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Galvanic synthesis of copper selenides $Cu_{2-x}Se$ and CuSe in alkaline sodium selenosulfate aqueous solution

Yu Jun Yang · Shengshui Hu

Abstract Spherical copper selenide nanoparticles (NPs) were prepared by a simple reaction of sodium selenosulfate with metal copper at room temperature in alkaline Na_2SeSO_3 aqueous solution. It is a galvanic process that operates on a coupled anodic copper oxidation and selenosulfate reduction. 1-Thioglycerol is found to catalyze this reaction. With gold and graphite as the positive electrodes, nanocrystallites of nonstoichiometric copper selenide ($Cu_{2-x}Se$) and stoichiometric copper selenides (CuSe) were produced, respectively. The XRD study shows that the produced CuSe and $Cu_{2-x}Se$ are in the pure hexagonal phase and clausthalite phase, respectively. Transmission electron microscopy images show that the diameters of the produced CuSe and $Cu_{2-x}Se$ NPs are in the range of 10~20 and 5~15 nm, respectively.

Keywords Copper selenide · Nanoparticles · Galvanic cell · Semiconductors · Catalysis

Introduction

In the past few decades, the semiconductor copper selenide has received great attention due to its particular photo-electrical properties and wide applications in electronic and optoelectronic devices, such as the solar cell, optical filter, super ionic conductors, thermo-electric converters, etc. [1–7]. Interestingly, as a kind of binary compound, copper selenide can exist in a wide range of stoichiometric compositions (CuSe, Cu_2Se, $CuSe_2$, Cu_3Se_2, Cu_5Se_4, Cu_7Se_4, etc.) and nonstoichiometric compositions ($Cu_{2-x}Se$) [8–11] and can be constructed into several crystallographic forms (monoclinic, cubic, tetragonal, hexagonal, etc.) [12]. The attraction of this material also lies in the feasibility of producing the ternary material $CuInSe_2$ [13, 14] and as an important surface impurity in Cu-rich $CuInSe_2$ [15]. Recently, Dusastre et al. [16] reported a route to selenides by the reaction of Se with elemental metals in amine solutions. Subsequently, several improved wet chemical methods were suggested by Zhang et al. [17] to prepare later transition metals and many main group metal sulfides and selenides. However, some of these approaches need special containers and/or high pressure, corrosive solvents (ethylenediamine) and/or chelating agents, and long reaction times [18–20]. All of these methods produce small nanoparticles, which are useful for optical signal processors and switches. Copper selenides in different stoichiometries are semiconductors with p-type conductivity and have been widely used in optical filters and superionic materials [21–23]. It has been reported that the thermal stability and the band gaps of copper selenides vary depending on their stoichiometries or phases [24, 25]. The composition and the crystal structure of the final products are usually dependent on the preparation methods [26–28]. $Cu_{2-x}Se$ is reported to possess a direct band gap of 2.2 eV and an indirect band gap of 1.4 eV for $x = 0.2$ [29]. The indirect band gap being near the optimal value for solar cell applications [30], the material could offer a high efficiency of conversion. Therefore, developing new methods for preparing high quality copper selenide crystals and to achieve control of their size or shape is of great importance.

Y. J. Yang · S. Hu (✉)
College of Chemistry & Molecular Sciences, Wuhan University,
Wuhan City 430072, People's Republic of China
e-mail: sshu@whu.edu.cn

Y. J. Yang · S. Hu
State Key Laboratory of Transducer Technology,
Chinese Academy of Sciences,
Beijing 100080, People's Republic of China

Herein, copper selenide nanoparticles (NPs) have been successfully prepared via a novel galvanic route with copper foil reacting with Na_2SeSO_3 in pH 7.4 aqueous solution. With copper foil as anode, highly stable CuSe and $Cu_{2-x}Se$ colloid solutions were produced with graphite and gold as the cathodes, respectively. This galvanic reaction operates on spontaneous anodic copper oxidation and cathodic selenosulfate reduction at room temperature. Further study reveals that 1-thioglycerol (TG) plays a crucial role in this reaction. TG not only acts as the capping agent of the produced copper selenide NPs but also catalyzes this reaction.

Experimental

A copper foil (1 cm×5 cm×0.25 mm) of analytical grade was used as anode. A gold foil or a graphite rod was used as the cathode. The copper foil was degreased with acetone, treated with 10% (wt.%) nitric acid to remove the oxide layer, polished with soft tissue paper, rinsed with distilled water, and then dried with high purity nitrogen gas. Both gold foil and graphite rod were polished with soft tissue paper and then washed with distilled water.

