**Highly efficient adsorption/photodegradation of organic pollutants
using $\text{Sn}_{1-0.25x}\text{Cu}_x\text{S}_2$ flower-like as a novel photocatalyst**

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Abstract

Hierarchical nanostructures $\text{Sn}_{1-0.25x}\text{Cu}_x\text{S}_2$ flower-like photocatalyst with high visible-light photocatalytic activity and absorption capacity was synthesized via a facile one-pot solvothermal method. The morphology, crystal structure, optical and photocatalytic property of the as-prepared samples were thoroughly investigated by various means. XRD results indicated that Cu ions entered into the crystal lattice of SnS_2 without deteriorating the original crystal structure. The adsorbing capacity of obtained $\text{Sn}_{1-0.25x}\text{Cu}_x\text{S}_2$ photocatalyst was 7.2 times and 2.9 times higher than SnS_2 for the removal of organics pollutants, respectively. Furthermore, $\text{Sn}_{1-0.25x}\text{Cu}_x\text{S}_2$ photocatalytic exhibited much higher photocatalytic activity than the pure SnS_2 towards the degradation of RhB and DB under visible light ($\lambda \geq 420 \text{ nm}$), more than 95 % DB and RhB molecules could be eliminated within 2 h. The enhanced adsorption capacity of the $\text{Sn}_{1-0.25x}\text{Cu}_x\text{S}_2$ for organic pollutants was attributed predominantly to its high specific surface areas and appropriate pore size distribution. Superior photocatalytic activity profited from the large light responded region and efficient separation of photo-generated electron-hole pairs. A possible visible light photocatalytic mechanism of $\text{Sn}_{1-0.25x}\text{Cu}_x\text{S}_2$ was proposed. Therefore, the $\text{Sn}_{1-0.25x}\text{Cu}_x\text{S}_2$ flower-like photocatalyst could be a potential applications for water splitting, new fuels synthesis and environmental remediation under natural sunlight.

Keywords: $\text{Sn}_{1-0.25x}\text{Cu}_x\text{S}_2$, one-pot solvothermal method, hierarchical nanostructures, degradation, adsorption, visible light

1. Introduction

Energy crisis and environmental pollution, which come from the rapid development of the economy, have been two severe issues for human beings. Since Honda and Fujishima found that water can be split into hydrogen (H_2) using titanium dioxide (TiO_2) as photoanode in 1972 [1], semiconductor photocatalysis have attracted widespread attentions to the scientists. However, TiO_2 possessing large band gap (3.2 eV) could only absorb ultraviolet light, which accounts for only 4 % of the solar spectrum resulting in low visible light photocatalytic activity. Therefore, it is urgent to develop novel visible-light-driven (VLD) photocatalysts to make better use of solar energy.

Consequently, various photocatalysts, Such as metal oxide semiconductor (MOS), metal sulfide, saline minerals, were investigated and synthesized to enlarge the visible light response and increase the photoactivity [2-4]. In particularly, nanometer sized metal sulfide semiconductor compounds have received considerable attention owing to their novel physicochemical properties, optical and electronic properties [5, 6]. Among a large amount of metal sulfide, tin disulfide (SnS_2), an n-type semiconductor with a band gap of around 2.2 eV, has been comprehensively studied during the recent years for its narrow band gap, non-poisonous, low cost and chemical stability [7]. However, despite its excellent photocatalytic activity under ultraviolet irradiation, SnS_2 was not active enough in degradation of certain organic compounds under visible light irradiation. In order to synthesize SnS_2 with a high quantum yield, numerous studies have been carried out on charge trapping and recombination. Such

as dopant, surface modification and coating [8-10].

Recently, ternary chalcogenides were considered as promising alternatives to traditional semiconductor photocatalysts. Ternary chalcogenides also have a great flexibility in tuning the optical properties, their narrow band-gap and low toxic elements, which have been extensively investigated and reported over the past decades [11-15]. Thus, they have gained tremendous concern attributed to their potential applicability in solar cells, lithium batteries, hydrogen generation and environmental purification [16-19]. Ternary semiconductor systems, possessing strong photoluminescence stems from irradiative recombination of excited electrons in Cu or in vacancies, which is easy to change by means of varying the excitation wavelength [20-23]. In general, many ternary semiconductors were synthesized using traditional solid-state reaction methods. For example, Cu_2SnS_3 was prepared with Cu_2S and SnS_2 as raw materials at 1123 K for 48 hours [24]; Cu_4SnS_4 could be synthesized when SnS - CuS were heated and melted stoichiometric at 588-673 K. However, the obtained products of above methods have lots of defects, such as in irregular shapes and conglomerations with large size-distributions, which might affect their future applications.

