Preparation and Characterization of Cu_2SnSe_4 Nanoparticles Using a Microwave-Assisted Polyol Method

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The microwave-assisted polyol method has been applied to the preparation of nanosized Cu_2SnSe_4. Cheap materials such as CuCl (or $CuCl_2·2H_2O$), Sn and Se were used as starting materials. Polyethylene glycol (PEG) is the only solvent in which the reaction takes place and the materials did not react in ethylene glycol, tri-, or tetraethylene glycol. Mössbauer spectroscopic measurements revealed a single doublet whose isomer shift of 1.81 mm/s is typical of that seen in tetravalent covalent tin semiconductors. The final product was characterized by X-ray powder diffraction, transmission electron microscopy (TEM), high resolution TEM (HR-TEM), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and electron paramagnetic resonance (EPR) spectroscopy.

Introduction

In recent years, there has been special interest in new multinary metal chalcogenido materials.$^{1-3}$ These compounds have the specific properties that are required for technological devices and have been used in optoelectronic devices, lasers and solar cells.[4,5] The compound Cu_2SnSe_4, or more precisely $Cu_2Sn\square Se_4$, where $\square$ denotes the cation vacancy that is included to maintain the same number of cations and anion sites, belongs to one of the families of fourfold defect derivatives of the $A^{II}B^{VI}$ binary semiconductors.[6] It is expected, that in order to maintain an average of four valence electrons per lattice site, the copper atoms should be divalent (Cu^{+2}) in Cu_2SnSe_4.

The multinary metal chalcogenides can be divided into two main groups. In the first group the metal is an alkali metal, and these materials can be prepared either by reactive-flux methods at temperatures between 300−600 °C or by the solvothermal method at relatively low temperatures.[2,7] The second group of multinary metal chalcogenides consists mostly of transition metals instead of alkali metals. These compounds can be synthesized by a simple combination of the elements followed by heating to high temperatures for a prolonged period of time.[8] Marcano and co-workers[9] have prepared ingots of Cu_2SnSe_4 by the vertical Bridgman−Stockbarger technique. The mixture of Cu, Sn and Se, in the ratio of 2:1:4 was sealed in an evacuated quartz ampoule, and heated to 1150 °C for 24 h. Later, it was annealed at 500 °C for 120 h and then cooled to room temperature. Bulk compounds with large sized particles have been prepared using this method, but it is unsuitable for the synthesis of nanomaterials.

Recently, two solvothermal reactions were described by Qian's group.[10,11] B. Li et al.[10] prepared Cu_2SnSe_4 nanocrystals at 140 °C for 15 h using $CuCl_2·2H_2O$, $SnCl_2·2H_2O$ and Se as the reagents and Q. Li et al.[11] also synthesized nanocrystals in a similar solvothermal process using $CuCl_2·2H_2O$, Sn, and Se as the reactants in ethylenediamine (en) at 180 °C for 12 h. They also investigated the effect of different solvents on the formation of the product. Ethylenediamine, diethylamine, benzene, and ethanol were examined as solvents in a sealed autoclave maintained at 140 °C for 15 h. The disadvantage of this method is the need for relatively high pressures and prolonged heating.

In our continuing effort to prepare semiconducting nanoparticles we have developed a general method, the so-called microwave-assisted polyol method, which is general and very efficient. We have applied this method to the preparation of binary and ternary nanosized chalcogenides (selenides and tellurides).[12−14] In most experiments the microwave reaction is complete within a few minutes, the maximum duration being one hour.

The polyol method has been developed over the past two decades and has been applied to the preparation of submicrometer nanoparticles of the easily reducible transition metals.[15] This method is based on alcohols (such as ethylene glycol as well as other glycols) reducing metallic cations to form the corresponding metals. In almost all the reactions, the polyol also plays the role of the solvent.