Sodium selenosulfate solution was prepared as follows: Dissolve 0.05 mol sodium sulfite in 100 mL distilled water. Then, add 0.005 mol elemental selenium into the solution. Reflux the solution under stirring in nitrogen gas for 72 h. The solution has to contain an excess of sodium sulfite to prevent selenosulfate from decomposing and selenium precipitating. The presence of excess sulfite produces two advantages. First, excess sulfite ions are able to stabilize the selenosulfate solution due to their reducing properties. Second, excess sulfite ions eliminate dissolved oxygen: $2SO_3^{2-} + O_2 \rightarrow 2SO_4^{2-}$ and the oxidation of copper by oxygen is safely avoided.

The solution was prepared as follows: A 10-mL beaker was used as the cell. Dissolve 10^{-4} mol TG in the Na_2SeSO_3 solution in 5 mL water. Adjust the solution pH to 7.0 with NaOH solution. Then, transfer 2 mL of the as-prepared Na_2SeSO_3 aqueous solution into the beaker. Finally, add water to make the final volume of 10 mL. The pH of the obtained solution is 7.4.

The setup of the galvanic cell is extremely simple. Connect anode (copper foil) and cathode (gold foil or graphite rod) with a conductive wire (copper wire in this experiment) and subsequently immerse them into the prepared solution under magnetic stirring. The distance between the cathode and anode was kept as 5 mm throughout the experiment. The color of the solution changed to black after 3 h of reaction at room temperature. Centrifuge the obtained colloid solution and wash the

precipitate with water and ethanol for several times. Black powder was obtained after being dried in vacuum oven at room temperature.

The open circuit potential (V_{OC}) of this galvanic cell was measured with a CHI660b Electrochemistry Workstation. The potential of the electrodes was measured with respect to the saturated calomel reference electrode throughout the experiment. The products were characterized using powder X-ray diffraction (XRD) and transmission electron microscopy (TEM). Powder X-ray diffraction (XRD) data were collected using a Siemens X-ray diffractometer at a scanning rate of 4°/min (the step size is 0.02° and the count time/step is 0.3 s) in the 2θ range from 10° to 90°, with graphite monochromatized Cu Kα radiation ($\lambda=$ 1.54056 Å). TEM images were obtained using a JOEL 100CX transmission electron microscope, operating at an accelerating voltage of 100 kV. The samples used for TEM were prepared by dispersing some products in ethanol followed by ultrasonic vibration for 30 min. One drop of the suspension was placed on a copper net, which was dried carefully in vacuum oven. Morphology study of the films on the copper electrode surface was carried out with a Quanta 200 scanning electron microscope (SEM; FEI Company, Holland).

Results and discussion

The reaction in this experiment is a galvanic reaction, which occurs immediately as both anode and cathode electrodes were immersed in the solution. Along with the oxidation of copper, Na_2SeSO_3 was reduced into Se^{2-}. In this experiment, TG favors the redox process on the electrodes surface. Copper can react directly with $SeSO_3^{2-}$ to form $Cu_{2-x}Se$ film on the surface [2]. However, copper selenide NPs were produced in the solution only upon the introduction of TG. Without the addition of TG, only black copper selenide thin films formed on the copper surface and the reaction is very slow. The solution remained transparent and no copper selenide NPs were produced in the solution even after 3 h of reaction under hard stirring. However, after the addition of TG, the reaction between copper and $SeSO_3^{2-}$ was significantly improved. The color of the solution changed from light green to brown immediately and finally to totally black after 3 h of reaction at room temperature. It is very clear that TG not only acts as the capping agent of the CuSe NPs but also catalyzes this reaction. We have reported the preparation of PbS nano-materials with a galvanic cell via the reaction between Pb and $Na_2S_2O_3$ under the catalysis of TG [31, 32]. The catalytic mechanism of TG on the hydrolysis of $SeSO_3^{2-}$ has also been investigated in our previous research [33]. In
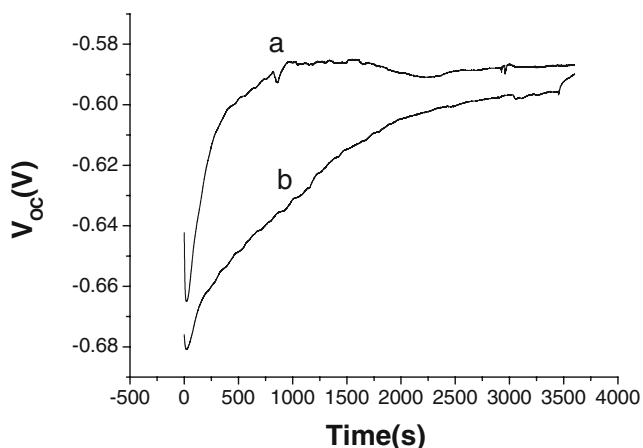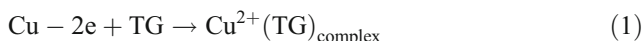
Fig. 1 Open circuit potential (V_{OC}) vs. time of the galvanic cell with copper as anode, graphite (*a*) and gold (*b*) as cathode in pH 7.4, 10^{-3} M Na_2SeSO_3 and 10^{-2} M TG aqueous solution without stirring

