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Preparation and characterization of nanocrystalline $Cu_{2-x}Se$ by a novel solvothermal pathway

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A novel solvothermal method has been developed to obtain nanocrystalline $Cu_{2-x}Se$ at low temperature; CuI and Se were placed at 90 °C for 4 h in an autoclave with ethylenediamine as solvent and the product was characterized by XRD, TEM and XPS. The results revealed that as prepared $Cu_{2-x}Se$ grains were nearly homogeneously spherical and the average grain size was *ca.* 18 nm. Ethylenediamine coordinated to Cu^+ probably plays an important role in the formation of nanocrystalline $Cu_{2-x}Se$. It is reasonable to expect that this simple one-step solvothermal route can be extended to obtain other nanocrystalline materials.

Extensive attention has been paid to the preparation and characterization of selenides, owing to their interesting properties and potential applications. Copper selenide has been widely used in solar cells,[1,2] as an optical filter[3] and as a superionic material.[4] Many methods have been utilized to synthesize copper selenide, such as heating Cu and Se powder mixtures to 400–470 °C in flowing Ar,[5] using toxic H_2Se as source,[3] or mechanical alloying of Se and Cu with a high energy ball mill.[6] Parkin and coworkers reported a room temperature route to selenides by the reaction of selenium with elemental metals in liquid ammonia in thick walled glass vessels.[7,8] In this method, many operations must be carried out at −77 °C, and because reactions in liquid ammonia have been known to explode,[7,8] all operations should be conducted with care and behind a safety screen.

Obtaining materials under mild conditions has been a goal of many scientists. Traditional methods usually need high temperature, and/or high pressure, and/or inert atmosphere protection, and/or toxic organometallic precursors and it is difficult to grow nanocrystalline materials under such conditions. However, nanoscale materials are becoming important for studying the variation of a material's property with size. The solvothermal pathway is a newly developed route, which does not require organometallic or toxic precursors and is carried out at comparatively low temperature. The organic solvent plays an important role in the formation of nanocrystalline materials. Compared with other methods, this method is convenient, simple and mild and we have obtained many kinds of non-oxide nanocrystalline materials at low temperature in this way.[9,10] In this paper we report a novel solvothermal method to form nanocrystalline $Cu_{2-x}Se$ at low temperature.

Powdered CuI (11 mmol) and Se (5 mmol) were placed in a Teflon lined stainless steel autoclave, then the autoclave was filled with ethylenediamine up to 90% of its capacity. The autoclave was kept at 90 °C for 4 h, and then allowed to cool to room temperature. The precipitate was filtered, washed with distilled water and dried in vacuum at 50 °C for 4 h. The final black product was collected for characterization.

X-Ray powder diffraction (XRD) patterns were collected on a Japan Rigaku D/max γA rotation anode X-ray diffractometer with Ni-filtered Cu-Kα radiation. Fig. 1 shows the XRD pattern of as prepared nanocrystalline $Cu_{2-x}Se$. All peaks in the pattern could be indexed to cubic $Cu_{2-x}Se$. After refinement, the cell constant was calculated to be $a = 57.4$ nm, close to the reported value.[11] The grain size of the sample, as calculated from the half-width of the diffraction peaks using the Scherrer equation, was 20 ± 5 nm.

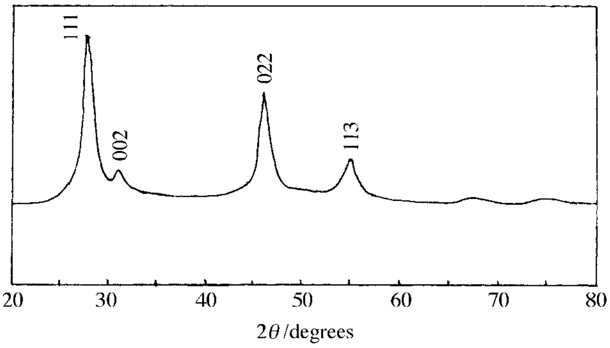

Fig. 1 XRD pattern of as prepared nanocrystalline $Cu_{2-x}Se$.

The morphology and grain size were determined by transmission electron microscopy (TEM). The TEM image was taken with Hitachi H-800 transmission electron microscope. Fig. 2 shows a TEM microphotograph of a typical sample of nanocrystalline $Cu_{2-x}Se$. It was obvious that the nanocrystalline $Cu_{2-x}Se$ grains were nearly homogeneously spherical. The grain sizes varied from 15 to 20 nm, and the average size was *ca.* 18 nm, close to the result from XRD.

