Synthesis and Spectroscopic Studies of Copper Selenide Nanoparticles

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Abstract

Copper selenide nanoparticles were synthesized using solvothermal route at different temperatures using ethylenediamine as a solvent. The study of the molecular structure by FTIR spectroscopy indicated that the cupper complex with ethylenediamine through the nitrogen atom was formed when the sample prepared at 140°C. The cupper selenide nanoparticles were formed at temperatures 160, 170 and 200°C. The X-ray diffraction data revealed that, all samples exhibit crystalline nature and the particle size depends on the temperature. At the same time transmission electron microscope was used in studying of the morphology and particle size. The particle size estimated by XRD and TEM was consistent and the two in nanorange. The obtained results reveal that the CuSe nanoparticles were formed with particle size 13, 15 and 21 nm at temperatures 160, 170 and 200°C respectively.

Introduction

Nanostructures materials were defined as systems having at least one dimension between 1 and 100 nm. The special properties of nanomaterials have been attracted much interest [1,2]. They had received growing interest due to their peculiar properties and applications superior to their bulk counterparts [3]. The nanostructure materials were characterized by strong chemical bonds delocalization of valence electrons and can vary with size [4]. The structural changes with size variation give different chemical and physical properties, depending on size. The properties include electrical, optical, melting points, specific heats, and surface reactivity. The size-dependent on excitation or emission, quantized conductance, Coulomb blockade single-electron tunneling and metal-insulator transition were studied by many authors [5-8]. Significant progress had regard to two, one dimensional wires and zero-dimensional nanostructures (quantum dots) in the past two decades [9,10]. There were many different chemical and physical methods for preparation of metal selenide [11-18]. The solid state reaction usually require high temperature (>500°C) and gaseous H_2Se to prepare metal selenide compounds, such process was dangerous and highly toxic [14]. Also, mechanical alloying using ball milling had been used to prepare nanosize particles at room temperature [15], but the product quality was difficult to be controlled [16-18]. Copper selenide has been used in solar cell [19], as an optical filter [20] and as super ionic material [21]. Several methods have been used to prepare copper selenide, including the thermolysis of copper and selenium powder mixtures at 400-470°C in flowing argon [22], mechanical alloying of Se and Cu in a high energy ball mill [23] and reaction of Se with elemental Cu in liquid ammonia [24,25]. Malik *et al.* have reported the preparation of tri-n-octylphosphine oxide (TOPO)-capped CuSe nanoparticles via a single-source route in which a solution of Cu(EtCNSE), the single-source precursor, was injected into hot TOPO at 250°C and then was heated for 45 min at this temperature [26]. Micro-sized rod-like crystal and nanocrystalline were prepared by hydrothermal method based on the reaction of $CuCl_2 \cdot 2H_2O$ with elemental selenium in dilute aqueous ammonia [11,27]. Wang *et al.* have prepared nanocrystalline CuSe using solvothermal

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method, in which powdered CuI and Se are heated at 90°C in an autoclave, with ethylenediamine as a solvent [28]. We have recently employed a solvothermal in the preparation of some metal selenides such as: CdSe, CdTe, CoSe, CoTe nanocrystalline and studied the effect of reaction time on the particle size [29]. Also, the effect of the preparation temperature of CuSe nanocrystalline on the optical properties was studied [30]. We now extended these work to study the dependence of the particle size on the preparation temperature.

Experimental

Appropriate amount of cupper chloride and selenium powder was put into a Teflon-lined autoclave of 100 ml capacity. The autoclave was filled with ethylenediamine up to 85% of the total volume. Then the autoclave was maintained at 140°C for 10 hrs, and then naturally cooled to room temperature. After filtering and washing with distilled water, and absolute ethanol, to remove the impurities the final product was dried in vacuum at 60°C for 4 hrs. The same procedure was repeated at 160, 170 and 200°C for the same sample.

Infrared spectra were measured in the wavenumber range (400-4000 cm^{-1}) using FTIR spectrometer model "Jasco 470", Japan and in the range (200-400 cm^{-1}) using FTIR-FT Raman Spectrometer (Nicolet USA), laser source 0-2 W, exposure power 0.6 W. KBr and CsI disk technique were used in the two ranges (4000-400 cm^{-1}) and (400-200 cm^{-1}) respectively with concentration 1%.

X-ray powder diffraction (XRD) patterns were recorded using Diano Corporation made in (USA) equipped with Co K$_\alpha$ radiation λ = 1.79026 nm, scanning rate 0.1° in the 2θ range from 20° to 80°, step time = 1 sec.

