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Preparation and characterization of TiO_2 photocatalysts co-doped with iron (III) and lanthanum for the degradation of organic pollutants

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ABSTRACT

Titanium dioxide photocatalysts co-doped with iron (III) and lanthanum were prepared by a facile sol–gel method. The structure of catalysts was characterized by X-ray diffraction (XRD), Raman spectroscopy, UV–vis diffuse reflectance spectroscopy and X-ray photoelectron spectroscopy (XPS). The photocatalytic activities of the samples were evaluated by the degradation of methylene blue in aqueous solutions under visible light ($\lambda > 420$ nm) and UV light irradiation. Doping with Fe^{3+} results in a lower anatase to rutile (A–R) phase transformation temperature for TiO_2 particles, while doping with La^{3+} inhibits the A–R phase transformation, and co-doping samples indicate that Fe^{3+} partly counteracts the effect of La^{3+} on the A–R transformation property of TiO_2. Fe-TiO_2 has a long tail extending up the absorption edges to 600 nm, whereas La-TiO_2 results in a red shift of the absorption. However, Fe and La have synergistic effect in the absorption of TiO_2. Compared with Fe^{3+} and La^{3+} singly doped TiO_2, the co-doped simple exhibits excellent visible light and UV light activity and the synergistic effect of Fe^{3+} and La^{3+} is responsible for improving the photocatalytic activity.

1. Introduction

Photocatalytic degradation of organic pollutants on semiconductor surfaces offers a viable approach to the solution of a variety of environmental problems. Semiconductor TiO_2 is the most widely used material because of its advantages such as high oxidation rate, low material cost, non-toxicity, chemically stability, and ecological friendliness [1–4]. However, a major drawback of pure TiO_2 anatase phase is that the bandgap (E_g) is about 3.2 eV, which requires excitation wavelengths of $\lambda < 376$ nm. Therefore, only 5–8% of sunlight photons have the enough energy to activate the catalyst [5]. In addition, the high recombination rate of photoinduced electron-hole pairs results in poor efficiency of photocatalytic reactions. In that case, the overall efficiency of pure TiO_2 is quite low, and the practical application is limited [6–9]. To deal with these problems, several strategies have been involved such as depositing noble metals on TiO_2 surface and doping with foreign species [10]. Among them, doping could be the effective way to improve the photocatalytic activity of TiO_2 under the visible light irradiation [6].

Transition metal dopants have been widely used to improve the photoefficiency of the electronic process as well as the response to the visible part of the spectrum. Iron is frequently employed owing to its unique half-filled electronic configuration, which might narrow the energy gap though the formation of new impurity energy levels [11,12]. Choi et al. [13] evaluated the effect of 21 different kinds of metal ions doping on the photoreactivity of TiO_2. Fe^{3+} dopant showed to be better than other metal ions. The most accepted explanation for improved photocatalytic performance of Fe^{3+}-doped samples is that Fe^{3+} dopant can form shallow charge traps within the TiO_2 crystal lattice through the substitution of Ti^{4+}, which reduced the electron–hole recombination and improved the photocatalytic efficiency [14–16].

Transition metal-doped TiO_2 photocatalysts are active under visible-light irradiation; however, the efficiency is insufficient for practical use due to low thermal instability [1]. Recently, doping rare earth metals such as La, Eu and Ce has received much attention [17–19]. In the published work, the report proved that TiO_2 with rare earth metal dopants shows significant improvement on both the photocatalytic activity and the thermal stability usually [20–22].

Doping with transition metal or rare earth metal elements has its respective advantage. The previous research showed that two dopants had more synergistic effect than a single one for enhancing the absorption in the visible-light region and improving the photocatalytic activity of TiO_2 [23,24]. The sample may possess the better photocatalytic performance if transition metal and rare earth metal elements are codoped into TiO_2. Here, we prepared TiO_2 photocatalysts codoped with Fe^{3+} and La^{3+} by a facile sol–gel method and its photocatalytic activities have been tasted for degradation of organic compound under both UV light and visible light irradiation.

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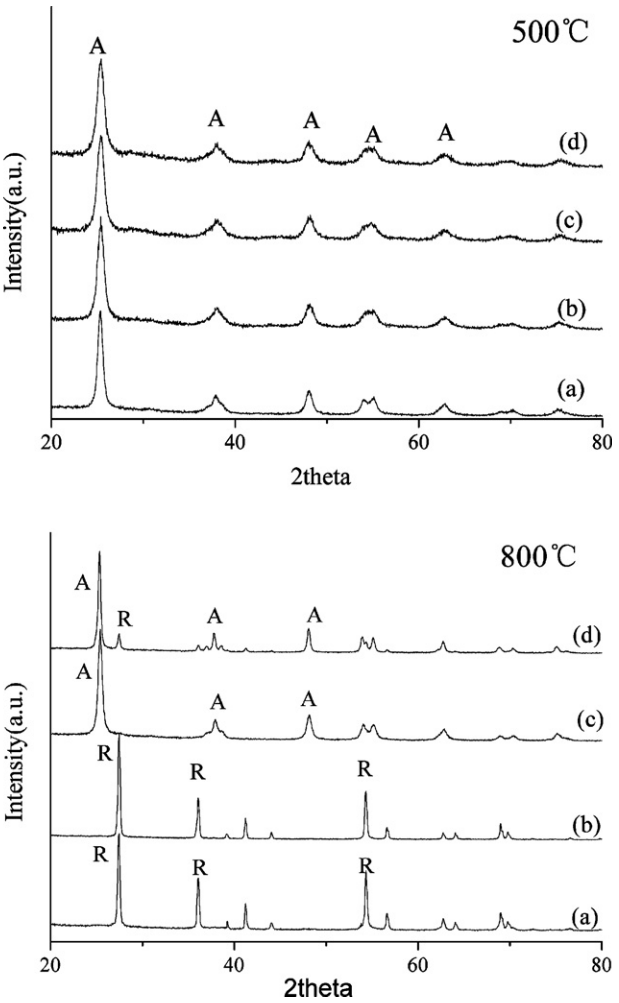

Fig. 1. XRD patterns measured for (a) pure TiO_2, (b) Fe-TiO_2, (c) La-TiO_2 and (d) Fe-La-TiO_2 with different calcination temperature (at 500 and 800 °C).