Against this background, herein we fabricated $\text{Sn}_{1-0.25x}\text{Cu}_x\text{S}_2$ solid solution photocatalyst via a facile one-pot solvothermal method. The as-prepared $\text{Sn}_{1-0.25x}\text{Cu}_x\text{S}_2$ exhibited an enhanced photocatalytic performance and stronger adsorption capacity toward organic dyes under visible light irradiation. The $\text{Sn}_{1-0.25x}\text{Cu}_x\text{S}_2$ hierarchical nanostructures photocatalyst showed the highest

photodegradation efficiency in degradation of RhB and DB, which was about 4.6 and 5.4 times higher than pure SnS_2 , respectively. Further studies revealed that as-prepared $\text{Sn}_{1-0.25x}\text{Cu}_x\text{S}_2$ photocatalyst has a strong light absorption which could be expand to 1014 nm. We also explored PL and EIS to investigate the as-prepared $\text{Sn}_{1-0.25x}\text{Cu}_x\text{S}_2$ and SnS_2 , which ulteriorly indicated the introduction of Cu ion could reduce the recombination rate of photoinduced electrons and hole.

2. Experimental

2.1. Materials

Materials of all chemical reagents used in this experiment were analytical reagent grade and without further purification. Tin chloride pentahydrate ($\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$), Cupric chloride dehydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$), Rhodamine B (RhB) and direct blue (DB) were obtained from Aladdin Industrial Corporation. Thioacetamide ($\text{C}_2\text{H}_5\text{NS}$) and ethanol were obtained from Sinopharm Chemical Reagent Co. Ltd. Deionized water was used throughout the work.

2.2. Samples preparation

In a typical preparation, 797 mg of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ and 375 mg of $\text{C}_2\text{H}_5\text{NS}$ were completely dissolved into 30 mL ethanol dispersion under stirring; Next, 78 mg of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ was added into above solution under stirring for 1 h. Then the resulting suspension was transferred to 50 mL Teflon-lined stainless steel autoclaves for a solvothermal reaction at 180 °C for 12 h. The resulting material was washed 3 times with ethanol and water before drying in vacuum, respectively. For comparison, 876

mg of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ and 375 mg of $\text{C}_2\text{H}_5\text{NS}$ were completely dissolved into 30 mL ethanol under stirring for 1 h. Then the resulting suspension was transferred to 50 mL Teflon-lined stainless steel autoclaves for a solvothermal reaction at 180 °C for 12 h. The resulting material was washed 3 times with ethanol and water before drying in vacuum, respectively. In this work, the samples were also synthesized with molar ratios ($r = 1:5$) of Cu and Sn.

2.3. Characterization methods

The crystal structures of the samples were tested by X-ray diffraction (D/max 2550, Rigaku Corporation). The morphologies of the as-prepared samples were examined by scanning emission microscopy (Nova Nano SEM 230, FEI Electron Optics B.V) and field emission transmission electron microscopy (JEM-2100F, Japanese electronics co. LTD). The UV-Vis spectra of the catalysts were obtained on a UV-Vis spectrometer (Evolution 220, Thermo Fisher Scientific). Electrochemical impedance spectra (EIS) and photocurrent characterization were conducted on the electrochemical workstation (CHI660E, CH Instruments, China). Surface chemical compositions and chemical status were analyzed by X-ray photoelectron spectroscopy (K-Alpha 1063, Thermo Fisher). The photoluminescence (PL) spectra were measured at room temperature on a fluorescence spectrometer (F-4600, Japan's Hitachi LTD) under the excitation of 325 nm. The N_2 -BET (Barrett-Emmett-Teller) surface was measured with a Micromeritics ASAP 2010 system at 77.3 K. An Evolution 220 UV-Vis spectrophotometer (Thermo scientific) was made use of recording the UV-Vis

absorbance spectra in the region of 200 to 1100 nm. BaSO₄ was utilized as the reflectance standard material.

2.4. Batch adsorption measurements

The primary aqueous solution containing 100 mg L⁻¹ of various organic contaminants (DB and RhB) were prepared, respectively. To test the various organic contaminants adsorption capacities, 10 mg of SnS₂ NFs and Sn_{1-0.25x}Cu_xS₂ NFs were dispersed in a 50 mL beaker with different organic contaminants of concentrations ranging from 10 mg L⁻¹ to 100 mg L⁻¹, respectively. After 10 h, the solid phase was separated from the solution by centrifugation at 13000 rpm for 5 min. The concentrations of different organic contaminants in the supernatant were determined. The pollutant adsorption capacity was calculated from the difference between the initial concentration (C₀) and equilibrium concentration (C_e) ($q_e = (C_0 - C_e)/m \cdot V$, where q_e is the amount of pollutant adsorbed on per weight of SnS₂ NFs or Sn_{1-0.25x}Cu_xS₂ NFs, V is the mass of the adsorbent). All batch adsorption experiments were carried out in the dark to avoid photocatalytic reaction.

