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PCBM supported on titania used as an efficient photocatalyst by visible light driven

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Abstract

[6,6]-phenyl-C61-butyric acid methyl ester (PCBM)-modified TiO₂ photocatalyst is prepared by a simple facile chemisorption approach. The photocatalytic activity was obtained for the degradation of nonbiodegradable azodyes methylene blue (MB) under visible light irradiation and the as-prepared samples show an excellent photocatalytic activity. After being modified by PCBM, the optimum synergetic effect is found at a weight ratio of 2.4 wt % (PCBM/TiO₂) and the photocatalytic activities increase about 3.72 and 2.89 times for the degradation of MB under visible light irradiation compared to pure PCBM and TiO₂, respectively. The enhanced photocatalytic activity for PCBM-modified TiO₂ comes from the high separation efficiency of photoinduced electron-hole which is produced by the interaction of TiO₂ and PCBM with the conjugative π -system.

Introduction

During recent decades, much attention has been focused on photocatalysis because it is an emerging successful technology for purifying wastewater from industries and households.¹⁻⁴ Among the photocatalysts, TiO₂ has been intensively investigated for the complete degradation of recalcitrant organic pollutants, as it is easily available, nontoxic, low-cost and chemically stable.⁵⁻⁷ As well known, there are two main disadvantages for TiO₂ photocatalyst. One is the wide band gap of TiO₂ (3.2eV) which limits the effective utilization of solar light.⁸ Thus, enormous efforts

have been devoted to improving the utilization of solar light by extending the photoresponse of TiO_2 to the visible region, such as metal or non-metal ion doping of this semiconductor.⁹⁻¹⁰ Non-metal ion doping, replacing oxygen in the titania lattice by anions (N, C, S, P) causes the mixing of the p states of these anions with the O_{2p} states. This, in turn, brings about a shift of the valence band edge upwards and narrows the band gap energy of TiO_2 .¹¹ For metal ion doping, substituting Ti^{4+} ions in the crystal lattice with metal ions with partially filled d-orbitals creates impurity energy levels within the band gap, thus facilitating the absorption in the visible.¹² Although doping technique plays an important role for visible light responsive it often produces new recombination centers which will decrease the photocatalytic activity of TiO_2 .¹³ The other drawback for TiO_2 photocatalyst is the high electron-hole recombination rate which decreases the photocatalytic activity. The deposition of noble metals¹⁴⁻¹⁶ or loading some materials with delocalized conjugated structures (C60) on the surface of TiO_2 reduces the rate of electron-hole recombination because these deposits may capture the conduction band electrons.¹⁷ Recently, several research groups have reported the preparation of C60 nanoparticles modified TiO_2 and their applications in splitting water and photodegradation of organic pollutants. One of the most remarkable properties of C60 in electron-transfer processes is that it can efficiently arouse a rapid photoinduced charge separation and a relatively slow charge recombination.¹⁸

[6,6]-phenyl-C61-butyric acid methyl ester (PCBM) has attracted our attention for their various interesting properties due to their delocalized conjugated structures¹⁹ and electron-accepting ability and it has been widely applied in organic solar cells²⁰. This is the first time we employed PCBM to modify TiO_2 thanks to its good electron accepting capability, high electron mobility and similar properties to those of C60. Previous studies showed that the photocatalytic activities of TiO_2 were improved remarkably after C60 modification,²¹ the combination of PCBM and TiO_2 may provide an ideal system to achieve an enhanced charge separation by photoinduced electron transfer.

In this study, we synthesized PCBM-modified TiO_2 by chemically adsorbing

PCBM on the surface of TiO₂. The work involves the preparation and photocatalytic activities of a series of PCBM supported on TiO₂ photocatalysts with varying PCBM content. Compare with pure TiO₂ and PCBM, the photodegradation results of dyes over PCBM-modified TiO₂ under visible-light irradiation show that the photocatalytic activity can be significantly enhanced. The promotion of photocatalytic activity may be ascribed to the effective separation of electron-hole pairs.

