Ce-doped titania nanoparticles: The effects of doped amount and calcination temperature on photocatalytic activity

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Abstract. A series of Ce-doped TiO₂ nanoparticles with different doped amount and calcination temperature were prepared by sol-gel method. These obtained samples were characterized with X-ray diffraction (XRD), transmission electron microscope (TEM) and ultraviolet-visible diffuse reflectance spectra (DRS), and their photocatalytic activities were evaluated by the photocatalytic degradation of methyl orange. Results showed that Ce doping inhibits the growth of crystal size and the phase transformation from anatase to rutile, leads to lattice distortion and expansion of TiO₂. Furthermore, Ce doping brings the red-shift of absorption profile and the increase of photons absorption in the range of 400-600 nm. Photocatalytic degradation of methyl orange shows that Ce doping improves the photocatalytic activity of TiO₂. The optimal doped amount is 0.05 mol% and the optimal calcined temperature is 600 °C for the maximum photocatalytic degradation efficiency in our experiment.

1. Introduction
As a promising photocatalyst, TiO₂ has been intensely researched for the treatment of environmental pollution in recent decades. However, there are still some problems which restrict its application in practical industry, such as restrictive light absorption due to its large band gap, the fast recombination of photo-generated electrons and holes [1]. Therefore, it is of great interest to develop new photocatalysts with visible-light response and effective separation of electron-hole pairs.

Recently, some reports have demonstrated that doping TiO₂ with suitable metal or nonmetal ions is a useful strategy to improve the mentioned above two performances of TiO₂ [2]. Due to incompletely occupied 4f and empty 5d orbitals, rare earth metals are often used as catalyst or promote catalysis. Some results have shown that doping TiO₂ with rare earth metals or their oxides is an effective method to improve the photocatalytic activity of TiO₂ [3]. As one of the rare earth metals, Ce has been used as a dopant to enhance the photocatalytic activity of the TiO₂ [4]. However, there is an example that Ce-doping brought negative effect on the photocatalytic performance of TiO₂ [5].

In order to clarify the effects of Ce-doping, in current work, a series of Ce-doped TiO₂ nanoparticles with different doped amount and calcination temperature were prepared by sol-gel method. The obtained samples were characterized by X-ray diffraction (XRD), transmission electron microscope (TEM) and ultraviolet-visible diffuse reflectance spectra (DRS), and their photocatalytic activities were investigated by photocatalytic degradation methyl orange (MO) in water.
2. Experimental

2.1. The preparation of photocatalysts

All reagents used in this experiment are analytical grade without further purification. Ce-doped TiO$_2$ nanoparticles were prepared by a sol-gel route. In a typical procedure, 17.0 mL tetra-n-butyl titanate was firstly dissolved in 30.0 mL ethanol under vigorous stirring. Another solution containing 28.3 mL ethanol, 7.2 mL distilled water, 20.0 mL acetic acid, and a certain weight of Ce(NO$_3$)$_3$·6H$_2$O was slowly added into the above solution under magnetic stirring at room temperature. The mixture was hydrolyzed for 60 min under vigorous stirring, and then the transparent sol was obtained. The sol was aged for 6 h at 60°C to obtain gel, and then the gel was dried at 80°C in a vacuum oven to remove the solvents. The dry gel was milled into powders in a mortar, and then was calcined in a muffle furnace at different temperature for 2 h, resulting Ce-doped TiO$_2$ nanoparticles. Un-doped TiO$_2$ was prepared by the same procedure without Ce(NO$_3$)$_3$·6H$_2$O addition. For convenience, Ce-doped TiO$_2$ samples were labelled as TiCe(X)Y and un-doped TiO$_2$ sample was labelled as TiY, where X stood for the molar percentage of Ce in theoretical product and Y referred to the calcined temperature. For example, a sample doped with 0.05 % Ce and calcined at 600°C, we labelled it as TiCe(0.05)600.

2.2. Characterizations

XRD patterns of all samples were obtained at room temperature with a Holand X’pert PROMPD diffractometer (Cu K$_\alpha$, radiation, $\lambda$ = 1.5406 Å). The crystal size was estimated by applying the scherrer equation $D = K\lambda/(\beta\cos\theta)$ to the full width at half maximum (FWHM) of the (101) peak of anatase, where $K$ is a constant (shape factor, about 0.89), $\lambda$ is the X-ray wavelength, $\beta$ is the FWHM of the diffraction line, and $\theta$ is the diffraction angle. Transmission electron microscope (TEM) was carried out on JEM-2012. A Shimadzu spectrophotometer (TU1901, China) equipped with an integrating sphere was used to record DRS of the samples. The baseline correction was done using a calibrated sample of barium sulfate, and the spectra was recorded at room temperature in air in the range of 240-600 nm.

