



Copper Selenide (CuSe and Cu₂Se) Nanocrystals: Controllable Synthesis Through a Facile Ultrasonic Chemical Route†

HANMEI HU^{1,2,*}, XINQING GE¹, CHONGHAI DENG³, MEI SUN¹, HAN XUAN¹ and KEHUA ZHANG¹

¹School of Materials and Chemical Engineering, Anhui University of Architecture, Hefei, Anhui Province, P.R. China

²Anhui Key Laboratory of Advanced Building Materials, Anhui University of Architecture, Hefei, Anhui Province, P.R. China

³Department of Chemical and Materials Engineering, Hefei University, Hefei, Anhui Province, P.R. China

*Corresponding author: E-mail: hmhu@ustc.edu

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Copper selenide (CuSe nanoflakes, Cu₂Se nanoeartworms) nanocrystals have been successfully fabricated using hydrazine hydrate as a reducing agent through an ultrasonic-assisted chemical route in one-pot solution. The as-prepared products are characterized by X-ray diffraction, field-emission scanning electron microscopy, transmission electron microscopy and UV-visible absorption spectrum. The experimental results reveal that the appropriate reaction molar ratio of copper salt to selenium powder in the solution plays a critical role in controlling the phase and morphology of copper selenide. The chemical reaction processes for explaining the formation of copper selenide are simply studied. UV-VIS absorption spectra indicate that the synthesized flake-shaped CuSe and earthworm-like Cu₂Se nanocrystals have good optical properties.

Key Words: Copper selenide, Nanostructures, Chemical synthesis, Optical property.

INTRODUCTION

Copper selenide, a *p*-type important semiconductor, has been studied interestingly due to their potential applications in various fields, such as solar cells¹, gas sensors², super ionic conductors³ and thermoelectric converters⁴. Recently, considerable efforts have been devoted to preparing copper selenide (CuSe, Cu₂Se) nanocrystals with various morphologies. Huang *et al.*⁵ fabricated CuSe nanosnakes by a bovine serum albumin-assisted room temperature method. Vinod *et al.*⁶ synthesized hexagonal CuSe nanoplatelets through a solution-phase synthetic route. Xiao *et al.*⁷ synthesized CuSe hexagonal nanoplates by developing a one-pot solution strategy. Kumar *et al.*⁸ prepared CuSe and Cu₂Se hexagonal nanoplates *via* a solvothermal method. Liu *et al.*⁹ prepared Cu₂Se hexagonal flakes by a hydrothermal co-reduction path. Low *et al.*¹⁰ obtained Cu₂Se nanocrystals from a single-source precursor of homoleptic copper (I) phenylselenolate polymer. Rong *et al.*¹¹ synthesized Cu₂Se nanoparticles by the reaction of selenium nanoparticles sol with copper sulfate solution containing ascorbic acid at room temperature. However, to our best of knowledge, a feasible and environmental-friendly method for controllable synthesis of copper selenide (CuSe, Cu₂Se) in one-pot solution reaction system is still a great challenge. In the present work,

we provide a convenient and eco-friendly one-pot solution route to controllably synthesize copper selenide (CuSe and Cu₂Se) with special morphology by adjusting the reaction molar ratio of copper salt to selenium powder.

EXPERIMENTAL

In a typical procedure, 1 mmol Cu(CH₃COO)₂·H₂O was dissolved in 40 mL distilled water to obtain solution A. Meanwhile, 1 mmol (or 0.5 mmol) Se powder was dissolved in 20 mL N₂H₄·H₂O (85 %) to obtain solution B. Then, solution B was added into the solution A under stirring. After continuous stirring for 20-30 min, the reaction mixture was transferred into a 100 mL autoclavable bottle, which was sealed and then put into a sonication bath with the water bath temperature of 90 °C and irradiated for 20-40 min by ultrasound wave. After cooling down to room temperature and standing overnight, CuSe (or Cu₂Se) precipitation was filtered out, washed several times with anhydrous ethanol and distilled water and then dried in a vacuum at 60 °C for 8 h.

