



Visible-light-driven titania/silica photocatalyst co-doped with boron and ferrum

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ABSTRACT

The sol–gel route was employed to prepare a titania/silica photocatalyst co-doped with boron and ferrum. The microstructure and the optical property of the photocatalyst were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), UV–vis diffusive reflectance spectroscopy (DRS), Fourier transform infrared spectroscopy (FT-IR), and N₂ adsorption–desorption isotherm. The decomposition of phenol under visible light irradiation was used as probe reaction to evaluate the photocatalytic activity. The results revealed that the dopants could inhibit phase transformation of TiO₂, and that there were intimate molecule-level interactions between titania and silica. The doping boron led to the response to visible light. The doping ferrum, which existed in the form of Fe₂O₃ and dispersed on the surface of TiO₂, increased photoquantum efficiency and resulted in the enhancement of catalytic performance. The photocatalytic activity related to the annealing temperature and component. The synergistic effects of co-doping and intimate interaction between titania and silica were responsible for the increase of photoactivity.

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1. Introduction

In the past decades, TiO₂ photocatalysis was intensively investigated because irradiation of TiO₂ using light with greater energies than its band energy could trigger electron transition from the valence band to the conduction band, leaving the photo-generated electron–hole pairs, which might degrade many pollutants [1–4]. However, titania photocatalysis faces several significant limitations because of its high energy band gap (ca. 3.2 eV for anatase) and low photoquantum efficiency resulting from low interfacial charge-transfer rate of photogenerated carriers and high recombination of photoinduced electron–hole pairs [5,6]. For the purpose of solving these problems, some strategies including loading noble metal over titania [7], doping with metal [5,8], doping with nonmetal [2,6,9,10], and compound-titania/silica [11,12] have been proposed. Based on the previous researches reported in the literature, the doping metal atoms present individual phases dispersed into TiO₂, trapping temporarily the photogenerated charge carriers and inhibiting the recombination of photoinduced electron–hole pairs when the electron–hole pairs migrate from the inside of the photocatalyst to the surface [8]. The doping nonmetal atoms can enter into TiO₂ lattice and decrease the band gap, possibly resulting in the response to the visible light [2,6,9,13]. As for titania/silica mixed

oxide, there are the intimate molecule-level interactions between titania and silica, which may lead to many new physicochemical properties, such as quantumsized crystallites, high surface area, and high adsorption capability to the pollutants [12,14,15]. Zhao et al. [16] prepared the B–Ni co-doped photocatalyst using the modified sol–gel method. They pointed out that incorporation of B into TiO₂ could extend the spectral response to the visible region and that Ni doping could increase greatly the photocatalytic activity. Ling et al. [17] prepared the boron and nitrogen co-doped titania photocatalyst. They reported that the photocatalytic activity of the B and N co-doped photocatalyst for degradation of phenol under visible light irradiation was much higher than that of P25. Jung et al. [18] prepared the B₂O₃–SiO₂/TiO₂ ternary oxides by sol–gel route. They reported that the photoactivity of titania/silica mixed oxides was improved by the addition of boron oxide and that boron was partially incorporated into the framework and replaced Ti–O–Si with Si–O–B bond. They pointed out that the quantization was observed in the B₂O₃–SiO₂/TiO₂ ternary mixed oxides in which the boron content was less than 5%. When the boron content was over 10%, the blue shift disappeared and the absorption spectrum became equal to the pure titania. These indicated that either doping of titania or mixing titania/silica might be an effective method to improve the photoactivity of titania. It is imagined that if two methods are combined together to prepare photocatalyst, higher photoactivity can be readily achieved. Therefore, it is expected that the cooperative action of co-doping with metal and nonmetal can be used to modify titania/silica mixing oxide which is a class of promising materials and to raise

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the photoactivity. On the basis of the consideration, we investigated the titania/silica photocatalyst co-doped with metal and nonmetal and succeeded in preparing the titania/silica photocatalyst co-doped with B and Fe by the sol-gel method. The as-prepared samples were characterized by XRD, XPS, DRS, FT-IR, N_2 adsorption-desorption isotherm. The degradation of phenol under visible illumination was employed to evaluate the photocatalytic performance. We find that there are few reports on this aspect so far among the impressive number of publications. Therefore, it should be a meaningful work to investigate the preparation and photoactivity of the co-doped titania/silica photocatalyst.

2. Experimental

2.1. Photocatalyst preparation

Tetrabutyl titanate was chemically pure and others were analytically pure, and they were used as received without any further purification. Water used was deionized water.

A certain amount of boric acid (H_3BO_3) and ferric nitrate enneahydrate ($Fe(NO_3)_3 \cdot 9H_2O$) were dissolved in a mixture of 10 mL of deionized water, 8 mL of glacial acetic acid (CH_3COOH) and 30 mL of ethanol (CH_3CH_2OH) at room temperature to obtain solution 1. The mole ratio of Ti to Si was fixed (1:0.3). 17.02 g of tetrabutyl titanate ($Ti(O-nC_4H_9)_4$) and 3.12 g of ethyl silicate ($(C_2H_5)_4SiO_4$) were dissolved in 50 mL of anhydrous ethanol to form solution 2. Then, the solution 2 was added drop-wise into the solution 1 within 60 min, keeping the reaction mixture vigorously magnetically stirred. Subsequently, the sol was stirred continuously for 2 h and aged for 72 h at room temperature to prepare the gel. The resulting gel was dried for 12 h at 100 °C under reduced pressure to gain the xerogel, which was milled to obtain powder. The powder was annealed at desired temperature for 2 h to remove the residual organic compounds. Thus, the co-doped titania/silica photocatalyst was obtained. The as-prepared sample was kept in a vacuum until the time of use. The sample was labeled as $B(x)Fe(y)TiO_2/SiO_2-T$, where x and y corresponded to the initial mole ratios of B to Ti and Fe to Ti, respectively, and T was the corresponding temperature of calcination (°C).

