Carbon nanotubes/TiO$_2$ nanotubes composite photocatalysts for efficient degradation of methyl orange dye

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ABSTRACT

A series of carbon nanotubes/TiO$_2$ nanotubes (CNTs/TNTs) composite photocatalysts were successfully prepared by incorporation of CNTs in HNO$_3$ washing process. These photocatalysts were characterized by XRD, N$_2$ physical adsorption, UV–vis diffuse reflectance spectroscopy, TEM and Raman spectroscopy, respectively, and their photocatalytic activities were tested by using methyl orange (MO) as a model compound. Also, the effects of amount of CNTs incorporated, calcination temperature and amount of catalyst on the photocatalytic activity of the composite photocatalyst were systematically investigated. The results show that the CNTs/TNTs composite exhibits much higher photocatalytic activity than that of the TNTs or CNTs alone.

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1. Introduction

With the rapid development of industrialization, certain hazardous effects on environment and human survival have emerged besides its benefit. Effluents from the use of pesticides, the textile, petrochemical, dyeing, plastic and paper industries are high toxic, carcinogenic and recalcitrant (Anandan, 2008; Lam, Sin, & Mohamed, 2010), and yet not readily degradable. Environmental purification has increasingly become a global concern calling for considerable attention. In recent years, many strategies have been devised to remove these pollutants, including treatment methods such as biological oxidation, chemical and physical methods for degradation of these effluents (Panda, Sahoo, & Mohapatra, 2011; Robinson, McMullan, Marchant, & Nigam, 2001). However, these traditional methods are often costly, may cause secondary pollution, thus greatly limiting their large-scale implementation. More efficient and economic methods need to be developed.

The initial discovery of photoelectrochemical water splitting on TiO$_2$ electrodes by Fujishima and Honda (1972), opened a new area in the destruction of organic pollutions. Photocatalytic oxidation is an alternative means for pollutant treatment in air and in water, and heterogeneous photocatalysis by semiconductors has attracted much attention (El-Sharkawy, Solimanb, & Al-Amer, 2007; Tian, Zhang, Tong, & Chen, 2008; Wang, Feng, et al., 2006;

Zou et al., 2004). Among the various semiconducting photocatalysts, TiO$_2$ has been the focus due to its non-toxicity, photoelectric conversion, photocatalytic activity and high stability (Biskupski, Herbig, Schottner, & Moos, 2011; Kazemi & Mohammadizadeh, 2011; Tennakone & Wijiayantha, 2005). However, photoefficiency and photoresponse of TiO$_2$ are not sufficient to compensate for its low photon utilization efficiency, small surface area and narrow spectrum responsive range ($\lambda < 388$ nm). Compared to TiO$_2$ powder, TiO$_2$ nanotubes (TNTs) have both large surface area (Gao, Le, Wang, & Chen, 2006) and high adsorptive capacity, both serving to improve photoelectric conversion efficiency and photocatalytic property of TiO$_2$ (Costa & Prado, 2009; Wang, Li, Wang, Quan, & Chen, 2009). To improve photocatalytic efficiency, different methods have been proposed, such as modification with metal ions (Li, Zou, Qu, Zhao, & Wang, 2011; Sun, Li, Wang, Li, Chen, et al., 2009; Sun, Li, Wang, Li, Lai, et al., 2009; Zhao, Li, Chu, Jiang, & Yin, 2009), doping non-metals (Park, Kim, & Bard, 2006) and semiconductor nanoparticle modification (Chen et al., 2006; Hossain, Biswas, Zhang, & Takahashi, 2011).

Researchers found that the addition of co-sorbent carbon materials can enhance the photocatalytic efficiency of TiO$_2$ (Liu, Chen, & Chen, 2007; Sakthivel & Kisch, 2003; Zhang, Fu, & Zhu, 2008). As a new member of the carbon family, carbon nanotubes (CNTs) with one-dimensional and hollow structure have received considerable interest since their discovery (Iijima, 1991) due to their outstanding structural characters, e.g., mechanical strength (Yu, Files, Arepalli, & Ruoff, 2000), excellent thermal conductivity, unique electronic properties (Cha et al., 2008) and thermal stability (Serp, Corrias,

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& Kalck, 2003). CNTs can be used as a promising material for environmental cleaning. To our best knowledge, CNTs/TiO$_2$ composite catalysts have been successfully prepared and used widely in degradation of organic dye pollutants (Kuo, 2009; Wang, Serp, Kalck, & Faria, 2005; Wang & Zhou, 2011). However, synthesis and application of CNTs/TNTs composite photocatalyst have seldom been reported.

The present work aimed at the synthesis of CNTs/TNTs composite photocatalyst with varying amount of CNTs. We studied the degradation of methyl orange (MO) using CNTs/TNTs composite as photocatalyst. Our CNTs/TNTs composite photocatalyst exhibited much high photocatalytic activity as compared to CNTs or TNTs alone. The effects of CNTs content incorporated in the composite, calcination temperature, and dosage of catalyst on photocatalytic activity of the CNTs/TNTs composite catalyst were also investigated.

2. Experimental

2.1. Materials

Chemicals including sodium hydroxide, nitric acid, MO, sodium dodecyl sulfate (SDS), sodium silicate, cobalt chloride, cetyltrimethyl ammonium bromide (CTAB), ethanol, hydrofluoric acid and concentrated sulfuric acid, were purchased from Shanghai Chemical Reagent Corporation, PR China. All reagents were of analytical grade. TiO$_2$ (P25, consisting of *ca.* 80% anatase-type TiO$_2$ powder and 20% rutile-type TiO$_2$ powder) was purchased from Degussa Corporation, Germany. Carbon nanotubes (CNTs) were made in our laboratory using chemical vapor deposition (CVD) with a purity >95%. To modify the material characteristics of the CNTs it was post-treated in concentrated nitric acid for 4 h.

