Solvothermal Synthesis Route to One-Dimensional Nanostrucutes

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Solvothermal processes have emerged as powerful tools for the controlled syntheses of one-dimensional (1D) nanostructures. This paper provides a survey of our recent work concerning the controlled solvothermal syntheses of one-dimensional nanostructures in different solvents or with the assistant of the polymers, especially those with large-scale production, high aspect ratio and novel morphologies. For example, the syntheses of thin single-crystal tellurium nanobelts and nanotubes, nanotubes of C, Sb, and Bi, urchin-like patterns of Bi_2S_3 nanorods, and La_2S_3 nanorods in single solvent; the preparation of Sb_2E_3 (E = S, Se) nanowires, ultralong Bi_2S_3 nanoribbons, and $Cu_{2-x}Se$ nanotubes in a mixed solvent; and the fabrication of CdE (E = S, Se, and Te) nanowires, closed PbS nanowires, $VO_x \cdot nH_2O$ nanoribbons, $Y(OH)_3$ nanotubes, Sb_2Se_3 nanoribbons, and Te nanowires in the presence of a suitable polymer. Of all the synthesis parameters in solvothermal system that affect the nano-morphologies, the solvents are specially highlighted here. Now that an appropriate procedure has been established, the solvothermal route is efficient, selective and timesaving.
Key words: solvothermal synthesis, one-dimensional, nanostructures, polymer, crystal growth.

1. INTRODUCTION

The synthesis of one-dimensional (1D) nanostructures in controllable fashion has been the goal of much active research due to the need of both current fundamental research and upcoming development of nanodevices [1]. Thereby, to develop the controlled synthetic methods of 1D nanostructures has been the most attractive aspect in nanomaterials science over the past decade. Of the methods employed in 1D nanostructure synthesis solvothermal processes have emerged as powerful tools for generalizing and systematizing controlled syntheses of nano-morphologies [2,3]. One outstanding characteristic of solvothermal method is that, in particular when the starting materials exposed to unusual conditions, some quite unexpected reactions can be carried out accompanied by the formation of nanoscopic morphologies, which cannot be achieved by classical reactions [4,5]. Moreover, the nanoscopic morphologies can usually be controlled by varying the parameters in solvothermal reaction system, such as choice of solvents, control of reaction temperature, change of PH value, introduction and removal of templates and other additives, etc. [6].

Among all these parameters, the solution structures depended on the used solvent and some additives are essential for synthetic processes because they reflect the basic characteristic of solvothermal method. The physical and chemical properties of the solvents can influence the solubility, reactivity, and diffusion behavior of the reagents [7], in particular, their polarity and coordinating properties can dramatically affect the morphology of nanocrystals [8]. To date, various effective solvents, such as benzene [9], ethylenediamine [10], n-butylamine [11], polyol [12], and water (specially termed "hydrothermal", as it is used) [6], and so on, have been successfully employed to form 1D nanostructures.

In most cases, the solvents were composed of only one component in each synthetic process [9-11], whereas our experimental results showed that, in some cases, the mixed solvents, composed of two or more components (inc. water acting as one component), were much more effective alternatives, by using which some 1D nanostructures with uniform morphologies, or high aspect ratios and or novel structures were accessible. Comparatively, the properties of a mixed solvent have much larger scope that can be adjusted by changing the components and molar ratios thereby some favorable synthetic conditions for the growth of 1D nanostructures can be achieved. Moreover, when using some additives in the solvothermal process, such as polymers and surfactants, some novel 1D nanostructures of various materials can also be obtained [13-15].

In this paper, we discuss the controlled solvothermal syntheses of various 1D nanostructures in different solvents (a single or mixed solvent) or with the assistant of the polymers.