Morphology and the particle distribution was studied using Transmission electron microscope (TEM) type ZEISS, EM10, West Germany power 60 kV. The samples were prepared by making a suspension from the powder in distilled water. The suspension was centrifuged to collimate the large size particles. A drop of the suspension was put into the carbon grid and left to dry [31].

Results and Discussion

Figure 1 show the infrared absorption spectra in the wavenumber range (400-4000 cm^{-1}) of CuSe prepared at 140, 160, 170 and 200°C respectively. From this figure it is clear that, the two bands appeared at about 3433 and 1637 cm^{-1} for the sample prepared at 140°C disappeared at T = 160, 170 and 200°C. These two bands were stronger than those of usual N–H vibration. This may be due to the superimposed of N–H vibration with the (OH) vibrations, corresponding to adsorption of water on the surface of the sample. In fact, the adsorption of water is very common in powder samples with high surface area which had been exposed to the atmosphere. The band appeared at about 1034 cm^{-1} was assigned to the C–N stretching vibration. The two absorption peaks at about 2850 and 1458 cm^{-1} corresponding to the (C–H) stretching and bending vibration respectively. The band appeared at about 583 cm^{-1} may be due to the coordination of cupper to nitrogen in ethylenediamine to form a complex structure. The whole process can be expressed as follows [32,33]:

$$Cu(en)_3^{2+} + Se^{2-} \rightarrow CuSe(en)_m \leftrightarrow$$
$$\leftrightarrow CuSe(en)_{m-n} + n(en)$$
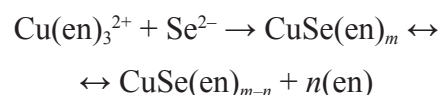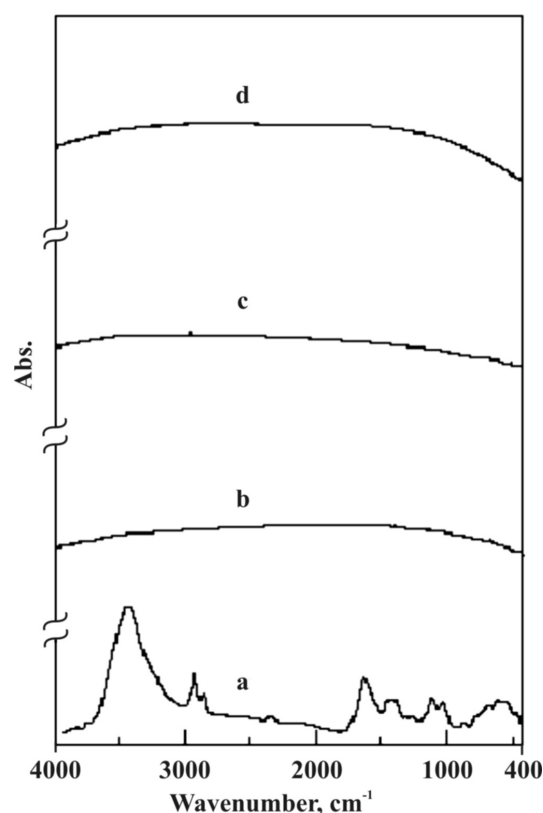
where en – ethylenediamine.

Fig. 1. FTIR spectra of CuSe prepared at (a) 140 (b) 160 (c) 170 (d) 200°C in the wavenumber range 400-4000 cm^{-1}.

This indicates that, Cu^{2+} ion coordinated with ethylenediamine molecule to form $Cu(en)_3^{2+}$ at 140°C. By comparing the spectrum of the compound $Cu(en)_3^{2+}$ prepared at 140°C with the compounds prepared at 160, 170 and 200°C it was noticed that, no absorption bands appeared in the wavenumber region (400-4000 cm^{-1}). This indicates that the reaction between $Cu(en)_3^{2+}$ and Se produced CuSe powder with its surface-adsorbed ethylenediamine molecule. However, the interaction between the ethylenediamine and Cu^{2+} on the surface of CuSe was weak when the ethylenediamine molecule was in the trans conformation. The dissociation of the ethylenediamine molecule from the surface of CuSe resulted in the evolution process of the morphology when the prepared temperature ≥ 160, 170 and 200°C.

