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TiO_2-loaded activated carbon fiber: Hydrothermal synthesis, adsorption properties and photo catalytic activity under visible light irradiation

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TiO_2-loaded activated carbon fibers (ACF) were prepared by a hydrothermal method. The samples were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectrometry and UV–vis diffuse reflectance spectra (DRS). SEM images showed that the TiO_2 nanoparticles were deposited on the surface of ACF, and the particle size and loading amount of TiO_2 were varied by changing the initial concentration of tetrabutyl titanate (TBOT). The results of an ash experiment showed that the loading amounts of TiO_2 were 18.4%, 43.3%, 52.5%, 75.1%, and 91.1% for initial concentrations of TBOT of 0.07, 014, 0.21, 0.28, and 0.35 mol/L, respectively. Physical interactions played an important role in the formation of TiO_2/ACF composite fibers that absorb UV and visible light. Compared with those of ACF, improved adsorption and photocatalytic activity toward Rhodamine B (RhB) were observed for TiO_2/ACF composite fiber. The Rhodamine B could be removed efficiently by TiO_2/ACF composite fibers, and the TiO_2 loading amount had a significant effect on the photocatalytic activity of TiO_2/ACF composite fibers.

1. Introduction

Using semiconductor photocatalysts to remove environmental pollutants has attracted extensive interest over the past decades. Among various semiconductor catalysts, titanium dioxide (TiO_2) has been widely investigated because of its strong photocatalytic ability, stable chemical properties, easy accessibility, and low cost. However, TiO_2 nanoparticles tend to agglomerate during the photocatalytic process due to their high surface energy, which consequently reduces their photocatalytic activity. Furthermore, the separation and recovery of TiO_2 photocatalysts from the treated water represent one of the main practical challenges remaining to be overcome. As an alternative method, some studies have focused on loading the nanosized TiO_2 onto much larger supports. An assortment of porous materials, such as silica, alumina, zeolites, and activated carbon, has been used to immobilize TiO_2 nanoparticles. The supports serve as good pollutant adsorbents and promote photocatalytic efficiency.

Activated carbon fiber (ACF) is widely used as a support in various applications because of its uniform pore structure and high adsorption ability (Huang, Chen, & Yuan, 2008; Lin, Cheng, Liu, & Chen, 2011; Macías-Pérez, Lillo-Ródenas, Bueno-López, Salinas-Martínez de Lecea, & Linares-Solano, 2008; Puma, Bono, Krishnaiah, & Collin, 2008; Zhang et al., 2012). ACF has also been selected as a support for TiO_2 loading, which can help to enrich the organic substances around the TiO_2 catalysts and promote photodegradation efficiency (Shi, 2009; Shi, Zheng, Wu, & Ji, 2008; Yao, Li, & Shi, 2010; Yuan, Guan, & Zheng, 2005; Zhang et al., 2010). For example, Shi et al. (2008) prepared TiO_2/ACF samples and found that methyl orange (MO) could be removed rapidly from water with those samples under UV irradiation. Yuan et al. (2005) prepared TiO_2-loaded ACF and studied its photocatalytic efficiency toward β-cyclodextrin. Their results showed that a tight and stable fixation between TiO_2 and ACF was essential for practical applications. Despite the above reports, some advancements still need to be made in this field, such as the development of a simple synthesis method, the promotion of the interfacial interaction between ACF and TiO_2 nanoparticles, an understanding of the relationship between the structure and photocatalytic activity and improvements in the performance of the TiO_2/ACF system.

The sol–gel process is a common method used to synthesize TiO_2/ACF composite fibers (Shi et al., 2008; Yao et al., 2010; Zhang et al., 2010). TiO_2 sol or gel was mixed with ACF fibers to form composite fibers, and a subsequent sintering treatment

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was essential to produce TiO_2 with an anatase structure. However, the sintering process might easily cause the agglomeration of TiO_2 nanoparticles and the decomposition of ACF at temperatures over 400 °C. Alternatively, hydrothermal techniques can be performed in a closed system at a higher autogenous pressure and can directly produce the crystalline structure without further annealing processes. In addition, the hydrothermal process is also useful to produce fine particles with unique morphology and unusual properties (Wu, Wang, Liu, & Gu, 2008). Using hydrothermal processes in the preparation of composite fibers might deposit uniform TiO_2 nanocrystallines on the ACF fibers, which will be helpful to improve the photocatalytic efficiency. Furthermore, the hydrothermal method has been seldom reported in the preparation of TiO_2/ACF composite fibers.

In this paper, TiO_2 nanoparticles were immobilized on ACF by a hydrothermal process. The adsorption properties and photocatalytic performances under visible light irradiation were investigated by using Rhodamine B (RhB) as a target compound. The effects of the TiO_2 loading amount on the photocatalytic properties of the composite samples are discussed. This type of material combines the excellent photocatalytic activity of TiO_2 nanoparticles and the high adsorption of ACF fibers and has many potential applications in the practical treatment of pollutants.

2. Experimental

2.1. Materials

Activated carbon fiber (ACF) with a specific surface area of 900–1800 m^2/g was purchased from the Yuheng carbon fiber corporation (Shenyang, China). Tetrabutyl titanate (TBOT), titanium isopropylate (TTIP), absolute alcohol, acetic acid, hydrochloric acid (HCl, 36.5%), sodium hydroxide (NaOH), and Rhodamine B were purchased from the Sinopharm Chemical Reagent Corporation (Shanghai, China). All chemicals were of analytical grade and were used without further purification. Deionized water was used throughout the experiments.

