RESEARCH ARTICLE

Efficient photocatalytic desulfurization of thiophene under visible light irradiation over flower-like AgBiS$_2$ photocatalyst

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Here, we report the production of hierarchical flower-like AgBiS$_2$ nanostructures by an amino acid-modified polyol route. This work indicates that by changing the polyol process conditions including kind of capping agent, reaction time and reflux temperature, the sheet-like, cone-like, sphere-like and flower-like morphologies of AgBiS$_2$ micro/nanostructures can be prepared. The phase, elemental composition, morphology and optical characteristics of as-prepared AgBiS$_2$ nanostructures were analyzed by UV–Vis, FESEM, XRD, and EDS techniques. After characterization of the products, the AgBiS$_2$ nanostructures were employed as novel photocatalysts for oxidative desulfurization of thiophene/n-octane solution as model fuel under visible light illumination. Results demonstrate that hierarchical flower-like AgBiS$_2$ photocatalyst with desirable band gap energy (2.44 eV) has high photocatalytic desulfurization performance of about 89% after 2 h of visible light irradiation. As well as, the effects of morphology, photocatalyst dosage and reusability of the AgBiS$_2$ nanostructures on the photocatalytic performance were evaluated. The excellent photocatalytic activity of AgBiS$_2$ photocatalyst can be attributed to the strong visible light absorption, high separation rate of electron–hole pairs, special hierarchical structures and suitable band gap energy. Moreover, a reliable photo-oxidation desulfurization mechanism was discussed according to the active species trapping experiments, which revealed the photo-generated h$^+$ and $\cdot$O$_2^-$ radicals were the main active species in the photocatalytic desulfurization process.

INTRODUCTION
The critical weather problems arising from atmosphere pollutants have gained extensive attentions, especially the ignition of sulfur-containing gasoline fuels in the automobile engines, which causes the release of extraordinary amounts of sulfur oxides (SO$_x$) into the air. These harmful compounds seriously threat the plants, animals and human health [1-3]. Hence, many countries have investigated the diverse desulfurization processes, which can produce “zero” sulfur fuels, including hydrodesulfurization, adsorption desulfurization, biosulfurization, catalytic desulfurization, oxidative desulfurization, extraction desulfurization, alkylation and sono-hybrid techniques [4-10]. Among them, the photo-oxidative desulfurization (PODS) route as one of the potential methods for the ultra-deep desulfurization of fuels has received widespread attentions because of the benefits of using the sunlight sources, performance under moderate conditions (low temperature and pressure), using air or H$_2$O$_2$ as oxidant, non-use of H$_2$, high-yield and selectivity, affordable and eco-friendly [1-3, 9-12]. As well known, in the photocatalytic desulfurization process, photocatalyst plays the main role for the oxidation reactions of sulfur atoms to sulfoxides and sulfones [1, 13]. For this reason, preparation of efficient nanophotocatalysts...
with the suitable band gap in visible light range, low recombination value of electron-hole pairs, and good stability is essential for the ultra-deep desulfurization process.

In recent years, photocatalytic nanomaterials have attracted extensive considerations due to their applications in various environmental and industrial areas, including solar cells, water treatment, oxidation reactions, desulfurization, catalysis, photocatalysis, etc. In a general photocatalysis process, a photocatalyst with the use of solar photons can produce electron-hole (e⁻-h⁺) pairs and subsequently generate powerful active species which can oxidize the organic compounds. However, the traditional photocatalysts suffer from their wide band gaps and high recombination of charge carriers, which only excited under UV illumination. Hence, many efforts have been made to fabricate nanoscale photocatalysts with appropriate band gaps for the effective absorption of visible light radiation to eliminate the environmental pollutants [14-20].

