JOURNAL OF Materials CHEMISTRY Communication

Synthesis of closed PbS nanowires with regular geometric morphologies†

Dabin Yu, Debao Wang, Zhaoyu Meng, Jun Lu and Yitai Qian*

Laboratory of Nanomaterials and Nanochemistry, Department of Chemistry, University of Science and Technology of China, Hefei, Anhui, 230026, P. R. China.
E-mail: ytqian@ustc.edu.cn; dabinyu@mail.ustc.edu.cn

Received 12th December 2001, Accepted 22nd January 2002
First published as an Advance Article on the web 1st February 2002

Closed PbS nanowires with regular geometric morphologies (ellipse and parallelogram shape) were synthesized in the presence of poly[*N*-(2-aminoethyl)acrylamide] in ethylenediamine/H_2O (3 : 1, v/v) solvent at 110–150 °C.

It is well known that semiconductor nanowires have attracted great research interest in materials science for several years due to their potential in microelectronic, electronic, optical and magnetic devices.[1,2] The challenge in this field is still the development of synthetic methods, control of morphology, and assembly of desired nanostructures of nanowires.[3–5] As an important IV–VI semiconductor, PbS has attracted considerable research interest for many decades due to its special semiconductive and optical properties, especially since the improvement of the experimental measurements in 1960s.[6–7] Its small band gap energy (0.41 eV) and large exciton Bohr radius (18 nm) permit size-quantization effect to be clearly evident even for large particles or crystallites.[8] The non-linear optical properties of PbS nanoparticles show potential application in high-speed switching.[9] PbS nanoparticles have been investigated in glasses,[10] micelles,[11] sol–gels,[12] Langmuir–Blodgett films,[13] *etc.* However, one-dimensional nanostructures have been seldom reported. Schneider *et al.*[11] have synthesized PbS needles in polystyrene-*b*-poly(4)vinlpyridine micelles. Recently, Wang and Yang[14] prepared oriented PbS nanorods in polymer films.

In this communication, we report the synthesis of closed PbS nanowires (PbS CNWs) with ellipse and parallelogram structures in presence of poly[*N*-(2-aminoethyl)acrylamide] in ethylenediamine/H_2O (*ca.* 3 : 1, v/v) as solvent. Experimentally, all of the reagents and solvents were analytical grade purity. 30 ml ethylenediamine, 10 ml distilled H_2O, and 0.02 mol acrylamide were mixed in a flask. This reaction process was exothermic and the temperature of the mixture increased rapidly to about 70 °C. When the temperature decreased to about 40 °C, the mixture was transferred into a Teflon-lined stainless-steel autoclave. Then 2 mmol $Pb(NO_3)_2$, 2 mmol thiourea and 0.010 g 2,2′-azobisisobutyronitrile (AIBN) were added into the autoclave and stirred sufficiently. The autoclave was put in a furnace at 110–150 °C for 24 h. After washing completely with absolute ethanol and distilled water several times, part of the sample was preserved in absolute ethanol for TEM and HRTEM analysis, while the other part was vacuum dried at 80 °C for 4 h.

The XRD pattern, recorded on a MAC Science MXP18AHF X-ray diffractometer (λ = 1.54056 Å), indicates that the product is cubic PbS with lattice constant a = 5.9343 Å, in agreement with the literature value (JCPDS 5-592). No obvious impurity phase could be found. The strong and sharp peaks indicate that the PbS CNWs are well crystallized.

Fig. 1(a)–(d) show TEM images of the PbS CNWs, taken on a Hitachi H-800 TEM at an acceleration voltage of 200 kV. The PbS CNWs have two typical geometrical morphologies: ellipse [Fig. 1(a) and (b)] and parallelogram [Fig. 1(c) and (d)] shapes. The diameters of the nanowires are in the range of 80–200 nm while the perimeters of the two types of closed structures are 15–25 µm. It can be clearly seen that the ellipse PbS CNWs have high symmetry along their major axes, and two vertexes at the ends of the major axes. The parallelogram PbS CNWs have four identical angles and sides. On the outside of the PbS CNWs, there are apparent symmetrical crystal faces at the vertexes of the elliptic PbS CNWs and the angles of the parallelogram PbS CNWs. Energy dispersive X-ray fluorescence analysis (EDAX), performed with an EDAX system attached to the Hitachi model H-800 TEM, shows that in both types of nanowires the atomic ratio of Pb to S is 1.01 : 1, close to the stoichiometry of PbS.

