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Preparation of lanthanum and boron co-doped TiO_2 by modified sol–gel method and study their photocatalytic activity

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ABSTRACT

Lanthanum and boron co-doped TiO_2(La–B–TiO_2) was successfully prepared by modified sol–gel method aiming at enhancing the visible-light photocatalytic performance by improving the quantum efficiency of the photocatalytic reaction and extending the absorption in the visible-light region. The prepared photocatalysts were characterized by different techniques. The results indicated that boron doping could narrow the band gap of titania, and lanthanum doping could suppress the phase transformation and hinder the crystallization of titania. In addition, lanthanum doping could not only increase the adsorption of organic pollutants on the surface of catalyst, but also improve the separation of photogenerated holes and electrons and consequently promote the formation of hydroxyl radicals. The photocatalytic activities of the series samples were evaluated for degradation of Acid Orange 7 (AO7). Compared with the lanthanum doped TiO_2 and boron doped TiO_2 samples, the 1%La–B–TiO_2 photocatalyst exhibited outstanding visible-light activity and it was found that there would be synergistic effects of lanthanum and boron, which was responsible for improving the photocatalytic activity.

1. Introduction

With the development of industrialization, environmental pollution is increasingly becoming a major problem to the globe [1–3]. Semiconductor photocatalysis, as one of the advanced physicochemical process, has been studied extensively for solving the environmental problems [4]. Many organic compounds have shown to be oxidized to CO_2, water and mineral acid by photocatalysis method. TiO_2, as a typical semiconductor photocatalyst, has received a great deal of attention due to its chemical stability, non-toxicity, low cost, and other advantageous properties [5–7]. However, a major disadvantage is its ineffectiveness under visible-light irradiation: the band gap of anatase is 3.2 eV, which requires excitation wavelengths of $\lambda < 387.5$ nm [8,9]. On the other hand, the photocatalytic acitivity of TiO_2 is limited by fast charge carriers recombination and low interfacial charge-transfer rates of photogenerated carriers [10]. The main focus of the researchers is to modify TiO_2 in an effort to combat above problems so as to render it usable at industrial level in environmental protection.

In recent years, many studies have been carried out to improve the photocatalytic performances, including non-metal [11–13], rare earth metal [14–16] and transition metal doping [17–19], noble metal deposition [20], semiconductor coupled [21] and dye sensitization, etc. Recently, the co-doped TiO_2 with rare earth and non-metal element has aroused our great attention [22–24]. Ma et al. reported that Sm and N co-doped TiO_2 with high photocatalytic activity was successfully prepared by co-precipitation method. They suggested that the probable mechanism was a synergistic effect of Sm and N co-doping. Nitrogen doping could extend the absorption to visible region and samarium doping suppressed the anatase-to-rutile phase transformation and retarded the growth of crystallite [25]. Xing et al. prepared lanthanum and carbon co-doped TiO_2, using glucose as the carbon-doping source and {0 0 1}-facet-controlling agent through a simple one-step hydrothermal method. They indicated that glucose played an important role in the formation of {0 0 1} facets and the co-doped TiO_2 performed the excellent photocatalytic performance under both UV and visible-light irradiation, which is due to the synergistic effect of co-doping [26]. Cong et al. prepared the nanoparticles of TiO_2 modified with lanthanum and nitrogen by homogeneous

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precipitation-hydrothermal method. Superior photocatalytic activity of La–N co-doped TiO_2 was observed for the decomposition of Rhodamine B under visible-light irradiation. They indicated that nitrogen and lanthanum co-doping could produce a synergistic effect. The La^{3+} doping could accelerate the separation of photo-generated electrons and holes, while the nitrogen doping could narrow the band gap of TiO_2 and improve the efficiency of light quantum [27]. However, few studies involved lanthanum and boron co-doped TiO_2 [28]. It is found that doping TiO_2 prepared by sol–gel method is more stable and better crystalline than that prepared by hydrothermal method, because the samples prepared by sol–gel method were heated at high temperature and doping ions are easily to enter the lattice of TiO_2. Our previous works have found that La doped TiO_2 presented high visible-light performance and the carbon and nitrogen photosensitization showed great effects on its efficient photocatalytic activity [26,27].

In the present study, we reported a modified sol–gel method to prepare lanthanum and boron co-doped TiO_2. Both boron and lanthanum doping could show efficient visible-light photodegradation of acid orange 7 (AO7). Compared with La-doped TiO_2, B-doped TiO_2 and pure TiO_2, the La–B co-doped TiO_2 photocatalyst manifested higher photocatalytic activities. The resulting photocatalysts were systematically investigated by various techniques. Based on the characterization, the synergistic effect of La and B co-doping were discussed.

