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Morphology-controlled preparation of Bi_2S_3-ZnS chloroplast-like structures, formation mechanism and photocatalytic activity for hydrogen production

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ABSTRACT

Chloroplast-like structures of Bi_2S_3-ZnS was prepared by facile and convenient solvothermal process. The controlled morphology was achieved by regulating the concentration of PVP in the reaction mixture and reaction time. Role of PVP and its effect on morphology has been explored by varying it concentration in the reaction mixture. The formation mechanism has been probed, proposed and discussed through time-dependent study. The photocatalytic activity of the prepared product was evaluated for hydrogen production under visible light irradiation. The successful synthesis of chloroplast-like structures of Bi_2S_3-ZnS may provide some insight to design the other semiconductors for their potential photocatalytic activity.

1. Introduction

The use of solar light driven semiconductors for hydrogen production by splitting water is one of the important ways to fulfill the future energy requirement [1–5]. It is getting more interest due to environmentally sound fuel source and facile route for hydrogen production. Many efforts have been devoted for seeking potential photocatalysts. However, most of the reported catalysts exhibit limited photocatalytic activities under visible light or active only in UV light. So there is need to develop photocatalysts which can show promising activity under visible light. Metal sulfides are considered important photocatalysts for hydrogen production under visible light [6–18].

Recently, synthesis of heterostructured nanomaterials with controlled morphologies and sizes have been a subject of intensive research. Such nanomaterials have been getting more attraction and concern owing to their distinctive properties and prospective applications [19–22]. The heterostructures semiconductor with controlled morphologies and sizes can modulate the properties of materials with potential applications in nanodevices, biomedicine and photocatalysis [23–26]. Numerous kinds of semiconductor-based heterostructures have been designed and fabricated owing to their potential applications. Therefore, to prepare the catalysts with controlled morphologies and crystal size has become an interesting topic [27,28].

The self-assembly of nanomaterials is considered an efficient route to construct the functional materials having diverse morphologies. So, surfactant assisted synthesis of self-assembly of nanomaterials is an important way to control the morphologies of the nanomaterial [29,30].

Bi_2S_3 is an ideal semiconductor for solar cells and photo-detectors in the visible region due to its narrow band gap (1.3–1.7 eV) [31,32]. ZnS is also an important semiconductor with direct wide band gap energy of 3.66 eV. However, due to wide band gap, its light absorption ability is restricted to UV region only [33].

Herein, I employed a facile solvothermal method to synthesize the chloroplast-like structures of Bi_2S_3-ZnS with the aid of the surfactant (PVP) and proposed the possible formation mechanism of Bi_2S_3-ZnS chloroplast-like structures. The prepared product was applied for photocatalytic hydrogen production under visible light irradiation. This method can be extended to the synthesis of other heterostructures semiconductors with controlled morphologies.

2. Experimental section

2.1. Materials and methods

Analytical grade $BiCl_3$, $Zn(CH_3COO)_2$. $2H_2O$, ethylene glycol, thiourea, polyvinyl pyrrolidone (PVP-K30) and ethanol were

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purchased from the local suppliers and used without further purification.

2.2. Preparation

0.5 mmol of $BiCl_3$ and 1 mmol of $Zn(CH_3COO)_2{\cdot}2H_2O$ was added into 20 mL of ethylene glycol followed by the addition of 3 mmol of thiourea and 0.5 g polyvinyl pyrrolidone (PVP-K30). The mixture was stirred well at room temperature and then transferred into Teflon-line autoclave and heated in an electric oven at 200 °C for 20 h. Autoclave was then cooled naturally, product was centrifuged and washed several times with deionized water and ethanol and dried at 60 °C for 24 h.

2.3. Characterizations

Powder X-ray diffraction (XRD) patterns were obtained using a Philips PW/1840 diffractometer (40 kV, 25 mA) with Cu-Ka radiation, k = 1.542 A. Data was collected in the 2θ angle range of 20–70° at a rate of 2°/min. The morphologies of the as-synthesized product were characterized by field emission scanning electron microscope (FE-SEM; Hitachi, S-4800) at an acceleration voltage of 10.0 kV. The element composition was determined by a Horiba EX250 X-ray energy-dispersive (EDX) spectrometer associated with the FE-SEM. UV–vis diffuse reflectance spectra of the product was obtained on a UV–vis spectrophotometer (UV-2550, Shimadzu, Japan). $BaSO_4$ was used as a reflectance standard in a UV–vis diffuse reflectance experiment and the spectra is recorded in a range 200–800 nm.