The application of microwaves to inorganic chemistry began only in the late 1980s.[16] Ethylene glycol (and other glycols) has been proposed as a solvent for microwave di-

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electric heating because it is highly susceptible to microwave radiation due to its high permanent dipole and high dissipation factor.[17] An added advantage is that ethylene glycol is a good reducing agent only at high temperatures. The metallic particles that are produced as intermediates in the polyol reaction are also susceptible to microwave radiation, and therefore undergo rapid heating. While the solvent temperature is expected to be that of boiling ethylene glycol, it is likely that the temperature in the reaction cell will be much higher than that of the surrounding liquid. Mingos and Whittaker[18] recently reported that high boiling point alcohols are superior solvents in microwave-assisted reactions because they help prevent arcing, which is known to lead to the decomposition of solvents resulting in carbon and carbonaceous residues. Arcing is considered the main source of the high levels of impurities that are found in the end-products.

In this study, the microwave-assisted polyol method has been shown to be an excellent method for the preparation of Cu_2SnSe_4 nanoparticles. Their crystal structure, morphology, and properties have been investigated using various analytical techniques, and the results are reported below.

Results and Discussion

Powder XRD Studies

The XRD patterns of the prepared and annealed products are shown in Figure 1 (a and b), respectively. The prepared product was not obtained as clean Cu_2SnSe_4 but as a mixture of about 90% Cu_2SnSe_4 (face-centered cubic, PDF: 78−0600), and 10% $SnSe_2$ (PDF: 23−0602), the latter being obtained as a secondary phase. To purify the material, the mixture was heated at 450 °C for 12 h. The X-ray diffraction patterns of the annealed product are presented in Figure 1 (b). No evidence for any impurity was detected and only diffractions characteristic of polycrystalline Cu_2SnSe_4 (PDF: 78−0600) were indexed. To check for other impurities in the annealed compound, we carried out an elemental analysis for carbon and hydrogen. It was found that the levels of carbon and hydrogen impurities after the annealing of Cu_2SnSe_4 were less than 0.2%. The Scherrer equation was used to calculate the particle dimensions.[19] The sizes of the Cu_2SnSe_4 particles are ≈ 40 nm. The calculated lattice parameter found for the compound is a = 5.71 Å. These results are in agreement with previously published data.[9−11] Additional analyses were conducted in order to verify the stoichiometry of the heated sample. Elemental analysis is especially important for Cu_2SnSe_4, because of the secondary phase that was observed for the prepared material. The stoichiometric ratio of Cu:Sn:Se in the annealed sample, measured using EDS, is 2.01:1:3.3. The EDS results show a deficiency of Se. It cannot be claimed that the product is Cu_2SnSe_3 because the positions of the diffraction peaks of this compound are very different from those of Cu_2SnSe_4.[20] For example, Cu_2SnSe_3 has a remarkably intense diffraction peak at $2\theta = 36.50°$, which was not observed in our measurements. By analyzing the XRD and the EDS measurements we confirmed Cu_2SnSe_4 to be the sole product of the heated sample.

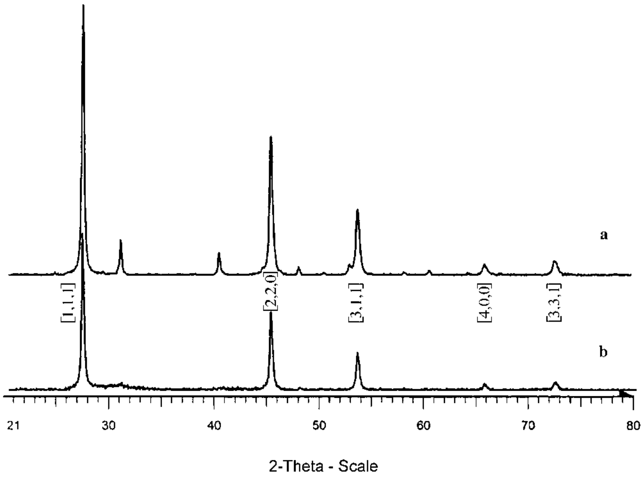

Figure 1. Powder XRD patterns of: (a) Cu_2SnSe_4 compound prepared in PEG and (b) annealed face-centered cubic product after heating at 450 °C for 12 h

TGA Measurements

The thermogravimetric measurements of the prepared product in the temperature range of 30 to 600 °C revealed two main mass losses. The first loss was ca. 1.6% and occurred in the temperature range of 240−450 °C. This loss can be attributed to the removal of PEG from the surface of the product. A second mass decrease of 4.3% was seen over the range 480−600 °C. This loss may perhaps be due to the removal of $SnSe_2$.

