Facile Fabrication and High Photoelectric Properties of Hierarchically Ordered Porous TiO$_2$

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ABSTRACT: This paper presents the first successful fabrication of hierarchically ordered porous (HOP) TiO$_2$. Poly(styrene-co-acrylic acid) colloidal spheres and triblock copolymer P123 were used as macro- and mesoporous structure-directing agents, and titanium chloride and titanium tetraisopropoxide were used as sources of titania. When the mixture of polymer spheres, P123, and titania precursors were cast on substrates, and conducted for complete solvent evaporation, followed by thermal treatment, large-scale HOP TiO$_2$ can be directly fabricated. The in situ chelate effect between the titania precursors and the poly(styrene-co-acrylic acid) plays a key role in the fabrication of HOP TiO$_2$. The as-obtained HOP TiO$_2$ exhibits 50% and 70% greater the highest photocurrent under UV and visible lights, respectively, and far higher photoelectrocatalytic property than commercial TiO$_2$ (P-25).

KEYWORDS: hierarchically ordered porous structure, TiO$_2$ photoelectric properties

INTRODUCTION: Nano TiO$_2$ has many important uses in dye-sensitized solar cells, photocatalyses, electrocatalyses, self-cleaning and antibacterial coatings, and gas sensors.

Over the past few decades, two issues have been the focal points of TiO$_2$ research. The first is the fact that nano TiO$_2$ can only be excited by UV light at a wavelength shorter than 387 nm, which only occupies 3% of the solar spectrum because of its wide band gap (3.2 eV). One approach to increasing the utilization efficiency of sunlight is to sensitize TiO$_2$ by using a narrower band gap semiconductor with a higher conduction band, such as cadmium sulfide (CdS) and ultimately its photoelectrochemical properties, even though nano TiO$_2$ is one of the most promising photoelectric and catalytic materials. In fact, TiO$_2$ with hierarchically porous structure has been prepared by spin coating, hydrothermal methods, phase separation, and nanocasting. The supported TiO$_2$ photocatalyst has less surface area than suspended TiO$_2$, which cause its lower photoelectric degradation efficiency.

Recently, hierarchically ordered porous (HOP) materials have received increasing interest. With the merit of larger specific surface area, higher porosity, easier mass transport, HOP carbon, HOP silica, and their hybrids with other materials have been successfully fabricated and applied in catalysis, adsorption, batteries, and waste disposal. However, little research involves the fabrication of the TiO$_2$ materials with hierarchically ordered porous structure (HOP TiO$_2$) and their properties, even though nano TiO$_2$ is one of the most promising photoelectric and catalytic materials. In fact, TiO$_2$ with hierarchically porous structure has been prepared by spin coating, hydrothermal methods, phase separation, and nanocasting. Yet the as-obtained porous TiO$_2$ was always disordered with respect to either distribution of pores or pore size, which dramatically affected its properties, and most of these fabrication processes are time-consuming and laborious. Moreover, TiO$_2$ with well ordered mesoporous structure has been successfully prepared through evaporation-induced self-assembly. Titania precursors (titanium chloride, titanium tetraisopropoxide, etc.) can serve as the titania resources and commercial Pluronic triblock copolymers, such as P123 (EO$_{20}$PO$_{70}$EO$_{20}$) or F127 (EO$_{106}$PO$_{70}$EO$_{106}$), can serve as...
the mesopore templates. But this approach is very sensitive to preparation conditions, such as solvent purity, temperature, and relative humidity, which can affect the sol–gel process of titania precursors and thus the mesoporous structure.\textsuperscript{24,25} Besides, TiO\textsubscript{2} arranged in an ordered macroporous structure is usually fabricated using a nanocasting approach with polymer spheres or silica crystal arrays as templates and titania precursors or TiO\textsubscript{2} nanoparticles as infilling materials.\textsuperscript{26} Unfortunately, the weak interaction between the templates and titania precursors, and the shrinkage of titania precursors during the process of calcination often lead to a disordering macropore structure.\textsuperscript{27} In short, because of the difficulty in controlling the hydrolysis and condensation of titania precursors and of the assembly of amphiphilic copolymer templates and the further problems created by weak interactions between polymer templates and titania precursors, it remains difficult to fabricate TiO\textsubscript{2} materials with HOP structures.\textsuperscript{23d}

