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Short Communication

TiO_2 supported on bamboo charcoal for H_2O_2-assisted pollutant degradation under solar light

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ABSTRACT

Composite TiO_2/bamboo charcoal materials were prepared using a sol–gel method. The composites were characterized using X-ray powder diffraction, Fourier-transform infrared spectroscopy, scanning electron microscopy, transmission electron microscopy, and nitrogen adsorption–desorption isotherm techniques. They were then evaluated for degradation of methyl orange in water under solar light. The composite can be recycled up to 30 times and retains high photocatalytic activity.

1. Introduction

In 1977, Bard successfully oxidized CN^- to OCN^- and laid the foundation for photocatalytic treatment of waste water [1]. TiO_2 as a photocatalyst is inexpensive, non-toxic, abundantly available, and stable under solar irradiation [2]. Numerous studies of catalyst carriers have been conducted, ranging from economical synthesis to detailed physical and chemical characterization [3].

Worldwide, over 700,000 t of dyes and pigments are produced annually, of which approximately 20% is industrial effluent from textile dyeing and finishing processes. Most of these dyestuffs have complicated polyaromatic structures and they cannot be treated successfully by conventional degradation methods [4,5]. However, azo dyes such as methyl orange (MO) are photodegradable [6–11].

TiO_2 as a photocatalyst has some drawbacks such as phase separation after reaction and fast recombination of photoinduced electrons and holes [12]. For convenient TiO_2 separation and reuse, photocatalysts are often immobilized on porous materials such as electron acceptors and adsorbents that provide good dispersion of TiO_2 on their surface [13–17]. The high adsorption capacity of porous materials helps in pooling the pollutants to the vicinity of TiO_2 surface [18].

In the present study we uses bamboo charcoal (BC) as a support for TiO_2 to increase its efficiency in treatment of dye wastewater. We used MO as a model compound to establish the photocatalytic degradation conditions over a composite photocatalyst under solar irradiation in aqueous suspension.

2. Experimental

2.1. Materials and methods

All chemicals were purchased from Xi'an Fuchen Chemical Reagent Company as analytical reagent grade and were used without further purification. All solutions were prepared with high-purity deionized water (Shanghai Hetai Instrument Company) generated using a Millipore device.

BC was purchased from the Yihuang Bamboo Charcoal Company and was used without further purification. BC is prepared from bamboo by carbonization at 800 °C. BET

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analysis revealed a specific surface area of 108 m^2/g for the BC material, indicating that it is porous.

2.2. Preparation of TiO_2/BC composites

TiO_2/BC composites were prepared by a sol–gel method [19,20]. Typically, 10 ml of tetrabutyl titanate was dissolved in 40 ml of anhydrous ethanol at room temperature under a nitrogen flow and stirring to prepare solution A. To prepare solution B, 4.0 ml of 0.21 M ferric nitrate was mixed with 20 ml of anhydrous ethanol and 5 ml of glacial acetic acid. Solution B was then added to solution A under vigorous stirring within 30 min. The mixture was stirred for a further 10–30 min and aged for 12 h at room temperature. The required amount of BC granules was admixed with the TiO_2 gel at 32 °C under ultrasonication (45 Hz) and is thoroughly mixed. The samples were first dried at 80 °C and then calcined at 550 °C for 3 h (heating rate 3 °C/min) under a nitrogen flow of 10 ml/min.

2.3. Characterization

TiO_2 and TiO_2/BC composites were characterized using X-ray powder diffraction (XRD), field-emission transmission electron microscopy (FETEM), and scanning electron microscopy (SEM) techniques. The surface properties of BC and TiO_2/BC were measured in terms of N_2 adsorption using an Autosorb 1C Quantachrome physical adsorption system. The specific surface area and pore volume were calculated using the BET and Barrett–Joyner–Halenda (BJH) [8] methods, respectively. XRD patterns were recorded on a Rigaku D/max-2500 diffractometer (36 kV, 20 mA) using Cu K_α radiation (λ=0.154 nm) over the 2θ range 10–80°. For SEM analysis, samples were mounted on an aluminum support using double-sided adhesive tape and observed in Germany SUPRA-55 SEM unit.

