

Structure, luminescence properties and photocatalytic activity of europium doped-TiO₂ nanoparticles

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As a promising photocatalyst, semiconductor TiO₂ is the focus of numerous studies owing to its attractive characteristics in the treatment of environmental contaminants over the past 20 years. Unfortunately, its bad photocatalytic activity due to the fast recombination of photogenerated electron-hole pairs limits the commercialization of this technology. In recent years, in order to enhance the photocatalytic activity, modification of TiO₂ by rare-earth-element has become of an increasing interest because of their special photoluminescence and catalytic properties [1–4]. In this paper, europium is selected as a representative of rare earth elements to study the effects of Eu³⁺ ion doping on the structure, luminescence properties, and photocatalytic activity of TiO₂.

Europium doped-TiO₂ nanoparticles were prepared by sol-gel method using tetrabutyl titanate and Eu₂O₃ as the precursors. Eu₂O₃ powder was dissolved in hydrochloric acid to form EuCl₃ solution. A solution consisting of the EuCl₃ solution, 20 ml ethanol, and 1.06 ml deionized water was added dropwise to another solution containing 10 ml tetrabutyl titanate and 26 ml ethanol under vigorous stirring, and a titania sol was obtained. The sol was dried under an infrared lamp and then milled to powder, followed by calcining at different temperatures for 2 hr. Undoped TiO₂ was prepared in the same way except for the Eu₂O₃. Eu³⁺-doped TiO₂ nanoparticles are designated as TEX, where X is the mole percent of Eu³⁺ ions.

Fig. 1a and b show the XRD patterns of undoped TiO₂ and TE0.3 calcined at different temperatures, respectively. It can be seen that undoped TiO₂ calcined at 500 °C is a mixture of anatase (ca. 68.5%) and rutile (ca. 31.5%), while Fig. 1b shows that TE0.3 calcined at 500 °C is pure anatase phase, and in TE0.3 calcined at 700 °C, the major crystal phase is anatase (ca. 81.0%) accompanied by a rutile phase (ca. 19.0%). Compared with undoped TiO₂, the appearance temperature of rutile for TE0.3 is obviously increased. The transformation of anatase to rutile in undoped TiO₂ occurs from

300 to 500 °C, lower than that of TE0.3 (500–700 °C). The anatase phase can be observed in TE0.3 until the temperature is increased to 900 °C, showing a strong inhibition effect for the phase transformation. It is expected that the surrounding europium ions will inhibit the transition of the anatase-to-rutile through the formation of a Ti–O–Eu bond [1, 4].

When Eu³⁺ ions are doped into the TiO₂ matrix, there are two possible states: one is that Eu³⁺ ions replace or are replaced by Ti⁴⁺ ions; the other is Eu³⁺ in the gap of TiO₂ matrix. No matter what is true, it could enhance the local distortion of crystal lattice because the ionic radius of Eu³⁺ ion (0.95 Å) is larger than that of Ti⁴⁺ ion (0.68 Å). Crystal lattice parameters were measured to determine whether Eu³⁺ ions enter the lattice to form solid solution. Table I shows the crystallite size of anatase, lattice parameter, and cell volume of undoped TiO₂ and TE0.3. It can be seen that the lattice parameters and cell volume of TiO₂ in TE0.3 are larger than those of undoped TiO₂ calcined at the same temperature, meaning that the entering of Eu³⁺ into the TiO₂ lattice results in the distortion and dilation of crystal lattice. Additionally, europium oxide phase, Eu₂O₃, is not found in TE0.3 calcined at different temperatures. Europium titanium oxide, Eu₂Ti₂O₇, appears in TE0.3 calcined at 1200 °C.

The particle size is calculated by using Scherrer's formula and the results are listed in Table I. It can be seen that the crystalline size of TE0.3 is smaller than that of undoped TiO₂ calcined at the same temperature. It is evident that the particle growth is restrained by europium doping. A given amount of Eu³⁺ enters the lattice of TiO₂ and the Eu–O–Ti bonds are formed on the surface of TiO₂ during calcination, which retards the contact of particles and the transfer and rearrangement of Ti and O in particles.

Fig. 2 shows the excitation spectra of Eu³⁺ in TE0.3 calcined at 400, 900, and 1000 °C (The monitor wavelength is 612 nm). In the spectra of TE0.3 calcined at 400 °C, the peaks at 394, 414, 464, 532 nm correspond