Experimental

Materials

All the reagents were used without further purification.

Preparation of Photocatalysts

PCBM (molecular weight ~1031.01) was purchased from Jilin Zhengji Corp (P.R. China), TiO₂ (P-25, particle diameter 30 nm, surface area 50 m² g⁻¹) was obtained from Degussa Corp (Germany). All other reagents were analytical pure and used without further purification. PCBM-modified TiO₂ sample was prepared as follows: an appropriate amount of PCBM was added into toluene and sonicated for 30 min to make PCBM totally disperse. The P25 powder (1 g) was added into the above solution and stirred for 24 h. The solvent was evaporated at 80 °C for 10 h and opaque powder was obtained after drying. PCBM-modified TiO₂ samples with other different mass ratio from 0.65 to 3.00% were prepared by following a similar procedure.

Characterization

The phase purity of these PCBM-modified TiO₂ samples was confirmed by X-ray diffraction (XRD). XRD patterns were obtained with a MO3XHF22 X-ray diffractometer (MAC Science, Japan) equipped with Ni-filtrated Cu K α radiation (40 kV, 30 mA). The 2 θ scanning angle range was 10–80° at a scanning rate of 5° min⁻¹. UV-vis diffuse reflectance spectra (UV-vis DRS) were obtained for the dry-pressed disk samples using Specord 2450 spectrometer (Shimadzu, Japan) equipped with the integrated sphere accessory for diffuse reflectance spectra, using BaSO₄ as the reflectance sample.

Photocatalytic Performance

The photocatalytic activities were evaluated for the degradation of MB solution under visible light irradiation. A 500 W xenon lamp ($\lambda > 290$ nm Institute of Electric Light Source, Beijing) with a 420 nm cutoff filter was used as light resource, and the average light intensity was $30 \text{ mW} \cdot \text{cm}^{-2}$. 100 mg of the PCBM-modified TiO_2 photocatalyst was dispersed in $10 \text{ mg} \cdot \text{L}^{-1}$ MB solution (100 mL). Prior to irradiation, the suspension was magnetically stirred in dark for 20 min to ensure the establishment of an adsorption/desorption equilibrium. During the photodegradation reaction, stirring was maintained to keep the mixture in suspension. Samples were withdrawn 8 mL every 30 min and immediately centrifuged to separate photocatalysts for analysis. The MB concentration was monitored by measuring the absorption intensity at its maximum absorbance wavelength of $\lambda = 664$ nm using a UV-visible spectrophotometer in a spectrometric quartz cell.

Results and Discussion

Structure of PCBM-modified TiO_2 Photocatalyst

The typical TEM and HRTEM images of 2.4%PCBM/ TiO_2 photocatalyst are shown in Fig. 1, revealing clearly that the lattice structure of TiO_2 was clear from the center to the boundary. It was also found a coverage layer with noncrystal structure adsorbed evenly and stably on the TiO_2 with the thickness of about 2.5 nm.

X-ray diffraction analysis

The XRD patterns of the as-prepared pure PCBM, TiO_2 and PCBM-modified TiO_2 are shown in Fig. 2. We can see that the dominate structure in these samples is anatase TiO_2 (JCPDS: NO. 21-1272).²² It is noteworthy that no PCBM related peak could be observed in the XRD spectra indicating the absorption of PCBM did not influence the lattice structure of anatase TiO_2 .

UV-vis diffuse reflectance spectra (DRS)

The UV-vis absorption spectra of TiO_2 , PCBM and PCBM-modified TiO_2 with different mass ratios are depicted in Fig. 3. TiO_2 sample showed an absorption edge around 400 nm, which could be responsible for the only ultraviolet light induced photocatalytic activity. However, the PCBM sample exhibited a great light response

throughout the whole spectrum consistent with the brown color of the sample. It can be clearly seen that a drastic increase of the absorption intensity in the visible region with the increasing of PCBM/TiO₂ weight ratio from 0.6 to 2.4%, but the increment was not obvious from 2.4 to 3.0%. This suggested that the ratio of 2.4% may be the optimum quantity to get the monolayer dispersed PCBM on TiO₂ surface.²³ This also suggests that the absorption in the visible region is due to the well dispersed PCBM nanoparticles and not to any modification of the band gap of the TiO₂.