2. Experimental

2.1. Preparation of samples

The lanthanum and boron co-doped samples were prepared by modified sol–gel method. Tetrabutyl titanate was used as a starting material, lanthanum nitrate as a lanthanum source, boric acid as a boron source. 3.4 mL tetrabutyl titanate was dissolved into 20 mL of anhydrous ethanol (solution A). Under continuous stirring, boric acid, different amounts of lanthanum nitrate and 3.6 mL of distilled water were dissolved into 35 mL of anhydrous ethanol (solution B). Then, solution A was added drop-wise to solution B under mechanical stirring. The resultant mixture was stirred at room temperature for 4 h and then aged 1 h until the sol was obtained. The sol was poured into a Petri dish and following heated at 60 °C for 16 h to get the dry glue, which was ground to the powder. After the prepared powder was calcined at 400 °C for 3 h, the catalysts were obtained. A series of La–B-doped TiO_2 catalysts were prepared by varying the La/Ti mole ratio. For the convenience, the obtained photocatalysts were labeled as *x*%La–B–TiO_2, where *x*% corresponded to the mole ratio of doped La to Ti, which was varied from 0.1% to 2.0%. The atomic ratio of B/Ti was fixed at 3%. In addition, the pure TiO_2 was prepared by the similar process in the absence of $La(NO_3)_3$ and H_3BO_3 for comparison.

2.2. Characterization of photocatalysts

X-ray diffraction (XRD) patterns of all samples were collected in the range 10–80° (2θ) using Rigaku Ultima IV (Cu Kα radiation, λ = 0.15406 nm), operated at 40 kV and 40 mA. The crystallite size was estimated by applying the Scherrer equation to the full width at half-maximum (FWHM) of the (1 0 1) peak of anatase, with α-silicon (99.9999%) as a standard for the instrumental line broadening. The UV–vis reflectance spectra were recorded with absorbance spectra UV–vis spectrophotometer (Shimadzu UV-2450) in the range of 200–800 nm. $BaSO_4$ powder was used as a reference, and the spectra were recorded in the 200–800 nm. The surface properties of TiO_2 samples were characterized by X-ray photoelectron spectroscopy (XPS) in a Perkin-Elmer PHI 5000 C ESCA system with Al Kα source and a charge neutralizer. All binding energies were referenced to the C 1s peak (284.6) arising from adventitious carbon. Photoluminescence (PL) analysis was conducted using a Spectrofluorophotometer (Shimadzu RF-5301PC) at room temperature with an excitation wavelength at 300 nm. The Fourier transform (FTIR) spectra were measured using a Nicolet Magna 550 spectrometer, which was recorded with KBr disks containing the powder sample with the FTIR, in the range of 4000–400 cm^{-1}. Measurements of Raman spectra were performed on a Renishaw inVia Reflex Raman spectrometer with 514 nm excitation light in the range 100–1400 cm^{-1}. N_2 adsorption–desportion isotherms were measured on a Micromeritics ASAP 2020 system. The samples were degassed at 453 K in N_2 for 10 h prior to the measurement. The pore size distribution of mesopores in the samples was analyzed by the BJH method.

Table 1
The crystalline size of the photocatalysts.

	La (mol%)	*x*La–TiO_2 (nm)	*x*La–B–TiO_2 (nm)
1	0	16.1	12.8
2	0.2	14.6	13.8
3	0.5	12.6	11.0
4	1	11.1	10.8
5	1.5	10.8	10.7
6	2	10.7	10.5

2.3. Photocatalytic activities test

The photocatalytic activities of samples were evaluated in terms of the degradation of azo-dye acid orange 7 (AO7) under visible-light illumination. AO7 is an azo-dye, which is difficult to decolorize and frequently used in textile industry [29]. In a typical photocatalytic reaction, 0.06 g of sample was suspended in 60 mL of aqueous 20 mg L^{-1} AO7. A 500 W commercial tungsten halogen lamp was used as the visible light with a UV cutoff filters (>420 nm) to remove radiation below 420 nm. And there was a quartz cylindrical jacket around the lamp, in which the running water was used to keep the ambient temperature during the photocatalytic reaction. Before irradiation, the obtained solution was first stirred for 30 min in dark in order to reach the adsorption–desorption equilibrium. The change of AO7 concentration as a function of the maximum (483 nm) was analyzed by a UV–vis spectrophotometer with 1 h intervals for a total irradiation time of 5 h.

3. Results and discussion

3.1. Phase structures of TiO_2

Fig. 1 shows the XRD patterns of *x*La–TiO_2 and *x*La–B–TiO_2 nanoparticles with different La amount calcined at 400 °C. All of samples consist of anatase as a unique phase. However, no separate B_2O_3 or La_2O_3 phases were observed for the boron-containing or lanthanum-containing samples, possibly ascribing to the low B and La concentration. The average crystalline sizes of all these samples were determined by analyzing the most intense (1 0 1) XRD peaks and using the well-known Scherrer formula, summarized in Table 1 [30]. Compared to La–TiO_2, the crystallite size of La–B–TiO_2 was smaller, which indicated that boron doping would bring a little distortion in the crystalline structure. And the particle size of La–TiO_2 photocatalysts got smaller with the increasing lanthanum doping. It indicates that lanthanum doping prolongs the crystallization of anatase since the crystallinnity of La–TiO_2 is lower than that of TiO_2.

Fig. 2 shows the Raman spectra recorded under ambient conditions for pure TiO_2, 1%La–B–TiO_2. It is shown that the positions of the peaks are similar while Raman intensities are different between

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