Electron Microscopy Studies (TEM, SEM and HR-TEM)

The morphology of the heated sample was studied by TEM and SEM measurements. The TEM image of Cu_2SnSe_4 is shown in Figure 2. The diameters of most of the particles are in the 30−50 nm range. We also observed agglomerated particles with an average diameter of about 150 nm. The prepared nanoparticles were also found to be

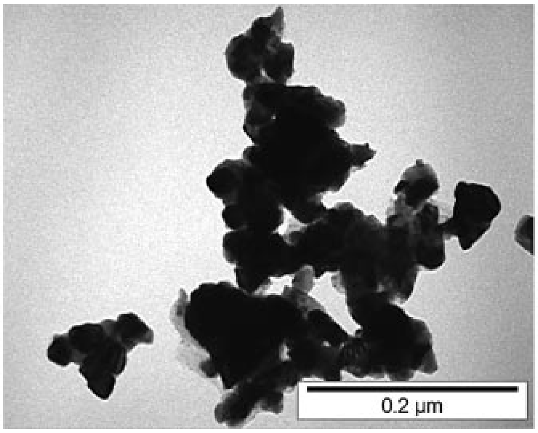

Figure 2. TEM image of the heated Cu_2SnSe_4 sample

aggregated and the aggregation mode changed only slightly upon annealing. The size of the individual particles, of 30−50 nm, is in agreement with the results calculated from the XRD data. The polycrystalline nature of Cu_2SnSe_4 was established from electron diffraction measurements. The SEM micrograph of the product (Figure 3) is consistent with the overall view of the TEM image. It also showed aggregated nanoparticles resulting in large clusters.

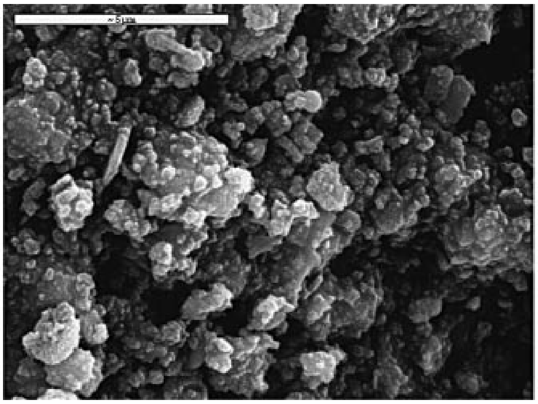

Figure 3. SEM image of the heated Cu_2SnSe_4 sample (scale bar equal to 5 μm)

The HR-TEM is depicted in Figure 4 and provides further evidence for the identification of the product as Cu_2SnSe_4. The micrograph shown in Figure 4 is a picture of the edge of the Cu_2SnSe_4 particle. The image was recorded along the [111] zone. It illustrates the perfect arrangements of the atomic layers and the lack of defects. The measured distance between these [111] lattice planes is 0.315 nm, which is very close to the distance between the planes reported in the literature (0.328 nm) for the face-centered cubic lattice of Cu_2SnSe_4 (PDF: 78−0600). An outer amorphous shell was also observed at the edge of the nanocrystalline Cu_2SnSe_4 particles and is marked by an arrow. The thickness of this shell measured for many particles is approximately 1 nm. The Fast Fourier Transform filtered (FFT) image of this lattice is shown in the insert.

