny nanoparticle subunits

throughout the TiO_2 mesocrystal nanoparticle. Second, on account of its high porosity, each pore in the mesocrystal can be used as an isolated reaction center so that long-range electron transfer through the adjacent pore wall was not always compulsory, resulting in the enhancement of photoexcited charge carriers. Third, the high crystallinity and oriented subunit alignment led to the absence of grain boundaries that can act as recombination centers for electrons in the mesocrystal structure facilitating long-range electron transport, thus promoting the separation efficiency of photoexcited charge carriers. Lastly, a huge specific surface area can effectively promote the reaction space, offering a plentiful opportunity of spatial contact between reactant and photocatalytic active species. To sum up, all these synthetic factors were responsible for the remarkable enhanced photocatalytic activity of QOAMs in comparison with P25, which suggested the QOAM is desirable for designing and fabricating a high-performance PEC sensor.

Electrochemical Measurements of Different Modified Electrodes. The stepwise construction process of the sensor was monitored by EIS using $\text{K}_3\text{Fe}(\text{CN})_6/\text{K}_4\text{Fe}(\text{CN})_6$ as the redox probe. As demonstrated in Figure 3A, the Nyquist plot of

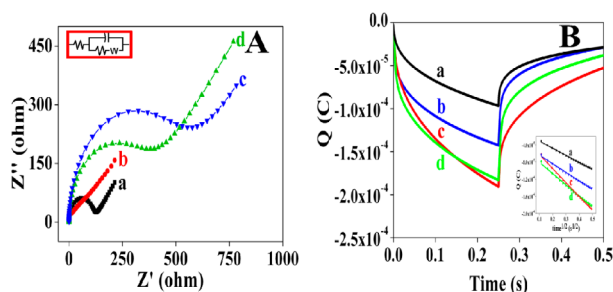


Figure 3. (A) Nyquist diagrams of EIS recorded from 0.1 Hz to 10 kHz for different electrodes in 0.1 M KCl containing 5.0 mM $\text{K}_3\text{Fe}(\text{CN})_6/\text{K}_4\text{Fe}(\text{CN})_6$ (1:1), (B) chronocoulometries of 0.5 mM $\text{K}_4\text{Fe}(\text{CN})_6$ (0.1 M PBS (pH = 7.0)) at different electrodes. Then, the linear relationship between the charges and the square roots of the times was inset: (a) bare GCE, (b) CNHs/GCE, (c) CNHs-PLC-QOAMs/GCE, and (d) CNHs-PLC/GCE.

the CNH-modified electrode (curve b) showed a sharply decreased diameter of the high frequency semicircle compared with that of GCE (curve a), indicating that the immobilized CNH film promoted the electron transfer process on the electrode surface, owing to the big surface area, high porosity, and excellent electron mobility of the CNHs. The result also showed that the CNHs were successfully immobilized on the electrode surface. The diameter significantly increased (curve d) after the electrochemical polymerization of CNHs/GCE, attributing to a PLC layer that impedes the transfer of an electron was successfully formed on the surface of the CNH electrode. Subsequently, the CNHs-PLC/GCE was immersed into a centrifuge tube containing 500 μL of 3 mg mL^{-1} of QOAM solution for 10 min, with the resistance further increased attributing to the strong bonding interaction between PLC and the QOAM, which illustrated that the QOAM was successfully self-assembled to the modified electrode.

The chronocoulometry was performed to compare the electroactive areas of different modified electrodes by the linear relationship between the charges having subtracted the background and the square roots of the scan times from Figure 3B following the Anson equation:³⁵

$$Q(t) = kt^{1/2} + Q_{\text{ads}} (k = 2nFAc\sqrt{D/\pi}) \quad (2)$$

where Q is the charge at the planar electrode, k is the slope in the corresponding Anson equation, t is the time, Q_{ads} is Faradaic charge, n is the number of electrons involved in the reaction, F is the Faraday constant, A is the efficiency surface area of the working electrode, c is the concentration of the oxidized species, and D is the diffusion coefficient. From Figure 3B, we can see clearly that the slope of CNHs-PLC-QOAMs/GCE (c) was the maximal, indicating that the CNHs-PLC-QOAM-modified electrode has the largest effective surface area. That is to say, the electroactive area of CNHs-PLC-QOAMs/GCE was 6.69 times that of GCE (a), 4.95 times that of CNHs/GCE (b) and 3 times that of CNHs-PLC/GCE (d). These values concretely embodied the character of the modified electrode that had larger surface area resulting in providing additional sites at the semiconductor-electrolyte interface, which leads to the enhancement of the photocurrent. The result also showed that the modified electrodes were fabricated successfully, which is in well accordance with the result of EIS.

