

Thiamine-assisted hydrothermal synthesis of Ag₂S microcrystals and their optical properties

Xingyu Cui¹, Chen Yuan¹, Sha Li² ✉, Tong Hu¹, Jiehua Bao¹, Shuwei Chen¹

¹College of Chemistry and Chemical Engineering, Taiyuan University of Technology, Taiyuan 030024, People's Republic of China

²College of Textile Engineering, Taiyuan University of Technology, Taiyuan 030024, People's Republic of China

✉ E-mail: lisha@tyut.edu.cn

Published in Micro & Nano Letters; Received on 22nd March 2017; Revised on 9th May 2017; Accepted on 18th May 2017

Facile thiamine-assisted hydrothermal synthesis of silver sulphide (Ag₂S) microcrystals in the water/ethanol binary solution is reported. The reaction conditions including the contents of reactants, solvents and reaction times, were optimised. The morphology, phase composition and optical properties of the as-prepared Ag₂S product were characterised with scanning electron microscopy, transmission electron microscopy, X-ray diffraction, Raman spectrometry and photoluminescence (PL). The results indicate that the synthesised cubic Ag₂S microcrystals have strong PL in the blue-light range. A possible synthesis mechanism was proposed for the cubic Ag₂S microcrystals. It is noteworthy that no toxic hydrogen sulphide was released from the environmentally friendly synthesis reaction proposed in the present work. This is for the first time that thiamine, an ordinary and cheap biomolecule, was used as the S source for the preparation of Ag₂S microcrystals.

1. Introduction: Recently, great efforts have been made in regards to the development of semiconductor nano/microcrystals due to their tunable properties with their sizes, shapes and morphologies in order to explore the novel electronic properties [1, 2]. Among them is silver sulphide (Ag₂S), an important chalcogenide semiconductor with a direct and narrow bandgap. It has good chemical stability and excellent optical limiting properties, making it an effective semiconductor material for photocatalytic applications [3, 4].

The tunable plasmonic properties of Ag₂S have received much attention [5]. Various methods have been developed for the preparation of metal sulphide nanostructures. The shape of nanoparticles can be controlled by appropriate templates or capping agents and the latter are simpler and usually give higher yields [6, 7]. However, the preparation of Ag₂S polyhedral nanocrystals such as nanocubes is still a challenge. Among these methods, air-sensitive and expensive complexes or surfactant agents are utilised to synthesise faceted and cubic Ag₂S nanocrystals [8, 9]. Yang *et al.* has reported that heterostructures of cadmium sulphide nanorods and Ag₂S domains were obtained with ultrasonic activation without using any reductant [10]. Moreover, sulphur, sodium sulphide, thioacetamide and thiourea are the conventional sulphur sources, which release toxic hydrogen sulphide during the reaction for the preparation of metal sulphides. Therefore, a simple, efficient and environmentally friendly approach with low cost for the preparation of metal sulphide nano/micromaterials is highly desired.

Biomolecules have special structures and fascinating abilities to self-assemble, therefore, can be used as structure-directing agents or reactant sources. Various biomolecule-assisted synthesis methods have been developed for preparation of metal sulphides. For example, Komarneni *et al.* synthesised highly ordered snow flake like structures of bismuth sulphide (Bi₂S₃) nanorods under microwave irradiation using glutathione as both directing molecules and a sulphur source [11, 12]. Xie's group achieved flower-like Bi₂S₃ nanoparticles and the porous spongy-like nickel sulphide nanoparticles for the electrochemical hydrogen storage, and network-like γ -manganese sulphide nanostructures for optical applications with L-cysteine as a directing agent [13–15].

In sum, biomolecule-assisted synthesis method is a novel, environmentally friendly and promising strategy for the preparation of

various nanomaterials. Thiamine is one of essential vitamin containing a sulphur atom, hence can be used as a sulphur source to prepare sulphides. In addition, the self-assembling ability makes it an excellent structure-directing agent for the morphology controlling. Therefore, in the present work, Ag₂S microcrystals were synthesised in a binary solution with the assistance of thiamine, an ordinary and cheap biomolecule. This is for the first time that thiamine was used as S source for the preparation of Ag₂S. The reaction conditions including the contents of reactants, solvents and reaction time were optimised. We also present the characterisation of Ag₂S microcrystals: temperature-dependence photoluminescence (PL) and Raman spectroscopy. It is noteworthy that the whole process is environmentally friendly and controllable.