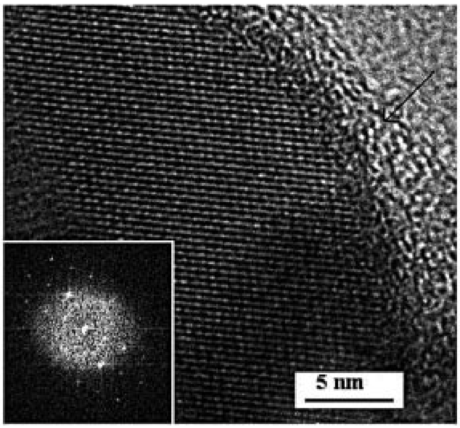

Figure 4. HR-TEM image of the heated Cu_2SnSe_4 sample. The FFT image of this lattice and the computer generated diffraction pattern is shown in the insert

The aggregated nature of the product was also evident from BET measurements. The surface area measured was 5.7 m^2g^{-1}.The surface area for a 40 nm sphere of Cu_2SnSe_4, assuming a density of 5.1 gcm^{-3}, was calculated as 29.4 m^2g^{-1}. This indicates the aggregated nature of the product. However, the aggregated initially prepared material or the aggregated annealed material both form colloidal solutions upon dissolving in 2-mercaptoethanol.

XPS Measurements

X-ray photoelectron spectroscopy (XPS) is known to probe only the surface of the particles. In XPS, excitation by X-rays enables core atomic levels to be probed, and the resultant chemical shift provides an indication of the oxidation state of the surface materials. In Figure 5 (a) we present the wide XPS spectrum of the heated sample. The overall XPS spectrum of the Cu_2SnSe_4 nanoparticles is in agreement with previously published data.[11] The binding energies obtained in the XPS analysis were corrected for specimen charging by referencing the C 1s to 285.2 eV, and are presented in Table 1. Peaks for carbon and oxygen were also observed, and we have assigned them to organic impurities adsorbed on the surface of the powders due to solvent decomposition. The XPS picture of the peaks of the doublet of Sn in Cu_2SnSe_4 nanoparticles is shown in Figure 5 (b). The energy of the Sn $3d_{5/2}$ band is 486.6 eV, and is probably an average value between that of Sn^{+4} in SnO_2 (486.9 eV) and that of Sn^{+2} in SnO (486.3 eV).[21,22] According to the recent literature, Sn undergoes a chemical shift of at least 0.4 eV when reduced from Sn^{+4} to Sn^{+2}.[23] We have attributed the presence Sn^{+2} ions to the reduction that the Sn^{+4} undergoes upon X-ray irradiation. Similar examples are well documented in the literature.[24,25] It can therefore be concluded that the XPS measurements cannot confirm unequivocally that the oxidation state of Sn in the prepared or annealed materials is Sn^{+4}. We therefore required another spectroscopic tool in order to determine the oxidation state of the Sn in the heated sample.

Mössbauer Spectroscopic Measurements

In order to verify our conjecture that the oxidation state of Sn in the heated sample of Cu_2SnSe_4 nanoparticles is +4, Mössbauer spectroscopic measurements were performed. The Mössbauer spectrum of Cu_2SnSe_4 at room temperature is shown in Figure 6. A similar spectrum was obtained at 90 K. The spectrum was analyzed in terms of two quadrupole doublets, one corresponding to Cu_2SnSe_4 (isomer shift: 1.81 mm/s relative to $BaSnO_3$, and quadrupole splitting: 0.90 mm/s), while the second (less than 5%) is perhaps due to an Sn^{+2} impurity, which was also observed in the XPS spectrum. The value obtained for the isomer shift of ^{119}Sn in Cu_2SnSe_4 is typical of Sn^{+4} in essentially covalent semiconductors,[26] and quite similar to the $SnSe_2$ system.[27] This conclusion leads to the determination of the oxidation state of the copper as +2 in Cu_2SnSe_4. The oxidation states of the Sn and Cu as determined by Mössbauer spectroscopy are bulk properties, which are different from the surface values.

