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Facile fabrication of SnS_2 quantum dots for photoreduction of aqueous Cr(VI)

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ABSTRACT

Visible-light active SnS_2 quantum dots photocatalyst with average diameter of 6.5 nm was prepared successfully via a facile one-pot hydrothermal route by using tin tetrachloride and L-cysteine as precursors. Benefiting from the strong visible-light absorption and high surface area, the as-prepared SnS_2 quantum dots can act as a highly-efficient photocatalyst for photocatalytic reduction of aqueous Cr(VI) without additional reducing agents or hole scavengers, a maximum removal efficiency of 92% was observed after 120 min of visible light irradiation. This work demonstrates that the as-synthesized SnS_2 quantum dots is a promising photocatalyst for photocatalytic reduction of Cr(VI).

1. Introduction

Photocatalytic Cr(VI) reduction has attracted wide attention because it provides an efficient and cost-effective separation method for Cr(VI) toxicant. During the past decades, a great number of semiconductor photocatalysts have been developed and investigated for photocatalytic Cr(VI) reduction [1–3]. Among these semiconductor photocatalysts, SnS_2 has attracted a great deal of scientific interest due to its suitable band gap (E_g=2.2 eV), considerable chemical stability and harmlessness [4,5]. From the practical point of view, a further improvement in photocatalytic performance of SnS_2-based photocatalysts is still needed. Therefore, the ongoing development of SnS_2 photocatalyst with novel structure to enhance the photocatalytic activity is very essential.

Semiconductor quantum dots (QDs) have recently appeared at the forefront of photochemistry due to their unique properties amenable to applications in light-harvesting and charge-separation [6]. Compared to bulk semiconductors, the QDs exhibit high extinction coefficient of light absorption and size-dependent bandgap, which should lead to improved light-harvesting performance. More importantly, the quantum dots with large surface-to-volume ratios can significantly enhance the surface amplitude of photoexcited electrons and hole for photochemical reaction. Herein, we report a visible-light-driven Cr(VI)-to-Cr(III) conversion system by using SnS_2 QDs as the photocatalyst-the first such use of QDs photocatalyst in a heterogeneous photocatalytic system for visible-light-driven photoreduction of Cr (VI) to Cr (III).

2. Experimental section

SnS_2 QDs was prepared by a simple hydrothermal approach. In a typical synthesis process, 1 mmol (225 mg) $SnCl_4 \cdot 5H_2O$ and 1 mmol L-cysteine were dissolved in 10 ml of distilled water, and then the mixture was sealed in a Teflon-lined stainless-steel autoclave of 50 ml capacity for hydrothermal treatment at 180 °C for 16 h. After the mixture was cooled to room temperature naturally, the resulting brown product was collected by centrifugation and washed with deionized water and absolute ethanol to remove the residue of reactants, and lastly dried at 60 °C for 5 h in air. The details regarding photocatalytic experiments can be found in Supplementary material.

3. Results and discussion

As shown in Fig. 1a, the X-ray diffraction peaks at 2θ values of 15.1°, 28.3°, 32.1°, 41.8°, 50.1°, 52.5°, 55.1°, 60.8° and 67.3°, which can be attributed to the (001), (100), (101), (102), (110), (111), (103), (201) and (202) crystal planes of hexagonal SnS_2 [7],

