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Synthesis and comparison of the photocatalytic activities of $ZnSe(en)_{0.5}$, ZnSe and ZnO nanosheets

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ABSTRACT

$ZnSe(en)_{0.5}$ (en = ethylenediamine) nanosheets were successfully synthesized via a facile solvothermal method using en-water mixture as solvent. When $ZnSe(en)_{0.5}$ composite were calcined at 300 °C in air atmosphere, $ZnSe(en)_{0.5}$ nanosheets first converted to ZnSe nanosheets. When the calcination temperature was increased to 400 °C, ZnSe nanosheets completely converted to porous ZnO nanosheets. The possible conversion mechanism was proposed based on X-ray diffraction (XRD), scanning electron microscope (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and Brunauer-Emmett-Teller (BET) analysis of the as-prepared samples. ZnSe and porous ZnO nanosheets had the same hexagonal wurtzite crystal structure and maintained the shape and size of $ZnSe(en)_{0.5}$ nanosheets. The optical and photocatalytic properties of $ZnSe(en)_{0.5}$, ZnSe and ZnO nanosheets were compared. The experiment of rhodamine B (RhB) photodegradation revealed that ZnSe exhibited the highest photocatalytic activity compared to other samples under ultraviolet (UV) light irradiation.

1. Introduction

In the past few decades, photocatalysis has attracted considerable attention for a long time in the field of photochemistry due to its potential application in solving many current environmental problems such as air and water pollution [1–3]. Among various semiconductor photocatalysts, ZnO with wide band gap energy of 3.37 eV has been extensively investigated because of their relatively high photocatalytic activity and low cost [4–6]. Similarly, ZnSe with a direct band gap of 2.67 eV is another important semiconductor photocatalyst. Recently, ZnSe nanostructure materials have also attracted extensive attention owing to their advantageous properties of decomposition of organic materials [7–11]. Qian et al. reported that ZnSe nanobelts exhibited superior photocatalytic activity than that of TiO_2 nanoparticles in photodegradation of fuchsin acid solution under UV light irradiation [7]. Thus, ZnSe nanostructure materials are an excellent candidate as a photocatalyst for the degradation of organic dye pollutants.

As we know, the applications of nanoscale ZnO or ZnSe depend strongly on their morphologies [8,12,13]. A lot of efforts have been devoted to the fabrication various morphologies nanoscale ZnO or ZnSe with novel or enhanced properties for their further applications [14,15]. Among various synthesis methods, solvothermal method has attracted great interest because it is simple and environmentally friendly. A typical organic-inorganic composite of $ZnQ(en)_{0.5}$ (Q = S, Se, or Te) have been synthesized as nanocrystals by solvothermal method [16–19]. Different morphologies ZnSe, such as nanosheets [20,21], nanoparticles [22], nanobelts [7,23], nanoflowers [10,12], nanoplates [24], hollow microspheres [25,26] and nanoribbons [27] were synthesized by thermal treatment of $ZnSe(en)_{0.5}$ in N_2 or Ar atmosphere. However, the thermal decomposition $ZnSe(en)_{0.5}$ composite under air atmosphere was rarely studied. Meanwhile, Lee et al. [28] reported the topotactic transformation from $ZnS(en)_{0.5}$ complex to porous ZnS and ZnO nanoplates when $ZnS(en)_{0.5}$ was heated under air atmosphere. We deduce that $ZnSe(en)_{0.5}$ will have the similar topotactic transformation because of the similar structure between $ZnS(en)_{0.5}$ and $ZnSe(en)_{0.5}$. Furthermore, porous structure nanomaterials with high surface areas have been highly attracted by scientists in recently years because of their significantly enhanced photocatalytic properties [29–31]. So, fabricating porous structure nanomaterials by a simple and low-cost synthetic strategy and

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studying their photocatalytic properties is an intensive and hot research topic currently.

In this paper, the precursor $ZnSe(en)_{0.5}$ nanosheets were prepared by a solvothermal route using en-water (v/v = 2:1) as reactant solvent, and ZnSe and porous ZnO nanosheets were obtained through thermal treatment of $ZnSe(en)_{0.5}$ composite. XRD, SEM, TEM, XPS and BET analyses were applied to characterize the composition and morphology of the as-prepared samples. The shape and dimension relationship between $ZnSe(en)_{0.5}$ and ZnSe (or ZnO) was investigated. The mechanism of topotactic conversion from $ZnSe(en)_{0.5}$ composite to ZnSe or ZnO was proposed. The photocatalytic activities of $ZnSe(en)_{0.5}$, ZnSe and porous ZnO nanosheets were compared by degradation of RhB dye under UV light.

2. Experimental section

2.1. Preparation

All chemicals used in this experiment were analytical grade and used without further purification. For the $ZnSe(en)_{0.5}$ composite, 2 mmol of $Zn(NO_3)_2 \cdot 6H_2O$ and 2 mmol of selenium (Se) powder were dissolved in 60 ml en-water (v/v = 2) solution under magnetic stirring. Subsequently, the mixture solution was transferred into a Teflon-lined autoclave of 80 ml capacity, and maintained at 180 °C for 12 h. After being cooled to room temperature naturally, the precipitate was collected after filtering, washing, and drying at 60 °C for 12 h. The as-synthesized $ZnSe(en)_{0.5}$ composite was named S0. The other samples obtained by annealing the as-synthesized $ZnSe(en)_{0.5}$ composite at 300, 350, 400 and 500 °C for 2 h under air atmosphere were named S3, S35, S4 and S5, respectively.

