

Catalytic property of TiO₂/PS complex nanoparticles prepared via a novel TSM

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Abstract. With an average size of 7 nm and good catalytic property under the natural light, TiO₂/PS complex nanoparticles were successfully prepared through a novel two-step method (TSM) from TiCl₄, used as both the catalyst for polymerization of styrene and Ti source, and styrene monomer and characterized by TG-DTA, XRD, IR, TEM and UV-Vis techniques. Its catalytic property was evaluated by the decolourization and degradation of dye MB solution under the natural light. From its TEM, the particles with an average size of 7 nm were observed without the separation of TiO₂ and PS phases, i.e., TiO₂/PS was hybrid material in nanosize scale. IR spectrum of TiO₂/PS showed increase of unsaturated degree and growth of the group C=O on the chain of PS and Ti–O–C coordination bond between TiO₂ and PS. The nanosize of the TiO₂/PS complex particles and the conjugated structure and polar groups of PS were advantageous to good adsorptive property and strong interaction of PS and TiO₂. And they brought multi-functions of inorganic and organic materials in the single material. Catalytic experiments indicated that the complex nanoparticles could catalytically degrade dye MB solution in 10 min under the natural light while P25 basically showed adsorptive property for MB molecules under the same conditions.

Keywords. TiO₂; PS; complex nanoparticles; preparation; catalytic property; natural light.

1. Introduction

Semiconductor photocatalysis had received considerable attention as an alternative remediation technology of hazardous wastes, contaminated groundwater, and air contaminants. In recent years, considerable efforts had been put into TiO₂ due to its unique properties (Hoffmann *et al* 1995) such as inexpensive, safe, biologically and chemically inert, stable with respect to photo-corrosion. Although titanium dioxide was the most popular photocatalytic material (Monredon *et al* 2002), it was active only in the ultraviolet (UV) region because of its wide bandgap ($E_g=3.2$ eV). Therefore, many researchers (Wang *et al* 1998; Chen *et al* 2000; Asahi *et al* 2001; Ohno *et al* 2003; Wang *et al* 2003) had attempted to modify the electronic properties of TiO₂ in order to improve its catalytic activity under natural/sun light.

Although the dye-sensitized TiO₂ showed excellent power conversion performances, their catalytic applications were still limited due to stability problems such as the

dissolubility and the photocatalytic degradation of the dye. The capability of some polymers such as PPVs and PTS (Savenije *et al* 1998, 2000; Salafsky *et al* 1998; van Hal *et al* 1999) to act as sensitizer of TiO₂ had been demonstrated for the visible light. The photo-induced charge transfer from the polymers to TiO₂ had been found to be possible when the thickness of the polymer was below the exciton diffusion length (~20 nm) (Savenije *et al* 2000). However, the major problem, which had to be solved in order to improve the performance of polymer/TiO₂ materials, was the poor interaction and adsorptive properties of the polymer to nanosized TiO₂.

In this paper, we have reported a novel two-step method (TSM) and successfully prepared TiO₂/PS complex nanoparticles with an average size of 7 nm from TiCl₄ and monomer styrene (S), in which TiO₂ and PS were closely linked by Ti–O–C bond. The sample was characterized by TG-DTA, XRD, IR, TEM, UV-Vis and catalytic experiments under natural light. TiO₂/PS complex nanoparticles showed very good catalytic property for the degradation of methylene blue (MB) solution. The nanoparticles fully degraded dye MB solution in 10 min under the natural light while P25 basically showed adsorptive property.

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2. Experimental

2.1 Reagents

Titanium chloride (TiCl_4), monomer styrene (S), and methylene blue (MB) were of reagent grade; anhydrous ethanol (EtOH) and deionized water were used thoroughly. Commercial Degussa P25 was a mixture of anatase (80%) and rutile (20%) and its particle size was in the range of 20–40 nm.

2.2 Preparation of TiO_2/PS complex nanoparticles

TiO_2/PS complex nanoparticles were prepared via a novel two-step method (TSM), developed by our group and described as follows: (I) *Ionic polymerization step*: Under room temperature and vigorous stirring conditions, a suitable amount of $\text{TiCl}_4/\text{EtOH}$ solution was slowly added dropwise to 20 ml styrene (S). S was catalytically polymerized to produce polystyrene (PS) and during the polymerizing process, Ti^{4+} was spontaneously mixed into PS base to form the orange precursor Ti^{4+}/PS due to the coordination between Ti^{4+} and S/PS. The coordination of $\text{S/PS} \rightarrow \text{Ti}^{4+}$ was formed by S and/or PS with π electrons as electron donors and Ti^{4+} with unoccupied valence orbits as electron acceptor. (II) *Heat conversion step*: This precursor Ti^{4+}/PS was calcinated at 300 °C for a proper time under air atmosphere and the black sample, called TiO_2/PS , was obtained. Appropriate treatment could bring about the conversion of Ti^{4+} to TiO_2 (as seen in XRD of TiO_2/PS) and a new structure of PS (seen from IR spectrum of TiO_2/PS).

