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Sonochemical Synthesis and Mechanistic Study of Copper Selenides $Cu_{2-x}Se$, β-CuSe, and Cu_3Se_2

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Nanocrystallites of nonstoichiometric copper selenide ($Cu_{2-x}Se$) and stoichiometric copper selenides (β-CuSe and Cu_3Se_2) were synthesized in different solutions via sonochemical irradiation at room temperature. The influence of solvents, surfactants, and ultrasonic irradiation on the morphology and phase of products has been investigated. The morphological difference of the products was mainly affected by the solvents and surfactants, which can self-aggregate into lamellar structures or microemulsions, and then these unique structures can act as both supramolecular template and microreactor to direct the growth of copper selenides. On the other hand, it was also found that the sonochemical irradiation and solvents played an important role in the formation of different phases of copper selenides. The proposed formation mechanism of copper selenides is discussed.

Introduction

In the past decades, extensive attention has been paid to the preparation and characterization of semiconductor selenides, owing to their interesting properties and potential applications.[1,2] Among these materials, copper selenides are very important semiconductors with p-type conductivity, which have potential applications in solar cells,[3] as an optical filter,[4] and as a supersonic material.[2] $Cu_{2-x}Se$ was reported to possess a direct band gap of 2.2 eV and an indirect band gap of 1.4 eV for $x = 0.2$,[5] which can offer a high efficiency of conversion. Therefore, considerable progress has been made in the study of copper selenides and many methods have been applied to prepare these important semiconductors, such as heating the mixture of Cu and Se powders up to 400−470 °C in flowing Ar gas[6] or using toxic H_2Se as selenium source.[4] Copper selenide thin films with different compositions were obtained by the mild chemical deposition route.[7−11] Our group[12−14] reported solvothermal and γ-irradiation routes to nonstoichiometric $Cu_{2-x}Se$ nanocrystallite, but in their synthetic processes, the Teflon-lined autoclave and ^{60}Co source have to be used, respectively.

In the past years, sodium selenosulfate, as a promising Se source, has been widely used to prepare metal selenides,[15] which are often nanocrystallites, such as CdSe[16] and PbSe.[17] Lakshmi et al.[7] and Nair and co-workers[8] have also reported the preparation of chemically deposited copper selenide ($Cu_{2-x}Se$ and Cu_3Se_2) thin films, using sodium selenosulfate as the Se source. Currently, the sonochemial process has been proved to be a useful technique for generating novel materials with unusual properties.[18] The chemical effects of ultrasound, which arise from acoustic cavitation, formation, growth, and implosive collapse of bubbles in a liquid, will produce unusual chemical and physical environments. Ohtani et al.[19] reported that the ultrasonic irradiation could accelerate the

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(1) Lakshmikvmar, S. T. *Sol. Energy Mater. Sol. Cells* **1994**, *32*, 7.
(2) Korzhuev, A. A.; Khim, F. *Obrab. Mater.* **1991**, *3*, 131.
(3) Hiroto, U. *Jpn. Kokai Tokkyo Koho* JP 01 298 010, 1989.
(4) Toyoji, H.; Hiroshi, Y. *Jpn. Kokai Tokkyo Koho* JP 02 173 622, 1990.
(5) Hermann, A. M.; Fabick, L. *J. Crystal Growth* **1983**, *61*, 658.
(6) OshitasiAkira. *Jpn. Kokai Tokkyo Koho* JP 61 222 910, 1986.
(7) Lakshmi, M.; Bindu, K.; Bini, S.; Vijayakumar, K. P.; Kartha, C. S.; Abe, T.; Kashiwaba, Y. *Thin Solid Films* **2000**, *370*, 89.
(8) Garcia, V. M.; Nair, P. K.; Nair, M. T. S. *J. Crystal Growth* **1999**, *203*, 113.
(9) Mondal, A.; Pramanik, P. *J. Solid State Chem.* **1983**, *47*, 81.
(10) Mondal, A.; Pramanik, P. *J. Solid State Chem.* **1984**, *55*, 116.
(11) Padam, G. K. *Thin Solid Films* **1987**, *150*, 189.
(12) Zhang, W. X.; Zhang, X. M.; Zhang, L.; Wu, J. X.; Hui, Z. H.; Cheng, Y. W.; Liu, J. W.; Xie, Y.; Qian, Y. T. *Inorg. Chem.* **2000**, *39*, 1838.
(13) Wang, W. Z.; Yan, P.; Liu, F. Y.; Xie, Y.; Geng, Y.; Qian, Y. T. *J. Mater. Chem.* **1998**, *8*, 2321.
(14) Qiao, Z. P.; Xie, Y.; Xu, J. G.; Liu, X. M.; Zhu, Y. J.; Qian, Y. T. *Can. J. Chem.* **2000**, *78*, 1143.
(15) Kitaev, G. A.; Khvorenkova, A. Z. *Russ. J. Appl. Chem.* **1998**, *71* (8), 1325.
(16) Kale, S. S.; Lokhande, C. D. *Mater. Chem. Phys.* **2000**, *62* (2), 103.
(17) Kitaev, G. A.; Khvorenkova, A. Z. *Russ. J. Appl. Chem.* **1999**, *72* (1), 55.
(18) Suslick, K. S. *Ultrasound: Its Chemical, Physical and Biological Effects*; VCH: Weinheim, Germany, 1988.
(19) Ohtani, T.; Nonaka, T.; Araki, M. *J. Solid State Chem.* **1998**, *138*, 131.