2.3. Photocatalytic activity testing

The experiment of the photo degradation was carried out in a photoreaction system. Ultraviolet irradiation was offered by a 500-W high-pressure mercury lamp with major emission at 365 nm. The reactive bottle was a 250-mL cylindrical vessel with a water-cooled quartz jacket, and the lamp was located in the center of the quartz jacket. A magnetic stirrer was equipped at the bottom of the reactor to achieve effective dispersion. Air was bubbled through the reaction solution from the bottom to ensure a constant dissolved O$_2$ concentration. The amount of catalysts was 2 g/L. The initial MO concentration was 40 mg/L, and 250 mL MO solution was used for the photocatalytic degradation every time. Some aqueous samples were withdrawn at different intervals. The residual concentration of MO was measured at 465 nm with a spectrophotometer (DR/2500, America HACH Company).

3. Results and discussions

3.1. The effects of Ce-doped amount

In order to investigate the effects of doped amount, Ce-doped TiO$_2$ samples with different doped amount (i.e. 0.05%, 0.10%, 0.50% and 2.00%) and calcined at 500°C were prepared. Figure 1A shows the XRD patterns of these samples. Only the single anatase TiO$_2$ was detected in all samples. With the increase in Ce-doped amount, the diffraction peaks of anatase phase become broader in width and weaker in intensity, which implies that Ce doping inhibited the growth of nanocrystallite size. In addition, the mean crystalline sizes calculated by the Scherrer equation were summarized in Table 1, from which it is observed that the crystalline size decreased with the increase in Ce-doped amount, which can be ascribed to that a given amount of Ce ions has entered into the lattice of TiO$_2$ and the Ti-O-Ce bonds have formed on the surface of TiO$_2$ during calcination, which retarded the contact of
particles, the transfer and rearrangement of Ti and O in particles [6]. Smaller crystal size means more powerful redox ability due to the quantum size effect, and smaller crystal size is in favour of the shifting of photogenerated carriers to the surface of photocatalyst and reacting with reactant. That is, Ce doping improved the transfer efficiency of photogenerated carriers to surrounding supports, and then, enhanced the photocatalytic activity of TiO\textsubscript{2}. From Table.1, it can be seen that unit cell volumes and lattice distortion of Ce-doped TiO\textsubscript{2} particles were larger than that of un-doped TiO\textsubscript{2}, meaning that the entering of Ce ions into the TiO\textsubscript{2} lattice resulted in the distortion and expansion of crystal lattice. It is well known that oxygen molecules are easy to be adsorbed as electron trap on the sites of structure defects brought by distortion and expansion of crystal lattice. Therefore, the recombination rate of electron and hole pairs can be reduced, which has a positive influence on the photocatalytic activity of TiO\textsubscript{2} [7].

![Figure 1](image1)

**Figure 1.** (A) XRD patterns of samples (A: Anatase): (a) Ti500, (b) TiCe(0.05)500; (c) TiCe(0.10)500; (d) TiCe(0.50)500; (e) TiCe(2.00)500; (B) TEM image of TiCe(0.05)500.

| Sample       | Crystal size (nm) | Matrix distortion (%) | Crystal parameter |
|--------------|-------------------|-----------------------|-------------------|
|              |                   |                       | a (nm)            | c (nm)            | V (nm\textsuperscript{3}) |
| Ti500        | 18.2              | 0.8595                | 0.3892            | 0.8084            | 0.1225             |
| Ti600        | 51.9              | 0.3012                | 0.3888            | 0.8166            | 0.1234             |
| Ti700        | 79.1              | 0.1976                | 0.3898            | 0.8127            | 0.1235             |
| Ti800        | 101.8             | 0.1534                | 0.3884            | 0.8221            | 0.1240             |
| TiCe(0.05)500| 16.3              | 0.9610                | 0.3892            | 0.8119            | 0.1230             |
| TiCe(0.10)500| 16.2              | 0.9669                | 0.3883            | 0.8302            | 0.1252             |
| TiCe(0.50)500| 15.4              | 1.0719                | 0.3897            | 0.8197            | 0.1245             |
| TiCe(2.00)500| 13.6              | 1.1481                | 0.3891            | 0.8154            | 0.1234             |
| TiCe(2.00)600| 13.2              | 1.1838                | 0.3886            | 0.8235            | 0.1244             |
| TiCe(2.00)700| 15.3              | 1.0208                | 0.3878            | 0.8286            | 0.1246             |
| TiCe(2.00)800| 41.0              | 0.3816                | 0.3888            | 0.8276            | 0.1251             |

