

Preparation of Ce–TiO₂ catalysts by controlled hydrolysis of titanium alkoxide based on esterification reaction and study on its photocatalytic activity

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Abstract

The Ce–TiO₂ catalysts were prepared by controlled hydrolysis of Ti(OC₄H₉)₄ with water generated “in situ” via an esterification reaction between acetic acid and ethanol, followed by hydrothermal treatment. The samples were characterized by X-ray diffraction (XRD), UV–vis diffuse reflectance spectroscopy (DRS), scanning electron microscopy (SEM), atomic absorption flame emission spectroscopy (AAS), and nitrogen adsorption–desorption methods. Both of undoped TiO₂ and Ce–TiO₂ samples exclusively consist of primary anatase crystallites, which further form spherical aggregates with diameters ranging from 100 to 500 nm. The photocatalytic activity of Ce–TiO₂ was investigated for the photocatalytic degradation of Rhodamine B (RB) aqueous solution both under UV and visible light irradiation. Doping of Ce⁴⁺ effectively improves the photocatalytic activity under both UV light irradiation and visible light irradiation with an optimal doping concentration of 0.2 and 0.4%, respectively. The photocatalytic mechanisms of Ce–TiO₂ catalysts were tentatively discussed.

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Keywords: Titanium dioxide; Photodegradation; Esterification reaction; Visible light; Ce⁴⁺ doping

1. Introduction

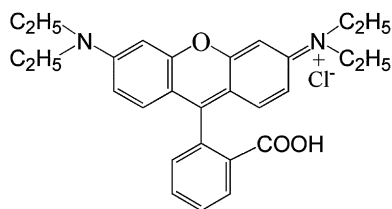
Since the discovery of photoelectrochemical splitting of water on *n*-TiO₂ electrodes [1], photocatalysis has attracted extensive interest owing to its great advantages in the complete mineralization of organic pollutants in waste water and air. As a popular catalyst, TiO₂ has been widely used because of its various merits, such as optical and electronic properties, low cost, chemical stability and nontoxicity [2,3]. However, it is unavoidably facing two issues for its practical applications, one of which is to improve the low photo-quantum efficiency of TiO₂ that arises from fast recombination of photoinduced electrons and photoinduced holes; another is to further extend its photoresponse in visible light regions. Some reports indicated

that doping with a group of transitional metal ions [4–9], depositing some noble metals such as Au and Pt [10–13], and coupling metallic oxides [14,15] with d electronic configuration into TiO₂ lattice are effective strategies for eliminating the recombination of electron–hole pairs significantly and also extending the light response of TiO₂ in visible regions.

Recently, doping lanthanide ions/oxides into TiO₂ has also become one research hotspot [16–19] because they do not only improve the separation efficiency of electron–hole pairs of TiO₂ [20,21], but also extend the photoresponse in visible regions [18,22]. Furthermore, lanthanide ions can form complexes with various Lewis bases including organic acids, amines, aldehydes, alcohols, and thiols by the interaction of the functional groups with their f orbital [21,23]. Thus, doping lanthanide ions into a TiO₂ matrix can concentrate organic pollutants on the semiconductor surface and therefore improve the photoactivity. Among the lanthanide oxides, cerium oxides have received much research attention due to the redox couple

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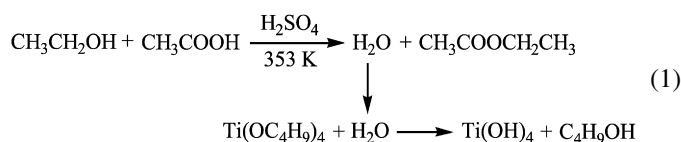
E-mail address: jlzhang@ecust.edu.cn (J. Zhang).



Scheme 1. Molecular structure of Rhodamine B.

$\text{Ce}^{3+}/\text{Ce}^{4+}$ with the ability of ceria to shift between CeO_2 and Ce_2O_3 under oxidizing and reducing conditions [19]; the different electronic structures between Ce^{3+} ($4f^15d^0$) and Ce^{4+} ($4f^05d^0$) would lead to different optical properties and different catalytic properties [24–26].

As for the preparation method, sol–gel process based on the hydrolysis and polycondensation reactions of titanium alkoxides have been extensively employed to prepare Ce-doped TiO_2 catalysts. However, the high hydrolysis rate of titanium alkoxides may cause uncontrolled local precipitation, resulting in photocatalytic losses in TiO_2 -based material [27]. Since the work of Larbot et al. [28], excellent control of the hydrolysis rate of titanium alkoxides has been realized with “in situ” water generated in esterification reactions [29–31]. However, to the best of our knowledge, preparation of lanthanide ions doped TiO_2 with this method has not reported. In the present work, Ce– TiO_2 catalysts with high crystallinity and regular shapes were prepared by excellent controlling the hydrolysis rate of titanium tetrabutoxide via an esterification reaction between acetic acid and ethanol (Eq. (1)). The prepared samples have been characterized by XRD, SEM, UV–vis DRS, AAS, and nitrogen adsorption–desorption methods. The photodegradation of Rhodamine B (RB, Scheme 1) dye was chosen as a probe reaction to measure the photocatalytic activity of different samples. Photocatalytic mechanisms for Ce– TiO_2 catalysts under UV light irradiation and visible light irradiation were tentatively discussed.



