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Influence of sulfur source on properties of CuSbS2 particles

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Abstract

CuSbS2 is a direct p-type semiconductor with a two-dimensional layered structure of orthorhombic system, excellent electrical performance, and a band gap of 1.1–1.5 eV, which has a light absorption coefficient of more than 10⁴ cm⁻¹ in the visible light range. CuSbS2 particles were synthesized by microwave irradiation method, and the effects of different sulfur sources on the phase structure, morphology and electrochemical performance of CuSbS2 particles were studied. The results showed that the sample prepared by thiourea as sulfur source was CuSbS2 phase, and the morphology was composed of flower-like microspheres and rod-like particles. However, nanorod-like CuSbS2 particles were obtained using L-cysteine or 3-thiopropionic acid as sulfur sources, and the phase of samples contained CuSbS2 and Sb2S3 phase. Electrochemical tests showed that L-cysteine based CuSbS2 particles had the largest photocatalytic response, a photocurrent density of 1.03 μA cm⁻² and impedance of 14.66 Ω.

1. Introduction

Our society is facing two important problems of energy shortage and environmental pollution. However, photocatalysis technology, as a main mean to solve these two problems, can realize not only the degradation of organic pollutants, but also the photocatalytic decomposition of water to produce hydrogen. Highly efficient photocatalyst plays a very important role in photocatalysis technology. From the perspective of maximizing use of solar energy, it is very necessary to develop the visible-light photocatalyst. Sulfide semiconductors are widely concerned by researchers, due to their narrow band gap and appropriate valence band position. Copper sulfide antimony (CuSbS2) is a kind of I-V–IV semiconductor materials, with a two-dimensional layered structure, the ideal band gap of 1.1–1.5 eV, and the light absorption coefficient larger than 10⁻⁴ cm⁻¹ [1, 2]. Therefore, CuSbS2 is a very potential visible light photocatalyst.

There are lots of technologies to prepare CuSbS2 particles, such as hydrothermal method [3], solvothermal method [4], mechanochemically method [5] and so on. Among them, microwave irradiation method with low-cost, rapid reaction and safety is an ideal method. Furthermore, the morphology and phase composition of nanomaterials have a great influence on their photocatalytic performance. There are some reports on the controllable morphology and phase structure of CuSbS2 nanoparticles by adjusting reaction temperature, reaction time and the ratio of metal to sulfur in the precursor solution [6–8]. John B et al [9] prepared CuSbS2 nanoparticles by solvothermal method, and explored the effect of reaction temperature on the phase structure of CuSbS2 nanoparticles. Shima M et al [10] reported tuning sulfur to metallic precursor ratio might be an efficient approach to control shape and size of CuSbS2 nanoparticles by hot injection method. Swathi S et al [11] prepared CuSbS2 nanorods by hydrothermal method, and electrochemical performance were changed by addition of PVP. Chandini B et al [12] obtained pure CuSbS2 nanoplates and CuSbS2 nanoplates decorated with Cu3SbS4 nanoparticles synthesized using hot-injection method by changing the sulfur precursor.

As far as we know, there is little report on regulating the morphology and phase structure of CuSbS2 particles by changing sulfur sources in the precursor solution using microwave irradiation method. Therefore, CuSbS2

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particles were prepared by microwave irradiation method. Thiourea, 3-thiopropionic acid and L-cysteine were used as sulfur sources, respectively. The influence of various sulfur sources on the phase structure and properties of particles were explored.

2. Experimental

2.1. Starting materials
Analytical ethylene glycol (C₂H₆O₂) was purchased from Sinopharm Chemical Reagent Co. Ltd., China. Copper nitrate trihydrate (Cu(NO₃)₂·3H₂O, ≥99.0%), antimony chloride (SbCl₃, ≥90%), thiourea (CH₄N₂S, ≥99%), L-cysteine (HSCH₂CH(NH₂)CO₂H, 3-mercaptopropionic acid (C₃H₆O₂S, ≥98%), ≥98%) were purchased from Aladdin.