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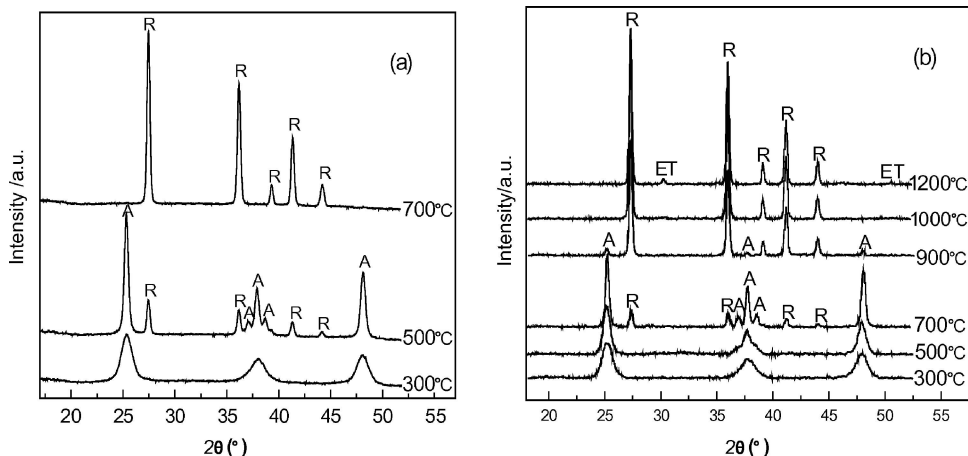


Figure 1 XRD patterns of TiO₂ (a) and TE0.3 (b) calcined at different temperatures. A: anatase R: rutile ET: europium titanium oxide.

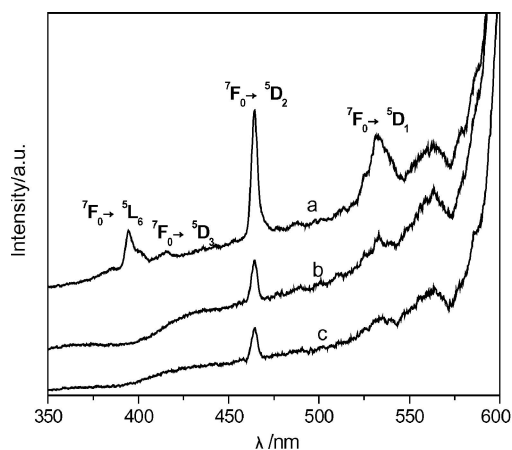


Figure 2 Excitation spectra of Eu³⁺ ions in TE0.3 calcined at 400 (a), 900 (b), and 1000 °C (c).

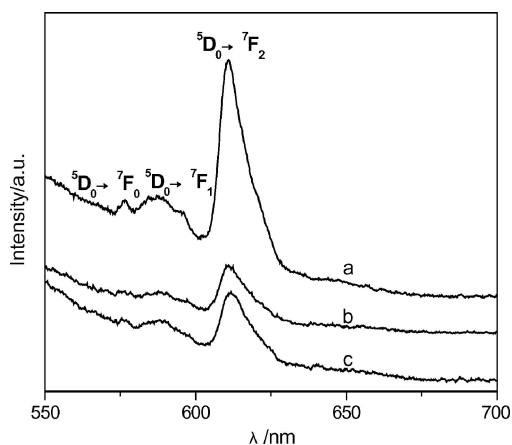


Figure 3 Emission spectra of Eu³⁺ ions in TE0.3 calcined at 400 (a), 900 (b), and 1000 °C (c).

to ${}^7F_0 \rightarrow {}^5L_6$, ${}^7F_0 \rightarrow {}^5D_3$, ${}^7F_0 \rightarrow {}^5D_2$, ${}^7F_0 \rightarrow {}^5D_1$, respectively. However, no ${}^7F_0 \rightarrow {}^5L_6$ transition was found in the spectra of TE0.3 calcined at 900 and 1000 °C, and no luminescence was detected in TE0.3 calcined at 1200 °C. From the results of XRD, it is known that TE0.3 calcined at 400 °C is anatase, while TE0.3 calcined at 900 and 1000 °C is rutile, and TE0.3 calcined at 1200 °C is a compound of rutile TiO₂ and Eu₂Ti₂O₇. Comparison of their excitation spectra shows that the excitation intensity decreases with anatase transformation to rutile. After the rutile phase forms, the enhancement of local symmetry, contraction of cell volume, and reduction of porosity could result in the increase of local concentration of Eu³⁺ ions, which contributes to the fluorescent intensity decrease [5].

The electronic structure of the rare earth element Eu is the f⁶ electronic configuration. The first fluores-

cence metastable state of Eu³⁺ ions is 5D_0 , and the ground state is 7F_j ($j = 0, 1, 2, 3, 4, 5, 6$). Among the abundant emission spectra, ${}^5D_0 \rightarrow {}^7F_1$ and ${}^5D_0 \rightarrow {}^7F_2$ transitions are the characteristic emission bands, whose peak sites are independent of the species of host matrix. The emission spectra of TE0.3 after an excitation of 464 nm, with peaks at 587 and 611 nm, correspond to ${}^5D_0 \rightarrow {}^7F_1$ (magnetic dipole transition) and ${}^5D_0 \rightarrow {}^7F_2$ (electronic dipole transition), respectively, as shown in Fig. 3. The intensity of the ${}^5D_0 \rightarrow {}^7F_2$ transition is strong in low site symmetry, whilst that of ${}^5D_0 \rightarrow {}^7F_1$ is strong in high site symmetry. The ratio (R value) of the intensity of ${}^5D_0 \rightarrow {}^7F_2$ to that of ${}^5D_0 \rightarrow {}^7F_1$ reflects the chemical bond and site symmetry of particles around Eu³⁺ ions [6]. The R values of TE0.3 calcined at 400, 900, and 1000 °C are 6.14, 4.37, and 3.91, respectively. The R value becomes smaller