In this paper, we report for the first time the fabrication of HOP TiO\textsubscript{2}, using a one-pot self-assembly method by the aid of in situ chelate interaction between polymer templates and titania precursors. In this approach, monodisperse colloidal poly(styrene-co-acrylic acid) (PSA) polymer spheres and triblock copolymer P123 served as the macro- and mesoporous structure-directing agents, respectively. PSA rather than the commonly used polystyrene colloidal spheres was used as the macroporous template. In this way, the carboxylic groups on the PSA spheres could be employed as coordination agent during the assembly process to tie titania precursors surrounding the surfaces of polymer spheres. This chelation effect was able to both control the fast hydrolysis and condensation reaction of titania precursors and ensure the assembly of polymer templates and the subsequently formation of the titania wall around the polymer surfaces during thermal process. This directly produced HOP TiO\textsubscript{2}. The as-obtained HOP TiO\textsubscript{2} exhibited considerably better photoelectrochemical properties and photoelectrocatalytic activity than commercial TiO\textsubscript{2} (P-25).

**EXPERIMENTAL SECTION**

**Materials.** Styrene (St, \(\geq 99\%\)), acrylic acid (AA, \(\geq 98\%\)), ammonium persulfate (APS, \(\geq 98\%\)), potassium hydroxide (KOH, \(\geq 90\%\)), and absolute ethanol (EtOH, \(\geq 99.7\%\)) were purchased from Sinopharm Chemical Reagent Corp. Titanium chloride (TiCl\textsubscript{4}, \(\geq 99\%\)), titanium tetraisopropoxide (Ti(OiPr)\textsubscript{4}, \(\geq 98\%\)), sodium sulfide (Na\textsubscript{2}S, \(\geq 98\%\)), and cadmium chloride (CdCl\textsubscript{2}, \(\geq 98\%\)) were purchased from Aladdin Chemical Reagent Corp. The triblock poly(ethylene oxide)-block-poly(propylene oxide)-block-poly(ethylene oxide) copolymer P123 (EO\textsubscript{30}PO\textsubscript{70}EO\textsubscript{30}, \(M_\text{w} = 8000\)) was purchased from Aldrich. TiO\textsubscript{2} nanopowder P-25 was purchased from Degussa. All chemicals were used as received without further purification. Millipore water was used in all experiments.

**Synthesis of Colloidal Polymer Spheres.** Monodisperse colloidal PSA spheres were synthesized by soap-free emulsion polymerization of styrene and acrylic acid. Briefly, 10 g of styrene, 0.5 g of acrylic acid, and 120 g of deionized water were charged into a 250 mL round-bottom flask equipped with a mechanical stirrer, thermometer with a temperature controller, N\textsubscript{2} inlet, Graham condenser, and heating mantle. This mixture was stirred and deoxygenated with bubbling nitrogen gas at room temperature for 0.5 h and then heated to 75 °C, and then aqueous APS solution was added (0.200 g of APS in 10 g of water). This reaction was conducted at 75 °C for 10 h to finish the polymerization. PSA polymer spheres with diameters of 180 nm were obtained. By adjusting the concentrations of monomers and APS, PSA latex with sizes of 300 and 420 nm were produced in the same way. The resultant colloidal suspension of PSA spheres was centrifuged and washed five times with ethanol and then dialyzed in ethanol for 24 h to remove the residual water. The final PSA colloid in ethanol with solid content of 20% was obtained for further use.

**Fabrication of HOP TiO\textsubscript{2}.** HOP TiO\textsubscript{2} was prepared using a one-pot in situ self-assembly strategy. In a typical experiment, 0.08 g of P123, 5 g of ethanol, 0.144 g of TiCl\textsubscript{4}, 0.056 g of Ti(OiPr)\textsubscript{4}, and 0.5 g of PSA ethanolic dispersion were mixed and stirred at room temperature for 2 h. The homogeneous mixture was then transferred into Petri dishes. Solvent was allowed to evaporate at room temperature for 24 h, and then the monolith was pretreated at 80 °C for 48 h and finally calcinated at 400 °C in air for 2 h to remove PSA templates.