PEC Characterizations of Modified Electrodes. As exhibited in Figure 5A, the different modified electrodes as photoanodes were investigated in the different light switching states. The QOAMs/GCE (curve a) in 0.1 M PBS containing 10 μM 4-MID showed a photocurrent density of 0.17 $\mu\text{A cm}^{-2}$ under the optimum experimental conditions (Figure 4), which

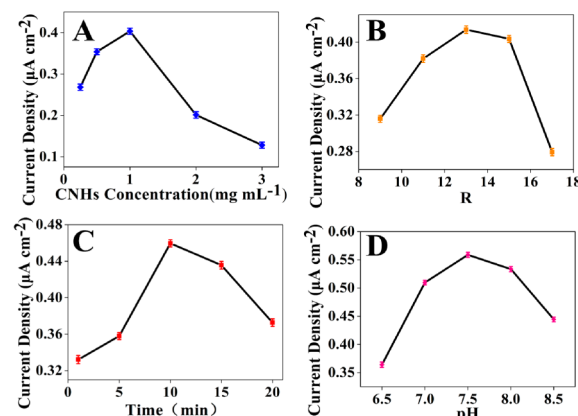


Figure 4. Effect of (A) the concentration of CNHs, (B) electro-polymerization cycles, (C) QOAM self-assembly time, and (D) pH to the photocurrent density of CNHs-PLC-QOAMs/GCE in 0.1 M PBS containing 10 μM 4-MID.

revealed the QOAMs can function as an excellent photoactive material. The CNHs-QOAMs/GCE displayed a photocurrent density of 0.27 $\mu\text{A cm}^{-2}$, indicating CNHs efficiently enhance the photocatalytic performance, owing to not only the extraordinary electric conductivity of the CNH superstructure but also the good contact between the CNH superstructure and the TiO_2 superstructure that accelerated the transfer of electrons and inhibited the recombination of photogenerated electron-hole pairs. Obviously, the photocurrent density of CNHs-PLC-QOAMs/GCE (d) is almost 2 times larger than that of CNHs-QOAMs/GCE. The remarkably enhanced photocurrent probably on account of the formation of a stable adherent polymer between CNHs and QOAMs, leading to much QOAMs absorbed to the matrix by interaction between the TiO_2 mesocrystal and the thiol group in PLC. It is

interesting to note the tremendous enhancement of the photocurrent density by comparing the CNHs–PLC–QOAMs/GCE in the presence (d) with that in the absence (c) of 4-MID, attributing to that the 4-MID working as quencher of photogenerated holes was oxidized, consuming the photogenerated holes, benefiting the electron–hole separation, leading to the enhancement in photocurrent. Consequently, the concentration of 4-MID can be quantified by the photocurrent density.

Parameter Optimization. To obtain good performance in this PEC process for 4-MID detection, several experimental parameters including the CNH concentration, electropolymerization cycles, QOAM self-assembly time, and pH were optimized. As seen in Figure 4A, the photocurrent density increased quickly with the increasing amount of the CNH concentration and then tends to level off. Therefore, the optimal CNH concentration was set at 1 mg mL⁻¹. From Figure 4B–D, the number of electropolymerization cycles of 13, the QOAM self-assembly time of 10 min, and the pH of 7.5 were selected for 4-MID detection. (Relevant descriptions were presented in the Supporting Information.)

Calibration Curve, Linear Range, and Detection Limit. As shown in Figure 5B, under the optimum experimental

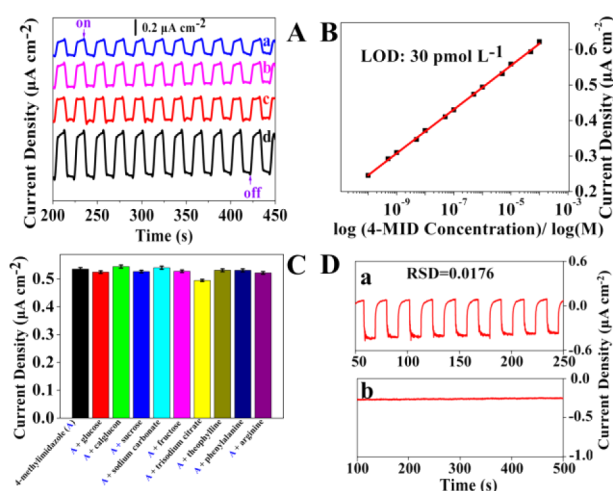


Figure 5. (A) Photocurrent density of (a) QOAMs/GCE, (b) CNHs–QOAMs/GCE, and (d) CNHs–PLC–QOAMs/GCE in 0.1 M PBS in the presence and (c) CNHs–PLC–QOAMs/GCE in the absence of 10⁻⁵ M 4-MID with light on and off. The applied potential was 0.2 V, and the excitation wavelength was 390 nm. (B) Corresponding calibration curve of different concentrations of 4-MID (0.0001, 0.0005, 0.001, 0.005, 0.01, 0.05, 0.1, 0.5, 1, 5, 10, 50, and 100 μM) on the differential photocurrent density. (C) Selectivity of the proposed assay to 4-MID by comparing it to the interfering substances at the 1 mM level: fructose, glucose, calglucon, sucrose, sodium carbonate, fructose, trisodium citrate, theophylline, phenylalanine, and arginine in 10⁻⁵ M 4-MID. (D) Photocurrent density of (a) the CNHs–PLC–QOAMs/GCE measured at 0.2 V at repeated on and off cycles of simulated sunlight illumination and (b) under continuous simulated sunlight illumination.

