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NOVEL ROUTES OF ADVANCED MATERIALS PROCESSING AND APPLICATIONS

Synthesis of nanorods and nanowires using biomolecules under conventional- and microwave-hydrothermal conditions

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Abstract In this paper, we review our work on the synthesis and characterization of one-dimensional (1D) nanorods/nanowires and assemblies of inorganic materials with the assistance of several biomolecules under conventional- or microwave-hydrothermal conditions. Two classes of biomolecules have been investigated. One is sugars and their derivatives, and the other is amino acids and their polymers, peptide, and protein. With the assistance of sugars or their derivatives, different kinds of 1D elemental tellurium (Te) and selenium (Se) nanostructures with different sizes and morphologies have been obtained. With the assistance of amino acids or their polymers, 1D semiconductor sulfides and oxide nanowires and assemblies have been successfully synthesized. By providing confined spaces or serving as functional templates for site-specific nanomaterials nucleation or binding, biomolecules appear to direct the growth and/or the assembly of the nanomaterials.

Introduction

Nanomaterials are getting more and more attention from not only the scientific community, but also the public because of their special properties, which may lead to novel and exciting applications. These properties could differ markedly from those of the bulk materials and are sensitively dependent on their size, morphology, and assembly behaviors [1, 2]. Therefore, materials scientists are focusing on developing facile and effective synthetic techniques for fabricating nanomaterials with controlled size, morphology, and assembly behaviors and hence, tailoring their properties.

One-dimensional (1D) nanostructures, such as nanorods, nanowires, and nanobelts, make up an important class of the nanomaterials. These anisotropic nanostructures are of great interest due to their promising applications in both fundamental research and nanodevices fabrication [3–7] and have compelled more and more scientists to pursue direct and simple methods to accomplish synthesis with high yield [8–11]. Until now, remarkable progress has been achieved to control the morphology of nanomaterials and a range of different 1D nanostructures have been synthesized through various techniques, such as vapor–liquid–solid (VLS) growth [12], hydrothermal and solvothermal routes [13], hard template directing technique [14] and surfactant-assisted approach [15]. On the other hand, as nanotechnology has been developing to a higher level, guiding these 1D nanostructures into well-defined two-dimensional (2D) or three-dimensional (3D) ordered superstructures or complex architectures is increasingly gaining interest because it is a critical step toward the realization of chemical, optical, magnetic and electronic nanodevices and would bring possibilities to brand-new properties and applications that result from the spatial orientation and

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arrangement of the nanocrystals [16–26]. Although so far some kinds of complex nanorod-based structures including multi-armed [16–18], dendritic [19, 20], self-sustained [21] and penniform [22] structures of inorganic materials have been synthesized, the alignment and the patterning of the 1D nanostructures on a large scale are still very difficult for materials scientists to realize and the development of generally simple and rational construction approaches for macroscopic-scaled interconnection of nanoscale building blocks into desired structures is still a significant challenge in nanoscience and nanotechnology.

Biomolecules have distinct structures with typical size matching the scale of nanomaterials [27]. They also have several fundamental features, such as specific and strong complementary recognition interactions, several binding sites, etc. and can interact with nanomaterials through physical adsorption, electrostatic binding, specific recognition, and covalent coupling, which make them important future building blocks for nano-architectures [28, 29]. With the biomolecules, organisms have built complex molecules and nanoscale organelles for about 3.8 billion years [30, 31]. Inspired from biology, harnessing biomolecules' amazing abilities to mimic the way nature makes materials would offer an unmatched alternative to conventional fabrication methods for nanostructured materials [32–36]. By providing confined spaces or serving as effective templates for site-specific nanomaterials nucleation or binding, biomolecules would play an important role in directing the growth and/or the assembly of the nanomaterials. Until now, this biomolecule-assisted approach has been employed to assist the synthesis of single crystal nanowires and the assembly of nanocrystals into 1D nanowires, 2D or 3D ordered structures. In 1997, Mann et al. pioneered the use of self-assembled bacteria S-layers to synthesize cadmium sulfide superlattices [37]. Recently, protein cytochrome c_3 has been confirmed to have linking function in the synthesis of polycrystalline Se nanowires [38]. Polypeptide glutathione-assisted reaction was used to produce single-crystal Se nanowires [39]. DNA, an attractive biomolecule with special cylindrical double-helical structure, has also been explored in templated-synthesis of gold and copper nanoparticle-nanowires [40–43] or to assemble gold nanorods [44]. However, this outstanding approach is still in its early stage of development. Full investigation of the effects of these selective biomolecules on nanomaterials syntheses is of great importance in the development of novel materials and would offer great opportunities to fabricate nanocrystals with desired shapes and construct complicated superstructures from a single functional structure.

