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# Scalable low temperature in air solid phase synthesis of porous flower-like hierarchical nanostructure $SnS_2$ with superior performance in the adsorption and photocatalytic reduction of aqueous Cr(VI)

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ABSTRACT

Nanosheets-constructed porous flower-like hierarchical nanostructure $SnS_2$ (which was labeled as F-$SnS_2$) was synthesized by heating the mixture of $SnCl_2{\cdot}2H_2O$ and thiourea in air at 170 °C for 2 h, in combination with a subsequent washing with water. F-$SnS_2$ exhibited much more adsorption and faster visible-light (wavelength > 420 nm)-irradiated photocatalytic reduction of aqueous Cr(VI), as compared with $SnS_2$ nanoparticles, nanoplates-assembled flowerlike hierarchical structure $SnS_2$ synthesized by hydrothermal method, Fe, N and C tri-doped $TiO_2$, and hydrothermally treated g-$C_3N_4$. The underlying reasons for the far superior performance of F-$SnS_2$ were proposed, based on the comparison of the microstructure, specific surface area, optical, electrochemical impedance, photocurrent, surface charge, and Cr(VI) adsorption properties of F-$SnS_2$ and $SnS_2$ nanoparticles. Besides, the photocatalytic reusability and stability of F-$SnS_2$, as well as the effects of photocatalytic testing parameters (including dosage of photocatalyst, initial pH and concentration of $K_2Cr_2O_7$ aqueous solution) on the Cr(VI) removal efficiency by F-$SnS_2$ were also studied. This work may advance our knowledge on the scalable low temperature solid phase synthesis of $SnS_2$ nanomaterial, and contribute to the application of $SnS_2$ in treating the Cr(VI)-polluted water.

## 1. Introduction

Hexavalent chromium (Cr(VI)) is a common and intractable pollutant in the effluents from electroplating, leather tanning, chromate manufacturing and metallurgy, etc. Cr(VI) has high toxicity, high solubility and high mobility in water, and has been classified as a priority pollutant by China and many other countries [1–10]. The reduction of Cr(VI) to Cr(III) can greatly lessen its toxicity and mobility in the environment. Therefore, it is very worthwhile to develop an effective, environmental-friendly and economical method for the reduction of aqueous Cr(VI). Now, photocatalytic reduction has been widely recognized as a promising substitution for the traditional chemical reduction, because it has many outstanding advantages, such as (i) direct utilization of sunlight to activate the photocatalytic reactions under ambient conditions, (ii) no consumption of any reducing agents and no secondary pollution, (iii) reusability, and (iv) low cost [11–18]. However, so far, most of the synthesized photocatalysts are inefficient in photocatalytic reduction of aqueous Cr(VI) under visible-light (above 46% of sunlight energy) irradiation [19]. Hence, for industrial application of photocatalytic reduction in treating large-scale Cr(VI)-containing wastewaters, there is a pressing need to synthesize new high efficiency visible-light photocatalysts.

$SnS_2$ is a $CdI_2$-type layered semiconductor with a medium bandgap of around 2.2 eV [20]. It has recently attracted great research interest as a promising visible-light photocatalyst, due to its abundant source materials, easy synthesis, low cost, nontoxicity, good stability, and relatively high visible-light photocatalytic activity [21–32]. So far, a variety of methods have been proposed for synthesis of $SnS_2$ with different features [21–32], and $SnS_2$ has been studied as a photocatalyst for many purposes, such as degradation of organic compounds [21–26], reduction of Cr(VI) [27–30], reduction of $CO_2$ [31], and production of $H_2$ from $H_2O$ [32]. Previous studies revealed that the photocatalytic performance of $SnS_2$ strongly depends on its synthesis methods and synthesis conditions, as well as the application objects [21–32]. However, most of the reported synthesis methods have difficulties in realizing the low cost large-scale production of $SnS_2$ with high visible-light photocatalytic activity [21–32]. Hence, it is still very meaningful to develop a simple low cost mass-production method to synthesize $SnS_2$ with high visible-light photocatalytic activity.