Figure 2A shows the evolution of DRS of TiO\textsubscript{2} doped with different Ce amount and calcined at 500 °C. Compared with the spectrum of un-doped TiO\textsubscript{2}, a red-shift of the absorption profile and photons absorption increase in the range of 400-600 nm in the Ce-doped TiO\textsubscript{2} were observed, and the red-shift extent increased with the increase in Ce-doped amount. This red-shift can be attributed to the charge-transfer transition between the rare earth ion f electrons and the TiO\textsubscript{2} conduction or valence band [8]. During the photocatalytic process, electrons are excited and transferred from valence band to conduction band when photons are absorbed by photocatalyst, thus electron-hole pairs generate. The electrons in the conduction band are captured by oxygen molecules dissolved in the suspension, and
the holes in the valence band are captured by OH or H₂O species adsorbed on the surface of catalysts, to produce the hydroxyl radical. So the catalysis activity is related with the number of electron-hole pairs in TiO₂. The more electron-hole pairs exist on the surface of TiO₂, the more highly efficiency obtains the catalysis activity in decolorization [9]. The number of electron-hole pairs depends on optical property of samples. The longer wavelength light can be absorbed, under the same light irradiation, the more electron-hole pairs will be formed on the surface of TiO₂. Ce doping leads to red-shift of the absorption profile and photons absorption increase in the range of 400-600 nm, which are advantaged to generating of electron and hole under light irradiation.

![Figure 2](image1.png)

Figure 2. (A) DRS spectra of samples; (B) Degradation curves of MO over samples.

The photocatalytic activities of the samples were measured by the degradation MO solution without concerning the degradation intermediates in detail. The residual concentration ratios \( C_t/C_0 \) of MO versus time under mercury lamp irradiation are obtained and shown in Figure 2B. Where, \( C_t \) and \( C_0 \) (mg/L) are signed as \( t \) time and the initial concentrations of MO in solutions, respectively. It can be seen that doping with proper Ce ions can improve the photocatalytic activity of TiO₂, and the reasons may be attributed to the smaller crystallite size, lattice distortion, the red shift of the absorption profile, and photons absorption increase in the range of 400-600 nm because of Ce doping. The optimal doped amount is 0.05 mol% for the maximum photocatalytic degradation efficiency.

3.2. The effects of calcination temperature

Figure 3 shows the XRD patterns of un-doped TiO₂ and Ce-doped TiO₂ calcined at different temperature. It can be seen that all samples presented anatase structure except for Ti800, in which 11 wt% rutile structures appeared, indicating that phase transition from anatase to rutile was inhibited due to Ce doping. It can be seen from Table. 1 that the crystal size increased with the increase in calcination temperature, and the increased velocity of un-doped TiO₂ was more rapid than that of Ce-doped TiO₂, implying that Ce doping inhibited the growth of crystal size.

![Figure 3](image2.png)

Figure 3. XRD patterns of samples calcined at different temperature (A: Anatase; R: Rutile).
Figures 4A and B show the effect of calcination temperature on the DRS results of un-doped and Ce-doped TiO$_2$ (doped amount is 0.05%), respectively. Some red-shift of the absorption profile was observed with calcination temperature increase from Figure 4A. The red-shift extent of the sample calcined at 800 °C was the biggest among the four samples, which can be attributed to the appearance of rutile structure confirmed by XRD pattern. Compared with the spectrum of un-doped TiO$_2$, the red-shift of the absorption profile and photons absorption increase in the range of 400-600 nm of Ce-doped TiO$_2$ were also observed from Figure 4B.

Figure 4C shows the photocatalytic degradation results of Ce-doped and un-doped TiO$_2$ calcined at different temperature. In comparison with un-doped TiO$_2$, Ce doping improved the photocatalytic activity of TiO$_2$ markedly. The effects of calcination temperature on photocatalytic activity of un-doped TiO$_2$ and Ce-doped TiO$_2$ were very obvious. The optimal calcined temperature was 600 °C. Furthermore, the Ce-doped sample revealed its higher catalytic activity. The reason may be ascribed to the restraining of crystal size increase, the lattice distortion and expansion, the red-shift of the absorption profile and photons absorption increase in the range of 400-600 nm.

**Figure 4.** (A) DRS spectra of TiO$_2$ calcined at different temperature; (B) DRS spectra of Ce-doped TiO$_2$ calcined at different temperature; (C) Degradation curves of MO over samples calcined at different temperature.

### 4. Conclusions

Ce doping decreases the crystal size of TiO$_2$ nanoparticles, which is in favour of the shifting of photogenerated carriers to the surface of photocatalyst and reacting with reactant. Ce doping leads to lattice distortion and expansion of TiO$_2$, which reduces the recombination of electron and hole, and then produces more hydroxyl radical. Furthermore, Ce doping brings a red-shift of the absorption profile and photons absorption increase in the range of 400-600 nm, which is advantageous of the generation of electron and hole under light irradiation. Therefore, Ce doping is an effective mean to improve the photocatalystic activity of TiO$_2$ for degradation organic pollutants in water.

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