JOURNAL OF
Materials
CHEMISTRY

Microwave-assisted elemental direct reaction route to nanocrystalline copper chalcogenides CuSe and Cu_2Te†

Yong Zhang, Zheng-Ping Qiao* and Xiao-Ming Chen*

School of Chemistry and Chemical Engineering, Sun Yat-Sen University, Guangzhou 510275, P. R. China. E-mail: cescxm@zsu.edu.cn (X.-M. Chen)

Received 10th June 2002, Accepted 3rd July 2002
First published as an Advance Article on the web 5th August 2002

Nanocrystalline copper chalcogenides, CuSe and Cu_2Te, have been synthesized by reactions between elemental Cu and Se or Te under microwave irradiation for several minutes. The products have been characterized by XRD, TEM, and XPS.

Introduction

Copper selenide has been used in solar cells,[1] as an optical filter[2] and as a superionic material.[3] 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,[4] mechanical alloying of Se and Cu in a high energy ball mill,[5] and reaction of Se with elemental Cu in liquid ammonia.[6,7] Wang *et al.* have prepared nanocrystalline CuSe using a solvothermal method, in which powdered CuI and Se are heated at 90 °C in an autoclave, with ethylenediamine as solvent.[8] 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.[9]

Tellurides are attractive materials for thermoelectric applications due to their very high thermopower values and the fact that both p- and n-type materials can be obtained by doping.[10] Tellurides are generally synthesized by solid-state reaction at high temperature,[11] the organic precursor method,[12] elemental reaction in liquid ammonia,[13] or solvothermal reaction.[14] Recently, Li *et al.* have reported the sonochemical synthesis of nanocrystalline copper tellurides,[15] in which Te and $CuCl_2 \cdot 2H_2O$ were sealed in a reactor and irradiated with a high-intensity ultrasonic probe for 3 h with ethylenediamine as solvent.

As a faster, simpler and very energy efficient method, microwave (MW) irradiation has been used for the acceleration of organic chemical reactions and the synthesis of inorganic materials.[16–18] More importantly, the method can cause molecular-level heating, which leads to homogeneous and quick thermal reactions. Thus, MW heating has recently become very attractive for chemists as a new method for preparing nano-sized inorganic particles and is a very rapidly developing area of research.[19,20] Furthermore, it is very easily to use microwave equipment for continuous synthesis of large quantities of products. This is significant for obtaining products in bulk amounts in industry.[21] We have recently employed a straightforward approach in the preparation of two non-stoichiometrical copper sulfides, Cu_9S_8 and Cu_7S_4.[22] We now extended this approach to the synthesis using MW irradiation of nanocrystalline CuSe and Cu_2Te, which are much more difficult to prepare by other methods and have not been synthesized before by a MW-assisted reaction.

Experimental

All reagents were of analytic purity and were used without further purification. Powdered Cu (5 mmol) and Se (5 mmol) or Te (2.5 or 5 mmol) were mixed with ethylenediamine (5 ml). Then the mixture was put into a microwave oven (Spectra 900 W) in air, one-third of the output power of the microwave was used to irradiate the mixture for 2 min. After cooling to room temperature, the precipitate was filtered out, washed three times with distilled water, ethanol, CS_2 (for CuSe) or hot potassium hydroxide solution (for Cu_2Te), and then dried with anhydrous diethyl ether. The products generated from Se and Te were labeled as samples **1** and **2**, respectively.

X-Ray powder diffraction patterns of the products were obtained using a D/max-IIIA X-ray diffractometer equipped with graphite monochromatized Cu-Kα radiation (λ = 1.54056 Å). A scanning rate of 0.05° s^{-1} was used to record the patterns in the 2θ range from 20 to 60°. The TEM images were taken with a Hitachi Model H-800 transmission electron microscope, using an accelerating voltage of 200 kV. Powdered CuSe and Cu_2Te were ultrasonically dispersed in aqueous ethanol, then a drop of the suspension was placed on a copper grid and dried in air before observation. The electronic binding energy of the copper chalcogenides was examined by X-ray photoelectron spectroscopy (XPS) on an ESCALab MKII instrument with Al(Mg)-Kα X-rays as the excitation source.

