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The Solvent Synthesis, Growth Mechanism, Photocatalytic Properties of $AgInS_2$ Nanoplate and Nanoparticle

Yue Wang[1]*, Yongfang Shi[2]*, Dongwei Li[1], Tao Zhang[1], Xiaochuan Zou[1] and Yucen He[1]

[1]*School of Biological and Chemical Engineering, Chongqing University of Education, Nan'an District, Chongqing, China*
[2]*Fujian Institute of Research on the Structure of Matter, Key Laboratory of Research on Chemistry and Physics of Optoelectronic Materials, Chinese Academy of Sciences, Fuzhou, Fujian Province, China*

ABSTRACT

Orthorhombic $AgInS_2$ nanoplate and nanoparticle were synthesized using pyridine and 1-dodecanethiol as the solvent. The obtained products were characterized by X-ray diffraction (XRD), field-emission scanning electron microscope (FESEM), field-emission transmission electron microscope (FETEM), and the possible growth mechanism of $AgInS_2$ was also proposed by the exploration of reaction temperature and time. Meanwhile, the band gap of $AgInS_2$ were calculated by the UV-vis diffuse reflectance spectrum, and the photocatalytic activity was also investigated. Those experimental results indicate that the reaction temperature, reaction time and solvent have an influence on the phase and morphology of $AgInS_2$, and both $AgInS_2$ nanoplate and nanoparticle have some ability on photocatalytic degradation of organic dyes under visible light irradiation.

Keywords: Orthorhombic $AgInS_2$, Nanostructure, Solvent method, Growth mechanism, Photocatalysis

INTRODUCTION

With the development of society, people pay more and more attention to the pollution caused by industrial waste water [1]. The semiconductor photocatalytic method, especially using cheap sunlight as the light source, to realize visible photocatalytic degradation of pollutants is a new technology of low energy consumption and environmental protection. As an important I-II-VI group semiconductor material, ternary metal sulfide, $AgInS_2$, has gradually become a research hotspot, due to its unique photoelectric and catalytic performance, which has potential application prospect in the field of light-emitting diodes, nonlinear optical devices, solar cells, photocatalysis, biological labelling [2-7]. Currently, the preparation methods of $AgInS_2$ are hot pressing method [8], hot-wall epitaxial growth method [9], hydrothermal method [10], solvothermal method [11], hot injection method [12], and thermolysis method [13], etc. The previous works focus on the 0D $AgInS_2$ quantum dots, but few studies of 2D and 3D nanostructures [4]. In our previous work [13,14], the metastable orthorhombic $AgInS_2$ flower-like microsphere was successfully prepared by the pyrolysis of organometallic precursors at 250~280°C. However, considering the high temperature (above 200°C) needs the high energy consumption, and the products should be heated more uniformly in the solvent, as well as the solvent has important influence on the morphology of the product, so we try to disperse the precursor in different solvent to obtain $AgInS_2$ nanostructures with different morphology at lower temperature. The results indicate that $AgInS_2$ nanoplate and nanoparticle can be obtained at lower temperature (120~150°C) using pyridine and 1-dodecanethiol as the solvent. Meanwhile, the obtained products were characterized by X-ray diffraction (XRD), field-emission scanning electron microscope (FESEM), field-emission transmission electron microscope (FETEM), and the possible growth mechanism of $AgInS_2$ was also proposed by the exploration of reaction temperature and time. Finally, the bandgap of $AgInS_2$ were calculated by the UV-vis diffuse reflectance spectrum, and the photocatalytic activity was also investigated, as well as its possible photocatalytic mechanism.

MATERIALS AND METHODS

Experimental

Chemicals

Silver nitrate ($AgNO_3$), indium nitrate hydrate ($In(NO_3)_3 \cdot 4.5H_2O$), carbon disulfide (CS_2), potassium hydrate (KOH), ethanol (C_2H_5OH), chloroform ($CHCl_3$), dichloromethane (CH_2Cl_2), and pyridine (C_5H_5N), dichloromethane (CH_2Cl_2), 1-dodecanethiol ($C_{12}H_{25}SH$), ethylenediamine ($C_2H_8N_2$), and oleic acid ($C_{18}H_{34}O_2$) were purchased from Shanghai Chemical Co.. $[CH_3(CH_2)_7]_2NH$ (Alfa, A.R.) was used. All reactants were used as received.