Besides the interesting morphologies, PbS CNWs have a special crystal structure. Fig. 1(e) shows a selected area electron diffraction (SAED) pattern of individual PbS CNWs. The pattern can be indexed to the cubic phase PbS [100], the diffraction spots of which indicate highly arrayed atoms in crystal lattice revealing the single crystalline property of the PbS CNWs. Furthermore, the SAED patterns along the loop in different areas of individual PbS CNWs are almost the same as shown in Fig. 1(e), which indicates an interesting phenomenon that the crystal orientation ([100] direction) of the individual PbS CNWs is almost unchanged along the wire.

High-resolution transmission electron microscopy (HRTEM) images of individual PbS CNWs were obtained on a JEOL-2010 TEM at an acceleration voltage of 200 kV. The fringe spacing shown in Fig. 1(f) is estimated to be 0.292 nm, which is close to the (200) lattice spacing of PbS, indicating that the crystal growth is preferential in the [100] direction. This growth pattern has been observed by Waller's group[11] and Yang *et al.*[14] in PbS needles and rods. Upon investigating the crystal growth at different vertexes and angles of individual PbS CNWs, this was found to occur preferentially in the [100] direction. Further investigation of the crystal growth in different areas along the loop of individual CNWs, also indicated a preferential [100] direction, and the (200) lattice planes in different areas were almost parallel to those in the vertexes and angles as related above. Therefore, individual PbS CNWs had identical crystal orientation, although the axial orientation of the individual PbS CNWs changes by 360°. We also found that the crystal

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†Electronic supplementary information (ESI) available: XRD pattern of the PbS CNWs, FTIR spectrum of the polymer, TEM images of more PbS CNWs. See http://www.rsc.org/suppdata/jm/b1/b111187f/