Solid phase synthesis is a promising alternative method for

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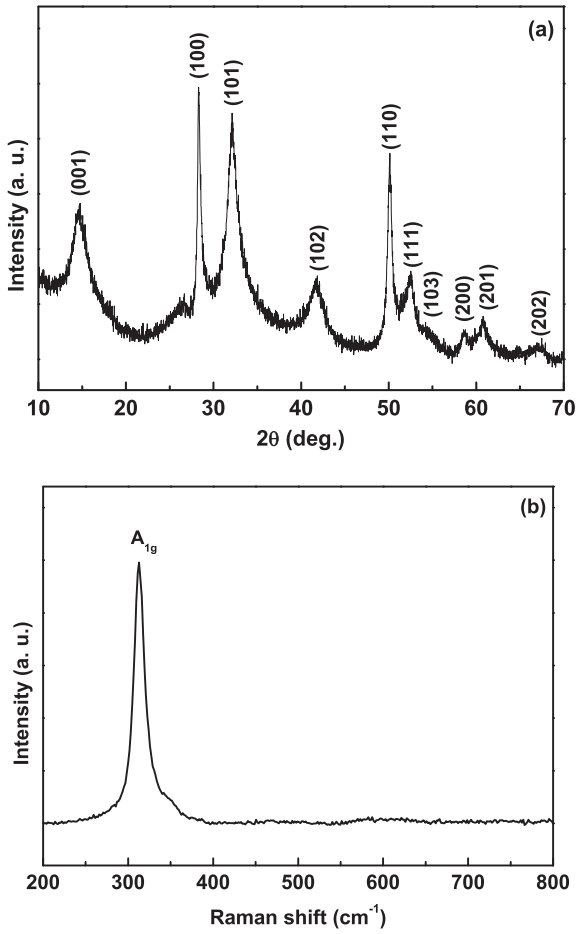