Synthesis of Ag(OTC) and In(OTC)$_3$ Precursors

Precursors were prepared according to the reactions shown in **Scheme 1**. Below 0°C, CS_2 had reacted with $[CH_3(CH_2)_7]_2NH$ and KOH to produce enough dithiocarbamate salt in ethanol (**Reaction 1**). Then, an ethanol solution with excess $In(NO_3)_3 \cdot 4.5H_2O$ was added to generate white suspension $In[S_2CN(C_8H_{17})_2]_3$ (**Reaction 2**). After stirring for 5 min, an ethanol solution with an appropriate amount of $AgNO_3$ with a mole ratio of M^+:In^{3+} = 1:1.25 was added and stirred for another 2 h to ensure the complete reaction to form In(OTC)$_3$ and Ag(OTC) precursors (**Reaction 3**) and make them mix evenly. A solid was obtained after the rotary evaporation of ethanol and then dissolved in $CHCl_3$ and filtrated. Then, this $CHCl_3$-filtration was rotary evaporated to generate the Ag(OTC)/In(OTC)$_3$ precursor, a soil-like solid. Finally, the precursors were washed by acetone. The precursor color is yellow.

Synthesis of the AgInS$_2$

In a typical process, the precursor was added into a solution containing pyridine or other solvents. The mixture was stirred for 15 min at room temperature in air, and then poured into a 25 ml Teflon-lined stainless autoclave. The autoclave was heated at 120~150°C for 17.5~20 h under autogenous pressure, and then air-cooled to room temperature. The resulting precipitates were collected and washed with CH_2Cl_2 and ethanol thoroughly and dried at room temperature in air. The $AgInS_2$ product is dark red.

Characterization

X-ray powder diffraction (XRD), transmission electron microscopy (TEM), high-resolution TEM (HRTEM), and scanning electron microscopy (SEM) were used to characterize the structure, composition, size, and shape of the synthesized nanoproducts, respectively. The XRD patterns were collected with the aid of a PANalytical X'Pert Pro diffractometer at room temperature, at 40 kV and 40 mA with Cu *Kα* radiation. The TEM images were obtained using a JEM 2010 TEM equipped with a field emission gun operating at 200 kV. Images were acquired digitally using a Gatan multipole scanning CCD camera with an imaging software system. The EDX analyses were performed on a carbon-film-coated Cu grid with the aid of a JEM 2010 TEM equipped with an Oxford INCA spectrometer. The optical diffuse reflectance spectrum was measured at room temperature using a Perkin-Elmer Lambda 900 UV–vis spectrophotometer equipped with an integrating sphere attachment and $BaSO_4$ as reference. The UV-vis spectra were measured on a Perkin-Elmer Lambda-35 spectrophotometer.

Photocatalytic activity test

The photocatalytic activities of the samples were investigated by the decomposition rate of methyl orange (MO) or Methylene blue (MB) in an aqueous solution under UV-vis light irradiation. Briefly, 100 mg of $AgInS_2$ nano powders was dispersed in 100 mL of MB or MO solution with an initial concentration of 10 ppm. Prior to irradiation, the suspension was stirred in the dark for 1 h to ensure the establishment of the adsorption-desorption equilibrium. The assembly was continuously stirred and irradiated by a 300 W halogen-tungsten lamp. At an irradiation time interval of 1 h, 4 mL of the suspension was collected and then the slurry samples including the photocatalyst and MO or MB solution were centrifuged to remove the photocatalyst particles. The concentration of MO or MB was analyzed by measuring the absorbance at 664 nm wavelength for MB (or 463 nm wavelength for MO) using a UV-VIS spectrophotometer.

RESULTS AND DISCUSSION

Phase and microstructure

The XRD patterns of the as-synthesized products prepared using pyridine as the solvent at 120°C for 20 h (**Figure 1a**) and using 1-dodecanethiol as the solvent at 150°C for 17.5 h (**Figure 1b**) can be indexed to the ICDD pattern (PDF#25-1328). We can see that the position of all the diffraction peaks corresponds to (120), (002), (121), (202), (320), (123) and (322) plane and are in agreement with the orthorhombic phase of $AgInS_2$. The difference between those patterns is that the intensity of (002) plane in **Figure 1a** is much higher than one in **Figure 1b**, which is probably due to their different morphology.

