Interface engineering of TiO₂@PANI nanostructures for efficient visible-light activation

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Abstract. Core-shell-structured TiO₂@PANI composites were fabricated using negatively charged titanium glycolate (TG) precursor spheres, which were decorated using hydrochloric acid; subsequently, the uniform polyaniline (PANI) layer could be attached onto the surface of the polystyrene spheres by *in situ* chemical oxidative polymerization and finally, the resulting PANI-grafted TG were allowed to hydrolyse by treating the material with hot water. The TGs were transformed to porous TiO₂, leading to the formation of core-shell TiO₂@PANI composites. The resulting TiO₂@PANI composite photocatalysts were characterized by X-ray diffraction, scanning electron microscopy, ultraviolet-visible diffuse reflection spectroscopy and photoluminescence spectroscopy. Significantly, the TiO₂@PANI composite photocatalysts exhibited dramatically enhanced photo-induced electron-hole separation efficiency, which was confirmed by the results of photocurrent measurements. PANI was dispersed uniformly over the porous TiO₂ surface with an intimate electronic contact on the interface to act cooperatively to achieve enhanced photocatalytic properties, indicating that core-shell TiO₂@PANI composite photocatalysts could be promising candidate catalysts under visible-light irradiation. The mechanism of enhancing photocatalytic activity was proposed on the basis of the experimental results and estimated energy band positions.

Keywords. Photocatalysis; TiO₂-based materials; heterojunction; efficient charge separation.

1. Introduction

Semiconductor photocatalysis has received worldwide interest in the field of completely degraded or mineralized organic pollutants in recent decades [1,2]. Fujishima and Honda published relevant reports on discovering a novel photocatalytic evolution method for TiO₂ electrodes in 1972. Since then, TiO₂-based hybrid materials have become popular due to environmental viability with great chemical stability, they also can absorb photons and then produce photo-excited charges and they can drive catalysis reactions for wastewater treatment. However, the fast recombination rate of photo-generated electrons (e⁻) and holes (h⁺) in bulk TiO₂ and the confined utilization of solar light impair their further applications.

To overcome the problems mentioned above, tremendous efforts have been made to enhance sunlight-harvesting, reduce the recombination of photo-induced carriers, including doping elements, combining with polymers, coupling with foreign semiconductors and inducing defects [3–5]. Polyaniline (PANI) has been considered as a significant photocatalyst to expand spectral responses of TiO₂ effectively [6–8]. In the photocatalytic system PANI/TiO₂, PANI shows unique properties with a rapid charge separation capability, relatively slow

charge recombination rate and good stability and thus has a wide range of potential industrial applications. Moreover, PANI is an excellent h⁺ transporting material which behaves like a p-type semiconductor [9,10]. According to previous reports, a large number of approaches have been developed to synthesize TiO₂/PANI composites which exhibit low control on particle size and dispersion [11,12]. For example, it was reported that PANI/TiO₂ nanocomposites were prepared by mixing commercial TiO₂ nanopowders and PANI through chemical oxidative polymerization. The composites were evaluated to degrade methylene blue under visible light [13]. It is worth noting that PANI plays an important role in photocatalytic performance, because the presence of PANI molecules could prevent TiO₂ aggregation, and at the same time sensitize TiO₂ NPs in comparison with bare TiO₂ NPs. Unfortunately, the disordered dispersion of particles and unclear composite structures using a physical mixing method may lead to adverse effects. In order to avoid above disadvantage, Li *et al* [14] have fabricated a strong PANI layer *via* self-assembled monolayers of aminopropyltriethoxysilane on the surface of TiO₂ nanoparticles. The PANI/SAM-TiO₂ nanocomposites exhibit much better photodegradable ability of methyl orange (MO) than bare-TiO₂ NPs under sunlight. Similar results were also reported by Liao *et al* [15], who reported on a core-shell

PANI/M-TiO₂ photocatalyst combined with a hydrothermal method and a chemisorption approach. Based on band matching and interface engineering, the as-prepared catalysts afford high catalytic activity for MO under UV-light and sunlight irradiation. However, the photocatalytic efficiencies of these conducting polymer-modified TiO₂ nanoparticles are somewhat limited by low visible-light harvest efficiency. To enhance the efficiency of visible-light absorption for sensitized TiO₂ hybrids, porous TiO₂ spheres would be beneficial for visible-light enhancement owing to the large surface area which can enhance mass transport, and unique optical properties allowing intense scattering and light trapping.