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reaction between Cu and Se powders and found that the interparticle collisions induced by the ultrasonic irradiation could impinge upon the surface of Cu and Se, which produced a freshly exposed and highly reactive surface. Furthermore, the transient high temperature generated from the interparticle collisions had an important influence on the impact points. Therefore, the ultrasonic irradiation accelerated the reaction between Cu and Se, and meanwhile reduced the reaction time from the natural 3 days to 8 h. Gedanken and co-workers[20] and Suslick et al.[21] have used sonochemical irradiation to produce a variety of nanostructural materials, which are often amorphous. On the basis of previous research, our group has successfully expanded this method to prepare nanoscale metal chalcogenides.[22,23] Here, we successfully obtained the different pure phases of copper selenides in water/ethanol or water/hexanol solutions via the sonochemical irradiation method under ambient conditions using CuI and Na_2SeSO_3 as the raw materials.

Experimental Section

Sodium selenosulfate (Na_2SeSO_3) was prepared according to the literature.[24] A typical procedure is as follows: appropriate amounts of CuI (0.5 g, 2.6 mmol) and excess Na_2SeSO_3 (20 mL, 5 mmol) were added to a 120 mL titanium container filled with distilled water and absolute ethanol or hexanol and sodium dodecyl sulfate (SDS) or cetyltrimethylammonium bromide (CTAB) as surfactants up to 80 vol % of the capacity. The solution was purged with nitrogen for 30 min and then the container was sealed and kept in a circulating water bath to maintain the temperature of the bulk solution at 20 ± 5 °C. The solution was irradiated with high-intensity ultrasound (Model R = 1 cm, Ti horn, 40 kHz, ≈100 W/cm^2) 4 h. The black-brown precipitates were collected and washed with aqueous ammonia, distilled water, and absolute ethanol in turn to remove the residues, and then the final products were dried in a vacuum at 50 °C for 10 h.

X-ray powder diffraction (XRD) patterns were collected on a Japan Rigaku D/max-rA X-ray diffractometer with Cu Kα radiation (λ = 1.54178 Å). The scan rate of 0.05°/s was applied to record the pattern in the 2θ range of 10−70°. The morphology and size of as-prepared products were observed by transmission electron microscope (TEM) images, which were taken on a Hitachi Model H-800 instrument, with an accelerating voltage of 200 kV. The X-ray photoelectron spectra (XPS) of the products were collected on an Escalab MKII instrument, with Mg Kα X-ray as the excitation source.

Results and Discussion

Under ultrasonic irradiation, several interesting copper selenide phases, such as $Cu_{2-x}Se$, β-CuSe, and Cu_3Se_2, are produced by the reaction of CuI and Na_2SeSO_3 in different solutions, and the experimental conditions are listed in Table 1. The products are characterized by X-ray powder diffraction (XRD), transmission electron microscopy (TEM), X-ray photoelectron spectra (XPS), and electronic diffraction (ED) techniques. The XRD patterns for cubic $Cu_{2-x}Se$ (a), orthorhombic β-CuSe (b), and tetragonal Cu_3Se_2 (c) are shown in Figure 1. All the reflection peaks in the XRD patterns can be indexed to the corresponding pure phases,[25] and all the lattice parameters are very close to the reported data, which are shown in Table 2. Comparison of Figure 1b with the corresponding reflections in standard samples of β-CuSe reveals a preferential alignment along the (006) plane. The adsorption of the surfactant molecules on the (111) plane prevents any side interconnections with more copper selenides, thus inhibiting further growth.[26] In the case of $Cu_{2-x}Se$, the average size of particles calculated from the Scherrer