Sonication was performed using a locally supplied ultrasonicator (KQ-50, 40 kHz, 50 W). The samples were analyzed by X-ray diffraction on a Philips X'Pert PRO SUPER X-ray diffractometer. Field-emission scanning electron microscope (FESEM, JSM-6700F) and transmission electron

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microscope (TEM, H-7650) were used to investigate the morphology of the obtained products.

RESULTS AND DISCUSSION

The crystal structure of as-prepared copper selenide products was characterized by X-ray diffraction analysis, as shown in Fig. 1. The six diffraction peaks of sample A (the reaction molar ratio of $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ to Se is 1:1) can be indexed to (101), (102), (006), (110), (108), (116) crystal planes of hexagonal CuSe (JCPDS card, No. 86-1240). The three prominent XRD peaks of sample B (the reaction molar ratio of $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ to Se is 2:1) can be indexed to (111), (220), (311) crystal planes of Cu_2Se with face-centered cubic structure (JCPDS card, No. 88-2043). The XRD results reveal that two copper selenide (CuSe and Cu_2Se) are successfully obtained by only tuning the reaction mole ratio of copper salt to selenium powder in the present designed ultrasonic-assisted chemical reaction system.

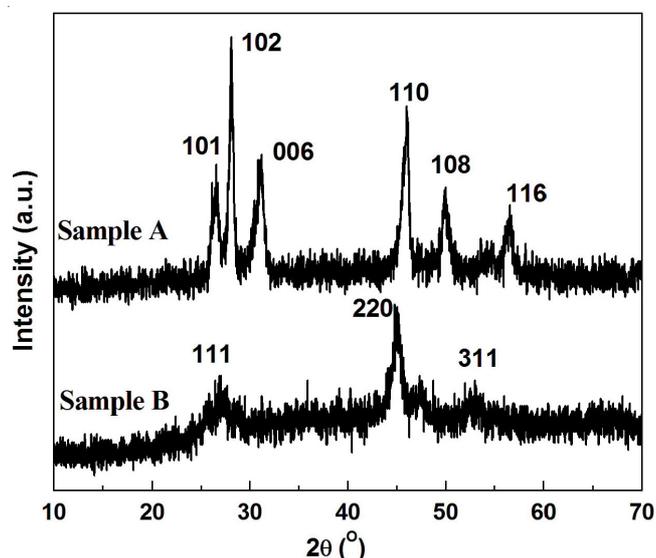


Fig. 1. XRD patterns of as-prepared copper selenide products

Fig. 2(a) and (b) display the FESEM images of CuSe products obtained by controlling the molar ratio of $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ to Se with 1:1 in the ultrasonic-assisted chemical reaction solution, which indicate that most of the CuSe products are irregular flake-like nanostructures with the sizes of 200–600 nm and the thicknesses are estimated to be 30–50 nm. Some hexagonal nanoflakes are also observed in the products [indicated by the white dashed circle in Fig. 2(b)]. Fig. 2(c) and (d) show the morphology of Cu_2Se products prepared by controlling the molar ratio of $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ to Se with 2:1 in the present ultrasonic-assisted chemical reaction solution, which exhibit that uniform tiny earthworm-like nanocrystals are found in the products [see enlarged image in Fig. 2(d)].

TEM images of CuSe [Fig. 3(a) and (b)] clearly shows that the synthesized CuSe products are 2D nanoflakes, including regular and deformed hexagonal shape. These thin nanoflakes stack with each other through van der Waals force to minimize the surface energy. The inset image of Fig. 3(b) displays a comparatively regular hexagonal nanocrystal. Fig.