2.2. Hydrothermal synthesis of TiO_2/ACF composite fibers

The ACF fibers were pre-treated with 1 mol/L acetic acid, deionized water and 1 mol/L sodium hydroxide in turn. Then, a certain volume of TBOT was dissolved in 20 mL of absolute alcohol into which 20 mL of 1 mol/L acetic acid had been added; the mixture was continuously stirred for 2 h. The obtained transparent TiO_2 sol and pre-treated ACF were transferred into a sealed reactor and heated at 150 °C for 8 h. Finally, the prepared composite fibers were separated and dried at room temperature. The initial concentration of TBOT was varied within 0.07–0.35 mol/L to obtain TiO_2/ACF hybrid fibers with different TiO_2 loadings.

2.3. Characterization

The morphology of TiO_2/ACF was observed on an SSX-50 scanning electron microscope (SEM, Shimadzu, Japan). The X-ray diffraction pattern was obtained with a XRD instrument (D/max-2500PC, Rigaku, Japan) (Cu Kα, tube voltage of 50 kV and tube current of 100 mA). FT-IR analyses were performed on a FT-IR spectrometer (Spectrum One, Perkin-Elmer, USA) using samples dispersed in anhydrous KBr. The UV–vis spectra and UV–vis diffuse reflectance spectra (DRS) were measured with a UV–vis spectrophotometer (Lambda 35, Perkin-Elmer, USA).

2.4. Adsorption and photocatalytic experiments

The adsorption experiments on TiO_2/ACF fibers were carried out under darkness. A fiber sample (2 cm × 2 cm) was immersed in 5 mg/L RhB solution (80 mL) under stirring, and the UV–vis spectrum was measured at regular intervals to determine the concentration change of RhB. The characteristic peak of RhB was observed at 554 nm. The effect of the contact time on the adsorption rate was studied. The adsorption rate of RhB was calculated according to Eq. (1):

$$Ads\% = \frac{c_0 - c_e}{c_0} \times 100, \tag{1}$$

where c_0 and c_e are the initial and final concentrations of RhB, respectively.

The photocatalytic experiments were carried out using a xenon short arc lamp (CHF-XM35-500W) as a excitation light source, and a glass filter was used to allow visible light ($\lambda > 400$ nm) to pass through. The TiO_2/ACF fibers (2 cm × 2 cm) were placed in 80 mL of a 5 mg/L RhB solution. Before illumination, the solutions were stirred for 30 min under darkness to achieve adsorption equilibrium. The UV–vis spectrum was also used to monitor the reaction process, and the concentration change of RhB was determined by analyzing its absorbance at 554 nm.

3. Results and discussion

3.1. Morphology and structure of TiO_2/ACF composite fibers

The morphologies of ACF and TiO_2/ACF composite fibers are presented in Fig. 1. As shown in Fig. 1(a), the average diameter of ACF is approximately 10 μm, and the surface of ACF is rough and has a large amount of long grooves, which are the active sites for surface adsorption (Diaz-Flores, Leyva-Ramos, Guerrero-Coronado, & Mendoza-Barron, 2006). Fig. 1(b)–(f) shows SEM images of TiO_2/ACF composite fibers prepared with different TiO_2 loading amounts. Compared with Fig. 1(a), the TiO_2 nanoparticles are deposited with good dispersity on the surface of ACF, and the loading amounts of TiO_2 increase as the concentration of TBOT increases from 0.07 to 0.28 mol/L (Fig. 1(b)–(e)). However, when the concentration of TBOT is increased up to 0.35 mol/L (Fig. 1(f)), the amount of immobilized TiO_2 is apparently reduced, which may be caused by the agglomeration of TiO_2 nanoparticles into large TiO_2 particles that are separated from the ACF fibers. A high-magnification portion of the SEM image in Fig. 1(b) is shown in Fig. 1(g), and the size of the immobilized TiO_2 nanoparticles is approximately 100 nm. To further clarify the morphology of the immobilized TiO_2, the TiO_2 particles were prepared under the same hydrothermal conditions but without ACF; the TEM results are shown in Fig. 1(h). The average size of TiO_2 nanoparticles is approximately 18 nm. Therefore, the immobilized TiO_2 particles in Fig. 1(b) and (g) might be composed of several smaller particles.

The XRD pattern of TiO_2/ACF composite fibers is shown in Fig. 2. The characteristic diffraction peaks at $2\theta = 25.3°$, 37.9°, 48.4°, 54.3°, and 62.8° correspond to the indices (1 0 1), (0 0 4), (2 0 0), (1 0 5), and (2 0 4), respectively, and the values are in good agreement with JCPDS data of anatase TiO_2 (No. 21-1272). Apart from the above diffraction peaks, there is a broad peak at $2\theta = 20°–35°$ that is caused by the amorphous ACF fibers. The sizes of the TiO_2 particles can be calculated according to Scherrer's equation: $D = K\lambda/(\beta \cos \theta)$ ($K = 0.89$ and $\lambda = 0.154056$ nm); the crystalline size of TiO_2 is approximately 15.6 nm based on the data from the (1 0 1) plane.