conditions, the anode photocurrent density was proportional to a logarithmic value of the 4-MID concentration. The dynamic range of this PEC sensor covered from 10⁻¹⁰ to 10⁻⁴ M with a good linear relationship. The linear regression equation was j (μA cm⁻²) = 6.10 + 0.44log C (M, r^2 = 0.999) with a detection limit (LOD) of 30 pM at a signal-to-noise ratio of 3. The dynamic range of 10⁻¹⁰ to 10⁻⁴ M was wider than those of

other strategies for the quantitative detection of 4-MID, and the LOD was much lower than the earlier report, obtaining the sensitive determination for 4-MID (Table S-1, Supporting Information).^{36–38} Thereby, the prepared PEC sensor showed promise for application in the sensitive monitoring of 4-MID with a low LOD and a wide concentration range.

Interference, Reproducibility, Precision, and Stability.

To estimate the selectivity of the proposed sensor, the influence of some potential interfering substances were investigated in 10 μM 4-MID solution containing 1 mM glucose, calglucon, sucrose, sodium carbonate, fructose, trisodium citrate, theophylline, phenylalanine, and arginine, respectively (illustrated in Figure 5C). The results suggested that they had no evident influence on the determination of 4-MID, revealing the high selectivity of the present sensor for 4-MID detection.

The reproducibility of the sensor was evaluated by determining 10 μM 4-MID with three sensors prepared at the same electrode. A relative standard deviation (RSD) of 3.58% was attained from three parallel measurements (Figure S-6, Supporting Information), giving an acceptable fabrication reproducibility of the sensors and indicating a distinctive precision.

As demonstrated in curve a of Figure 5D, the photocurrent responses of the modified electrode were recorded as the illumination light was turned on and off in 0.1 M PBS (pH 7.5) solution containing 10 μM 4-MID at the applied potential of 0.2 V. The strong and stable photocurrent responses were observed with a RSD of 1.76%, which denoted that the modified electrode had good stability. No evident descend in the photocurrent was observed after 15 days of storage at 4 °C, implying that the fabricated sensor possessed good storage stability.

Furthermore, as can be seen from curve b in Figure 5D, the photocurrent was highly stable under continuous light radiation for 500 s without observable deterioration, validating distinctive chemical and structural stability of the proposed sensor.

Practical Application. To evaluate the analytical reliability and application potential of this sensor, 10 μL of the samples, Coca Cola, without any pretreatment process, was diluted with PBS (pH 7.5) to 2 mL and analyzed. The result showed a total amount of 4-MID in Coca Cola was estimated to be 95 μg L⁻¹, which was close to the 101.6 μg L⁻¹ value given in the instructions, denoting acceptable accuracy of the sensor. Subsequently, an amount of standard 4-MID was gadded into the above solution, and the recovery of the added 4-MID was in the range from 91.67% to 94.76% (Table 2S, Supporting Information), revealing that this sensor can be successfully used for the monitor of 4-MID in the beverage sample.

CONCLUSIONS

In summary, the hierarchical-structured TiO₂ mesocrystal with high porosity, huge specific surface, and extraordinary photocatalytic activity was first applied to the PEC detection. The presence of the CNH superstructure enhanced the photocatalytic efficiency of QOAMs due to the excellent electric property of the CNH superstructure and the matchable energy band position between QOAMs and CNHs. On the basis of the photoelectrochemical sensing principle, we reported a new and facile strategy for the fabrication of a ternary hybrid and a highly efficient photocatalyst for selective and sensitive sensing of 4-MID. The proposed PEC sensor has the advantages of low cost, easy fabrication, rapid response, high sensitivity, very broad linear range, rather low LOD, and excellent reproducibility.

bility. Furthermore, the utilization of visible light avoids the inactivation of biological identification devices in the UV range, expanding the applications of mesocrystals to biosensing in PEC detection, and relevant research is being conducted in our laboratory. Hopefully, this report would offer new advances into valid design and application of mesocrystals as photocatalysts for a wide variety of PEC detection and more importantly will afford beneficial lessons in research fields ranging from solar cells to photocatalysis.

■ ASSOCIATED CONTENT

■ Supporting Information

Photocurrent density of CNHs–PLCY–QOAM/GCE in different solutions; XRD patterns of the TiO₂ mesocrystal; cyclic voltammograms at CNHs/GCE during the electropolymerization in 0.01 M L-cysteine solution; photocurrent densities and cyclic voltammograms of different modified electrodes in different solutions; table of comparable figures of determining 4-MID; and table of the results of the addition recovery test. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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