3(c) and (d) are the TEM images of Cu_2Se 1D nanocrystals, which demonstrate that these tiny earthworm-like nanocrystals are flexible and entangle with each other to form a network-like microstructure. The diameters and lengths of Cu_2Se nanoeartworms are estimated to be 5–8 nm and 30–40 nm.

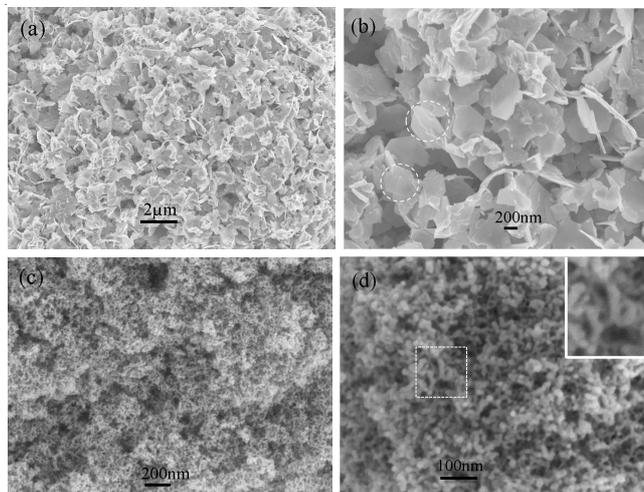


Fig. 2. (a, b) FESEM images of CuSe products, (c, d) FESEM images of Cu_2Se products

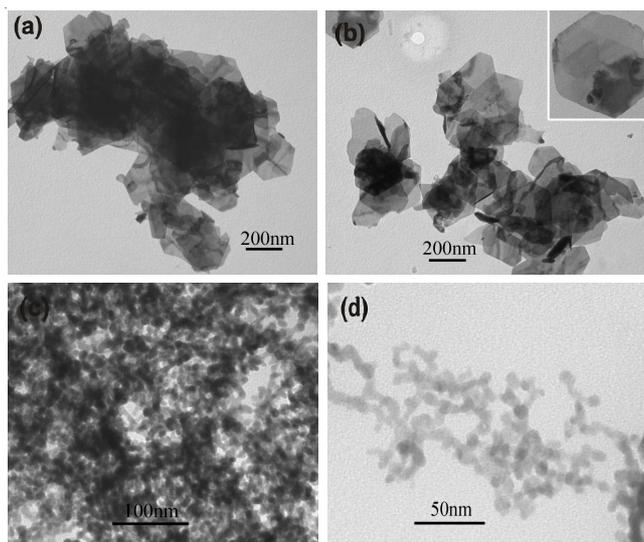


Fig. 3. (a, b) TEM images of CuSe products, (c, d) TEM images of Cu_2Se products

Besides as a solvent, hydrazine hydrate acts as a mild reducing reagent and alkaline amine benefitting the reduction of Se powder and Cu^{2+} ion in the present designed ultrasonic-assisted chemical reaction solution. The reaction mechanisms for controllably synthesizing CuSe and Cu_2Se are proposed as follows: The elemental Se could be firstly dissolved and reduced to Se^{2-} by $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$. Cu^{2+} in the solution rapidly reacts with new-produced Se^{2-} to form CuSe product in the solution with 1:1 molar ratio of $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ to Se [eqns. (1) and (2)]. When the molar ratio of $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ to Se is changed to 2:1 keeping other conditions constant, abundant Cu^{2+} can also be reduced to Cu^+ by $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ [eqn. (3)], which is a key step for the formation of Cu_2Se . Finally, the as-reduced active Cu^+ combines with Se^{2-} to generate Cu_2Se

compound [eqn. (4)]. Surely, the exact reaction mechanism is worthy to be further studied. The possible chemical reaction processes are described as follows:

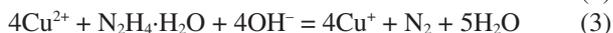
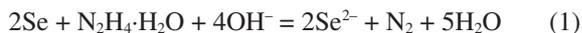