2.2. Preparation and purification of CNTs

According to our previous publication (Zhao et al., 2010), the synthesis of CNTs was carried out by CVD using ethanol as carbon source and using CoMCM-41 mesoporous molecular sieve (Jiang et al., 2008) as catalytic template in a fixed bed flow-reactor consisting of a tubular furnace with a quartz tube with an inside diameter of *ca.* 30 mm. Typically, approximately 100 mg of the CoMCM-41 catalyst was put into a ceramic boat, which was put in the middle of the quartz tube placed horizontally inside the tubular furnace. The tubular furnace was heated at a rate of 20 °C/min, and then nitrogen was introduced into the quartz tube at a flow rate of 60 mL/min to keep the reactor under inert environment. When the furnace reached a temperature of 700 °C, a mixture of ethanol vapor and N$_2$ was introduced into the quartz tube, the flow of ethanol vapor being controlled by adjusting the temperature of ethanol vaporizing furnace (at 80 °C in this study). After the reaction had proceeded for 30 min, ethanol vapor was stopped. The reactor was then cooled down to room temperature in nitrogen to harvest carbon nanotubes.

The as-prepared carbon nanotubes need to be purified before they are used in the preparation of CNTs/TNTs composite. In a typical acid treatment procedure, the carbon nanotubes were first treated by ultrasonication for 1 h with 40% hydrofluoric acid at ambient temperature, and were then refluxed using concentrated nitric acid at 120 °C, to yield a product designated as CNTs.

2.3. Preparation of CNTs/TNTs composites

One gram of P25 was mixed with 80 mL of 10 mol/L NaOH solution, and the mixture was transferred into a 100 mL Teflon-lined stainless steel autoclave and was crystallized at 150 °C for 48 h in an oven. Then, the autoclave was cooled to room temperature, and the precipitate was filtered, washed with deionized water until a neutral precipitate was obtained, which was dispersed in 0.1 mol/L nitric acid by ultrasonic dispersion for 30 min to obtain solution A. At the same time, a given amount of CNTs was dispersed in 100 mL of 0.1 mol/L SDS aqueous solution by ultrasonic dispersion for 1 h to obtain solution B. Then, solution B was added into the solution A, and the mixture were continuously stirred for 3 h and aged for 1 d at room temperature. After that, the resulting precipitate was washed with deionized water until the pH was neutral and dried at 80 °C in an oven for 24 h to obtain a dried sample, namely CNTs/TNTs(x), where x is the mass ratio of CNTs to P25 in the composite synthesis process from 0.05, 0.10 to 0.15. The CNTs/TNTs(x) sample was calcined at 350, 450 and 550 °C for 3 h in nitrogen atmosphere, respectively. The calcined samples were designated as CNTs/TNTs(x)-350, CNTs/TNTs(x)-450 and CNTs/TNTs(x)-550, correspondingly.

For comparison, the pure TiO$_2$ nanotubes can also be obtained in a similar manner without the incorporation of CNTs, denoted as s-TNTs. Then, a certain amount of s-TNTs was calcined at 450 °C for 3 h in ambient nitrogen, marked as TNTs.

2.4. Characterization

The XRD patterns of samples were recorded on a Rigaku D/MAX 2500PC powder X-ray diffraction instrument with Cu Kα radiation ($\lambda = 0.15418$ nm) over the scanning range $2\theta = 20$–$60°$ for wide angle XRD at a voltage of 40 kV and 200 mA. Specific surface areas were measured by using a NOVA2000e analytical system made by Quantachrome Corporation (USA) and were calculated by the Brunauer–Emmett–Teller (BET) method. UV–vis diffuse reflectance spectra (DRS) were recorded on a UV-3100 spectrophotometer made by Shimadzu Corporation (Japan) with spherical diffuse reflectance accessory, using BaSO$_4$ as a reference. Raman spectroscopy was recorded on a JYHR800 Raman spectrometer with a 488 nm argon ion laser (France JY Company) at laser wavelength of 514 nm. Transmission electron microscopy (TEM) morphologies of samples were observed with a Philips TEMCNAl-12 with an acceleration voltage of 100–120 kV.

2.5. Photocatalytic activity test

The photocatalytic activities of the composite catalysts were evaluated by degradation of MO dye as a target pollutant, in a cylindrical reactor with magnetic stirring (SGY-1, China). A 300 W middle-pressure mercury lamp (MPML) with maximal emission at 365 nm was used as an internal centered light source, surrounded by MO solution with a quartz thimble, and the reactor was cooled *via* a jacket to keep the chamber temperature at 20–25 °C, 200 mg of catalyst was added into 1000 mL of MO solution (20 mg/L), and the resulting solution was dispersed ultrasonically for 20 min and was then poured into the reactor. Air flow rate was 240 mL/min, and 30 min for adsorption and desorption was needed for equilibrium before irradiation. During reaction, 8 mL of mixed solution was withdrawn periodically from the reactor, followed by centrifugation and filtration, and the obtained clear solution was analyzed by UV-spectroscopy (756CRT). The degradation rate of MO was calculated by the equation, $d\% = (C_0 - C)/C_0\%$, where C_0 stands for the initial concentration of MO solution, and C, at any other time (Mohamed, Ismail, Othman, & Ibrahim, 2005).