



Preparation of polypyrrole/TiO₂ nanocomposites with enhanced photocatalytic performance



Fei Gao, Xianhui Hou, Aolan Wang, Guangwen Chu, Wei Wu*, Jianfeng Chen, Haikui Zou

State Key Laboratory of Organic-Inorganic Composites, Beijing University of Chemical Technology, Beijing 100029, China

ARTICLE INFO

Article history:

Received 17 April 2015

Received in revised form 22 June 2015

Accepted 17 July 2015

Available online 13 January 2016

Keywords:

PPy/TiO₂

Polypyrrole (PPy)

Nanocomposite

Photodegradation

Methanol

ABSTRACT

A simple in situ method was developed to synthesize polypyrrole (PPy)/TiO₂ nanocomposites having high photocatalytic activity under simulated solar light. The structure and morphology of the PPy/TiO₂ nanocomposites were characterized by X-ray powder diffraction (XRD), transmission electron microscopy, UV–vis diffuse reflectance spectroscopy, and Fourier transform infrared spectroscopy. The visible light photocatalytic properties of the nanocomposites were demonstrated by Rhodamine B degradation and by the production of methanol from CO₂. The XRD analysis showed that the coating of PPy did not change the crystallinity of the TiO₂. The UV–vis diffuse reflectance spectra indicated that the light adsorption range of the TiO₂ was enlarged after modification. Energy-dispersive X-ray spectroscopy analysis confirmed the presence of PPy and TiO₂ in the nanocomposite catalyst. The RhB degradation using the nanocomposites was increased by 41% and the methanol yield was enhanced by 34 wt% in comparison with those obtained with pure TiO₂. The improvements were considered to originate from the increased separation efficiency of hole–electron pairs from TiO₂ and the enhancement of the light adsorption range by the introduced PPy.

© 2015 Chinese Society of Particuology and Institute of Process Engineering, Chinese Academy of Sciences. All rights reserved.

Introduction

In current society, phenomena associated with environmental pollution have been increasing seriously (Paoletti et al., 2010). For example, the dyeing and printing industries produce a large amount of dye wastewater that can cause serious water pollution if discharged into the environment without suitable treatment (Schwarzenbach, Egli, Hofstetter, Von Gunten, & Wehrli, 2010). Similarly, massive emission of CO₂ has been a severe problem toward the green-house effect (Bose, 2010). Photocatalytic technologies using nanosized oxide semiconductor particles as catalyst have been considered as an effective green route for degrading organic pollutants and reducing CO₂ producing organic substances (Serpone & Emeline, 2012).

Nanoscale titanium dioxide (TiO₂) particles have many excellent properties, such as low cost, simple preparation, good stability, non-toxicity, and better photodegradation ability (Chen & Mao, 2007), making it a good prospect for application in solar cells (Bach et al., 1998; Mor, Shankar, Paulose, Varghese, & Grimes, 2006), photocatalysis (Linsebigler, Lu, & Yates, 1995), and photocatalytic

hydrogen production (Thompson & Yates, 2006). However, the wide band gap of pure TiO₂ nanoparticles means that they not only have a low sunlight energy conversion efficiency but also a high rate of photogenerated hole and electron recombination. Therefore, improvement of the photocatalytic properties of TiO₂ is essential.

There are many routes to enhance the photocatalytic properties of TiO₂, such as metal or non-metal doping (Duong Vu, Mighri, & Aji, 2014), compositing with other semiconductors (Gómez-Cerezo, Muñoz-Batista, Tudela, Fernández-García, & Kubacka, 2014), compositing with conductive materials such as graphene (Gómez-Cerezo et al., 2014) or carbon nanotubes (Woan, Pyrgiotakis, & Sigmund, 2009), sensitization with organic dyes and conductive polymers, such as polyaniline (Sarmah & Kumar, 2011), polythiophene (Xu, Zhu, Jiang, & Dan, 2010), and polypyrrole (PPy) (Sun, Shi, Li, Li, & Wang, 2013). Among these routes, sensitization with organic dyes and conductive polymers is thought to be the most effective (Deng, Min, Luo, Wu, & Luo, 2013), because it can reduce the recombination rate and band gap simultaneously. Because organic dyes are always unstable (Park, Lee, Kang, & Choi, 2010), conductive polymer sensitizers have been extensively studied (Wang, Li et al., 2012).