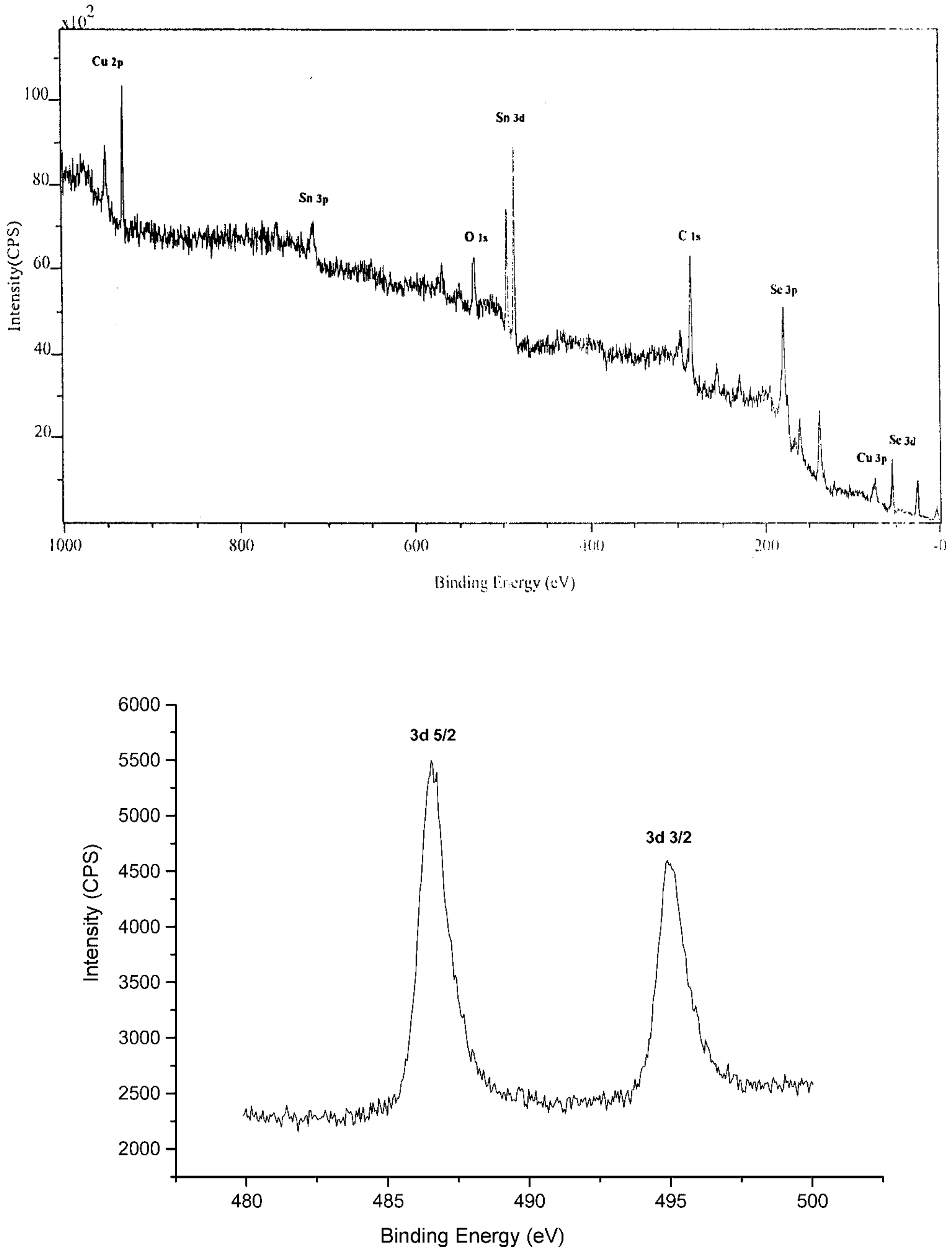

Figure 5. a) Wide XPS spectrum of the Cu_2SnSe_4 heated sample; b) the XPS picture of the peaks of the doublet of Sn in Cu_2SnSe_4 nanoparticles