2.5. Evaluation of photocatalytic activity

Photocatalytic decomposition of direct blue and Rhodamine B was performed at visible light irradiation after adsorption. For decomposition RhB, 10 mg catalysts was added to 15 mL aqueous solution containing 60 mg L⁻¹ RhB in a reactor of double layer cooled by running water to keep the temperature unchanged. Before irradiation, the vial containing catalysts and the aqueous solution of RhB was stirred in the dark for 2 h to assure the establishment of an adsorption/desorption equilibrium between

the catalyst and organic pollutant. Then, the suspension was irradiated by a Xe lamp (BL-300) combined with a UV cutoff filter ($\lambda \geq 420$ nm) under stirring. At the given intervals time, about 4 mL aliquots were sampled, centrifuged with 13000 rpm, and filed through a 2.5 mL membrane filter to remove the remaining particles. The organic concentration after adsorption equilibrium is regarded as the initial concentration (C_0).The degradation of DB was similar as above production. Except the concentration of DB was 50 mg L⁻¹.Hence the degradation efficiency can be calculated by the following equation.

$$\% \text{ Degradation} = (C_0 - C_t) / C_0 * 100\% \quad (1)$$

Where C_0 is the concentration of organic pollutants after adsorption equilibrium and C_t is the concentration of organic pollutants after exposed to visible light.

2.6. Photoelectrochemical measurement

12 mg of composite and 20 μ L of nafion solution (5 wt %) were dispersed into 200 μ L of alcohol and sonicated for 30 min to form a uniform catalyst emulsion .Then, 60 μ L of the catalyst emulsion were deposited onto areas of ca. 1 cm² of the tin-doped indium oxide (ITO) conductive glass. Then, we put the prepared samples into pipe furnace with Ar system at 573.15 K. Photoelectrochemical characterization was conducted on a CHI660E electrochemical workstation (CH Instruments, China) with a standard three-electrode system. The prepared samples served as the working electrode with an active area of ca. 1 cm² of the tin-doped indium oxide (ITO) conductive glass to form the working electrode. The counter and reference electrodes were Pt plate and Ag/AgCl electrode, 0.1 M Na₂SO₄ was used as electrolyte. A

Microsol AR300 lamp was used to provide UV light. Electrochemical impedance spectra (EIS) were recorded under an AC perturbation signal of 5mV over the frequency range of 1 MHz to 100 mHz.

3. Results and discussion

3.1 Morphology, crystalline structure and chemical composition of typical sample

To investigate the shape and morphology of as-synthesized photocatalysts, the SEM image of (a) SnS_2 NFs and (b) $\text{Sn}_{1-0.25x}\text{Cu}_x\text{S}_2$ NFs was shown in Fig.1. From the images, the microstructure of as-obtained samples were well defined flower-like sphere self-assembled by nanosheets. During the solvothermal process, the addition of Cu ion directly affected the morphology of Cu-SnS₂. The average size of SnS_2 NFs is about 4.5 μm bigger than $\text{Sn}_{1-0.25x}\text{Cu}_x\text{S}_2$, which is about 2 μm , as determined from SEM images (Fig. 1 (a) and (b)). From a view in Fig. 1 (b), the individual flower-shaped sphere consists of a large number of uniform nanoplate architectures as building blocks. These quantities of nanoplates with interpenetrating growth order are connected to each other to build a flower-like structure [25]. That is to say, the $\text{Sn}_{1-0.25x}\text{Cu}_x\text{S}_2$ NFs possessed compact texture when Cu was added. Besides, the microstructure of as-synthesized samples were tested by high resolution transmission electron microscopy (HRTEM). As shown in Fig.2 (a), the obtained SnS_2 NFs had a uniform lattice fringe which was measured with a spacing 0.32 nm, corresponding to the (100) plane of SnS_2 . However, the HRTEM image of Fig.2 (b) revealed that the

lattice fringes were observed measuring with a spacing of 0.34 nm and 0.26 nm, corresponding to the (100) and (011) planes of SnS₂.