For this purpose, we have prepared core-shell-structured TiO₂@PANI composites on the surface of titanium glycolate (TG) precursor spheres *via* electrostatic interaction. We also examined the activity of TiO₂@PANI in the photocatalytic degradation of MO under visible-light irradiation. Based on a series of systematic investigations, we proposed a possible mechanism for enhancing photocatalytic activity. Compared with conventional PANI-modified TiO₂ photocatalysts, we expected that the large specific surface area and unique core-shell porous structure of TiO₂@PANI could be beneficial for the harvest of visible light. Meanwhile, a heterojunction built between the PANI and TiO₂ could facilitate the separation of photo-generated charges.

2. Materials

Tetrabutyl titanate (TBOT), ethylene glycol (EG), ammonium persulfate (APS), aniline (C₆H₇N), acetone and acetic acid were purchased from Sinopharm Chemical Reagent Company (Shanghai, China).

2.1 Preparation of TG precursor spheres

TG precursor spheres were synthesized according to the route reported previously [16]. In detail, a certain amount of Ti(OBu)₄ was dropped into 50 ml of EG and the mixture was stirred for 4 h. Then, 140 ml of acetone, 2.3 ml of deionized water and 2 ml of acetic acid were mixed together and kept under vigorous stirring again for another 3 h and obtained a white precipitate by means of centrifugation. The products were thoroughly washed with ethanol.

2.2 Preparation of core-shell TiO₂@PANI composites

In a typical procedure, the as-prepared TG powders were suspended in 20 ml of 0.01 mol l⁻¹ HCl solution under ultrasonication for 30 min to reduce the aggregation of the TG nanoparticles, termed solution A. The desired amount (Ti/ANI = 1:0.3) of aniline was dissolved in 20 ml of HCl (0.01 mol l⁻¹) solution and termed solution B. We then mixed the above two solutions A and B and stirred for another hour. After that, 10 ml of HCl (0.01 mol l⁻¹) solution containing APS with an equimolar ratio of aniline was slowly added

dropwise to a well-dispersed suspension with continuous stirring at 0°C in an ice-water bath. After 4 h, an ideal degree of polymerization was gained, and a dark-green precipitate was obtained after centrifugation. Then, the precipitate was washed repeatedly with ethanol and deionized water. Finally, core-shell TG@PANI composites were achieved by drying the as-obtained precipitate under vacuum at 60°C for 12 h.

0.4 g TG@PANI composite was dispersed in 50 ml of deionized water, and refluxed at 100°C for 6 h under ultrasonic vibration conditions. A porous TiO₂@PANI composite was obtained after the centrifugation of the mixtures, washing the precipitates several times with deionized water and ethanol and drying the powders at 80°C for 12 h.

2.3 Fabrication of porous TiO₂ nanoparticles

A certain amount of TG nanoparticles was dispersed in 50 ml of deionized water, and refluxed at 100°C for 6 h under ultrasonic vibration conditions. Mesoporous TiO₂ nanoparticles were obtained after the centrifugation of the mixtures, washing the precipitates several times with deionized water and ethanol and drying the powders at 80°C for 12 h.

2.4 Photocatalytic activities

The photocatalytic activities of samples were examined by degradation of MO under visible light using a 300 W xenon lamp (Beijing Perfectlight, PLS-SXE 300c). In the experiment, 100 mg of photocatalyst was added into MO solution (10 mg l⁻¹) in a quartz reactor, which was equipped with circulating water, thus the heating effect can be ignored during the reaction. The suspension was stirred in the dark for 30 min to reach equilibrium before illumination. 3 ml of aliquots was collected at given time intervals and the change of MO absorbance was analysed quantitatively by monitoring its absorbance at 465 nm using a UV-Vis spectrophotometer (Shimadzu UV-2450).

2.5 Photoelectrochemical measurement

The electrochemical measurements were conducted in a conventional three-electrode system. The counter electrode was a Pt plate and an Ag/AgCl electrode acted as a reference electrode. The working electrode was prepared on a glassy carbon electrode. Typically, the sample powder (4 mg) was ultrasonicated in 2 ml of anhydrous ethanol and Nafion mixture to obtain a slurry. Then, the slurry was dropped on the surface of the glassy carbon electrode. After drying, the three-electrode cell system was immersed in a 0.2 M Na₂SO₄ aqueous solution. A 300 W Xe lamp was used as a light source. The photocurrent-time-dependent experiments were conducted under chopped irradiation with 25 s light on/off cycles at an open-circuit potential. Electrochemical impedance spectroscopy (EIS) tests were conducted through a CHI-660e electrochemical workstation and the electrolyte contains 0.01 M K₃[Fe(CN)₆]/K₄[Fe(CN)₆] and 0.1 M KCl.

Figure 1. Schematic illustration of preparation of TiO_2 @PANI composites.