Table 1. Experimental Conditions and Results of Reaction of CuI with $NaSeSO_3$[a]

no.	solvent	volume ratio	surfactant	products
1	water			β-CuSe
2	water/ethanol	1:1	SDS (0.2 M)	β-CuSe
3	water/ethanol	1:1	none	Cu_3Se_2
4	water/hexanol	1:1	CTAB (0.03 M)	$Cu_{2-x}Se$
5	water/hexanol	1:9	CTAB (0.003 M)	$Cu_3Se_2(Cu_{2-x}Se)$
6	water/hexanol	2:98	none	$Cu_3Se_2(Cu_7Se_4)$
7	water/cyclohexane	4:2	CTAB (0.003 M)	$Cu_{2-x}Se$
8	water/ hexanol	1:4	CTAB (0.003 M)	$Cu_{2-x}Se$
9	water/enthano l	1:1	dodecylamine (0.015 M)	none
10	water/heptane	1:1	PVP (0.0015 M)	none

[a] Reaction time was 4 h in all cases listed.

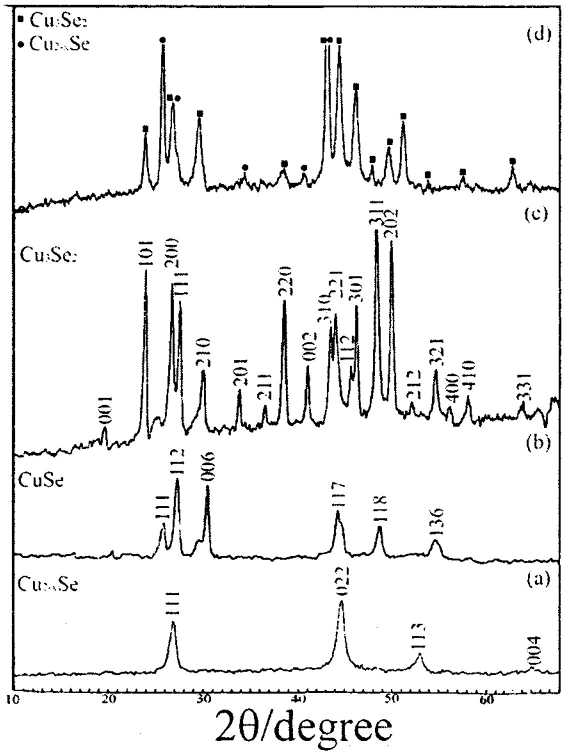

Figure 1. XRD patterns of (a) $Cu_{2-x}Se$, (b) β-CuSe, (c) Cu_3Se_2, and (d) $Cu_{2-x}Se$ and Cu_3Se_2 mixture phase nanocrystals.

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(20) (a) Dhas, N. A.; Gedanken, A. *Chem. Mater.* **1999**, *11*, 806. (b) Ramesh, S.; Koltypin, Y.; Prozorov, R.; Gedanken, A. *Chem. Mater.* **1997**, *9*, 546.

(21) (a) Suslick, K. S.; Fang, M.; Hyeon, T. *J. Am. Chem. Soc.* **1996**, *118*, 11960; (b) Mdleleni, M. M.; Hyeon, T.; Suslick, K. S. *J. Am. Chem. Soc.* **1998**, *120*, 6189.

(22) Li, B.; Xie, Y.; Huang, J. X.; Qian, Y. T. *Ultrason. Sonochem.* **1999**, *6*, 217.

(23) Li, B.; Xie, Y.; Huang, J. X.; Liu, Y.; Qian, Y. T.; Liu, X. M. *Chem. Mater.* **2000**, *12*, 2614.

(24) Pejova, B.; Najdoski, M.; Grozdanov, I.; Dey, S. K. *Mater. Lett.* **2000**, *43*, 269.

(25) JCPDS file numbers are 6-680 for $Cu_{2-x}Se$, 27-184 for β-CuSe, and 19-402 for Cu_3Se_2.

Table 2. Cell Parameters and Particle Size of Copper Selenides

products	cell parameters/Å		phase	JCPDS file	morphology
	calcd	theor			
β-CuSe	$a = 3.960$ $b = 6.969$ $c = 17.194$	$a = 3.948$ $b = 6.958$ $c = 17.239$	orthorhombic	27-184	flakelike
Cu_3Se_2	$a = 6.416$ $c = 4.259$	$a = 6.406$ $c = 4.282$	tetragonal	19-402	grainlike
$Cu_{2-x}Se$	$a = 5.74$	$a = 5.72$	cubic	6680	grainlike

formula is 25−30 nm. Figure 1d shows one mixed XRD pattern for $Cu_{2-x}Se$ and Cu_3Se_2.