The XRD patterns of the samples SnS₂ NFs and Sn_{1-0.25x}Cu_xS₂ NFs were shown in Fig.3. From the diffraction peaks of the samples SnS₂ NFs and Sn_{1-0.25x}Cu_xS₂, it is found that the characterized diffraction peaks correspond to the crystal plane of (001), (100), (002), (101), (003), (110), (111) and (200). Besides, all patterns of samples exhibited sharp diffraction peaks, indicating that all samples were highly crystalline. The obtained product displays only the characteristic XRD peaks of hexagonal phase SnS₂ (JCPDS card No. 23-677) [26]. From the XRD analysis of SnS₂ NFs and Sn_{1-0.25x}Cu_xS₂ NFs in Fig.3, compared with the as-obtained SnS₂ NFs, it indicated that no other obvious phases could be observed in the XRD patterns of Sn_{1-0.25x}Cu_xS₂ NFs. That is to say, the sample of as-obtained Sn_{1-0.25x}Cu_xS₂ NFs was a pure phase. XRD results indicated that Cu ions entered into the crystal lattice of SnS₂ without deteriorating the original crystal structure.

As we all know, XPS was used to study the chemical states of sample. In Fig. 5 (a)–(d), XPS spectra of showing survey spectra of S 2p, Sn 3d and Cu 2p levels were presented and the obtained binding energy values are given. In Fig. 5a, the presence of Sn, C, Cu, S and O were shown in the survey spectrum of as-obtained Sn_{1-0.25x}Cu_xS₂ NFs, while the survey spectrum of as-obtained SnS₂ NFs showed the presence of Sn, C, S and O. From Fig.5 (b) and (c), the two strong peaks of SnS₂ NFs at around 161.68 and 163.78 eV displayed in Fig. 5b could be indexed to S 2p_{1/2} and 2p_{3/2}, respectively. The two strong peaks of SnS₂ NFs at around 486.88 and 497.78

eV displayed in Fig. 5c could be indexed to Sn 3d_{3/2} and 3d_{5/2}, respectively. However, the two strong peaks of Sn_{1-0.25x}Cu_xS₂ NFs at around 160.98 and 163.08 eV displayed in Fig. 5b could be indexed to S 2p_{1/2} and 2p_{3/2}, respectively. The two strong peaks of Sn_{1-0.25x}Cu_xS₂ NFs at around 486.08 and 497.38 eV displayed in Fig. 5c could be indexed to Sn 3d_{3/2} and 3d_{5/2}, respectively. The spectrum of the Cu 2p region is shown in Fig. 5d. The binding energy of the Cu 2p_{3/2} and Cu 2p_{1/2} peaks are located at around 932.50 eV and 952.42 eV. It was obvious to get that the binding energy of S and Sn lowered when Cu was presented. Electronegativity of Cu was bigger than Sn, it contributed to reduce the binding energy of atoms. It was also a crucial reason to choose Cu element. There were no “shake-up” peaks in the higher binding energy direction, which rules out the coexistence of Cu(II) in the samples [27]. Therefore, the Cu ions were presented in the +1 valence state in the Sn_{1-0.25x}Cu_xS₂ NFs. The formation of Cu⁺ can be ascribed to the presence of cysteine, a molecule with a moderate reducing ability.

Nitrogen gas adsorption-desorption isotherms and Barrett-Joyner-Halenda (BJH) methods characterization further verified the adsorption ability of the Sn_{1-0.25x}Cu_xS₂ NFs (Fig.5 (a) and (b)). Compared with as-obtained SnS₂ NFs, Sn_{1-0.25x}Cu_xS₂ NFs possessed larger specific surface areas and possible hierarchical pore structures. From the describing of Fig. 5(a), it indicated that SnS₂ NFs displayed a type-II adsorption-desorption isotherm. However, Sn_{1-0.25x}Cu_xS₂ NFs showed a type-IV isotherm with a hysteresis loop in the range of 0.5-1.0 P/P₀ was in accordance with the assembled plate-like structure and Barrett-Joyner-Halenda (BJH) method could

calculated the pore size distribution curves [28]. As shown in Fig.5b, for $\text{Sn}_{1-0.25x}\text{Cu}_x\text{S}_2$ NFs, their pore size distribution curves were quite broad (several nanometers) and larger ones (dozens of nanometers). The smaller mesopores reflected pores within nanosheets, whereas larger ones could be correlated to pores formed between stacked nanosheets. Almost no mesopores existed in SnS_2 NFs. The quantitative calculation shows that the BET surface area of as-prepared SnS_2 . The increased surface area may be attributed to the small assembled hierarchical building blocks. This type of hierarchical 3D architecture with high surface area is beneficial for the applications as catalyst or for water treatment. The synthesized SnS_2 NFs and $\text{Sn}_{1-0.25x}\text{Cu}_x\text{S}_2$ NFs had a BET surface areas of 30.37 and $73.45\text{m}^2\text{g}^{-1}$, respectively.