Photoluminescence (PL) spectroscopy was conducted using terephthalic acid (TA) as a probe molecule.

2.6 Characterization

The characterization of crystal structure of photocatalysts with $\text{Cu K}\alpha$ radiation was carried out using powder X-ray diffraction (XRD, Bruker D8). A field-emission scanning electron microscope (SEM, Zeiss Supra 55VP) was utilized to determine the surface morphology and crystal microstructures of samples. UV-vis diffuse reflectance spectroscopy (DRS) was carried out on a spectrophotometer (SOLID 3700, Shimadzu). The PL spectra of samples were probed on a fluorescence spectrophotometer (Hitachi F-4500). Surface area and porosity of samples were calculated using nitrogen adsorption on a surface analyser (Micromeritics ASAP 2020). The ζ -potentials of aqueous samples were measured using a Zetasizer Nano ZS 128 system (Malvern Instruments).

3. Results and discussion

TGs were first synthesized following a previously reported procedure [16]. As illustrated in figure 1, monodisperse TG nanospheres were immersed in a dilute hydrochloric acid system forming positive charges on their surface, and then aniline was adsorbed onto TG spheres by *in situ* oxidative copolymerization of aniline monomers in the presence of APS as the oxidant. The resulting PANI-grafted TGs were allowed to hydrolyse by treating the material with hot water. The TGs were transformed to porous TiO_2 leading to the formation of core-shell TiO_2 @PANI composites.

The crystal structure of TiO_2 particles and PANI shell can be further explored by XRD. The XRD patterns of the synthesized TG (A), TiO_2 nanospheres (B) and TiO_2 @PANI (C) are displayed in figure 2. It reveals that the TG precursors are amorphous with no characteristic diffraction peaks (figure 2A). After reflux heating, the main peaks at 2θ values of 25.3, 37.9, 48.1, 54.0, 55.2 and 62.8° in curve B can be indexed to the (101), (004), (200), (105), (211) and (204) crystal planes of anatase, which match well with JCPDS 21-1272 [17]. Moreover, figure 2C shows that TiO_2 particles exist in the PANI shell and also indicates that the crystal structure of TiO_2 can be well maintained during the PANI polymerization process under acidic conditions. The XRD patterns of

Figure 2. XRD patterns of the synthesized TG (A), TiO_2 nanospheres (B) and TiO_2 @PANI (C).

PANI@TiO_2 composites show that the peak positions hardly changed compared with the TiO_2 , indicating that the modification with PANI has no impact on the lattice structure of TiO_2 [18].

Figure 3 shows the representative SEM images of the prepared TiO_2 spheres and TiO_2 @PANI composites. Based on the SEM images of figure 3A and B, we can find that the average diameter of TiO_2 spheres is about 300 nm, and the size distribution is highly uniform. As shown in figure 3C and D, after the chemical oxidative polymerization of aniline, PANI is deposited onto the surface of TiO_2 spheres, and the surface of TiO_2 @PANI spheres becomes rough compared with that of original TiO_2 template spheres.

ζ -Potential measurements can quantify this surface charge on TG precursors and hence help in establishing the dispersion stability. For ζ -potential measurements, the surface potential of TG showed a range varying from 45 mV at pH 2 to -40 mV at pH 12, as shown in figure 4. TiO_2 @PANI nanocomposites were synthesized by treating with TG and aniline suspension at room temperature in acidic medium. In this acidic pH range, ζ -potentials of TG are determined to be negative. By electrostatic interaction, aniline can easily adsorb and wrap TG molecules, and then APS can provide a further *in-situ* surface oxidative graft polymerization to form a dense PANI

Figure 3. Morphology of TiO_2 spheres (A, B) and $\text{TiO}_2\text{@PANI}$ (C, D) at different magnifications.

Figure 4. Zeta potential of TG colloid systems as a function of pH.

layer, so as to offer an opportunity for close contacts between the two components.

The porosity and surface area of samples were measured using nitrogen adsorption–desorption isotherms. The N_2 adsorption–desorption isotherm of TiO_2 (A) and $\text{TiO}_2\text{@PANI}$ (B) yielded a characteristic type-IV isotherm with a small hysteresis loop. This indicated that the materials have a mesoporous structure. It is easier to obtain nanoporous TiO_2 by treating the TG precursor with water *via* refluxing, without

the addition of any surfactant as the template. The pore-size distribution of TiO_2 calculated based on the adsorption branch of the isotherm (figure 5B) revealed a narrow pore-size distribution with an average value of 13 nm. For $\text{TiO}_2\text{@PANI}$, the pore-size distribution curve reveals two sharp peaks were found with a pore diameter of 18.5 and 22 nm. The BET and Langmuir surface areas of the TiO_2 and $\text{TiO}_2\text{@PANI}$ were found to be 113 and 182 $\text{m}^2 \text{g}^{-1}$, respectively, due to the large voids created between the crystallites found on the surface areas of TiO_2 and $\text{TiO}_2\text{@PANI}$ (figure 3).