For samples prepared for photoelectrochemical measurement, the mixture was directly assembled on the fluorine-doped SnO\textsubscript{2} conductive glass, followed by the same procedure described as above. For the sake of comparison, a commercially available TiO\textsubscript{2} powder (Degussa P-25) was used to prepare thin particulate films with the same mass of TiO\textsubscript{2} as the HOP TiO\textsubscript{2} by deposition of P-25 suspension in ethanol on the fluorine-doped SnO\textsubscript{2} conductive glass followed by calcination at 450 °C for 0.5 h.\textsuperscript{28} The as-obtained TiO\textsubscript{2} electrodes were sensitized with CdS quantum dots by sequential chemical bath deposition. The electrodes were dipped consequently into 100 mL of 0.5 M CdCl\textsubscript{2} aqueous solution, deionized water, 100 mL of 0.5 M Na\textsubscript{2}S aqueous solution, and deionized water for 30 s each, in that order. This cycle was repeated for various lengths of time. After the deposition, the as-prepared samples were dried in a N\textsubscript{2} stream for photocatalytic activity. For photocatalytic measurement, the electrodes were prepared using the same method as above but without the CdS sensitizing process. The film thickness of sample could be controlled by pasting Scotch tape around a given FTO glass to form a certain area of groove and fixing the volume of suspension.

**Characterization.** Scanning electron microscopy (SEM) was conducted with a Philips XL 30 field emission microscope at an accelerating voltage of 10 kV. Transmission electron microscopy (TEM) images were taken with a Philips CM200FEG field emission microscope. For the TEM observations, samples were dispersed in ethanol and then dried on a holey carbon film Cu grid. The phase and composition of the as-prepared products were measured using XRD patterns recorded in a Rigaku D/max-kA diffractometer with Cu K\(\alpha\) radiation. The UV–vis adsorption spectra were obtained using Hitachi U-4100 spectrophotometry. Nitrogen adsorption–desorption iso-
therms were determined at 77 K using an ASAP 2010 analyzer. The surface areas were calculated according to the Brunauer–Emmett–Teller (BET) method, and the pore volumes and pore size distributions were obtained using the Barrett–Joyner–Halenda (BJH) model.

Measurement of Photoelectric Properties. The electrochemical properties of TiO₂ electrodes were analyzed using an electrochemical workstation in a quartz cell with a three-electrode configuration, a Pt coil as the counter electrode, a saturated Ag/AgCl as the reference electrode, and 1 M KOH as the electrolyte. A 70 mW UV lamp (OMRON ZUV-C30H, 365 nm) and a 300 mW lamp (CCS HLV-24, 445 nm) provided the UV and visible light, which penetrated the quartz circular window mounted in one side of the cell and illuminated the working electrode.

■ RESULTS AND DISCUSSION

Fabrication of HOP TiO₂. HOP TiO₂ was fabricated via one-pot in situ self-assembly process. As shown in Scheme 1, TiCl₄ and Ti(OiPr)₄ were first mixed with the ethanol solution of copolymer P123, followed by the addition of PSA colloid to produce a stable dispersion. This dispersion was then cast on the Petri dishes and conducted for solvent evaporation at room temperature for 24 h, followed by pretreated at 80 °C for 48 h and finally calcinated at 400 °C in air for 2 h to directly produce HOP TiO₂.

When 180 nm PSA colloid in ethanol was poured into a Petri dish and underwent solvent evaporation at room temperature, these polymer spheres formed a large-area, three-dimensional periodic array with few defects, as shown in Figure S1. When the mixture of PSA colloid, triblock copolymer P123, and titania precursors in ethanol was cast on a substrate for solvent evaporation, followed by thermal treatments, the product presented three-dimensional interconnections of the ordered macropores with small windows, as shown in Figure 1a (top view) and Figure 1b (cross-sectional view), indicating that the macrostructure of the colloidal polymer crystals can be retained well. This structure appeared to be a typical face-centered cubic (fcc). That is, each macropore is surrounding by six equal macropores in layers perpendicular to the (111) direction. These ordered macropores are connecting each other by the TiO₂ wall. The center-to-center distance between two neighboring pores estimated from SEM is about 170 nm, around 5.5% of shrinkage of the lattice structure compared to polymer templating spheres. The TEM image further indicates an open macropore structure (Figure 1c). The size of the macropore can be easily tunable by using polymer templating spheres of different sizes. For example, macropores 270–370 nm in diameter can be produced by polymer templating spheres 300–420 nm in diameter (Figure S2). The high resolution TEM (HRTEM) image in Figure 1d shows characteristic projections of mesopore structure along with the curvature of macropore wall surface, indicating a hierarchically ordered porous structure. The size of the mesopore, as estimated from the HRTEM image, is about 3.5 nm.