In this paper, we investigate the effects of some biomolecules on the syntheses of 1D inorganic nanorods/nanowires/nanobelts and assemblies under conventional- or microwave-hydrothermal conditions. Two classes of biomolecules have been studied. One is sugars and their derivatives, and the other is amino acids and their polymers. With the assistance of sugars or their derivatives, such as glucose, sodium gluconate, and starch, different kinds of 1D elemental tellurium (Te) and selenium (Se) nanostructures with different sizes and morphologies have been obtained. With the assistance of amino acids such as aspartic acid and serine, multi-arm horn-like and bi-pyramid-like architectures of complex PbS nanorod-based structures have been realized under conventional hydrothermal conditions, respectively. Glutathione (GSH), a polypeptide, can be used not only as a sulfur source, but also as an assembling agent for the synthesis of an unusual, highly ordered snowflake-like structure that is assembled with Bi_2S_3 nanorods under microwave-assisted hydrothermal conditions. Lysozyme, a protein, has also been found to be a new morphology-directing agent to direct the growth of single-crystal bismuth sulfide and oxide nanowires.

Experimental

Synthesis of one-dimensional nanostructures

We mainly used sugars, amino acids, peptide, and protein-assisted conventional- or microwave-hydrothermal techniques to synthesize 1D nanostructures. The detailed description of the methods was reported elsewhere in our previous publications [45–50].

Sugars- or their derivative-assisted synthesis of 1D nanostructures of Te/Se

For all the syntheses of the Te/Se nanostructures, appropriate amounts of $H_2TeO_4 \cdot 2H_2O/Na_2SeO_3$ and sugars/sugar derivatives were dissolved in 10 mL distilled water and then transferred into a Teflon-lined stainless steel autoclave. After keeping at 160 °C for 15 h, the autoclave was cooled to room temperature in air. The precipitate was collected, washed with distilled water and alcohol, and dried in air at ambient temperature.

Amino acid-assisted synthesis of PbS nanostructures

In a typical process, 0.15 g $PbCl_2$, 0.04 g thiourea, and 0.05 g aspartic acid or serine were mixed with 10 mL of distilled water in a Teflon-lined stainless steel autoclave. After sealing, the autoclave was kept at 150 °C for 15 h and then cooled to room temperature. The products were collected by centrifugation and washed with distilled water and alcohol several times, followed by drying in air at room temperature.

Peptide-assisted synthesis of Bi_2S_3 nanostructures

This synthetic reaction was carried out under microwave-assisted hydrothermal conditions. Typically, 0.06 mmol $Bi(NO_3)_3{\cdot}5H_2O$ and 0.16 mmol glutathione were put into a Teflon vessel of a double-walled digestion vessel with 0.45 mol distilled water. The double-walled digestion vessels have an inner liner and cover made up of Teflon PFA and an outer high-strength shell of Ultem polyetherimide. After sealing, the vessel was treated at 120 °C for 1 h using a microwave digestion system, MARS-5 (CEM Corp.). The product was collected, and washed with distilled water and alcohol. Then the black powders were dried at room temperature.

Protein-assisted synthesis of Bi_2S_3 and Bi_2O_3 nanowires

For Bi_2S_3 nanowires, 0.15 g $Bi(NO_3)_3{\cdot}5H_2O$, 0.04 g thiourea, and 0.05 g lysozyme were put into a Teflon-lined stainless steel autoclave. The autoclave was then filled with 10.0 g distilled water and maintained at 160 °C for 15 h. After the hydrothermal treatment, the vessel was cooled to room temperature, the product was collected, filtered and washed with absolute alcohol and distilled water for several times, and dried at room temperature. The synthesis procedure for bismuth oxide is quite similar to that of the bismuth sulfide but without the addition of thiourea.