The optical absorptions of the as-prepared TiO_2 (a), mixture of PANI and TiO_2 (b) and $\text{TiO}_2\text{@PANI}$ (c) were recorded using a UV–vis spectrometer and are shown in figure 6. Pure TiO_2 shows absorption from the UV range up to 400 nm matched well with the band gap of TiO_2 (3.28 eV). The estimated band gap values of the mixture of PANI and TiO_2 (b) and $\text{TiO}_2\text{@PANI}$ (c) are 3.12 and 2.96 eV, respectively. Integration of PANI onto TiO_2 results in stronger absorption at wavelengths longer than 400 nm in the visible region, and the red shift was assigned to exciton formation in the quinoid rings after the *in situ* formation of PANI polymers.

The variations of MO concentrations with irradiation time over samples are shown in figure 7. For comparison, the photodegradation of MO without a photocatalyst (blank) and with PANI, TiO_2 spheres as well as the mixture of PANI and TiO_2 spheres as the reference photocatalysts has been investigated. The reaction mixture was stirred for 30 min in darkness in order to reach adsorption/desorption equilibrium.

Figure 5. Nitrogen adsorption–desorption isotherms and the BJH pore-size distributions of TiO₂ (A, B) and TiO₂@PANI (C, D).

Figure 6. (A) UV–vis DRS and the corresponding plot of $(\alpha h\nu)^2$ vs. $h\nu$ (B) for TiO₂ (a), mixture of PANI and TiO₂ (b) and TiO₂@PANI (c).

The concentration of MO was nearly unchanged in the dark for blank and PANI, however, the other three may show different adsorption ability for MO during the initial dark irradiation, which may be attributed to these different degradation processes. Mainly, TiO₂@PANI with great adsorption capacity is due to its porous structure. There is only a slight degradation of MO by pure PANI and TiO₂ spheres under visible-light irradiation. In contrast, TiO₂@PANI exhibited

excellent photocatalytic degradation activity. As observed in figure 7A, it can be seen that 81% of MO was decomposed in 110 min when TiO₂@PANI was used as the photocatalyst, while only 58% of MO was degraded by the mixture of PANI and TiO₂ spheres. The photocatalytic degradation rate constants (k) are shown in figure 7B. The reaction kinetics in the photocatalytic process follows the first-order kinetics equation: $\ln(C/C_0) = kt$, where k is the apparent rate constant

Figure 7. Photodegradation of MO aqueous solution (A) and the pseudo-first-order kinetic plots (B) of different samples.

[19]. The rate constants corresponding to TiO_2 spheres, the mixture of PANI and TiO_2 spheres and $\text{TiO}_2@\text{PANI}$ were estimated to be 0.0007, 0.0082 and 0.0149 min^{-1} , respectively. The excellent photocatalytic performance of $\text{TiO}_2@\text{PANI}$ can be attributed to its enhanced absorption in the visible-light region, which implies that more photogenerated e^- and h^+ can be created to take part in the photocatalytic reaction process. Moreover, core-shell-structured $\text{TiO}_2@\text{PANI}$ contains two phases in which the interface heterojunction between the TiO_2 and PANI phases can accelerate the separation of charge carriers and improve the transfer rate of the photogenerated e^- and h^+ [6].

PL spectroscopy is carried out to study the efficiency of decrease in the recombination for the photo-induced e^- and h^+ pairs of the materials [20]. A sharp emission intensity indicates that the photo-induced e^- and h^+ are prone to recombination and the lifetime of the photo-induced e^- and h^+ [21,22]. In figure 8, the $\text{TiO}_2@\text{PANI}$ showed less intense PL peaks compared to TiO_2 . In light of the above results, it can be concluded that PANI decreases the PL intensity, leading to a lower e^- - h^+ recombination rate.