2.3 Apparatus and characterization

TG–DTA analysis (DT-40) was used. Transmission electron microscopy (TEM) image was obtained with a JEM-100SX Electron Microscope. The sample was dispersed in anhydrous ethanol and cast on carbon-coated copper grid. XRD technique (Rigaku D/max-3 C) was used for studying the phase structure. IR spectra were recorded on Nicolet NEXUS 670 FT–IR spectrophotometer. UV–Vis absorption spectra of the solid samples were carried out and recorded on an UV-240 spectrophotometer using diffuse reflection technique. The UV–Vis spectra of the solutions were recorded on HITACHI U-3400 spectrophotometer in the range of 200–800 nm.

2.4 Catalytic experiments

The catalytic property of the sample was evaluated by measuring the decolourizing efficiency and UV-vis spectra

of MB solution at different decolourizing times. The catalytic reaction was performed in a flask under mild conditions such as the natural light and room temperature. 30 mg sample powder was added in 30 ml MB solution of 10 mg/l, the system was stirred for some time, and then the solution, from which the powder was removed, was analysed by recording its UV–Vis spectra and measuring its decolourizing efficiency (D_t %). D_t % was calculated based on the following equation:

$$D_t\% = (A_0 - A_t)/A_0 \times 100\%$$

in which, A_0 and A_t the absorption values of dye solution at initial time, $t=0$ and reaction time, t at 663 nm (the max absorption wavelength of MB solution), respectively.

3. Results and discussion

3.1 Characterization

TG–DTA property of the precursor Ti^{4+}/PS was investigated and the curves are shown in figure 1. Below 230 °C, the loss of weight could be assigned to the release of HCl and monomer S and adsorbed water and H_2O from Ti-OH . The slight loss occurring in the range of 230–390 °C, was due to the polymer crosslink. And in the range of 390–438 °C, the loss was related to breaking main chain and side group of PS. Residue up to 450 °C was TiO_2 . So treating Ti^{4+}/PS at 300 °C for a proper time did not lead to the decomposition of PS while it could bring about the conversion of Ti^{4+} to TiO_2 (as seen in XRD of the sample in figure 2) and the formation of a new structure of PS via the crosslink of PS chains (seen as IR spectrum of the sample in figure 3).

XRD pattern of the sample, TiO_2/PS , is shown in figure 2. In TiO_2/PS , PS was amorphous. In the range of 30–40°, a wide reflection peak indicated the formation of TiO_2 by treating the precursor Ti^{4+}/PS at 300 °C and the directed growth of TiO_2 crystalline along a certain direction under the existence of the polymer PS. In addition, the characteristic

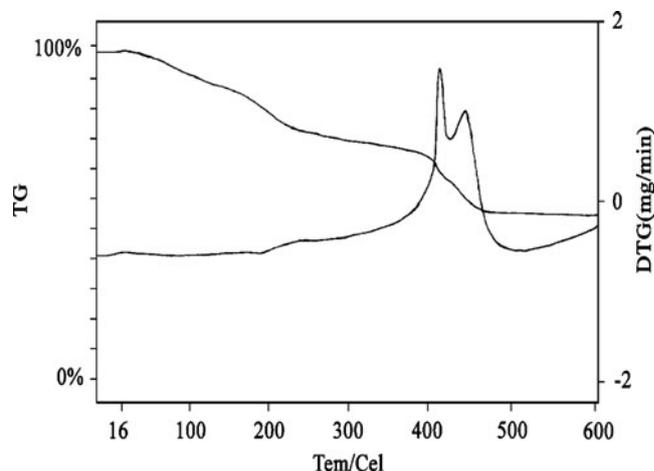


Figure 1. TG–DTA curves of precursor Ti^{4+}/PS .