TABLE I XRD results of photocatalysts

Catalysts	Calcination temperature (°C)	Anatase content (%)	Crystallite size of anatase (nm)	a (nm)	c (nm)	Cell volume (nm ³)
TiO ₂	300	100	11.9	0.378 53	0.947 45	0.135 753 2
	500	68.5	30.7	0.378 03	0.948 93	0.135 608 9
TE0.3	300	100	10.4	0.379 85	0.953 62	0.137 597 4
	500	100	22.1	0.379 67	0.954 14	0.137 540 2
	700	81	40.4	0.378 62	0.953 73	0.136 717 3

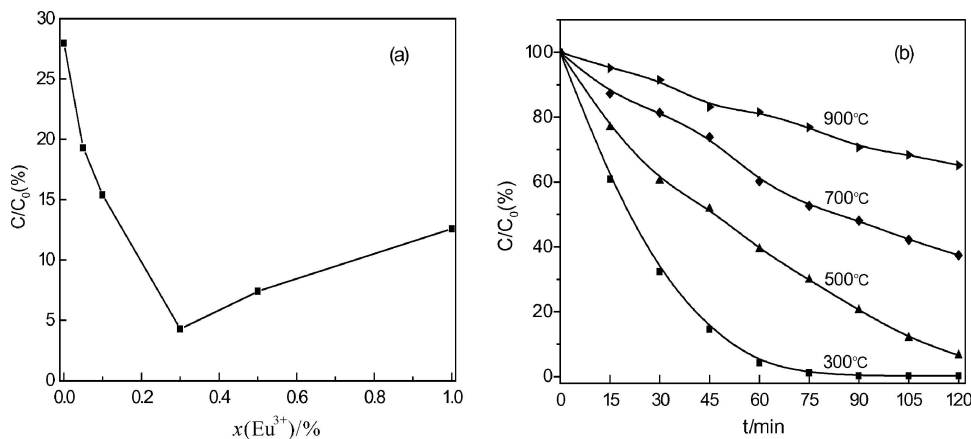


Figure 4 Effect of doping content (a) and calcination temperature (b) on the photocatalytic activity of Eu^{3+} -doped TiO_2 .

with the increase of calcination temperature, suggesting that the site symmetry increases after the transformation from anatase to rutile TiO_2 . Thus it can be concluded that the crystalline phase composition of TiO_2 may be estimated by the excitation and emission spectra of Eu^{3+} ions.

The gaseous photocatalytic activities of samples were tested on the degradation of heptane. We applied Eu^{3+} -doped and undoped TiO_2 to the reaction system containing heptane (1000 ppm), oxygen (20%), and ultrapure nitrogen. The band gap radiation was provided by a 400 W high-pressure mercury lamp. As shown in Fig. 4a, after irradiation for 60 min, all Eu^{3+} -doped TiO_2 with various Eu^{3+} ion concentrations (from 0.05 mol% to 1 mol%) exhibit higher photoactivities than that of undoped TiO_2 , and TE0.3 shows the highest photocatalytic activity, which suggests that the Eu^{3+} doping enhances the photocatalytic activity of TiO_2 and there is an optimum doping content of Eu^{3+} ions in TiO_2 particles. The photocatalytic activities of TE0.3 decrease with increasing calcination temperature, as shown in Fig. 4b. It is known that the photocatalytic activity of TiO_2 nanoparticles is influenced by many factors: (1) in general, the larger expansion of crystal lattice and greater cell volume could produce more defects in the lattice or on the surface, resulting in a corresponding increase in photoactivity. From the data of cell parameter and cell volume in Table I, it is supposed that the photocatalytic activity of Eu^{3+} -doped TiO_2 is higher than that of undoped TiO_2 calcined at the same temperature; (2) the crystalline phase of TiO_2 is closely related to its photoactivity. It has been reported that anatase is more active than rutile in photocatalysis because anatase possesses a slightly higher Fermi level and a high degree of surface hydroxylation [7, 8]. Thus it is not surprising that the photoactivities of anatase TE0.3 calcined at lower temperatures are superior to those of rutile TE0.3 calcined at higher

temperatures; (3) in the case of the same phase, when the particle size is very small, the specific area is large and the reactive sites are adequate to absorb the molecular pollutants. On the other hand, the small particle size makes the diffusion of the photoexcited electron-hole pairs to the surface faster than in the large particles and gives rise to a decrease in the probability of recombination. The photocatalytic activity of Eu^{3+} -doped TiO_2 with smaller particle size is greater than that of undoped TiO_2 . Moreover, for TE0.3, the photoactivity decreases with increasing calcination temperature, partially because the size increases.

Acknowledgements

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