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Journal of Solid State Chemistry

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Electrospun nanofibers of Er³⁺-doped TiO₂ with photocatalytic activity beyond the absorption edge



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ARTICLE INFO

Article history:

Received 5 August 2013

Received in revised form

17 November 2013

Accepted 21 November 2013

Available online 2 December 2013

Keywords:

Er³⁺-doped TiO₂

Electrospinning

Photocatalytic activities

Absorption edge

ABSTRACT

Er³⁺-doped TiO₂ nanofibers with different Er³⁺ contents were prepared via electrospinning and characterized by X-ray diffraction, scanning electron microscopy, ultraviolet–visible diffuse reflectance spectroscopy and photocurrent measurement. Photocatalytic activities of the as-prepared samples were evaluated by the decolorization of methyl orange aqueous solution under simulated solar light irradiation. The results indicated that the photocatalytic activity of Er³⁺-doped TiO₂ nanofibers was much higher than that of the undoped one, and the optimal dosage of Er³⁺ at 1 mol% achieved the highest degradation rate. Moreover, the photocatalytic activity of Er³⁺-doped TiO₂ nanofibers under the irradiation of light with the wavelength beyond the absorption edge of TiO₂ was explored by the decolorization of a dye, rhodamine B and the photodegradation of a typical colorless pollutant, phenol. The results further revealed the mechanism of the enhanced photocatalytic activity through Er³⁺ doping in TiO₂ nanofibers.

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1. Introduction

Titanium dioxide (TiO₂) has been widely explored to photo-degrade many kinds of organic pollutants for its relatively high catalytic reactivity, physical and chemical stability, low cost and so on [1]. However, the wide band gap and high recombination rate of the photogenerated electron–hole pairs resulting in a low quantum efficiency hamper to a great extent its commercial applications in the environmental purification [2]. Therefore, it is necessary to adopt proficient modified methods to enhance the photocatalytic performance of TiO₂. Commonly, the modification is mainly aimed at two aspects, one is to extend the light absorption range of TiO₂ to the visible light region [3] and the other is to suppress the recombination rate of photogenerated electron and hole pairs [4].

Doping with rare earth ions has been proven to be a potential route to improve photocatalytic activity of TiO₂. The unique 4f electron structure endows rare earth ions with multi-electron configuration, and lanthanide ions are known for their ability to form complexes with various Lewis bases (e.g. acids, amines, aldehydes, alcohols, thiols, etc.) in the interaction of these functional groups with *f*-orbitals of the lanthanides [5]. Some investigations have shown that the photocatalytic activity of TiO₂ could

be improved by rare earth metals doping [6–9]. Zeinhom et al. [5] synthesized lanthanide ions (La³⁺, Nd³⁺, Sm³⁺, Eu³⁺, Gd³⁺, and Yb³⁺) doped TiO₂ nanoparticles and found that lanthanide ions can enhance the photocatalytic activity of TiO₂ to some extent as compared with pure TiO₂. Liang et al. [10] fabricated pure TiO₂ and Er³⁺-doped TiO₂ photocatalysts by sol–gel method, and the results showed that Er³⁺-TiO₂ photocatalysts had higher adsorption equilibrium constants and better adsorption capacity than pure TiO₂. Furthermore, many researches have focused on trivalent lanthanide ions doped solid hosts, which are characterized by high density of energy levels in the IR–UV range that allows a variety of upconversions to occur [9,11]. Among all the trivalent lanthanide ions, Er³⁺ has attracted considerable attention due to its favorable electronic level scheme with equally spaced, long-lived excited states [12]. At present, the photocatalytic activities of rare-earth-doped photocatalysts are mainly evaluated by a photodegradation process under simulated solar light or UV light irradiation. There are rare reports on the photocatalysis beyond the absorption edge of the doped photocatalysts.

It is well accepted that nano-catalysts always present a superior activity due to their large surface-to-volume ratios [3]. Among all the nanostructures, fibrous nanostructures are favorable for practical applications in environmental remediation. Compared to conventional film and particulate photocatalysts, nanofibrous photocatalysts not only possess high specific surface area, which allows for their surface active sites to be accessible for reactants more efficiently, but also owe high length-to-diameter aspect

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ratio, which makes the separation of photocatalysts more easily [13]. Among the methods of producing nanofibers, electrospinning is a unique technique that is able to yield abundant quantities of continuous nanofibers, which can be readily prepared as mats with favorable recycling characteristics for the application of photocatalysis [14]. Therefore, electrospun TiO₂ based nanofibers are considered as good candidates due to their high photocatalytic activity and ease of removal. However, to the best of our knowledge, the electrospinning approach for Er³⁺-doped TiO₂ photocatalyst has not been reported.

In present study, a series of Er³⁺-doped TiO₂ photocatalysts by doping Er³⁺ into TiO₂ structure with different contents via the electrospinning technique have been prepared. It was demonstrated for the first time that visible light beyond the absorption edge of TiO₂ can be used as the driving source for photocatalysis. The photocatalytic activity of the as-prepared samples was investigated by the photodegradation of methyl orange (MO) under simulated solar light, and the influence of Er³⁺ doping on photocatalytic decolorization of rhodamine B (RhB) and degradation of a colorless pollutant phenol was studied under green LED ($\lambda=517\text{--}522\text{ nm}$) irradiation. The proposed mechanism of the improved activity in Er³⁺-doped TiO₂ was also discussed.