2.2. Preparation of CuSbS₂ particles
In a typical experiment, 1 mmol of Cu(NO₃)₂·3H₂O, 2 mmol of SbCl₃, and 9 mmol of sulfur sources (thiourea, 3-mercaptopropionic acid, L-cysteine) were dissolved in 50 ml of ethylene glycol under magnetic stirring. After it was completely dissolved, the precursor solution was transferred to a reactor and then placed in a microwave oven. The microwave irradiation power was maintained at 400W for 4 min, and then adjusted to 240W for 6 min. After the reaction, the solution was cooled down to room temperature in air. The precipitates were separated from the solution by centrifugation at 10000 rpm for 8 min and washed with de-ionized water and ethanol several times. Then the precipitates were washed by 0.2 mol/L Na₂S solution to remove Sb₂S₃ impurity and dried under vacuum at 70 °C for 6 h.

2.3. Characterizations
X-ray diffractometer (XRD, Bruker D8 advance diffractometer with Cu-Kα) was used to analyze the phase structure and crystallinity of the prepared particles. The micro-morphology of the samples was observed by transmission electron microscope (TEM, G2 F20 FEI Tecnai). The optical properties of the samples were analyzed by ultraviolet visible spectrophotometer (UV–vis, UV-3600 Shimadzu company, Japan).

2.4. Electrochemical characterizations
To prepare the CuSbS₂ electrode, 20 mg CuSbS₂ was dispersed equably in 1 ml ethyl alcohol and 20 μl Nafion solution by ultrasound, and then dried in air at room temperature. The electrochemical tests of the electrode were studied by an electrochemical station (CHD760e, Shanghai) with a standard three-electrode system. It consisted of the as-obtained electrode as the working electrode, the Pt (1 × 1 cm) sheet as the counter electrode and a standard saturated Ag/AgCl electrode as standard saturated. The Mott-Schottky analysis and electrochemical impedance spectroscopy (EIS) (0.5 Hz to 1000 kHz and a perturbation amplitude of 5 mV) were performed in the three-electrode system with 1 M KOH solution (pH = 14). The HER activity was evaluated using linear sweep voltammetry (LSV) tests with a sweep rate of 1 mV s⁻¹ under visible light (50 mW cm⁻²).

Figure 1. XRD patterns of CuSbS₂ particles prepared using different sulfur sources.
irradiation by xenon lamp optical system (CEL-S500, Beijing China Education AuLight Technology). The photocurrent-time curve was tested under with chopped illumination from visible light (50 mW cm\(^{-2}\)). All the measured potentials versus the SCE were converted to RHE by the Nernst equation \(E_{\text{RHE}} = E_{\text{SCE}} + 0.0591pH + 0.197\).

3. Results and discussion

Figure 1 shows the XRD patterns of CuSbS\(_2\) particles prepared using different sulfur sources. As shown in the figure, the XRD diffraction peaks of the samples at \(2\theta = 28.73^\circ, 29.94^\circ, 39.02^\circ, 40.31^\circ, 42.61^\circ, 47.87^\circ, 49.79^\circ, 52.37^\circ\) are attributed to the (410), (301), (501), (201), (321), (002), (521), (212) planes of CuSb\(_2\) (JCPDS 44–1417) [13]. When the sulfur source is L-cysteine, the sample contains CuSb\(_2\) phase and Sb\(_2\)S\(_3\) secondary phase. This may be due to many functional groups in L-cysteine, such as -COOH, -SH and -NH\(_2\), which have strong coordination with metals cations [14]. The C-S bond of L-cysteine is broken and gradually released S\(^{2-}\) during the reaction. Under the condition of rich Sb, S\(^{2-}\) combines with Sb\(^{3+}\) to form Sb\(_2\)S\(_3\). When the sulfur source is 3-mercaptopropionic acid, the sample is still CuSb\(_2\) phase and Sb\(_2\)S\(_3\) secondary phase. The S-H group and carboxyl group in 3-mercaptopropionic acid also have a strong coordination with Sb\(^{3+}\), so metal ions coordinate with 3-mercaptopropionic acid by bidentate coordination, and then complexes are thermally decomposed into Sb\(_2\)S\(_3\) [15]. There is no obvious Sb\(_2\)S\(_3\) phase in the samples prepared with thiourea as the sulfur source, because thiourea tends to form complexes with Cu\(^{2+}\) during the reaction. In the precursor solution, Cu\(^{2+}\) is reduced to Cu\(^{+}\) with ethylene glycol. Cu\(^{+}\) is soft Lewis acid, and Sb\(^{3+}\) is intermediate Lewis acid. According to hard soft acids base, the S precursor is more reactive to Cu\(^{+}\) than Sb\(^{3+}\). More Cu-Tu complexes are involved in the reaction to form copper sulfide as nucleation seeds. Compared with Cu-Tu complex, less Sb-Tu complex is reacted to form antimony sulfide [16]. XRD patterns show that the Sb_S\(_2\) secondary phase diffraction peak of 3-mercaptopropionic acid as sulfur source is stronger than that of L-cysteine, indicating that its Sb\(_2\)S\(_3\) crystallinity is better, which may be related to the preferred orientation of sample particles prepared using different sulfur sources.

