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Preparation and photocatalysis of TiO_2 nanoparticles co-doped with nitrogen and lanthanum

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Nanoparticles of TiO_2 powder co-doped with La and N were prepared using a coprecipitation method followed by being two hours calcinated at a temperature ranging from 500 to 600°C in NH_3/Ar atmosphere. Uniformly co-doped TiO_2 nanocrystalline was 5–15 nm with surface area 65–125 m^2/g. Optical absorption along with the microstructural investigation for monodoped and co-doped catalyst provided that a part of O vacancy of Ti_5O_9 was occupied by N, which is responsible for the band-gap narrowing of TiO_2, while La^{3+} doping prevents the aggregation of powder in process of nitrification. Superior catalytic activity was observed in the co-doped TiO_2 under visible light ($350 < \lambda < 450$ nm). 20 mg/l methyl orange solution could be docomposed completely within 1 h using the 0.5 at.% La^{3+} doped TiO_2 calcinated in NH_3 for 2 h. © *2004 Kluwer Academic Publishers*

1. Introduction

Titanium dioxide (TiO_2) is widely known to be the best photocatalyst due to its chemical stability, low cost and no toxicity. It acts by UV irradiation at around 360 nm region ($E_g = 3.2$ eV for anatase) and gives rise to excited-state electrons and holes at conduction band and valance band respectively, which can initiate various redox reactions at the semiconductor surface or interface. Nanometer TiO_2 provides large-scale surface with broad band gap because of the quantum size effect of nanoparticles [1]. In recent years, impurity doping has been widely performed by chemical synthesis in order to create photocatalysts operating under visible light irradiation [2–8]. For example, Choi *et al.* [5] found that TiO_2 doping with Fe^{3+}, Mo^{5+}, Ru^{3+}, Os^{3+}, Re^{5+}, V^{4+}, and Rh^{3+} increased photo-reactivity in the liquid-phase photo-degradation of $CHCl_3$, Jooho Moon *et al.* [6] showed that superior catalytic activity was observed in the Sb-doped TiO_2. But doped TiO_2 samples heated above 200°C show lower reactivities than the undoped TiO_2. Also, Asahi *et al.* [7] reported that nitrogen-doping nanometer thin film shifts the absorption edge to the visible region. But after being treated by NH_3 above 600°C, the surface area of the TiO_2-xNx was only 25% of pure TiO_2. Akihiko Hattori and Hiroaki Tada [8] found that the absorption coefficient for ultraviolet light increased in F-doped TiO_2 film, but the effect of dopanting with transition metal and nonmetal was not reported.

Rare earth ions have larger radii than Ti^{4+}, so they are mainly distributed on the surface when deposited onto TiO_2, that keep large surface areas of TiO_2 when treaded at high temperatures. TiO_2 co-doped with La^{3+} and Nitrogen is first reported in this paper. The effect of two dopants leads to significant enhancement in photodegradating of methyl orange.

2. Experiments

2.1. Catalyst preparation

Nanocrystalline La^{3+} doped TiO_2 catalyst was prepared by coprecipitation from titanium tetrachloride. In a typical experiment, $TiCl_4$ was added dropwise under vigorous stirring to distilled water (<15°C, pH = 1.5) adjusted with HCl. The concentration of $TiCl_4$ premature hydrolysis was 1.1 $mol \cdot L^{-1}$. 0.1 $mol/L^{-1}LaCl_3$ was dissolved in nitric acid, which was used as a precursor of the dopant. Different quantity of $TiCl_4$ solution and $LaCl_3$ solution were mixed to make the content of La^{3+} in the mixed solution to be predetermined values. Then the mixtures were heated at 90°C for 1 h, precipitated upon neutralization with NH_4OH, cooled to room temperature, allowed to stand for 24 h under stirring and filtered. The precipitated products were washed three times with distilled water and alcohol, then dried at 100°C for 12 h. The dried precipitates were calcined at 500°C for 2 h in air.

2.2. Nitrification of TiO_2 powder

La-doped TiO_2 were heated to temperature ranging between 500 and 600°C (heating rates of 5°C/min) in a flow of dry NH_3(67%)/Ar atmosphere in a quartz tube.

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The samples were held for 2 h and then cooled to room temperature in a flow of Ar gas.

For convenience, the samples were labeled as TL(x), TN(y) for La^{3+} and N-doped TiO_2, respectively, and TL(x)N(y) for La^{3+} and N co-doped TiO_2, where x and y refer to the nominal atom content of La^{3+} and the peak temperature of nitrification, respectively.