**Fig. 1.** (a) XRD and (b) Raman spectra of F-$SnS_2$.

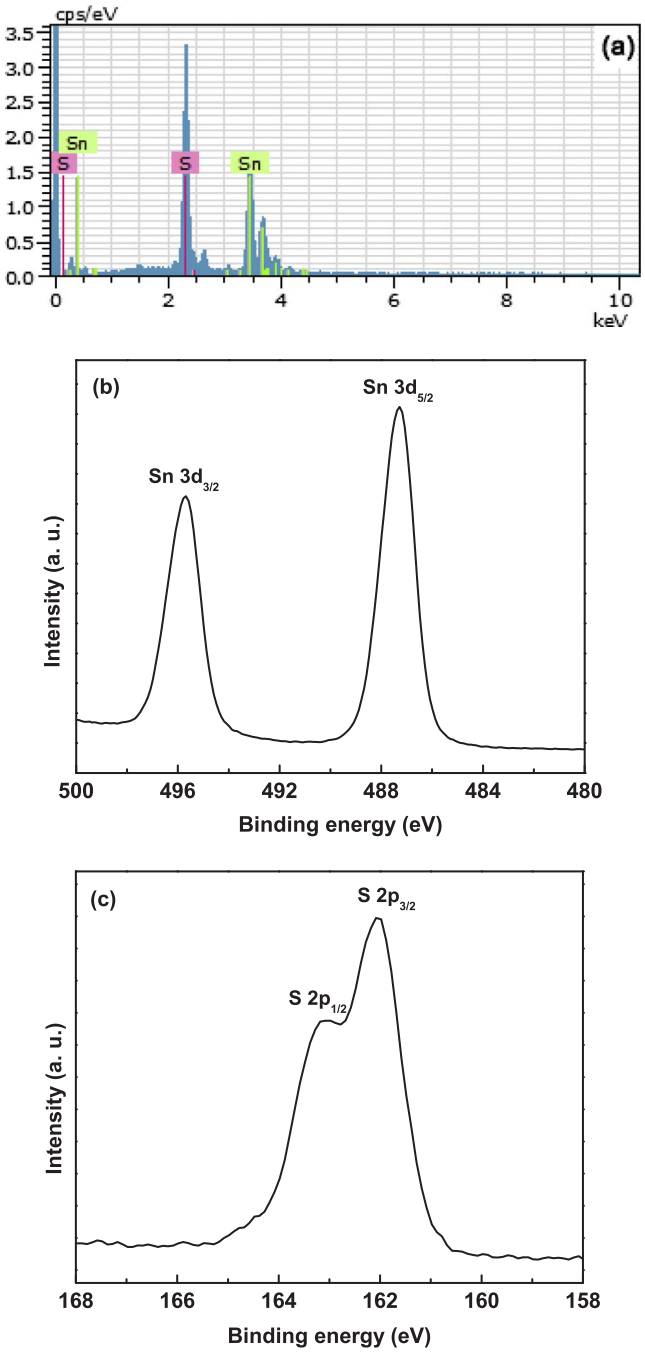


**Fig. 2.** (a) EDX spectrum, and high resolution XPS spectra of (b) Sn 3d and (c) S 2p of F-$SnS_2$.

manufacturing semiconductor nanomaterials [33–35]. It not only has the advantages of no use of solvent, simple procedure, low cost, and mass-production, but also can control the particle morphology and size of the resulting product by employing suitable precursor, reaction temperature and time [33–35]. Here, we report a scalable synthesis of $SnS_2$ porous flower-like hierarchical nanostructures constructed with nanosheets (F-$SnS_2$), by heating the mixture of $SnCl_2{\cdot}2H_2O$ and thiourea in air at 170 °C for 2 h, in combination with a subsequent washing with water. The performance of F-$SnS_2$ was evaluated in the dark adsorption and visible-light (wavelength > 420 nm)-irradiated photocatalytic reduction of aqueous Cr(VI), and compared with those of $SnS_2$ nanoparticles [1], nanoplates-assembled flowerlike hierarchical structure $SnS_2$ synthesized by hydrothermal method [36], Fe, N and C tri-doped $TiO_2$ [37], and hydrothermally treated g-$C_3N_4$ [38]. Moreover, the underlying reasons for the far superior performance of F-$SnS_2$ were proposed, based on the comparison of the microstructure, specific surface area, optical, electrochemical impedance, photocurrent, surface charge, and Cr(VI) adsorption properties of F-$SnS_2$ and $SnS_2$ nanoparticles. Besides, the photocatalytic reusability and stability of F-$SnS_2$, as well as the effects of photocatalytic testing parameters (including dosage of photocatalyst, initial pH and concentration of $K_2Cr_2O_7$ aqueous solution) on the Cr(VI) removal efficiency by F-$SnS_2$ were also studied.

## 2. Experimental

### 2.1. Synthesis

2.2565 g of $SnCl_2{\cdot}2H_2O$ and 1.9030 g of thiourea were mixed and ground in a carnelian mortar for about 30 min for uniform mixing of the reactants. Subsequently, the reactant mixture was transferred to a 50 mL corundum crucible, and heated in an electric hot air drying oven at 170 °C (the optimum temperature among 160, 170, 180 and 190 °C to synthesize phase-pure $SnS_2$ with the highest photocatalytic activity, as can be seen from Figs. S1–S3 in the Supplementary materials) for 2 h. After it was naturally cooled to room temperature, the resulting fluffy powder was washed with deionized water to remove the impurities such as $NH_4Cl$ (Figs. S1 and S2), and dried in air at 90 °C, thus yellow $SnS_2$ (F-$SnS_2$) was obtained.

For comparison, $SnS_2$ nanoparticles were synthesized via the hydrothermal reactions of $SnCl_4{\cdot}5H_2O$, thioacetamide and citric acid at 150 °C for 12 h, according to our previous report [1]. Nanoplates-assembled flowerlike hierarchical structure $SnS_2$ was synthesized using a biomolecular L-cysteine-assisted hydrothermal method [36]. Fe, N and