XPS is used to study the valence state of elements present in as-prepared particles using different sulfur sources (figure 2). The survey scan spectra of the all samples are displayed in figure 2(a) and these visible peaks can be ascribed into Cu, Sb, S and C element of samples. Among them, C might be generated by contamination.
and residual solvent reaction. As for Cu element in samples, figure 2(b) shows two distinct peaks at about 951.6 eV and 931.7 eV with a separation of 19.8 eV, in accordance with Cu$^{2+}$ and Cu$^{2+}$, respectively. The positions of the two peaks and their separation are in consistent with Cu$^{2+}$ [17]. Figure 2(c) presents three pairs of Sb 3d peaks with a separation of 9.4 eV, which are attributed to Sb$^{3+}$. Furthermore, the lower binding energy at 538.3 eV and 528.9 eV can be attributed to CuSbS$_2$ [18], the high binding energy red peaks may be caused by surface dangling bond from Na$_2$S chemical etching. The core level spectra of S (in figure 2(d)) show the typical peaks with separation of 9.4 eV of S$^{2-}$ [18]. Similarly, the high binding energy green peaks may be caused by Na-S$. Thus, different sulfur sources will affect the surface chemical bond of the sample, thus changing the morphology of the sample. That may be caused by the difference of complexation with metal ions. Hence, XPS analysis further confirms the valence states of the components are identified as Cu$^{+}$Sb$^{3+}$(S$^{2-}$)$_2$.

Figure 3 presents TEM and HRTEM images of as-prepared particles with different sulfur precursors. The sample prepared with thiourea as sulfur source is composed of nanorod and spherical structure, in which the diameter and length of nanorod structure is 0.6 μm and 2.1 μm, respectively. In the high-resolution image (figure 3(b)), it can be calculated that the crystal plane spacing is 0.190 nm, corresponding to the (002) crystal plane of CuSbS$_2$ [19]. The sample prepared with L-cysteine as sulfur source is rod-like and sheet-like particles. The diameter of rod-like particle is about 300 nm. It can be calculated that the crystal plane spacing is 0.131 nm, which corresponds to the (410) crystal plane of CuSbS$_2$ [20]. Figure 3(e) shows the TEM image of CuSbS$_2$ particles prepared with 3-mercaptopropionic acid as the sulfur source. It can be seen that the size of rod structure is smaller than that of the rod structure with thiourea as the sulfur source. Moreover, its diameter is about 0.4 μm, and length is about 0.65 μm. It can be calculated that the crystal plane spacing is 0.374 nm, which corresponds to the (310) crystal plane of CuSbS$_2$ (as shown in figure 3(f)). The difference of complexation with metal ions causes the variety chemical configuration, further effect the difference morphology.
The optical properties and band gap of photocatalysts prepared using three kinds of sulfur sources were studied by UV–vis spectroscopy. The difference phase and morphology of samples cause the difference absorbance, and the deficiency of Sb$_2$S$_3$ phase might cause the low absorbance at less than 600 nm. As shown in figure 4, the absorption edges of the samples are at 1400–1500 nm, which have good absorption in the range of visible light. The band gap of CuSbS$_2$ as a direct band gap semiconductor can be calculated as the following formula:

\[
(ahv)^2 = A(hv - E_g)
\]

Where, $E_g$ is the band gap, $h$ is the photon energy, $A$ is a constant \cite{21}. The band gaps of samples are 1.42 eV (for thiourea), 1.40 eV (for L-cysteine) and 1.39 eV (3-mercaptopropionic).