2.3. Catalyst characterization

Powder X-ray diffraction (XRD) patterns were obtained at room temperature with Cu K_α radiation for crystal phase identification and crystallite size estimation of doped TiO_2. The particle size was also determined by a Philips Tecnai transmission electron microscope (HRTEM) operating at 200 kV. Surface area of samples was determined by BET adsorption measurements on ST-03A adsorption meter. UV-Vis absorption spectra of samples were recorded on 760CRT spectrophotometer.

2.4. Photoactivity measurement

The photodegradation reaction was carried out in a Pyrex glass vessel with 0.10 g of each catalyst suspended in 100 ml methyl orange aqueous solution (20 mg/ml, pH = 5.0) adjusted with HNO_3. The catalysts were ultrasonically agitated for 10 mim in methyl orange solution in absence of light to attain the equilibrium adsorption on the catalyst surfaces. A 200-W high pressure Hg lamp was used as source of UV illumination. The incidence of the UV light was perpendicular to the surface of the solution at a distance of 10 cm with constant magnetic stirring. The wavelength selection was achieved with a filter transmitting only 350–450 nm. After a given irradiation time, the catalysts were separated from the supernatant by centrifugation. A UV-vis spectrophotometer was utilized to measure absorbances of methyl orange at 490 nm.

In this paper, the chemical reagents were all of analytical regent grade. All the measurements of photoactivity were carried out at room temperature.

3. Results and discussion

3.1. Characterization of the doped TiO_2 powders

The X-ray phase analysis of the samples prepared under different conditions is given in Fig. 1. It can be seen that a mixed structure of anatase and rutile crystalline phases coexisted at both 0.5% La-doped TiO_2 and La, N co-doped TiO_2, with the weight percent of anatase phase 85–88% according to the intensity of highest peak of the two phases. No rutile phase appear in undoped TiO_2. The average grain size calculated from the broadending of the (101) peak of anatase using Scherrer's equation was 5–15 nm.

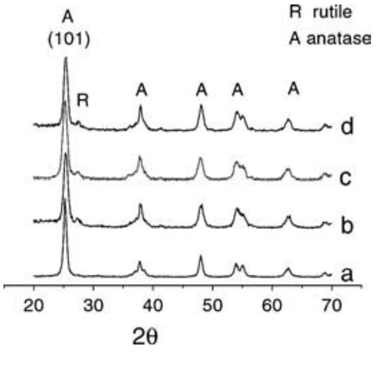

Figure 1 XRD patterns of the TiO_2 samples: (a) TiO_2, (b) TL(0.5), (c) TL(0.5)N(550) and (d) TL(0.5) N(600).

Fig. 2 shows HRTEM micrographs of nanocrystalline TiO_2. The average particle size of pure TiO_2 was approximately 7 nm for the Fig. 2a, 5 nm for Fig. 2b, 13 nm for Fig. 2c and 15 nm for Fig. 2d, respectively. These size is well matched with the XRD results.

Pure and 0.5%La-doped TiO_2 powders changed from white to yellowish after being annealed in NH_3/Ar gas at 500 to 600°C for 2 h. Oxynitride $TiO_{2-x}N_x (x \ll 1)$ appeared in Fig. 2c, d showing that part nanostalline of cubic or rhombus exist, it means that a part of TiO_2 changed into TiN, though XRD analysis showed no difference. According to Kamiya and co-workers [9, 10], the nitrification of the TiO_2 starts by the thermal dissociation of ammonia,

$$2NH_3 + \text{heat} \rightarrow N_2 + 3H_2$$

then several successive reduction steps occurs at high temperature [11].

$$TiO_2 + H_2 \rightarrow Ti_5O_9(\rightarrow Ti_4O_7 \rightarrow Ti_3O_5 \rightarrow TiO_3) + H_2O$$

Futher, the O vacancy of Ti_5O_9 will be occupied by N, the Oxynitride $TiO_{2-x}N_x$ has the same crystalline structure as TiO_2 when $x \ll 1$, or TiN when $x > 0.5$.

$$Ti_5O_9 + NH_3 \rightarrow TiO_{2-x}N_x + H_2O$$

The value of x can be controlled convenient by the treated temperature, time, or pressure of NH_3.

The radii of La^{3+} and Ti^{4+} are 0.115 and 0.068 nm, respectively, so it is likely that La^{3+} ion are mainly distributed on the surface of the TiO_2 nanoparticles, preventing the aggregation of powder when calcined at high temperature. Therefore the doped TiO_2 powder had smaller particle size and large surface area than pure TiO_2 as shown in Table I. La^{3+} doping also produced more oxygen vacancies on the surface of TiO_2 which are responsible for the temperature of nitrification decreasing by 100°C or so than pure TiO_2.