2. RESULTS AND DISCUSSION

2.1 Solvothermal Process in a single solvent
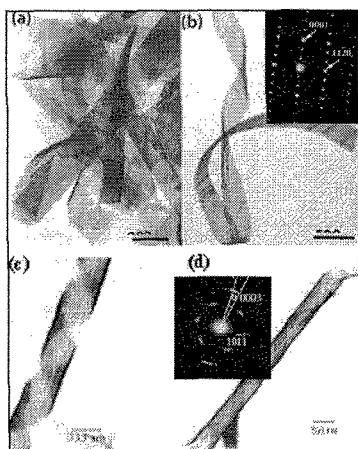
In our recent work, many 1D

Fig. 1 TEM images of: (a) tellurium nanobelts; (b) a twisted individual nanobelt, (inset) a typical ED pattern, showing the single-crystal nature of tellurium nanobelts; (c) a nanobelt with helical twisting shape; (d) a typical belt-rolled nanotube, (inset) a representative ED pattern obtained with the incident electron beam perpendicular to both walls of a tube.

nanostructures with high quality have been prepared by solvothermal process in a single solvent (inc. water). Some typical cases are illustrated as following.

Single-crystal tellurium nanobelts and nanotubes were synthesized hydrothermally on the basis of a simple disproportionation of Na_2TeO_3 in aqueous ammonia at 180 °C for 36 h (Fig. 1) [16]:

$$3Na_2TeO_3 + H_2 \rightleftharpoons Te + 2Na_2TeO_4 + 2NaOH$$
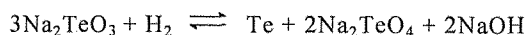
The nanobelts, with thickness of ca. 8 nm and widths of 30-500 nm, have the tendency to roll into a characteristic ripple-like structure (Fig. 1b). Most interestingly, there is the same shape of ripple-like contrast in the TEM images of the nanotubes (Fig. 1d), moreover, there were still some ripple-like helical belts attached on the ends of nanotubes. These show that the tellurium nanotubes resulted from the twist of the nanobelts, then the growth and join of the helical nanobelts along the edges. Thus, a twist-join-growth mechanism has been, for the first time, suggested for the formation of nanotubes. It is worth noting that the tellurium nanobelts and nanotubes were formed without the presence of any other additives. Thus, ammonia and water are undoubtedly responsible for the formation of the tellurium nanobelts and nanotubes.

A catalytic-assembly benzene-thermal route was used to synthesize carbon nanotubes [17]. Hexachlorobenzene was reduced by potassium in the presence of Co/Ni catalyzer at 350 °C to form hexagonal carbon clusters. The carbon clusters were then assembled into nanotubes and caused axial growth. Meanwhile, because the geometry structure of hexagonal carbon clusters is simlar to that of a carbon nanotube wall built from a hexagonal lattice of sp2-bonded carbons, the
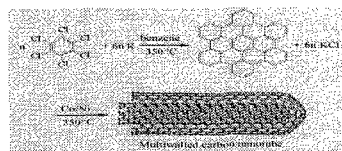
Scheme 1. Multiwall carbon nanotube synthesis via a low temperature benzenethermal route.

epitaxial growth of newly reduced hexagonal carbon clusters on the nanotube wall is favorable. This results in the formation of multiwall nanotube under a relatively low temperature benzene-thermal process. The reaction is illustrated in Scheme 1, and the TEM image of a multiwall carbon nanotubes is shown in Figure 2a.

Nanotubes of the main group metals can also be prepared by a solvothermal process. A rational complexing-reduction route was developed to synthesize Sb nanotubes under controlled solvothermal conditions [18]. In this synthetic system, acetylacetone was selected as both solvent and complexing agent. Antimony chloride, taken as the antimony source, was coordinated with acetylacetone to form Sb-acetylacetone complexes, which were then reduced in situ to antimony products by zinc powder under certain conditions. The yield of Sb nanotubes is *ca.* 50 %. The as-prepared Sb nanotubes have inner diameters of 15-80 nm, wall thickness of 10-30 nm, and lengths of up to several micrometers with obvious open end (Figure 2b). Single-walled aligned Bi nanotube arrays have been successfully synthesized by a solvothermal method through the reduction of bismuth oxide (Bi_2O_3) by ethylene glycol (EG) [19]. Here the EG is serviced as both the solvent and the reductant. The diameter of the Bi nanotubes is about 3–6 nm and length is up to 500 nm (Figure 2c and 2d).