2. Experimental

2.1. Preparation of photocatalysts

Commercial erbium nitrate pentahydrate (Er(NO₃)₃·5H₂O, *M*_w 443.35, 99.95%), poly(vinyl pyrrolidone) (PVP, *M*_w $\approx 1.3 \times 10^6$) and tetrabutyl titanate (Ti(OC₄H₉)₄, *M*_w 340.36, 98%) were purchased from Shanghai Chemical Company and used without any further purification. In a typical process, 5 mL of ethanol and 1 mL of acetic acid were mixed together in a beaker, then certain amount of Er(NO₃)₃·5H₂O was added into the mixture. The mixture was ultrasonicated for a few minutes till Er(NO₃)₃·5H₂O dissolved completely. About 1 g of Ti(OC₄H₉)₄ (the atomic ratio of Er:Ti ranged from 0.5% to 2.5%) and 0.25 g of PVP were added into the above solution respectively under vigorous stirring to form a transparent solution for electrospinning.

The electrospinning setup consisted of a syringe and needle, a ground electrode and a high voltage supply. The applied voltage was set at 13.5 kV with a tip-to-collector distance of 20 cm. After electrospinning, the as-collected fibers were calcined at 773 K for 2 h in air. The as-synthesized samples were denoted as *x* mol%Er:TiO₂, where *x* refers to the molar ratio of Er:Ti. The TiO₂ nanofibers were prepared by the same method as described above without adding Er(NO₃)₃·5H₂O.

2.2. Characterization

The phase and composition of the as-prepared samples were measured by X-ray diffraction (XRD) using a D/MAX 2250 V diffractometer with Cu K α radiation under 40 kV and 100 mA and with the 2θ ranging from 20° to 80° (Rigaku, Japan). The morphologies and microstructures were performed on a JEOL JSM-6700 F field emission scanning electron microscope (SEM). UV–vis diffuse reflectance spectra (DRS) of the samples were recorded with a UV–vis spectrophotometer (Hitachi U-3010) using BaSO₄ as reference.

2.3. Photocatalytic test

Photocatalytic activities of the Er³⁺-doped TiO₂ samples were evaluated by photocatalytic degradation of methyl orange (MO), rhodamine B (RhB), and phenol. A Xe lamp of 500 W and a LED of

3 W were used as the light sources. The reaction vessel was a beaker of 50 mL and the distances from the Xe lamp or LED to the solution were 12.5 cm or 1.0 cm, respectively. The initial pH value of the solution was about 7 and was not adjusted.

The MO photodegradation experiments were performed under a 500 W Xe lamp as the light source. The experiments were performed as follows: 0.025 g of photocatalyst was added into 25 mL MO solution (10 mg/L). Before illumination, the suspensions were magnetically stirred for 1 h in the dark to ensure the adsorption–desorption equilibrium between the photocatalyst and MO. At given time intervals, a small amount of suspensions were sampled and centrifuged to remove the photocatalyst. The change of absorption at 465 nm was applied to identify the concentration of MO using a UV–Vis Spectrophotometer (Hitachi U-3010), and the concentration of MO was measured as a function of irradiation time.

For the degradation of RhB and phenol, a 3 W LED ($\lambda=517\text{--}522\text{ nm}$) was used as the light source. About 0.05 g of the photocatalyst was added into 50 mL of RhB solution (10^{−5} mol/L) or 50 mL of phenol solution (20 mg/L). Then the photodegradation process was performed just as that of MO. The absorption spectrum of the centrifuged solution was recorded using a Hitachi U-3010 UV–vis spectrophotometer. The concentration variation of RhB was obtained according to the linear relation between the absorbance (at 552 nm).

2.4. Photocurrent measurement

Photocurrent spectra were performed in a three-electrode cell with 0.1 M Na₂SO₄ as an electrolyte at a potential of 0.6 V. A Pt ring was used as the counter electrolyte, a saturated calomel electrode (SCE) as the reference electrode and the photocatalyst as the working electrode. A CHI 660C electrochemical workstation was used for the photocurrent measurements. As for light sources, A 500 W Xe lamp and a 3 W LED ($\lambda=517\text{--}522\text{ nm}$) were used.

3. Results and discussion

3.1. Crystal structure

The crystal phases of the as-prepared samples were investigated by performing XRD analysis. Fig. 1 shows the XRD diffraction

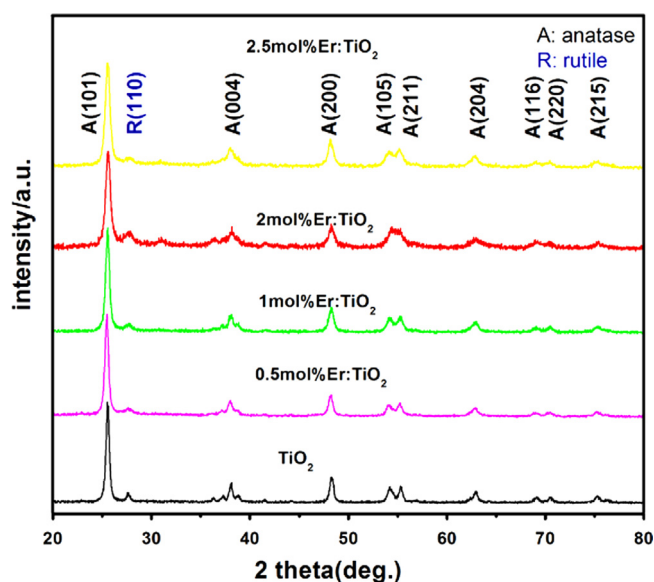


Fig. 1. XRD patterns of the as-prepared products.

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