In the last few decades, silver bismuth sulfide (AgBiS₂) compounds belonging to I–V–VI group ternary chalcogenides have attracted extensive interest due to their excellent properties in thermoelectric, optoelectronic, optical recording, photoconductivity, dielectric constant, magnetic, and especially in visible light absorption [21-26]. Because of such features, AgBiS₂ semiconductors have been widely employed as electrodes or sensitizers in solar cells, catalysts for polymerization of alkyllsilanes, photovoltaic absorbers, materials for optoelectronic and thermoelectric devices, and photocatalysts for hydrogen evolution and degradation of Doxycycline [24-29]. Moreover, AgBiS₂ nanocrystals possess energy band gap of ∼1.2 eV, high absorption coefficient of α ≈ 105 cm⁻¹ (at λ = 600 nm), earth-abundance and non-toxicity, which make them as good potential candidates for visible-light-driven photocatalytic applications [23, 30, 31]. Moreover, it is well known that the hierarchical micro/ nanostructures exhibit interesting features including favorable optical properties, high specific surface area, impressive charge carriers separation, plentiful transport paths for e⁻-h⁺ pairs, superior photocatalytic performance and reusability [32-35]. Hence, adopting an efficient approach for the preparation of hierarchical architectures in nanoscale building is important. So far, several methods have been reported for the synthesis of AgBiS₂ structures with various morphologies including microwave, solid-state reaction, hydro/solvothermal, sonochemical, biomolecule-assisted synthesis, template, hot-injection, and polyol route [21, 22, 27, 36-40]. Among these approaches, the polyol technique with benefits like less-energy demanding, simplicity, effectiveness, low-temperature, versatility and environmentally friendly has proved very attractive process for the preparation of nanoscale structures [41, 42].

Herein, hierarchical flower-like AgBiS₂ nanostructures were prepared by a polyol approach in the presence of various amino acid as capping agent. The results showed that by controlling the process conditions such as kind of capping agent, reaction time and reflux temperature, the porous flower-like AgBiS₂ nanostructures can be formed. Furthermore, for the first time, the AgBiS₂ nanostructures were applied as novel photocatalysts for the desulfurization of thiophene under visible light illumination. Results indicate that the flower-like AgBiS₂ nanostructures have high photocatalytic desulfurization performance (about 89%) after 2 h of visible light irradiation. Also, the photodesulfurization mechanism was described based on the radical trapping experiment. This photocatalyst provides new design strategy and versatile research prospect for application in the photocatalytic oxidation desulfurization.

**EXPERIMENTAL**

**Materials and Equipments**

All the reagents used for the fabrication of AgBiS₂ nanostructures including Bi(NO₃)₃·5H₂O, AgNO₃, thiourea, ethyleneglycol (EG), glutamic acid, and methanol were of analytical grade and purchased from Sigma-Aldrich company. The particle size and shape of the samples were studied by field emission scanning electron microscope (FE-SEM, Mira3 Tescan) equipped with an energy dispersive X-ray spectroscopy (EDS). The phase and grain size of the samples were determined by X-ray diffraction (XRD) analysis on a Philips-X’PertPro, X-ray diffractometer using Cu-Kα radiation (λ=0.15418 nm). UV-Vis diffuse reflectance spectra (UV-Vis-DRS) was obtained using a Shimadzu UV-2550 UV-Vis spectrophotometer. The quantity of sulfur in the photo-desulfurized samples was calculated with X-ray fluorescence sulfur meter (Tanaka Scientific RX-360SH).
Synthesis of AgBiS₂ nanostructures

In order to synthesize the AgBiS₂ nanostructures a facile refluxing polyol approach was employed. For this purpose, certain amounts of Bi(NO₃)₃·5H₂O and AgNO₃ (with 1:1 mole ratio) were dissolved in 20 ml of EG under constant magnetic stirring. Then, 10 ml of EG solution of thioacetamide with 1:1:2 mole ratio to Ag:Bi:S was added into the above mixture and process was carried out for 6 h at 200 °C under reflux. After completion of polyol reaction, the precipitates were filtered and washed with deionized water and ethanol to remove the other impurities. After drying at 60 °C for 6 h, the AgBiS₂ powders were obtained. Scheme 1 shows the schematic synthesis of the AgBiS₂ nanostructures in presence of tryptophan as capping agent (sample no. 3) and its photocatalytic desulfurization performance. Furthermore, the effect of polyol reaction time, capping agent and reflux temperature on the morphology of the AgBiS₂ compounds were examined and the results are shown in Table 1.