this experiment, TG molecules catalyze the reaction by facilitating the lost of electrons from copper via the formation of a stabilized complex with the Cu^{2+}:

$$Cu - 2e + TG \rightarrow Cu^{2+}(TG)_{complex} \quad (1)$$

Meanwhile, the production of Se^{2-} occurred on the electrodes surface:

$$SeSO_3^{2-} + 2e \xrightarrow{TG} SO_3^{2-} + Se^{2-} \quad (2)$$
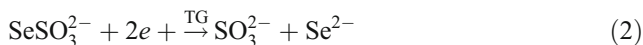
The cations and anions thus reacted to form CuSe:

$$Cu^{2+}(TG)_{complex} + Se^{2-} \rightarrow CuSe(TG)_{capping} \quad (3)$$

It is well known that the galvanic reaction rate is increased by the following factors: high conductivity of the medium, large potential difference between anode and cathode, low polarizability of anode and cathode, large area ratio of cathode to anode, and small distance from anode to cathode. As a galvanic reaction, it also occurs without connecting the cathode and anode electrodes in this experiment. However, the introduction of the cathode with a large surface area significantly accelerates the reaction rate. It is due to the fact that the relative areas of the anode and the cathode have an important effect on the galvanic reaction that occurs. A large cathode coupled with a small area of copper anode results in rapid penetration of copper because the galvanic current density at the small copper anode is very high, and anodic polarization in the solution is very limited. Just immersing the copper film in the solution under stirring, the solution turned into black copper selenide colloid solution after 8 h of reaction. After introducing the cathode, at pH 7.4, the light green and transparent solution changed into black colloid solution in less than 3 h under stirring. No deposition of copper selenide was observed on the copper foil surface. Without

stirring, thin copper selenide films visible to naked eyes were observed after 3 h of reaction. It can be concluded that the formation of the copper selenide thin films was prevented effectively by stirring. During this experiment, a competition between two different anode surface processes exists. One process is the formation of copper selenide particles, and the other is the deposition of copper selenide on anode. The employment of magnetic stirring greatly enhances the formation of copper selenide particles and effectively reduces the latter process.