A rapid polyol process has been developed to synthesize self-supported urchin-like patterns of Bi_2S_3 nanorods with only $Bi(NO_3)_3 \cdot 5H_2O$ and thiourea (Tu) as the reagents and ethylene glycol (EG) as the solvent at 197 °C for 30 min [12]. The reaction is based on the formation of Bi–thiourea complexes and then the thermal decomposition of these complexes to give the final Bi_2S_3 product. The product appears as uniform urchin-like pattern with spherical symmetry, and the individual Bi_2S_3 nanorods is about 50 nm in diameter (Figure 3a). Though several geometrical
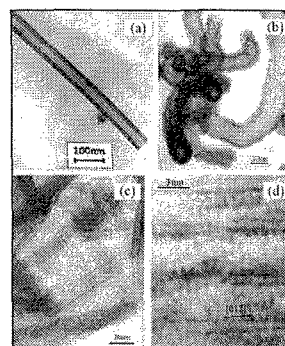

Fig. 2 Representative TEM images of the as-prepared a multiwall carbon nanotube (a), Sb nanotubes (b) and Bi nanotubes arrays (c); and a HRTEM image of the bundle of Bi nanotubes showing that lattice fringe is the (0 12) faces.
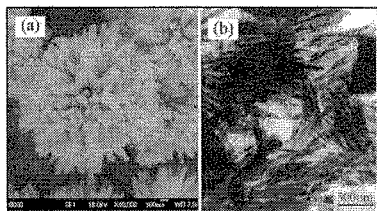
Fig. 3. (a) SEM images of as-prepared product, which shows large scale urchin-like patterns of three-dimensional aligned Bi_2S_3 nanorods. (b) TEM image of the β-La_2S_3 nanorods

urchin-like patterns, including Bi_2S_3, have been presented, our synthetic process is relatively rapid, simple and efficient and may provide a novel method for large-scale synthesis and studies of the potential physical and chemical properties of novel materials with special nanomorphologies.

β-La2S3 nanorods, with diameters of 30-50nm and lengths of 600-1000 nm (Figure 3b), were successfully prepared via a solvothermal route at 260-280 °C for 10 h using ethylenediamine (en) as the solvent [20].

2.2 Solvothermal Process in a mixed solvent

Since the mixed solvents usually consist of two or more components and each component contains special molecular structure, polarity and ligands, the properties of the solvents can be easily adjusted by varying the sorts and ratios of the components to meet the need of the 1D growth of nanocrystals. In particular, when there are combinatorial performances between or among the different components in one solvothermal route, some unexpected experimental results can be obtained. Our recent work demonstrates a suitable mixed solvent is very efficient for the synthesis of 1D nanostructures.

Sb_2E_3 (E = S, Se) nanowires were synthesized by refluxing $SbCl_3$ with elemental E (E = S, Se) in a mixed solvent of en/diethylene glycol at 200 °C for 1.5 h (Fig. 4a and 4b) [21]. There are a few solvothermal routes to Sb_2E_3 (E = S, Se) nanowires (nanorods) due to the fact that the infinite chains in the crystal structure of Sb_2E_3 are favorable for their 1D growth [22,23]. Comparatively, this is a timesaving synthesis since the synthetic process can be carried out within a short time of 1.5 h, moreover, this route can result in large-scale and well-crystallized
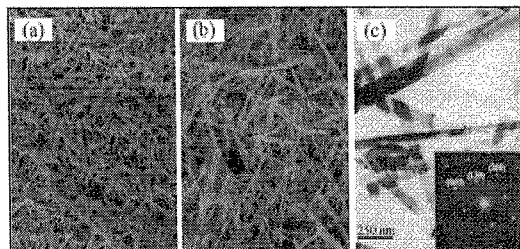
products. Experimental results showed that the formation of the Sb_2E_3 nanowires in this synthetic route was attributed to the combinatorial action of en and diethylene glycol. Although en accounted for only a small part of the solvent (ca. 5%, volume), it played a crucial role in the synthetic process. Without the presence of en, some elemental E will present in the final products even after a much longer reaction time. Since en is strongly basic, elemental E can be readily activated by a nucleophilic attack of the amines to form E^{2-}, which can make the synthetic reaction go smoothly [24]. Diethylene glycol can complex and stabilize the surface of the nanoparticles to avoid the agglomeration of the nuclei, which is favorable for the oriented growth of the nanowires [25]. This route has been successfully extended to synthesize other 1D semiconductor nanostructures, for instance, SnSe nanowires were synthesized by almost the same process (Fig. 4c) [26].