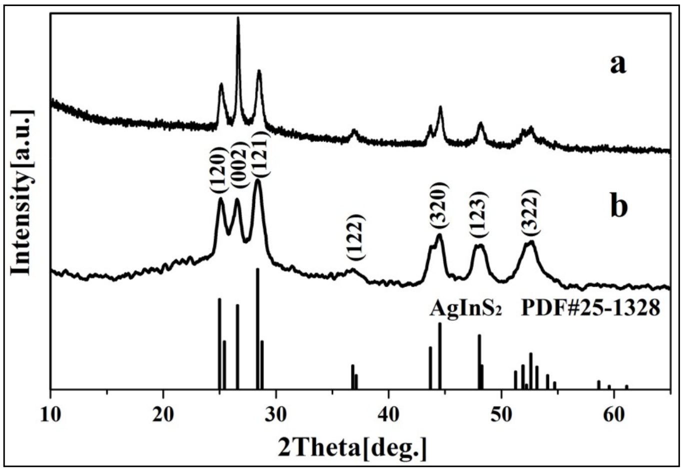

Figure 1: XRD pattern of as-prepared $AgInS_2$ samples: (a) 120°C/20 h, pyridine as the solvent; (b) 150°C/17.5 h, 1-dodecanethiol as the solvent.

As shown in **Figures 2a** and **2b,** the $AgInS_2$ produced in pyridine at 120°C for 20 h are nanoplates with width of 300~500 nm, and thickness of about 40 nm, which are stacked and not well dispersed. However, $AgInS_2$ produced in 1-dodecanethiol at 150°C for 17.5 h are irregular nanoparticles (SEM: **Figure 2c**), which is severely agglomerated and the dispersity is still not well even after ultrasonic concussion (TEM: **Figure 2d**). Comparing with 0D nanoparticle, the 2D nanoplate takes a preferred orientation for powder diffraction, so the intensity of (002) diffraction peak is greatly increased, which also explains why the peak in **Figure 1a** is significantly higher than that in **Figure 1b**. A typical HRTEM image of the edge of such a nanoparticle is shown in **Figure 2e**, indicating the size of those particles is about 14 nm (calculated by the red circle). Clear lattice fringes (**Figure 2f**) can be observed after FFT inversion and the single-crystal natures of the nanoparticles are revealed. The interplanar spacing is about 0.357 nm, in good agreement with the distance (0.356 nm) of (120) planes of orthorhombic $AgInS_2$.

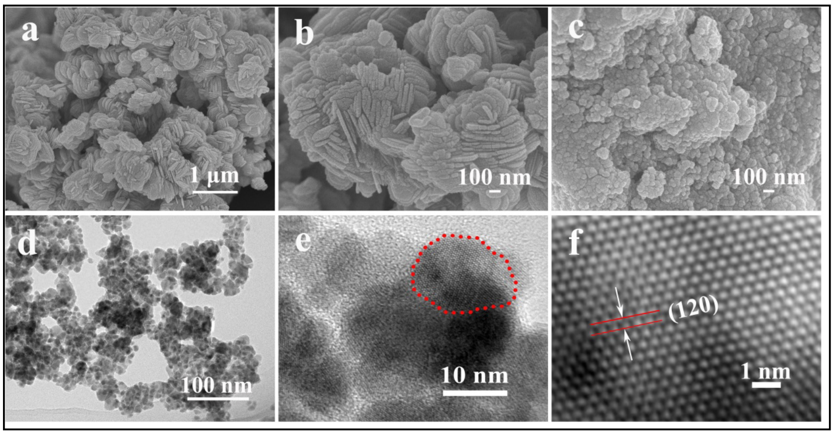

Figure 2: (a, b) SEM images of $AgInS_2$ samples prepared at 120°C for 20 h, using pyridine as the solvent; (c,d) SEM and TEM images of $AgInS_2$ samples prepared at 150°C for 17.5 h, using 1-dodecanethiol as the solvent; (e,f) HRTEM images of particle in picture d, indicating that the size of particle is about 14 nm (calculated by the red circle), and the interplanar spacing is 0.357 nm, in good agreement with the distance (0.356 nm) of (120) planes of orthorhombic $AgInS_2$.

