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Aqueous preparation of surfactant-free copper selenide nanowires

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ABSTRACT

Uniform surfactant-free copper selenide (Cu_{2-x}Se) nanowires were prepared via an aqueous route. The effects of reaction parameters such as Cu/Se precursor ratio, Se/NaOH ratio, and reaction time on the formation of nanowires were comprehensively investigated. The results show that Cu_{2-x}Se nanowires were formed through the assembling of CuSe nanoplates, accompanied by their self-redox reactions. The resultant Cu_{2-x}Se nanowires were explored as a potential thermoelectric candidate in comparison with commercial copper selenide powder. Both synthetic and commercial samples have a similar performance and their figures of merit are 0.29 and 0.38 at 750 K, respectively.

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1. Introduction

Transition-metal chalcogenides have attracted considerable attentions due to their unique structures, novel properties and wide applications ranging from energy conversion/storage to biomedical field [1–4]. For example, both bulk and nano-scale copper selenides, despite their simple chemical formula, have very complicated crystal structures (e.g. tetragonal-, orthorhombic-, and cubic structures) and variable composition (Cu_{2-x}Se , $0 \leq x \leq 1$), which offer an incredible wealth of properties for diverse applications such as thermoelectric conversion, lithium-ion battery, photocatalysis, quantum-dot-sensitized solar cells, and photoacoustic imaging [5–14]. Nano-scale copper selenides exhibit some unusual properties due to the large surface area, high ratio of surface atoms, and quantum confinement effects. An example is the cuprous selenide (Cu_2Se) nanoparticles, which are easily oxidized into non-stoichiometric $\text{Cu}_{1.8}\text{Se}$, and become into surprisingly good *p*-type semiconductor with over 3000 times of enhancements in electrical conductivity [2]. In order to tune the properties of nano-scale copper selenides, a number of techniques and strategies, such as hydro- or solvo-thermal approach [2,15,16], sonochemistry [17], electrochemical-deposition [18], microwave-assistant route [19], ball milling technique [6], and chemical welding method [5], have been developed to prepare nanocrystals [20], nanotubes/wires [15,21–23], nanocages [24], dendrimers [16,25], and nanosheets

[26] with well-defined size, morphology, crystal structure, and composition. However, most syntheses are complicated and the resultant nanostructures are stabilized with organic ligands, which could influence their properties (e.g. conductivity) and have to be removed in some applications. There are few reports on synthesis of surfactant-free copper selenide nanostructures, which can be used without post surface treatment [27].

In comparison with zero dimensional (0D) and bulk counterparts, one dimensional (1D) semiconductor nanostructures have many unique characteristics including asymmetric structure, intrinsic polarization anisotropies, long (macroscopic) length, band and/or ballistic transport etc. [28–34]. The electrons in nanowires are quantum confined laterally and thus occupy energy levels that are different from the traditional continuum of energy levels or bands found in bulk analogues. 1D semiconductor nanostructures show great potential in fabrication of various optical and electronic nanodevices [35]. For example, stoichiometric cuprous selenide nanowires have been utilized to fabricate catalytic electrode for oxygen reduction reaction [36], and non-stoichiometric ones have been used to construct the photoluminescence type sensor of humidity [37]. In this work, we successfully synthesized uniform surfactant-free copper selenide (Cu_{2-x}Se) nanowire bundles on gram-scale via an aqueous route. The resultant Cu_{2-x}Se nanowire bundles have diameters of 100–300 nm and lengths of tens of micrometers. The evolution of Cu_{2-x}Se nanowires demonstrates they were formed through assembling of CuSe nanoplates accompanied by redox reaction. This gram-scale synthesis offers enough pristine nanowires for exploring their properties and potential applications. The nanowires were sintered into pellets for investigation of their thermoelectric properties, which show higher

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electrical conductivity, smaller Seebeck coefficient, and lower thermal conductivity than commercial Cu_2Se powder which was sintered and measured under the same conditions. The obtained ZT is comparable with that of commercial sample, and reach to 0.29 at 750 K.

2. Material and methods

2.1. Materials

Selenium powder (–325 mesh, 99.5%, Alfa Aesar), sodium hydroxide (low chloride, 97.0%, Alfa Aesar), copper nitrate 3-hydrate (99.5%, Aldrich), copper(I) selenide (99.95%, Alfa Aesar), copper powder (–40 mesh, 99.5%, Aldrich), and Milli-Q water (18.2 M Ω cm) were used for the synthesis.

2.2. Synthesis of Cu_{2-x}Se nanowires

In a typical synthesis, 0.158 g Se powder, 4.8 g NaOH (Se/NaOH = 1/60), and 20 mL Milli-Q water were loaded into a 100 mL round-bottomed flask. The mixture was heated to 90 °C under magnetic stirring. After the selenium was completely dissolved (deep red), 1.5 mL $\text{Cu}(\text{NO}_3)_2$ aqueous solution (0.5 M) (Se/ $\text{Cu}(\text{NO}_3)_2$ = 2.5/1) was quickly added into the selenium solution. The black suspension was transferred into a 100 mL beaker, and then put into an oven at 100 °C until the water was completely evaporated. The black precipitate was washed with hot distilled water and centrifuged. The washing/centrifugation was repeated several times, and the purified sample was dried at 60 °C to constant weight. The yield is around 90%.