Figure 2 demonstrates that the XRD pattern of the typical HOP TiO₂ has seven well-resolved diffraction peaks. These can be indexed to the 101, 004, 200, 105/211, 204, 116/220, and 215 reflections of anatase [JPDF no. 21-1272], and no rutile phase was observed. The crystalline size estimated using the Scherrer equation from the full width at half-maximum of the (101) peak (2 theta = 25.4°) was about 8.8 nm. This suggests that the amorphous TiO₂ can be converted into the anatase phase by heating at 400 °C despite the mole ratios of two kinds of titania precursor, as shown in Figure S3.
The N₂ adsorption–desorption isotherm of the HOP TiO₂, as shown in Figure 3, reveals a type IV curve, typical for mesoporous materials according to the IUPAC nomenclature.²⁹ Besides, the isotherm displays two hysteresis loops. The hysteresis loop at low relative pressure between 0.40 and 0.80 is of type H2. This can be ascribed to capillary condensation in mesopores generated by triblock copolymer P123. The other loop, at a higher pressure of between 0.88 and 1.0, has a type H3 shape, which may have been due to interparticle pores within the sample.³⁰ The estimated pore volume of the sample was 0.206 cm³ g⁻¹, and the BET surface area was 135 m² g⁻¹, nearly three times as large as that of P-25 (50 m² g⁻¹). The pore distribution, as shown in the inset of Figure 3, shows a narrow Gaussian pore size distribution, implying that the TiO₂ possess very regular pore channels in the mesoporous region. The mean mesopore size of the HOP TiO₂ is 3.4 nm calculated by BJH model, which corresponds closely to the results of HRTEM.

**Effects of Titania Precursors.** The concentration of titania precursors has obvious impact on the nanostructure of TiO₂. As shown in Figure 4, when the concentration was too low, such as at a weight ratio of 2:3 for titania precursors and PSA, a collapsing skeleton was observed (Figure 4a). When this weight ratio was increased to 4:3, a continuous TiO₂ with porous nanostructures was observed (Figure 4b). When more titania precursors, i.e., 2:1 and 4:1 for titania precursors and PSA, were used, more TiO₂ derived from the hydrolysis and condensation reaction of titania precursors was accumulated around the surfaces of PSA spheres, finally forming integrated and periodic porous structure after calcination. The thickness of the TiO₂ wall increased from 15 to 30 nm, as shown in Figure 4c and d. This suggests that the TiO₂ grows from the surfaces of PSA spheres and becomes thicker and thicker to fill the interstitial voids between PSA spheres as the concentration of titania precursors increases. However, when too much titania precursor, i.e., weight ratio of 8:1 for titania precursor and PSA, was present, the window became much smaller, even closing completely (Figure 4e). This means that the infiltration of TiO₂ into the voids between polymer spheres plays a critical role in the successful fabrication of HOP TiO₂ in our in situ self-assembly approach. Too little of titania precursors is not enough for the formation of an integrated TiO₂ framework, but excess titania precursors would impede the contact between neighboring polymer spheres except for filling in the voids between polymer spheres and even form a TiO₂ domain.

When Ti(OiPr)₄ was used as the sole titania precursor, a continuous TiO₂ bulk with irregular pores was obtained (Figure S4). This can be attributed to the low reactivity of Ti(OiPr)₄.
When TiCl₄ was used as the sole titania precursor, bulks of flocculation appeared because of the overly fast hydrolysis and condensation reaction of TiCl₄ in ethanol under carboxylic acid-catalysis. This showed that TiCl₄ and Ti(OiPr)₄ are best used together as titania precursors on the basis of the acid−base pair concept, wherein they serve as hydrolysis−condensation controllers.