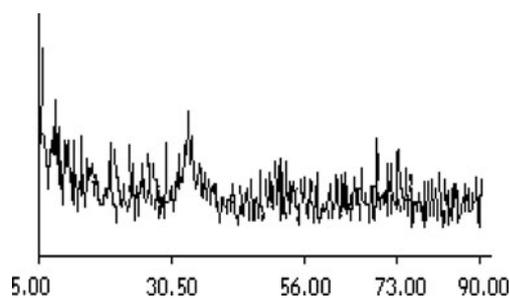


Figure 2. XRD pattern of TiO₂/PS.

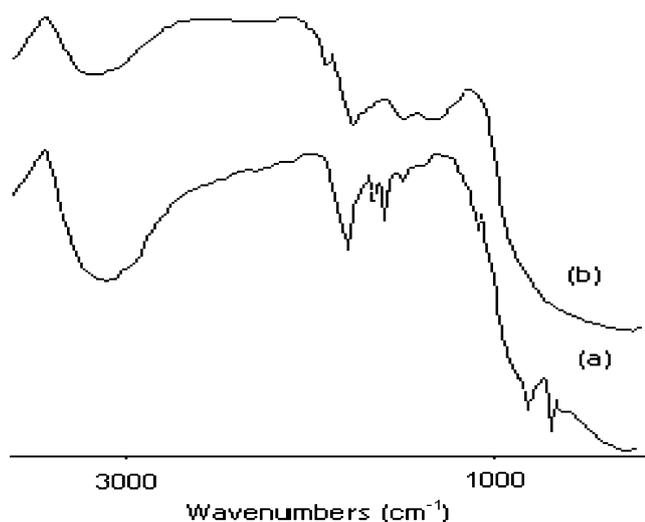


Figure 3. IR spectra of Ti⁴⁺/PS (a) and TiO₂/PS (b).

reflection peaks were considerably broadened, indicating that the crystal lattice of TiO₂ was distorted because of the strong interaction of TiO₂ and PS (Ohno *et al* 2003) and also suggesting a small crystalline size (Xie and Yuan 2003; Zhang and Gao 2003) in agreement with that from TEM.

IR spectra of Ti⁴⁺/PS (a) and TiO₂/PS (b) are shown in figure 3. In the IR spectra of Ti⁴⁺/PS, the broad band at about 3185.19 cm⁻¹ was formed by the peak overlap of -C-H and =C-H of PS and O-H of the adsorbed H₂O. The peaks near 1600·60, 1491·17 and 1449·45 cm⁻¹ were assigned to the characteristic skeleton vibration peak of phenylring (Duan *et al* 2003). The peaks at about 748 and 697 cm⁻¹ were related to single-substrate of phenyl ring. So the styrene was catalytically polymerized by Ti⁴⁺ via an ionic polymerization route. Comparing the IR spectra of TiO₂/PS and Ti⁴⁺/PS, it could be found that the peaks at 1600·60, 1491·17 and 1449·45 cm⁻¹ attributed to the characteristic skeleton vibration (figure 3a), became a broadening and red-shifting band (figure 3b), indicating the increase of conjugated degree on the chain of PS (Zhang and Mou 1994; Jang *et al* 2000; Duan *et al* 2003) and C = O peak at 1700·61 cm⁻¹ and C-O-Ti band at 1265·78 cm⁻¹ (Gao *et al* 2001) appeared in figure 3b. The polar bonds/groups, led to asymmetric structure of π electron on the chain of a conjugated polymer, were found to be advantageous in the effective separation of the photo-generated charges.



Figure 4. TEM image of TiO₂/PS.

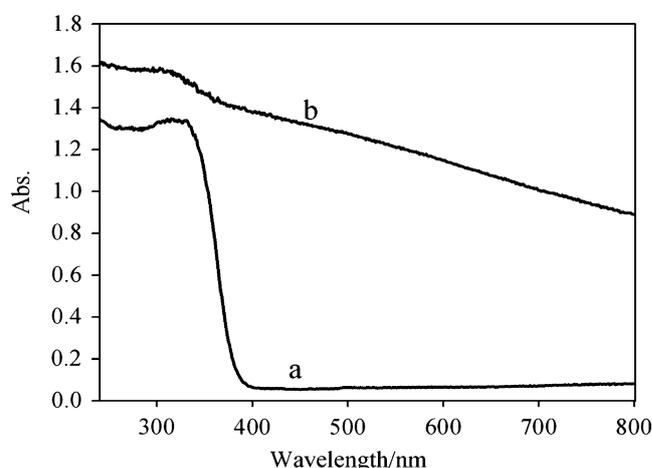


Figure 5. UV-vis spectra of TiO₂ (a) and TiO₂/PS (b).