2. Experimental details

2.1. Thiamine-assisted hydrothermal synthesis: All analytical grade chemical reagents were purchased from the Tianjin Kemiou Chemical Company (Tianjin, China) and used without further purification. Typical experiments were conducted as follows: 0.051 g of silver nitrate (AgNO₃) (analytical reagent (AR), $\geq 99.8\%$) (0.3 mmol) and 0.504 g of thiamine (C₁₂H₁₇ClN₄OS·HCl) (AR, $\geq 98.0\%$) (1.5 mmol) were dissolved, respectively, in 10 ml of distilled water and then mixed under stirring. Subsequently, 10 ml of ethanol (C₂H₆O) (AR, $\geq 99.7\%$) was added into the mixture and stirred magnetically for 10 min. The resulting solution was transferred into a 50 ml Teflon-lined autoclave, heated at 180°C for 12 h and cooled to room temperature. The black precipitate was collected by centrifugation and washed with distilled water and absolute alcohol. The washing process was conducted for several times. The residue was dried in a vacuum at 50°C for 6 h.

2.2. Characterisation: The morphologies of samples prepared above were imaged with a Hitachi S4800 field emission scanning electron microscopy (SEM). Transmission electron microscopy (TEM) images were obtained with a JEM100CXII TEM operated at 100 kV. The crystal structures of the as-prepared samples were characterised by X-ray diffraction (XRD) with a Rigaku D/MAX-2500 V/PV using Cu-K α radiation (40 kV and 200 mA) at a scanning speed of 4°/min over the 2 θ range of 20–70°. The samples were evaluated by Raman spectroscopy

(DXR Raman microscope). PL measurements were carried out on a FluoroMax-4 luminescence spectrometer equipped with a pulsed xenon lamp.

3. Results and discussion

3.1. Optimised reaction conditions: The solution including water, water/EA, water/ethanol, the reactant concentration of AgNO_3 and thiamine was first optimised in Figs. S1 and S2. The reaction solvent can significantly affect the morphology of Ag_2S . Ag_2S displayed a significantly aggregated quasi-circular structure in water. The introduction of EA to the water produced larger aggregated micron particles. In the water/ethanol binary solution, well-structured and relatively uniform cubic materials were formed (Figs. S1c and d) and the size of the cubic structure was mainly about 1 μm . As shown in Fig. S2a, irregular small aggregates were formed with 2 mM AgNO_3 and 10 mM thiamine. Increasing the concentrations of AgNO_3 and thiamine to 10 and 50 mM resulted in cubic Ag_2S (Fig. S2b). Large amounts of cubic aggregates and irregular particles were formed with 20 mM AgNO_3 and 100 mM thiamine, indicating excessive use of the reactants.

The morphological evolution of Ag_2S during the reaction was determined to understand the growth mechanism of cubic structure. As shown in Fig. 1, irregular-layered particles were formatted at the early reaction stage (Fig. 1a) and bulk-layered aggregates were formed and stacked on each other with further reaction, indicating the occurrence of self-assembling between the Ag_2S crystals (Fig. 1b). Cubic Ag_2S crystals were formed at the reaction time of 8 h and became a perfect cubic crystal structure at 12 h (Fig. 1c). By increasing the reaction time to 24 h, cracks were formed on the crystal surfaces. This growth process of cubic Ag_2S followed the oriented attachment mechanism. Monocrystalline particles at different orientations were alternated to the same orientation by particle rotation, and grew into bigger monocrystalline by oriented attachment. The crystal growth mechanism is similar with the literatures [16, 17]. The dislocations and defects occurred during the oriented attachment resulted in different shapes of crystallites.