The copper electrode was kept above the solution during the assembly of the cell. It was immersed into the solution just before the open circuit potential (V_{OC}) measurement, which was carried out without magnetic stirring. The plot of V_{OC} vs. time (Fig. 1a) shows that, for the galvanic cell with graphite as the cathode, V_{OC} decreased very quickly at early times, then leveled off after 500 s. Compared to the
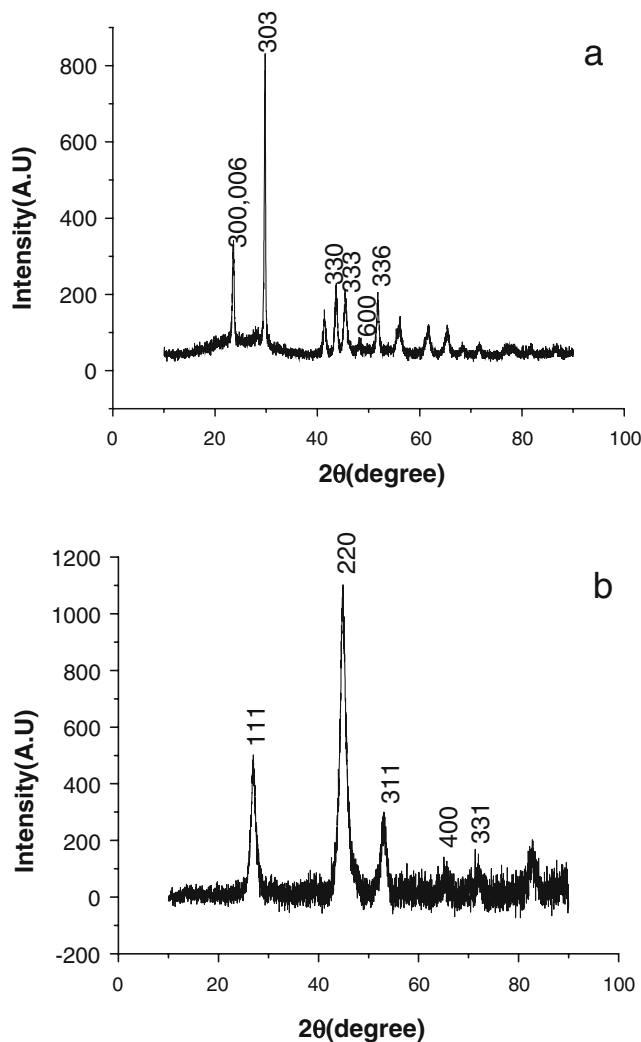

Fig. 2 XRD pattern of the CuSe (**a**) and $Cu_{2-x}Se$ (**b**) NPs synthesized with graphite and gold as the cathode, respectively, in pH 7.4, 10^{-3} M Na_2SeSO_3 and 10^{-2} M TG aqueous solution under magnetic stirring
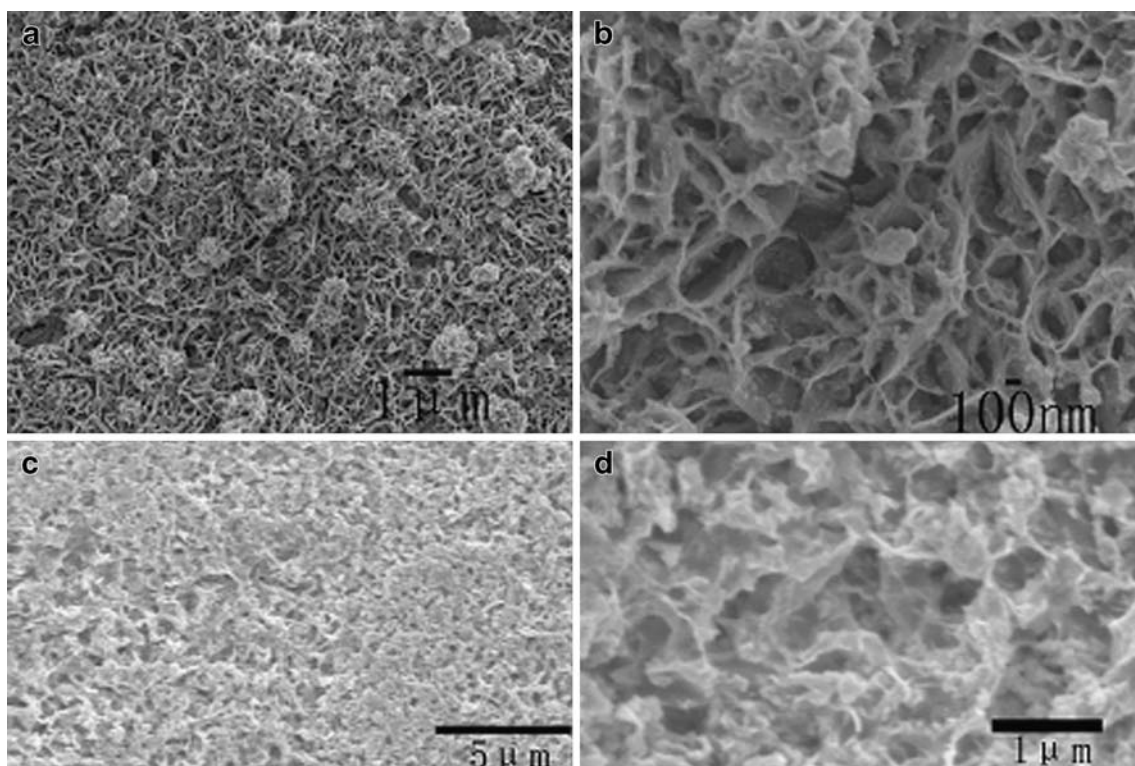
Fig. 3 SEM images of the CuSe (**a**, **b**) and $Cu_{2-x}Se$ (**c**, **d**) films deposited on the copper electrode surface in pH 10.0, 10^{-3} M Na_2SeSO_3 and 10^{-2} M TG aqueous solution under magnetic stirring; **a**, **c** coverage of the copper surface; **b**, **d** copper selenide films in greater details