3.2 Optical and photocatalytic properties of the as-obtained $\text{Sn}_{1-0.25x}\text{Cu}_x\text{S}_2$ architectures

To investigate the difference of the adsorption capability of the as-synthesized SnS_2 NFs and $\text{Sn}_{1-0.25x}\text{Cu}_x\text{S}_2$ NFs, we carried out a series of systematic experiments to examine the removal of organic pollutants (RhB and DB). From Fig.6, compared with as-synthesized SnS_2 NFs, it can be obviously seen that the adsorption capacity had a highly increase on RhB and DB, no matter what the concentration of organic pollutants (RhB and DB). Relative to a maximum adsorption capacity of as-synthesized SnS_2 NFs, as-synthesized $\text{Sn}_{1-0.25x}\text{Cu}_x\text{S}_2$ NFs exhibited superior adsorption capacity for organic pollutants (RhB and DB). The adsorption capacities of as-synthesized SnS_2 NFs and $\text{Sn}_{1-0.25x}\text{Cu}_x\text{S}_2$ NFs on RhB and DB were presented in Table 1. As-synthesized $\text{Sn}_{1-0.25x}\text{Cu}_x\text{S}_2$ NFs achieved a maximum adsorption capacity

of 78.96 and 64.14 mg g⁻¹, corresponding to the organic pollutants of RhB and DB, respectively. However, As-synthesized SnS₂ NFs achieved a maximum adsorption capacity of 26.99 and 8.9 mg g⁻¹, corresponding to the organic pollutants of RhB and DB, respectively. Based on above experimental results of BET and pore size distribution, high specific surface areas and appropriate pore size distribution of Sn_{1-0.25}XCu_XS₂ NFs improved the adsorption ability of organic pollutants. Both Langmuir ($q_e = bq_{\max}C_e/(1+bC_e)$) and Freundlich ($q_e = kC_e^{1/n}$) models were applied to describe the adsorption of organic pollutants on Sn_{1-0.25}XCu_XS₂ NFs (where C_e is the equilibrium concentration of pollutants in aqueous solution (mg·L⁻¹), q_e represents the amount of pollutants adsorbed on per weight of Sn_{1-0.25}XCu_XS₂ NFs (mg·L⁻¹); $q_{\max}$ is the maximum adsorption capacity calculated by Langmuir equation to form a complete monolayer coverage on the surface, b is enthalpy of sorption and should vary with temperature (L·mg⁻¹), and k and $1/n$ are the Freundlich constants associated with the adsorption capacity and adsorption intensity, respectively) [29]. Table 1 showed the related parameters calculated from Langmuir and Freundlich isotherm models. From Table 1, the adsorption of organic pollutants on Sn_{1-0.25}XCu_XS₂ NFs fitted very well by the Langmuir model ($R^2 > 0.97$), indicating that the as-synthesized Sn_{1-0.25}XCu_XS₂ NFs had a homogeneous distribution of active sites and the adsorption sites possess equal adsorbate affinity. Therefore, as-synthesized Sn_{1-0.25}XCu_XS₂ NFs exhibited excellent adsorption capacity and could be used as an appropriate material for the pre concentration and removal of organic pollutants.

Table 1 Parameters of the Langmuir and Freundlich isotherm model for organic

pollutants on SnS₂ NFs and Sn_{1-0.25X}Cu_XS₂ NFs.

Samples	Organic pollutants	Langmuir			Freundlich		
		q _{max} (mg/g)	b(L/mg)	R ²	k	n	R ²
SnS ₂	DB	8.9	0.1386	0.997	1.884	2.425	0.968
	RhB	27.0	2.238	0.970	21.467	14.067	0.818
Sn _{1-0.25X} Cu _X S ₂	DB	64.1	2.746	0.991	48.402	10.696	0.709
	RhB	79.0	0.7896	0.980	63.926	15.311	0.756

To demonstrate the photocatalytic activity of as-obtained Sn_{1-0.25X}Cu_XS₂ NFs as a novel integrated photo catalytic adsorbent (IPCA) [32], photodegradation experiments of organic pollutants (RhB and DB) were carried out with visible irradiation after adsorption. Representatively, total concentrations of organic pollutants were determined by the maximum absorption measurements by UV-Vis spectroscopy. C/C_0 was used to describe the degradation (C and C_0 were organic pollutants concentrations at time t and 0, respectively). As shown in Fig.7, Sn_{1-0.25X}Cu_XS₂ NFs not only exhibited much higher adsorption, but also better photocatalytic activity.