2. Experimental

2.1. Materials

The chemicals used in this study were titanium tetrabutoxide ($\text{Ti}(\text{OC}_4\text{H}_9\text{-}n)_4$, 98%, Lingfeng Chemical Reagent Co., Ltd., China) as a titanium precursor, ammonium cerium(IV) nitrate ($(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$, 99%, Shanghai Chemical Reagent Co., China) as Ce source, anhydrous ethanol ($\text{C}_2\text{H}_5\text{OH}$, 99.7%, Jiyi Chemical Reagent Co., Ltd., China), glacial acetic acid (HAc, 99.5%, Shanghai Jinghua Sci. & Tech. Institute, China), concentrated sulfuric acid (H_2SO_4 , 98%, Shanghai Jinghua Sci. & Tech. Institute, China).

Degussa P25 ($45\text{ m}^2\text{ g}^{-1}$, nonporous, 70% anatase and 30% rutile, purity >99.5%) used as a reference photocatalyst was supplied by Degussa Company.

2.2. Experimental procedure

The synthetic procedure was as follows: under magnetic stirring, 20 ml HAc was added dropwise to a flask containing 10 ml of $\text{Ti}(\text{OC}_4\text{H}_9\text{-}n)_4$ diluted in 30 ml $\text{C}_2\text{H}_5\text{OH}$, followed by addition of 1 ml of H_2SO_4 and a specific amount of $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$. Then, the obtained clear liquid was sonicated in an ultrasonic cleaning bath (Elma, T660/H, 35 kHz, 360 W) at 313 K for 1 h and 333 K for 3 h, resulting in the formation of a milk-like sol, which was further transferred into a 100 ml Teflon-inner-liner stainless autoclave and kept at 393 K for 13 h. The resulting precipitates were separated from the mother liquor by centrifugation, washed thoroughly with deionized water and ethanol several times, and then dried at 373 K in air for 12 h. Finally, the obtained powders were calcined at 733 K for 2 h and designated as $x\%\text{Ce-TiO}_2$, where x stands for the mass percentage of cerium in theoretical product (between 0.1 and 1 wt%). The undoped TiO_2 were prepared by the same procedure, except no $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ was added.

2.3. Characterization

The phases present and crystallite sizes of as-prepared samples were characterized by X-ray diffraction (XRD) performed on a Rigaku D/max 2550 VB/PC X-ray diffractometer at room temperature. The patterns were recorded over the angular range $20^\circ\text{--}80^\circ$ (2θ), using a scan rate of $2^\circ/\text{min}$ and $\text{CuK}\alpha$ radiation ($\lambda = 0.154056\text{ nm}$) with working voltage and current of 40 kV and 100 mA, respectively. The content of Ce in Ce^{4+} doped TiO_2 samples was determined by atomic absorption flame emission spectroscopy (AAS) (Shimadzu AA-6400F). Scanning electron microscopy with energy dispersive spectroscopy (SEM–EDS) measurements were performed on a Hitachi S-520 scanning electron microscope equipped with an EDAX-9100 energy-dispersive spectrometer. UV–vis diffuse reflectance spectra (DRS) were obtained using a Scan UV–vis–NIR spectrophotometer (Varian Cary 500) equipped with an integrating sphere assembly, using polytetrafluoroethylene as a reference material. The Brunauer–Emmett–Teller (BET) specific surface areas (SBET) of the samples were determined through nitrogen adsorption (Micromeritics, ASAP 2010). All the samples were degassed at 200°C before the measurements.

2.4. Photocatalytic activity measurement

Photodegradation reaction were carried out using a home-made setup, for which the lamp was cooled with flowing water in a quartz cylindrical jacket around the lamp, and a fan was fixed for maintaining an constant temperature during the photocatalytic reaction. UV light and visible light irradiation were achieved using a 300 W high-pressure Hg lamp and halogen-tungsten lamp with UV cut-off filter, respectively. For each test, 0.05 g of catalyst sample was suspended into a 70 ml quartz tube containing 50 ml of 20 mg/L RB. The concentration of the catalyst was 1 g/L. After sonicated for 10 min, the pH value of the suspension was adjusted to 3.5 with 0.1 M HCl. Then, the above suspension was stirred in the dark for 30 min to attain the

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