2.3. Crystal structure and morphology evolution of Cu_{2-x}Se nanowires

In order to investigate the evolution of the morphology and crystal structure, a group of experiments was designed to prepare Cu_{2-x}Se nanowires and collect the intermediate samples at different reaction times. The preparation procedure was the same as in the above process. Typically 1.5792 g Se powder, 48 g NaOH (Se/NaOH = 1/60), and 200 mL Milli-Q water were loaded into a 500 mL sealed round-bottomed flask. After the selenium was completely dissolved at 90 °C, the solution was equally divided into 10 beakers (20 mL in each beaker). After adding the same amount of 0.5 M $\text{Cu}(\text{NO}_3)_2$ aqueous solution (1.5 mL) (Se/ $\text{Cu}(\text{NO}_3)_2$ = 2.5/1), all beakers were kept in an oven at 100 °C, with the individual samples taken out at different times (i.e. 1 min, 40 min, 60 min, 90 min, 3.5 h, 5 h, 7 h, 9 h, 13 h, and 18 h).

In addition to normal oven, fan-forced oven and oil bath were also used to investigate the influence of heating manners on the evaporation of water. In this group of experiments, 0.316 g Se powder, 9.6 g NaOH, and 40 mL Milli-Q water were loaded into a 100 mL sealed round-bottomed flask. After the selenium was completely dissolved at 90 °C, the solution was equally divided and loaded into 2 beakers. After 1.5 mL $\text{Cu}(\text{NO}_3)_2$ aqueous solution (0.5 M) was quickly added into the selenium solution, the beakers were put into an oil bath in fume cupboard and a fan-forced oven separately at 100 °C until the water completely evaporated.

The influence of other reaction parameters on nanowires was also investigated. The procedures are similar and the resultant products were purified using the same process as described above.

2.4. Synthesis of Cu_{2-x}Se from as-synthesized CuSe in alkaline solution

CuSe powder was synthesized by a solvent-mediated method, as described elsewhere.[38] 0.285 g CuSe powder was dispersed into 20 mL NaOH solution (0.12 M) (CuSe/NaOH = 1/60). The

suspension was kept in an oven at 100 °C for 18 h. The resultant products were purified using the same process as described above.

2.5. Characterization

Powder X-ray diffraction (PXRD) patterns for all samples were collected using $\text{Cu K}\alpha_1$ radiation ($\lambda = 1.5406 \text{ \AA}$) at 40 kV and 25 mA with a position-sensitive detector. Energy dispersive X-ray spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS), and inductively coupled plasma atomic emission spectroscopy (ICP-AES) were used to characterize the chemical composition and crystal structure of the samples. The field emission scanning electron microscope (FE-SEM) images of all samples were collected using a JEOL JMS 7500-FA microscope with an accelerating voltage of 5 kV and a secondary electron detector. The transmission electron microscope (TEM) images were recorded on a JEOL 2011 microscope operated at 200 kV. The as-synthesized copper selenide nanowires were loaded into a graphite die with a diameter of 20 mm and sintered into a pellet at 703 K under 65 MPa for 10 min by the spark plasma sintering (SPS) technique. The resultant pellet was cut into pieces and polished into parallelepipeds with dimensions of $\sim 2 \text{ mm} \times 3 \text{ mm} \times 10 \text{ mm}$. The parallelepipeds were coated with a layer of boron nitride to protect the instrument against evaporation of the elements. The electrical conductivity and the Seebeck coefficient were measured simultaneously under helium atmosphere from room temperature to 750 K using an Ozawa RZ2001i (Japan). A Linseis LFA1000 (Germany) instrument was used to determine the thermal diffusivity of samples that were cut and polished into a round shape with a diameter of 10 mm and a thickness of 1 mm. The thermal conductivity (κ) was calculated using Eq. (1):

$$\kappa = D \times C_p \times \rho \quad (1)$$

where D is the thermal diffusivity, C_p is the heat capacity, and ρ is the mass density of the specimen. The ρ values used here were calculated using the geometrical dimensions of the specimens and their masses. The heat capacity was determined using the differential scanning calorimetry (DSC) method.

3. Results and discussion

Copper selenide nanowires were prepared from copper nitrate and selenium in sodium hydroxide solution. Fig. 1 shows the X-ray diffraction (XRD) pattern, and scanning and transmission electron microscope (SEM and TEM) images of the resultant nanowires. Compared with the standard diffraction peaks of copper selenide, all the peaks of our nanowires match well with those of face-centered-cubic Cu_{2-x}Se (JCPDS 06-0680) with a lattice constant of 0.5728 nm (Fig. 1(a)). The strong and sharp diffraction peaks suggest that the as-synthesized nanowires are well crystallized. The absence of other peaks indicates high purity and the single-phase nature of these nanowires. The typical field emission SEM (FESEM) image in Fig. 1(b) clearly shows a large quantity of uniform bundles with lengths up to tens of micrometers and diameters of 100–300 nm. A typical bundle is displayed in Fig. 1(b) as an inset. A high-resolution SEM image reveals that each bundle is assembled from many thin nanowires (Fig. S1 in the Supporting Information). The TEM image in Fig. 1(c) also confirms that these bundles have a uniform diameter and that they are made up of many thin nanowires. The high-resolution TEM (HRTEM) image clearly shows the lattice fringes with a spacing of 0.33 nm (Fig. 1(d)), which matches well with that of (111) planes of Cu_{2-x}Se . Both XRD and HRTEM prove that the resultant nanowires are non-stoichiometric Cu_{2-x}Se rather than stoichiometric Cu_2Se . The energy-dispersive X-ray spectrum (EDS) in Fig. S2 shows that

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