Results and discussion

The XRD patterns of the as-prepared CuSe and Cu_2Te are shown in Fig. 1. In each pattern, all peaks are consistent with those of the corresponding standard samples (JCPDS file no.

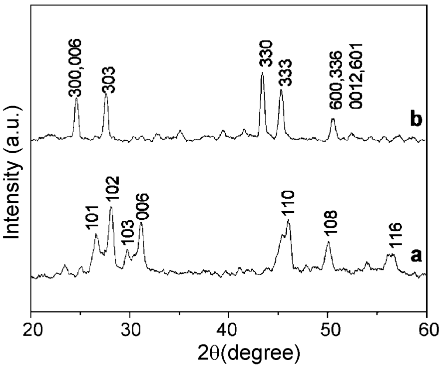

Fig. 1 XRD patterns of the products: (a) CuSe; (b) Cu_2Te.

---

†Electronic supplementary information (ESI) available: XPS spectra of the products. See http://www.rsc.org/suppdata/jm/b2/b205558a/

DOI: 10.1039/b205558a

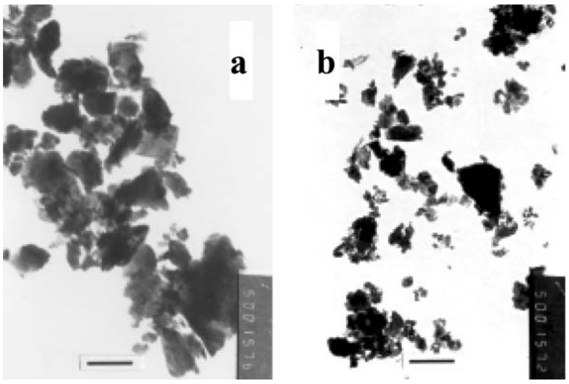

Fig. 2 TEM images of the products: (a) CuSe; (b) Cu_2Te. In each case, the scale bar represents 200 nm.

20-1020 for CuSe and file no. 10-421 for Cu_2Te). The CuSe and Cu_2Te crystallite sizes are 22 and 29 nm, respectively, as calculated from the half-width of diffraction peaks using the Scherrer formula.

TEM pictures of the samples are presented in Fig. 2, showing that CuSe and Cu_2Te aggregate due to their high surface energy. The CuSe particles in sample **1** are sheet-like, while the Cu_2Te particles in sample **2** have an average size of 30 nm.

XPS analysis of samples **1** and **2** gives binding energy values of 934.85 eV for Cu $2p_{3/2}$ and 54.75eV for Se 3d in CuSe, and 932.65 eV for Cu $2p_{3/2}$ and 572.75 eV for Te $3d_{5/2}$ in Cu_2Te (see ESI). The survey indicated that the products were pure. The Se_{3d} and Te_{3d} region showed that the valences of Se and Te were -2. The Cu_{3p} region demonstrated that the valences of the copper in sample **1** and sample **2** were $+2$ and $+1$, respectively. Quantification of peaks gave a Cu to Se ratio of 0.97 : 1 in **1** and a Cu to Te ratio of 2.05 : 1 in **2**, which are consistent with the formulae for the as-prepared products within experimental error. The low valence of the copper in sample **2** is due to the lesser oxidation ability of elemental Te as compared to Se.

It has been found that ethylenediamine is an important solvent in the preparation of metal chalcogenides.[8,13] To study the function of ethylenediamine, we also carried out the reactions in other media, such as diethylamine, benzene, and glycol, but no copper chalcogenides were formed. Copper chalcogenide powders were only deposited in ethylenediamine. Ethylenediamine, which is an N-chelating ligand, can dissolve Cu to form a complex. This is supported by the observation that Cu powder slowly dissolved in ethylenediamine under MW irradiation and the solution colour changed from transparent to light blue, and finally to dark blue. The diamine solvent plays a critical role in activating the metal and chalcogenide surfaces, effectively allowing good contact between the elements.