Photocatalytic desulfurization experiment

The photocatalytic desulfurization performance of the AgBiS₂ nanostructures was investigated using...
50 mg of the photocatalyst and 50 ml of model fuel (thiophene/n-octane with sulfur content ~ 600 ppm) utilizing visible 400 W Osram lamp. Before the illumination, the suspension was continuously stirred in the dark for 30 min to establish an adsorption/desorption equilibrium and air as oxidant was pumped into the mixture. At certain time intervals, 5 ml of desulfurized solution were withdrawn, centrifuged and then was extracted by methanol as extractant to remove the oxidized thiophene. The desulfurization efficiency (η) of thiophene solution was calculated according to the following formula:

\[ η = \frac{(C_0 - C_t)}{C_0} \times 100 \]  

where \( C_0 \) and \( C_t \) are the sulfur concentrations of model fuel for initial and \( t \) times, respectively. In addition, to investigate the participating species in the photocatalytic desulfurization process, radical trapping study was carried out in the same procedure in presence of various kinds of scavengers, such as Na₂-EDTA (as quencher of \( h^+ \)) and BQ (as quencher of \( \cdot O_2^- \)).

RESULTS AND DISCUSSION

The phase purity and composition of the AgBiS₂ nanostructures was studied using X-ray diffraction (XRD) measurement. The XRD pattern (Fig. 1) exhibits that the as-prepared sample no. 3 is cubic phase of AgBiS₂. The main diffraction peaks at 27.2°, 31.7°, 45.4°, 53.8°, 56.4° and 66.1°, are corresponding to (111), (200), (220), (311), (222) and (400) crystal planes, which are in good agreement with the standard JCPDS card No. 21-1178. In addition, there are no characteristic peaks attributable to other impurities, e.g. Ag₂S,
Bi$_2$S$_3$, etc., in the pattern, indicating that the AgBiS$_2$ products are pure crystalline. The broadening of the peaks demonstrates that the crystalline size of the sample is very small. By using Scherrer formula from the diffraction peaks widths at half maxima, the average diameter of the AgBiS$_2$ crystals was calculated as ~16 nm.

Energy dispersive spectroscopy (EDS) was also applied to determine the elemental composition of the as-synthesized AgBiS$_2$ nanostructures (sample no. 3). As can be seen in Fig. 2, only the peaks of Ag, Bi, and S elements are present in the EDS spectrum, and the atomic ratio of Ag:Bi:S is 1.04:1.16:2.19, which is close to the stoichiometry of 1:1:2 for AgBiS$_2$ structures. This result is in good agreement with the result of XRD pattern.

In order to study the effect of the reaction time, capping agent and reflux temperature on the morphology of the AgBiS$_2$ nanostructures, field emission scanning electron microscopy (FESEM) was used. As shown in Table 1, to examine the influence of the polyol reaction time, the AgBiS$_2$ samples were prepared for 1 h (sample no. 1), 3 h (sample no. 2) and 6 h (sample no. 3) at 200 °C in the presence of tryptophan as capping agent. As seen from the Figs. 3a-c, the reaction time of 1 h was not enough to form the flower-like nanostructures. In this time, initial agglomerated particles of AgBiS$_2$ were formed (Fig. 3a). By prolonging the reaction time to 3 h, very fine sheet-like structures were prepared (Fig. 3b). It seems that, by increasing the reaction time to 3 h, primary particles had enough time to stick together and form the nanosheets. When the refluxing time was extended more to 6 h, nanosheets had enough time to orientated attachment growth and finally the uniform flower-like nanostructures were obtained (Fig. 3c).

Moreover, the effect of the reflux temperature on the size and shape of the AgBiS$_2$ samples was investigated. For this purpose, polyol process was performed at 100 °C (sample no. 4) and 150 °C (sample no. 5) for 6 h. As seen in Fig. 4a, at 100 °C, the intertwined sheet structures were obtained. Whereas, by increasing the reaction temperature to 150 °C, non-assembled sheet-like nanostructures were formed (Fig. 4b). A possible formation mechanism of flower-like AgBiS$_2$ nanostructures can be proposed. First, the thioacetamide complexes with Ag and Bi ions were formed under the reflux conditions. Second, the as-obtained complexes undergo thermal decomposition at optimum reaction temperature and time. Third, in the presence of the capping agent, the orientation growth of AgBiS$_2$ nanosheets was carried out in the nucleation and growth stages [22, 41, 43]. Finally, the hierarchical flower-like AgBiS$_2$ nanostructures aggregated from a large number of nanosheets were prepared.