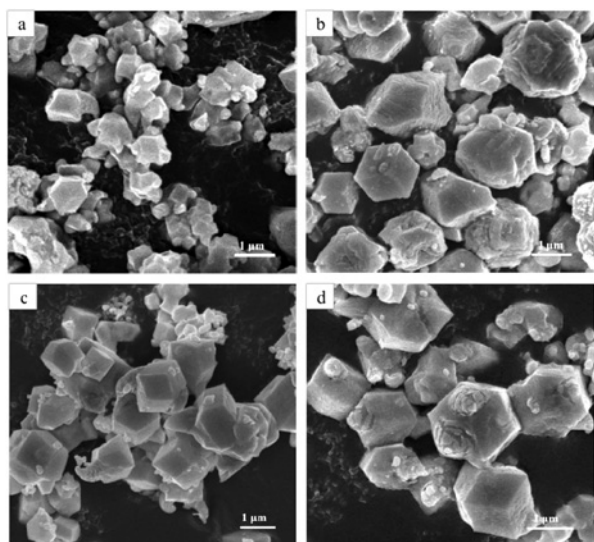


Fig. 1 SEM images of Ag_2S produced at the reaction time of

a 1 h

b 4 h

c 8 h

d 24 h

Reaction conditions: $C_{\text{AgNO}_3} = 10 \text{ mM}$, $C_{\text{thiamine}} = 50 \text{ mM}$, $V_{\text{AgNO}_3} = 10 \text{ ml}$, $V_{\text{thiamine}} = 10 \text{ ml}$, $V_{\text{ethanol}} = 10 \text{ ml}$ and $T = 180^\circ\text{C}$

3.2. Structure characterisation of cubic Ag_2S microcrystals: Fig. 2a shows the XRD patterns of the cubic Ag_2S produced under the optimal conditions. All peaks in the diffraction patterns can be indexed to monoclinic $\alpha\text{-Ag}_2\text{S}$ (JCPDS Card No. 14-0072). No peaks of impurities were detected, indicating the high purity of the products. Fig. 2b shows the Raman spectra of the cubic Ag_2S . The bands at 93 and 147 cm^{-1} were attributed to silver lattice vibrations. It is worth noting that strong resonant Raman scattering with high-order longitudinal optical (LO) modes were obtained on the cubic Ag_2S (Fig. 3). The Raman peaks at 284 and 490 cm^{-1} , which is due to the fact that phonon vibration corresponds well to the first- and second-order LO phonon modes in Ag_2S , respectively. The bands at 1377 and 1567 cm^{-1} resulted from the photo-decomposition of the Ag_2S due to its photo-sensitivity [18].

3.3. Synthesis mechanism of cubic Ag_2S microcrystal: In the present work, the growth of cubic Ag_2S crystal underwent the initial nucleation stage and the subsequent growth phase. During the initial reaction, Ag^+ and thiamine molecule formed the precursor molecules. The C–S–C in the thiamine was then broken in the 180 $^\circ\text{C}$ hydrothermal reactors and –S– was released from the precursor molecules, which combined with Ag^+ to form the nuclei of the Ag_2S microcrystals.

In our previous work, we used the density functional theory to calculate the complex formed by Cu^{2+} and thiamine, and the bond lengths of Cu–S indicated that the interaction between Cu and S is significant [2]. It is well known that there are three Ag_2S forms: monoclinic $\alpha\text{-Ag}_2\text{S}$ at room temperature, body-centred cubic $\beta\text{-Ag}_2\text{S}$ at 176–600 $^\circ\text{C}$ and face-centred cubic $\gamma\text{-Ag}_2\text{S}$ at