DOI: 10.1039/b111187f

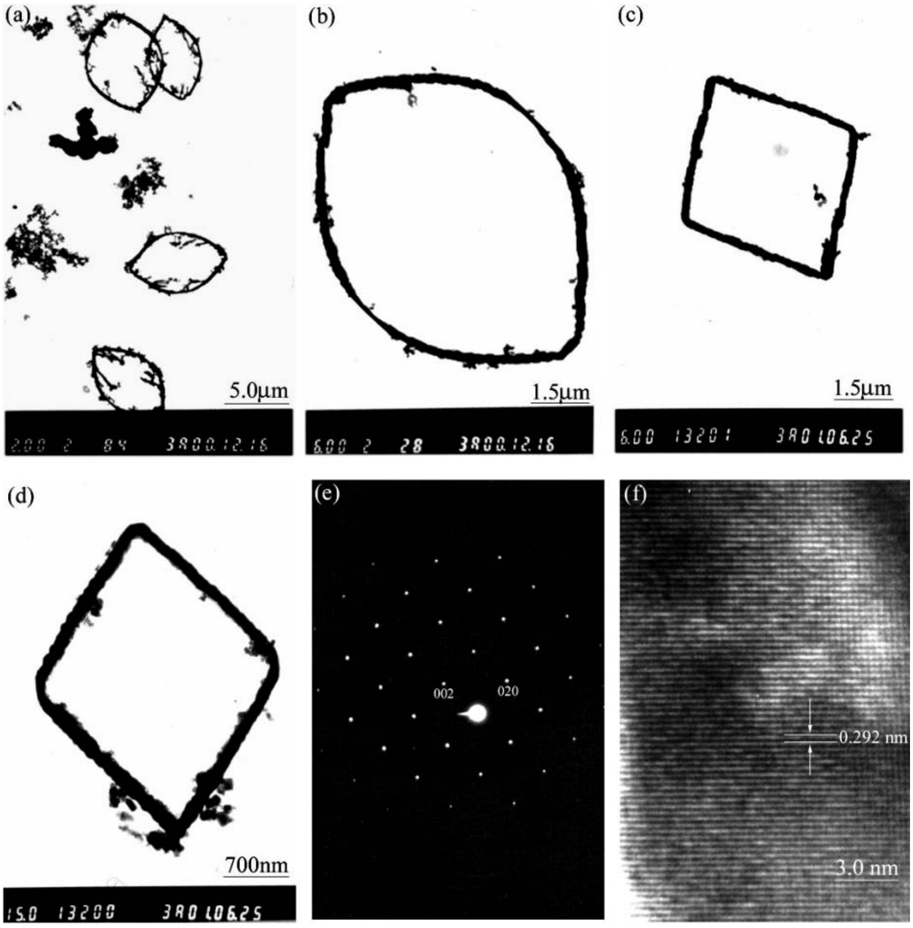

Fig. 1 TEM and HRTEM analyses of the PbS CNWs: (a) and (b) PbS CNWs with ellipse structure, (c) and (d) PbS CNWs with parallelogram structure, (e) selected-area diffraction pattern of individual PbS CNWs, (f) HRTEM image of the individual PbS CNWs.

faces at the vertexes and the angles consisted of (200) lattice planes.

In the synthesis process, the possible reactions can be described as follows

$$CH_2{=}CHCONH_2 + NH_2CH_2CH_2NH_2 \rightarrow CH_2{=}CHCONHCH_2CH_2NH_2 + NH_3\uparrow \quad (1)$$

$$n\,CH_2{=}CHCONHCH_2CH_2NH_2 \rightarrow [CH_2CH{-}CONHCH_2CH_2NH_2]_n \quad (2)$$

$$CS(NH_2)_2 + 3\,H_2O \rightarrow 2\,NH_4{}^+ + HS^- + HCO_3{}^- \quad (3)$$

$$Pb^{2+} + HS^- \rightarrow PbS + H^+ \quad (4)$$

When ethylenediamine, H_2O and acrylamide were mixed in the flask, an amine-exchange reaction took place immediately between acrylamide and ethylenediamine accompanied by the release of a large amount of gaseous NH_3 as shown in eqn. (1). The FTIR spectrum of the sample obtained from the solvent after separating the PbS CNWs and fully evaporating the small molecules (H_2O, NH_3 and ethylenediamine) was measured on a Bruker Vector-22 FT-IR spectrometer. This showed a characteristic peak of –CO–NH–R at 1566 cm^{-1} resulting from the combination of the bending vibration of NH and the stretching vibration of C–N, confirming that the amine-exchange reaction had token place. Under the heating conditions used the other three reactions [eqns. (2)–(4)] proceeded in the autoclave. Because the molar ratio of ethylenediamine to acrylamide was $>10:1$ and the NH_3 volatilized from the solution, acrylamide could be fully converted into *N*-(2-aminoethyl)acrylamide. Poly[*N*-(2-aminoethyl)acrylamide] probably acts as both a stabilizer and a "soft template'[15,16] for the formation of PbS CNWs, due to the fact that no PbS CNWs were fabricated under the same synthetic conditions when it was substituted by other polymers. A coordinative action of poly[*N*-(2-aminoethyl)acrylamide] and the solvent (ethylenediamine) also is probably responsible for the formation of PbS CNWs. The detailed mechanism for the formation of PbS CNWs is still not fully understood and further investigation is still in progress. Upon changing the amount of acrylamide and the synthetic temperature, the morphologies of the products could be controlled. With 0.015–0.03 mol acrylamide added into the autoclave, PbS CNWs with ellipse and parallelogram structures were prepared in the range 110–130 and 130–150 °C, respectively, in yields of 10–40%.

Acknowledgement

This work is supported by the National Science Foundation of China. We greatly thank Prof. S.Y. Zhang, G. E. Zhou, and X. M. Liu for the beneficial discussion about the crystal structure.

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