



Preparation and photocatalytic activity of TiO₂ nanoparticles co-doped with Fe and La

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ABSTRACT

The catalysts of un-doped, single-doped and co-doped titanium dioxide (TiO₂) nanoparticles were prepared by a sol–gel method with Ti(OC₄H₉)₄ as a Ti source material. The photo-absorbance of the obtained nanoparticles was measured by UV–vis diffusive reflectance spectroscopy (UV–vis DRS), and the photocatalytic activity of the prepared samples under UV and visible light was estimated by measuring the degradation rate of phenol (50 mg/L) in an aqueous solution. The effect of Fe and La co-dopants on the material properties was investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM) and N₂ adsorption–desorption isotherm measurement. It was shown that the co-doped TiO₂ could be activated by visible light and could thus be used as an effective catalyst in photo-oxidation reactions. The photocatalytic activity of TiO₂ co-doped with Fe and La is markedly improved due to the synergistic actions of the two dopants.

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1. Introduction

Titanium dioxide (TiO₂) is a well known n-type metal oxide semiconductor, transparent to visible light with a high refractive index. Due to its unique optical property and chemical stability, TiO₂, especially its anatase phase, has attracted much attention for its potential application in degradation of various environmental pollutants, both gaseous and liquid (Ao, Lee, Yu, & Xu, 2004; Fujishima, Rao, & Tryk, 2000; Hoffmann, Martin, Choi, & Bahnemann, 1995; Ochuma, Fishwick, Wood, & Winterbottom, 2007; Rodrigues et al., 2008; Strini, Cassese, & Schiavi, 2005; Thompson & Yates, 2006). However, its shortcomings include a large band gap (~3.2 eV) which causes most of the solar spectrum unutilized. To extend the optical absorption of TiO₂ to the visible region, various dopants have been added to the oxide to improve its photocatalytic and solar efficiency (Asahi, Morikawa, Ohwaki, Aoki, & Taga, 2001; Burda et al., 2003; De Vos, Dams, Sels, & Jacobs, 2002; Martyanov, Uma, Rodrigues, & Klabunde, 2004; Sakthivel & Kisch, 2003). Many previous investigations focused on the transition metals as dopants (Sun, Reddy, & Smirniotis, 2005; Wang, Böttcher, Bahnemann, & Dohrmann, 2004; Wu & Chen, 2004; Xu, Lu, Guo, & Li, 2005; Zhang, Li, Zhu, & Wang, 2004). Rare earth metals having incompletely occupied 4f and empty 5d orbitals have

been found to promote catalysis, that is, photocatalytic activity of TiO₂ (Baiju et al., 2005; Xie & Yuan, 2004; Xu, Gao, & Liu, 2002). Wang, Yin, Komatsu, and Sato (2005) and Zhang, Wang, Zakaria, and Ying (1998) indicated that introducing two or more appropriate elements into nanocrystalline TiO₂ particles could improve the photocatalytic effect of TiO₂, showing the salutary effect of co-doping with transition and rare earth metals into nanocrystalline TiO₂.

In the present paper, we used tetrabutyl titanate (Ti(OC₄H₉)₄), Fe(NO₃)₃·9H₂O and La(NO₃)₃·6H₂O as the sources of titanium, iron and lanthanum to prepare titanium dioxide photocatalyst co-doped with Fe and La (Fe, La–TiO₂) by a sol–gel method. The photocatalytic activity was evaluated by photodegradation of phenol in solution under UV and visible light. Co-doping with Fe and La was found to enhance the photocatalytic activity for the phenol degradation under UV and visible light irradiation of TiO₂. The synergistic effect of the two dopants that leads to the significant enhancement of photodegradation is to be discussed.

2. Experimental

2.1. Photocatalyst preparation

Anatase TiO₂ was prepared by a sol–gel method at low temperature using tetrabutyl titanate (Ti(OC₄H₉)₄, analytic grade, Shanghai Xingta Co., Ltd., China) as precursor. A solution was prepared as follows: Ti(OC₄H₉)₄ (0.02 mol) was added to anhydrous ethanol

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(50 mL) under vigorous stirring. Then triethylamine (0.01 mol) was added as a stabilizer, and the solution was stirred at 200 r/min for 2–3 min in an inert atmosphere of flowing argon. A second solution was prepared as follows: hydrochloric acid (3.0 mL) and water (0.72 mL) were added to anhydrous ethanol (50 mL) and mixed well with a magnetic stirrer at 200 r/min. The two solutions were then mixed together and stirred vigorously for 30 min under flowing argon. The TiO₂ sol formed is transparent, quite stable and highly sensitive to triethylamine and water. It was subsequently kept at room temperature for 2 weeks until a white powder was obtained, which was dried for 96 h at 80 °C and then calcined at 500 °C for 1 h with a heating rate of 15 °C/min.

Doped TiO₂ nanoparticles were synthesized using the same method. The appropriate amount of Fe(NO₃)₃·9H₂O or La(NO₃)₃·6H₂O was dissolved in anhydrous ethanol, which was added dropwise into the distilled water prior to the hydrolysis of Ti(OC₄H₉)₄ under vigorous stirring.

