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Polyvinylbutyral assisted synthesis and characterization of kesterite quaternary semiconductor $Cu_2ZnSnSe_4$ nanofibers by electrospinning route

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ABSTRACT

Kesterite quaternary semiconductor $Cu_2ZnSnSe_4$ nanocrystals were successfully prepared via a relatively simple electrospinning route and characterized using X-ray powder diffraction (XRD), scanning electron microscopy (SEM), thermogravimetric analysis (TGA) and transmission electron microscopy (TEM). Semiconductor $Cu_2ZnSnSe_4$ nanofibers were obtained for PVB/ $Cu_2ZnSnSe_4$ precursor at an applied voltage of 20 kV after annealing treatment at 500 °C for 2 h. The optical property of $Cu_2ZnSnSe_4$ nanocrystals was also recorded by means of UV–vis absorption spectroscopy. It was shown that the dimension effect of composites could be enhanced by increasing the electrospinning conditions (voltage, distances, concentrations, viscosity) and the CZTSe nanofibers prepared at annealing process exhibited more intense optical properties. Temperature dependent studies were conducted and the annealing of composites was found to be the key factor in determining the phase formation.

1. Introduction

The composition of a crystalline copper zinc tin selenide (CZTSe), a direct band gap semiconductor, is a quaternary chalcogenide semiconductor with high absorption coefficient in the visible region (over 104 cm^{-1}). CZTSe is reported as a good candidate for photovoltaic applications due to its high absorption coefficient, good radiation stability, low toxicity, and high photovoltaic efficiency. CZTSe can significantly affect its structural, optical, and electrical properties [1–4] and ultimately the performance of the resulting thin film solar cells [5–7]. Because nanocrystals (NCs) solution can be spin-coating, spraying, or drop-casting onto substrates directly and easily, solution-based method to synthesize CZTSe NCs has attracted extensive attention [8,9]. The most common phase structure obtained for CZTSe is the zinc blende derived structures, of which kesterite and stannite are the two low-energy polytypes. The traditionally obtained quaternary I_2-II-IV-VI_4 NCs are always in the kesterite or stannite phase, which features a tetragonal crystal cell [10–13]. Both theoretical calculation and experimental work have shown that the kesterite structure is the lower energy form and is thus more thermodynamically stable than the stannite structures [14,15]. Recently, several groups have reported the synthesis of kesterite phase I_2-II-IV-VI_4 NCs by sputtering, thermal evaporation, spray pyrolysis, solution coating, electrodeposition, and so on [16–23]. However, the vacuum process synthetic procedure still requires relatively complex and costly operation. Therefore, a facile and inexpensive method for the preparation of high quality, monodisperse, and pure phase kesterite CZTSe nanofibers is still highly demanded. The large surface-to-mass ratio of nanofibers provides an advantage of higher loading per mass, and thus higher charge conductivity per mass [24,25]. This improved performance is associated with the excellent compositional and shape control achieved by electrospinning in such complex quaternary materials. We expect that these nanofibers with a uniform width and very high surface-to-volume ratio will be developed into novel green nanomaterials.

Herein, we describe a low-cost and convenient method for the preparation of pure phase kesterite CZTSe nanofibers under atmospheric conditions. Electrospinning is a simple and cost-effective technique to fabricate 1D nanostructures [26–29]. The proposed method was carried out at relatively low annealing temperature and did not require vacuum condition. The annealing process is usually applied to mixtures of polymers/inorganic precursors and it is based on an oxidative conversion of the polymeric component by heat treatment. During the formation of pure phase kesterite CZTSe nanofibers, electrospinning plays an important role in the process of the CZTSe shape transition from nanoparticles to nanofibers structures. Transmission electron microscopy (TEM), energy dispersive spectrometry (EDS), X-ray diffraction (XRD), X-ray photoelectron

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spectroscopy (XPS), and UV–vis absorption characterizations confirm the structure, composition, morphology, and optical properties of the kesterite CZTSe nanofibers. Thus, the obtained kesterite CZTSe nanofibers are more suitable and potential in high-efficiency for absorber materials applications.

2. Experimental section

2.1. Materials

All chemicals were used as received without further purification. Copper(I) chloride (CuCl; 99.99%), elemental selenium powder (99%) from Sigma Aldrich; zinc(II) chloride ($ZnCl_2$; 99.5%) from Alfa, tin(II) chloride ($SnCl_2$; 99.5%) from Mallinckrodt; ethanol absolute and hydrochloric acid were from PA Panreac; Polyvinylbutyral (PVB) (average $M_v \sim 40$ kDa) was obtained from ChangChun Group Company.

2.2. Preparation of electrospinning solution and $Cu_2ZnSnSe_4$ nanofibers

In a nitrogen-filled glovebox, a typical reaction is carried about by adding 2 mmol of CuCl, 4 mmol of elemental Se, 1 mmol of $ZnCl_2$ and 1 mmol of $SnCl_2$, 24 wt% PVB(PVB/ethanol content ratio=6:19), 30 ml ethanol absolute and 1 ml hydrochloric acid to a 50-ml three-neck flask with attached condenser and stopcock valve in a nitrogen-filled glovebox, while magnetically stirred at room temperature for 2 h, followed by N_2 bubbling at 60 °C for 2 h while stirring to obtain a homogenous precursor of PVB/ $Cu_2ZnSnSe_4$ composites.

