Improving the photocatalytic activity of benzyl alcohol oxidation by Z-scheme SnS/g-C₃N₄†

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Until now, the effective photocatalytic oxidation of benzyl alcohol to benzaldehyde with high selectivity is still a great challenge. It is reported that the carrier separation rate is the key factor affecting the photocatalytic activity, and the formation of heterojunction is an effective solution to hinder electron–hole recombination. SnS with a narrow band gap has excellent light absorption performance, which covers the whole visible light region. After compounding with g-C₃N₄, the light utilization of the SnS/g-C₃N₄ photocatalyst is effectively improved. In addition, a Z-scheme heterojunction is formed between SnS and g-C₃N₄ due to the matched energy levels, which accelerates the separation of electrons and holes and improves the conversion of benzyl alcohol effectively. In this paper, the charge separation is accelerated to promote the reaction by the in situ construction of Z-scheme heterojunctions; the preparation method, reaction mechanism and energy level structure of the photocatalyst can play a certain guiding role in the organic conversion reaction.

1. Introduction

Benzaldehyde (BAD) is the most commonly used aromatic aldehyde in industry. It is widely used as an intermediate in the production of spices, medicines, and dyes, and its consumption is increasing year by year. However, in industry, its preparation method usually requires noble metal catalysts (e.g., Au, Pd, etc.) or strong oxidants (e.g., KMnO₄, V₂O₅ or K₂Cr₂O₇), which will cause high energy consumption and environmental pollution. Therefore, the development of a green and low-cost method to achieve selective alcohol oxidation is of great significance. In order to solve these problems, the photocatalytic oxidation of benzyl alcohol (BA) to BAD has become a new hotspot.

Photocatalysis mainly drives the redox reaction by the excitation of carriers, and the rapid separation of photogenerated carriers can accelerate the reaction rate. A variety of effective strategies such as noble metal loading, element doping, surface defect formation, and the construction of heterojunctions have been developed to speed up the separation of electron–hole pairs. Of the strategies mentioned above, the construction of heterojunctions has been demonstrated as an effective way to enhance the light energy utility rate and facilitate the charge carrier separation. Recently, Z-scheme heterojunctions have been widely studied in the field of photocatalysis due to their unique electron–hole transfer pathway. The transition of electrons and holes to CB and VB energy levels in opposite directions makes the electron-rich CB of one semiconductor and the hole-rich VB of the other. The existence of Z-scheme heterojunction can promote the separation of electrons and holes in space, which ensures that specific photocatalytic reactions can take place at their corresponding active sites. These advantages make the construction of Z-scheme heterojunctions one of the effective strategies to improve the catalytic activity.

SnS has the typical features of low cost, wide spectrum absorption and non-toxic nature. Due to its narrow band gap (1.3–1.6 eV), the absorption boundary of SnS is close to 1000 nm, covering the whole visible region, which can effectively increase the utilization of light. However, the rapid recombination rate of the photogenerated electrons and holes in SnS will lead to poor photocatalytic efficiency, which limits its practical application. g-C₃N₄ has been widely studied in the field of photocatalysis because of its environmental friendliness and high chemical stability. Due to the matching band structure, the combination of g-C₃N₄ and SnS may form the Z-scheme structure, which can improve the reactivity.

In this paper, SnS with narrow band gap was compounded with g-C₃N₄ using a simple in situ synthesis method, which effectively improved the light absorption ability of the catalyst. In addition, the formation of Z-scheme heterojunction was verified by activity test and band structure measurement, which effectively improved the efficiency of photo generated carrier...
separation. The optimal conversion of 0.5-SnS/g-C_3N_4 is much higher than that of pure g-C_3N_4, and the selectivity is >99.9% after 6 h. The design of the catalyst will provide a new idea for the design and construction of efficient photocatalytic oxidation system.

2. Experimental section

2.1 Preparation of photocatalysts
Preparation of g-C_3N_4: 1 g of dicyandiamide and 5 g of ammonium chloride were mixed and ground evenly, put into a porcelain crucible, heated to 550 °C in a muffle furnace at a heating rate of 3 °C min⁻¹ and calcined for 4 h.