2.2. Photocatalyst characterization

A D/max-RA X-ray diffractometer with Cu target $K\alpha$ radiation ($\lambda = 0.15406$ nm) as X-ray source was used to record the powder X-ray diffraction patterns, which were compared with the standard diffraction charts of anatase and rutile. The scan speed was at 2° min^{-1} in a 2θ range of 20° – 70° . The accelerating voltage and the applied current were 40 kV and 100 mA, respectively. In addition, crystallite sizes were estimated through the widths of half-height according to the Scherrer equation and the lattice constants were calculated using full profile structure refinement of XRD data.

A Thermo Escalab250 X-ray photoelectron spectroscope equipped with Al $K\alpha$ excitation was employed to obtain the XPS spectra of the co-doped titania/silica photocatalyst. Binding energies were calibrated with respect to the signal for adventitious carbon (284.6 eV). The chemical forms of the doped atoms at the surface of TiO_2 were analyzed by means of binding energies from XPS.

A Shimadzu (Japan) DUV-3700 UV-vis-NIR Recording Spectrophotometer equipped with integrating sphere attachment was used to measure the UV-vis diffusive reflectance spectra of samples in the wavelength range of 200–800 nm. $BaSO_4$ was used as a reference.

FT-IR transmittance spectra of samples were measured by a Nicolet 5700 spectrometer (Thermo Electron Corporation) using KBr discs in the region of 4000 – 400 cm^{-1} at ambient conditions.

The N_2 adsorption-desorption isotherms were determined by Autosorb-1 at 77 K. Prior to measurement, the samples were outgassed in an evacuation chamber for 8 h at 423 K.

2.3. Photocatalytic activity test

Phenol is widely used in industry and agriculture and it is a common pollutant. Therefore, phenol was chosen as model pollutant in order to evaluate the photocatalytic performance. The degradation of phenol was conducted in a 100 mL of self-designed quartz vessel, which contained 50 mL of 50 mg/L phenol solution and 50 mg of photocatalyst. The vessel was immersed in a thermostatic circulation bath (30.0 °C) for the purpose of keeping the temperature of photoreaction constant. The reaction system was exposed in the air and the reaction mixture was magnetically stirred. A 150 W metal halide lamp was used as the light source, which was filtered by a 410 nm cut filter (L41, KenKo Co.) to remove the UV light. The lamp was located at 5 cm above the reactor. Prior to illumination, the suspension was ultrasonicated for 5 min and stirred for 60 min in the dark to reach a state of adsorption equilibrium of phenol. The decomposition experiment was carried out for 3 h. A 5 mL of suspension was periodically sampled every hour and centrifuged. The solution was determined at the characteristic wavelength of phenol ($\lambda = 270.0$ nm) by a 751GD UV-vis spectrophotometer. The photocatalytic activity is evaluated by:

$$\text{conversion} = \left(\frac{A_0 - A}{A_0} \right) \times 100\% \quad (1)$$

where A_0 and A represent the initial absorbance before irradiation and the absorbance at irradiation time t , respectively.

3. Results and discussion

3.1. XRD spectra of samples

The XRD patterns of typical samples, including $B(0.01)Fe(0.01)TiO_2/SiO_2-600$, $B(0.01)TiO_2-600$, $Fe(0.01)TiO_2-600$ and pure TiO_2-600 are shown in Fig. 1. One could conclude that the samples $B(0.01)Fe(0.01)TiO_2/SiO_2-600$, $B(0.01)TiO_2-600$, and $Fe(0.01)TiO_2-600$ contained only anatase. As for the sample pure TiO_2-600 , a characteristic peak ($2\theta = 27.4^\circ$) assigned to rutile (1 1 0) was to be observed, demonstrating that pure TiO_2-600 existed in the states of anatase and rutile. Undoubtedly, one could deduce that the doping

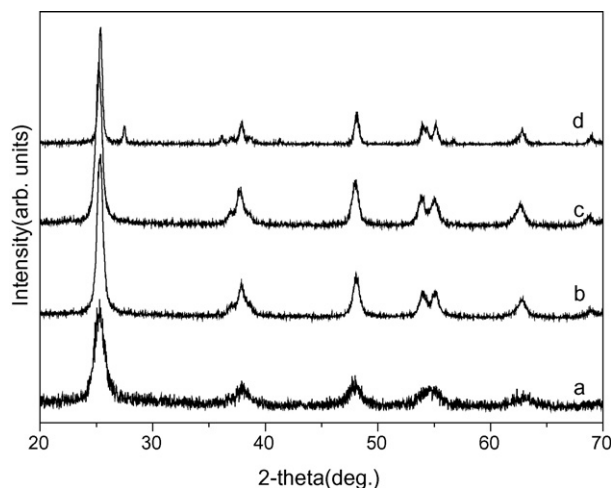


Fig. 1. XRD patterns of (a) $B(0.01)Fe(0.01)TiO_2/SiO_2-600$, (b) $B(0.01)TiO_2-600$, (c) $Fe(0.01)TiO_2-600$, (d) pure TiO_2-600 .

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