Table 1. Spin orbit components and respective binding energies of the elements in Cu_2SnSe_4 nanoparticles

Elements	Cu	Sn	Se
Spin orbit component	2p 3/2 2p 1/2	3d 5/2 3d 3/2	3d
B.E. (eV)	932.3 952.1	486.6 494.6	54.7

EPR Measurements

The electron paramagnetic resonance (EPR) spectrum of the heated sample of Cu_2SnSe_4 nanoparticles was measured at room temperature (not shown here). The Cu_2SnSe_4

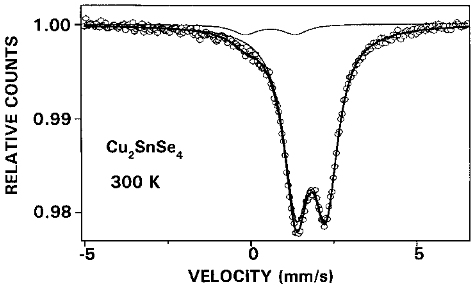

Figure 6. The ^{119}Sn Mössbauer spectrum of Cu_2SnSe_4 nanoparticles at room temperature

sample showed a peak-to-peak separation (ΔHpp) of 320 G and a *g* value 2.178. The *g* factor is equal to 2.00232 for the unbound electron.[28] The paramagnetic resonance signal in Cu_2SnSe_4 is associated with the paramagnetic nature of Cu^{+2}. This is consistent with the fact that copper atoms should be divalent in Cu_2SnSe_4 in accordance with the Sn oxidation state of +4 obtained from the Mössbauer measurements. The experimental *g* value of 2.178 for this sample is within the experimental error of the *g* values reported for Cu^{+2}.[29]

Reaction Mechanism

The main question regarding the preparation of Cu_2SnSe_4 is the mechanism of its formation. In previous work, we proposed a mechanism for the formation of $CuInSe_2$ (CIS) and $CuInTe_2$ (CIT) nanoparticles.[14] The proposed mechanism was based on the fact that the reduced metallic particles react with a second metallic element and with the chalcogenide under microwave irradiation in order to form a ternary chalcogenide compound. For the above-mentioned compounds, CIS and CIT, the additional metallic element was indium. We refer to these reactions as "wet solid-state reactions". A control experiment in which metallic copper powder, an In^{+3} salt, and Se (or Te) reacted together ($Cu/In^{3+}/Se$ or Te), did not result in ternary chalcogenides (a binary copper selenide was obtained instead).

Copper(I) or copper(II) are known from previous experiments to be reduced by the ethylene glycol to the corresponding metallic nanoparticles. This was demonstrated when CuCl or $CuCl_2$ were treated with EG in the absence of Se and Sn, yielding copper nanoparticles as the sole products. In the current reaction, both copper(I) and copper(II) yielded the same product, Cu_2SnSe_4, when treated with Sn and Se. The mixture reacted in the microwave field forming Cu_2SnSe_4 nanoparticles. As in previous cases, we have attributed the ability of the two metals (Cu and Sn) to reduce Se to their strong interaction with microwave radiation. The experiments to reduce tin salts under the same reaction conditions were unsuccessful. In another control experiment, metallic copper powder, a Sn^{+2} salt, and Se reacted together but did not yield the ternary compound (instead a binary copper selenide was obtained). We also tried to synthesize Cu_2SnTe_4 using the same starting materials but replacing Se with Te but only copper telluride was obtained. We could not find any report in the literature of the synthesis of bulk or nanoparticles of Cu_2SnTe_4.

Finally, we discuss the role of the PEG in this reaction. We could not synthesize Cu_2SnSe_4 when Cu^{II} or Cu^{I} was treated with Sn and Se in ethylene glycol, triethylene, or tetraethylene glycol. The only solvent *in* which these materials react and *with* which these materials react is PEG. We have attributed these observations to the higher boiling temperature of PEG (around 400 °C) compared with those of ethylene glycol (198 °C) and the other glycols.

