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Solar photocatalytic degradation of methylene blue using doped TiO_2 nanoparticles

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Abstract

Doped-TiO_2 nanoparticles (M:TiO_2: Fe, Zn, Zr, Sb, Ce and *n*M:TiO_2: B, C, N, P, S) with anatase structure were prepared by sol–gel method and characterized by X-ray diffraction (XRD), Transmission electron microscopy (TEM), X-ray photoelectron spectra (XPS), Brunauer–Teller method (BET), UV–Vis diffuses reflectance spectroscopy (DRS). Results revealed that the anatase structure is highly stable for all doped TiO_2 prepared compounds with enhancement in the surface area. UV–Vis diffuse reflectance spectra showed that these dopants were responsible for narrowing the band gap of TiO_2 and shifting its optical response from ultraviolet to visible-light region. The photocatalytic activities of these multi-doped TiO_2 catalysts were investigated by degradation methylene blue in aqueous solution under solar-light illumination. The results showed an appreciable enhancement in the photoactivity of the C-doped TiO_2 as compared to other multi-doped TiO_2 because of the formation of Ti^{+3} species which prevent the recombination of electron–hole pairs in C-doped TiO_2.

Keywords: Carbon; Iron; Solar photocatalysis; Methylene blue

1. Introduction

Heterogeneous photocatalysis has received great attention as an advanced oxidation process for the removal of toxic organic and inorganic contaminants from water (Sharma et al., 2012; Wang et al., 2010; Gernjak et al., 2004; Gambhire et al., 2011). However, the development of a practical photocatalytic system focused on the cost effectiveness by the use of renewable solar energy source. Photocatalytic degradation of organic contaminants using solar irradiation could be highly economical compared with the processes using artificial UV–Vis irradiation which required substantial electrical power input. Hence, development of solar light active photocatalytic materials is a subject of extensive current research in this field.

Doping TiO_2 with transition metals having electronic coupling capability (Naseri et al., 2011; Choi et al., 1994) or non-metals such as Boron (Begum et al., 2008), Carbon (Xiao et al., 2008; Khan et al., 2002), Nitrogen (Asahi et al., 2001; Gole et al., 2004), Sulfur (Wang et al., 2007;

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Umebayashi et al., 2002) is known to enhance their photocatalytic response in the visible light region. Choi et al. (1994) studied the effects of 21 different dopants on the photocatalytic activity of TiO_2, Fe dopant proved to be better than Ru, V, Mo, Os and Re. Asahi et al. (2001) reported that N-doping shifted the absorption edge of TiO_2 to visible light region, thereby exhibiting photocatalytic degradation of MB solution and gaseous acetaldehyde under visible irradiation. Wang et al. (2007) reported the shift of photo response of TiO_2 from UV to the visible region by a C-dopant. Irie et al. (2003) prepared carbon-doped anatase TiO_2 nanoparticles by oxidative annealing of TiC under O_2 flow at 600 °C. The modification of TiO_2 by co-doping with metal and non-metal and the cooperative actions of co-doping were also investigated to improve the photocatalytic activity (Rengifo-Herrera and Pulgarin, 2010; Zhao et al., 2004; Sakatani et al., 2003; Xiao et al., 2008). At present, the doping of one kind of atom into TiO_2 has gained much attention due to superior control on the concentration of dopant and fabrication of efficient, cost-effective photocatalysts in order to ease global environmental issues. However, there are few publications reporting the comparative study on photocatalytic degradation of MB using multi-doped TiO_2. Furthermore, most of the research work has been carried out by irradiating catalyst suspension with artificial visible light (Lv et al., 2013) or by using UV light irradiation (Liu et al., 2011) and it is not feasible and economical for the treatment of huge quantity of industrial effluents. The present study focuses on the efficient use of sunlight and the ability of prepared photocatalyst to destroy MB under solar light irradiation.