Preparation of SnS/g-C_3N_4. Add 0.2 mmol SnCl_2·H_2O to 3.2 M/L HNO_3, stir to dissolve (solution A), and then add different amounts of g-C_3N_4 to mix evenly. Dissolve 0.2 mmol Na_2S·9H_2O in 20 mL H_2O (solution B), slowly drop solution B into solution A under stirring, and heat the final mixed suspension at 50 °C for 3 h. Centrifuge the suspension to separate the solid catalyst and wash it with water and ethanol for three times, then dry at 60 °C for 2 h. During the experiment, 0.3, 0.4, 0.5 and 0.6 g of g-C_3N_4 were added, respectively, so the different catalysts were named 0.3, 0.4, 0.5 and 0.6-SnS/g-C_3N_4.

Preparation of SnS. Pure SnS was obtained without adding g-C_3N_4 in the above preparation process.

2.2 Characterization
The composition of the catalyst was obtained using an X-ray diffractometer (XRD, Germany Brook AXS Co., Ltd); the light absorption properties of the catalyst were determined using a UV-3600 plus ultraviolet visible near infrared spectrophotometer (DRS UV-Vis, Japan Shimadzu company); the electronic lifetime of the catalyst was obtained using a LifeSpec II Ultra Fast Time Resolved Fluorescence Lifetime Spectrometer (Edinburgh Instruments, UK). The reaction activity in the experiment was detected using a GC9720 gas chromatograph (Zhejiang Fulic Analytical Instrument Co., Ltd); the element composition and valence of the catalyst were determined using a Thermo ESCALAB 250XI X-ray photoelectron spectrometer (XPS, PerkinElmer Company, USA); JEM-2100plus transmission electron microscope (TEM, Japan Electronics Co., Ltd) was used to observe the morphology of the catalyst; Brooke A300 electron paramagnetic resonance (EPR, Germany Brooke Technology Co., Ltd) was used to test the free radicals produced in the reaction process, and then the reaction mechanism was studied.

Photoelectrochemical (PEC) measurements were performed on a CHI660E electrochemical workstation produced by Chenhua Instrument in Shanghai, China. It was performed using a conventional three-electrode configuration with Pt foil (1 × 1 cm) as the counter electrode and Ag/AgCl as the reference electrode. For the working electrode, few photocatalyst is dispersed in a mixed solution of Nafion perfluorinated resin and ethanol, then 30 µL is taken on the FTO electrode and dried at room temperature. On the basis of the three-electrode system, choose IMPE-impedance-potential technology in technique to obtain the curve, and the Mott–Schottky curve can be obtained by converting the curve.

2.3 Photocatalytic activity
60 mg of the catalyst was dispersed in 10 mL acetonitrile solution containing 0.2 mmol BA, oxygen was passed for 30 minutes, and then the reaction was carried out under a 300 W xenon lamp (AM 1.5G filter). After the reaction, the supernatant was collected by centrifugation and analyzed using GC-9720. For stability test, 60 mg of photocatalyst was used to complete the reaction, and the solid was recovered by centrifugation, washed and dried with water and ethanol for further reaction. In order to further understand the photocatalytic mechanism of SnS/g-C_3N_4, different sacrificial agents were used for trapping experiments, such as AgNO_3 as electron scavenger, benzoquinone (BQ) as O_2 scavenger, triethanolamine (TEA) as hole scavenger and isopropanol (IPA) as OH scavenger. The selectivity and conversion of BA to BAD were calculated according to the following formula:

\[
\text{BA conversion} (\%) = \frac{(C_0 - C_1)}{C_0} \times 100
\]

\[
\text{BAD yield} (\%) = \frac{C_2}{C_0} \times 100
\]

\[
\text{BAD selectivity} (\%) = \frac{C_2}{(C_0 - C_1)} \times 100
\]

where, \(C_0\) is the benzyl alcohol concentration at the beginning, \(C_1\) is the BA concentration after the reaction for 6 h, and \(C_2\) is the benzaldehyde concentration obtained after the reaction.

3. Results and discussion

3.1 Preparation and characterization of SnS/g-C_3N_4
Fig. S1 (ESI†) shows the XRD patterns of pure g-C_3N_4, SnS and x-SnS/g-C_3N_4 (x = 0.3, 0.4, 0.5, 0.6) composite catalysts. For pure g-C_3N_4, the obvious diffraction peak at 27.5° is expressed as the (002) crystal plane of g-C_3N_4, which can be attributed to the special stacking reflection between planes in the conjugated aromatic system, while the stacking of the interlayer structure points to the diffraction peak at 13.1° and is denoted as the (100) crystal plane of g-C_3N_4. In the XRD pattern of SnS, the obvious diffraction peaks at 32.2° and 39.6° correspond to the (111) and (131) crystal planes of SnS, respectively, which is consistent with the peak described in the JCPDS card (39-0354). In different proportions of x-SnS/g-C_3N_4 (x = 0.3, 0.4, 0.5, 0.6), the diffraction peaks at 32.2° and 39.6° of SnS decrease with the increase in g-C_3N_4, which proves the successful preparation of g-C_3N_4 and SnS.