2.4. Photocatalytic experiments

Experiments were carried out between April and May 2013 at Xi'an, China. Natural solar irradiation (intensity ~90 mW cm^{-2} at ~31 °C) between 13:00 and 15:00 h was used in static experiments over a 2-h cycle. Before light experiments, MO adsorption was allowed to reach equilibrium for 1 h in the dark under continuous stirring.

3. Results and discussion

3.1. Characterization

Fig. 1 shows high-angle XRD patterns for TiO_2/BC and TiO_2. All the diffraction peaks can be indexed to anatase TiO_2 with tetragonal lattice parameters of a=3.785 Å and c=9.514 Å (JCPDS card 21–1272). The composite shows one diffraction peak located at ~25° corresponding to the (0 0 2) reflection of carbon. This clearly indicates that BC is amorphous in nature. The presence of dispersed titania peaks confirms that TiO_2 was supported over BC.

Fig. 2 shows SEM and TEM images of BC and the TiO_2/BC composite. BC exhibits a well-developed pore structure and

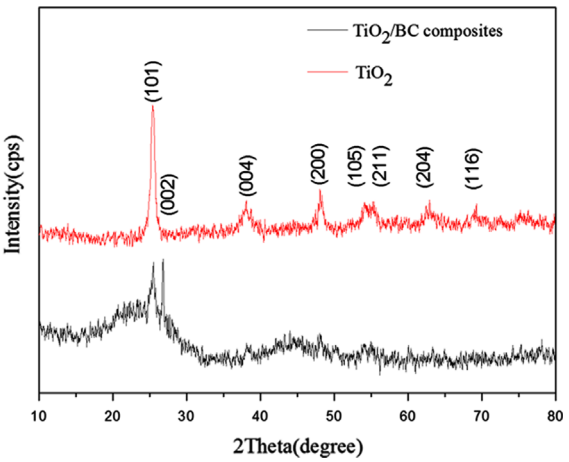

Fig. 1. XRD patterns for TiO_2 and the TiO_2/BC composite.

TiO_2 particles are dispersed on its surface and in its pores. This well-ordered nanochannel and pore structure is an excellent catalyst support. It provides numerous adsorption sites and thus promotes photocatalytic kinetics for pollutant molecules [18].

Representative N_2 adsorption–desorption isotherms and the corresponding BJH pore-size distribution (calculated from adsorption data) for TiO_2/BC are shown in Fig. 3a. The sample exhibits a typical type IV isotherm (IUPAC definition), which is characteristic of a mesoporous structure. The specific surface area is 108 m^2/g for BC and 55 m^2/g for TiO_2/BC. The decrease in surface area on TiO_2 loading is due to dispersion of TiO_2 particles over the surface and inside the support.

To further investigate the TiO_2/BC composite, the surface chemical compositions of composite was measured by XPS analysis. For XPS profiles at a depth of 1 nm (Fig. 3b), no strong Fe signals were detected, whereas strong O and Ti signals are apparent, indicating that Fe is more likely to be situated in the interior rather than on the surface of the composite.

Fig. 4 shows FT-IR spectra of BC, TiO_2, and the TiO_2/BC composite. The absorption band at ~3420 cm^{-1} observed in all the spectra can be ascribed to stretching of surface hydroxyl groups. The absorption at ~1630 cm^{-1} can be assigned to bending of adsorbed H_2O molecules [18]. Since TiO_2 crystallites are very small, Ti–OH bonding is not homogeneous, which explains widening of the band at 3170 cm^{-1}. For TiO_2/BC, transmission dips between 450 and 800 cm^{-1} confirm that TiO_2 is adsorbed to the BC surface, because the broad absorption bands at 450–800 cm^{-1} correspond to Ti–O–Ti stretching vibrations [22]. For TiO_2/BC, a strong peak at ~1200 cm^{-1} is observed. Peaks between 1000 and 1300 cm^{-1} can be assigned to C–O stretching. Thus, C–O are formed by treatment at 550 °C for 3 h.

3.2. Photocatalytic activity

MO adsorption on BC and TiO_2/BC was allowed to equilibrate in the dark. pH is an important parameter because it