Figure 5(a) demonstrates linear sweep voltammetry of particles with different sulfur precursors. When the current density reaches 10 mA cm$^{-2}$, the potentials of as-prepared samples for thiourea, 3-mercaptopropionic...
acid and L-cysteine as different sulfur sources are 1543 mV, 1609 mV and 1521 mV, respectively. It shows that the initial potential of the sample using L-cysteine as sulfur source is lower. The difference in initial potential is due to the different surface morphology, resulting in different crystal plane exposed on the surfaces and different active sites. In order to further obtain more kinetic information, the Tafel curves of CuSbS2 electrodes prepared using different sulfur sources were analyzed, as shown in figure 5(b). It can be found that the Tafel slopes of samples using thiourea, 3-mercaptopropionic acid and L-cysteine as sulfur sources are 384 mV/dec, 362 mV/dec and 347 mV/dec, respectively. In conclusion, the higher catalytic activity of the sample using L-cysteine as sulfur source means the stronger hydrogen evolution ability.

The recombination rate of photoinduced carriers could be explained by photoluminescence (PL), and the low intensity of the peak implies a lower recombination rate (figure 6(a)) [17]. Thus, the sample with thiourea as sulfur source has stronger carrier migration ability, and the samples prepared using different sulfur sources have different energy level defect, which may be caused by different band gap and defect type. Figure 6(b) indicates the ESI of particles prepared using different sulfur sources. The semicircle in the figure represents charge transfer resistance at interface between the electrode and electrolyte, and belongs to the high-frequency region. The size of the arc radius can reflect the electron transfer efficiency within the electrode. The smaller arc radius indicates smaller charge transfer resistance between the electrode and the electrolyte interface, and the higher the electron transfer efficiency. It can be seen that the sample prepared with L-cysteine as the sulfur source has the lowest impedance, and its impedance is only 14.66 Ω calculated by the analog circuit, indicating that the sample has good conductivity. The difference of electron transfer efficiency of samples comes from phase, morphology and defect. The sample prepared by 3-mercaptopropionic acid has a larger impedance, and the impedance value reaches 65.4 Ω, which may be due to Sb2S3 secondary phase. The conductivity of Sb2S3 is worse than that of CuSbS2. From the TEM images, it can be seen that the particles synthesized with L-cysteine as the sulfur source have relatively uniform morphology, while the nanorod CuSbS2 particles prepared with thiourea as the sulfur source have different sizes and poor uniformity, indicating that the sample has large surface defect concentration and carrier recombination. And the Cu ratio of L-cysteine is clearly lower than others (figure 2(b)), which explains the high concentration VCu of samples. It can improve the electrical conductivity of CuSbS2 [22].

Compared with thiourea as sulfur source, the particles prepared with L-cysteine as sulfur source have lower surface defects and weaker carrier scattering. Therefore, CuSbS2 particles with L-cysteine as sulfur source have the best conductivity.

As shown in figure 7, Mott Schottky (M-S) test was carried out on different electrode samples. The M-S plots show the capacitance of interface between photocathode electrode and electrolyte. The slope of Mott Schottky plots is negative, which further confirms that the prepared samples are p-type conduction. The flat band potentials of CuSbS2 photoelectrodes prepared with L-cysteine, 3-mercaptopropionic acid and thiourea as sulfur sources are 0.47 eV, 0.27 eV and 0.22 eV respectively, and the corresponding valence band maximum of 0.57 eV, 0.37 eV and 0.32 eV. According to the band gap, the corresponding conduction band minimum can be calculated as −0.83 eV, −1.03 eV and −1.07 eV, respectively. The conduction band minimum of the sample prepared with 3-mercaptopropionic acid as the sulfur source is more negative than the others. It can be deduced from the formula that the current density is directly proportional to the slope of the M-S plot (equation (2)) [23]. Thus, the larger slope presents the larger carrier concentration. The slope of M-S plot of the sample with L-cysteine as the sulfur
source is the largest, so the carrier concentration is the largest, which increases the photogenerated holes concentration on the surface of photoelectrode, thereby improving photoelectrochemical properties.