Using pyridine as the solvent, we can observe the formation of orthorhombic $AgInS_2$ by adjusting the reaction time under the condition of 120°C. When the reaction time was 5 h, a small amount of Ag_2S (**Figure 3a**) with weak diffraction peak of XRD was obtained, and there were only two obvious peaks; when the reaction time was increased to 10 h, the peak intensity of XRD (**Figure 3b**) had significantly enhanced, in good agreement with that of monoclinic Ag_2S (ICDD PDF# 14-0072). It can be seen from **Figure 3d** that the Ag_2S also contains two morphologies, namely, the hexagon with a length of about 100 nm and the particle with size of about 50 nm, and the amount of particles is significantly more than the hexagon. When the reaction time was further extended to 15 h, the obvious diffraction peak of orthorhombic $AgInS_2$ appeared (**Figure 3c**), and its intensity is higher than that of Ag_2S, indicating that most of the Ag_2S have been transformed into $AgInS_2$. Furthermore, the amount of the original small particles greatly reduced, but both the number and size of the hexagonal sheet increased (**Figure 3e**). This result shows that, as the reaction time is increased, the newly generated monoclinic Ag_2S gradually transforms into orthorhombic $AgInS_2$, accompanied by the transformation from particles to hexagonal plate. This point can be verified that pure orthorhombic $AgInS_2$ nanoplates are obtained when the reaction time is extended to 20 h (**Figures 1a** and **2a**).

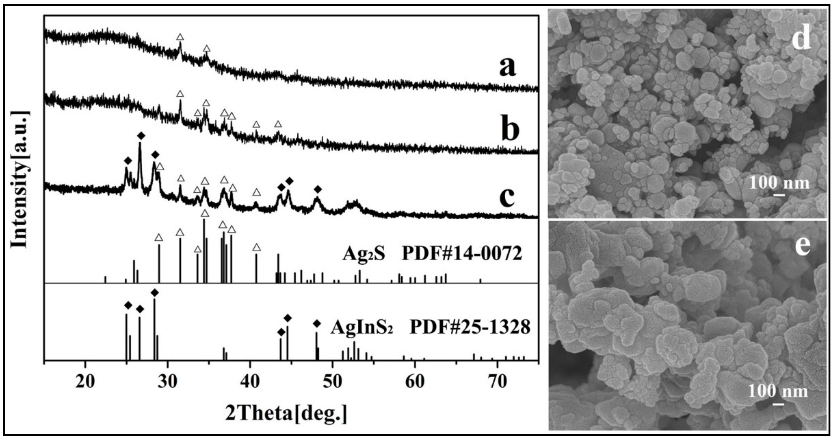

Figure 3: XRD patterns and SEM images of products prepared at 120°C for different time: (a) 5 h, weak diffraction peak, monoclinic Ag_2S; (b,d) 10 h, monoclinic Ag_2S, similar quantity of nanoplate and nanoparticle; (c,e) 15 h, the major orthorhombic $AgInS_2$ with minor monoclinic Ag_2S, and the quantity of nanoplate is much larger than nanoparticle.

According to the above experimental facts, combined with the previous work [15] and results obtained by our group [16,17], we has proposed the possible growth mechanism of orthorhombic $AgInS_2$, and the reactions are as follows (HNR_2, R= $-C_8H_{17}$):

$$HNR_2 + KOH + CS_2$$

$$\rightarrow KS_2CNR_2 + H_2O \tag{1}$$

$$KS_2CNR_2 + AgNO_3 \rightarrow AgS_2CNR_2 + KNO_3 \tag{2}$$

$$KS_2CNR_2 + In(NO_3)_3 \rightarrow In(S_2CNR_2)_3 + KNO_3 \tag{3}$$

$$AgS_2CNR_2 \rightarrow Ag_2S + \text{others} \tag{4}$$

$$Ag_2S + In(S_2CNR_2)_3 \rightarrow AgInS_2 + \text{others} \tag{5}$$

Scheme 1: Reactions to generate $AgInS_2$

The as-prepared KS_2CNR_2 (**Reaction 1**) was coordinated with Ag^+ and In^{3+} to form the corresponding complex AgS_2CNR_2 (**Reaction 2**) and $In(S_2CNR_2)_3$ (**Reaction 3**). Since these complexes were formed in solution and have been fully stirred, it should not be a simple mechanical mixture in the final solid form, but rather a uniform mixture at the molecular level. As the reaction temperature increased, AgS_2CNR_2 began to decompose into corresponding Ag_2S (**Reaction 4**), because Ag^+ has a high diffusivity under high temperature, which can move freely in the lattice of cation hole [18]. Therefore, In^{3+}, released slowly from $In(S_2CNR_2)_3$, can replace part of Ag^+ in the Ag_2S lattice, leading to form orthorhombic $AgInS_2$ gradually (**Reaction 5**). On the other hand, when using pyridine as the solvent, the as-prepared Ag_2S particles wrapped by pyridine, would grow anisotropically into lamellar structure; while using