Furthermore, the AgBiS$_2$ nanostructures were synthesized by various capping agents including glutamic acid (sample no. 6), glycine (sample no. 7) and tryptophan (sample no. 3), and in the
Fig. 3. FESEM images of the (a) sample 1, (b) sample 2 and (c) sample 3, synthesized in different reaction times.

Fig. 4. FESEM images of the (a) sample 4 and (b) sample 5, synthesized at different reaction temperatures.
absence of any capping agent (sample no. 8) at 200 °C for 6 h. It can be clearly seen from Figs. 5a-c, that the non-uniform cone-like structures (Fig. 5a), irregular sphere-like nanostructures (Fig. 5b), flower-like nanostructures (Fig. 5c) and agglomerated microstructures (Fig. 5c) were prepared in the presence of the glutamic acid, glycine, tryptophan and without using of capping agent, respectively. These amino acids with various spatial arrangements, can play the role of capping agents. It can be concluded that tryptophan with the highest steric hindrance effect can provide an oriented growth pathway to formation of flower-like AgBiS$_2$ nanostructures [44].

The light absorption property of the as-fabricated AgBiS$_2$ nanocrystals was studied by UV–Vis diffuse reflectance spectroscopy (UV–Vis DRS). The DRS spectra of the AgBiS$_2$ semiconductor (sample no. 3) has been illustrated in Fig. 6a. It can be seen that a broad and strong peak ranging from 200 to 700 nm has appeared. Specially, it shows a continuous absorption spectrum in the whole visible light area. Thus, the amount of photo-generated charge carriers in the AgBiS$_2$ photocatalyst can further augmented, which leads to increase the catalytic yield under visible light illumination. Furthermore, the sample has an absorption peak located at 410 nm in wavelength, which compared to the absorption band of the bulk AgBiS$_2$ (~1050 nm) exhibits a large blue-shift, due to the very small crystalline size of the nanostructures [37]. Commonly, the gap energy ($E_g$) of the crystalline semiconductors can be computed based on the following equation:

$$ahv = A(hv - Eg)^2$$

(2)

where $a$ is the absorption coefficient, $h$ is the photonic energy, and $A$ is energy-independent constant. The energy band-gap of the product was
calculated by the Tauc plot of \((\alpha h\nu)^2\) versus \(h\nu\). The \(E_g\) value of the sample no. 3 was determined to be 2.44 eV (Fig. 6b), which is in agreement with the band gap of the reported value [24]. Therefore, it is obvious that the AgBiS\(_2\) nanostructures can be applied as a potential photocatalyst in the visible region.

The catalytic oxidative desulfurization activity of the AgBiS\(_2\) nanostructures was studied by monitoring the photo-oxidation of thiophene/n-octane solution as model fuel using \(O_2\) as the oxidant and methanol as extraction solvent under visible light irradiation. Up to now, the desulfurization performance of the AgBiS\(_2\) compound has not been reported. The blank experiments showed that in the absence of AgBiS\(_2\) photocatalyst or visible light irradiation, thiophene molecules could not be oxidized (Fig. 7a), that indicated the oxidation process was mainly due to photocatalytic reactions. As illustrated in the Table 1, the results exhibited that the sample no. 3 with particular morphology has better desulfurization efficiency about 89\% after 2 h of visible light irradiation (Fig. 7a). The proposed mechanism of photocatalytic desulfurization process of the AgBiS\(_2\) nanostructures is shown by the following equations [12, 45]:

\[
\text{AgBiS}_2 + h\nu \text{(Vis)} \rightarrow (\text{AgBiS}_2)^* + e^- + h^+ \quad (3)
\]

\[
O_2 + e^- \rightarrow O_2^- \quad (4)
\]

\[
O_2^- + \text{Thiophene} \rightarrow \text{Oxidized thiophene} \quad (5)
\]

\[
h^+ + \text{Thiophene} \rightarrow \text{Thiophene}^+ \quad (6)
\]

\[
\text{Thiophene}^+ + O_2^- \rightarrow \text{Oxidized thiophene} \quad (7)
\]

As shown in Scheme 2, the AgBiS\(_2\) can adsorb the photons and instantly produce the electrons and holes on its conduction band (CB) and valence band (VB), respectively. Afterward, the electrons accumulated in the CB can react with \(O_2\) molecules and generate reactive oxygen anion superoxide (\(O_2^-\)). These oxidative radicals can attack to the sulfur atoms in the thiophene and generate the oxidized compounds. Simultaneously,
thiophene can combine with the holes (h+) to form ‘thiophene’, which is then oxidized by active ‘O2’ radicals [4, 46]. The excellent photocatalytic performance of the AgBiS2 nanostructures can be ascribed to the lower charge carrier recombination, appropriate band gap energy and more active sites of the photocatalyst [1, 47].

