Synthesis of Ag₂O and Ag co-modified flower-like SnS₂ composites with enhanced photocatalytic activity under solar light irradiation

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Abstract: Three-dimensional Ag₂O and Ag co-modified flower-like SnS₂ composites have been synthesized through a facile hydrothermal and photoreduction process. The physical and chemical properties of Ag₂O and Ag co-modified flower-like SnS₂ composites were carefully studied by using XRD, SEM, TEM, UV-vis diffuse reflectance spectra (DRS) and XPS. The photocatalytic activity of the as-prepared products was evaluated by photocatalytic decolorization of Rhodamine B (Rh B) aqueous solution at ambient temperature under solar light irradiation. The photocatalytic result shows that Ag₂O and Ag co-modified flower-like SnS₂ composites exhibit enhanced photocatalytic activity compared with that of pure SnS₂. Three of the Ag₂O and Ag co-modified flower-like SnS₂ composites form the Z-scheme systems, because of their unique charge-carrier transfer process, the oxidation/reduction ability of photogenerated holes and electrons could be enhanced. Therefore, the new Ag₂O and Ag co-modified flower-like SnS₂ composites possess a favorable photocatalytic activity, and it can be a promising candidate for the solar energy conversion process.

Key words: SnS₂; Flower-like; Co-modified; Synthesis; Photocatalysis

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1. Introduction

Semiconductor-based photocatalysis, owing to its high efficiency, safety, cost-effectiveness and simplicity with the inexhaustible solar light as a driving force, **has being became** an efficient green technology to solve environmental problems and energy crisis [1-4]. However, the commonly studied photocatalysts, such as TiO_2 [5-7] and ZnO [8], have limited practical applications due to their wide band gap and the high recombination of photogenerated electron-hole pairs. Thus, numerous **attempts have being made** to develop efficient visible-light-active photocatalysts [9-10]. Recently, metal sulfide, such as MoS_2 [11] and SnS_2 [12], have been widely used in photocatalytic degradation of organic dyes [13] and water splitting [14]. Typically, SnS_2 , a layered CdI_2 -type structure semiconductor with a band gap of 2.2~2.35 eV [15], was reported to be a relatively stable and efficient visible-light-activated photocatalyst [16-18]. SnS_2 has unique properties, such as non-toxic, cheap, good stability in acid and neutral aqueous media as well as oxidative and thermal stability in air. It exhibits a rich portfolio of applications as anode materials for Li-ion batteries [19], photoelectrodes, photoconductors and, importantly, photocatalysts. Recently, the flower like SnS_2 has enhanced photocatalytic activity towards methyl blue (MB) degradation [20]. The graphene like SnS_2 film can achieve the degradation rate of rhodamine B of 90% only irradiated for 20 min [21]. More recently, 2D SnS_2 nanosheets are reported to have both adsorption and photocatalytic activities for different organic pollutants [22]. Cocatalyst modification is an efficient strategy to improve the photocatalytic efficiency of photocatalysts by promoting the effective separation of photogenerated electrons and

holes. However, most of the cocatalysts are restricted to noble metals (e.g., Ag, Au, Pt [23-24]) and few investigation have been focused on their oxides [25]. Y.C. Huang et al. fabricated metallic oxide composite photocatalyst or cocatalyst materials for degrading organic pollutant and they show varying degree of enhanced photocatalytic activity [26-30].

In this paper, we reported a facile hydrothermal and photoreduction process to synthesize three-dimensional Ag₂O and Ag co-loaded SnS₂ composites without any templates or surfactants. Furthermore, we proposed a photocatalytic mechanism based on XRD, TEM and XPS analyses of the Ag₂O and Ag co-modified flower-like SnS₂ composites, the as-obtained Ag₂O and Ag co-modified flower-like SnS₂ composites exhibit enhanced photocatalytic activity for the degradation of Rh B.

2. Experimental

2.1 Materials

All chemicals were analytical grade without further purification. Tin (IV) chloride pentahydrate (SnCl₄·5H₂O, A. R.) and thiourea (NH₂CSNH₂, A. R.) were purchased from Tianjin Chemical Reagent Co., Ltd., China, silver nitrate (AgNO₃, A. R.) was purchased Guanghai Chemical Reagent Co., Ltd, China, ethanol (≥99.5%, A.R.) were obtained from Xi'an Chemical Reagent Co., China.