Photocatalytic Performances

The visible light photocatalytic performances of TiO₂ loaded with different concentration of PCBM photocatalysts were evaluated by degradation of MB in aqueous solution (Fig. 4). It was clearly seen that the degradation rate of MB is almost zero without photocatalyst (Fig. 4, curve a). For pure PCBM (Fig. 4, curve b) and TiO₂ (Fig. 4, curve c) only 26.7% and 34.4% MB can be photodegraded under visible light. Notably, when the loading amount was below 2.4%, the photocatalytic activities increased with the increase of loading amount of PCBM. The photocatalytic degradation rate for the 0.6%PCBM/TiO₂ (Fig. 4, curve d), 1.2%PCBM/TiO₂ (Fig. 4, curve f), 1.8%PCBM/TiO₂ (Fig. 4, curve g) and 2.4%PCBM/TiO₂ (Fig. 4, curve h) photocatalysts with the irradiation for 4.5 h are 76.46%, 84.19%, 87.76% and 99.44%, respectively. The enhancement of photocatalytic activity may be ascribed to the fast transferring of the photoinduced electrons and low recombination of electron-holes pairs. When the loading amount of PCBM exceeded 2.4%, the photocatalytic activity of samples decreased. As mentioned in the result of DRS, PCBM tended to aggregate on the surface of TiO₂ when the mass ratio of PCBM above 2.4%, which resulted in the slower transmission of the photoinduced electrons. So, the optimal loading value of PCBM on TiO₂ for increasing the photocatalytic activity was 2.4%. The photocatalytic activity of TiO₂ modified by 2.4%PCBM was enhanced by about 3.72 and 2.89 times compared with those of pure PCBM and TiO₂ samples. This result implied that the interaction between PCBM and TiO₂ photocatalyst took an important role in the enhancement of photoactivity. After photocatalysis, the as-prepared photocatalysts display a XRD pattern nearly identical

to that of the original one, implying that the stability towards photocatalysis is excellent (see from Fig. 2.).

Photocatalytic Mechanisms

As discussed above, the PCBM-modified TiO_2 photocatalyst showed a high photocatalytic activity under visible light irradiation and the photocatalytic mechanism of PCBM/ TiO_2 is proposed. The reason should be closely due to the interaction between TiO_2 and PCBM which increased the photogenerated electron transfer rate in TiO_2 . In this work, PCBM molecule was mainly covered on the surface of TiO_2 and acted as an electron shuttle.²⁴ Illumination of photocatalysts by photons with energy equal to or greater than its band gap can excite electrons from the valence band to the conduction band of TiO_2 . The photogenerated electrons in the modified TiO_2 photocatalyst could easily transfer by PCBM from the inner region to the surface to take part in the surface reaction. Based on the above discussion, the schematic of photocatalytic mechanism was shown in Fig. 5(a). Usually, photoluminescence (PL) spectra (see from Fig. 5(b)) have been used to investigate the effect of the recombination of e^-/h^+ . The PL spectra of pure TiO_2 and PCBM/ TiO_2 samples were measured at room temperature in the wavelength between 450 and 570 nm. There were three emission peaks at about 460, 480 and 528 nm for the as-prepared sample with the excitation wavelength of 256 nm, which were assigned to the radiative recombination process of self-trapped excitons.²⁵ The position of the emission peaks of TiO_2 remained almost unchanged after being modified with PCBM on the surface, suggesting that the interaction between PCBM and TiO_2 was chemical absorption. Furthermore, the PL intensity of PCBM/ TiO_2 samples was weaker than pure TiO_2 . It was suggested that recombination efficiency of photogenerated electrons excited in TiO_2 under visible light were inhibited successfully after modifying with PCBM.