\[
\frac{1}{C^2} = -\frac{2}{eA^2\varepsilon_0\varepsilon}\left(E - E_{fb} - \frac{kT}{\varepsilon}\right)
\]  

(2)

Where \(C\) is the capacitance, \(e\) is the electric charge, \(\varepsilon_0\) is the vacuum permittivity, \(\varepsilon\) is the dielectric constant of \(\text{CuSbS}_2\), \(N_d\) is the carrier density, and \(A\) is the effective area.

Figure 8 shows photocurrent-time curves of \(\text{CuSbS}_2\) particles prepared using different sulfur sources. It was found that when L-cysteine was used as sulfur source, the photocurrent response was the largest, and the
photocurrent density was 1.03 $\mu$A cm$^{-2}$, with good stability. However, the photocurrent density of particles using thiourea as sulfur source is 0.21 $\mu$A cm$^{-2}$. There are two reasons for the result. Firstly, the particles prepared with L-cysteine as sulfur source have relatively uniform morphology, but the morphology of particles with thiourea as sulfur source is not uniform. Due to the differences in the exposed active sites caused by different morphologies, the exposed active sites may better adsorb H$^+$, -OH and other groups in the solution, and may catalyze to decrease the activation energy of reduced hydrogen, which is more conducive to hydrogen evolution. Secondly, due to the difference of energy level position, the energy level position of the sample prepared by L-cysteine is relatively negative from the hydrogen level, and the electron reduction ability is relatively strong, which is easier to hydrogen evolution. However, the energy level position of particles prepared with 3-mercaptopropionic acid as sulfur source is relatively more negative (less than $O_2/O_2^\cdot -0.33$ eV) [24], which may be more inclined to form H$_2$O$_2$, and the electrode has a large impedance, resulting in no obvious photocurrent response.

4. Conclusion

In this paper, CuSbS$_2$ particles were successfully prepared by microwave irradiation method, and the effects of sulfur sources on the phase structure, micro-morphology and photocatalytic properties of CuSbS$_2$ particles were discussed. The sample prepared with thiourea as sulfur source is composed of nanorod structure and spherical particles, and the particles prepared with L-cysteine and 3-mercaptopropionic acid as sulfur source are rod-like. The particles prepared with L-cysteine as sulfur source have good electrochemical performance ($362$ mV/dec, $1.03$ $\mu$A cm$^{-2}$ photocurrent density), stable photocurrent response and low impedance (impedance of $14.66\Omega$).

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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References