A schematic setup of the electrospinning route used in this study is shown in Fig. 1. In the electrospinning of polymer/inorganic mixture solutions, the fiber formation process is characterized by the formation and thinning of the liquid jet and the solidification and deposition of fibers on the collection target. A stainless steel electrode was connected to a high voltage power supply (You-Shang Technical Corp.), which can generate a DC voltage of up to 30 kV. The applied voltage between the tip and collector were set at 20 kV with a tip-to-collector distance of 18 cm. The applied voltage overcomes the liquid surface tension to form a jet, which then bends and spirals into a large looping path as it thins into fine fibers and solidifies. Homogeneous precursor solutions of PVB/$Cu_2ZnSnSe_4$ composites were prepared and used immediately for electrospinning. Finally $Cu_2ZnSnSe_4$ nanofibers were obtained by annealing at 500 °C for 2 h.

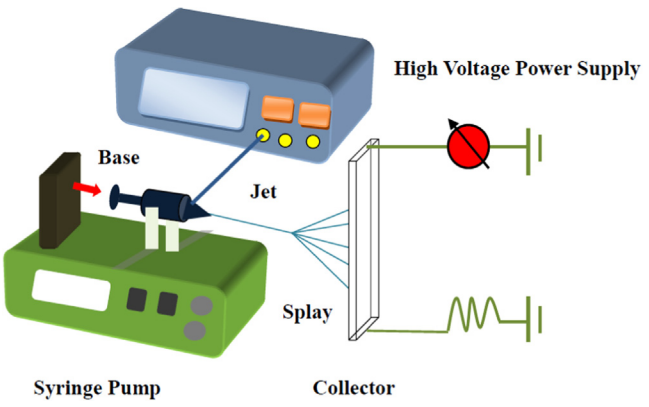

Fig. 1. Schematic diagram of electrospinning device.

2.3. Morphologies of $Cu_2ZnSnSe_4$ nanofibers

The as-prepared samples were characterized by X-ray powder diffraction (XRD), scanning electron microscopy (SEM), a thermogravimetric analysis (TGA), and transmission electron microscopy (TEM), respectively. XRD was carried out on a D/MAX-500 X-ray powder diffraction system with Cu Ka radiation (λ=1.5418 Å). A scanning rate of 0.02°/s was applied to record the patterns in the 2 Theta range of 15–80°. TEM characterization was conducted on a JEM-2000EX system using an acceleration voltage of 160 kV. A Hitachi scanning electron microscopy (SEM) with at an acceleration voltage of 5 kV was employed to characterize the morphologies.

3. Results and discussion

3.1. Morphologies of electrospinning PVB/ $Cu_2ZnSnSe_4$ composite fibers formation

Fig. 2(a)–(e) shows a series of SEM images of PVB/$Cu_2ZnSnSe_4$ nanofibers obtained from precursor solutions with concentration ratios of 16 wt%, 20 wt%, 24 wt%, 26 wt% (PVB/ethanol content ratio) and anneal-treated fibers. As can be seen in Fig. 2(a), no fibers were obtained when the ratio was 16 wt%. Because of the ratio increased, the conductivity of fibers decreased, the viscosity of fibers increased, and bead-on-string structures appeared. High viscosity prohibits the electrospinning by the instability of flow, which is caused by the high cohesiveness of solution. At low viscosity, only droplets are formed due to the lack of chain entanglement [30]. When the ratio further increased, the beads on fibers decreased. The results showed that high concentration preferred generated fibers ratios increased. The high conductivity solvent is helpful to the ion diffusion and reduces resistance. The high viscosity solvent can cause the diffusion of ions not to be easy, to reduce the conductivity [31]. When the concentration of PVB was increased, bead-on-string structures were observed, as shown in Fig. 2(b)–(d), and the bead density decreased. $Cu_2ZnSnSe_4$ nanofibers with smooth surfaces were obtained after annealing when the PVB/ethanol ratio was 24 wt% (Fig. 2e). PVB acted as the capping agent, which in the PVB/ $Cu_2ZnSnSe_4$ composite nanofibers exists states is adsorbed polymer chains induce not only steric repulsion but also bridging attraction. Pure PVB fibers are shown in Fig. 2(f); their morphology is smooth than those of PVB/$Cu_2ZnSnSe_4$ fibers.

The effect of the parameters of the solution on the morphology of nanofibers was investigated. The diameter of PVB/$Cu_2ZnSnSe_4$ composite fibers obtained at various work distances and concentrations are shown in Fig. 3. With increasing concentration ratio, the diameter of PVB/$Cu_2ZnSnSe_4$ composite fibers decreased and bead-on-string structures appeared. When the concentration ratio was further increased, the beads on fibers decreased, as shown in Fig. 3 (blue line; triangle). Compared with various concentrations, the capping agent forms stable complexes with the precursor, which the rapid formation of small nanoparticles as the crystal nuclei and slow crystal growth to form nanofibers from the crystal nuclei according to the inherent crystal structure. In this instance, the work distance from the tip of the needle to the collector is enough long for the elongation and solidification of the jet to form fibers, as shown in Fig. 3 (black line; cubic). However, when the work distance was shortened, the fiber diameter increased. That is, the morphology of the electrospinning structure transformed quickly and one was the evaporation of solvent in the jet was partly suppressed. The whipping instability, which facilitated the diffusion of the jet, was greatly suppressed [32]. The results show that a large work distance is preferred for electrospinning.