Chemical Physics 490 (2017) 38–46

Contents lists available at ScienceDirect

Chemical Physics

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

Hydrothermal synthesis, characterization and enhanced visible-light photocatalytic activity of Co-doped Zn_2SnO_4 nanoparticles

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ARTICLE INFO

Article history:
Received 20 December 2016
In final form 6 April 2017
Available online 10 April 2017

Keywords:
Co-doped Zn_2SnO_4 nanoparticles
Hydrothermal method
Photocatalytic activity
Visible light irradiation
Mechanism

ABSTRACT

Various molar concentrations of Co-doped Zn_2SnO_4 nanoparticles were synthesized by hydrothermal method. The as-prepared samples were characterized by XRD, XPS, FESEM, TEM, UV–Vis and PL. The result of XPS revealed that the Co dopant displayed a chemical state of Co^{2+} in Zn_2SnO_4 lattice. UV–Vis results revealed that the absorption edge of samples shifted towards visible light region gradually with the increase of Co doping content. The PL intensity weakened significantly for the Co-doped Zn_2SnO_4, which indicates that the recombination of photo-generated electrons and holes was suppressed strongly. The photocatalytic activity of Zn_2SnO_4 was observed by photodegradation of RhB under visible light irradiation. The influences of Co doping content on photocatalytic activity of Zn_2SnO_4 were investigated. The experiment results indicated that the maximum degradation rate of RhB was 93% in 120 min when Co^{2+} molar concentration was 2 mol%. Furthermore, a possible mechanism of photocatalytic degradation of RhB was discussed.

1. Introduction

As is known, photocatalysis has attracted considerable attentions for their potential applications in solar energy conversion and environment purification [1]. Particularly, photocatalysis is regarded as one of the most effective techniques for restoring the polluted environment. Inverse spinel Zn_2SnO_4 (ZTO) is a significant ternary oxide n-type semiconductor with high electron mobility, high electrical conductivity and favorable stability. Based on the above advantages, ZTO can be used as gas sensors [2,3], photoelectrical devices [4], an anode materials for dye sensitized solar cells [5,6] and lithium-ion battery [7,8]. Besides, ZTO can effective degrade Benzene [9], Rh6G [10], Methylene blue (MB) [11] and RhB [12] under ultraviolet light (UV) or visible light irradiation. Although the above examples clearly demonstrate the significance of ZTO as a potential candidate for degradation of various pollutants, most of these researches focused on the UV irradiation rather than visible light irradiation. In general, the photocatalytic activity of pure ZTO under visible light irradiation is not desirable due to its wide band gap (Eg = 3.6 eV [13]) and high recombination rate of electrons and holes. Consequently, it is necessary to adopt some effective ways to extend visible light responsive range and reduce the recombination rate of photo-generated carriers.

In recent years, it has been reported that the photocatalytic activity of some semiconductor can be enhanced by metal doping [14–19]. Particularly, doping with transition-metal ions is a widely used method to transform the activities of photocatalysts. It is worth mentioning that doping with transition-metal ions can greatly influence the electronic structure of host matrix of semiconductor [20]. Among various transition-metals, Co is regarded as an appropriate candidate as dopant. On the one hand, the ionic radius of Co^{2+} (0.745 Å) is similar to that of Zn^{2+} (0.74 Å), hence Co^{2+} can enter into ZTO crystal lattice to substitute Zn^{2+} easily. On the other hand, Co^{2+} can serve as carrier trap to restrain the recombination of photo-generated electron-hole pairs, and indirectly enhance the photocatalytic activity of ZTO. As far as we know, although there are numerous literatures about ZTO modification, only few literatures reported Co-doped ZTO. S. Sumithra et al. studied the effects of Co on structural, optical and magnetic behavior of ZTO [20]. Bu investigated the effects of Co doping on photocatalytic properties of ZTO thin films [21].

So far, ZTO have been synthesized by numerous techniques, such as thermal evaporation method [22], co-precipitation method [23,24], sol-gel synthesis [25], and hydrothermal synthesis

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http://dx.doi.org/10.1016/j.chemphys.2017.04.001

[26–28]. Among these methods, hydrothermal method permits dopants into crystal lattice of products easily. In our work, Co-doped ZTO nanoparticles were synthesized by a hydrothermal method. The influences of Co doping content on crystalline phase, morphology, UV–Vis absorption spectra, photoluminescence properties and photo-degradation efficiency of RhB dye were investigated. Furthermore, a possible mechanism of ZTO photodegradation RhB dye under visible light irradiation was proposed.

2. Experimental

2.1. Materials

All the reagents used to synthesize ZTO nanoparticles were of analytical grade without any further purification. Zinc acetate dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$), Tin chloride pentahydrate ($SnCl_4{\cdot}5H_2O$), Cobalt nitrate hexahydrate ($Co(NO_3)_2{\cdot}6H_2O$).