In addition, trapping experiments of radicals and holes were used to detect the main oxidative species in the photocatalytic process (seen from Fig. 6). Noticeably, the photodegradation for MB on 2.4%PCBM/ TiO_2 under visible light without the addition of scavenger can reach 99.44%. However, with the addition of 1mM EDTA (holes scavenger) the photodegradation of MB was hardly suppressed while it was

obviously prevented after the injecting of 1mM iso-propyl alcohol (IPA, radicals scavenger). This suggested that oxygenous radical were the main active species. The electrons react with O_2 in the air to yield O_2^- and subsequently react with H_2O to yield hydroxyl ($\cdot OH$) and superoxide radicals ($\cdot O_2^-$), which can possess strong oxidation ability and can react readily with surface adsorbed organic molecules to CO_2 and H_2O .

Conclusion

In summary, PCBM-modified TiO_2 photocatalyst was formed by a simple facile chemisorption method for the first time. Based upon the synergetic effect between PCBM and TiO_2 the efficient separation of electron-hole pairs came true and the photocatalytic activity of PCBM-modified TiO_2 photocatalyst was remarkably enhanced under visible light. The modified photocatalyst is a promising photocatalytic material with high activity which has good potential applications for environmental purification.

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Captions for Figures

Fig. 1 (A) TEM and (B) HRTEM image of 2.4%PCBM/TiO₂ photocatalyst

Fig. 2 X-ray diffraction patterns of TiO₂, PCBM and PCBM/TiO₂ samples with various mass ratios.

Fig. 3 UV-vis diffuse reflectance spectra of TiO₂, PCBM and PCBM/TiO₂ samples with various mass ratios. Inset: changes of absorbance (450 nm) as a function of mass ratio PCBM / TiO₂

Fig. 4 Photocatalytic degradation of MB by TiO₂, PCBM and PCBM/TiO₂ samples under visible light irradiation ($\lambda > 450\text{nm}$)

Fig. 5 (a) Possible Pathway of the Photoelectron Transfer Excited by Visible Light Irradiation Including Photocatalytic Process for PCBM-modified TiO₂; and (b)Photoluminescence (PL) spectra of TiO₂, PCBM and PCBM/TiO₂ samples.

Fig. 6 Plots of photogenerated carriers trapping in the system of photodegradation of MB by 2.4%PCBM/TiO₂ under visible light irradiation ($\lambda > 450\text{ nm}$)