To synthesize 1D nanostructures with high aspect ratio is in the focus of current research interests. Large-scale ultralong Bi_2S_3 nanoribbons with length up to several millimeters were synthesized by using $Bi(NO_3)_3 \cdot 5H_2O$, NaOH and $Na_2S_2O_3$ as starting materials, glycerol/H_2O (v/v, 2:1) as mixed solvent at 160 °C for 20 h (Fig. 5) [27]. According to our experimental experience and theoretical investigations, the formation of the nanoribbons seems to follow a "solid-solution-solid transformation" mechanism but is not completely similar to the cases reported previously because a intermediate [28], $NaBiS_2$, was found in the synthesis process and played a vital role in the formation of the nanoribbons. The formation of Bi_2S_3 nanoribbons was basically carried out in two steps. First, glycerol acted as the coordination agent to form the complex $Bi(C_3O_3H_5)$, which further reacted with $Na_2S_2O_3$ and NaOH to produce an intermediate, polycrystalline $NaBiS_2$ flakes. Then, the intermediate decomposed into Bi_2S_3. The chemical reactions can be described as the following.

$$Bi^{3+} + C_3O_3H_8 + 3OH^- \rightleftharpoons Bi(C_3O_3H_5) + 3H_2O$$

$$Bi(C_3O_3H_5) + 3S_2O_3^{2-} + Na^+ + 3OH^- \rightleftharpoons$$
$$NaBiS_2 + 4SO_3^{2-} + C_3O_3H_8$$

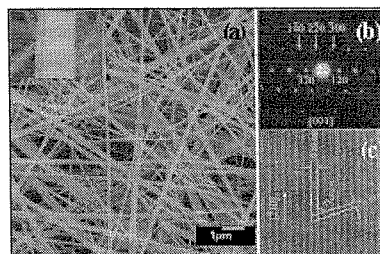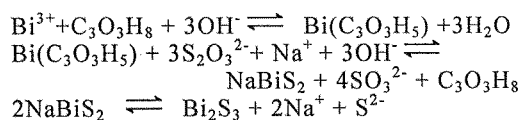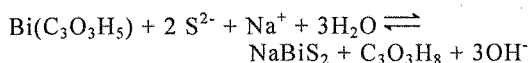$$2NaBiS_2 \rightleftharpoons Bi_2S_3 + 2Na^+ + S^{2-}$$

Fig. 5 (a) SEM image of Bi_2S_3 nanoribbons, (the inset) the rectangular cross section of a typical individual nanoribbon with large magnifications; (b) A SAED pattern obtained from [001] direction; (c) HRTEM image of a nanoribbon, the lattice spacings of 0.39 and 0.50 nm corresponding to the distances of (220) and (120) planes, respectively.