Characterizations of one-dimensional nanostructures

Transmission Electron Microscopy (TEM) images were obtained with a Philips 420 transmission electron microscope with an accelerating voltage of 120 kV. High-resolution TEM (HRTEM) micrographs and selected area electron diffraction (SAED) patterns were taken on a JEOL-2010F transmission electron microscope operated at 200 kV. Scanning Electron Microscopy (SEM) images were obtained with a Hitachi S-3500N Scanning Electron Microscope.

Results and discussion

Sugars and their derivatives

Sugars and their derivatives, such as glucose, sodium gluconate, and starch, are one kind of the most common biomolecules in our general life and are wide-spread in nature [51]. They have been extensively used in medicine, pharmacy, and food industry. The side hydroxyl groups of these biomolecules have chelating functions, which have been utilized to adsorb metal ions, and might provide the possibility to direct the synthesis of nanostructures, especially the controlled growth of 1D nanomaterials [51]. Herein we report the synthesis of 1D tellurium/selenium nanostructures with the assistance of sugars or their derivatives as both reducing and morphology-directing agents.

Monosaccharides

Glucose is the most common and simplest sugar and classified as a monosaccharide. Figure 1a and b shows the typical TEM images of tellurium sample prepared with glucose as reducing agent from $H_2TeO_4{\cdot}2H_2O$ (the ratio between $H_2TeO_4{\cdot}2H_2O$ and glucose is 0.1 g/0.1 g). It can be seen clearly that the obtained sample has wire-like morphology (>90%) and according to its SAED pattern (Fig. 1c), these nanowires are crystalline tellurium of hexagonal phase. These nanowires are uniform and with average diameter of about 15 nm and length of up to 3 μm. The HRTEM image (Fig. 1d) confirms that the nanowire is single crystalline and the calculated spacing of the lattice perpendicular to the growth direction is 0.59 nm, which is equal to the spacing of (001) planes. It suggests that the nanowires might have a preferred growth direction of [001], in agreement with the results reported in the previous literature [52]. The concentration of glucose is quite important to the formation of tellurium nanocrystallites. When the concentration is low, the obtained samples are amorphous. But a higher concentration of glucose (such as the ratio between $H_2TeO_4{\cdot}2H_2O$ and glucose is 0.1 g/0.2 g) showed more effects on the assembly of nanowires or nanorods and led to the formation of tassel-like structures assembled by tellurium nanorods. Its TEM images are shown in Fig. 1e, f. The center diameter of these tassels is ranging from 200 to 400 nm and the length is up to 5 μm. According to the magnified TEM image (Fig. 1f), these tassels are assembled by uniform nanorods with diameter of about 15 nm. Further increase in the concentration of glucose in the system was not found to be beneficial to the growth of 1D tellurium nanowires as it led to the formation of particle-like morphology.

As a derivative of glucose, sodium gluconate (referred to hereinafter as gluconate) is also a green and safe chemical with very strong chelating function [51], which has not been used for the synthesis of nanomaterials to the best of our knowledge. Here we also exploit gluconate to control the 1D-preferred growth of tellurium. Figure 2a