**Effects of Thermal Treatment Temperature.** During the preparation of HOP TiO₂, the monolith was pretreated at 80 °C, which can accelerate the hydrolysis and condensation of titania precursors to form the TiO₂ framework around the surfaces of PSA spheres. The surrounding TiO₂ particles restrained the deformation and coalescence of these polymer spheres during the subsequent calcinations, which caused monodispersed and spherical polymer spheres to pile tightly into three-dimensionally ordered arrays. Without this pretreatment, only bulk TiO₂ was obtained (Figure S5). Because the glass transition temperature of PSA is only about 100 °C, the pretreatment temperature should not be too high. Calcination temperature also has an important influence on the nanostructure of the products. When this temperature was increased from 400 to 500 °C, crystallinity increased (Figure S6). However, higher calcination temperatures caused the deformation of the mesoporous structure of the HOP TiO₂. As
shown in Figure S7, for the N\textsubscript{2} adsorption−desorption isotherms of the 500 °C-calcined sample, this isotherm curve can be classified as type III according to the IUPAC nomenclature. It was unclear what type of H\textsubscript{2} hysteresis loop appeared at low relative pressure between 0.5 and 0.8, suggesting that there is little capillary condensation because of the deformation of mesoporous structure. The mesopores ranged widely in size, by as much as 3–50 nm, and the BET surface area was only about half of the value of the sample calcined at 400 °C because of the collapse of the mesoporous pores.

Formation Mechanism of HOP TiO\textsubscript{2}. Based on above experimental results and discussion, a possible formation mechanism of HOP TiO\textsubscript{2} is deduced. As shown in Scheme 2, when the materials were mixed together, a series of reversible equilibrium reactions could happen between TiCl\textsubscript{4}, Ti(O\textsubscript{iPr})\textsubscript{4}, PSA, and EtOH. First, TiCl\textsubscript{4} can react with EtOH to form TiCl\textsubscript{4−x−y}(OEt)\textsubscript{x}(OH)\textsubscript{y} species (Scheme 2a).\textsuperscript{32} Upon the addition of Ti(O\textsubscript{iPr})\textsubscript{4}, a reaction of redistribution of the chloride and alkoxide substituents around the titanium atoms formed an equilibrated mixture of TiCl\textsubscript{4−x−y}(OPr)\textsubscript{x}(OEt)\textsubscript{y} species because the cleavage of the oxygen−metal bond in the intermediate Lewis adduct caused an exchange reaction\textsuperscript{32} (Scheme 2b). Acetic acid, however, is a well-known chelating agent for titanium alkoxide, which is generally used to control the hydrolysis and condensation reaction of titanium precursors.\textsuperscript{33,34} Herein, the PSA spheres with hydrophilic carboxylic groups constituting the shell provided adequate carboxylic acid groups for titanium due to the chelating effect between titanium and carbonyl groups.\textsuperscript{35} There are two kinds of chelation reactions between titanium alkoxides and carboxylic acid groups, covalent interactions and coordination reactions, both of which are shown in Scheme 2c.\textsuperscript{36} These cause a tightly coalescent structure with PSA core and titanium species thin layer. During the pretreatment process, the titanium species surrounding the PSA spheres were further thermopolymerized into TiO\textsubscript{2}, which fixed the position of PSA position during the calcination process.

To verify that this chelating effect takes place, PSA polymer spheres and the PSA/titania hybrid materials left over from the assembly process were vacuum-dried and taken for FTIR scans. As shown in Figure S8a, the broad peak between 3100–3700 cm\textsuperscript{-1} created by carboxylic acid was dramatically decreased after chelation with titania precursors. There was also a slight shift...
for the peak of carbonyl stretching vibration, from 1740 cm\(^{-1}\) for pure PSA to 1735 cm\(^{-1}\) for the PSA/titania hybrids caused by the chelating effect. Because of the low content of poly(acrylic acid) (only 5% based on the formula) in PSA polymer spheres, the changes of other peaks in FTIR spectra were difficult to detect. To investigate this reaction further, poly(acrylic acid) (PAA) was used instead of PSA under the same conditions. As shown in Figure S8b, for pure PAA, the characteristic absorption band of carbonyl (C=O) was 1722 cm\(^{-1}\). After PAA had chelated with the titania precursors, we observed one absorption band of 1720 cm\(^{-1}\) from the carbonyl (C=O) of poly(acrylic acid) and a new peak at 1712 cm\(^{-1}\) for PAA/titania hybrids. This peak appeared because of the coexistence of an ester group and a carboxylic acid group.\(^{37}\) Another new peak appeared at 1250 cm\(^{-1}\) for the PAA/titania hybrid, which is a typical antisymmetric stretching vibration for the C–O bond of ester. These results confirm the chelating effect between titania precursors and carboxylic acid groups.