It has been widely accepted that the e^- - h^+ separation efficiency has great impact on the activity of a photocatalyst and it can be revealed by its corresponding photoelectrochemical behaviour [23]. Therefore, the transient photocurrent responses of electrodes were recorded *via* several on-off cycles under visible-light irradiation (figure 9). It was noted that the photocurrent increased sharply upon light irradiation. Subsequently, it rapidly decreased to zero on removing irradiation. The TiO_2 sphere electrode shows almost no photocurrent density which is attributed to the weak response under visible light and the fast e^- - h^+ recombination in the TiO_2 . The photocurrent intensity of $\text{TiO}_2@\text{PANI}$ was nearly 1.4 times higher than that found for the mixture of TiO_2 and PANI. This demonstrated that a more effective separation of the photo-induced e^- and h^+ and a faster interfacial

Figure 8. PL spectra of TiO_2 and $\text{TiO}_2@\text{PANI}$ at an excitation wavelength of 325 nm.

charge transfer occurred in the heterostructures and therefore the higher photocatalytic activity.

$\text{TiO}_2@\text{PANI}$ photocatalysts can produce $\bullet\text{OH}$ radicals during the photocatalysis process using a method described previously [24]. As far as we know, the $\bullet\text{OH}$ radicals would react with TA in basic solutions to generate TAOH and then a fluorescence signal can be found centred at 426 nm [25]. Figure 10 shows significant fluorescence signals associated with TAOH, generated upon visible-light irradiation, which demonstrate that the photoexcited h^+ can oxidize surface-adsorbed hydroxyl groups and water to generate $\bullet\text{OH}$ radicals. Thus PANI might be responsible for the visible-light induced photocatalytic degradation by improving the photo-generated e^- and h^+ separation as well as charge migration,

Figure 9. Transient photocurrent–time ($I-t$) curves of samples in 0.2 M Na_2SO_4 aqueous solution under the irradiation of visible light ($\lambda \geq 420$ nm).

Figure 10. PL spectral changes with irradiation time for TiO_2 @PANI in 5×10^{-4} M basic solution of TA.

allowing both the e^- and h^+ to take part in the overall photocatalytic reaction.

As shown in figure 11, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of PANI were 0.8 and -1.9 V vs. NHE, respectively [26]. And the valence band and conduction band (CB) of TiO_2 was 3.0 and -0.2 V vs. NHE, respectively [12]. The energy levels of PANI matched well with the band gap of TiO_2 . Under visible-light irradiation, PANI can absorb visible light to induce the $\pi-\pi^*$ transition, exhibiting the excited-state e^- of the HOMO orbital to the LUMO orbital, the excited-state e^- from the PANI molecules injected into the CB of TiO_2 and finally react with adsorbed oxygen and water to yield superoxide radicals and hydroxyls, respectively. The generated hydroxyl and superoxide

Figure 11. Mechanism diagram of photocatalytic reaction of TiO_2 @PANI under visible light ($\lambda \geq 420$ nm).

Figure 12. EIS Nyquist plots of samples under visible-light irradiation.

radicals can oxidize MO. Therefore, the delocalized conjugated π structures cause a rapid separation of photo-induced charges and a slow charge recombination in e^- -transfer processes. Remarkable improvement of visible-light photocatalysis with conjugative π structure material-modified core-shell mesoporous TiO_2 microspheres was observed, which significantly enhances the photocatalytic activity of core-shell TiO_2 @PANI composites.

In order to investigate the e^- -transfer resistance and the charge separation process at the surface of the photoelectrodes, EIS measurements were performed [27]. Figure 12 presents a typical Nyquist plot for TiO_2 , mixture and TiO_2 @PANI under visible-light irradiation. The smaller radius of the Nyquist circle represents the lower charge-transfer resistance [28,29]. In this case, the TiO_2 @PANI showed a smaller arc radius compared to TiO_2 , mixture of TiO_2 and PANI under visible-light irradiation, which indicates the more effective separation of photogenerated e^-h^+ pairs and faster interfacial charge transfer on the surface of TiO_2 @PANI. Therefore, the TiO_2 @PANI are strongly affected by the photogenerated charge separation, which is related to the synergistic effect of PANI and TiO_2 .

4. Conclusions

In summary, we demonstrated a facile route to fabricate core-shell-structured TiO₂@PANI composites by *in situ* oxidative copolymerization of PANI monomers on the surface of TG precursor spheres *via* electrostatic interaction. Compared with pure TiO₂ and mixture of TiO₂ and PANI, core-shell TiO₂@PANI composites show a lower charge-transfer resistance, higher photocurrent and enhanced photoelectric properties. The superior photocatalytic effect of the TiO₂@PANI composites is attributed to the synergistic effect between the PANI and TiO₂ which promotes migration efficiency of the photo-generated carriers on the TiO₂-PANI interface. This hetero-junction results in an efficient charge separation at the interface, which is confirmed by the photoelectron test and PL spectroscopy. This work presents a simple and economical method to synthesize efficient and stable visible-light-responsive TiO₂ photocatalysts for wide applications in environmental remediation.

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