Fig. 4 (a) SEM image of Sb_2S_3, (b) SEM image of Sb_2Se_3, The scale bars in (a) and (b) are 14 and 3 μm, respectively. (c) TEM image of SnSe

$$Bi(C_3O_3H_5) + 2\ S^{2-} + Na^+ + 3H_2O \rightleftharpoons$$
$$NaBiS_2 + C_3O_3H_8 + 3OH^-$$

The reactions show that glycerol and H_2O not only act as reaction medium but actually take part in the reactions as well. The morphologies of the products were sensitive to the change of the volume ratio of glycerol to water. With other conditions unchanged, the volume ratio of ca. 2:1 was a best alternative for the formation of Bi_2S_3 nanoribbons

Nanotubes, with basic hollow morphology and several different areas of contact (borders, inner and outer surfaces, and walls), have been suggested as a kind of the most promising functional materials in the future [2,29]. One of our successful routes to nanotubes is the synthesis of $Cu_{2-x}Se$ nanotubes in a mixed solvent of en/hydrazine hydrate (2:1, volume ratio) [30]. Briefly, 0.01 mol CuO, 0.005 mol Se, and 45 ml mixed solvent were put into a glass container and kept at a temperature in the range of 20-60°C with constant stirring for 24 h. The $Cu_{2-x}Se$ nanotubes have straight and nearly uniform morphology with an average inner diameter of 20 nm, outer diameter of 30 nm and length up to several 100 nm (Fig. 6a). Mostly interestingly, the as-synthesized tubes have the nature of single crystal at least from the ED pattern of view (Fig. 6b). The ED pattern shows a typical second diffraction phenomenon when the electrons passed through the both walls of a tube. To infer from our recent research, the formation of the $Cu_{2-x}Se$ nanotubes can be attributed to the roll of the single-crystal flake-like $Cu_{2-x}Se$ (Fig. 6c), which has the tendency to roll on the edges as indicated by the arrows. The flake-like structure has the same ED pattern as the tube except for the second electron diffraction spots (inset in Fig. 6c). Moreover, some nanotubes with half rolled ends of the flake-like structure can still be found in the products, as indicated by the arrows in Fig. 6d, which further shows a direct evidence of the formation of the $Cu_{2-x}Se$ nanotubes resulting from the rolling flakes. Since the as-synthesized $Cu_{2-x}Se$ has a cubic phase [31], the formation of
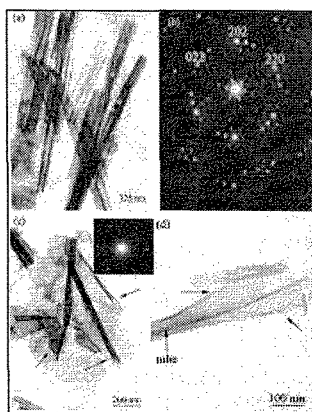
Fig. 6 (a) A typical TEM image of $Cu_{2-x}Se$ nanotubes; (b) a typical ED pattern of an individual nanotube; (c) TEM image of some flake-like $Cu_{2-x}Se$ with rolled edges as indicated by arrows, (inset) a corresponding ED pattern; (d) TEM image of nanotubes with half rolled ends of the flake-like $Cu_{2-x}Se$ as indicated by arrows.

such a two-dimensional layered structure and 1D nanotubes should be an interesting result.

The possible reaction can be expressed as follows:

$$CuO+N_2H_4 \cdot H_2O+Se \rightarrow Cu_{2-x}Se+NH_4+H_2O+OH^-+SeO_3^{2-}$$
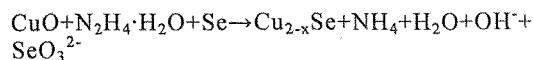
Therefore, not only was hydrazine hydrate one component of the mixed solvent, but also was responsible for the formation of Se^{2-} due to its reductive property [32]. Due to the strong coordinating ability of en, the stable complexes of $[Cu(en)_2]^{2+}$ and $[Cu(en)_2]^+$ were formed. However, the formation constant of $[Cu(en)_2]^{2+}$ ($k_2 = 10^{20}\ M^{-2}$) is $1 \times 10^{9.2}$ times that of $Cu(en)_2]^+$ ($k_2 = 10^{10.8}\ M^{-2}$) [33], that is, the concentration of free Cu^+ is much larger than that of free Cu^{2+} in the presence of the same concentration of en, which is benefit for the formation of $Cu_{2-x}Se$ so that a pure phase of cubic $Cu_{2-x}Se$ was finally obtained. The cooperative action of hydrazine hydrate and en resulted in the formation of the flake-like $Cu_{2-x}Se$ and the final nanotubes. Experimental investigations showed that the initial volume ratio of en to hydrazine hydrate ranging from 3 to 2 was a favorable condition for the synthesis of $Cu_{2-x}Se$ nanotubes.