1-dodecanethiol as the solvent, the as-prepared Ag_2S particles wrapped by 1-dodecanethiol, would grow isotropically into irregular particle with small size. Hence, when the In^{3+} partially replaces the Ag^+ in the Ag_2S lattice, it will not change the morphology, and finally the product grows into nanoplates or nanoparticles, respectively.

Effect of reaction temperature

In order to investigate the morphology-reaction temperature relationship, a batch of parallel reactions using pyridine as the solvent has been carried out, and some representative SEM images are displayed. The detailed experimental results are listed in **Table 1**. The results indicated that when temperature is increased to 150°C, the products are also pure orthorhombic $AgInS_2$ nanoplate (XRD: **Figure 4a**, SEM: **Figure 5a**), similar to that of 120°C; while at 170°C, besides of orthorhombic $AgInS_2$, minor tetragonal $AgInS_2$ (ICDD PDF# 25-1330) begins to appear, and lots of nanoparticles are observed (XRD: **Figure 4b**, SEM: **Figure 5b**), indicating that some orthorhombic $AgInS_2$ has transformed into tetragonal $AgInS_2$, namely metastable phase transformes into stable phase [19], so the morphology of products takes an obvious change. When the temperature continues to rise to 190°C, the relative intensity of the diffraction peak of tetragonal phase is not significantly improved (**Figure 4c**), showing that the percentage of tetragonal phase has not significantly enhanced. The products are also nanoparticles similar to that of 170°C, but almost none of nanoplate is observed (**Figure 5c**).

Table 1: Products synthesized using pyridine as the solvent at different temperature.

Tempreature (°C)	Time (h)	XRD	Phase	SEM	Morphology
150	17.5	Figure 4a	orthorhombic $AgInS_2$	Figure 5a	nanoplate
170	17.5	Figure 4b	orthorhombic $AgInS_2$ + tetragonal $AgInS_2$ (minor)	Figure 5b	nanoplate (minor) + nanoparticle
190	17.5	Figure 4c	orthorhombic $AgInS_2$ + tetragonal $AgInS_2$ (minor)	Figure 5c	nanoparticle

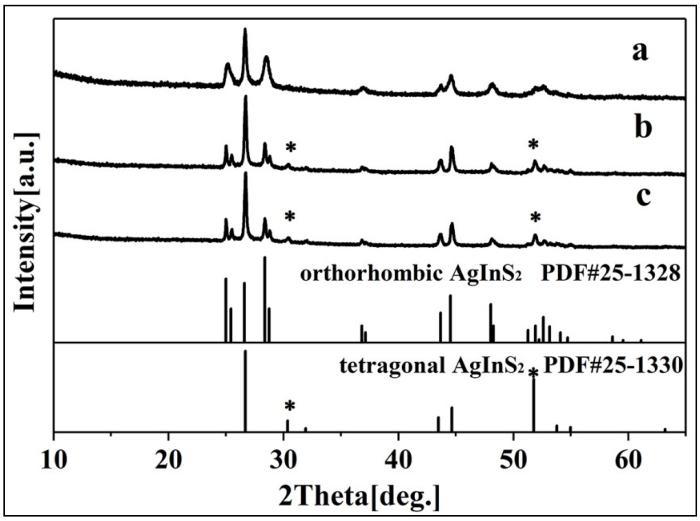

Figure 4: XRD patterns of products prepared at different temperature for 17.5 h using pyridine as the solvent: (a) 150°C, orthorhombic $AgInS_2$; (b) 170°C, orthorhombic $AgInS_2$ (major) + tetragonal $AgInS_2$ (minor) ; (c) 190°C, orthorhombic $AgInS_2$ (major) + tetragonal $AgInS_2$ (minor)

Therefore, using pyridine as the solvent, the optimal temperature range to synthesize orthorhombic $AgInS_2$ nanoplate is 120~150°C, and the optimal range of reaction time is 17.5~20 h. If the temperature is too low or the time is too short, the samples should not fully react to produce pure ternary sulfide $AgInS_2$. However, the higher temperature will make metastable $AgInS_2$ transform into tetragonal $AgInS_2$. It is interesting to find that when 1-dodecanethiol is used as the solvent, the orthorhombic $AgInS_2$ can be obtained at 120~190°C for 17.5~20 h, which indicates that the solvent also plays a certain role in the formation of $AgInS_2$.