TEM images for the as-prepared products are shown in Figure 2, which indicate the different morphologies of products. From Figure 2a, one can see that the product of $Cu_{2-x}Se$ consists of nearly spherical grains with an average size of about 25−30 nm, which is consistent with the XRD results. This can also prove that the broadening of the peaks is caused by the small particle size rather than lattice distortion in the nanocrystallite.[9] The corresponding electronic diffraction (ED) pattern of $Cu_{2-x}Se$ is shown in Figure 2b, in which three fringe patterns with plane distance of 2.86, 1.74, and 1.48 Å could be observed. They are consistent with the indices (002), (113), and (004) planes of pure cubic $Cu_{2-x}Se$. Figure 2 panels c and d show that the product of β-CuSe displays flakelike shapes with different widths and lengths. Figure 2e displays the ED image of as-prepared β-CuSe, which shows the products to be almost single crystals. (The incident beam is oriented along the direction of [100].) Spherical Cu_3Se_2 grains in Figure 2f show the presence of dense agglomerates because of the small dimensions and high surface energy of the nanocrystals.

Figure 3 shows the X-ray photoelectron spectra (XPS) of the as-prepared products. The binding energy values are 932.35 eV for Cu 2p and 54.00 eV for Se 3d in $Cu_{2-x}Se$ (a), 934.40 eV for Cu 2p and 53.75 eV for Se 3d in β-CuSe (b), and 934.10 eV for Cu 2p and 53.40 eV for Se 3d in Cu_3Se_2 (c), respectively. All of the observed binding energy values for Cu 2p and Se 3d are nearly in agreement with the reported data in the literature.[27] The shake-up peak of Cu(I) (Figure 3a, arrowed) indicates that parts of the surface of $Cu_{2-x}Se$ are oxidized. According to Figure 3a, one can see that Cu(I) and Cu(II) are all situated on the surface of $Cu_{2-x}Se$. The peaks (934.40 eV, Figure 3b, arrowed) come from β-CuSe, but the peak (931.70 eV) indicates that small Cu(I) exists on the surface of β-CuSe, which perhaps comes from the adhered raw materials Cu(I). Peak areas of these high-resolution scans are measured and used to calculate the Cu-to-Se ratio for the nanocrystals. The quantification of peaks gives atomic ratios of Cu to Se of 1.86:1, 0.91:1, and 1.48:1 for $Cu_{2-x}Se$, β-CuSe, and Cu_3Se_2, respectively, which are nearly consistent with the given formula for the as-prepared products within the experimental errors.

The influence of surfactants, solvents, and ultrasonic irradiation on the morphology and phase of the final products was carefully investigated in the sonochemical synthesis process. It is well-known that the presence of surfactants during the formation of nanomaterials has a great effect on the shape and size of the final products.[26,28] And the self-aggregated structures formed by surfactants in selective solvents would direct the growth of products. Therefore, much attention has been paid to the study of such supramolecular structures, which can act as both template and microreactor for the successive growth of products, and it has been proved to be an effective structure director to control the morphology of nanomaterials.[29] For example, sodium dodecyl sulfate (SDS) molecules can self-aggregate into a series of peculiar structures, such as cubic, hexagonal, and lamellar, with increasing concentration in solutions. It was reported that SDS would self-aggregate into lamellar structure when its concentration increased to a certain extent (ca. 0.2 mol/L).[29d] In this work, we used this unique SDS lamellar structure to provide special interlayer spaces to limit the preferential growth and direct arrangement of copper selenide particles in the two-dimensional direction. As a result, the flakelike β-CuSe was produced. A schematic illustration of the aggregation in lamellar structure of SDS molecules and the formation of flakelike β-CuSe are shown in Figure 4.

It is well-known that cetyltrimethylammonium bromide (CTAB) is a kind of effective surfactant, which has been widely investigated and applied to control the morphology of nanomaterials.[30] In the synthesis of $Cu_{2-x}Se$ in a water/CTAB/*n*-hexanol system, the use of sonication favors emulsification of the solutions.[31] The surfactant-covered water pools offer a unique microenvironment for the formation of nanoparticles,[29c] because the absorption of CTAB molecules on the surface of the particle inhibits the excess aggregation of copper selenides when the particle size is appropriate to that of the water pool. Therefore, the $Cu_{2-x}Se$ particles obtained in such a medium are very fine and highly monodispersive with diameters of ca. 25−30 nm.

