

Different effects of cerium ions doping on properties of anatase and rutile TiO₂

Guangqin Li^{a,b}, Chunyan Liu^{a,*}, Yun Liu^a

^aLaboratory of Organic Optoelectronic Functional Materials and Molecular Engineering, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100080, People's Republic China

^bGraduate School of the Chinese Academy of Sciences, Beijing 100806, China

Received 8 March 2006; received in revised form 26 April 2006; accepted 5 May 2006

Available online 19 June 2006

Abstract

Pure and Ce⁴⁺ doped anatase and rutile TiO₂ were prepared by hydrothermal methods and characterized by XRD, TEM, UV–vis diffusion spectroscopy, and XPS measurements. The photocatalytic reactivity of the catalysts was evaluated by the photodegradation of Rhodamine B (RB) under ultraviolet irradiation. The photocatalytic efficiency of the rutile sample doped with an appropriate amount of Ce⁴⁺ was enhanced while all Ce⁴⁺ doped anatase samples showed a much lower activity than pure anatase. The reasons were discussed

© 2006 Elsevier B.V. All rights reserved.

Keywords: Cerium ions; Doping; Anatase; Rutile; TiO₂

1. Introduction

Since the discovery of photoelectrochemical splitting of water on titanium dioxide electrodes [1], photocatalysis has caused much attention owing to its wide application in complete mineralization of various organic pollutants in waste water and air. Due to its desirable properties, such as chemical inertness, non-toxicity, low cost and high photocatalytic efficiency, TiO₂ remains the most promising material as photocatalysts, gas sensors, solar cells and white pigment materials [2–4]. However, the photocatalytic efficiency at the present stage is still very low, which is mainly caused by the fast recombination of photogenerated electron–hole pairs. Thus, further improving the photocatalytic efficiency is still a major challenge in the photocatalysis research field until now.

Doping metal ions in TiO₂ has been proven to be an efficient route to enhance the photocatalytic activity. Transition metal-ion-dopants in TiO₂, such as Fe³⁺, Mn²⁺, Ni²⁺, Pd²⁺, Pt⁴⁺, V⁵⁺, W⁶⁺ etc. have been investigated previously, but unifying conclusions are difficult to make because the photoreactivity of doped TiO₂ appears to be affected by many factors, such as

particle size, dopant concentration, the energy level of the dopants within TiO₂ lattice, their d electronic configuration, the light intensity for reactions and so on [5–11].

Recently, doping lanthanide ions into TiO₂ has become one research hotspot [12–17]. Lanthanide ions can form complexes with various organics by the interaction of the functional groups of the organic molecules with f-orbitals of lanthanides. Thus, doping lanthanide ions into a TiO₂ matrix could provide a means to concentrate organic pollutants on the semiconductor surface and therefore improve the photoreactivity, and doped lanthanide ions can improve the separation efficiency of electron–hole pairs by trapping photogenerated electrons [18,19]. Some visible light reactive TiO₂ photocatalysts prepared by doping with lanthanide ions have been prepared recently and red shifts of the absorption edge of TiO₂ by doping with lanthanide ions also have been reported [20–23].

Although lanthanide ions doped TiO₂ has been studied intensively, little attention has been paid to the different action of lanthanide ions doping on the activity of anatase and rutile TiO₂. In this work, pure and Ce⁴⁺ doped anatase and rutile TiO₂ were prepared by hydrothermal methods and RB was used as a probe molecule to evaluate the photocatalytic reactivity of the samples. The photocatalytic reactivity of commercial Degussa P-25 was also tested as a contrast. Results showed that the photocatalytic efficiency of the doped rutile TiO₂ with an

* Corresponding author. Tel.: +86 10 82543573; fax: +86 10 62554670.

E-mail address: cylu@mail.ipc.ac.cn (C. Liu).

appropriate amount of Ce^{4+} increased and was comparable to Degussa P-25 at the optimum doping content (0.5 at%), while the photocatalytic efficiency of the doped anatase samples greatly reduced.

2. Experimental

TiCl_4 (99%), $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ and Rhodamine B (RB) were all analytical grade and purchased from Beijing Chemical Factory. 1.5 M TiCl_4 aqueous solution was prepared by diluting TiCl_4 (99%) in an ice-water base. Degussa P25 (average particle size 30 nm and specific surface area of $50 \text{ m}^2 \text{ g}^{-1}$) was used as received. The structure of RB is given in Scheme 1. Deionized water was used for solution preparation in our experiment.

Pure and Ce^{4+} doped anatase TiO_2 were prepared by a hydrothermal process. The detailed process was described as the following. Under wild stirring, 10 ml deionized water was added to a certain amount of TiCl_4 aqueous solution (1.5 M). Then, 10 M NaOH was added slowly until the pH value of the solution was about 7. Subsequently, the above solution was diluted with deionized water to make the concentration of Ti^{4+} was 0.46 M, then transferred to an autoclave and heated to 453 K at a heating rate of about 3 K/min, maintained at 453 K for 2 h. After the autoclave treatment, the resulted powders were rinsed repeatedly by osmosis until the system was free of Cl^- (tested by 10^{-2} M AgNO_3 solution). The prepared powders were dried at 353 K for about 12 h in air. For the sample of Ce^{4+} doped anatase TiO_2 , stoichiometric $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ was added to the TiCl_4 aqueous solution along with 10 ml deionized water.