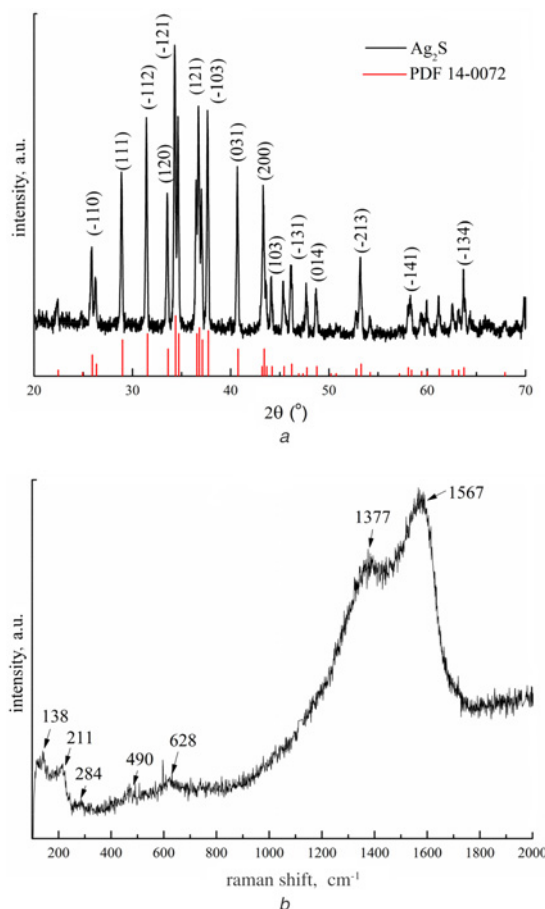


Fig. 2 Structure characterisation of cubic Ag_2S microcrystals

a XRD pattern

b Raman spectrum of cubic Ag_2S microcrystals

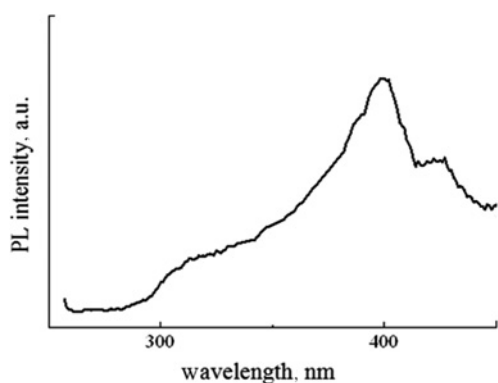


Fig. 3 Fluorescent emission spectrum of cubic Ag_2S microcrystals

temperatures higher than 600°C . The growth direction of the crystal surface depends on its surface energy. The cubic morphology of Ag_2S microcrystals was formed at 180°C in ethanol/water binary solution with the ratio of growth rate (R) along the $\{100\}$ plane to that along $\{111\}$ plane < 0.58 [19]. No cubic Ag_2S microcrystal was formed without ethanol in the reaction solution, indicating that ethanol molecules in the reaction system were critical for the formation of cubic Ag_2S . Ag_2S microcrystals grew along the $\{100\}$ plane to form the cubic structure. Thiamine has three functions for the formation of the cubic Ag_2S microcrystals. It functioned as an S source to provide S atom in the formation of Ag_2S microcrystals. Thiamine functioned as the directing agent to form stable complex with Ag^+ , inhibiting the excessive reaction between S^{2-} and Ag^+ and decreased the nucleation rate and growth rate to form the uniform morphologies of the Ag_2S microcrystals. In addition, thiamine was a protecting agent for the reaction. The excessive thiamine adsorbed on the surface of Ag_2S by the electrostatic interaction between the lone pair of S atom and Ag_2S could prevent the aggregation of the microcrystals, producing monodispersed microcrystals.

3.4. Optical properties of cubic Ag_2S microcrystals: The fluorescence properties of the as-prepared cubic Ag_2S microcrystals in ethanol were determined with a fluorescence spectroscopy to understand its optical properties. Two emission peaks at 400 and 435 nm in the purple region were obtained under the excitation at 247 nm. This recombination luminescence process was attributed to the electron transitions from the conduction band into the electron hole. Therefore, cubic Ag_2S microcrystals emitted fluorescence under the excitation of ultraviolet light [20].

4. Conclusions: In summary, we have obtained Ag_2S microcrystals by the thiamine-assisted hydrothermal synthesis in water/ethanol binary solvent at 180°C with small biomolecule, with thiamine as a sulphur source and AgNO_3 as a silver source. The effects of the reactant concentration, solvent system and reaction time on the morphology of Ag_2S were determined with SEM and TEM, and the reaction condition was optimised. The results indicate that monodisperse cubic Ag_2S microcrystals can be formed with 10 mM AgNO_3 and 50 mM thiamine in the ethanol/water binary solution. The synthesis mechanism of the cubic Ag_2S microcrystals was explored by recording the morphological evolution of the produced particles during the reaction. The two strong emission peaks of the cubic Ag_2S microcrystals at 400 and 435 nm indicate that it can be used as an excellent kind of optical semiconductor material.

5. Acknowledgments: The financial support from the National Natural Science Foundation of China (grant nos. 21406153 and 21546009) and the Shanxi Province Science Foundation for Youths (grant no. 2014021014-2) are greatly appreciated. This work was also supported by the Program for the Outstanding Innovative Teams of Higher Learning Institutions of Shanxi.