2.2 Preparation of monodispersed flower-like SnS₂ microspheres.

The flower-like SnS₂ microspheres were prepared by a hydrothermal process of SnCl₄·5H₂O and NH₂CSNH₂ in ethanol. In a typical experiment, 0.35g SnCl₄·5H₂O were dissolved in 100 mL of ethanol and stirred for 20 min, followed by addition of

0.46g thiourea and continuously stirring for 30 min. The reactions were finished and then the mixed solution was transferred into the Teflon-lined stainless steel autoclave and maintained at 180°C for 24 h. The resulting powders were centrifuged, and then washed with distilled water and ethanol for several times. The washed products were dried on a vacuum oven at 60°C for 12 h.

2.3 Preparation of Ag₂O and Ag co-modified flower-like SnS₂ composites.

Briefly, 0.25g as-prepared SnS₂ powders were dispersed into 50 mL deionized water and sonicated for 20 min, then a given amount of AgNO₃ solution [31] (the concentration of 10 g/L) was added to the mixture with continuous stirring for 10 min at room temperature. The amount of AgNO₃ is 5, 10 and 15 mL, respectively. The mixture was stirred for 1 hour under the solar light (500 W Xenon lamp) irradiation. The precipitate was and then washed with distilled water and ethanol for several times. The washed products were dried on a vacuum oven at 60°C for 12 h. To make a comparison, the sample of pure flower-like SnS₂ microspheres was also prepared. The preparation process of the pure flower-like SnS₂ microspheres was same as the above experimental section 2.2. In order to facilitate the later statement, the Ag₂O and Ag co-modified flower-like **SnS₂ composites were** hereinafter denoted as SnS₂-A-V, e.g., SnS₂-A-5, SnS₂-A-10, SnS₂-A-15.

2.4 Characterization.

XRD patterns were recorded on a Rigaku D/max 2200pc diffractometer using Cu Ka radiation of wavelength $\lambda=0.15418\text{nm}$ at 40kV and 40mA. FE-SEM (field-emission scanning electron microscope) analysis was performed on a Hitachi S-4800 electron

microscopy. TEM images were conducted on a FEI Tecnai G2 F20 transmission electron microscope operated at 200kV. UV-visible absorbance spectra were obtained for the dry-pressed disk samples with a UV-visible spectrophotometer (Lambda-950, PerkinElmer Corporation, American). BaSO₄ was used as a reflectance experiment. X-ray photoelectron spectroscopy (XPS) measurements were performed by using an ultrahigh vacuum VG Scientific Corp MK-II electron spectrometer equipped with a multichannel detector. The spectra were excited using Mg Ka (1253.6 eV) radiation (operated at 200 W) of a twin anode in the constant analyzer energy mode with a pass energy of 50 eV.

2.5 Measurements of photocatalytic activities.

The photocatalytic activity of the samples was evaluated in terms of the degradation of Rh B. For each test, we carefully prepared 80 mL Rh B solution (the concentration of Rh B is 10 mg/L) previously, then the as-prepared Rh B solution was equally transferred into eight quartz photoreactors, which ensured that each quartz tube contained 10mL Rh B and 10mg photocatalyst in eight all quartz photoreactors, respectively. The mixture was sonicated for 20 min and stirred for 30 min in the dark in order to reach the adsorption-desorption equilibrium. A 500 W Xenon lamp was used as a solar light source. After the photocatalytic action, 10 mL of solution was taken and centrifuged. After removing the sediment (photocatalyst particles), the supernatant was used to analyze. The concentration of the residual Rh B was analyzed by checking the absorbance at 553 nm with a UV-vis spectrophotometer.