TABLE I Characterization of TiO_2 samples treated at different temperature for 2 h

Sample	Crystalline size (nm)	Surface area (m^2/g)	Temperature (°C)
TiO_2	7.5	103.2	500
TN(600)	18.2	32.3	600
TL(0.25)	6.4	116.7	500
TL(0.5)	5.4	122.6	500
TL(0.5)(500)	7.1	96.4	500
TL(0.5)N(550)	10.3	87.9	550
TL(0.5)N(600)	13.5	58.7	600

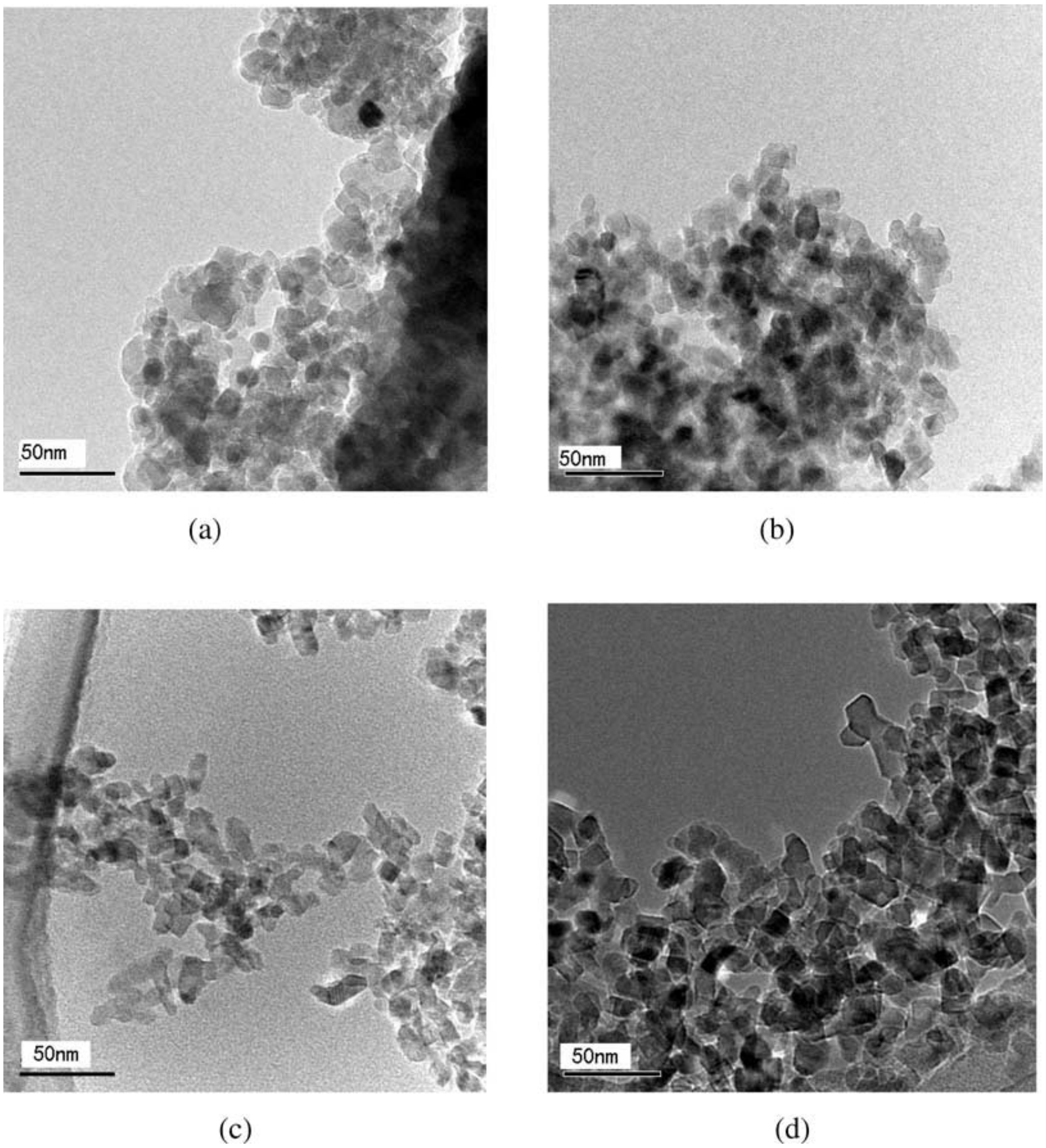

Figure 2 HRTEM micrographs showing nanocrystalline doped TiO_2: (a) TiO_2, (b) TL(0.5), (c) TL(0.5)N(550) and (d) TL(0.5)N(600).