Fig. 4(a) shows the UV-VIS absorption spectrum of CuSe nanoflakes, two absorption bands located at 360 nm and 510 nm are found. The shape of absorption curve is similar to that of reported CuSe hexagonal nanoplatelets⁷. It is reported that the increase in absorbance at the lower wavelength region originates from the indirect band gap of the semiconductor¹². Fig. 4(b) displays the UV-VIS absorption spectrum of Cu₂Se nanoeartworms, two absorption peaks at 280 nm and 478 nm are observed, which is blue-shifted compared with that of reported Cu₂Se nanoparticles¹¹.

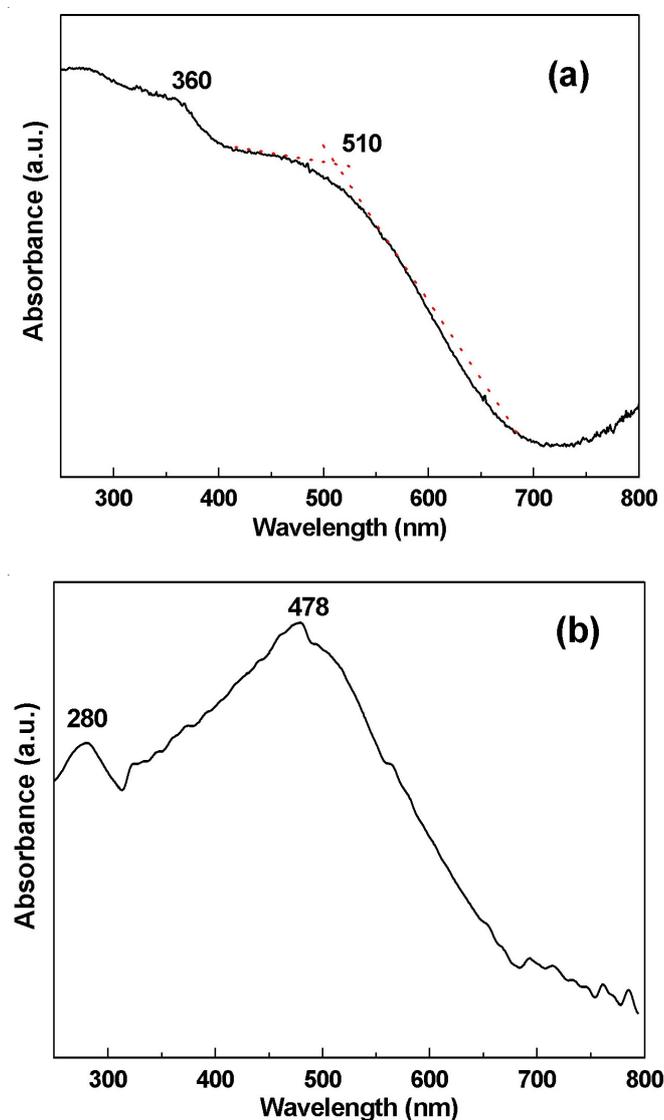


Fig. 4. UV-VIS absorption spectrum of (a) CuSe nanoflakes and (b) Cu₂Se nanoeartworms

Conclusion

In this work, we present a simple one-pot ultrasonic chemical reaction method to controllably prepare flake-shaped CuSe and earthworm-like Cu₂Se nanocrystals in the presence of reducing agent N₂H₄·H₂O. The molar ratio of Cu(CH₃COO)₂·H₂O to Se is important for controlling the phase and morphology of copper selenide. The synthesized CuSe products are 2D nanoflakes with sizes of 200–600 nm and thicknesses of 30–50 nm, including regular and deformed hexagonal shape. The obtained Cu₂Se are 1D nanoeartworms with diameters and lengths of 5–8 nm and 30–40 nm. UV-VIS absorption spectra indicate that the synthesized copper selenide nanocrystals have good optical properties.

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