The product purity and composition (to a sensitivity of <0.5 atom%) were detected by X-ray photoelectron spectra (XPS) recorded on an ESCALab MKII instrument with Mg-Kα radiation as the exciting source. The binding energies obtained in the XPS analysis were corrected for specimen

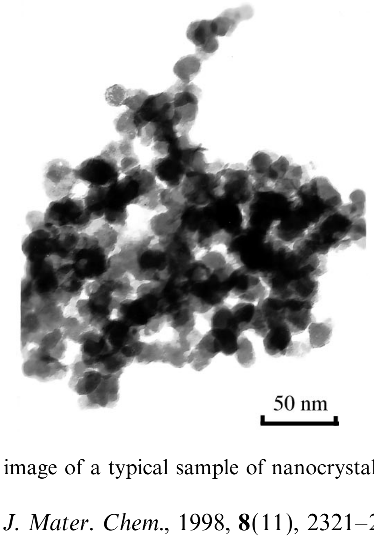

Fig. 2 TEM image of a typical sample of nanocrystalline $Cu_{2-x}Se$.

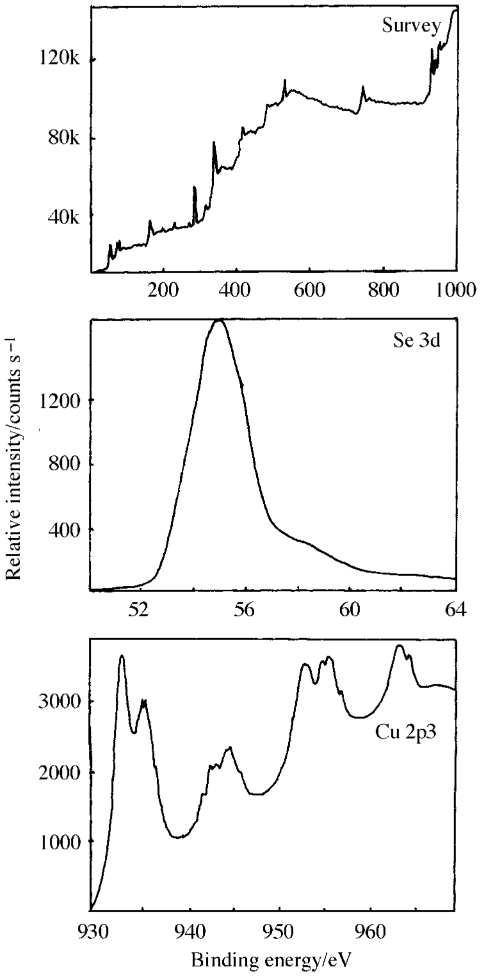

Fig. 3 XPS analysis of nanocrystalline $Cu_{2-x}Se$.

charging by referencing the C 1s to 284.60 kV. Results are shown in Fig. 3 and no obvious peaks for copper oxides, iodides or selenium oxide were observed indicating high product purity. Quantification of peaks gave a ratio of Cu to Se of 1.83:1.

In the experimental process, several factors affected the product quality. The reaction occurring is as follows:

$$(4-2x)\ \mathrm{CuI}+2\ \mathrm{Se} \xrightarrow[90\,^{\circ}\mathrm{C},\ 4\ \mathrm{h}]{\mathrm{H_2NCH_2CH_2NH_2}} 2\ \mathrm{Cu_{2-x}Se}+(2-x)\ \mathrm{I_2}$$

Optimum conditions for preparing nanocrystalline $Cu_{2-x}Se$ were at 90 °C for 4 h in the autoclave. Lower temperatures or shorter times led to incomplete reaction with decreased yield and crystallinity with a large amount of unreacted Se and CuI being present (XRD). When the temperature was lower than 50 °C, the reaction can not be initiated. On the other hand, the resultant grains were much bigger at higher temperatures or longer times. When the reaction was carried out at 180 °C for 4 h, the grain size reached 100 nm (XRD). In general the grain size varied with the reaction temperature and time.

In the solvothermal process, the solvent plays an important role in the formation of nanocrystalline $Cu_{2-x}Se$. Ethylenediamine(en) was selected as solvent because it is a N-chelating ligand which dissolves CuI to form a complex. This was supported by the fact that CuI powder slowly dissolved after addition of ethylenediamine and the solution color changed from transparent to light then to dark blue. As Cu^+ dispersed into the solution, the reaction surface area greatly increased, which promotes the reaction between CuI and Se. Thus nanocrystalline $Cu_{2-x}Se$ formed at relatively low temperature. There is a related report that $[Cu(en)_2]^{2+}$ reacts with thiourea to produce amorphous CuS.[12] Furthermore, the solvent absorbed the heat produced during the reaction, so leading to smooth reaction. Ethylenediamine limits the product size and mediates the reaction.

In the solvothermal process, CuI reduced Se to Se^{2-}. To our knowledge, the reducibility of I^- has been seldom utilized to prepare nanocrystalline materials at comparatively low temperatures. Although the reducibility of I^- is low ($E_{I_2/I^-}^{\ominus}=0.535$ V ($E_{Se/Se^{2-}}^{\ominus}=-0.78$ V), the reaction goes to completion since the $Cu_{2-x}Se$ formed precipitates out of solution. The by-product I_2 was removed from the product by washing and has no effect on the product purity. It is reasonable to expect that iodides can be widely used as reductants to obtain other nanoscale materials at low temperatures in solvothermal processes.

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