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Rapid Communication

Sonochemical synthesis of mass single-crystal PbS nanobelts

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Abstract

Based on sonochemical technique, large-scale PbS nanobelts are successfully synthesized in the mixed solution of $PbCl_2$ and $Na_2S_2O_3$. These nanobelts are characterized using X-ray diffraction, scanning electron microscopy, transmission electron microscopy (TEM), selected area electronic diffraction, energy dispersive X-ray spectroscopy, and high-resolution TEM. The as-synthesized PbS nanobelts have width of about 80 nm, length up to several millimeters, and width-to-thickness ratio of about 5. In addition, the growth mechanism of PbS nanobelts is suggested.

Keywords: Nanobelt; Sonochemistry; Semiconductor; Single crystalline

1. Introduction

The discovery of nanobelts of semiconducting oxides in 2001 has initiated intense experimental interest in such belt (ribbon)-like nanostructures because of their great potential for addressing some basic issues about dimensionality and space-confined transport phenomena as well as possible applications in electronics, mechanics and biomedicine [1]. Various nanobelts (ribbons) including oxide compound nanobelts [2–5], nitride composite nanobelts [6,7], sulfide compound nanobelts [8–10], titanate compound nanobelts [11], and single element nanobelts, [12–14] have been synthesized by a simple thermal evaporation route. Also, based on the same technique, we have fabricated GaN nanowires [15,16], GaN nanowhiskers [17], and $Cd_xZn_{1-x}S$ nanowhiskers [18] and Meng et al. (the third author of our paper) have formed ZnS nanobelts [9,10]. However, one of the problems with this technique is that it is difficult to purify the products and have good reproduction, owing to high temperature. Therefore, it is indispensable to fabricate such nanobelts by some other suitable energy instead of the thermal energy.

For the last decade of the 20th century, the sonochemical method developed by Suslick [19,20] has proved a useful technique for making novel materials with unusual properties [21–29]. The extremely high temperature (about 5000 K), pressure (>20 MP), and cooling rate ($>10^9$ K/s) attained during acoustic cavitation within the collapsing bubbles lead to many unique properties in the irradiated solution [19–29]. Recently, this technique has extensively been used to fabricate various nanostructured materials [21–29]. For example, we have successfully prepared large-scale single-crystalline PbS nanorods and CdS nanorods via sonochemical reaction [21,29] and Zhang et al. have synthesized CdS nanocrystallines of controlled phases [22], and that nanostructured gold/monolithic mesoporous silica assembly through sonochemistry [23] has been reported. In addition, sonochemical syntheses of Bi_2S_3 nanorods [24], HgS and PbS nanoparticles [25], Telluride silver nanocrystallines [26], photochromic nanocomposite thin film [27], as well as single-crystalline trigonal selenium

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nanowires [28] have been reported. Therein, ultrasound irradiation energy instead of thermal energy, has been applied to induce them to grow for the corresponding nanoscales in solution.

PbS is a direct narrowband gap semiconductor with $E_g = 0.41$ eV (at room temperature) and an exciton Bohr radius of 18 nm [21,25]. The small band gap and large exciton Bohr radius make PbS an interesting system for studying the effect of size confinement [21,25]. PbS nanostructures may be one of the most potential candidates for optical devices such as light-emitting diodes and optical switches due to its exceptional third-order nonlinear optical properties [21,25]. This material is also potentially useful for making devices that require small band gap semiconductors with optical absorption and emission in the red and near-infrared region of the spectrum [21,25]. However, the preparation of PbS nanobelts has rarely been reported to date. As discussed in this paper, the key to the synthesis of such nanostructures is the control of the reaction conditions in solution, and we employ this method to synthesize belt-like PbS. The as-synthesized PbS nanobelts with single-crystalline face-centered phase each have width of about 80 nm and length up to several millimeters where they are well dispersed in ethylenediamine tetraacetic acid (EDTA) solution. Since the whole process is carried out at ambient pressure and temperature, our prepared products are reproducible, easily purified, and low cost, and friendly environment, and this technique might be very useful for both fundamental research and future manufacture of semiconductor nanodevices.