Among the various conductive polymers, PPy is one of the most promising owing to its superior conductivity, high absorption coefficient in the visible part of sunlight, high charge carrier mobility,

* Corresponding author.

E-mail address: wuwei@mail.buct.edu.cn (W. Wu).

and good environmental stability (Yan et al., 2006). Therefore, PPy is suitable for use as a stable photosensitizer to improve the photocatalytic activity and solar light conversion efficiency of TiO₂. There are many methods of preparing PPy/TiO₂ nanocomposites, for example, anodic co-deposition (Ferreira, Domenech, & Lacaze, 2001), self-assembly techniques (Tai, Jiang, Xie, Yu, & Zhao, 2007), photoelectrochemical polymerization (Okano, Itoh, Fujishima, & Honda, 1987), and hydrothermal methods (Sedláček, Mrlík, Pavlínek, Sába, & Quadrat, 2012). However, in situ chemical oxidation has good promise owing to its simplicity, good reproducibility, and easy scale up. Moreover, PPy/TiO₂ nanocomposites are mainly used in solar cells and for the photocatalytic degradation of organic species, while their application to the photoreduction of carbon dioxide is rarely reported.

In this study, PPy modified TiO₂ (PPy/TiO₂) nanocomposites were synthesized through simple chemical oxidation of pyrrole in a prepared TiO₂ sol solution. The photocatalytic activity of the as-synthesized nanocomposites for the degradation of Rhodamine B and the reduction of CO₂ was studied. The results showed that the PPy/TiO₂ composites exhibited better photodegradation and photoreduction properties than those of pure TiO₂.

Experimental

Materials

Pyrrole monomer (98%) was purchased from Sinopharm Chemical Reagent Co. Ltd, China. Ferric chloride (FeCl₃·6H₂O) and tetrabutyl titanate (Ti(OC₄H₉)₄, 98%) were supplied by Tianjin Fucheng Chemical Reagent Plant, China. Acetic acid, HCl, NaOH, and absolute ethanol were obtained from Beijing Chemical Plant, China. The pyrrole was distilled twice under reduced pressure and refrigerated in the dark before use. All other reagents were of analytical grade and used without further purification.

Synthesis of PPy/TiO₂ nanocomposites

Ten milliliters of tetrabutyl titanate and 2 mL of acetic acid were dissolved in 12 mL ethanol. After vigorous magnetic stirring for 5 min at room temperature, a mixed solution of 4 mL of water, 4 mL of acetic acid and 6 mL of ethanol was slowly added under stirring. The resulting mixed solution was stirred for 3 h and then aged at room temperature to gel. The aged wet gel was dried at 100 °C for 12 h, and then calcined at 500 °C for 3 h in a muffle furnace under air to remove organic impurities.

The preparation process of the PPy/TiO₂ nanocomposites is illustrated in Fig. 1. The as-prepared TiO₂ nanoparticles were dispersed in 100 mL of 1.0 M aqueous HCl solution and sonicated for 30 min. Pyrrole was then injected into the suspension at 0 °C under constant stirring. Then, 0.4 g of FeCl₃·6H₂O was dissolved in 100 mL of 1.0 M aqueous HCl to form a clear solution which was subsequently added drop-wise to the above reaction mixture. The resulting mixture was allowed to react at 0 °C for 3 h, after which it was filtered and washed with 1 M HCl and a large amount of deionized water. Finally, the obtained product was dried at 100 °C until a constant mass was reached. In the experiment, the molar ratio of pyrrole to FeCl₃ was 1:2, whereas that of pyrrole to TiO₂ was varied from 1:20 to 1:140.

