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Effect of solvent on the synthesis of $AgBiSe_2$ nanostructures

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ABSTRACT

A facile solution chemical route has been developed for synthesis of $AgBiSe_2$ nanostructures in a controllable manner via employing porous anodic aluminum oxide (PAA) as a template. Single-crystalline $AgBiSe_2$ nanowires or nanocrystals with even size can be controlled synthesized by changing the solvent in the reaction. Nanowires growth direction is perpendicular to the (104) planes. The variation of the morphology of $AgBiSe_2$ from nanowires to uniform nanoparticles may be due to the effect of solvent on the nanocrystals nucleation and growth.

1. Introduction

As a I–V–VI_2 ternary compound and a typical polymorphous semiconductor, $AgBiSe_2$ has been paid much attention recently because of its unique properties [1–5]. For example, $AgBiSe_2$ shows interesting phase behavior, structural variability and high degree of Ag or Bi bimetal ions disordering in the high temperature lattice [6]. Being a dimetal chalcogenide, $AgBiSe_2$ can exchange the bimetal atoms during the phase transition, which could induce some complicated and unusual electrical or thermal transport behavior [7,8]. Nanoscale materials have been actively studied and many novel features have been found [9,10]. Recently, a few research investigations about nanoscale $AgBiSe_2$ have been conducted. $AgBiSe_2$ nanoplates and nanoparticles have been prepared successfully via solution approaches [5,6]. However, shape-selective synthesis of $AgBiSe_2$ nanowires and nanoparticles with even size has not been reported as far as we know. It is known that chemical reactions occur in nanoconfined spaces sometimes show outstanding properties compared to the same processes involving macroscopic systems. Higher stability and more favorable thermodynamic properties may originate from the nanoconfinement effect induced by nanospace [11,12]. In particular, as a result of nanoconfinement effect, reactions can happen under milder conditions; particle agglomeration and phase segregation can be avoided and tailoring the particle shape and size becomes more available by choosing an appropriate template. Template materials with nanoscale pores are usually used to provide nano space from the small pores for nanoconfined chemical reactions. Among various types of templates, porous anodic aluminum oxide is a particularly desirable template because of its advantages including monodisperse size distribution, high pore density, nearly parallel porous structures and easily controlled pore diameter [13]. Here we reported a facile solution chemical route for synthesis of $AgBiSe_2$ nanostructures in a controllable manner. All synthesis process is conducted in nanoconfined space provide by porous anodic aluminum oxide template. We found that single-crystalline $AgBiSe_2$ nanowires or uniform nanocrystals can be controlled synthesized by simply changing the solvent used in the reaction condition.

2. Experimental section

For the typical synthesis $AgBiSe_2$ nanowires, a precursor solution was prepared by adding 0.75 mmol $AgNO_3$, 0.75 mmol $BiCl_3$, 1.5 mmol selenourea and 25 mL ethylene glycol into a flask under stirring. In the case of synthesis of $AgBiSe_2$ uniform nanoparticles, 20 mL oleylamine is used to replace ethylene glycol. In a typical procedure, PAA template (Whatman Co., channel sizes of 200 nm in diameter) was put in the solution, and then sonication was conducted for about 10 min to eliminate air in PAA channels. The flask was connected to a Schlenk line. Rough vacuum and nitrogen bubbling for 10 min each were done in alternately for several times at room temperature. The mixture solution was refluxed at 190 °C for 100 min under N_2 protection. After reaction, the PAA template

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was washed 3 times with distilled water and ethanol, finally air-dried for characterization.

X-ray powder diffraction (XRD) pattern was carried out on a Rigaku Dmax-γA X-ray diffractometer with Cu κα radiation (λ = 1.54178 Å). Field emission scanning electron microscope (FESEM) images were taken on a JEOL JSM-6300F SEM. TEM images were taken with a Hitachi H-800 transmission electron microscope. The high-resolution transmission electron microscopy (HRTEM) images were taken with a JEOL-2010 transmission electron microscope. To prepare the SEM samples for observation of the morphology, 1 M NaOH solution were dropped onto the PAA to dissolve partial aluminum oxide in it. The PAA template was then rinsed with distilled water to remove residual NaOH solution. To prepare the TEM and HRTEM samples, the PAA template was submerged in 2 M NaOH solution and its aluminum oxide became dissolved in the strong basic environment. The $AgBiSe_2$ product was released from the PAA template and existed in the solution. Residual NaOH in the solution was removed by centrifugation. The $AgBiSe_2$ product was finally washed with distilled water and absolute ethanol. A drop of the $AgBiSe_2$ colloidal suspension was applied to a copper mesh covered with a carbon film.

3. Results and discussion

$AgBiSe_2$ nanowires could be obtained when ethylene glycol was used as the solvent in the synthesis process. X-ray diffraction pattern (XRD) pattern was taken to see phase information and purity of the sample. Fig. 1a shows a representative XRD pattern of the as-prepared product. The sample can be assigned to the hexagonal structured $AgBiSe_2$ in the space group $P\bar{3}$ m1 based on the reflection peaks. The lattice parameters of a = 4.178 Å and c = 19.676 Å were calculated from the XRD pattern. They are in good agreement with the standard data ($AgBiSe_2$ JCPDS card, No. 74-0842). The XRD pattern shows no impurity phase in the sample. Fig. 1b is a representative SEM image taken from the $AgBiSe_2$ product and it shows large-area straight long nanowires. All the $AgBiSe_2$ nanowires have even size and the average diameter of them is 200 nm.