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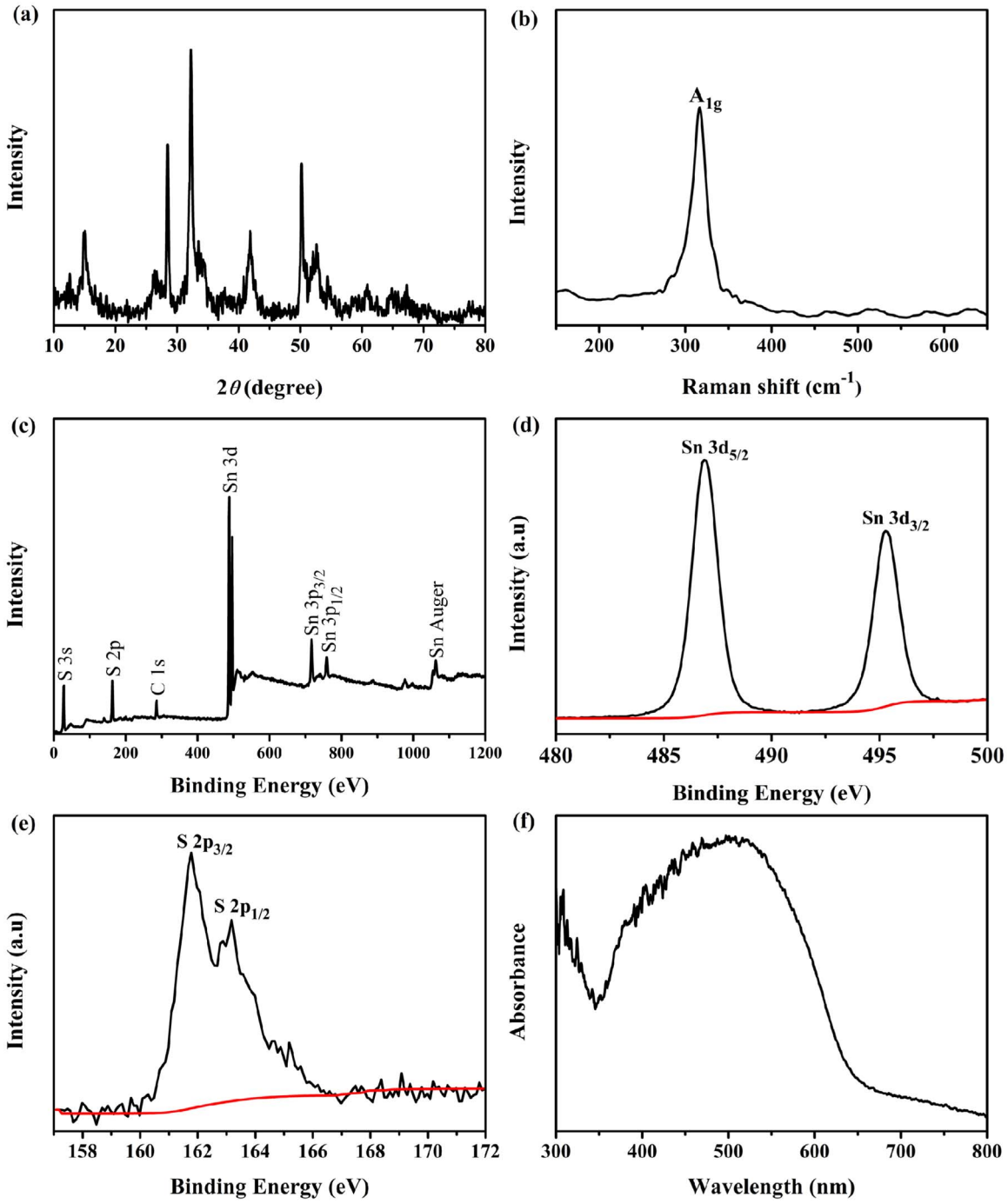

Fig. 1. (a) XRD pattern SnS_2 QDs; (b) Raman spectrum of the SnS_2 QDs; (c) Wide XPS spectrum of the SnS_2 QDs; (d) HR-XPS spectrum of Sn; (e) HR-XPS spectrum of S; (f) UV–vis absorption spectra of the SnS_2 QDs.

respectively. Raman spectroscopy was applied to further check the phase of the SnS_2 sample. As displayed in Fig. 1b, the as-synthesized SnS_2 QDs exhibits an intense peak at about 312 cm^{-1}, which can be assigned to the $A_{1\,g}$ Raman active vibration mode of SnS_2 [8]. XPS measurement was used to determine the exact surface state of as-prepared SnS_2 QDs. As shown in Fig. 1c, the full-range XPS spectra of SnS_2 QDs shows the binding energy peaks at 491.4 and 162.1 eV, which can be attributed to the Sn 3d and S 2p peaks, respectively [9]. More importantly, the XPS analysis reveals that the Sn:S atomic percentage was found to be 32.67% and 67.33%, which is close to the ideal value 1:2 of SnS_2. Fig. 1d shows the high-resolution XPS spectra of Sn 3d, which contains Sn $3d_{5/2}$ at 486.2 eV and Sn $2d_{3/2}$ at 495.3 eV. Meanwhile, the binding energies of S $2p3_{/2}$ and S $2p_{1/2}$ of SnS_2 QDs illustrated in Fig. 1e were located at 161.21 and 163.15 eV, respectively. The XPS result reveals the coexistence of Sn^{4+} and S^{2-} in the nanomaterial [10–12].

As shown in Fig. 1f, the SnS_2 has a strong absorption in visible light region with an absorption maximum at around 508 nm. The spectrum exhibits a relatively broad and intense absorption in the visible region indicates that the SnS_2 QDs is capable of harvesting visible light and hence act as a photocatalyst under visible light. Furthermore, the Brunauer-Emmett-Teller surface area of as-prepared SnS_2 QDs powder was measured to be 112 $m^2\,g^{-1}$ (Fig. S1), which is higher than those of both SnS_2 nanosheets and SnS_2 nanoflowers in previous literatures [2,11]. Fig. 2a-d represents the