This fixation effect has a pivotal effect on the maintenance of the ordered macropore structure of the HOP TiO\(_2\) materials. We prepared the TiO\(_2\) with the same procedure but using polystyrene spheres instead of PSA spheres, removing the chelating effect. As shown in the SEM image in Figure S9, a continuous bulk with smaller, more irregular pores was observed. This bulk took shape because of the disordered polymer spheres and the collapses of the TiO\(_2\) framework during the calcination process.

This chelating effect could also explain why no HOP structure was obtained when pure Ti(OiPr)\(_4\) or TiCl\(_4\) was used as the sole titanium source. Besides their own activity, the reactions of Ti(OiPr)\(_4\) and TiCl\(_4\) with PSA play an important role. This is because this chelating effect can decrease the reactivity of titanium species and increase colloidal stability due to the steric hindrance from polymer chains.\(^{36,39}\) The chelating effect between Ti(OiPr)\(_4\) and carboxyl groups was very strong, dramatically decreasing the reactivity of Ti(OiPr)\(_4\). For TiCl\(_4\), there was no such direct covalent bond between TiCl\(_4\) and PSA, so the chelating effect only occurred after partial alcoholysis of TiCl\(_4\). This weaker effect between TiCl\(_4\) and carboxylic acid groups could not obviously change the speed of the alcoholysis of TiCl\(_4\). Therefore, an appropriate ratio of TiCl\(_4\) and Ti(OiPr)\(_4\) was necessary to facilitate a moderately paced reaction and the formation of the HOP structure.

As the ethanol evaporated, the monodispersed PSA spheres, which were surrounded by a thin layer of the chelated titanium species, self-assembled into three-dimensional periodic structures. The residual titanium species and P123 infiltrated into the interstitial voids between polymer spheres. Further evaporation of ethanol induced the folding of P123 templates and the assembly of titanium species around the P123 to form the mesoporous structure (Scheme 2d). No isopropyl chloride was detected, indicating that the condensation between Ti–O–Pr and Ti–Cl groups did not occur at any significant rate at room temperature.\(^{32}\) This may be why no TiO\(_2\) formed during this assembly process.

During the pretreatment process at 80 °C, the condensation reactions between Ti–Cl and Ti–OR produced TiCl\(_4\)(OEt)\(_3\)O\(_x\)O\(_{1-x}\) species. As shown in Scheme 2e, an alkox group coordinates to the metal center of the second molecule; then the release of an alkyl halide molecule leads to an oxide linkage. At the same time, ligand-exchange reactions took place to balance the ratios of the titanium species.\(^{32}\) These condensation reactions were initiated from the surfaces of PSA spheres, on which the chelated titanium species condensed to form the TiO\(_2\) wall. As these condensation reactions proceeded, the TiO\(_2\) layer grew and filled the voids and formed an integrated TiO\(_2\) framework. When calcined at 400 °C to remove polymer templates, HOP TiO\(_2\) was fabricated easily.

**UV–Vis Absorbance and Photoelectrochemical Properties of HOP TiO\(_2\).** When the mixture of PSA colloid, triblock copolymer P123, and titania precursors was cast on the fluorine-doped SnO\(_2\) conductive glass and then treated using the procedure described above, HOP TiO\(_2\) photoelectrodes could be directly fabricated and further sensitized by CdS.