TEM image of the sample is shown in figure 4. It was observed that the average size was about 7 nm without the separation of organic and inorganic phases. The poor dispersion was possibly related to high surface energy of nanoparticles with such a small size. The nanometer size of TiO₂/PS was advantageous for closely linking TiO₂ and PS together and bringing their functions in the single material. At the same time, it could exhibit much larger efficient areas and more efficient active centres, in favour of pre-adsorption and activation of organic pollutants (Zhang *et al* 2001; Sung-Suh *et al* 2004; Wang *et al* 2004), which was important for the following degradation when it was used as a catalyst.

Therefore, this present method was successful for preparing the nanosized complex material with some strong interaction between TiO₂ and PS.

Figure 5 shows the UV-Vis spectra of TiO₂ (a) and TiO₂/PS (b). It could be concluded that TiO₂/PS could absorb light from UV to visible while TiO₂ only absorbs one below 400 nm due to its wide bandgap ($E_g = 3.2$ eV). Herein, the PS to act as sensitizer of TiO₂ was in agreement with that of PPVs, PTS (Salafsky *et al* 1998; Savenije *et al* 1998, 2000;

van Hal *et al* 1999) and PVC (Ma *et al* 2005). The absorption property of TiO₂/PS was attributed to long conjugated structure and narrow bandgap of PS. So hybridizing TiO₂ and PS with long conjugated structure could largely extend photo-response region of TiO₂ from UV to visible region and it was possible that TiO₂/PS complex material was a promising photocatalytic and photoelectric material for the full use of light, especially natural light.

3.2 Catalytic property

From figure 6, it was found that under the natural light, the decolourization efficiency of MB solution reached 93% in 10 min on TiO₂/PS, while on P25, the efficiency was about

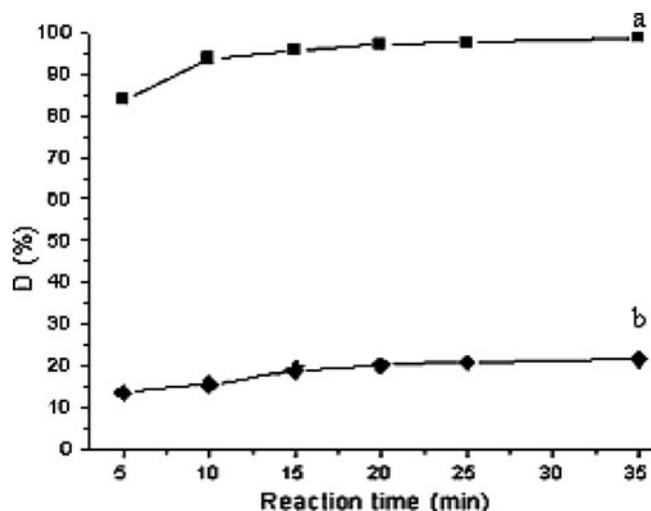


Figure 6. Decolourizing efficiency of MB solution on TiO₂/PS (a) and P25 (b).

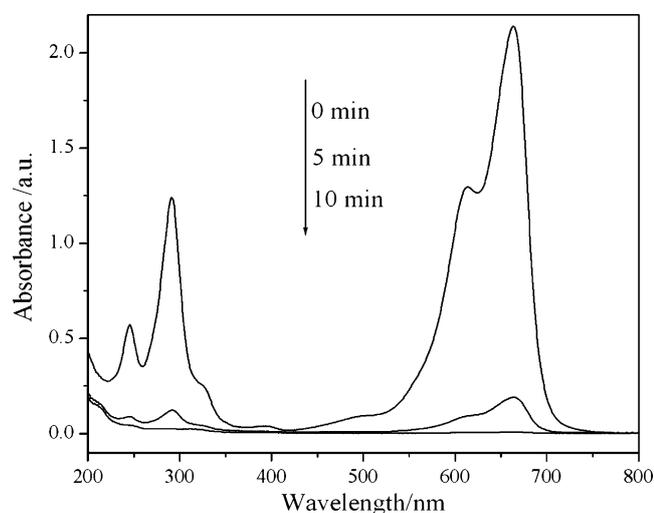


Figure 7. UV-Vis spectra of decolourized MB solution at different times on TiO₂/PS.

20 % in 20 min and basically did not change with further increase of time, which were attributed to the adsorption of MB molecules on the surface of P25 nanoparticles under natural light.