In order to further prove the preparation of SnS/g-C_3N_4, the chemical states of C, N, Sn and S were analyzed by XPS. In Fig. 1a, the C 1s spectrum can be divided into three characteristic peaks. The two peaks at 288.3 eV and 285.9 eV are mainly corresponding to the sp²-hybrid carbon atoms in graphite phase and the amorphous carbon in g-C_3N_4, while the peak at 284.6 eV corresponds to the carbon in sp³-bonded C of N=C—NH₂. As shown in Fig. 1b, the N 1s spectrum can be divided into two
peaks at 398.7 and 400.3 eV, which correspond to the sp²-hybrid nitrogen atom (C–N) and the nitrogen atom bridged with C in g-C₃N₄ (N–(C)₃), respectively. In the S 2p diagram (Fig. 1c), two characteristic peaks at 162.8 and 161.5 eV can be observed, corresponding to S²⁺ in SnS. The characteristic peaks of Sn 3d at 494.9 and 486.5 eV point to the Sn 3d 3/2 and Sn 3d 5/2 states of Sn²⁺ in SnS. The results of XRD and XPS indicate the existence of g-C₃N₄ and SnS, and the successful preparation of SnS/g-C₃N₄.

Transmission electron microscopy (TEM) was used to study the morphology of the catalyst. In Fig. 2a, the pure g-C₃N₄ is observed to have a thin sheet structure. After compounding with SnS (Fig. 2b), the nanoparticles are uniformly dispersed on the g-C₃N₄ sheet. Fig. 2c shows the HRTEM of 0.5-SnS/g-C₃N₄; the lattice spacing of 0.284 nm corresponds to the (111) crystal plane of SnS. Fig. 2d–i show the EDX mapping diagram of 0.5-SnS/g-C₃N₄, which can be further used to analyze the composition of the composite catalyst. It can be seen from the figure that C and N elements are uniformly and densely distributed in the g-C₃N₄ nanosheet, indicating the successful preparation of g-C₃N₄, while Sn and S are uniformly present in the small nanoparticles, indicating that the SnS nanoparticles exist in the g-C₃N₄ nanosheet.

### 3.2 Energy level structure analysis of SnS/g-C₃N₄

Optical properties are the key factors affecting the performance of photocatalysts. Fig. 3 shows the UV-vis diffuse reflectance spectra of different catalysts. It can be seen that SnS has an excellent absorption performance and wide spectral response, which are consistent with the reported results. Compared with SnS, the absorption boundary of g-C₃N₄ is about 454 nm, and the utilization of visible light is low. Therefore, the light absorption ability of the composite catalyst can be greatly improved by combining SnS with g-C₃N₄. As shown in Fig. 3, the light absorption performance of the SnS/g-C₃N₄ composite catalyst is gradually improved with the decrease in the amount of g-C₃N₄ added.

According to the UV-vis diffuse reflectance spectrum, the Tauc plots can be obtained to understand the band gap of SnS and g-C₃N₄. As shown in Figures S2a and S2b, the band gap of g-C₃N₄ is about 2.77 eV, and that of SnS is 1.60 eV. The narrow band gap of SnS is the main reason for its excellent light absorption ability. In order to further understand the band structure of the composite catalyst, Mott Schottky curves were measured (Fig. S2c and d, ESI†). The flat band potentials of g-C₃N₄ and SnS were −1.15 eV and 0.07 eV, respectively. In general, the conduction band (CB) position of the n-type semiconductor is about 0.1–0.3 eV lower than its flat band potential. In the literature, the CB position of SnS is about −0.1 eV, so the CB position of SnS is about −0.03 eV, and the CB position of g-C₃N₄ is about −1.25 eV. According to the formula $E_{VB} = E_g + E_{CB}$ ($E_{VB}$ is the catalyst valence band, $E_g$ is the catalyst band gap, and $E_{CB}$ is the CB of catalyst), the valence band (VB) of SnS is about 1.57 eV, and the VB of g-C₃N₄ is 1.52 eV.

