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Synthesis, electronic property and photocatalytic applications of mesoporous cobalt-doped ZnS and ZnO nanoplates

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ABSTRACT

Mesoporous cobalt-doped ZnS and ZnO nanoplates were fabricated by calcination of a $Zn_{0.95}Co_{0.05}S(en)_{0.5}$ complex (en = ethylenediamine), which was hydrothermally synthesized using ethylenediamine as a single solvent and chelating agent. When the as-prepared $Zn_{0.95}Co_{0.05}S(en)_{0.5}$ complex was calcined, mesoporous nanoplates of wurtzite $Zn_{0.95}Co_{0.05}S$ were formed, which then transformed to $Zn_{0.95}Co_{0.05}O$ platelets upon further oxidation. Photocatalytic performance of the as-prepared materials was investigated for decomposition of the azo dye (acid red 14) and photoelectrochemical current generation in aqueous Na_2S/Na_2SO_3 solution as probe reactions. The $Zn_{0.95}Co_{0.05}S$ calcined at 500 °C exhibited the highest photocatalytic activity under UV irradiation and also showed the photocatalytic performance under visible light irradiation.

1. Introduction

$ZnS(en)_{0.5}$ (en = ethylenediamine) is an inorganic–organic hybrid material possessing three-dimensional networks that are composed of monatomic ZnS layers as a source of semiconductor functionality and organic diamine molecules as linkers and confining agents [1–6]. Upon heat treatment, the complex is transformed to porous ZnS and ZnO materials with high surface areas [1,7], which are widely used as photocatalysts for eliminating environmental hazards [8–13]. Since ZnS and ZnO have wide band gaps of about 3.66 eV (or 3.80 eV) and 3.2 eV, respectively [14,15], they absorb only UV light. In order to utilize solar light containing ample visible light (46%), the band gap of ZnS and ZnO materials has to be narrowed by doping transitional metal ions such as Co, Ni or Mn [16–18] into the lattice of Zn.

In this work, we present a novel method to synthesize Co-doped ZnS and ZnO as effective visible light-responsive photocatalysts with Co-doped $ZnS(en)_{0.5}$ complex as a precursor. Thus, we synthesized the inorganic–organic hybrid material, $Zn_{0.95}Co_{0.05}S(en)_{0.5}$ complex via a solvothermal route using ethylenediamine (en) as a single solvent and obtained mesoporous $Zn_{0.95}Co_{0.05}S$ and $Zn_{0.95}Co_{0.05}O$ nanoplates through thermal treatment of the complex. In particular, the electronic and local structures of Zn and Co in $Zn_{0.95}Co_{0.05}S(en)_{0.5}$, $Zn_{0.95}Co_{0.05}S$ and $Zn_{0.95}Co_{0.05}O$ nanoplates were elucidated with X-ray absorption fine structure (XAFS) using the synchrotron radiation. Photocatalytic activity of the synthesized materials was measured with degradation of an organic dye and photoelectrochemical current generation.

2. Experimental

2.1. Preparation of powder materials

For solvothermal synthesis of $Zn_{0.95}Co_{0.05}S(en)_{0.5}$, 15.39 mmol $Zn(NO_3)_2{\cdot}6H_2O$, 0.81 mmol $Co(CH_3COO)_2{\cdot}4H_2O$ and 48.6 mmol thiourea NH_2CSNH_2 were added to a Teflon-lined stainless steel autoclave which had been filled with ethylenediamine (en) $NH_2(CH_2)_2NH_2$ to 70% of its volume. The autoclave reactor was maintained at 160 °C for 12 h and then allowed to cool to room temperature. The colored precipitate was filtered and washed with absolute ethanol and deionized water to remove the residual impurities such as organic solvent; then it was dried in an oven at 80 °C for 12 h. Obtained $Zn_{0.95}Co_{0.05}S(en)_{0.5}$ complex precursor were calcined at 500 and 600 °C for 2 h in an electrical furnace under ambient air; these samples are denoted as ZnCo500 and ZnCo600, respectively.

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