Characterization

The nanocomposite sample used for characterization was that of PPy/TiO₂ 1:100 unless otherwise stated. The morphologies of the TiO₂ and PPy/TiO₂ nanocomposite samples were characterized by transmission electron microscopy (TEM, H-800, Hitachi, Japan). The samples for TEM observation were prepared by dispersing the

product in ethanol using a sonicator bath for 15 min and dropping the resulting suspension onto a copper grid. The crystal structure of the samples was characterized by X-ray diffraction (XRD, D/max 2500 VB2+/PC, Rigaku, Japan) using Cu K α radiation. Fourier transform infrared (FT-IR) spectra of the samples were measured on a FT-IR spectrometer (Nicolet 8700, Thermo Scientific, USA) with KBr pellets as the sample matrix. UV-vis diffuse reflectance spectroscopy (DRS) of the samples was carried out using a UV-Vis spectrophotometer (UV-3600, Shimadzu, Japan) to determine their photo adsorption properties over the range 200–1000 nm. The sample powders for DRS were pressed into pellets and BaSO₄ was used as a reference standard for correction of the instrumental background. The photoluminescence emission spectra of the samples were recorded using a fluorescence spectrophotometer (F-7000, Hitachi, Japan) to investigate the efficiency of charge carrier trapping, migration, and transfer. Sample excitation was performed at 235 nm at room temperature, and the emission was scanned between 250 and 400 nm.

Evaluation of photocatalytic degradation activity

The photocatalytic activities of TiO₂ and PPy/TiO₂ were evaluated by measuring the photodegradation of Rhodamine B (RhB) in aqueous solution. Illumination was performed under simulated solar light created by a 500 W tungsten-halogen lamp. In the experiment, 0.15 g of catalyst was suspended in 150 mL of 10 mg/L aqueous RhB solution and stirred in the dark for 30 min to reach adsorption and desorption equilibrium. The suspension was then irradiated with the simulated solar light under continuous stirring. Samples for analysis were taken from the suspension every 30 min and centrifuged. The amount of RhB remaining in the supernatant was then determined by measuring its absorbance at 553 nm using a spectrophotometer (UV-5200 PC, Shanghai Metash, China).

CO₂ photoreduction experiments

CO₂ photoreduction reactions were carried out in a glass cell equipped with a water-cooled jacket and a central light source. Catalyst powder (250 mg) was suspended in 250 mL of 0.1 M NaOH aqueous solution. Illumination was carried out using simulated solar light created by a 500 W tungsten-halogen lamp. The reactor was tightly sealed during the reaction and stirred continuously with a magnetic stirring bar to prevent the sedimentation of the catalyst. CO₂ was bubbled through the reactor for at least 30 min to purge it of air and to saturate the solution before irradiation. Small samples of the liquid reaction mixture were taken at regular intervals during the irradiation with a syringe, filtered through a Millipore filter membrane (USA), and then analyzed. The methanol yield was determined by gas chromatography (GC) using a GC instrument (GC-4000A, Beijing Things Analysis Instrument Co., Ltd., China) equipped with a FID and a 50-m-long KB-FFAP column. Two blank reactions were conducted to prove that the methanol came only from the photoreduction of CO₂. The first was carried out in absence of the catalyst, whereas the second was carried out with the presence of catalyst but under dark conditions. No methanol was detected in either of the blank tests.

Results and discussion

Morphology

Representative TEM images of TiO₂ and PPy/TiO₂ are shown in Fig. 2(a) and (b). The pure TiO₂ particles had an irregular spherical structure and a particle diameter of about 12–15 nm. In comparison, the PPy/TiO₂ nanocomposites existed as relatively loose

Download English Version:

<https://daneshyari.com/en/article/671728>

Download Persian Version:

<https://daneshyari.com/article/671728>

[Daneshyari.com](https://daneshyari.com)