galvanic cell using graphite as cathode, the V_{OC} of the galvanic cell using gold as cathode decreased very slowly initially. This was followed by a gradual decrease of V_{OC} during the rest of the galvanic reaction. The decrease of V_{OC} is due to the deposition of copper selenide on the electrode surface and the passivation of anode by the copper selenide thin layer. Our supposition is further confirmed by the fact that V_{OC} remains constant when the solution is stirred.

Xie et al. have discovered that the employment of ultrasonic irradiation played an important role in the formation of different phases of copper selenides [20]. In this experiment, it was found out that the cathode materials of the cell play a key role in determining the phase of the final products. With graphite as cathode, copper was oxidized into Cu^{2+} ions, leading to the formation of CuSe. Meanwhile, with gold as cathode, $Cu_{2-x}Se$ was formed. It was also discovered that $Cu_{2-x}Se$ was produced when just immersing a copper foil in the solution under stirring, although the reaction rate was pretty low. V_{OC} is different with graphite and gold as cathode. The formation of different phases of copper selenides is probably due to the different potential differences between anode and cathode (V_{OC}). In a galvanic cell with copper anode, copper may be oxidized to Cu^+ and/

or Cu^{2+}. It was reported that both Cu^+ and Cu^{2+} ions may be present on the electrode surface and in the solution at the same time [34]. In this experiment, it is probable that the lower potential difference between gold and copper favors the oxidation of major Cu into Cu^+ to form $Cu_{2-x}Se$.

As shown in the powder XRD patterns of copper selenide (Fig. 2), with graphite rod and gold foil as the cathode (positive electrode), stoichiometric copper selenide (CuSe) and nonstoichiometric copper selenide ($Cu_{2-x}Se$) NPs were produced in the solution, respectively. The intensity and position of the diffraction peaks of CuSe are in good agreement with the literature value (JCPDS Card File, No. 20-1020), which was indexed to be pure hexagonal phase (Fig. 2a). The intensity and position of the diffraction peaks of $Cu_{2-x}Se$ are in good agreement with the literature value (JCPDS Card File, No. 6-354), which was indexed to be pure clausthalite phase (Fig. 2b). The average crystal size was estimated using the well-known Debye–Scherrer relationship [35]:

$$T = k\lambda / D\cos\theta \qquad (4)$$

Where θ is the Bragg angle, λ is the X-ray wavelength, T is the crystal size, k is the Scherrer constant (0.94) and D is
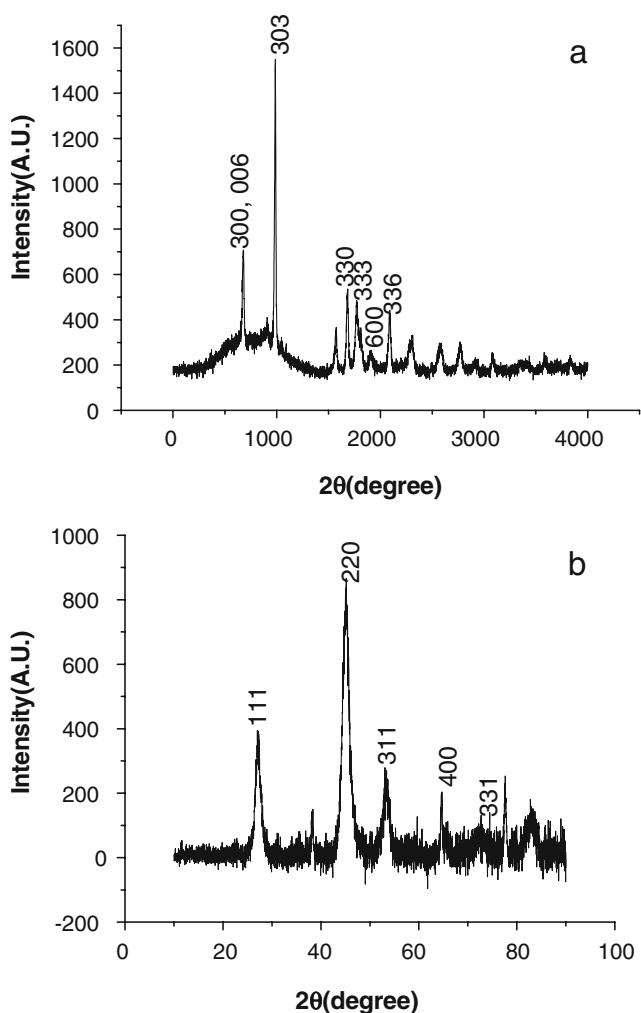
Fig. 4 XRD pattern of the CuSe (a) and Cu$_{2-x}$Se (b) films deposited on the copper electrode surface in pH 10.0, 10^{-3} M Na$_2$SeSO$_3$ and 10^{-2} M TG aqueous solution under magnetic stirring
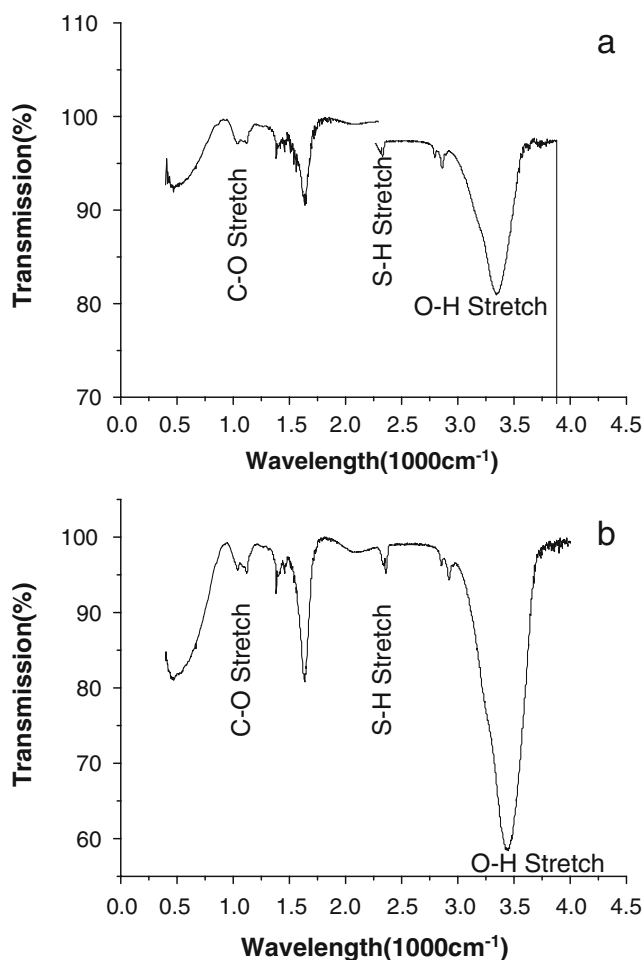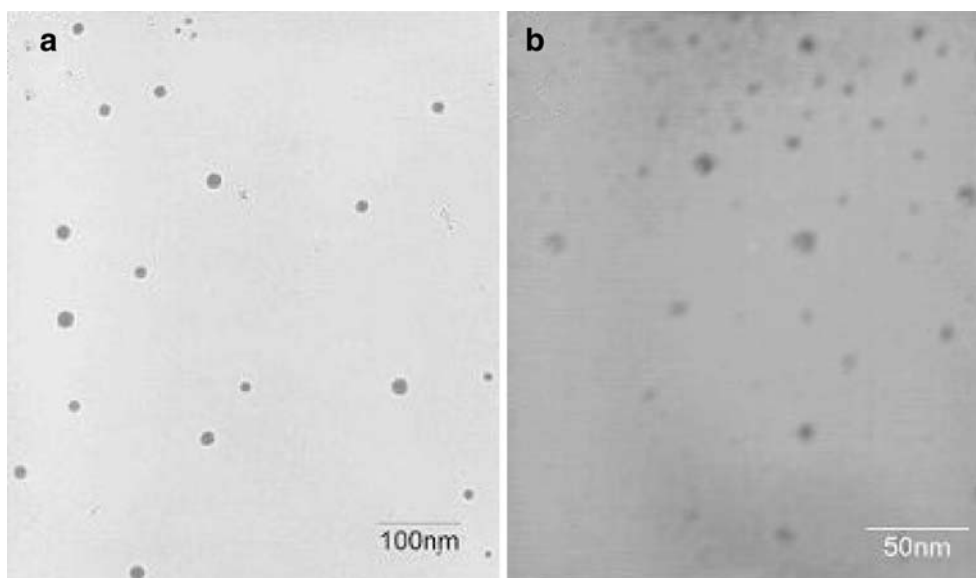