Moreover, to further revelation the photocatalytic desulfurization mechanism of flower-like AgBiS2 nanostructures, the radical trapping experiment was employed to characterize the contributor active species in the desulfurization process. It is well known that the superoxide radical (‘O2’−) and hole (h+) were generally considered as
the basic species in the photocatalytic reactions [48, 49]. Hence, the radical trapping was performed utilizing BQ and Na₂-EDTA as the scavengers of superoxide radical (•O₂⁻) and hole (h⁺), respectively. As shown in Fig. 7b, the benzoquinone notably repressed the photo-desulfurization process performance, whilst by adding the Na₂-EDTA, the desulfurization efficiency partially decreased. The amount of desulfurization efficiency was reduced from 89% to 21% and 69% in the presence of BQ and Na₂-EDTA, respectively. Therefore, this result suggested that the photo-generated superoxide radicals (•O₂⁻) has played the main role in the photocatalytic desulfurization of thiophene by AgBiS₂ nanostructures.

To examine the effect of AgBiS₂ photocatalyst dosage on the photocatalytic desulfurization efficiency, the values of 25, 50, 100 and 200 mg from the sample no. 3 were applied in desulfurization of thiophene solution (600 ppm) under 2 h of visible light irradiation. The photodesulfurization efficiency of thiophene in each amount of photocatalyst were approximate 65, 89, 85 and 74%, respectively. As shown in Fig. 8a, by adding the photocatalyst loading from 25 to 50 mg, due to the increase in the number of surface active sites and interactions, the desulfurization rate of thiophene was enhanced. Whereas, by further boosting in photocatalyst dosage to 100 and 200 mg, due to the high accumulation of nanoparticles and then decrement in surface active sites on the photocatalyst, the desulfurization performance of AgBiS₂ was reduced [50, 51].

In the industrial applications, the recovery and reusability of the catalysts is economically valuable. Therefore, the recyclability of the flower-like AgBiS₂ nanostructures (sample no. 3) was carried out for 5 runs of desulfurization experiment. From Fig. 8b, it is obvious that even after 5 recycles, the photocatalytic activity remained constant, which indicates that the AgBiS₂ nanostructure can be employed as a recyclable photocatalyst for the photocatalytic applications under sun light irradiation.

**CONCLUSIONS**

In the present study, hierarchical flower-like AgBiS₂ nanostructures have been synthesized by an amino acid-modified refluxing polyol process. We found that sheet-like, cone-like, sphere-
like and flower-like morphologies of the AgBiS₂ nanostructures can be achieved by controlling the reaction parameters including type of capping agent, reaction time and reflux temperature. Finally, we employed the AgBiS₂ photocatalysts with different morphologies to desulfurize the thiophene as model fuel in the presence of O₂ as oxidant and methanol as extraction solvent under visible light illumination. Results illustrate that the hierarchical flower-like AgBiS₂ photocatalyst with suitable band gap energy (~2.44 eV) has good photocatalytic desulfurization activity (~89%) after 2h of visible light irradiation. Also, the impacts of morphology, catalyst dosage and recyclability of the AgBiS₂ products on the photocatalytic efficiency were examined. The superior photocatalytic performance of AgBiS₂ photocatalyst can be ascribed to the good visible photon absorption, high separation efficiency of charge carriers, particular hierarchical structures and appropriate band gap energy. Moreover, the reliable photocatalytic mechanism was suggested according to the active species trapping experiments, which showed the photo-induced h+ and O₂− species were the dominant active species in the photocatalytic oxidation desulfurization process. The superior efficiency, low-cost, and simple synthesis of AgBiS₂ proves its promising potential for photodesulfurization applications.

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CONFLICT OF INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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