Figure 5 presents the UV–vis absorbance and photocurrent of the CdS-sensitized HOP TiO\(_2\) photoelectrode as a function of CdS deposition cycles under the irradiation of 365 nm UV light and an anodic bias of 0.4 V (vs Ag/AgCl). For the sake of comparison, a CdS-sensitized P-25 photoelectrode was also fabricated and measured for UV–vis absorbance and photocurrent. Both HOP TiO\(_2\) and P-25 films showed a rise and fall in photocurrent, which closely followed the intensity of the illumination. Although the two kinds of film showed increased absorbance in the visible light with the deposition cycles of CdS as shown in the UV–vis curve in Figure 5b and d, their photocurrents became drastically decreased after more than five deposition cycles of CdS for the HOP TiO\(_2\) films and three deposition cycles for P-25 films. This phenomenon could be attributed to the following two causes: i) The small CdS crystallites grew and aggregated into large crystallites with more CdS depositions, excessive growth, and aggregation of CdS crystallites will increase the chances of recombination of photoelectrons and holes, decreasing the magnitude of photoelectrochemical properties.\(^{7}\) ii) The transport of photoexcited electrons/holes on CdS becomes more difficult with thicker CdS.\(^{9}\) Even so, the HOP TiO\(_2\) film exhibited considerably higher photocurrent than the P-25 film. The highest photocurrent for the HOP TiO\(_2\) film (after 5 CdS deposition cycles) was 50% higher than that of the P-25 film (after 3 CdS deposition cycles). Increasing the number of CdS deposition cycles further expanded the difference between the two films. After 10 cycles, the photocurrent of the HOP TiO\(_2\) film was three times as large as that of the P-25 film. This means that nano TiO\(_2\) with HOP structure performs photoelectric conversion more efficiently under UV light than P-25.

Because both TiO\(_2\) (a band gap of ca. 3.2 eV) and CdS (a band gap of ca. 2.4 eV) can be photoexcited under UV irradiation, the CdS-sensitized TiO\(_2\) photoelectrode was found to have four types of electronic excitation and transfer under UV irradiation, as shown in Scheme 3: a) TiO\(_2\) absorbed UV light, became excited to its conduction band minimum (CBM), and then tunnelled into the fluorine-doped SnO\(_2\) substrate to form photocurrent. b) CdS absorbed UV light, became excited to its CBM, and formed a photocurrent. c) CdS absorbed UV light and became excited to its CBM, and then the photoexcited electrons flowed to the lower CBM of TiO\(_2\) and formed a photocurrent. This process is also called sensitization.\(^{8,10}\) d) TiO\(_2\) absorbed UV light and became excited to its CBM, then the photoexcited electrons recombined the holes of CdS which have a higher valence band maximum (VBM), and the remaining electrons on the CdS CBM then tunnelled into the current collector fluorine-doped SnO\(_2\) substrate. This process is also called the Z-scheme.\(^{9}\) For process (a) photoelectrochemical properties were determined solely by the morphology and structure of the TiO\(_2\) film. For processes (b), (c), and (d), TiO\(_2\)
was the main material for the photoelectrode and CdS was found to play the role of doping material. In this way, there existed a synergistic effect of TiO$_2$ and CdS on the electronic excitation and transfer. Accordingly, the distribution status of CdS within the TiO$_2$ film has an important influence on the final structure and function of the film. The hierarchically ordered macropore and mesopore structure certainly makes a positive contribution to the enhancement of photoelectric properties. As shown in Figure 6a and b, after 10 deposition cycles, CdS can still be equably deposited on the TiO$_2$ walls without blocking pores. The macropores of the HOP TiO$_2$ can provide a highway through which more Cd$^{2+}$ and S$^{2-}$ ions can access and distribute themselves evenly throughout the TiO$_2$ framework to form CdS nanocrystals. This hybrid nanostructure of TiO$_2$ and CdS can decrease the rate of recombination of the photoelectrons and holes and facilitate the transport of photoexcited electrons between CdS and TiO$_2$, increasing the photocurrent. For P-25 films (Figure 6c and d), after 10 deposition cycles, a layer of CdS became visible on the surface of the P-25 compact film. The phase separation caused the transport of photoexcited electrons and holes between TiO$_2$ and CdS, which had an adverse impact on the photoelectrochemical properties. Well-ordered three-dimensional pore structure in the HOP TiO$_2$ was still able to provide large amounts of specific surface area and high porosity. Accordingly, more Cd$^{2+}$ and S$^{2-}$ ions were adsorbed to form CdS. As a result, as shown in Figure 5b and d, the HOP TiO$_2$ film showed much higher absorbance at the visible region after the same number of CdS depositions, indicating that the ability of the HOP TiO$_2$ film to harvest light increases after sensitization with CdS.