Ultrasonic irradiation, a novel energy source, can drive chemical reactions such as oxidation, reduction, dissolution, decomposition,[18] and polymerization[32] to process under ambient conditions. In the liquid−solid heterogeneous system, the use of ultrasound can accelerate the solubility of CuI in the selenosulfate solution and enhance the speed of reactions. It is known that some reactions cannot proceed just due to surface limits, such as a passivated surface oxide coating. The effects of interparticle collision, microjet, and shock wave can drive high-speed jets of liquid to impinge

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(26) Salkar, R. A.; Jeevanandam, P.; Kataby, G.; Aruna, S. T.; Koltypin, Y.; Palchik, O.; Gedanken, A. *J. Phys. Chem. B.* **2000**, *104*, 893.

(27) Wagner, C. D.; Riggs, W. W.; Davis, L. E.; Moulder, J. F.; Muilenberg, G. E. *Handbook of X-ray Photoelectron Spectroscopy*; Physical Electronics Division, Perkin-Elmer Corporation: Eden Prairie, MN, 1979.

(28) (a) Jeevanandam, P.; Koltypin, Y.; Mastai, Y.; Gedanken, A. *J. Mater. Chem.* **2000**, *10*, 2143. (b) Lisiecki, I.; Billoudet, F.; Pileni, M. P. *J. Phys. Chem*. **1996**, *100*, 4160.

(29) (a) Huo, Q.; Margolese, D. I.; Ciesla, U.; et al. *Chem. Mater*. **1994**, *6*, 1176; (b) Tolbert, S. H.; Sieger, P.; Stucky, G. D.; et al. *J. Am. Chem. Soc.* **1997**, *119*, 8652; (c) Chen, D. H.; Wu, S. H. *Chem. Mater*. **2000**, *12*, 1354. (d) Qi, L. M.; Ma, J. M. *Chem. J. Chin. Univ.* **1999**, *20*, 507.

(30) (a) Schuth, F.; Ciesla, U.; Schacht, S.; Thieme, M.; Huo, Q.; Stucky, G. *Mater. Res. Bull*. **1999**, *34* (3), 483. (b) Nagy, J. *Colloids Surf.* **1989**, *35*, 201. (c) Wachhold, M.; Kanatzidis, M. G. *Chem. Mater*. **2000**, *12* (10), 2914. (d) Bonhommer, F.; Kanatzidis, M. G. *Chem. Mater*. **1998**, *10* (4), 1153.

(31) Beal, H. M.; Skauen, D. M. *J. Am. Pharm. Assoc.* **1955**, *44*, 487, 490.

(32) Kruus, P.; O'Neil, M.; Robertson, D. *Ultrasonics* **1990**, *28*, 304.

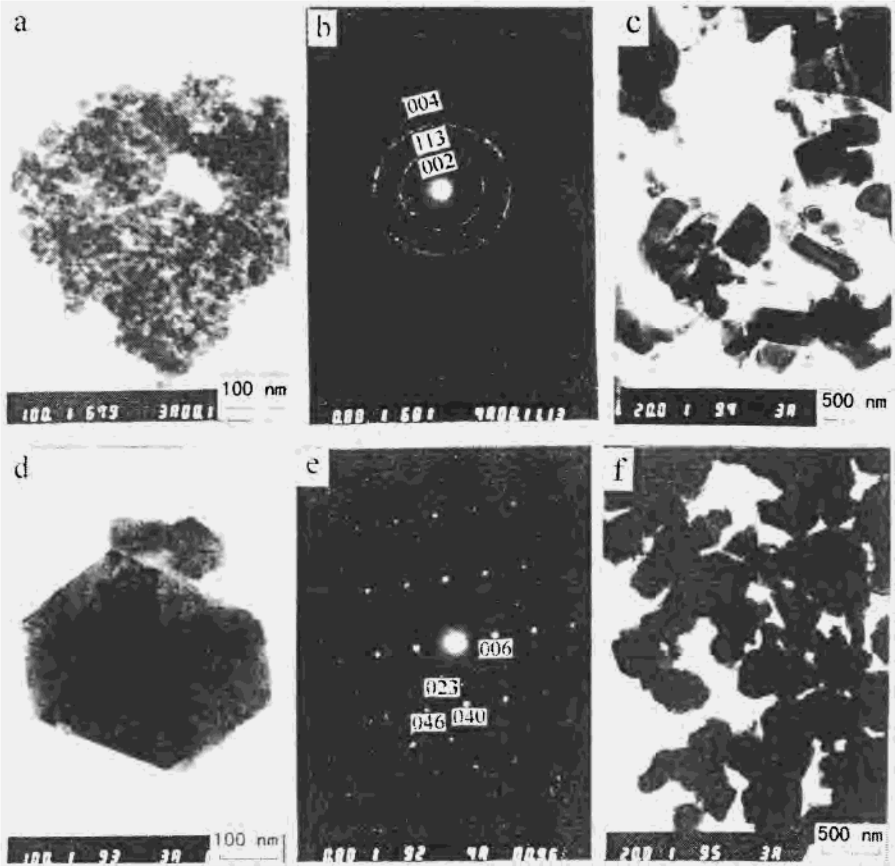

Figure 2. (a) TEM image of $Cu_{2-x}Se$. (b) ED pattern of $Cu_{2-x}Se$. (c) TEM image of β-CuSe with low magnification. (d) TEM image of β-CuSe with high magnification. (e) ED pattern of β-CuSe. (f) TEM image of Cu_3Se_2.