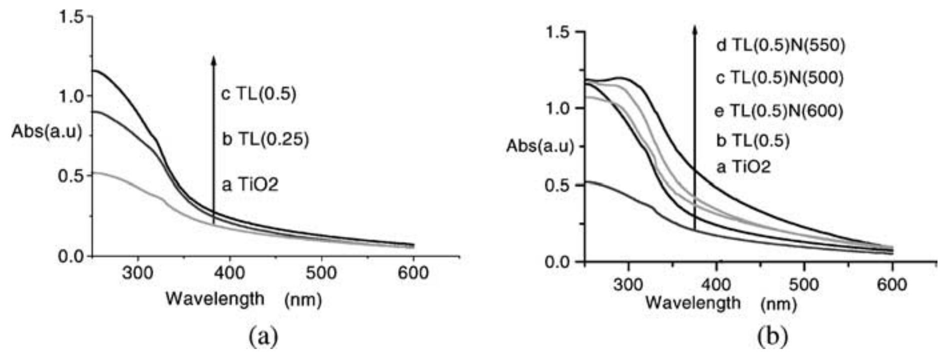

Figure 3 UV-Vis absorption spectra of suspend solutions of TiO_2, doped, and co-doped TiO_2.

The La^{3+} doping does not influence the band gap of the TiO_2 samples, but enhances the light absorption of the suspended solutions in water (Fig. 3a). This improvement can mainly be attributed to the increase in surface area by the La^{3+} doping. A significant red shift of the inset absorption of La and N co-doping TiO_2 samples were observed in Fig. 3b. It can be assigned to the substitutional N doping as Asahi [12] and co-workers had pointed out in their study, since N $2p_n$ to Ti d_{xy} instead of O $2p_n$ in TiO_2 nanostalline, a new energy level occurred on the top of the valence band and narrowed the band-gap of TiO_2. The light absorption increases with increasing nitrification temperature, but decreases in the absorption spectra was observed in sample TL(0.5)N(600). It may be attributed to a change in the crystal structure caused by the high

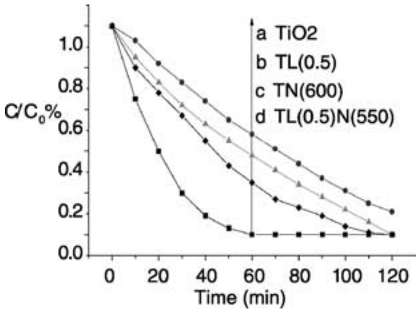

Figure 4 Decomposition rates of methyl orange in the water solution under visible light of 350 to 450 nm.

doping of N in the TiO_2 as the micrograph of (Fig. 2d) shows.

3.2. Characterization of photocatalytic

The photoreactivity of TiO_2, TL(0.5), TN(600), TL(0.5)N(550) are presented in Fig. 4. It shows that monodoped samples with La^{3+} or N (TL(0.5), TN(600)) both increase the decomposition of Methyl orange under visible light. At the same condition the photogradation rate of methyl orange for co-doped TiO_2 with La^{3+} and N is more than five times compared with the one produced by pure nanocrystalline TiO_2. The samples of TL(0.5)N(550) completely decomposed Methyl orange solution within 1 h. It can be attributed to the co-effect of N and La^{3+} in nanocrystalline TiO_2. As we described above, N-doping narrowed the band-gap to enhance the effectiveness of visible light, while La-doping not only increased the surface areas but also may serve as an electron trap in the oxide process. So the recombination of charge carriers is inhibited by such trapping and reaction efficiency is improved.

4. Conclusion

1. 0.5 at.% La^{3+} doping increased the surface areas of the samples and enhanced the absorption of UV light ($\lambda < 350$ nm).

2. N-doping narrowed the band-gap of TiO_2 nanocrystalline and enhanced the effectiveness of visible light (350 nm $< \lambda <$ 450 nm).

3. Superior catalytic activity was observed in the co-doped TiO_2 under visible light ($350 < \lambda < 450$ nm). Using the 0.5 at% La^{3+} doped TiO_2 calcinated in NH_3 for 2 h, 20 mg/l methyl orange solution could be docomposed completely within 1 h.

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