Effect of the solvent

To further understand the effect of the solvent, some other solvents are used instead of pyridine and 1-dodecanethiol. All these parallel reactions have been run at 150°C for 17.5 h. The detailed experimental results are listed in **Table 2**. When using ethylenediamine as the solvent, the product is a mixture containing lots of orthorhombic $AgInS_2$ and

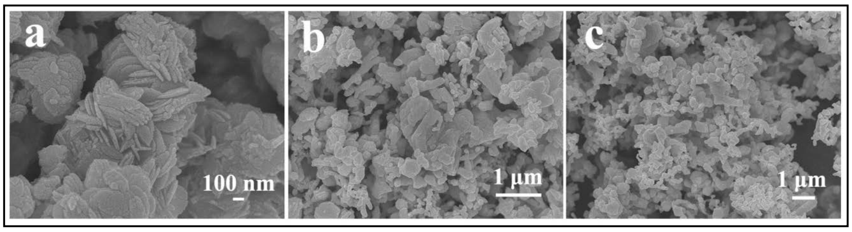

Figure 5: SEM images of products prepared at different temperature for 17.5 h using pyridine as the solvent: (a) 150°C; (b) 170°C; (c) 190°C.

Table 2: Products synthesized using other solvents at 150°C for 17.5 h.

Sample	Solvent	XRD	Phase	SEM	Morphology
1	Ethylenediamine	Figure 6a	orthorhombic $AgInS_2$ + tetragonal $AgInS_2$ (minor)	Figure 6c	square nanoplate + particle (minor)
2	Oleic acid	Figure 6b	orthorhombic $AgInS_2$ + monoclinic Ag_2S	Figure 6d	particle

a small amount of tetragonal $AgInS_2$ (XRD: **Figure 6a**); besides of a small number of particles, most of products are square sheet with the thickness of 30~60 nm (SEM: **Figure 6c**). While using oleic acid as the solvent, both orthorhombic $AgInS_2$ nanoparticles and monoclinic Ag_2S nanoparticles are observed (XRD: **Figure 6b**; SEM: **Figure 6d**), indicating that 150°C is too low, or 17.5 h is too short for as-prepared Ag_2S completely transforms to $AgInS_2$, which may be due to the strong adsorption properties of oleic acid. The oleic acid can be firmly adsorbed on the surface of as-prepared Ag_2S particles, which may hinder In^{3+} to replace the Ag^+, leading the conversion rate is greatly reduced, so it requires higher temperature or longer time to complete the transformation. This result shows that the solvent has a great influence on the phase and morphology of the products.

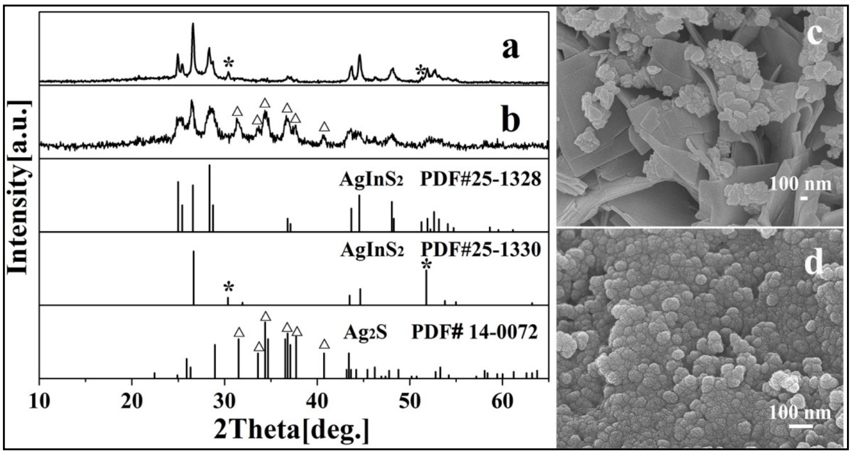

Figure 6: XRD patterns and SEM images of products prepared at 150°C for 17.5 h using other solvents: (a,c) ethylenediamine, orthorhombic $AgInS_2$ + tetragonal $AgInS_2$ (minor), square nanoplate + particle (minor); (b, d) oleic acid, orthorhombic $AgInS_2$ + monoclinic Ag_2S, nanoparticle.