upon the surface of CuI, removing this coating and creating a localized erosion to produce a newly exposed and highly reactive surface. At the same time, the ultrasound improves mass transport and causes particle (CuI) fragmentation, which substantially increase the surface of CuI. Hence, the reaction can proceed easily and rapidly at room temperature. Suslick et al.[33] reported that there are three regions of sonochemical activity: (i) the inside of the collapsing bubble ($T > 5000$K), (ii) the interface between the bubble and the liquid ($T \approx 1900$ K), and (iii) the bulk solution, which is at room temperature. If the reaction takes place inside the collapsing bubble, the products obtained are amorphous as a result of the high cooling rates ($>10^{10}$ K/s); on the other hand, if the reaction takes place at the interface, one expects to obtain crystalline products. In the liquid-state system, CuI and Na_2SeSO_3 are certainly involatile under normal conditions; the solution is ionic and has a low vapor pressure. Hence, the formation of crystalline phase was proposed to occur within the interfacial region. This can also be proved by the XRD and ED patterns, from which we can observe the products with high crystallinity.

The possible reaction steps and explanations for the sonochemical processing of copper selenides are described below. First, in the interfacial region Se^{2-} can be released from sodium selenosulfate due to the local high temperature. And water molecules generate $H^•$ and $OH^•$ radicals under ultrasound irradiation:

$$H_2O \xrightarrow{\text{ultrasound}} H^\bullet + OH^\bullet \qquad (1)$$

In the absence of any scavengers, the $H^•$ and $OH^•$ radicals readily recombine to produce H_2O_2:[34]

$$2H^\bullet/2OH^\bullet \rightarrow H_2/H_2O_2/H_2O \qquad (2)$$

Weissler[35] reported that the formation of H_2O_2 is easier in the presence of trace oxygen, simplified in the following equation:

$$HO^\bullet + OH^\bullet \rightarrow H_2O_2 \text{ (major)} \qquad (3)$$

The traces of oxygen in the solution would result in the formation of $HO_2^•$, which would also recombine to H_2O_2:[35]

$$H^\bullet + O_2 \rightarrow HO_2^\bullet \qquad (4)$$

$$HO_2^\bullet + HO_2^\bullet \rightarrow H_2O_2 + O_2 \qquad (5)$$

It is reported that the oxidant H_2O_2 and $OH^•$ radicals can initiate the oxidization of Fe^{2+} into Fe^{3+} in the sonochemical

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(33) (a) Suslick, K. S.; Hammerton, D. A.; Cline, R. E. *J. Am. Chem. Soc.* **1986**, *108*, 5641; (b) Grinstaff, M. W.; Cichowlas, A. A.; Choe, S. B.; Suslick, K. S. *Ultrasonics* **1992**, *30*, 168. (c) McNamara, W. B., III; Didenko, Y. T.; Suslick, K. S. *Nature* **1999**, *401*, 772.

(34) Gutierrez, M.; Henglein, A.; Dohrmann, J. *J. Phys. Chem.* **1987**, *91*, 6687.

(35) Weissler, A. *J. Am. Chem. Soc.* **1959**, *81*, 1077.