2.3 Polymer-assisted Solvothermal Process

The polymer has been successfully employed as stabilizing agent as well as structure-directing agent for the preparation of 1D nanostructures. For instance, Ag nanowires can be obtained in the solution via the reduction of $AgNO_3$ with EG in the presence of poly (vinyl pyrrolidone) (PVP) [34], Cu_2O nanowires can be produced by a reduction route in the presence of PEG [35]. In our recent work, various 1D nanostructures were also obtained by a special poly-assiasted solvothermal process.

Very long CdS nanowires were fabricated in a polymer matrix [13]. In the polymer, polyacrylamide (PAM), dosed with Cd^{2+}, the solvothermal reaction with thiourea was conducted at 170 °C for 10 days. The nanowires can grow as long as 100 with 40 nm thicknesses. The polymer may absorb ethylenedamine to form gel with many small pores. When sufficient solvent is absorbed, these pores connect and become continuous. The growth of CdS crystallites
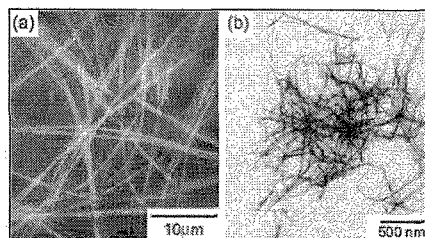
Fig. 7 (a) SEM image of CdS nanowires and (b) TEM image of CdSe nanowires.

is confined within the polymer matrix and axial growth along [001] direction is favorable. Using poly (vinyl alcohol) (PVA) instead of the PAM matrix, CdSe and CdTe nanowires with zinc blende structure have also been successfully prepared [36]. Figure 7a and 7b shows the SEM image of as-prepared CdS and the TEM image of CdSe nanowires, respectively.

In the above cases, the polymers seem to play a role similar to 'hard template', in which the nanowires can be formed. In another case of the synthesis of PbS closed nanowires, the used polymer, poly[N-(2-aminoethl)acrylamide], plays a distinct role as 'soft template' [37,38]. In this case, PbS closed nanowires with regular elliptic or parallelogrammic morphologies and nanorods were synthesized in the presence of poly[N-(2-aminoethl)acrylamide] in a mixed solvent of en/H$_2$O (3:1, v/v) in the range of 110-150 °C (Fig. 8) [37]. It is interesting that the closed structure has the single-crystal nature (the inset in Fig. 8b). Recently, it was found that formation of the closed nanowires has relation with an intermediate of frame-film structure [22], while the 1D growth of its nanorods is still not very clear. Without doubt, the results are attributed to the combinative performances of the exterior parameters on its crystal growth. The polymer was proved to be indispensable for the synthesis.

We have also successfully employed the polymer, polyethylene glycol (PEG), in the synthesis system to prepare oxide nanribbons and hydroxide nanotubes. In this case, the polymer seemed not to play a role as a template. VO$_x$·nH$_2$O (2.0≤x≤2.5) nanoribbons were prepared by direct hydrothermal reaction from the aqueous solution of NH$_4$VO$_3$ and polyethylene glycol 400 (PEG-400) at pH 3.5-5.5 and at 180 °C for 24 h [39]. The VO$_x$·nH$_2$O nanoribbons are up to ~200 μm in length, 100-150 nm in width, 20-30 nm in thickness (see Figure 9a). The ratios

Fig. 9 SEM images of VO$_x$·nH$_2$O nanoribbons (a) and Y(OH)$_3$ nanotubes (b).

of V^{4+} to V^{5+} in the products can be readily controlled by carefully adjusting the periods of reaction time. PEG carries the roles of both transport and reducing agent. A coordination self-assembly mechanism was proposed to elucidate the formation of the VO$_x$·nH$_2$O nanoribbons.