UV–VIS diffuse reflectance spectroscopy

For I-III-VI family compounds, most of them are direct-narrow-gap semiconductors with chalcopyrite structure [20]. $AgInS_2$ has chalcopyrite and orthorhombic phases, and the band gap values are 1.87 and 1.98 eV, respectively [21-23]. Because of its suitable bandgap, it has a good absorption in the visible range, so it is a good photocatalytic material. Fig.7 is the solid UV-vis diffuse reflectance spectra of $AgInS_2$ nanoplates and $AgInS_2$ nanoparticles. The band gap of $AgInS_2$ can be calculated according to the Equation 1[24]:

$$\alpha h\nu = (h\nu - E_g)^n \quad (1)$$

Here, α means absorption coefficient; $h\nu$ means photoelectron energy; the value of n is 1/2 for indirect bandgap compouds, while 2 for direct bandgap compounds, and E_g means bandgap. Taking $h\nu$ as the abscissa, with $(\alpha h\nu)^{1/n}$ as ordinate, the curve is extended to intersect with the abscissa, and the bandgap can be calculated. As seen in **Figure**

7a, the bandgap of $AgInS_2$ nanoplate is about 1.61 eV, close to the literature report of 1.58~1.63 eV[4,10,24]; while the bandgap of $AgInS_2$ nanoparticle is about 1.98 eV (**Figure 7b**), consistent with the band gap of $AgInS_2$ crystal. The difference between the two gaps is probably caused by the different particle sizes. Because the nanoplate has the larger size (thickness about 40 nm, width 300~500 nm), while the nanoparticle is only about 14 nm, which results in the blue shift of the absorption edge due to small size effect.

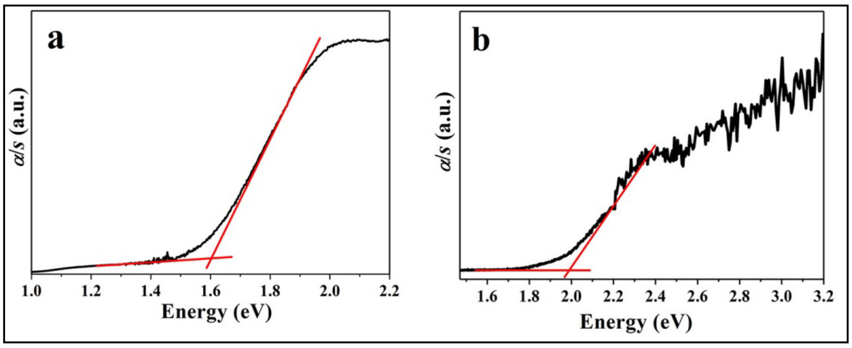

Figure 7: UV-vis diffuse reflectance spectrum of as-prepared products: (a) $AgInS_2$ nanoplate, synthesized at 120°C for 20 h using pyridine as the solvent, the bandgap is about 1.61 eV; (b) $AgInS_2$ nanoparticle, synthesized at 150°C for 17.5 h using 1-dodecanethiol as the solvent, the bandgap is about 1.98 eV.

Photocatalytic activity of the $AgInS_2$ samples

The photocatalytic activities of $AgInS_2$ samples are measured on the degradation of methyl blue (MB) or methyl oragne (MO) in water under UV-vis light irradiation. As shown in **Figure 8a**, with the advance of illumination time, the absorbance of MB in the solution is getting smaller and smaller, indicating that the concentration of MB is lower and lower. After 300 min of irradiation, the conversion of MB by $AgInS_2$ nanoparticles is about 66% (**Figure 8b**, red curve). However, the conversion of MO by $AgInS_2$ nanoplates is about 25% (**Figure 8b**, blue curve). The results show that $AgInS_2$ has the certain ability on photocatalytic degradation of organic dyes such as MB, and it is probably that