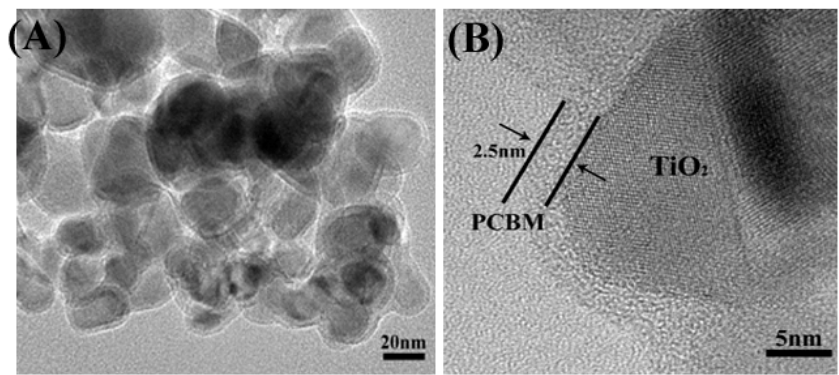


Fig. 1

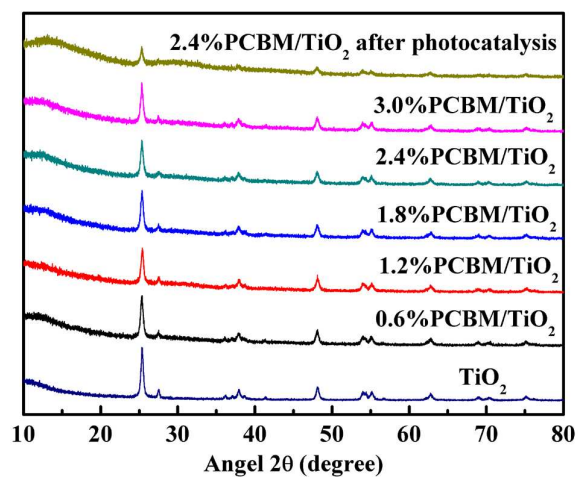


Fig. 2

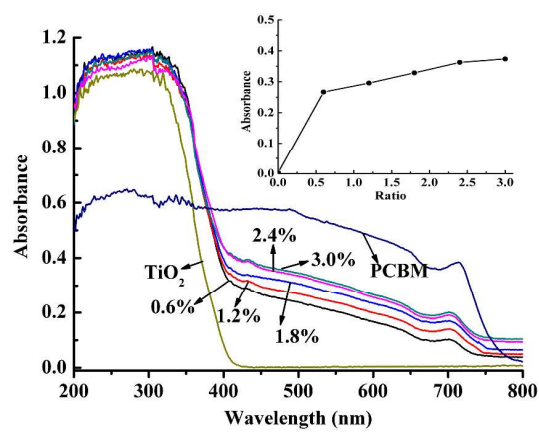


Fig. 3

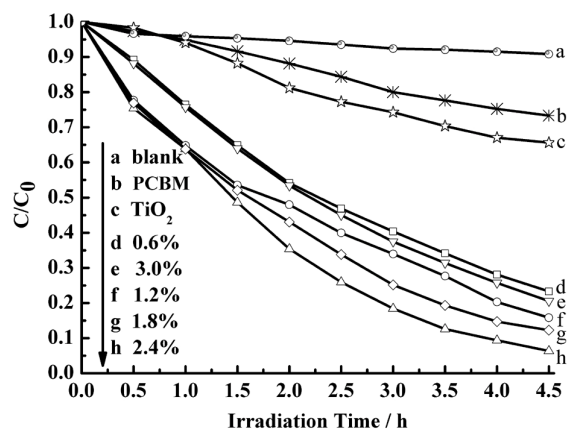


Fig. 4

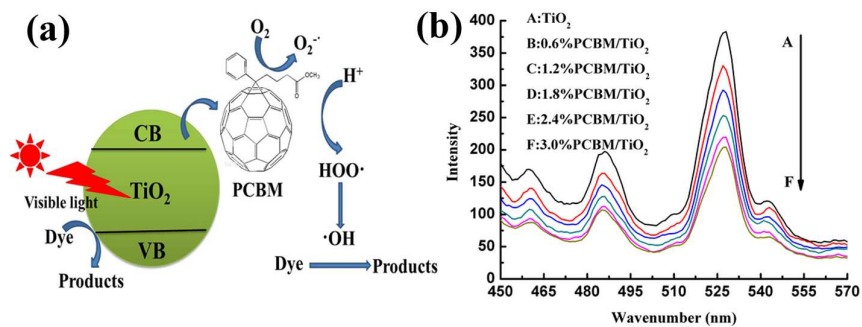


Fig. 5

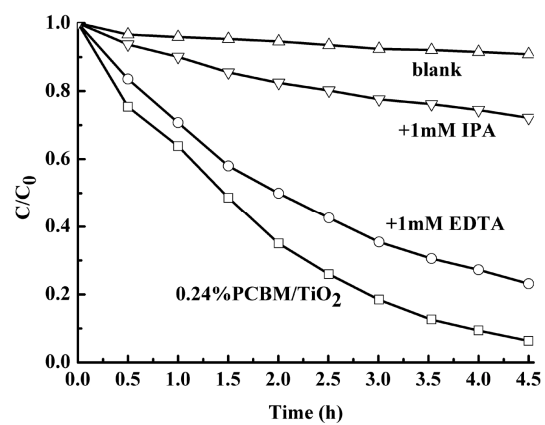


Fig. 6