Yttrium hydroxide (Y(OH)$_3$) nanotubes were hydrothermally synthesized via a metastable precusor, PEG-Y(NO$_3$)$_3$ complex [40]. The as-synthesized nanotubes have outer diameters ranging from 80 to 200 nm, wall thicknesses of about 30 nm, and lengths up to several micrometers (see Figure 9b). In the process of formation of Y(OH)$_3$ nanotubes, a metastable complex, PEG-Y(NO$_3$)$_3$, was believed to be initially formed in the hydrothermal system, and continuous feeding of Y(OH)$_3$ due to decomposition of PEG-Y(NO$_3$)$_3$ in alkali solution onto the surface of the initial formed nanorods sustained the growth of the nanotube with opposite direction. As a result, the well crystalline Y(OH)$_3$ nanotubes were achieved.

Sb$_2$Se$_3$ nanoribbons with diameters in the range of 25 to 100 nm and lengths of tens of micrometers were synthesized via a simple hydrothermal process in the presence of PVA [41]. Under the help of PVA, Te nanowires with uniform diameter of ~25 nm were produced by the hydrothermal reduction of Na$_2$TeO$_3$ in a mixture solution of ethanol and water at 100 °C [42]. Figure 10a and 10b show the SEM images of as-prepared Sb$_2$Se$_3$ nanoribbons and Te nanowires, respectively. In different reaction system, the polymer may play different role in the growth of 1D nanostructures. In the above two cases, polymers played an important role on
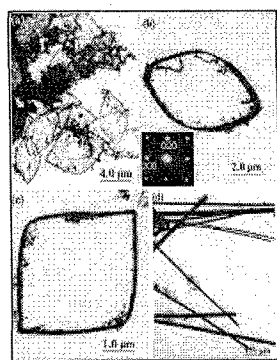

Fig. 8 (a)-(c) TEM images of closed PbS nanowires, (inset) a typical ED pattern, showing the single-crystal nature of the closed nanowires; (d) TEM image of PbS nanorods.
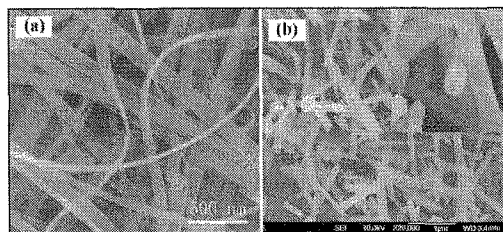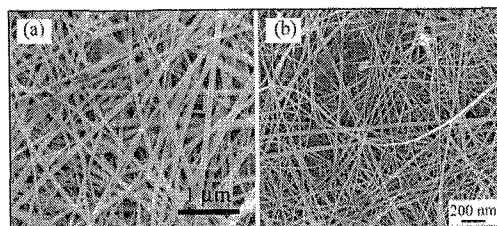

Fig. 10 SEM images of as-prepared Sb$_2$Se$_3$ nanoribbons (a) and Te nanowires (b).

the control of the nucleation and growth of silver nanowires through the selective adsorption on the facets of the growing particles. Such adsorption could significantly decrease the growth rate of these planes and also lead to a highly anisotropic growth.

3. CONCLUSION

In summary, the achievement of various 1D nanostructures with high aspect ratio, and novel morphologies demonstrates that the solvothermal technique should be attractive alternatives for the controlled syntheses of 1D nanostructures. The present solvothermal processes for various 1D nanostructures completely display the high flexibility and efficiency of the solvothermal route. In particular, although the detailed information about the performances of the mixed solvents and the polymers in some synthetic processes is still not very clear, it can be considered that the utility of mixed solvents and polymers in solvothermal processes has opened up other new perspectives for the controlled synthesis of 1D nanomaterials, which should be of importance in future nanomaterials research.

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