2.2. Characterization

X-ray diffraction (XRD) measurement was recorded by Rigaku-D/max-2500 automatic powder diffractometer equipped with Cu Kα radiation (λ = 1.5406 Å). The field-emission scanning electron microscope (FSEM) images of the samples were examined by a field emission scanning electron microscope (JEOL 7800F). Transmission electron microscopy (TEM), high-resolution TEM (HRTEM) analysis and element mapping imaging were performed by an FEI Tenai G^2 F20 microscope. X-ray photoelectron spectroscopy (XPS) analysis was accomplished using a Thermo Scientific ESCALAB 250Xi A1440 system. The room temperature photoluminescence (PL) spectra were obtained on a Renishaw inVia micro-PL spectrometer (325 nm, He-Cd laser). Surface areas of the samples were measured from nitrogen adsorption-desorption isotherms using a Quantachrome NOVA 2000e surface area analyzer, and the pore size distributions were estimated by the Barrett-Joyner-Halenda (BJH) method.

2.3. Photocatalysis

The photodegradation of RhB was performed under UV light to evaluate the photocatalytic activity of the as-prepared samples. A 250 W high-pressure mercury lamp (main emission wavelength λ = 365 nm) was used as UV light source. The as-synthesized samples (0.05 g) were added into 50 ml of RhB aqueous solution at a concentration of 10 mg/L. All experiments were carried out at room temperature. With stirring, the suspensions were placed under UV light. Prior to UV light exposure, the suspension was magnetically stirred in the dark for 30 min to establish an adsorption and desorption equilibrium between the catalysts and the organic molecules. For comparison, the blank experiment of absent catalyst was performed under the same experimental condition. Before and after different irradiation intervals, the solution concentration of RhB was measured by a UV–vis spectrophotometer (UV-5800PC, Shanghai Metash Instruments Co., Ltd).

3. Results and discussion

3.1. Characterization of samples

The XRD patterns of all as-synthesized samples are shown in Fig. 1. The XRD pattern of S0 shows that all the peaks are in good agreement with that of orthorhombic $ZnSe(en)_{0.5}$ reported in Refs. [21,23,32]. The strong and sharp diffraction peaks suggest good crystallinity and big particle sizes of $ZnSe(en)_{0.5}$. Fig. 1S3–S5 show the XRD patterns of samples obtained by annealing $ZnSe(en)_{0.5}$ composite at different temperatures in air atmosphere. The diffraction peaks of S3 can be well indexed to hexagonal wurtzite ZnSe (JCPDS cards No.80-0008) and no impurity peaks are observed, indicating that $ZnSe(en)_{0.5}$ completely converts to ZnSe via thermal annealing at 300 °C. In addition, the weak and wide diffraction peaks of S3 imply that ZnSe is formed by small crystalline grains. When the annealing temperature is increased to 350 °C, S35 consists of two sets of diffraction peaks hexagonal ZnSe and hexagonal wurtzite ZnO (JCPDS cards no. 36-1451), indicating that a part of ZnSe phase transforms into ZnO phase. Namely, both ZnSe and ZnO coexist in S35, and those two phases have the same hexagonal wurtzite structure. By further increasing the annealing temperature to 400 °C, all the diffraction peaks of S4 can be perfectly indexed to pure hexagonal ZnO, demonstrating that ZnSe completely transforms into ZnO. When the annealing temperature is further increased to 500 °C, only ZnO diffraction peaks are detected. Moreover, in comparison with S4, the diffraction peaks of S5 are rather strong and sharp, indicating that the crystallite size of S5 is larger than S4.

Fig. 2 shows the SEM images of all as-prepared samples. The low magnification SEM image in Fig. 2a exhibits that a sheet-like structure of the as-prepared $ZnSe(en)_{0.5}$ composite. However, the sizes of these nanosheets are irregular, and the lateral dimension is in the range of 1–10 μm. The high-magnification SEM image in Fig. 2b shows that the surface of $ZnSe(en)_{0.5}$ composite is perfectly smooth and the thickness of S0 is around 80 nm. Fig. 2c–j shows

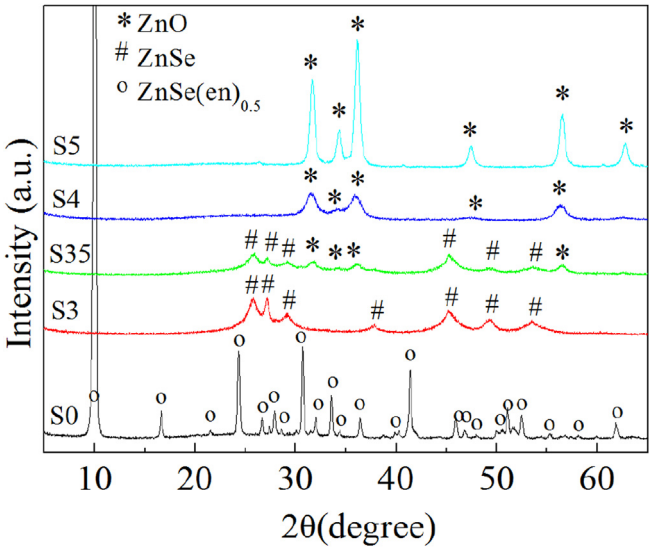

Fig. 1. XRD patterns of all as-prepared samples.