2.2. Synthesis of ZTO nanoparticles

In this paper, Co-doped ZTO nanoparticles were synthesized by hydrothermal method. A representative synthesis process was described as follows: appropriate amount of $Zn(CH_3COO)_2{\cdot}2H_2O$ and certain amount of $Co(NO_3)_2{\cdot}6H_2O$ were dissolved in 30 mL deionized water to form well-distributed solution. Then, 4 mmol of $SnCl_4{\cdot}5H_2O$ was also dissolved into 30 mL deionized water to form a transparent solution. Next, $SnCl_4{\cdot}5H_2O$ solution was dropwise added into the well-distributed solution under continuous stirring to compose mixture solution. Acting as a mineralizer, NaOH aqueous solution (2 M) was dropwise added into the mixture solution till pH = 9. After magnetic stirring of 30 min, the obtained slurry was transferred to a Teflon-lined stainless steel autoclave (100 mL capacity) and heated at 200 °C for 24 h. After the hydrothermal reaction, the autoclave was cooled to room temperature naturally. The precipitate was collected by a centrifugation method and washed by distilled water and absolute alcohol for several times. Finally, the products were dried at 80 °C for 10 h and the $Zn_{2\text{-}x}Co_xSnO_4$ ($x = 0, 0.005, 0.01, 0.02, 0.03, 0.05$) powders were obtained. Pure ZTO powders were synthesized by the same method without $Co(NO_3)_2{\cdot}6H_2O$. For convenience, ZTO powders doping with 0.0 mol%, 0.5 mol%, 1 mol%, 2 mol%, 3 mol% and 5 mol% Co^{2+} ions were labeled as P0, P1, P2, P3, P4 and P5 in sequence.

2.3. Characterization

The crystallinity and phase composition of as-prepared samples were investigated by X-ray diffraction analysis (XRD-7000, SHIMADZU) with Cu K_α radiation in the range of 10°-70° (2θ). The elemental composition and chemical state were investigated by energy dispersive spectrometry (EDS, X-Max50) and X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250), respectively. The morphology, particle size and crystalline structure of as-prepared samples were characterized by field emission scanning electron microscope (FE-SEM, JSM-7800F) and transmission electron microscopy (TEM, JEOLJEM-2100). The UV–Vis diffuse reflectance spectra of all samples were recorded by an UV–Vis spectrophotometer (UV–Vis, Lambda35). Photoluminescence (PL) spectra were measured by Hitachi F-7000 fluorescence spectrophotometer at the excitation wavelength of 260 nm.

2.4. Photodegradation of RhB under visible light irradiation

The photocatalytic activities of all prepared samples were evaluated by the degradation of RhB in an aqueous solution under a visible light irradiation (A 125 W mercury lamp was used as a light source to trigger the photocatalytic reaction). For the effective degradation of RhB, 100 mg of as-prepared catalyst was dispersed in 100 mL aqueous solution of RhB ($10^{-5}molL^{-1}$) under continuous stirring. Ahead of irradiation, the suspension was stirred for 30 min in dark condition to reach the absorption-desorption equilibrium between RhB solution and photocatalyst. Next, the suspension was exposed to visible light irradiation with continuous stirring. Finally, about 5 mL of the suspensions were sampled and centrifuged every 20 min. The degradation efficiencies of RhB were recorded by monitoring the variations of absorbance at the maximum absorption wavelength using a UV–Vis spectrophotometer (UV–Vis, Lambda35).

3. Results and discussion

3.1. Structural and phase analysis

The XRD patterns of pure and ZTO with different Co doping content were shown in Fig. 1(a). Nine significantly diffraction peaks which corresponding to (111), (220), (311), (222), (400), (331), (422), (511) and (440) planes are observed. It can be found that the positions and relative intensities of diffraction peak of all samples match well with the standard ZTO data (JCPDS file No. 24-1470). Neither diffraction peaks related to Co oxide nor impurities are detected in the XRD patterns, which can be ascribed to low ion doping content. A detailed comparison of XRD patterns of pure and Co-doped ZTO powders (Fig. 1(b)) exhibits tiny shifts of peak position toward lower 2θ angles, suggesting the variation in the unit cell volume caused by the possible substitution of Zn by Co. A possible lattice substitution of Zn^{2+} by Co^{2+} relying on a slight increase in cell volume since the ionic radii of Co^{2+} (0.745 Å) is more than that of Zn^{2+} (0.74 Å). In other words, the dopant of Co leads to the lattice expansion in a certain degree. Furthermore, the elemental composition analysis was investigated by EDS. The EDS patterns of Co-doped ZTO in Fig. 1(c) further demonstrate that the as-prepared nanoparticles are composed of Sn, Zn, O and Co.

Crystalline sizes can be calculated by Scherrer equation [29] applied to the most significant peaks relevant to the (311) plane. In principle, Scherrer equation is described as: $D = (k\lambda)/(\beta\cos\theta)$, where D is the average crystallite size, k is Scherrer constant which generally takes a value about 0.89, λ is the X-ray wavelength (0.15406 nm), θ is the Bragg diffraction angle and β is the full width at the half maximum (FWHM) of the diffraction peak, respectively. The values of crystalline size, the lattice constants, unit cell volume and density of $Zn_{2\text{-}x}Co_xSnO_4$ powders were listed in Table 1. As can be seen from Table 1, the crystallite sizes of Co-doped ZTO are slightly lower than that of pure, which indicates that the dopants cause a slight lattice distortion in the spinel structure.

3.2. XPS analysis

In order to investigate the chemical state of element and chemical composition of Co in the as-synthesized ZTO sample, X-ray photoelectron spectroscopy (XPS) measurements were implemented. The survey scan of XPS spectra of 2 mol% Co-doped ZTO is shown in Fig. 2(a), it is clear that the peaks of Zn, Sn, O, and Co, together with C can be observed. The XPS spectra of Zn is displayed in Fig. 2(b), the spectra of Zn 2p centered at around 1042.98 eV and 1019.88 eV can be attributed to the spin orbit split peaks of Zn $2p_{1/2}$ and Zn $2p_{3/2}$ respectively. These values are in good agreement with values of Zn^{2+} [30]. Fig. 2(c) presents the XPS spectra of Sn, a couple of well-defined peaks centered at around 492.88 eV and 484.58 eV originating due to the spin orbit coupling of 3d electrons corresponding to the binding energies of