Among the above photocatalytic experimental data, a pseudo first-order equation was adopted to describe the experimental data due to the very low initial concentrations of the substrates as follows [33]:

$$\ln (C/C_0) = -kt \quad (2)$$

Where k is a reaction rate constant. As is shown in Fig. 7 (b), the apparent rate constants calculated were 0.00783 min⁻¹ and 0.000734 min⁻¹ for Sn_{1-0.25X}Cu_XS₂ NFs and SnS₂ NFs on RhB. Among them, Sn_{1-0.25X}Cu_XS₂ NFs was about 10.7 times that of

over the SnS_2 NFs. Besides we also studied the photocatalytic activities of DB. As shown in Fig 7 (c) and (d), for degradation of DB, the as-prepared samples had the same laws. The apparent rate constants calculated were 0.0117 min^{-1} and $0.000765 \text{ min}^{-1}$ for $\text{Sn}_{1-0.25x}\text{Cu}_x\text{S}_2$ NFs and SnS_2 NFs on RhB on DB, $\text{Sn}_{1-0.25x}\text{Cu}_x\text{S}_2$ NFs was about 15.3 times that of over the SnS_2 NFs. In particular, the $\text{Sn}_{1-0.25x}\text{Cu}_x\text{S}_2$ hierarchical nanostructures photocatalyst showed the highest photodegradation efficiency for RhB and DB, which was 4.6 and 5.4 times higher than pure SnS_2 NFs, respectively.

The photocatalytic activity of a semiconductor was closely related to its energy band structure feature. Fig.8 (a) showed the UV-visible diffuse reflectance spectra of the as-synthesized SnS_2 NFs and $\text{Sn}_{1-0.25x}\text{Cu}_x\text{S}_2$ NFs at room temperature. Compared with as-synthesized SnS_2 NFs, the adsorption edge wavelength of as-synthesized $\text{Sn}_{1-0.25x}\text{Cu}_x\text{S}_2$ NFs increased. It almost absorbed all of visible light. It was one of the reasons for the photocatalytic activity enhancing. As we all know, the PL emission spectra resulted from the recombination of free hole and electron [30]. To investigate the role of photoinduced electron-hole pairs, we tried to examine the PL of the as-synthesized samples in Fig. 8 (b). The excitation wavelength was 375 nm at room temperature. To move forward a single step, it could be obviously observed that an emission peak was at around 470 nm. Compared to the as-synthesized SnS_2 NFs, as-synthesized $\text{Sn}_{1-0.25x}\text{Cu}_x\text{S}_2$ NFs had weak intensity of emission, indicating that Cu^{2+} suppressed the recombination rate of photoinduced electron-hole pairs. That is to say, lower PL intensity purported a higher photocatalytic activity. EIS measurement

was performed for SnS_2 NFs and $\text{Sn}_{1-0.25x}\text{Cu}_x\text{S}_2$ NFs to disclose the charge transfer resistance and the separation efficiency of the photoinduced electron-hole pairs [31]. As shown in Fig.8 (c) and (d), $\text{Sn}_{1-0.25x}\text{Cu}_x\text{S}_2$ NFs exhibited much lower resistance than the SnS_2 NFs which was evidenced by the drastically reduced diameter of the semicircle at the high-frequency region in the EIS patterns. It demonstrated that in the presented of $\text{Cu-Sn}_{1-0.25x}\text{Cu}_x\text{S}_2$ NFs could enhance the separation and transfer efficiency of photoinduced electron-hole pairs. This might be a favorable condition for improving the photocatalytic efficiency. Meanwhile, the TOC test were performed as shown in Fig. S1. The content of organic carbon reduced obviously in visible light, which indicated the dye was really degraded.

To investigate the photocurrent properties of the as-synthesized SnS_2 NFs and $\text{Sn}_{1-0.25x}\text{Cu}_x\text{S}_2$ NFs products, photoelectrochemical (PEC) cells were prepared by using the as-synthesized products as the corresponding photoelectrode, respectively. Besides, the electrolyte was 0.1 M Na_2SO_4 . Fig. 9 demonstrates the typical time-dependent current change curves of the PEC devices made of SnS_2 NFs and $\text{Sn}_{1-0.25x}\text{Cu}_x\text{S}_2$ NFs, respectively. All photocatalysts show photoresponse and the photocurrent density prominently increased from SnS_2 NFs of about $30 \mu\text{A}/\text{cm}^2$ to a stable value of $\text{Sn}_{1-0.25x}\text{Cu}_x\text{S}_2$ NFs of $55 \mu\text{A}/\text{cm}^2$. $\text{Sn}_{1-0.25x}\text{Cu}_x\text{S}_2$ NFs achieved higher efficiency in charge separation under visible light. The significant enhancement of the current density induced by electron-hole generation is around 2.5×10^2 . There are current transients in both the light-on state and the light-off state, which can be attributed to a typical sign of surface recombination processes according to previous

reports. It is also in good agreement with the PL and EIS (Fig. 7 (b) and (c)). Therefore, it is concluded that the high transfer rate of electrons also contributes to the high photocatalytic performance.