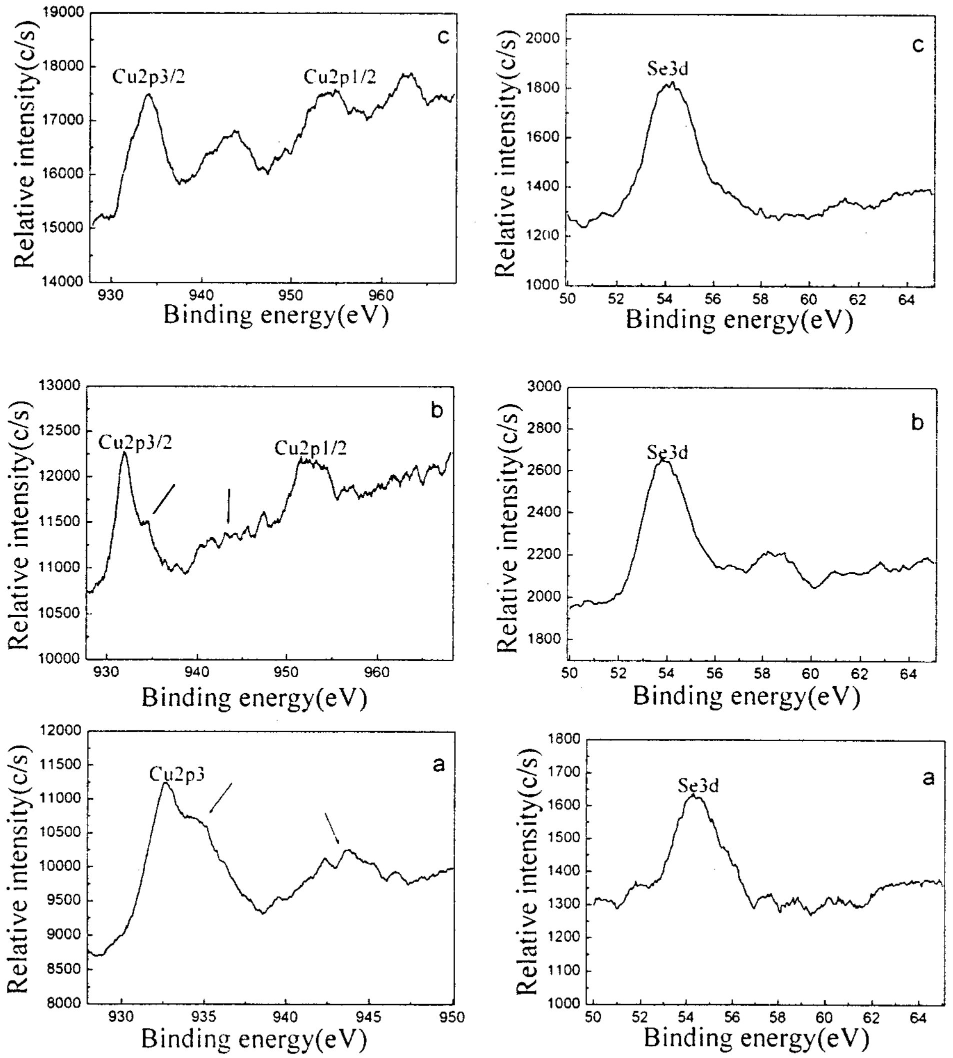

Figure 3. XPS spectra of (a) $Cu_{2-x}Se$, (b) β-CuSe, and (c) Cu_3Se_2.

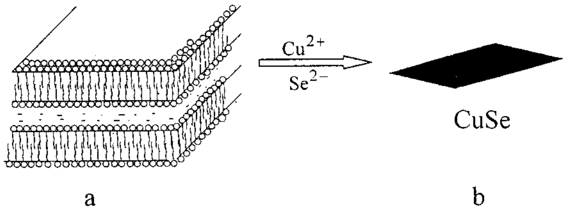

Figure 4. Schematic illustration of (a) the self-aggregated lamellar structure of SDS molecules at certain concentrations and (b) the formation of flakelike β-CuSe.

irradiation process.[36,37] Therefore, it is reasonable that H_2O_2 and $OH^\bullet$ radicals can also initiate the oxidation of Cu^+ into Cu^{2+} [$\varphi^0(Cu^{2+}/Cu) = 0.153\ V < \varphi^0(Fe^{3+}/Fe^{2+}) = 0.771\ V$]:

$$2Cu^+ + H_2O_2 \rightarrow 2Cu^{2+} + 2OH^- \quad (6)$$

$$Cu^+ + OH^\bullet \rightarrow Cu^{2+} + OH^- \quad (7)$$

$$Cu^{2+} + Se^{2-} \rightarrow CuSe \quad (8)$$

While CuI is only sparingly soluble in water, it is more soluble in selenosulfate, with which it can form complexes. The whole sonochemical irradiation process can be explicitly explained by Figure 5.

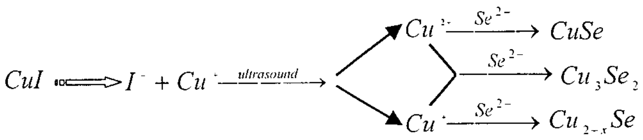

Figure 5. Schematic illustration of the formation of copper selenides by sonochemical irradiation.

