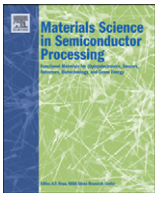
Materials Science in Semiconductor Processing 16 (2013) 288–294

Contents lists available at SciVerse ScienceDirect

Materials Science in Semiconductor Processing

journal homepage: www.elsevier.com/locate/mssp



Preparation and characterization of $BiFeO_3$@Ce-doped TiO_2 core-shell structured nanocomposites

Lixiu Gong [a], Zhufa Zhou [a,b,*], Shumei Wang [a,b,*], Ben Wang [a]

[a] College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, PR China
[b] National Engineering Laboratory of Modern Silk, Soochow University, Suzhou 215123, PR China

ARTICLE INFO

Available online 13 November 2012

Keywords:
Titania
$BiFeO_3$
Ce-doped
Synergistic effect
Photocatalysts

ABSTRACT

$BiFeO_3$@TiO_2–Ce composite nanoparticles with a $BiFeO_3$ core and a Ce-doped TiO_2 shell structure were fabricated via a sol–gel method. The nanoparticles were characterized by scanning electron microscopy with energy dispersive spectroscopy, X-ray diffraction, transmission electron microscopy and UV–vis diffuse reflectance spectroscopy. The results reveal that core-shell structured $BiFeO_3$@TiO_2–Ce nanoparticles show a significant redshift in the UV–vis absorption spectra in comparison with both Ce-TiO_2 and $BiFeO_3$@TiO_2 nanoparticles. The photocatalytic activities of the samples were tested in the degradation of methyl orange in aqueous solutions under visible light and UV light irradiations. The core-shell structured $BiFeO_3$@TiO_2–Ce sample exhibits higher photocatalytic activity, which is attributed to the synergistic effects of $BiFeO_3$ and cerium.

1. Introduction

Titanium dioxide (TiO_2) in different forms has attracted extensive interests in recent years owing to its high photocatalytic effects on decomposing various organic pollutants [1–4], which offers a viable approach to solve the variety of environmental problems. But the band gap of TiO_2 (3.2 eV for anatase) is so wide that it can only absorb ultraviolet (UV) light, which is only 5% in the sun source [5]. In addition, the photogenerated electron–hole pair recombining easily results in poor photocatalytic activity, and hence limits its applications. Several efforts have been made, such as replacing the oxygen position with nonmetallic or metal element to overcome the barriers [6–10]. Besides, various modifications have been performed to synthetize nanostructured composites such as $Fe_3O_4/SiO_2/TiO_2$, ZnO/TiO_2 and WO_3/TiO_2, which can efficiently hinder the recombination of the photogenerated electron–hole pairs [11–13]. In particular, exploiting a core-shell structured nanoparticles in which TiO_2 acted as shell and magnetic materials (such as Fe_3O_4, $MnFe_2O_4$, $BaFe_{12}O_{19}$) introduced as core is also an efficient way [14–16].

As we have known, $BiFeO_3$ has an excellent multiferroelectric properties at room temperature. In addition, It has been studied widely in the photocatalytic field due to its small bandgap. Zhang et al. synthesized $TiO_2/BiFeO_3$ heterostructures, and their results indicated $BiFeO_3$ weaken the recombination of electrons generated [17]. Shun Li et al. had prepared $BiFeO_3$@TiO_2 core-shell structure and found that the core-shell nanoparticles had a higher photocatalytic activity in contrast to pure TiO_2. $BiFeO_3$ act as electron carriers that can promote interfacial charge transfer in the composite systems [18]. Additionally the magnetic property of the composites helps recycle the photocatalysts from treated water. The core-shell $BiFeO_3$@TiO_2 nanoparticles have a lower energy gap that enhances visible light absorption. In order to overcome the recombination of photogenerated electron–hole pairs of $BiFeO_3$@TiO_2, many groups have been involved in doping rare earth ions into TiO_2 [19,20], among which cerium has been received much attentions because of the

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* Corresponding authors at: College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, PR China. Tel.: +86 512 65880963; fax: +86 512 65880089.
E-mail address: zhouzhufa@suda.edu.cn (Z. Zhou).

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http://dx.doi.org/10.1016/j.mssp.2012.10.009

following two reasons: (1) the redox couple Ce^{3+}/Ce^{4+} with the ability of ceria to shift between CeO_2 and Ce_2O_3 under oxidizing and reducing conditions; and (2) the easy formation of labile oxygen vacancies (OV) with the relatively high mobility of bulk oxygen species [21].

In this paper, a novel TiO_2-based $BiFeO_3$@Ce-doped TiO_2 core-shell nanocomposite was prepared through a sol–gel method. The crystal structure, optical property and morphologies of the nanocomposite were systematically characterized and investigated as well. Finally, the photocatalytic activity was measured via the degradation of MO under both UV light and visible light illuminations. Due to the synergistic effects of $BiFeO_3$ and Ce, the photocatalytic activity of these core-shell nanoparticles was dramatically enhanced. Additionally, under an external magnetic field, the nanocomposite could be easily separated and recycled from the treated water.