3. Results and discussion

3.1 XRD patterns

Fig. 1 displays the XRD patterns of the as-synthesized samples. As shown in Fig. 1, the x-ray diffraction peaks at 2θ values of 15.0° , 28.4° , 32.2° , 42.0° , 50.1° , 52.6° are corresponding to the (001), (100), (101), (102), (110), (111) crystal planes, respectively. The results confirmed that the synthesized materials were SnS_2 of hexagonal structure and all the diffraction peaks agree with the reported JCPDS data (Card NO. 23-0677), and the samples show sharp peaks because of the high crystalline characteristics (curve a). When the AgNO_3 solution was added to system (curve b, c, d of $\text{SnS}_2\text{-A-V}$), the background of the curve got deeper, which may be ascribed to the influence of Ag_2O and Ag on flower-like SnS_2 in the photoreduction process. Besides, the diffraction peaks for Ag species (38.1° , 44.2° , and 64.4°) were observed in all curves. Extra diffraction peaks appear at 26.8° and 32.4° in the XRD pattern of Ag_2O and Ag co-modified flower-like SnS_2 composites, which are respectively corresponding to the (110), (111) faces of Ag_2O as shown in JCPDS Card No. 41-1104. With the increase of the content of Ag_2O and Ag, the diffraction peaks of them is constantly increasing, the diffraction peaks of SnS_2 is constantly weakening, but the crystal structure of SnS_2 have not been changed by the Ag_2O and Ag particles.

3.2 Morphology of as-prepared photocatalysts

Fig. 2a demonstrates the SEM images of as-prepared pure SnS_2 . It can be observed that the samples are uniform flower-like spheres with average diameter of 1.5-2.0 μm , the surface of SnS_2 microspheres is smooth. As for Ag_2O and Ag co-modified flower-like SnS_2 composites (Fig. 2b, d and e), these microspheres shown

comparatively rough surface and attached few bright Ag_2O and Ag grains on the surface. To further confirm the presence of Ag and Sn in the composites, the element distribution is studied by EDX, O, S, Ag and Sn elements can be observed in element mapping studies of the SnS_2 -A-10 hybrid (Fig. 2h). Sn and S are assigned to SnS_2 , element Ag is due to metal Ag and Ag_2O , element O is due to Ag_2O , which indicating that the Ag_2O and Ag co-modified flower-like SnS_2 composites have been successfully synthesized. In order to get the detailed information in the Ag_2O and Ag co-modified flower-like SnS_2 composites, we performed TEM and HRTEM studies of Ag_2O and Ag co-modified flower-like SnS_2 composites (Fig. 2c and f), which increased specific surface area of the microspheres (Fig. S1). Besides, the large specific surface area of photocatalyst could lead to a more sufficient contact with Rh B in the photocatalytic reaction so as to enhance the activity of photocatalysis. As seen in Fig. 2f, the as prepared Ag_2O and Ag co-modified flower-like SnS_2 composites presented the clear lattice fringes owing to its excellent crystallization. The fringe interval of 0.28 nm of the microspheres was in accordance with the interplanar spacing of (101) crystal planes of hexagonal phase SnS_2 , and the d values of 0.2 nm and 0.24 nm were assigned to the crystal planes (200), (111) of 3C-silver [32], whereas that of 0.27 nm of (111) crystal planes corresponded to Ag_2O , which also confirmed that Ag, Ag_2O and SnS_2 species were all introduced into the hybrid system successfully. For one thing, the special structure is beneficial to facilitating the separation of photo-induced carriers and suppressing recombination of the electron-hole [33-34]. For another, the structure of Ag_2O and Ag co-modified flower-like SnS_2 composites were very stable, because its

TEM and HRTEM images were taken after intense ultrasonic dispersion in ethanol for 60 min.