In the sonochemical irradiation process, the concentration of H_2O_2 plays a key role in determining the phase of final products. A sufficient amount of H_2O_2 can oxidize all of the Cu^+ into Cu^{2+} ions, leading to the formation of CuSe. Meanwhile, insufficient H_2O_2 only oxidizes parts of Cu^+ into Cu^{2+} to form $Cu_{2-x}Se$ or Cu_3Se_2. Hengleinand Korman[38] reported that additive organic solvents such as hexanol, acetone, or methanol had a great effect on the yield of H_2O_2. Here, we selected hexanol to alter the yield of H_2O_2 under ultrasonic irradiation in order to control the phase of the final products. The addition of hexanol could reduce the yield of the H_2O_2;[38] thus only a part of Cu^+ ions were oxidized, which

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(36) Mizukoshi, Y.; Oshima, R.; Maeda, Y.; Nagata, Y. *Langmuir* **1999**, *15*, 2733.

(37) Miller, N. *Trans. Faraday Soc.* **1950**, *46*, 546.

(38) Henglein, A.; Korman, C. *Int. J. Radiat. Biol.* **1985**, *48*, 251.

can qualitatively explain the formation of $Cu_{2-x}Se$ in the water/hexanol/CTAB solution under ultrasonic irradiation. In our experiments, the influence of solvents on the phase of copper selenides has been studied in detail. The results, as listed in Table 1, show that increasing the concentration of organic solvents (hexanol or cyclohexane) in the solution favors the formation of low-valent copper selenides such as $Cu_{2-x}Se$ and Cu_3Se_2, but the particle size of $Cu_{2-x}Se$ prepared in water/cyclohexane/CTAB solution is much larger than that of the product prepared in the solution of water/hexanol/CTAB. In addition, we find that the solvents affect not only the phase of the final products but also their morphologies. During the formation of the final products, the periods of nucleation and growth of nuclei are quite different in different solutions. For a high-viscosity solvent (hexanol, 5.2 mPa•s, 20 °C), the rate of diffusion is slower than that of a low-viscosity solvent (ethanol, 1.2 mPa•s, 20 °C). The copper selenide molecules can form a new nucleus before they migrate to the surface of other nuclei, which prevents particles from growing. Therefore, $Cu_{2-x}Se$ prepared in water/hexanol has much smaller dimensions and higher monodispersity than those of Cu_3Se_2 prepared in water/ethanol.

To further understand the proposed mechanism of the formation of CuSe and the importance of ultrasonic irradiation to the morphology of the as-prepared products, control experiments have been carried out in the absence of the ultrasonic irradiation in various solvents and surfactants. All the products are characterized by the XRD and TEM techniques. The result show that the products are only low-valent copper selenides ($Cu_{2-x}Se$ and Cu_3Se_2) rather than $Cu^{II}Se$ in the absence of ultrasonic irradiation. The addition of appropriate amounts of H_2O_2 (ca. 1 mL) leads to the formation of a small quantity of CuSe, judging from the sharp contrast of relative intensity of the XRD patterns, which indicates that H_2O_2 does play an important role in the formation of CuSe. The result is consistent with the proposed formation mechanism of CuSe, but during the sonochemical process, the H_2O_2 can be continuously produced. And this ensures the sufficiency of H_2O_2 in the system. According to the TEM images, the morphologies of obtained products are quite different. The products obtained by vigorous stirring have much larger sizes and greater aggregation than those obtained under sonochemical irradiation. The control experiments further indicate that ultrasonic irradiation is not a prerequisite for the low-valent copper selenides but it accelerates the reaction, which is consistent with the results reported by Ohtani et al.[19] Meanwhile, for $Cu^{II}Se$, ultrasonic irradiation is a prerequisite.

Conclusion

A novel sonochemical approach to the preparation of different phases of copper selenides is reported. Here, the effects of the solvents, surfactants, and sonochemical irradiation have been investigated in the formation of different phases of copper selenides ($Cu_{2-x}Se$, β-CuSe, and Cu_3Se_2). It is found that the solvents and surfactants have a great effect on the morphology of the final products. In the higher viscosity solvent (hexanol), highly monodispersive products ($Cu_{2-x}Se$) with a diameter of about 25−30 nm can be obtained. The lamellar structure of surfactants, used as template, is an effective means to obtain the flakelike morphology. Sonochemical irradiation, which can produce $H^\bullet$ and $OH^\bullet$ radicals from H_2O that then recombine to H_2O_2, plays an important role in the formation of copper selenides (CuSe). Especially, H_2O_2 can oxidize Cu^+ ions into Cu^{2+} ions, and the yield of H_2O_2 can be altered by adding hexanol. The lower H_2O_2 concentrations, leading to minor efficiency of Cu^+ ion oxidization into Cu^{2+} ions, is the major factor in formation of low-valent copper selenides. The sonochemical irradiation method is expected to prepare other important transition metal chalcogenides.

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