Figure 7 shows the UV-Vis spectra of decolourized MB solutions at different times on the TiO₂/PS. By comparing with the spectrum of MB solution, the intensity of all peaks, corresponding to MB molecule, only decreased with the increase of decolourizing time without any shift in the whole region. This result reflected that MB molecules were strongly adsorbed and possibly destroyed and degraded to inorganic molecules on the TiO₂/PS nanoparticles.

In order to further prove the behaviour of the complex material for decolourizing dye MB solution, the IR spectrum of used TiO₂/PS were also studied. In the IR spectrum of used TiO₂/PS, any characteristic peaks of MB molecule or other degraded pieces did not appear and no distinct changes were observed. There were the characteristic peaks of MB molecules if they were only adsorbed on the surface of TiO₂/PS nanoparticles. This fact confirmed that TiO₂/PS played a role of catalyst by strongly adsorbing dye MB molecules onto its surface and thoroughly degrading them to inorganic molecules.

Under the natural light, high catalytic activity of TiO₂/PS for the decolourization of MB was related to many factors such as the nanosize, the introduction of PS into TiO₂, chemical bond between TiO₂ and PS, long conjugated structure and polar groups of PS, and so on. The smaller the catalyst size is, the higher its catalytic activity is.

As is well known, TiO₂ is induced to generate electron-hole pairs (process 1 in figure 8a) under UV light excitation and the electron-hole pairs bring about following reactions (Cho and Choi 2001). But the photo-generated electron-hole pairs easily recombine (process 2 in figure 8a), which decreases the photocatalytic activity of TiO₂.

In the TiO₂/PS with an average size of 7 nm, TiO₂ hybridized with the conjugated polymer PS on the nano-scale. Black PS had narrow energy gap and could generate electron-hole pairs by absorbing the visible light (process 1

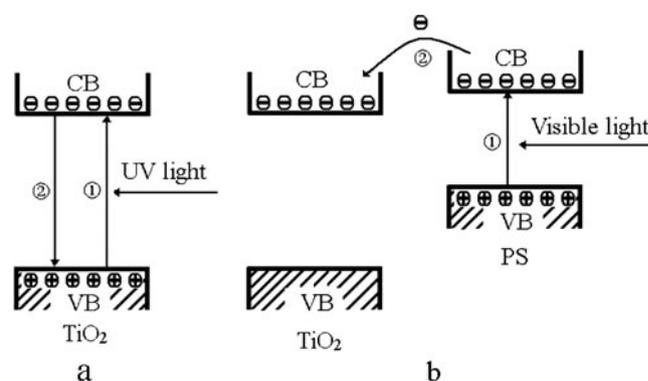


Figure 8. A schematic mechanism of photocatalytic reaction on TiO₂ (a) and TiO₂/PS (b).

in figure 8b) (Zhang *et al* 2009). And the pairs were easily separated by the electron transfer from the conjugated polymer PS to TiO₂ because of higher conductive band (CB) of the PS than TiO₂ and smaller nanosize of less than 20 nm (the exciton diffusion length) (Savenije *et al* 2000) and chemical band between TiO₂ and PS in the TiO₂/PS hybrid complex material. The separated charges brought about the reaction on the surface of the hybrid material. So the recombination of electrons and holes was greatly suppressed in the TiO₂/PS hybrid material because TiO₂ herein acted as a sink for the photo-generated electrons and the catalytic property of the material remarkably improved under natural light.

In addition, the complex catalyst was easily removed and showed good catalytic stability.

4. Conclusions

In summary, we first designed a novel two-step method (TSM) and successfully prepared a new TiO₂/PS complex material with an average size of 7 nm and chemical band between TiO₂ and PS through using the TSM. The catalytic experiment demonstrated that the complex nanoparticles showed extremely high catalytic activity for the decolourization of MB solution under natural light. The main reasons were listed as follows: (a) the small nanosize of the composite catalyst resulted in a larger interface, beneficial to the adsorption and activation of dye MB molecules; (b) hybridization of PS with a large conjugated structure and TiO₂ largely extended photo-response region of TiO₂ from UV to visible region, which greatly enhanced the use of light, especially natural light and increased the amount of photo-generated charges; (c) the photo-induced charges could be easily separated by electron transfer from PS to TiO₂ due to smaller nanosize of less than 20 nm (the exciton diffusion length) (Savenije *et al* 2000) and asymmetric structure of π electron on the chain of a conjugated polymer and the chemical band between TiO₂ and PS. Therefore, the polymer with large conjugated structure as an idea sensitizer could provide an effective modification of the electronic properties of TiO₂ and better catalytic property. So this complex hybrid material was a promising one for effective application in environment treatment under mild conditions without using any special UV light source.

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