2. Experimental

2.1. Materials and synthesis

All the chemicals used in the experiments were reagent grade and used as received without further purification. Tetrabutyl titanate, ferric nitrate and lanthanum nitrate were used as starting materials. The material was prepared via a facile sol–gel route as follows. First, 10 mL tetrabutyl titanate was mixed with 40 mL anhydrous ethanol (solution A). Solution B consisted of 1.0 mL deionized water, 10 mL anhydrous ethanol and 1 mL 70% HNO_3, ferric nitrate and lanthanum nitrate in the required stoichiometry (Fe: La: Ti = 0.002: 0.02: 1, molar ratio). Then solution A was added dropwise into solution B under vigorous stirring at room temperature for 12 h until the transparent sol was obtained. After being dried in air at 80 °C for 12 h, the obtained mixture was calcined at various temperature from 300 to 800 °C. The sample was designated as Fe-La-TiO2. Fe^{3+}, La^{3+} single doped TiO_2, and pure TiO_2 were prepared following the same procedure. They were designated as Fe-TiO_2, La-TiO_2 and pure TiO_2, respectively.

Table 1
Specific surface area and crystallite size property of undoped and doped samples.

Calcination temperature (°C)	Catalyst	Surface area ($m^2\,g^{-1}$)	Average crystallite size (nm)
500	Pure TiO_2	63	14
	Fe-TiO_2	78	12
	La-TiO_2	75	11
	Fe-La-TiO_2	84	10
800	Pure TiO_2	29	28
	Fe-TiO_2	25	30
	La-TiO_2	39	25
	Fe-La-TiO_2	46	22

2.2. Catalyst characterization

X-ray diffraction (XRD) patterns were obtained with a Rigaku D/Max diffractometer operating at 40 kV, 30 mA with Bragg–Brentano geometry using Cu Kα radiation (λ = 1.5405 Å). The scan ranged from 20 to 80° (2θ°) with a scan rate of 3° min^{-1}. The S_{BET} of the samples were determined through nitrogen physical adsorption at 77 K (Micromeritics ASAP 2010). All the samples were degassed at 150 °C before the measurement. Raman measurements were performed at room temperature using a Via+ Reflex Raman spectrometer with the excitation light of 514 nm. X-ray photoelectron spectroscopy (XPS) were performed on a SPECS ESCA system with Mg Kα source ($h\nu$ = 1253.6 eV) at 10.0 kV and 20.0 mA. Atomic absorption spectrometry (Varian Duo 220) was used to determine the dopant concentration in the powders after dissolving them in HF–H_2SO_4 solution. The UV–visible diffuse reflectance spectra were obtained using a scan UV–vis spectrophotometer (Varian Cary 500) equipped with an integrating sphere assembly, while $BaSO_4$ was used as the reference material and the analysis range was from 200 to 800 nm.

2.3. Photocatalytic activity

The photocatalytic activity of each simple was evaluated by the degradation of methylene blue (MB) in TiO_2 aqueous solution under UV and visible light irradiation. A 300-W high-pressure Hg lamp for which the predominated irradiation wavelength is 365 nm was used as a UV light source. A 1000-w halogen lamp equipped with a UV cut-off filters (λ > 420 nm) was used as a visible light source. The photocatalyst (0.10 g) was added into an 100-mL quartz photoreactor containing 80 mL of a 1.0×10^{-4} g L^{-1} MB solution which. The photoreactor was cooled with flowing water in a quartz cylindrical jacket around the reactor, and ambient temperature was maintained at 25 °C during the photocatalytic reaction. The suspension was stirred in dark for 30 min to in order to reach the adsorption–desorption equilibrium. Then the suspension was irradiated under UV and visible-light. Samples were withdrawn periodically from the reactor, then centrifuged and analyzed by recording variations in the absorption in the UV–vis spectra of MB using a Cary 500 UV–vis spectrophotometer at its characteristic wavelength (λ = 665 nm).

3. Results and discussion

3.1. X-ray diffraction

XRD measurements were performed to identify the crystalline phases synthesized by the sol–gel process at calcination temperatures ranging from 300 to 800 °C. Fig. 1 exhibits XRD patterns of pure TiO_2, Fe-TiO_2, La-TiO_2 and Fe-La-TiO2 calcinated at 500 and 800 °C. It can be seen that the diffraction peaks of all samples which calcinated at 500 °C are ascribed to the peaks of TiO_2 anatase phase. When the calcination temperatures increased to 800 °C, rutile phase appears in sample of pure TiO_2 and Fe-TiO_2, while anatase is still the unique phase in sample of La-TiO_2 and predominant phase in the sample of Fe-La-TiO2. No obvious diffraction peaks that could be attributed to the dopants are observed.