Fig. 1 XPS of (a) C 1s, (b) N 1s, (c) S 2p, and (d) Sn 3d of 0.5-SnS/g-C₃N₄.

Fig. 2 TEM images of (a) g-C₃N₄ and (b) 0.5-SnS/g-C₃N₄. (c) HRTEM image of 0.5-SnS/g-C₃N₄; the lattice spacing of 0.284 nm corresponds to the (111) crystal plane of SnS. Fig. 2d–i show the EDX mapping diagram of 0.5-SnS/g-C₃N₄, which can be further used to analyze the

Fig. 3 UV-vis diffuse reflectance spectroscopy (DRS) of g-C₃N₄, SnS and x-SnS/g-C₃N₄ (x = 0.3, 0.4, 0.5, 0.6).
3.3 Photocatalytic oxidation of BA to BAD on SnS/g-C₃N₄

Fig. 4a shows the experimental results of the oxidation of BA to BAD on different photocatalysts. It can be seen from the figure that on pure g-C₃N₄, the conversion of BA is 23.6% and the selectivity is >99.9% after illumination for 6 h, while the conversion of BA on pure SnS is 0 during the reaction, indicating that SnS does not have the ability to oxidize BA. When the amount of g-C₃N₄ increased from 0.3 to 0.5, the conversion increased from 48.6% to 72.5% gradually, while the selectivity remained >99.9%. However, when the amount of g-C₃N₄ further increased from 0.5 to 0.6, the conversion decreased to 63.8%, which may be due to the excessive amount of g-C₃N₄ affecting the transport of electrons and holes. Next, the stability of 0.5-SnS/g-C₃N₄ composite photocatalyst with the best performance was tested (Fig. 4b). After four cycles of reaction, the conversion and selectivity of the photocatalyst did not decrease significantly, indicating that the composite catalyst has good stability.

In order to verify the universality of 0.5-SnS/g-C₃N₄, the optimal composite photocatalyst 0.5-SnS/g-C₃N₄ was used for the oxidation of BA with different substituents (Table 1). It was found that the selectivity of all reactions was >99.9%. But for different electron-donating groups (–CH₃, –OCH₃) and electron-withdrawing groups (–Cl, –Br), the change of conversion is different. The electron-donating group can effectively increase the electron cloud density on the benzene ring and promote the reaction, so the conversion is improved. Similarly, the conversion of BA with an electron-withdrawing group on 0.5-SnS/g-C₃N₄ was decreased, but it was still about 67%. As for the effect of different substitution positions on the oxidation of BA (o-, m-), the –CH₃ substituent was taken as an example. The steric hindrance of o- and m- had a certain effect on the reaction, which made the conversion decrease slightly, but the overall conversion remained above 60%. The above results show that the composite catalyst 0.5-SnS/g-C₃N₄ has excellent general oxidation performance.

3.4 Photocatalytic mechanism on SnS/g-C₃N₄

In order to understand the active species in the reaction process, different free radical capture experiments were carried out (Fig. 5a). Firstly, most of O₂ in the reaction was removed by N₂, and the conversion of BA was only 9%, which indicated that O₂ was an important factor affecting the reaction results. AgNO₃ was used to capture the electrons generated in the reaction process. After adding AgNO₃, the conversion rate is reduced to about 8%, indicating that the photogenerated electrons play a key role in the reaction process. In general, electrons will reduce O₂ to superoxide radical (O₂⁻) in the reaction process. In order to verify the role of O₂⁻ in the reaction, benzoquinone (BQ) was added. The addition of BQ reduced the conversion rate to 15%, indicating that O₂⁻ is one of the key active species. Triethanolamine (TEA) and isopropanol (IPA) were used to eliminate h⁺ and *OH, respectively. The results showed that the effect of *OH was negligible compared with h⁺. The conversion of BA was almost reduced to 0% after the removal of h⁺; this proved that photogenerated h⁺ was another active species which played a key role in the photocatalytic process. The EPR spectrum further proves the above results. Fig. 5b shows that the amount of O₂⁻ produced by the 0.5-SnS/g-C₃N₄ composite photocatalyst under light is significantly larger than that of pure g-C₃N₄, and the amount of carbon centered radical generated by h⁺ oxidation on SnS/g-C₃N₄ is also larger than that of pure g-C₃N₄, which may be the reason why the reaction rate of the composite catalyst is much higher than that of pure g-C₃N₄.