2. Experimental details

2.1. Preparation of transition metals doped TiO_2 ($M:TiO_2$)

Fe(III), Zn(II), Zr(IV), Sb(III), and Ce(IV)-loaded (3 wt.%) TiO_2 nanomaterials were prepared by sol–gel process. Titanium butoxide (98%, Aldrich) was used as the precursor of TiO_2. In a typical procedure, 25 ml of titanium butoxide was hydrolyzed in 300 ml water containing 1.5 ml nitric acid. The cationic surfactant cetyltrimethylammonium bromide (CTAB), 20% (10 ml) in ethanol was dropped into the above solution. Gel formed was stirred continuously at room temperature to form a highly dispersed sol. To this, Fe, Zn, Zr, Sb, and Ce solutions (3 wt.%) were added separately and stirred again for about 5 h. After keeping the sol for aging (5 days), it was concentrated and dried at 80 °C. The samples, after overnight drying at 110 °C, were calcined for 2 h at 500 °C.

2.2. Preparation of non-metals doped TiO_2 ($nM:TiO_2$)

B, C, N, P and S doped TiO_2 samples were synthesized using the controlled hydrolysis of titanium butoxide. The dopant starting materials boric acid, mixture of ethylene glycol and citric acid, ammonia, ortho-phosphoric acid and thiourea were used for the preparation of the $nM:TiO_2$ samples, respectively. In a typical experiment, 0.1 mol of titanium butoxide was dissolved in 100 ml anhydrous ethanol to form solution. A certain amount of boric acid, ethylene glycol and citric acid, ammonia, ortho-phosphoric acid and thiourea were dissolved in a mixture of 50 ml deionized water containing 2 ml nitric acid and 50 ml of ethanol separately. To this, TiO_2 solution was added drop-wise under vigorous stirring to form the precipitate by simultaneous addition of ammonium hydroxide pH at 7 (excluding N-doped TiO_2 solution). After keeping the precipitate for aging (5 days), it was concentrated and dried. The samples, after overnight drying at 110 °C, were calcined for 2 h at 500 °C.

2.3. Characterization

X-ray powder diffraction (XRD) patterns have been recorded on a model D8 Bruker AXS with monochromatic Cu radiation (40 kV and 30 mA), over the 2θ collection range of 20–80°. The particle size of anatase was calculated from XRD measurement. Anatase to rutile ratio was estimated from integrated intensities of the reflection of 1 0 1 and 1 1 0 respective phases. BET surface area measurements were carried out using a Quantachrome NOVA 1200 instrument. The microscopic nanostructures were observed by transmission electron microscopy (TEM; FEI, Tecnai F30, HRTEM, FEG operated at 300 kV). FT-IR spectra were recorded on a Shimadzu-8400 spectrometer in the

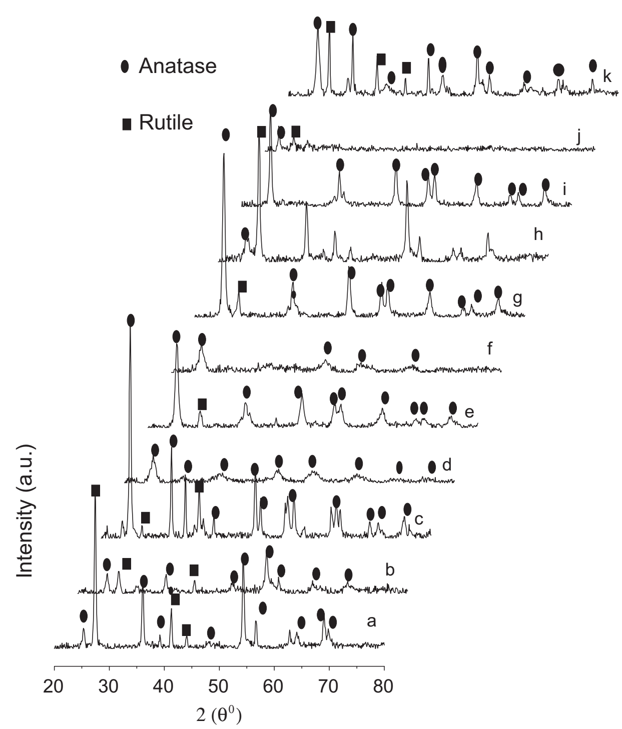

Fig. 1. XRD profiles of (a) pure TiO_2, (b) Fe–TiO_2, (c) Zn–TiO_2, (d) Zr–TiO_2, (e) Sb–TiO_2, (f) Ce–TiO_2, (g) B–TiO_2, (h) C–TiO_2, (i) N–TiO_2, (j) P–TiO_2, and (k) S–TiO_2, calcined at 500 °C.