Fig. 6 Fourier transform infrared spectra of TG protected CuSe (a) and Cu$_{2-x}$Se (b) NPs synthesized with graphite and gold as the cathode, respectively, in pH 7.4, 10^{-3} M Na$_2$SeSO$_3$ and 10^{-2} M TG aqueous solution under magnetic stirring

Fig. 5 TEM image of the CuSe (a) and Cu$_{2-x}$Se (b) NPs synthesized with graphite and gold as the cathode, respectively, in pH 7.4, 10^{-3} M Na$_2$SeSO$_3$ and 10^{-2} M TG aqueous solution under magnetic stirring

the half width of the diffraction peak. It was found that the average crystal sizes of CuSe and $Cu_{2-x}Se$ are calculated to be about 17 and 8 nm, respectively, according to the Debye–Scherrer equation.

The solution used in this experiment is alkaline. When the solution pH is above 7.0, it is light green and transparent. No evolution of elemental selenium was observed. However, if the solution pH is lower than 7.0, it became pink and turbid due to the decomposition of Na_2SeSO_3 and the release of elemental selenium. Thus, in order to obtain pure copper selenide NPs, this experiment must be carried out in alkaline solution.

Adjusting the solution pH with concentrated NaOH, further study showed that the solution pH had a great effect on the preparation of copper selenide NPs. Before the experiment, the solution is light green and transparent at pH 7.4. After the immersion of electrodes for 3 h, the solution turned into black and no deposition was observed on copper under magnetic stirring. The obtained colloid solution was highly stable and no precipitate was observed after even 1 month. As the solution pH increased, the deposition of copper selenide on the copper surface became more and more serious. At pH 10.0, the solution remained light green and transparent after 3 h of reaction under hard stirring, while the copper electrode surface was covered by copper selenide film (Fig. 3). When the stirring was stopped, only some very large black flakes were observed at the bottom of the cell. These flakes are parts of the selenide film, which peeled off from the copper surface. In other words, the copper selenide colloid solution cannot be obtained at pH 10.0. The SEM study showed that the copper selenide thin films deposited on copper (Fig. 3a and c). High magnification microscopy revealed the nano-porosity of these films (Fig. 3b and d). XRD analysis indicated that with graphite rod and gold foil as the cathode the films deposited on copper were CuSe (Fig. 4a) and $Cu_{2-x}Se$ (Fig. 4b), respectively.

The morphology of the produced NPs was studied with transmission electron microscopy. As shown in Fig. 5, the produced CuSe and $Cu_{2-x}Se$ NPs are spherical and the diameters of CuSe and $Cu_{2-x}Se$ NPs are in the range of 10~20 nm (Fig. 5a) and 5~15 nm (Fig. 5b), which were in good accordance with the results calculated from the XRD.

The FT-IR spectra of the produced CuSe (Fig. 6a) and $Cu_{2-x}Se$ (Fig. 6b) crystals show strong and broad O–H stretching bands at 3,500 cm^{-1}, weak S–H stretching bands at 2,400 cm^{-1}, and strong C–O stretching bands at 1,100 cm^{-1}. The FT-IR spectra confirm (a) that the copper selenide crystals were capped with TG and (b) that the TG molecule is not leached out during several washings of the copper selenide crystals.

Conclusions

A galvanic approach to the preparation of different phases of copper selenide is reported. Copper was found to spontaneously dissolve in the pH 7.4 solution containing Na_2SeSO_3, Na_2SO_3, and TG. The two half-cell reactions are the oxidation of copper and the reduction of seleno-sulfate. TG was discovered to catalyze this redox process. Here, the effect of V_{OC} has been investigated in the formation of different phases of copper selenide ($Cu_{2-x}Se$ and CuSe). Our experiment results suggest that this galvanic synthetic technique may be a cheap, convenient, and quick method to prepare copper selenide NPs.

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