Figure 7 depicts the photocurrent of HOP TiO$_2$ and P-25 photoelectrodes as a function of CdS deposition cycles under visible light irradiation at 445 nm. Both HOP TiO$_2$ and P-25 films showed a rise and fall pattern in the photocurrent, which closely matched changes in illumination over time. Because of its high band gap, TiO$_2$ could not be excited by the visible light, and the photocurrent of bare TiO$_2$ was almost zero under visible light irradiation. For this reason, there were only two possible types of electronic excitation and transfer under visible

Figure 6. SEM images of (a) bare HOP TiO$_2$, (b) HOP TiO$_2$ after 10 cycles of CdS coating, (c) bare P-25, and (d) P-25 after 10 cycles of CdS coating.
light irradiation, as shown in Scheme 3b and c. Thanks to its specific HOP structure, the HOP TiO2 film still showed much higher photoelectric conversion efficiency than the P-25 film under visible light irradiation. The photocurrent of HOP TiO2 decreased after more than seven cycles of CdS and that of P-25 decreased after three. The highest photocurrent of the HOP TiO2 film (after seven CdS deposition cycles) was around 70% higher than that of the P-25 film (after three CdS deposition cycles). After ten deposition cycles, the photocurrent of the HOP TiO2 film was four times higher than that of the P-25 film.

Therefore, the HOP TiO2 film exhibited much better photoelectrochemical properties and more pronounced light harvesting properties than the P-25 film under either UV or visible light irradiation, and it may be suitable for more applications.

**Photoelectrocatalytic Activity of HOP TiO2.** Nano TiO2 is a promising photocatalyst. However, when TiO2 nanoparticles are used as photocatalysts, they usually aggregate, which decreases photocatalytic activity. It is also difficult to separate and recycle the TiO2 nanoparticles from the solution, which largely limits their practical application. Herein, the as-obtained HOP TiO2 photoelectrode was found to be useful as a photoelectrocatalyst to overcome these problems. A comparison of the photoelectrocatalytic activity of HOP TiO2 and P-25 on Rhodamine B under UV irradiation is shown in Figure 8. As expected, the residual Rhodamine B content decreases with the increasing irradiation time. After the natural logarithm of residual phenol concentration vs UV irradiation time, the linear relationship of ln (C/C0) vs time shows that the photoelectrocatalytic degradation of Rhodamine B follows pseudo-first-order kinetics: ln (C/C0) = −kt, where C/C0 is the normalized Rhodamine B concentration, t is the reaction time, and k is the apparent reaction rate in min−1. The apparent photoelectrocatalytic degradation rate constant by the HOP TiO2 is 3.52 × 10−3 min−1, which is about two times as high as that by P-25, 1.85 × 10−3 min−1. This improved photoelectrocatalytic activity can be attributed to the ordered macropore and mesopore structure of the HOP TiO2 or to its large surface area and pore volume, which can facilitate the mass transport and the absorption/desorption process of Rhodamine B and oxygen.
CONCLUSION

Based on this study, we have successfully fabricated the HOP TiO2 by a one-pot self-assembly method. In this approach, when the mixture of monodisperse polymer colloid, triblock copolymer P123, and titania precursors are cast on a substrate for solvent evaporation, the polymer spheres can be assembled into three-dimensional ordered array, while the titania precursors can be in situ chelated and further catalyzed for hydrolysis and condensation by the carboxylic acid groups of polymer spheres to form TiO2 walls around the surfaces of polymer spheres, directly yielding large-area HOP TiO2 when treated with heat. This as-obtained HOP TiO2 shows far better UV−vis absorption, photoelectrochemical properties, and photoelectrocatalytic properties than commercial TiO2 (P-25) and may find more and better applications in photoelectrodes, dye-sensitized solar cells, and photoelectrocatalysts. This method can be extended for fabrication of other oxides (zinc oxide, zirconia, tin oxide) with hierarchically ordered porous structures.

ASSOCIATED CONTENT

Supporting Information

SEM images of PSA film prepared using the EISA method, SEM images, XRD, and nitrogen adsorption/desorption isotherm of TiO2 prepared with different conditions, FTIR spectra of PSA, PSA/titania hybrid, pure PAA and PAA/titania hybrid. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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