Conclusions

Cu_2SnSe_4 nanoparticles have been prepared by using the microwave-assisted polyol method. Two routes have been suggested for the synthesis. The starting materials did not react when ethylene glycol, tri-, or tetraethylene glycol were used as solvents. They did react, however, when PEG was used as a solvent, and the reaction took 2 h. The sizes of the nanoparticles measured from transmission electron microscopy are in the range of 30−50 nm, which is in agreement with the results calculated from the XRD data.

Experimental Section

Materials: All reagents were of the highest purity. Elemental Se, Sn, copper(I) chloride, $CuCl_2{\cdot}2H_2O$, polyethylene glycol (PEG) (MW = 400 g/mol), and 2-mercapto ethanol were all purchased from Aldrich and used without further purification.

Instrumentation: The X-ray diffraction patterns of the products were recorded using a Bruker AXS D8 Advance Powder X-ray Diffractometer (using Cu-K_α radiation, λ = 0.15418 nm at 40 kV/40 mA) with a secondary graphite crystal monochromator. The transmission electron micrographs (TEM) were obtained with a JEOL-JEM 100SX microscope, working at an 80 kV accelerating voltage, and a JEOL-2010 HR-TEM instrument using an accelerating voltage of 200 kV. EDS measurements were conducted using an X-ray microanalyzer (Oxford Scientific) built on a JSM-840 Scanning Electron Microscope (JEOL). Elemental analyses (Carbon) were carried out with an EA 1110 CHNS-O instrument. Thermogravimetric analyses (TGA) were performed with a Mettler−Toledo TGA/SDTA851 instrument using nitrogen or argon as the purging gas with a scanning rate of 5 °C/min. X-ray photoelectron spectra (XPS) were measured with an AXIS, HIS 165, Kratos Analytical, ULTRA instrument. Mössbauer spectroscopic studies of a Cu_2SnSe_4 sample were performed using a $Ba^{119m}SnO_3$ source (10 mCi) and a conventional constant acceleration Mössbauer drive. Electron paramagnetic resonance (EPR) spectra were recorded with a Bruker EPR spectrometer (ER083 CS) operating at X-band (υ = 9.77 GHz), with a 100-kHz magnetic field modulation. The Brunauer−Emmett−Teller (BET) surface area measurements were performed using a Micromeritics (Gemini 2375) surface area analyzer. The nitrogen adsorption and desorption isotherms were measured at a temperature of 77 K after heating the sample at 100 °C for 1 h.

Microwave-assisted reactions were conducted in a domestic microwave oven, Kenwood-900 W, 2.45 × 10^9 Hz working frequency, modified with a refluxing system. In all the experiments the microwave oven worked in the following cycling mode: on for 21 s, off for 9 s, and the total power was always 900 W. This cycling mode was chosen in order to prevent the violent "bump" boiling of the solvent. All reactions were conducted under a flow of nitrogen.

Preparation of Cu_2SnSe_4: CuCl (0.197 g, 2 mmol) was dissolved in PEG (50 mL) by gentle heating in the microwave oven for approximately 1 minute. The stoichiometric quantities of Sn (0.118 g, 1 mmol), and Se (0.315 g, 4 mmol) powder were then added. The system was purged for 10 minutes with nitrogen and then the microwave reactor was turned on. The process was carried out for 2 h.

In the post reaction treatment, the product was centrifuged once at 9500 rpm with the mother liquor to separate the powder from the liquid, and was then washed a few times with ethanol at 20 °C at 9500 rpm. The product was then dried overnight under vacuum. The sample was annealed under argon for 12 h at 450 °C.

Another attempt to fabricate Cu_2SnSe_4 nanoparticles was carried out using $CuCl_2{\cdot}2H_2O$ (0.341 g, 2 mmol) instead of CuCl under the same conditions as in the first route. The results discussed can be applied to samples prepared by either of these methods.

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