Figure 2 shows the infrared absorption spectra in the range (400-200 cm^{-1}) of the same samples. From this figure it is clear that, one band appeared at about 225 cm^{-1} for the sample prepared at 140°C. This band may be assigned to Cu–N bending vibration. This is due to the formation of cupper ethylindiamine complex. Two new bands appeared at 222 ± 2 cm^{-1} and 246 ± 2 cm^{-1} for the samples prepared at 160, 170 and 200°C. These two bands can be assigned as the symmetric and asymmetric stretching vibration of Cu–Se and this indicated to the formation of CuSe structure [13,34].

In the other hand The formation process of CuSe crystallite nanosized may be visualized as follows, the cupper chloride dissolves in ethylenediamine $(en)_n$ to form a complex ion $[Cu(en)_n]^{2+}$. The complex ions can be linked by hydrogen bonds, which exist in polyamine donor solvent, and they self-assembled to a chain form. Then, by the reaction of the complex ions with selenium, the intermediate which has a chain structure of metastable molecular-building blocks is formed. By increasing temperatures, the intermediate decomposes giving CuSe [35]. It is wroth mentioning that, the intermediate is stable up to 140°C and at higher temperature it decomposes into CuSe and the chemical reaction is,

$CuCl_2 + Se + 2Na \rightarrow CuSe + 2NaCl$

Figure 3 shows the X-ray diffraction pattern of CuSe system prepared at 160°C, 170°C and 200°C. The lattice parameters were estimated as shown in Table 1. From this table it was found that the CuSe prepared at 160°C and 200°C had cell constant a = 5.747 Å and a = 5.729 Å, respectively. The obtained values were close to those reported in the literature (a = 5.765 Å, JCPDS card, No. 71-0044). The lattice
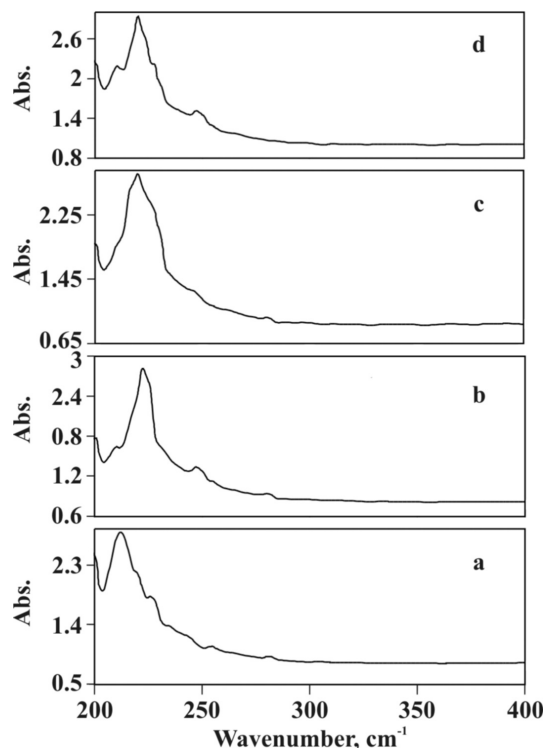

Fig. 2. FTIR spectra of CuSe prepared at (a) 140 (b) 160 (c) 170 (d) 200°C in the wavenumber range 200-400 cm^{-1}.

parameter for CuSe prepared at 170°C was found to be a = 11.388 Å which is close to that reported data (a = 11.414 Å, JCPDS card, No. 6-680). From this figure and cards it is clear that, all samples exhibit crystalline nature. The analysis of XRD patterns proves that, the formed crystals belong to cubic phase. However the samples prepared at 160°C and 200°C have the formula $Cu_{1.8}Se$. On the other hand and the sample prepared at 170°C exhibit the formula Cu_7Se_4.