[1] Khairy M, Jiang P P, Boulet P and Record M C 2022 Electron density and optoelectronic properties of copper antimony sulphur ternary compounds for photovoltaic applications J. Electron. Mater. 51 3903–18
[2] Kumara B H, Shajib S and Kumar M C S 2020 Effect of substrate temperature on properties of co-evaporated copper antimony sulfide thin films Thin Solid Films 697 137838
[3] Sathvik S et al 2022 Polyvinylpyrrolidone-assisted novel copper antimony sulphide nanorods for highly efficient hydrogen evolution reaction Fuel 314 123096
[4] John B et al 2019 Surfactant-mediated solvothermal synthesis of CuSbS$_2$ nanoparticles as p-type absorber material Indian J. Phys. 93 185–95
[5] Esperto L et al 2022 Structural and optical characterization of mechanochemically synthesized CuSbS$_2$ compounds Materials 15 3842
[6] Sugarthi S, Manikanand V S, Harish S, Bakiyaraj G and Navaneethan M 2022 Study on electrochemical performance of temperature-dependent Cu–Sb–S system J. Mater. Sci., Mater. Electron. 33 9650–9
[7] Sarilmat A, Genc E, Aslan E, Onen A, Yanalak G, Onel F and Patir I H 2020 Photocatalytic hydrogen evolution via solar-driven water splitting by CuSbS$_2$ with different shapes Journal of Photochemistry & Photobiology, A: Chemistry 400 112706
[8] Wang W, Zhi G W, Liu J J H, Hao L Y, Yang L, Zhao Y J and Hu Y F 2020 Effect of PVP content on photocatalytic properties of CuSbS$_2$ particles with chemical etching J. Nanopart. Res. 22 294
[9] John B, Silvena G G and Rajesh A L 2018 Influence of reaction time on the structural, optical and electrical performance of copper antimony sulphide nanoparticles using solvothermal method Physica B: Condensed Matter 537 243–50
[10] Moosakhani S, Alvari A A S, Mohammadpour R, Ge Y L and Hannula S P 2018 Solution synthesis of CuSbS$_2$ nanocrystals: a new approach to control shape and size J. Alloys Compd. 736 190–201
[11] Sathvik S, Yuvakkumar R, Kumar P S, Ravi G and Velauthapillai D 2022 Polyvinylpyrrolidone-assisted novel copper antimony sulphide nanorods for highly efficient hydrogen evolution reaction Fuel 314 123096
[12] Behera C, Samal R, Rout C S, Dhaka R S, Sahoo G and Samal S L 2019 Synthesis of CuSbS2 nanoplates and CuSbS2-Cu3SbS4 nanocomposite: effect of sulfur source on different phase formation Inorg. Chem. 58 15291–302
[13] Yang B, Wang L, Han J, Zhou Y, Song H B, Chen S Y, Zhong J, Lv L, Niu D M and Tang J 2014 CuSbS2 as a promising Earth-abundant photovoltaic absorber material: a combined theoretical and experimental study Chem. Mater. 26 3133–43
[14] Deshmukh S G and Kheraj V 2017 A comprehensive review on synthesis and characterizations of Cu3BiS3 thin films for solar photovoltaics Nanotechnology for Environmental Engineering 2 1–12
[15] Sharma V, Ilaiyaraja P, Dakshinamurthy A C and Sudakar C 2021 One step thermolysis of Sb-Mercaptopropionic acid complex in ambient air atmosphere for growing Sb2S3 thin films with controlled microstructure Mater. Sci. Semicond. Process. 121 105330
[16] Wang W, Hao L Y, Zhi G W, Lin Q and Tang Z X 2018 Investigation on preparation and formation mechanism of copper antimony sulphide particles by microwave irradiation Micro & Nano Letters 13 1036–9
[17] Zhi G et al 2022 ZnO/ZnO Heterojunction for Enhanced Photocatalytic Degradation of RhB ChemistrySelect 7 202202457
[18] Zhi G et al 2022 A method for improving performance of CuSbS2 anode materials by adjusting Cu/Sb ratio Ionics 28 2865–73
[19] Ramasamy K, Sims H, Butler W H and Gupta A 2014 Mono-, few-, and multiple layers of copper antimony sulfide (CuSbS2): a ternary layered sulfitde JACS 136 1587–98
[20] Zhi G, Wang W, Zhang M, Hao L Y, Yang L, Liu J H and Zhao Y J 2020 A novel CuSbS2-TiO2 nanoparticles synergy structure for photocatalysis J. Mater. Sci. Mater. Electron. 31 17036–43
[21] Syed A, Yadav L S R, Bahkali A H, Elgorban A M, Hakeem D A and Ganganagappa N 2020 Effect of CeO2–ZnO Nanocomposite for Photocatalytic and Antibacterial Activities Crystals 10 817
[22] Yang B et al 2014 CuSbS2 as a Promising Earth-Abundant Photovoltaic Absorber Material: A Combined Theoretical and Experimental Study Chem. Mater. 26 3133–43
[23] Jiang T F, Zhao Y, Liu M Y, Chen Y, Xia Z Q and Xue H G 2018 Enhancing the lifetime of photoinduced charge carriers in CuFeO2 nanoplates by hydrothermal doping of Mg for photoelectrochemical water reduction Physica Status Solidi (a) 215 1800056
[24] Kim D and Yong K 2021 Boron doping induced charge transfer switching of a G3N4/ZnO photocatalyst from Z-scheme to type II to enhance photocatalytic hydrogen production Appl. Catalysis B 282 119538