6 References

- [1] Toma O., Ion L., Ifimie S., *ET AL.*: 'Structural, morphological and optical properties of RF – sputtered CdS thin films', *Mater. Des.*, 2016, **100**, pp. 198–203
- [2] Yan X.L., Li S., Pan Y.X., *ET AL.*: 'A simple approach to the synthesis of $\text{Cu}_{1.8}\text{S}$ dendrites with thiamine hydrochloride as a sulfur source and structure-directing agent', *Beilstein J. Nanotechnol.*, 2015, **6**, pp. 881–885
- [3] Meng Z.D., Zhu L., Ullah K., *ET AL.*: 'Enhanced visible light photocatalytic activity of Ag_2S -graphene/ TiO_2 nanocomposites made by sonochemical synthesis', *Chin. J. Catal.*, 2013, **34**, pp. 1527–1533
- [4] Kalpana K., Selvaraj V.: 'Thiourea assisted hydrothermal synthesis of $\text{ZnS}/\text{CdS}/\text{Ag}_2\text{S}$ nanocatalysts for photocatalytic degradation of Congo red under direct sunlight illumination', *RSC Adv.*, 2016, **650**, pp. 4227–4236
- [5] Fang C.H., Lee Y.H., Shao L., *ET AL.*: 'Correlating the plasmonic and structural evolutions during the sulfidation of silver nanocubes', *ACS Nano*, 2013, **7**, pp. 9354–9365
- [6] Gao F., Lu Q., Zhao D.: 'Synthesis of crystalline mesoporous CdS semiconductor nanoarrays through a mesoporous SBA-15 silica template technique', *Adv. Mater.*, 2003, **15**, pp. 739–742
- [7] Hung C.Y., Hsieh S.J., Wang C.C., *ET AL.*: 'In situ growth of CdS nanocrystal arrays by self-assembling microporous templates from dendritic-linear PGMA-HPAM-r-PS copolymers', *React. Funct. Polym.*, 2013, **73**, pp. 789–795
- [8] Wen P.L., Zhang Z., Hong Y.L., *ET AL.*: 'Preparation of Ag_2S nanocrystals of predictable shape and size', *Angew. Chem., Int. Ed.*, 2004, **35**, pp. 5685–5689
- [9] Dong L., Ying C., Yang L., *ET AL.*: 'Synthesis of faceted and cubic Ag_2S nanocrystals in aqueous solutions', *J. Colloid Interface Sci.*, 2008, **317**, pp. 485–492
- [10] Miao Y.P., Jiang Z.X., Zhao Y., *ET AL.*: 'CdS– Ag_2S and CdS–Au heterostructures directly created via ultrasonic method', *J. Nanosci. Nanotechnol.*, 2016, **16**, pp. 9195–9202
- [11] Lu Q., Gao F., Komarneni S.: 'A green chemical approach to the synthesis of tellurium nanowires', *Langmuir ACS J. Surf. Colloids*, 2005, **21**, pp. 6002–6005
- [12] Lu Q., Gao F., Komarneni S.: 'Biomolecule-assisted synthesis of highly ordered snowflake-like structures of bismuth sulfide nanorods', *J. Am. Chem. Soc.*, 2004, **126**, pp. 54–55
- [13] Zhang B., Ye X., Hou W., *ET AL.*: 'Biomolecule-assisted synthesis and electrochemical hydrogen storage of Bi_2S_3 flower-like patterns with well-aligned nanorods', *J. Phys. Chem. B*, 2006, **110**, pp. 8978–8985
- [14] Zhang B., Ye X., Wei D., *ET AL.*: 'Biomolecule-assisted synthesis and electrochemical hydrogen storage of porous sponge-like Ni_3S_2 nanostructures grown directly on nickel foils', *Chem. Eur. J.*, 2006, **12**, pp. 2337–2342
- [15] Zuo F., Zhang B., Tang X., *ET AL.*: 'Porous metastable γ -MnS networks: biomolecule-assisted synthesis and optical properties', *Nanotechnology*, 2007, **18**, p. 215608
- [16] Marques V.S., Cavalcante L.S., Sczancoski J.C., *ET AL.*: 'Effect of different solvent ratios (water/ethylene glycol) on the growth process of CaMoO_4 crystals and their optical properties', *Cryst. Growth Des.*, 2010, **10**, pp. 4752–4768
- [17] Cavalcante L.S., Longo V.M., Sczancoski J.C., *ET AL.*: 'Electronic structure, growth mechanism and photoluminescence of CaWO_4 crystals', *CrystEngComm*, 2012, **14**, pp. 853–868
- [18] Hashmi L., Sana P., Malik M.M., *ET AL.*: 'Novel fork architectures of Ag_2S nanoparticles synthesized through in situ self-assembly inside chitosan matrix', *Nano Hybrids*, 2012, **1**, pp. 23–43
- [19] Wang Z.L.: 'Transmission electron microscopy of shape-controlled nanocrystals and their assemblies', *J. Phys. Chem. B*, 2000, **104**, pp. 1153–1175
- [20] Cavalcante L.S., Sczancoski J.C., Varela J.A., *ET AL.*: 'Photoluminescence properties of nanocrystals', *J. Nanomater.*, 2012, **2012**, pp. 143–149