2.2. Photocatalyst characterization

The morphologies of different samples were examined by a scanning electron microscope (SEM, Holland Philips, JSM-5800). X-ray diffraction (XRD) patterns of all samples were obtained at room temperature with a Rigaku D/max-r B X-ray diffractometer using Cu K α radiation which operated at 45 kV and 40 mA. Information about specific surface area, pore volume and adsorption–desorption curves of catalysts was obtained from nitrogen adsorption–desorption at 77K using the BET method (Gregg & Sing, 1982) with a Micromeritics 2000 instrument (ASAP 2000, Micromeritics, USA). The UV–vis diffusive reflectance absorption spectra were characterized using a UV-3000 spectrophotometer (Shimadzu, Japan).

2.3. Measurement of photocatalytic efficiency

The photocatalytic activity of the prepared catalysts under UV and visible light was estimated by measuring the degradation rate of phenol (50 mg/L) in an aqueous solution.

2.3.1. UV light irradiation

Experiments were carried out using a magnetically stirred quartz reactor and an ultraviolet mercury lamp (300 W, 365 nm) at ambient temperature of about 20 °C. The pH of the suspension was adjusted either with dilute 0.1 mol/L HCl or 0.1 mol/L NaOH. Sixty-minute adsorption time in dark condition was allowed before the start of photoreactions. Then, samples of the suspension were withdrawn after a definite time interval and filtered through 0.45 μ m filter paper. The filtrates were analyzed for residual phenol concentration using a UV–vis spectrophotometer (UV762, Shanghai Analysis Co.) at 269.5 nm.

2.3.2. Visible light irradiation

The experiments with visible light irradiation were performed at ambient temperature of about 20 °C by using a 300 W metal halide lamp as the light source, which was filtered by a L41 cut filter to assure cut-off of the UV light.

3. Results and discussion

3.1. XRD analysis

Fig. 1 shows the XRD patterns of both the doped catalysts and pure TiO₂. All samples prepared have the anatase structure, with no significant rutile form. The X-ray diffraction peak at 25.5° corresponds to the characteristic peak of crystal plane (1 0 1) of anatase.

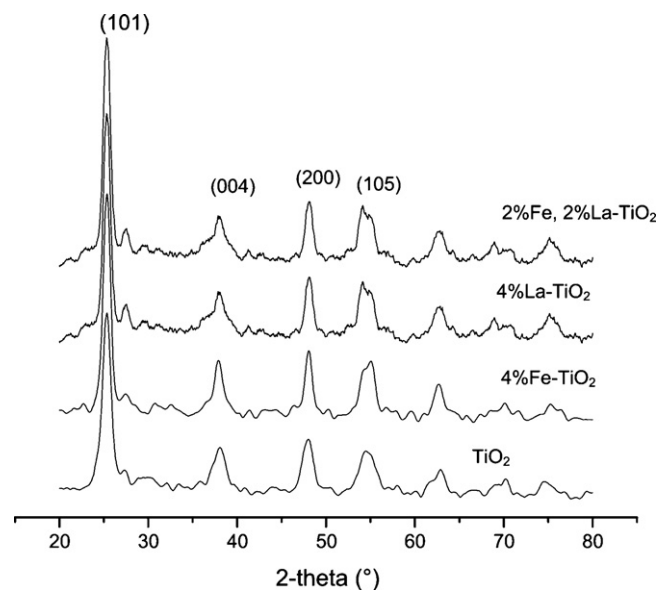


Fig. 1. XRD patterns of different samples.

No characteristic peak of Fe oxide or La oxide is found in the XRD patterns, implying that either both Fe and La ions are incorporated in crystalline TiO₂, or else, Fe oxide and La oxide are extremely small and highly dispersed.

The average crystallite size was calculated as a function of the full width at half maximum peak intensity based on Scherrer's formula. The physical properties determined from XRD data of the samples are listed in Table 1. The crystallite size decreases because of doping, implying that doping with Fe and La restrains increase of grain size and refines crystallite size. The change of crystal parameters becomes significant in the doped samples as compared to the un-doped crystals, implying that crystal matrix could be expanded.

3.2. Nitrogen adsorption–desorption measurement

To investigate the effect of doping with Fe and La on pore structure and adsorption ability of the photocatalysts, a set of N₂ adsorption–desorption measurements was carried out as shown by the isotherms in Fig. 2 for the co-doped photocatalyst (type IV hysteresis loop of Sing et al., 1985). The sharp decline in the desorption curve and the hysteresis loop at high relative pressure are indicative of mesoporosity. Barret–Joyner–Halenda (BJH) pore size distributions of different samples were calculated from the adsorption branch and represented in Fig. 3, indicating monomodal pore distribution with BJH average pore diameter of 10–15 nm for all samples, though doped photocatalysts had smaller mesopore size than the pure TiO₂ photocatalyst. Specific surface area and pore volume of catalysts were also calculated on the basis of N₂ adsorption–desorption isotherms and summarized in Table 2. The co-doped sample had lower surface area than that of pure TiO₂,

Table 1
XRD analysis result of the prepared samples.

Sample	Dopant content (%)	Crystallite size (nm)	Lattice parameters		
			a (nm)	c (nm)	V (nm ³)
Pure TiO ₂	0	13.1	0.3776	0.9486	0.1353
Fe–TiO ₂	4	12.5	0.3775	0.9499	0.1354
La–TiO ₂	4	10.9	0.3782	0.9492	0.1358
Fe, La–TiO ₂	2, 2	11.2	0.3785	0.9515	0.1363

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