2. Experimental

2.1. Materials

All the chemicals used in the experiments were analytically pure and used as received without further purification. Tetrabutyl titanate ($Ti(OC_4H_{9-n})_4$, 98%), cerium (III) nitrate hexahydrate ($Ce(NO_3)_3 \cdot 6H_2O$, 99%), bismuth nitrate pentahydrate ($Bi(NO_3)_3 \cdot 5H_2O$, 99%), and iron nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$, 98.5%) were obtained from Shanghai Chemical Corporation (Shanghai, China). Anhydrous ethanol (C_2H_5OH, 99.7%, Jiuyi Chemical Reagent Co., Ltd., China), nitric acid (HNO_3, 67%) and deionized water were used in all the experiments.

2.2. Sample preparation

The $BiFeO_3$ was synthesized according to the afore-published method [22]. The $BiFeO_3$ precursor was prepared from acetic acid based solution, using bismuth nitrate pentahydrate (5 mol% excess for the bismuth loss during the heating process), iron nitrate nonahydrate and acetic acid as the solutes and 2-methoxyethanol as the solution. After the solution became transparent, the precursor was dried at 80 °C for about 24 h to obtain the $BiFeO_3$ xerogel powder. Then the xerogel powder was annealed at 500 °C for 2 h and the $BiFeO_3$ nanoparticles were obtained.

The coating of Ce–TiO_2 on $BiFeO_3$ is as follows: solution A consisted of 10 ml tetrabutyl titanate, Ce $(NO_3)_3 \cdot 6H_2O$ in the required stoichiometry (0.5%, 1.0%, 2.0% and 4.0%, which was the mole percentage of Ce element in the theoretical TiO_2 samples) and 2 ml acetylacetone in 100 ml anhydrous ethanol, and the pH value was adjusted to 5–6 by dropwisely adding of HNO_3 (70%). Then the mixture was stirred vigorously until the solution became transparent. Solution B contained 4.65 g $BiFeO_3$ ($BiFeO_3$:TiO_2=1:2, molar ratio) and 150 ml anhydrous ethanol. In order to make the $BiFeO_3$ dispersed uniformly, the solution B was treated under an ultrasonic bath for 2 h. The Solution A was added dropwise into solution B under vigorous stirring. Then the mixture solution was under vigorous stirring at 40 °C for 5 h. The resulting transparent suspension was stirred for another 6 h and aged for 24 h until the transparent gel was obtained. The gel was dried at 80 °C for 24 h and then ground to form semisolid powder before sintering at 500 °C for 2 h in air condition. The resultant powders were $BiFeO_3$@TiO_2–Ce catalysts. Ce-doped TiO_2 was obtained in the same experimental conditions just like solution A. Meanwhile, $BiFeO_3$@TiO_2 was prepared in the absence of $Ce(NO_3)_3 \cdot 6H_2O$.

2.3. Characterizations

The phase structure of the as-synthesized particles were measured by X-ray diffraction (XRD) (Rigaku Co, Tokyo, Japan) with a Bragg-Brentano geometry using Cu Kα radiation (λ=1.5405 Å). The morphologies were observed by a scanning electron microscope (SEM, Hitachi S-4700, Japan) operated at 25 KV and a transmission electron microscope (TEM, FEI TecnaiG220, USA) with an accelerating voltage of 200 kV. An energy dispersive spectroscopy (EDS) was employed to examine the composition of the resultant nanocomposite photocatalysts. The UV–visible diffuse reflectance spectra (DRS) were obtained using a scan UV–vis spectrophotometer (Varian Cary 500) equipped with an integrating sphere assembly. The photocatalytic performance was evaluated by the degradation of methylene orange (MO) in aqueous solution. The particles were placed in quartz vessels and were irradiated under UV light (Hg lamp 300 W with a primary wavelength of 254 nm, Philips, China) and visible light (Xe lamp, 500 W; Visible cutoff filter $>$400 nm), the concentration of the dye solution was measured by a UV–vis spectrometer (Perkin-Elmer Lambda 900 UV/vis/NIR, Waltham, MA) at wavelength 500 nm. Magnetic measurements were carried out at room temperature using a vibrating sample magnetometer (VSM, Lakeshore 7307, USA).

3. Results and discussion

3.1. X-ray diffraction

XRD measurements are performed to identify the crystalline phases synthesized by the sol–gel process. The obtained TiO_2 and Ce–TiO_2 samples consist of anatase as a unique phase are shown in Fig. 1. No characteristic peaks of cerium oxides are observed in Ce–TiO_2 samples for the low dosage (Ce 2%) and the extremely high dispersion [21,23]. The $BiFeO_3$@TiO_2–Ce 2% sample shows that TiO_2 and $BiFeO_3$ phases coexistence at the present synthesis conditions, and there are no extra peaks, indicating that no new phase is formed between TiO_2 and $BiFeO_3$. Additionally, it is worth noting that the anatase (101) crystal plane peak became broad and weak as presented in the inset of Fig. 1. The average crystallite sizes of different samples are calculated by applying the Scherrer formula on the anatase (101) diffraction peaks. The values of pure TiO_2, TiO_2–Ce and $BiFeO_3$@TiO_2–Ce 2% were 11.0, 7.6 and 8.9 nm, respectively, suggesting that cerium doping inhibits crystal growth. The smaller size is beneficial to improve the photocatalytic activity.