According to the previous band structure of the composite catalyst, the CB and VB of g-C₃N₄ are −1.25 eV and 1.52 eV respectively, while the CB and VB of SnS are −0.03 eV and 1.57 eV respectively. Combined with the analysis of active species, the key factors in the reaction are O₂⁻ and h⁺, and the CB position of SnS makes it impossible for electrons to reduce O₂ to O₂⁻, which is also the reason why pure SnS cannot oxidize BA. Therefore, it is speculated that the Z-scheme heterojunction is formed between SnS and g-C₃N₄ while not type II heterojunction. In the band structure schematic diagram (Fig. 5d), the electrons on SnS are transferred to the VB of g-C₃N₄ and combine with h⁺, O₂ is reduced by the electrons generated on the CB of g-C₃N₄, and BA is oxidized by the h⁺ generated on the VB of SnS to form carbon.
centered radical, and finally $^{*}\text{O}_2^-$ combines with carbon centered radical to form BAD.

The existence of Z-scheme heterojunction can promote the separation of electrons and holes, which is also the reason for the acceleration of the reaction rate of the composite catalyst, as shown in Fig. 6. The steady-state fluorescence spectrum can be used to detect the carrier separation effect of a photocatalyst. In Fig. 6a, the peak value of pure g-C$_3$N$_4$ is the highest, while the peak value decreases with the addition of SnS. The peak value of the optimal catalyst 0.5-SnS/g-C$_3$N$_4$ is the lowest, indicating that the formation of heterojunction after SnS and g-C$_3$N$_4$ composite can hinder the recombination of photogenerated electrons and holes and improve the carrier separation efficiency. In the results of transient fluorescence (Fig. 6b), the carrier lifetimes of g-C$_3$N$_4$, SnS and 0.5-SnS/g-C$_3$N$_4$ are 0.399 ns, 0.022 ns and 0.447 ns, respectively. The carrier lifetimes of the

<table>
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<th>Entry</th>
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<th>Selectivity (%)</th>
<th>Conversion (%)</th>
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Reaction conditions: 60 mg of catalyst and 0.2 mmol reactant in 10 mL acetonitrile, then react for 6 h under illumination (300 W xenon with AM 1.5G filter).
composite photocatalyst are the longest, which is consistent with the steady-state fluorescence results. Photoelectrochemical characterization is also an effective method to test the efficiency of electron–hole pair separation. It can be seen from Fig. 6c that the photocurrent response value of 0.5-SnS/g-C3N4 is the highest when the light is turned on, and the radius value of 0.5-SnS/g-C3N4 in EIS Nyquist plot is the smallest, which indicates that the Z-scheme heterojunction can greatly improve the carrier separation rate, promote the reaction and then improve the conversion of BA.

Based on the above analysis, the oxidation mechanism of 0.5-SnS/g-C3N4 for BA is proposed in Fig. 7. The Z-scheme heterojunction is formed between SnS and g-C3N4, which can effectively improve the efficiency of electron–hole pair separation. Due to the special carrier transport path of the Z-scheme structure, the electrons on SnS will transfer to the VB of g-C3N4 and combine with the holes, so that the photogenerated electrons are in the CB of g-C3N4 and the photogenerated holes are in the VB of SnS. During the reaction, O2 will be reduced to *O2− in the CB of g-C3N4, BA will be oxidized to carbon centered radical in the VB of SnS, and finally *O2− will combine with carbon centered radical to form BAD.

4. Conclusions

The SnS/g-C3N4 composite photocatalyst with a Z-scheme heterojunction was prepared using a simple in situ synthesis method. The formed SnS nanoparticles are uniformly dispersed on the g-C3N4 layer, which is helpful for carrier separation. In addition, the narrow band gap of SnS (1.6 eV) greatly improves the light absorption capacity of the composite photocatalyst and the utilization of light. The existence of Z-scheme heterojunction makes the electrons in the CB of SnS transfer to the VB of g-C3N4 and compound with h+, so that the photogenerated electrons are in a relatively high position and the photogenerated holes are in a relatively low position to participate in the redox reaction, which is conducive to accelerating the carrier separation and promoting the reaction. The results of this study can provide some guidance for the development of efficient organic oxidation photocatalysts.

Author contributions


Conflicts of interest

There are no conflicts to declare.

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Notes and references