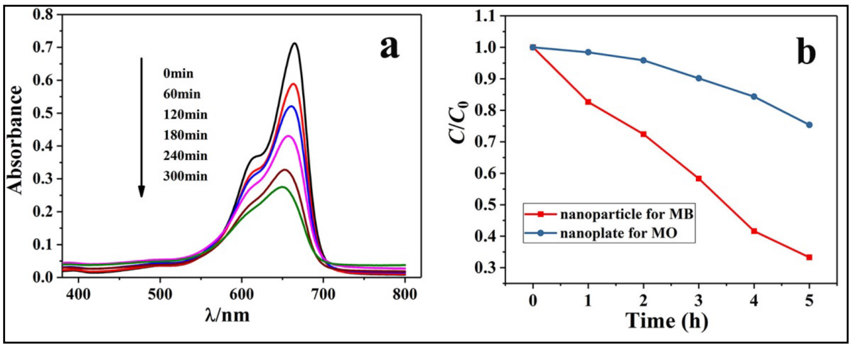

Figure 8: (a) Absorption spectra of MB photocatalytic degraded by $AgInS_2$ nanoparticle; (b) The relation between MB concentration and time photocatalytic degraded by $AgInS_2$ nanoparticle (the red curve), and the relation between MO concentration and time photocatalytic degraded by $AgInS_2$ nanoplate (the blue curve).

the low-power tungsten halogen lamp (300 W) used in the experiment causes unexciting conversion. The possible mechanism on photocatalytic degradation of MB by $AgInS_2$ can be explained by the following **Scheme 2**:

$$AgInS_2 + h\nu \leftrightarrow AgInS_2\,(h^+ + e^-) \quad (6)$$

$$e^- + O_2 \rightarrow \bullet O_2^- \quad (7)$$

$$2e^- + O_2 + 2H^+ \rightarrow H_2O_2 \quad (8)$$

$$H_2O_2 + \bullet O_2^- \rightarrow OH^- + \bullet OH + O_2 \quad (9)$$

$$\bullet OH/h^+/\bullet O_2^- + MB \rightarrow \text{intermediates} \rightarrow CO_2 + H_2O \quad (10)$$

Scheme 2: The possible mechanism on photocatalytic degradation of MB by $AgInS_2$ [25]

Under visible-light irradiation, the electrons transfer from valance band (VB) of $AgInS_2$ to the conduction band (CB), while the holes (h^+) generate in its VB (**Reaction 6**). The photogenerated electrons (e^-) can react with adsorbed O_2 to produce $\bullet O^{2-}$ (**Reaction 7**) and H_2O_2 (**Reaction 8**). H_2O_2 can further reacts with $\bullet O^{2-}$ and e^- to generate hydroxyl radicals ($\bullet$OH) (**Reaction 9**). All of $\bullet O_2^-$, h^+ and $\bullet$OH play a role in the degradation and mineralization of MB (**Reaction 10**).

CONCLUSION

Two kinds of orthorhombic $AgInS_2$ nanostructures with different morphologies have been successfully prepared by the solvent method using KS_2CNR_2, $AgNO_3$, and $In(NO_3)_3$ as reagents. When using pyridine as the solvent, by tuning the reaction temperature and reaction time, it is found that pure $AgInS_2$ nanoplates with relatively uniform morphology can be obtained at 120~150°C for 17.5~20 h; when the temperature is below 120°C or the reaction time is less than 10 h, most of the product is binary monoclinic Ag_2S, while there will be another ternary tetragonal $AgInS_2$ generated over 170°C. When using 1-dodecanethiol as the solvent, pure $AgInS_2$ nanoparticles with size of about 14 nm have been obtained at 120~190°C for 17.5~20 h, indicating that the solvent has a great influence on the phase and morphology, and this point has also been verified using ethylenediamine or oleic acid as the solvent. On the other hand, UV-vis diffuse reflectance spectra show that the bandgap of $AgInS_2$ nanoplates (1.61 eV) with larger size is less than that of $AgInS_2$ nanoparticles (1.98 eV) with smaller size, which is likely to be caused by the blue shift of the absorption edge due to the small size effect. Furthermore, the photocatalytic experiments show that $AgInS_2$ has certain ability on photocatalytic degradation of organic dyes such as MB.

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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