Fig. 2a shows a TEM image of as-prepared product. Straight $AgBiSe_2$ nanowires are revealed and the diameter of them is measured to be 200 nm, which according well to the SEM observation. Fig. 2b is a HRTEM image of the $AgBiSe_2$ nanowires, which discloses distinct lattice spacing. A line profile in Fig. 2d is used to measure the exact value of lattice distance and 0.29 nm is acquired. The 0.29 nm is in good agreement with the lattice spacing between (104) planes in hexagonal $AgBiSe_2$. A two dimensional Fast Fourier transform (FFT) has been done on a lattice-resolved part of a $AgBiSe_2$ nanowire in Fig. 2b, and the result is shown in inset. The spots in the FFT pattern are consistent with the zone axis $[\bar{4}\,\bar{1}\,1]$ and nanowires growth direction can be assigned to be perpendicular to the (104) planes. Fig. 2c shows a typical EDX pattern measured on the nanowires and obvious peaks originated from elements of Ag, Bi, Se can be found. This gives evidence that the chemical composition is Ag, Bi, Se. An average Ag/Bi/Se composition (%) of 22.44, 23.39, 54.17 can be obtained from the EDX quantitative analysis. This element ratio is near 1/1/2 and matches $AgBiSe_2$ chemical stoichiometry. STEM-EDX elemental mapping can provide spatial apportioning for compositional Ag, Bi, Se elements in nanowires. Inset of Fig. 2c shows a high-angle annular dark field (HAADF) image of a part of a nanowire and corresponding in–site EDX elemental mapping result of Ag, Bi, Se. A well-distributed spatial apportioning of the above three investigated elements is disclosed clearly.

The experimental results revealed that different solvent in the reaction can affect significantly final morphology of $AgBiSe_2$ product. When oleylamine is used as the solvent in the reflux system in a controlled experiment, uniform $AgBiSe_2$ nanocrystals can be obtained and nanowire could not be produced. The as-synthesized product of $AgBiSe_2$ nanocrystals has been characterized with XRD (as shown in Fig. 3). The reflection peaks in Fig. 3 confirm the $AgBiSe_2$ nanocrystals to be a hexagonal structure. XRD peaks are broadened in some degree compared with that of bulk sample in standard XRD pattern, which maybe induced by nanoscale size nature of $AgBiSe_2$ nanocrystals. XRD analysis of nanocrystals gave a size range of 8.9–10.7 nm according to the Scherrer equation, $D = (K\lambda)/\beta(\cos\theta)$, where K is a dimensionless shape factor of the nanocrystals, λ is the X-ray wavelength for the $K\alpha_1$ (1.540 Å), β is the line broadening at half the maximum intensity and θ is the Bragg angle. This calculated size data are in accordance with the following TEM investigation.

Fig. 4a is a lower-magnification TEM image. A lot of nanoparticles can be found enclosed in the PAA channels. Fig. 4b is a magnified TEM image, disclosing that $AgBiSe_2$ nanocrystals are of even size. The nanoparticle size is estimated to be in the range of 10.3 ± 1.2 nm. Distinct rings originated from the diffraction are shown in the SAED pattern (Fig. 4c). These rings match (102), (110) and (024) planes of hexagonal structured $AgBiSe_2$ (JCPDS 74-0842). Fig. 4e is an EDX pattern, disclosing chemical composition Ag, Bi, Se. Quantitative analysis based on the EDX data reveals the elemental composition Ag/Bi/Se ratio is near 1/1/2. Fig. 4d is a TEM HAADF image for $AgBiSe_2$ nanoparticles and elemental mapping results for Ag, Bi, Se are shown. The well-distributed spatial apportioning of Ag, Bi, Se elements in nanoparticles is illustrated evidently in the maps. Fig. 4f reveals a typical HRTEM lattice resolved pattern of

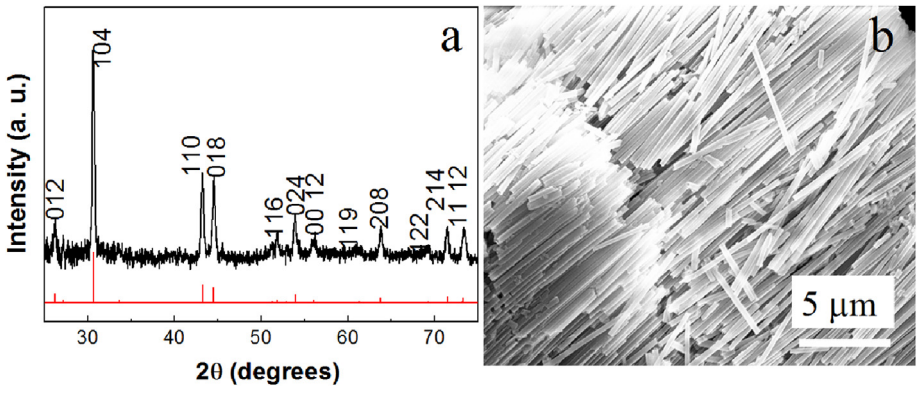

Fig. 1. (a) XRD analysis and (b) SEM image of $AgBiSe_2$ nanowires.