The stability of photocatalyst is one of the most important parts for its practical application. To study the stability of the as prepared samples, the used $\text{Sn}_{1-0.25x}\text{Cu}_x\text{S}_2$ was collected by high speed centrifugation (12,000 r/min). The product of centrifuge was washed with alcohol and deionized water for several times and then dried in 60 °C for a night. And the collected sample was examined in the same RhB degradation experiment like mentioned above without any treatment. As shown in Fig. 10, the photodegradation activity remained the similar level after three runs, which indicated that the $\text{Sn}_{1-0.25x}\text{Cu}_x\text{S}_2$ could maintain a high photostability. Furthermore the SEM image and XRD patterns of the $\text{Sn}_{1-0.25x}\text{Cu}_x\text{S}_2$ after the successive experimental was presented in Fig. S2 and 3.

3.3 Possible photocatalytic mechanism of $\text{Sn}_{1-0.25x}\text{Cu}_x\text{S}_2$ NFs

It's vital to determine the main oxidative species in the photocatalytic process for elucidating the photocatalytic mechanism, so active species trapping experiments were employed. As shown in Fig. 11 a, Disodium ethylenediamine tetraacetic acid (EDTA-2Na)、Isopropanol (IPA) and 1,4-benzoquinone (BQ) were used as the scavenger for photogenerated hole (h^+), hydroxyl radical ($\cdot\text{OH}$) and superoxide radical ($\cdot\text{O}_2^-$), respectively. The process of the trapping experiment was similar to the photocatalytic degradation process except for the presence of different scavenger (10 $\text{mmol}\cdot\text{L}^{-1}$) in RhB solution. These results showed the significant difference with the

different scavengers were added, which indicated that the $\cdot\text{OH}$ and $\cdot\text{O}_2^-$ were the active species for the degradation of RhB. Besides, the same experiment for degradation of DB had the similar results.

Based on the experimental and estimated results, a possible visible light photocatalytic mechanism of $\text{Sn}_{1-0.25x}\text{Cu}_x\text{S}_2$ was proposed in Scheme 2. The band gap energies of semiconductors were estimated by kubelka-munk transformation: [34]

$$\alpha h\nu = A (h\nu - E_g)^{n/2} \quad (3)$$

Where α , h , ν , and A are the absorption coefficient, planck constant, light frequency, and a constant. Besides, the n depends on the characteristics of the transition in a semiconductor. As previous report, the n values was 1. [35] Thus, the band gap of $\text{Sn}_{1-0.25x}\text{Cu}_x\text{S}_2$ was 1.35 eV and the band gap values of $\text{Sn}_{1-0.25x}\text{Cu}_x\text{S}_2$ were estimated to 1.69 eV as shown in Fig. 12 a and b. Many works reported approximated the band gap of the Sn-Cu-S. [36-38] The conduction band of $\text{Sn}_{1-0.25x}\text{Cu}_x\text{S}_2$ is 0.34 eV. Due to the standard reduction potential of 2.72 eV/NHE ($\cdot\text{OH}$, $\text{H}^+/\text{H}_2\text{O}$) and 2.38 eV/NHE ($\cdot\text{OH}/\text{OH}^-$), the E_{VB} level of $\text{Sn}_{1-0.25x}\text{Cu}_x\text{S}_2$ (1.69 eV/NHE) is not high enough to produce $\cdot\text{OH}$. Furthermore, compared with the standard reduction potential of -0.33 eV/NHE ($\text{O}_2/\cdot\text{O}_2^-$), the electron on the conduction band of $\text{Sn}_{1-0.25x}\text{Cu}_x\text{S}_2$ (0.34 eV/NHE) could not react with O_2 to form $\cdot\text{O}_2^-$ radicals. While the electron on the conduction band of $\text{Sn}_{1-0.25x}\text{Cu}_x\text{S}_2$ is high enough to react with O_2 to generate H_2O_2 for the reduction potential of $\text{O}_2/\text{H}_2\text{O}_2$ is 0.695 eV/NHE. This possible photocatalytic mechanism of $\text{Sn}_{1-0.25x}\text{Cu}_x\text{S}_2$ NFs was also proved by using scavenger method before.

