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Study on enhanced photocatalytic performance of cerium doped TiO_2-based nanosheets

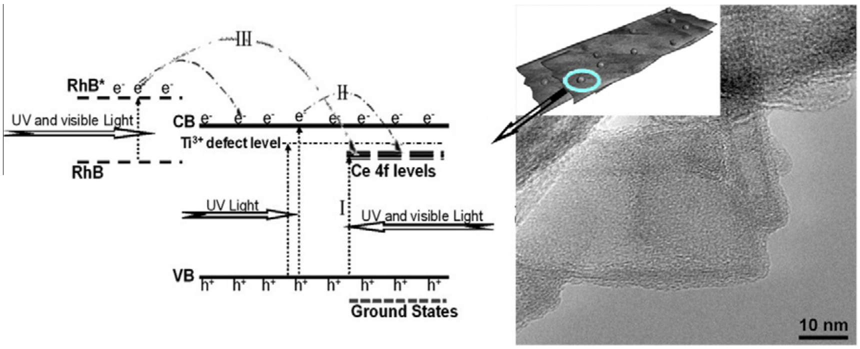
Yang Liu, Pengfei Fang *, Yunlang Cheng, Yuanpeng Gao, Feitai Chen, Zhi Liu, Yiqun Dai *

Department of Physics and Key Laboratory of Artificial Micro- and Nano-Structures of Ministry of Education, Wuhan University, Wuhan 430072, China

HIGHLIGHTS

- ▶ Ce doped TiO_2-based nanosheet (TNS) is prepared by hydrothermal method.
- ▶ Photoactivity of Ce-TNS is improved obviously with appropriate dosage.
- ▶ Photoactivity improvement of Ce-TNS concentrates in ultraviolet region.
- ▶ Ce doping leads to obviously increase of the Ti^{3+} ions content.
- ▶ Ce ions are useful electron traps to enhance the separation of electron–hole pairs.

GRAPHICAL ABSTRACT



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ABSTRACT

Cerium doped TiO_2-based nanosheets (Ce-TNSs) photocatalysts were prepared by a one-pot hydrothermal method using cerium nitrate as the cerium precursor. The photocatalysts were characterized by high-resolution transmission electron microscope (HRTEM), X-ray diffraction (XRD), Raman spectra, ultraviolet–visible light diffuse reflectance spectra (DRS), X-ray photoemission spectroscopy (XPS) and fluorescence spectra (FL). The results show that Ce^{3+} and Ce^{4+} co-exist in Ce-TNS. The doping leads to changes in binding energies of Ti and O. The concentration of Ti^{3+} increases gradually when the cerium doping amount keep increasing. Appropriate amount of cerium doping can significantly inhibit the recombination of electron–hole pairs, which is proved by the decline in the intensity of the fluorescence spectra. Ce-TNS with doping ratio of 0.5% (molar ratio) possesses the highest photocatalytic activity when degrading Rhodamine B (RhB), which is 5 times and 1.6 times of that of P25 and the undoped TNS, respectively. It is suggested that cerium ions are efficient electron trappers to improve the separation efficiency of electrons and holes.

1. Introduction

Photocatalytic technology is an important method of dealing with environmental pollution in recent years [1,2]. TiO_2-based photocatalysts are widely used for pollution control because they have many advantages such as high photocatalytic activity, high physical and chemical stability, low cost, and non-toxicity [3–5]. However, the traditional TiO_2 photocatalysts generally have two shortcomings: the low separation and migration efficiency of electron–hole pairs, and the narrow range of light absorbing. The insufficients are becoming bottlenecks restricting the large-scale applications of TiO_2-based photocatalysts.

Morphology control of TiO_2-based photocatalysts is usually one of the important research directions. The nanostructure of the photocatalyst has a great impact on the migration of the electrons and holes. Many new types of TiO_2-based photocatalysts have been reported in recent years, including nanorods [6], nanotubes [7], nanofibers [8], nanosheets (TNSs) [9,10], and nanoflowers [11]. The hydrothermal reaction of TiO_2 under high concentrated alkali

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* Corresponding authors. Tel./fax: +86 27 6875 2003.
E-mail addresses: fangpf@whu.edu.cn (P. Fang), dai@whu.edu.cn (Y. Dai).

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condition was known as a simple and convenient method to prepare TiO_2 nanotubes. Many studies [12–14] indicated that the hydrothermal reaction parameters, e.g., the reaction time, the alkali species, as well as the alkali concentration, can result in different morphologies of TiO_2-based nanomaterials, including nanosheets, nanofibers, nanorods, and nanobelts. Yao et al. [15] reported that the formation of TiO_2-based nanotubes under hydrothermal conditions is a transformation from 3D to 2D and finally 1D, which means nanotubes are curly nanosheets. By shortening the hydrothermal reaction time of preparing nanotubes, uniform nanosheets can be easily prepared. Research by our group [16] showed that, taking P25 as the starting material, controlling the reaction environment of 10 mol/L NaOH solution at 130 °C for 3 h, TNS with high specific surface area (339 m^2/g) can be prepared. The thickness of the single nanosheet has reached to only 5 nm. Photocatalytic degradation of Rhodamine B (RhB) under UV–vis light showed that the photocatalytic efficiency of TNS is much higher than that of the raw TiO_2 (P25). Its excellent photocatalytic performance in degradation of RhB is due to the high surface area, which is exposed to more light, and has more opportunities to contact with the dye molecules; in addition, thickness of only 5 nm can ensure the fast migration of electrons and holes to the surface.