2.4. Evaluation of photocatalytic activity

A closed gas circulation system equipped with an external-irradiation cell, which was placed about 20 cm under a 300 W xenon lamp, was employed for photocatalytic hydrogen production experiment. For photocatalytic experiment, 30 mg of catalyst was ultrasonically dispersed for 15 min in 80 mL aqueous solution containing 0.35 M Na_2S and 0.25 M Na_2SO_3. Prior to irradiation, the suspension of the catalyst in reactor were vacuumized for 15 min to remove the dissolved oxygen completely and ensure the reactor in an anaerobic atmosphere, the suspension was then irradiated by the Xe lamp. The amount of evolved gas after a given interval of irradiation was determined *in situ* by a gas chromatograph (TECHCOMP, GC 7890-II), equipped with a thermal conductivity detector containing an MS-5A column, which was connected to the closed gas circulating line using nitrogen as carrier gas.

3. Results and discussion

3.1. Structure analysis

The phase purity of the as-synthesized product was determined by powder X-ray diffraction (XRD). The XRD peaks pattern for the product by solvothermal process (Fig. 1a) can be indexed to orthorhombic phase of Bi_2S_3-ZnS. The ZnS peaks seem to be incorporated in Bi_2S_3 sites. The XRD patterns are in good agreement with those from the standard cards (JCPDS no. 65-2431). The EDX pattern of the as-synthesized product is presented in Fig. 1b, which contains Zn, S and Bi, confirming the composition

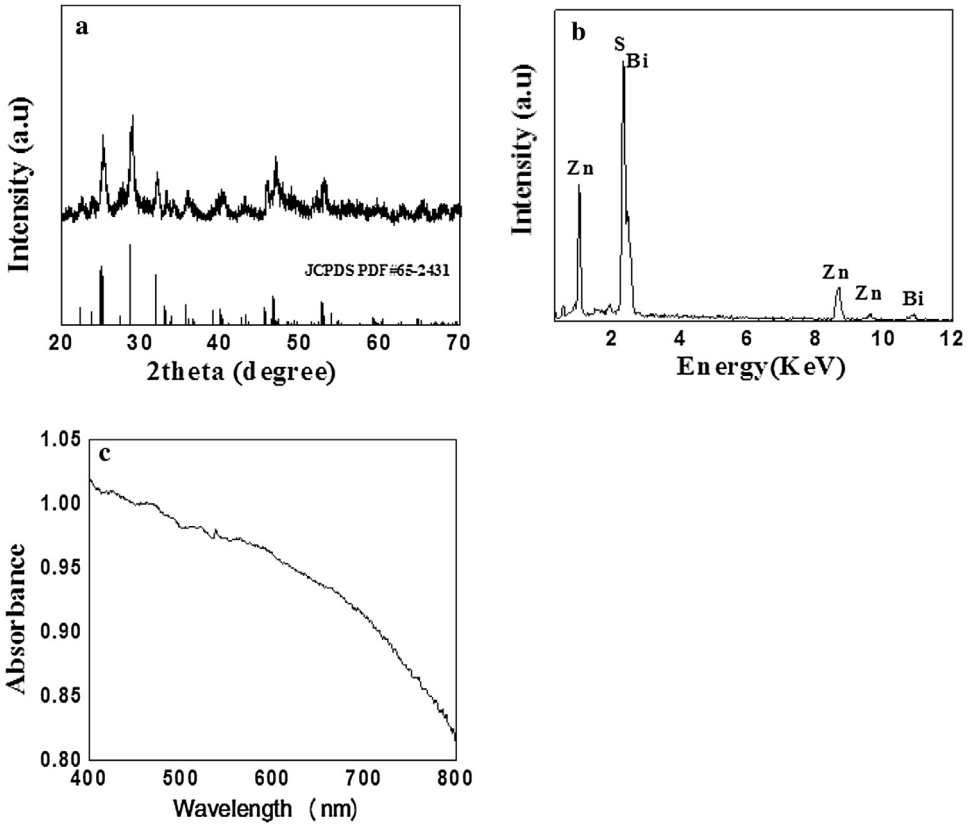

Fig. 1. (a) XRD pattern of Bi_2S_3-ZnS, (b) EDX pattern, (c) DR-UV–vis spectra.