Conclusions

A microwave-assisted approach for the rapid preparation of nanocrystalline CuSe and Cu_2Te in ethylenediamine by reaction between elemental Cu and Se or Te has been described. XRD, XPS, and TEM examinations show the products are pure phases and well crystallized, with average particle sizes of 22 and 29 nm for CuSe and Cu_2Te, respectively. The microwave-assisted method is very simple, energy and time efficient, and is suitable for continuous synthesis of large quantities of products. This method is expected to be useful for the preparation of other important transition metal chalcogenides.

Acknowledgements

This work was supported by the NSFC (no. 20131020) and the Foundation for University Key Teachers of the Ministry of Education of China.

References

1 S. T. Lakshmikvar, *Sol. Energy Mater. Sol. Cells*, 1994, **32**, 7.
2 H. Toyoji and Y. Hirohsi, *Jpn. Kokai Tokkyo Koho*, JP 02 1990, **173**, 622.
3 A. A. Korzhuev, *Fiz. Chim. Obrab.-Mater.*, 1991, **3**, 131.
4 O. Akira, *Jpn. Kokai Tokkyo Koho*, JP 61 1986, **222**, 910.
5 T. Ohtani and M. Motoki, *Mater. Res. Bull.*, 1995, **30**, 195.
6 G. Henshaw, I. P. Parkin and G. Shaw, *Chem. Commun.*, 1996, 1095.
7 G. Henshaw, I. P. Parkin and G. Shaw, *J. Chem. Soc., Dalton Trans.*, 1997, 231.
8 W. Wang, P. Yan, F. Liu, Y. Xie, Y. Geng and Y. Qian, *J. Mater. Chem.*, 1998, **8**, 2321.
9 M. A. Malik, P. O. Brien and N. Revaprasadu, *Adv. Mater.*, 1999, **11**, 1441.
10 K. Sridhar and K. Chattopadhyay, *J. Alloys Compd.*, 1998, **264**, 293.
11 R. Coustal, *J. Chem. Phys.*, 1958, **38**, 277.
12 D. W. Kisker, M. L. Steigerwald, T. Y. Kometani and K. S. Jeffers, *Appl. Phys. Lett.*, 1987, **50**, 1681.
13 V. Dusastre, B. Omar, I. P. Parkin and G. A. Shaw, *J. Chem. Soc., Dalton Trans.*, 1997, 3505.
14 B. Li, Y. Xie, J. X. Huang, H. L. Su and Y. T. Qian, *J. Solid State Chem.*, 1999, **146**, 47.
15 B. Li, Y. Xie, J. Huang, Y. Liu and Y. Qian, *Chem. Mater.*, 2000, **12**, 2614.
16 O. Palchik, J. Zhu and A. Gedanken, *J. Mater. Chem.*, 2000, **10**, 1251.
17 O. Palchik, R. Kerner, A. Gedanken, A. M. Weiss, M. A. Slifkin and V. Palchik, *J. Mater. Chem.*, 2001, **11**, 874.
18 Y. Wada, H. Kuramoto, J. Anand, T. Kitamura, T. Sakata, H. Mori and S. Yanagida, *J. Mater. Chem.*, 2001, **11**, 1936.
19 W. Yu, W. Tu and H. Liu, *Langmuir*, 1999, **15**, 6.
20 R. Kerner, O. Palchik and A. Gedanken, *Chem. Mater.*, 2001, **13**, 1413.
21 W. Tu and H. Liu, *Chem. Mater.*, 2000, **12**, 564.
22 Y. Zhang, Z.-P. Qiao and X.-M. Chen, *J. Solid State Chem.*, 2002, in press.