2. Experimental section

In a typical procedure, 5 mmol $PbCl_2$, 5 mmol $Na_2S_2O_3 \cdot 5H_2O$, and 5 mmol EDTA were dissolved in a conical flask with 500 mL deionized water where the PH value (~7) of the solution was controlled by a buffer solution ($NaH_2PO_4 + Na_2HPO_4$). The flask was degassed and then filled with Ar gas. First, the conical flask with the solution was sonicated in the ultrasonic irradiation device (Sonics & Materials VCX 600 Sonifier, 1 cm^2 titanium horn, 20 KHz, 40 W cm^{-1}) for 4 h at room temperature. During irradiation, flowing water was utilized to cool the flask. Subsequently, black wool-like products appeared in the flask and were collected by using centrifugation. PbS nanobelts obtained were still ultrasonically dispersed in ethanol and a drop of this solution was placed on a Cu grid coated with a holey carbon film for the characterizations of transmission electron microscopy (TEM) (JEOL-2010, working at 200 KV acceleration voltages, EDS attached to TEM, Japan), selected area electronic diffraction (SAED), and high-resolution TEM (HRTEM). After large-scale PbS samples were dried in an oven at 70 °C for 6 h and kept in a vacuum desiccator for 24 h, they were characterized by X-ray diffraction (XRD) (X'pert MRD-Philips diffractometer with Cu$K\alpha$ radiation, $\lambda = 1.54178$ Å, a scanning speed of 0.0335°/s in the 2θ range 15°–80°, Holland), scanning electron microscopy (SEM) (JEOL JSM-6300, Japan). In these experiments, all chemicals were of analytical grade and without additional purification.

3. Results and discussion

Firstly, the as-synthesized PbS products are characterized by using XRD as shown in Fig. 1, where all Miller indices of peaks are presented. The whole diffractogram can be indexed in peak positions to a crystalline PbS phase and a face-centered cubic phase with a lattice parameter ($a = 0.59$ nm) is indicated, which is consistent with that of a bulk PbS crystal (JCPDS Card File, No. 5-592). Moreover, no diffraction peaks from other impurities have been found in Fig. 1. A typical SEM image and cross-sectional SEM image are, respectively, shown in Figs. 2a and b, where belt-like PbS samples are clearly viewed. In addition, according to our calculation, the yield of the as-synthesized PbS nanobelts is about 80% (Based on the fact that there is only PbS belt-like morphology in Fig. 2, we deduce that PbS compound completely converts into PbS nanobelts. Therefore, the convertible rate of $PbCl_2$ is the yield.). Throughout SEM observation, the average width of sample is about 80 nm and length is up to several millimeters. Since the PbS samples acquired are large-scale nanobelts, one knows that belt-like nanostructures should be well distributed in solution. Morphology, structure and composition of these nanobelts are characterized in detail by using TEM, SAED, EDS, and HRTEM. Fig. 3b shows a typical TEM image of a single PbS nanobelt, where it is obvious that this nanobelt has a width of about 60 nm and a white round

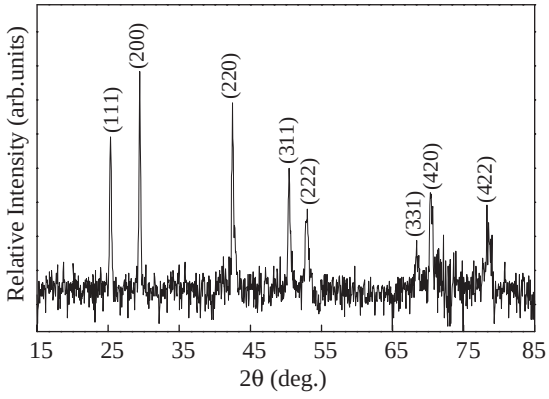

Fig. 1. XRD patterns of PbS nanobelts (width of about 80 nm and length up to several millimeters).