The broadening of peaks in the XRD pattern used to estimate the crystallite size using Scherer equation $D = K\lambda/\beta\cos\theta$; where D mean dimension of the crystallites, β is the broadening at half band width, λ is the wavelength and K is a constant approximately equal to unity [36]. The calculated values of crystallite size were listed in Table 1. The estimated values of D according to (111) indicated that the CuSe lies in the nanorange. The calculated crystallite sizes are 13, 15 and 21 nm for samples prepared at 160, 170 and 200°C respectively. The grain size increases with increasing temperature and this is due to the viscosity of the solution which is related to the critical temperature of the solvent. The critical temperature of ethylenediamine was 318°C,
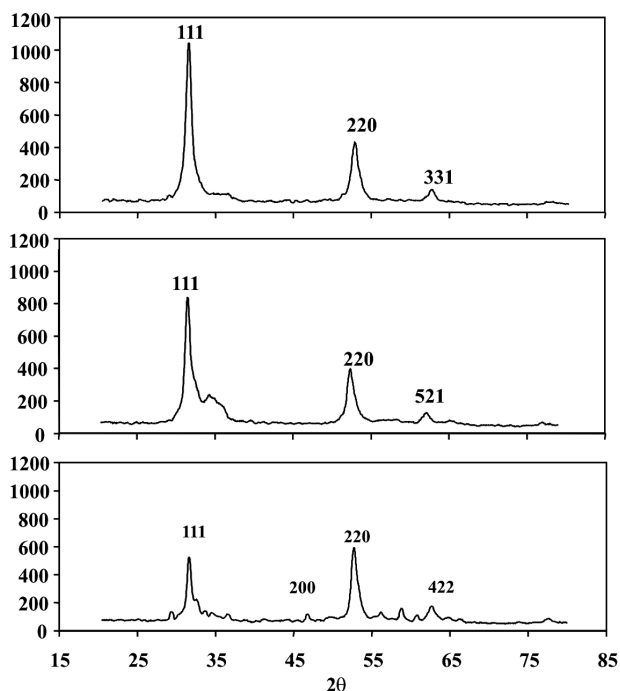
Fig. 3. X-ray diffraction pattern of CuSe prepared at (a) 160 (b) 170 (c) 200°C.

Table 1

Estimated values of the lattice parameter and grain size of CuSe prepared at 160, 170, 200°C from XRD

T, °C	Composite	Lattice parameter, Å		Grain size, nm
		Calculated	Literature	
160	$Cu_{1.8}Se$ (cubic)	$a = 5.747$	$a = 5.765$	13.300
170	Cu_7Se_4 (cubic)	$a = 11.388$	$a = 11.414$	15.230
200	$Cu_{1.8}Se$ (cubic)	$a = 5.729$	$a = 5.765$	21.314

so that the diffusion of ions in ethylenediamine at 170°C and 200 more rapid due to its lower viscosity [18]. This leads to acceleration in solubilization of starting materials and consequently the later crystal growth. On the other hand the XRD data for cupper selenide prepared at 160, 170, 200°C are listed in Table 2. Comparing between data listed in Table 2 and that reported (JCPDS card, No. 71-0044 and No. 26-0557) it was found that, preferred orientation was observed and the intensity of planes (111) and (220) is depending on the condition of preparation (temperature). The height ratio between planes (111) and (220) ($I_{111}/I_{220} = S$) was calculated and considered as a measure of orientation.

Table 2

X-ray data of CuSe prepared at 160, 170 and 200°C

	d	I/I_0	hkl
$Cu_{1.8}Se$ at 160°C	3.31	100	(111)
	2.86	5	(200)
	2.83	3.7	(400)
	2.07	5	(521)
	2.02	39	(220)
	1.73	8	(311)
Cu_7Se_4 at 170°C	3.29	100	(111)
	3.02	19	(321)
	2.01	43	(220)
	1.72	9.1	(311)
$Cu_{1.8}Se$ at 200°C	3.3	93	(111)
	2.86	9.5	(200)
	2.02	100	(220)
	1.72	20	(311)
	1.64	4.7	(222)
	1.43	5.7	(400)

Figure 4 represents the relative intensity ratio between planes (111) and (220) (S) as a function of temperature. By increasing temperature the degree of preferred orientation decreases and approaches the values of normal crystals. This means that the mechanism of growth depends on the temperature of preparation. It is worth mentioning that no characteristic peaks of other impurities were observed.
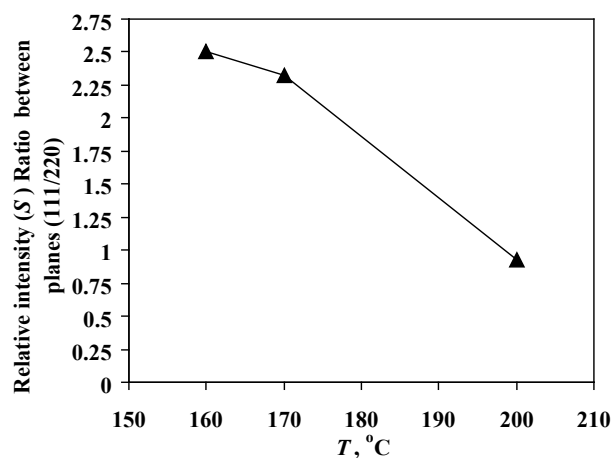

Fig. 4. Relation between the intensity ratios of planes I_{111}/I_{220} (S) and temperature for CuSe.