However, TNS may somewhat exist the similar shortcomings with regular titania, i.e., the low separation efficiency of electron–hole pairs, as well as narrow range of absorbing light. Ions doping was attempted for promoting an important way to enhance the separation of electron–hole pairs [17], and the light absorption capacity of photocatalysts [18,19]. As important dopant, cerium ions (Ce^{3+}/Ce^{4+}) have many advantages such as multi-electron energy levels, and variable valence states. In addition, CeO_2 and Ce_2O_3 themselves are p-type, wide band-gap semi-conducted photocatalysts [20], which may have the possibility of inducing some synergistic effects with TiO_2 (n-type semiconductor), such as heterojunction and semiconductor-sensitized effect. Until now, cerium doping was mostly attempted in TiO_2 particles [21–28] and TiO_2-based nanotubes [29]. According to the above analysis, it could be expected that applying cerium doping to TNS may be a promising way to prepare photocatalysts with high photoactivity, and may lead to different photocatalytic performance from cerium doped TiO_2 particles.

In this paper, cerium doped TiO_2-based nanosheets (Ce-TNSs) were synthesized by a one-pot hydrothermal method under alkaline conditions, for preparing TNS with higher photocatalytic activity. The photocatalysts were systematically studied by different techniques. The photocatalytic properties were evaluated using RhB as the target pollutant. At the same time, the optimal experimental parameters were obtained. The mechanisms on the separation of electron–hole pairs due to cerium ion doping were discussed.

2. Experiments

2.1. Materials and preparation

Titania P25 (TiO_2, 70% anatase, 30% rutile) was product of Degussa Co. CeO_2 was obtained from Baotou Ruike Rare Earth Co. (National Engineering Research Centre of Rare Earth Metallurgy and Function Materials). H_2O_2 (30%) and Rhodamine B (RhB) was purchased from Sinopharm Group Co. Ltd. Analytically pure NaOH, HNO_3 and HCl were used in the experiment. Deionized water was used in the experiments. All of these chemicals were used without further purification.

Photocatalysts were prepared by a one-pot hydrothermal method. 3 mol/L HNO_3 solution was heated to dissolve CeO_2 with appropriate amount of H_2O_2 to get 0.1 mol/L cerium nitrate solution. 0.8 g of P25 TiO_2 was dispersed in 50 mL of 10 mol/L NaOH solution. Precalculated amount of cerium nitrate solution was dropped slowly into the suspension. After ultrasonic dispersion for 30 min and magnetic stirred for 30 min, the mixture was transferred to a 100 mL Teflon reactor. The hydrothermal reaction was taken under 130 °C for 3 h. After the reaction, the samples were washed by deionized water for several times until pH = 7, and then proton exchanged by adding to 200 mL of 0.1 mol/L HCl. The mixture was kept stirring for 3 h. After the acid treatment, the samples were washed again by deionized water for several times until pH = 7. The photocatalysts were put in a drying oven at 70 °C for 12 h. The cerium doping ratios (molar ratio) were 0.1%, 0.25%, 0.5%, 1.0% and 2.0%. Undoped TNS was prepared without adding the cerium source.

2.2. Characterization

The result of high-resolution transmission electron microscopy (HRTEM) was obtained on a JEM-2010 FEF from FEI Company, with accelerating voltage of 200 kV. The X-ray diffraction (XRD) patterns were obtained by a Bruker D8 advance X-ray diffractometer using monochromatic Cu Kα radiation ($\lambda = 1.5406$ Å) with an accelerating voltage of 40 kV and current of 40 mA. The data were recorded with a step interval of 0.02° and scan rate of $2^\circ\ min^{-1}$ in the 2θ range from 20° to 80°. Ultraviolet–visible light diffuse reflectance spectra (DRS) were collected on a Shimadzu UV-2550 spectrophotometer with integrating sphere attachment using barium sulfate as a reference. A Raman spectrometer (Horiba LabRAM HR), with excitation wavelength of 488 nm and output power of 5 mW was used to characterize the structure of the samples. X-ray photoemission spectroscopy (XPS) was applied in the experiment. The spectra were collected on a Thermo VG Multilab2000 using Al Kα as the excitation source. The calibration of the binding energy and the corrections of the energy shift as a result of the steady-state charging effect were accomplished by assuming that the C 1s line lies at 284.6 eV. The XPS spectra were fitted by the software of XPS Peak 4.1, and analyzed by performing a Shirley background subtraction. A Hitachi FL4600 fluorescence spectrometer (FL) with voltage of 500 V and excitation wavelength of 205 nm was used to study the separation efficiency of electrons and holes. The record range was from 430 nm to 500 nm.

2.3. Photocatalytic performance evaluations

The photocatalytic activities of the samples were evaluated by degradation of RhB. The photoreaction was taken under a 160 W high-pressure Hg lamp (Shanghai Minghua Co.). The light focused onto a 200 mL beaker filled with 100 mL of 20 mg/L RhB solution and 0.10 g of photocatalyst. Before irradiation, the suspension was magnetically stirred in darkness for 1 h, making sure that the adsorption and desorption of RhB can reach an equilibrium. During the reaction, the suspension was kept magnetic stirring and the reactor was maintained at ambient temperature. Every 30 min, 1.6 mL of the suspension was collected, and then centrifuged at the speed of 12000 rad/min for 1 min to remove the photocatalyst. 0.8 mL of filtrate sample was diluted with 2.4 mL of deionized water. The whole reaction lasted for 3 h. The concentrations of RhB solutions were measured using the UV–vis absorbance spectra by measuring the absorbance. During the visible light photocatalytic reaction, a cutoff filter ($\lambda > 400$ nm) was put on the top of the beaker.