3.3 DRS analysis

The optical properties of the prepared samples were analyzed by the ultraviolet-visible diffuse reflectance spectra (DRS). The DRS result of pure SnS_2 , $\text{SnS}_2\text{-A-5}$, $\text{SnS}_2\text{-A-10}$, $\text{SnS}_2\text{-A-15}$, $\text{SnS}_2\text{-Ag}$ and $\text{SnS}_2\text{-Ag}_2\text{O}$ are demonstrated in Fig. 3. As for the pure SnS_2 sample, observation showed that the band-gap absorption in visible region with an adsorption edge at 580 nm. Pure SnS_2 itself can absorb visible light, indicating that SnS_2 is active under solar light irradiation. This is ascribed to the intrinsic band gap absorption of SnS_2 (2.35 eV). Moreover, it can be seen that the absorption band of $\text{SnS}_2\text{-Ag}$, $\text{SnS}_2\text{-Ag}_2\text{O}$, and co-modified samples exhibits somewhat red-shift of the absorption edge when compared to the pure SnS_2 (Fig. 3). It is worth mentioning that, compared to pure SnS_2 , a broad absorption covering the range of 400-800 nm appeared in the spectra of the Ag_2O and Ag co-modified samples, which should be attributed to the surface plasmonic resonance (SPR) effect of Ag (0) and the presence of Ag_2O . Therefore, the SPR effect of Ag nanoparticles and the presence of Ag_2O may have a significant contribution to the light-harvesting and using capacities, more electron-hole pair will be produced, and then promote the enhanced photocatalytic activity of Ag_2O and Ag co-modified samples.

3.4 XPS spectra

In order to clarify the interaction of the components in the composites, the corresponding XPS spectra provide further structural information for the $\text{SnS}_2\text{-A-10}$

photocatalyst, as shown in Fig. 4. Fig. 4a is a typical XPS survey spectrum of different atoms. The binding energies obtained in the XPS analysis are standardized for specimen charging using C1s as the reference at 284.6 eV. The survey XPS spectrum indicated that the samples were mainly composed of Sn, S, Ag and C (C is from adsorbed gaseous molecules and usually unavoidable in XPS measurements), except the element of oxygen from adsorbed gaseous molecules. Fig. 4b shows the high-resolution XPS spectrum of the Sn 3d. The two strong peaks at around 486.5 and 495.0 eV can be attributed to Sn 3d_{5/2} and Sn 3d_{3/2} [35], respectively, which is characteristic of Sn⁴⁺ in SnS₂. Compared with SnS₂, Sn 3d XPS peak in SnS₂-A-10 appears a slight offset. The binding energy is become little larger, may be the presence of Ag and Ag₂O nanoparticles change the chemical environment of Sn⁴⁺, it may be a further proof that there exists a special chemical bond between Sn and O atoms (i.e. the Sn-O bond). This phenomenon further suggests that there are strong interactions between Ag₂O and SnS₂. What's more, the binding energies of S 2p_{3/2} (161.7 eV) and S 2p_{1/2} (162.8 eV) of SnS₂ are all accorded with the reference values for SnS₂ [36](Fig. 4c). In Fig. 4d, it can be observed that the Ag 3d spectra of SnS₂-A-10 consist of two individual peaks at 373.9 and 367.92 eV, which can be attributed to the Ag 3d_{3/2} and Ag 3d_{5/2} binding energies, respectively. The Ag 3d_{5/2} peak for SnS₂-A-10 can be further divided into two different peaks at 368.2 and 367.6 eV, attributed to the peaks of metal Ag and Ag₂O, respectively [32, 37-38]. The O 1s spectrum is shown in Fig. 4e, two main peaks at 530.7 and 532.1 eV are attributable to oxygen of Ag₂O and oxygen atoms in absorbed water on the surface, respectively [39], which in agreement with the XRD results.

3.5 Photocatalytic activities

The photocatalytic performances of pure SnS₂, SnS₂-A-5, SnS₂-A-10 and SnS₂-A-15 are determined in Fig. 5. Fig. 5a shows the changes in the absorption spectra of an Rh B aqueous solution exposed to solar light for various time in the presence of SnS₂-A-10. The characteristic absorption band of the Rh B around 553 nm shows a slight blue shift and the peak intensity decreases rapidly in 85 min under solar light irradiation and the color of Rh B almost completely faded, which is much faster than that of pure SnS₂, and no new absorption bands appeared. (The structure of Rh B and the photographs of the time dependent degradation of Rh B for SnS₂-A-10 are seen inset in Fig. 5a). Figure 5b demonstrates the comparison of photocatalytic reduction curves of Rh B in the photocatalyst-free solution, pure SnS₂, SnS₂-A-5, SnS₂-A-10 and SnS₂-A-15 under solar light irradiation. The samples exhibit diversities in their degradation efficiency for Rh B in the photocatalytic reaction. The results show that the decrease in the concentration of Rh B without photocatalyst is negligible under solar light irradiation, testifying the stabilization of Rh B. The Rh B degradation percentage for pure SnS₂ after 85 min solar light irradiation approaches to 60%. The Rh B degrades almost completely within 85 min for SnS₂-A-10, a process much faster than that of pure SnS₂ (Fig. 5b). The degradation percentages of the as-prepared photocatalysts after 30 and 100 min irradiation are shown in Fig. 5d. The photocatalytic degradation kinetic was investigated and the linear simulation of degradation of dye concentration can be accounted for by a pseudo first-order model [40]. The relevant equation is:

$$\gamma = -\frac{dC}{dt} = k_{app}C = \frac{C}{t} \ln\left(\frac{C_0}{C_t}\right)$$

where γ is the degradation rate, C_t/C_0 is the ratio of the concentration of the dye after various intervals of time and at adsorption-desorption equilibrium, and k_{app} was the apparent first-order rate constant (min^{-1}). Obviously seen from Fig. 5c, we can obtain the pseudo-first-order kinetic rate constant k_{app} from the gradient of the graph of $\ln(C_0/C)$ versus time (t). The photocatalytic degradation rate constants were 0.0003, 0.0075, 0.0139, 0.0162, 0.0116, 0.0084, and 0.0076 min^{-1} for the cases of photocatalyst-free solution, pure SnS_2 , $\text{SnS}_2\text{-A-5}$, $\text{SnS}_2\text{-A-10}$, $\text{SnS}_2\text{-A-15}$, $\text{SnS}_2\text{-Ag}$ and $\text{SnS}_2\text{-Ag}_2\text{O}$ under solar light irradiation, respectively. The k_{app} value for the Ag_2O and Ag co-modified SnS_2 samples is larger than that of pure SnS_2 , $\text{SnS}_2\text{-Ag}$ and $\text{SnS}_2\text{-Ag}_2\text{O}$. It is obvious that the Ag_2O and Ag co-modified samples shows higher photocatalytic activity. The k_{app} value for the $\text{SnS}_2\text{-A-10}$ is about 2 times larger than that of pure SnS_2 (Fig. 5c). However, the content of silver should be moderate, if they are too much, silver particles will occupy the active sites on the surface of flower-like SnS_2 , it will reduce its photocatalytic performance. The photocatalytic performance of $\text{SnS}_2\text{-A-5}$ and $\text{SnS}_2\text{-A-15}$ is higher than that of pure SnS_2 but lower than that of $\text{SnS}_2\text{-A-10}$ (Fig. 5b, c and d). As a whole, the new Ag_2O and Ag co-modified SnS_2 composites possess a favorable photocatalytic activity, and it can be a promising candidate for wastewater purification.

The stability can be an important evaluation index for estimating the reusability and practical application of catalysts. Five cycles of photodegradation of Rh B were conducted taking pure SnS_2 and $\text{SnS}_2\text{-A-10}$ catalyst as typical samples. There covered $\text{SnS}_2\text{-A-10}$ was reused in the next cycle. Fig.6 shows no obvious performance

weakening for the as-prepared SnS₂-A-10 after five repeated cycles.

3.6 Mechanism on enhancement of photocatalytic activity

Scheme 1 schematically shows the proposed promotion mechanism of the photocatalytic degradation performance of the Ag₂O and Ag co-modified flower-like SnS₂ photocatalysts. Under the condition of illumination, silver nitrate was reduced to silver: $\text{AgNO}_3(\text{irradiation}) \rightarrow \text{Ag} + \text{NO}_2 + \text{O}_2$, and the part of the silver was oxidized to silver oxide in the air oxidation: $\text{Ag} + \text{O}_2 \rightarrow \text{Ag}_2\text{O}$, then the Ag₂O and Ag co-modified flower-like SnS₂ photocatalysts were prepared. On the one hand, owing to the surface plasmonic resonance effect, Ag nanoparticles can improve the utilization rate of quantum and expand the light response range. On the other hand, three of the Ag₂O and Ag co-modified flower-like SnS₂ composites form a Z-scheme systems [1, 41-42], which enhance the separation of electrons and holes thus improve the photocatalytic activity. From Scheme 1, an all-solid-state Z-scheme photocatalytic system was constructed by electron mediator Ag. Conductor Ag was inserted between Ag₂O and SnS₂ which formed Ohmic contact with low contact resistance [1]. Through the Ohmic contact, the photogenerated electrons (conduction band of Ag₂O) could directly recombine with the photogenerated holes (valence band of SnS₂) and then annihilate at Ag. It reduced the distance of Z-scheme electron transfer and increased the lifetime of photogenerated holes from Ag₂O and photoelectrons from SnS₂. The introduction of Ag₂O was useful for the improvement of visible light absorption and the enhancement of photon conversion efficiencies. At the same time, the strong reductive electrons would be left on the conduction band of SnS₂ and the strong oxidative holes would be