The morphology and the particle distribution of CuSe prepared at 160, 170, 200°C were investigated by the transmission electron microscopy (TEM) as shown in Fig. 5. From this figure, homogeneous distribution of the nanoparticles over a wide range of the samples was noticed; which are in the form of small spheres or faceted particles. The diameters of the particles were measured by an mm scale and the number of particles within 5 mm around different values of average diameters was counted. The particle size was calculated. The data were fitted to a log-normal distribution function [37]. These numbers were then plotted as a function of different average particle diameters to obtain the histogram [38].
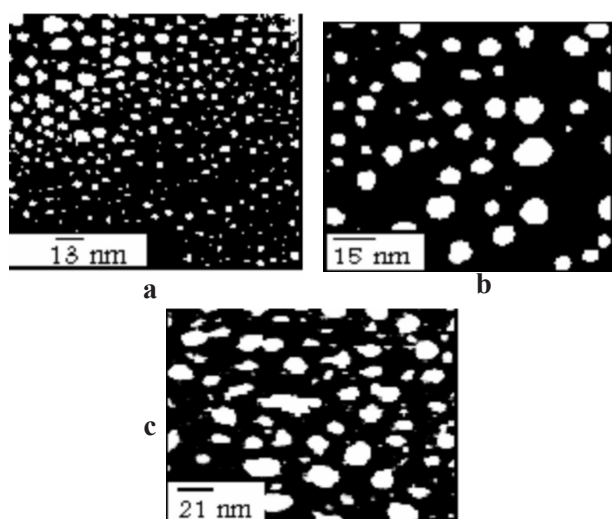

Fig. 5. TEM for CuSe prepared at (a) 160, (b) 170, (c) 200°C.

The histogram of particle size for CuSe was shown in Fig. 6. From these figures it was found that, the medium diameter obtained from TEM pictures are 13 nm, 15 nm and 22 nm for CuSe prepared at 160, 170 and 200°C respectively and this data are in agreement with the XRD data.

Conclusions

Cupper selenide was prepared in the nanorange by solvothermal route using ethylenediamine as a solvent and FTIR data indicated that, at 140°C a cupper ethylenediamine was formed due to the lone pair of electron between Cu^{2+} and nitrogen atom in ethylenediamine. $Cu(en)_3^{2+}$ and Se produced CuSe powder when the prepared temperature $\geq$ 160, 170 and 200°C. The grain size which calculated from
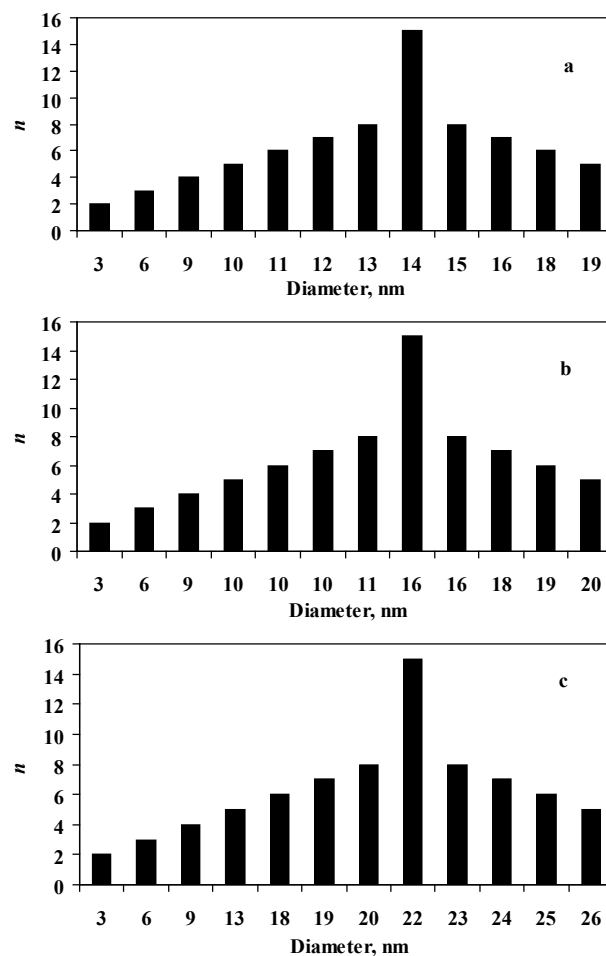

Fig. 6. Relation between number of grains n and avarege diameter for CuSe prepared at (a) 160, (b) 170, (c) 200°C.

X-ray data using Scherer equation and TEM images obtained that its increase with increasing prepared temperature.

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