4. Conclusions

In summary, the $\text{Sn}_{1-0.25x}\text{Cu}_x\text{S}_2$ hierarchical nanostructures were successfully prepared via a facile one-pot solvothermal process for the first time. The prepared $\text{Sn}_{1-0.25x}\text{Cu}_x\text{S}_2$ NFs showed a superior adsorption capacity for organic pollutants (RhB and DB), compared with SnS_2 NFs. And possessed higher photodegradation for organic pollutants (RhB and DB) in visible light ($\lambda \geq 420$ nm) irradiating, for its recombine of photoinduced electron-hole pairs were restrained. In particular, the $\text{Sn}_{1-0.25x}\text{Cu}_x\text{S}_2$ hierarchical nanostructures photocatalyst showed the highest photodegradation efficiency for RhB and DB, which was 4.6 and 5.4 times higher than pure SnS_2 NFs, respectively. Meanwhile, the photodegradation activity remained the similar level after three runs, which indicated that the $\text{Sn}_{1-0.25x}\text{Cu}_x\text{S}_2$ could maintain a high photostability. This work may provide an idea to design or fabricate efficient integrated photocatalytic adsorbent that can find potential applications in environmental pollution remediation and energy fields.

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Figure captions

Scheme 1 Possible growth mechanical scheme of the (a) SnS_2 and (b) $\text{Sn}_{1-0.25x}\text{Cu}_x\text{S}_2$ assembly flowerlike structure.

Scheme 2 Schematic illustration of the possible photocatalytic mechanism.

Fig. 1 SEM images of obtained samples (a) SnS_2 NFs and (b) $\text{Sn}_{1-0.25x}\text{Cu}_x\text{S}_2$ NFs.

Fig. 2 TEM images of obtained samples (a) SnS_2 NFs and (b) $\text{Sn}_{1-0.25x}\text{Cu}_x\text{S}_2$ NFs.

Fig. 3 XRD pattern of SnS_2 NFs and $\text{Sn}_{1-0.25x}\text{Cu}_x\text{S}_2$ at room temperature.

Fig. 4 (a) XPS survey spectra of samples SnS_2 NFs and $\text{Sn}_{1-0.25x}\text{Cu}_x\text{S}_2$ NFs; (b) XPS spectra of S 2p of samples SnS_2 NFs and $\text{Sn}_{1-0.25x}\text{Cu}_x\text{S}_2$ NFs; (c) XPS spectra of Sn 3d of samples SnS_2 NFs and $\text{Sn}_{1-0.25x}\text{Cu}_x\text{S}_2$ NFs; (d) Cu 2p core-level XPS spectrum of sample $\text{Sn}_{1-0.25x}\text{Cu}_x\text{S}_2$ NFs.

Fig. 5 (a) Nitrogen adsorption–desorption isotherms at 77.3 K and (b) the corresponding pore size distribution curves of SnS_2 NFs and $\text{Sn}_{1-0.25x}\text{Cu}_x\text{S}_2$ NFs.

Fig. 6 Adsorption isotherms of DB and RhB on (a) SnS_2 NFs and (b) $\text{Sn}_{1-0.25x}\text{Cu}_x\text{S}_2$ NFs.

Fig. 7 Photodegradation of (a) RhB and (c) DB and a natural logarithm C_0/C fitting curves of (b) RhB and (d) DB over SnS_2 NFs and $\text{Sn}_{1-0.25x}\text{Cu}_x\text{S}_2$ NFs under visible light irradiation ($\lambda \geq 420$ nm).

Fig. 8 (a) UV-visible diffuse reflectance spectra of the as-synthesized samples SnS_2 NFs and $\text{Sn}_{1-0.25x}\text{Cu}_x\text{S}_2$ NFs; (b) PL spectra of samples SnS_2 NFs and $\text{Sn}_{1-0.25x}\text{Cu}_x\text{S}_2$ NFs with the excitation wavelength of 325 nm at room temperature; (c) the Nyquist plots for samples SnS_2 NFs and $\text{Sn}_{1-0.25x}\text{Cu}_x\text{S}_2$ NFs; (d) the Nyquist plots for samples

$\text{Sn}_{1-0.25x}\text{Cu}_x\text{S}_2$ NFs.

Fig. 9 Amperometric I–t curves of SnS_2 NFs and $\text{Sn}_{1-0.25x}\text{Cu}_x\text{S}_2$ NFs under visible light ($\lambda \geq 420$ nm) with on/off cycles.

Fig.10 Cycle runs of $\text{Sn}_{1-0.25x}\text{Cu}_x\text{S}_2$ NFs for degradation of RhB under visible light irradiation ($\lambda > 420$ nm).

Fig. 11 Effects of different scavengers on degradation of (a) RhB and (b) DB over $\text{Sn}_{1-0.25x}\text{Cu}_x\text{S}_2$ NFs.

Fig. 12 (a) Plot of $(A\text{h}\nu)^{1/2}$ versus energy ($h\nu$) for the band gap energy of $\text{Sn}_{1-0.25x}\text{Cu}_x\text{S}_2$ NFs and SnS_2 NFs; (b) The VB-XPS of as-prepared $\text{Sn}_{1-0.25x}\text{Cu}_x\text{S}_2$ and SnS_2 NFs.

Figures

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