Pure rutile TiO_2 was also prepared by a hydrothermal method. The detailed process was described as the following. 0.5 M TiCl_4 solution was obtained by diluting a 1.5 M TiCl_4 . After stirred well, it was transferred to an autoclave and heated to 453 K at a heating rate of about 3 K/min, maintained at 453 K for 2 h. The resulted powder was rinsed repeatedly by osmosis until the system was free of Cl^- (tested by 10^{-2} M AgNO_3 solution). The prepared powders were dried at 353 K for about 12 h in air. For Ce^{4+} doped rutile TiO_2 , stoichiometric $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ was dispersed in water to dilute the 1.5 M TiCl_4 to make the 0.5 M TiCl_4 solution.

XRD measurements were carried out by a Rigaku D/MAX-Ra powder diffractometer with a nickel-filtered $\text{Cu K}\alpha$ radiation

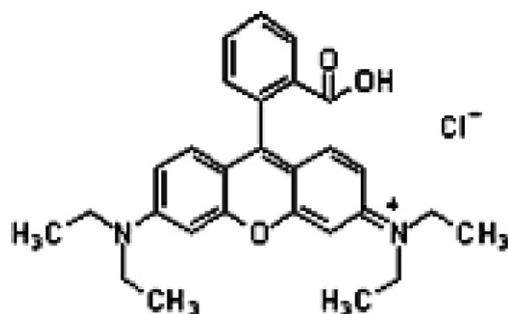
source ($\lambda = 1.54056 \text{ \AA}$) at a scan rate of 4° per second. The samples for XRD were supported on glass substrates. Transmission electron microscopy (TEM) was performed with a JEOL JEM-CX200 microscope operating at 160 KV. For TEM imaging, the samples were dispersed in deionized water by sonication and a drop of the suspension was placed onto a Formvar coated copper grid. Diffuse reflectance spectra (DRS) were obtained using a Hitachi 3010 UV–vis spectrophotometer. X-ray photoelectron spectroscopy data were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W AlK α radiation. The base pressure was about 3×10^{-9} mbar. The binding energies were referenced to the Cls line at 284.6 eV from adventitious carbon.

The photocatalytic activities of the samples were evaluated by the photodegradation of RB (analytical grade) in water. The photocatalytic activity of commercial Degussa P-25 was measured under identical conditions as a reference. The apparatus for the photocatalytic reaction consisted of a 50 ml cylindrical Pyrex glass reactor and a 500 w high-pressure mercury lamp with a main wavelength of $\lambda > 330 \text{ nm}$. The glass reactor was placed parallel to the lamp at a distance of about 10 cm.

The detailed photoreaction process was described as bellow. The TiO_2 powder was firstly added to deionized water to form a suspension. Then, a certain amount of RB solution (10^{-3} M) was added to the suspension. After sonicated for 10 min, the pH value of the suspension was adjusted to 3.5 by 0.1 M HCl. In this experiment, the concentration of the photocatalysts and RB were kept at 2 g/L and 8×10^{-5} M, respectively. Subsequently, the above suspension was firstly stirred in dark for 30 min to establish adsorption–desorption equilibrium. Then oxygen was bubbled into the reactor. After 10 min the solution was illuminated with a UV lamp. At a certain interval, 4 ml samples were taken from the suspension, centrifuged and then the concentration was monitored available on a Shimadzu UV-1601 PC UV–vis spectrophotometer using the characteristic absorption peak of RB at about 550 nm.

3. Results and discussion

The percentage of RB adsorption on TiO_2 was evaluated by the function of $(1 - C/C_0) \times 100\%$, where C and C_0 represented the dye concentration in the suspensions in the



Scheme 1. Structure of dye RB.

Table 1
Adsorption results of RB on P25 and the as-prepared photocatalysts

| Samples | Adsorption (%) |
|----------------------------------|----------------|
| P25 | 0.71 |
| Pure anatase (A) | 1.10 |
| 0.5 at% Ce^{4+} doped A | 0.90 |
| Lat% Ce^{4+} doped A | 0.73 |
| 1.5 at% Ce^{4+} doped A | 0.70 |
| Pure Rutile (R) | 1.10 |
| 0.5 at% Ce^{4+} doped R | 1.07 |
| Lat% Ce^{4+} doped R | 1.03 |
| 1.5 at% Ce^{4+} doped R | 1.0 |
| 3 at% Ce^{4+} doped R | 0.95 |

Download English Version:

<https://daneshyari.com/en/article/5369918>

Download Persian Version:

<https://daneshyari.com/article/5369918>

[Daneshyari.com](https://daneshyari.com)