left on the valence band of Ag₂O. The photogenerated electrons can reduce the H⁺ to ·OH, reduce O₂ to generate O₂^{·-} and the holes can oxidize the OH⁻ to ·OH. The produced ·OH was the main active specie in the photocatalytic reaction (Fig. S2). According to the Z-scheme charge-carrier transfer process, the oxidation ability of photogenerated holes and electrons could be enhanced, thus enhancing the catalytic ability.

The reaction includes the following [43-44]:

On the basis of the above, the enhanced photocatalytic activity of Ag₂O and Ag modified SnS₂ is attributed to the deposited Ag₂O and Ag nanoparticles. The Ag₂O and Ag modified SnS₂ exhibits higher photocatalytic activity than pure SnS₂ and the SnS₂-A-10 is the best.

4. Conclusions

The solar light driven Ag₂O and Ag co-modified flower-like SnS₂ photocatalyst was successfully synthesized by a combination of hydrothermal and photoreduction methods. In this research, Ag₂O and Ag nanoparticles dispersed on the flower-like SnS₂ microspheres with an average diameter of 1.5-2.0 μm, form a Z-scheme system. What's more, it is beneficial for the improvement of solar light absorption and increasing

photon conversion efficiencies. It also promoted the photocatalytic activity of Ag_2O and Ag modified SnS_2 composites and the SnS_2 -A-10 has the highest activity of 2 times of pure SnS_2 . However, the content of Ag_2O and Ag should be moderate, if they are too much, Ag_2O and Ag particles will occupy the active sites on the surface of flower-like SnS_2 , and it will reduce its photocatalytic performance. As a whole, the new Ag_2O and Ag co-modified flower-like SnS_2 composites possess a favorable photocatalytic activity, and it can be a promising candidate for wastewater purification.

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Figure Captions

Fig. 1. XRD patterns of samples: (a) pure SnS₂, (b) SnS₂-A-5, (c) SnS₂-A-10 and (d) SnS₂-A-15.

Fig. 2. SEM (a, b, d, e) and TEM (c, f) images of as-prepared samples: (a) pure SnS₂, (b-f) SnS₂-A-10. And its elemental mapping images of O, S, Ag and Sn of SnS₂-A-10 (h).

Fig. 3. UV-vis diffuse reflectance spectra of as-samples.

Fig. 4. XPS spectra of as-prepared samples.

Fig. 5. Photocatalytic degradation of 10mg/L Rh B (Rhodamine B) in the SnS₂-A-10 aqueous suspensions under visible light irradiation (a); comparison of the photocatalytic degradation curves of Rh B in the pure SnS₂, SnS₂-A-5, SnS₂-A-10 SnS₂-A-15, SnS₂-Ag₂O and SnS₂-Ag aqueous suspensions (b); kinetic plot with different samples (c); degradation percentages after 30 and 100 min irradiation (d). The inset of (a) shows the structure of Rh B and the photographs of the time dependent degradation of Rh B for SnS₂-Ag-10.

Fig. 6. Photocatalytic performances of SnS₂-Ag-10 in the first five reuse cycles.

Scheme 1 Proposed photocatalytic mechanism of 3D Ag₂O-Ag/SnS₂ microspheres.

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Figure 2 Zhenfeng Zhu et al

Figure 3 Zhenfeng Zhu et al

Figure 4 Zhenfeng Zhu et al

Figure 5 Zhenfeng Zhu et al

Figure 6 Zhenfeng Zhu et al

Scheme 1 Zhenfeng Zhu et al

Graphical Abstract