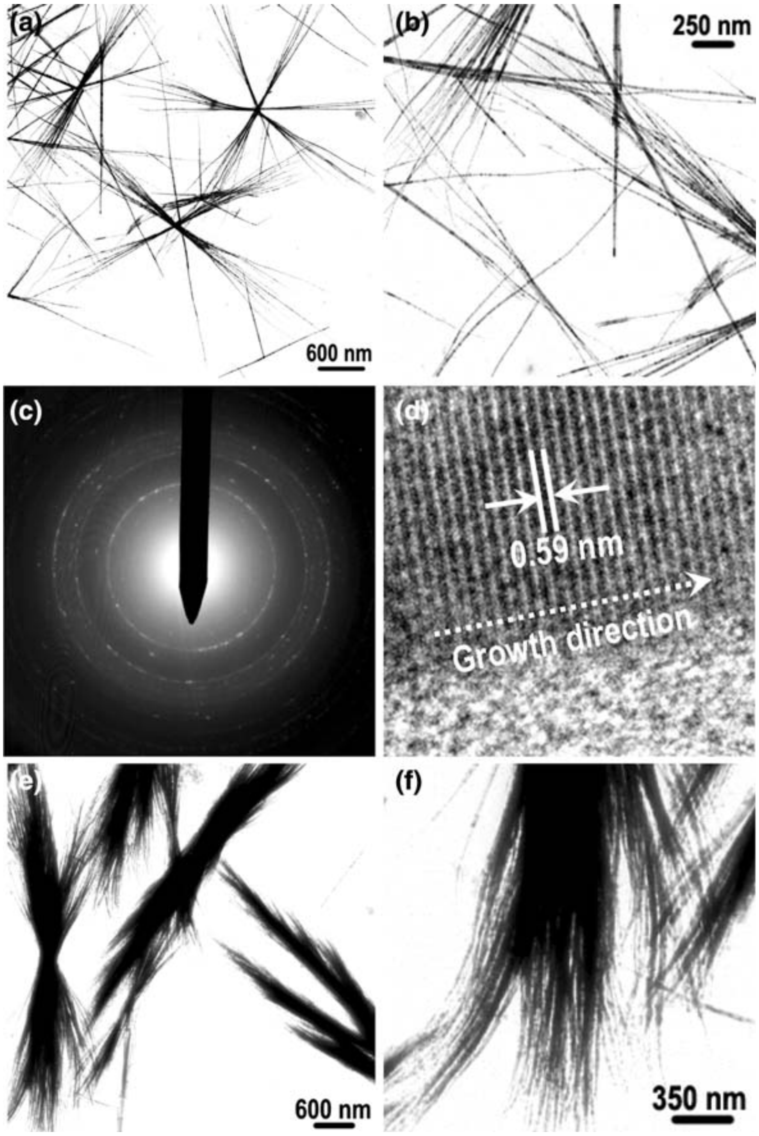


Fig. 1 (**a–d**) TEM images, SAED pattern and HRTEM image of the obtained Te sample prepared with glucose as reducing agent at a low reactants' concentration; (**e**, **f**) TEM images of the obtained Te sample prepared with glucose as reducing agent at a high reactants' concentration

is a TEM image of the tellurium nanorods prepared at low concentrations of reactants (weight ratio between $H_2TeO_4{\cdot}2H_2O$ and gluconate is 0.45 mmol/0.45 mmol). It clearly shows that almost all the sample has a relatively uniform, rod-like morphology with a tendency to arrange in parallel. About ten nanorods aggregated with a parallel arrangement. Figure 2b shows a clear view of laterally aggregated nanorods. These nanorods are uniform with an average diameter of ~20 nm and an average length of ~700 nm. The concentration of the reactants and the ratio between the reactants influenced the growth rate of 1D tellurium nanostructures and led to a change in their morphology. Figure 2c shows the TEM image of the tellurium nanowires prepared with a weight ratio of 0.90 mmol/0.90 mmol between $H_2TeO_4{\cdot}2H_2O$ and gluconate, in the other words, with increasing concentrations of H_2TeO_4 and gluconate but keeping the ratio between them unchanged. These nanowires have an average diameter of ~20 nm but lengths of up to ~5 μm. Compared with those nanowires prepared with weight ratio of 0.45 mmol/0.45 mmol between $H_2TeO_4{\cdot}2H_2O$ and gluconate, the lengths of tellurium nanorods increased but with their diameter almost unchanged. Thus controlling the concentration of starting chemicals might provide a simple way to adjust the length and the axis ratio of tellurium nanorods to some degree. On the other hand, increasing the ratio between gluconate and $H_2TeO_4{\cdot}2H_2O$ led to the increase of the lengths of tellurium nanorods and the decrease of their diameters. Figure 2d shows the TEM image of tellurium nanowires prepared with a weight ratio of 0.45 mmol/0.90 mmol between $H_2TeO_4{\cdot}2H_2O$ and gluconate. This sample consisted of fine nanowires with lengths up to 2 μm but with uniform diameter of ~10 nm.

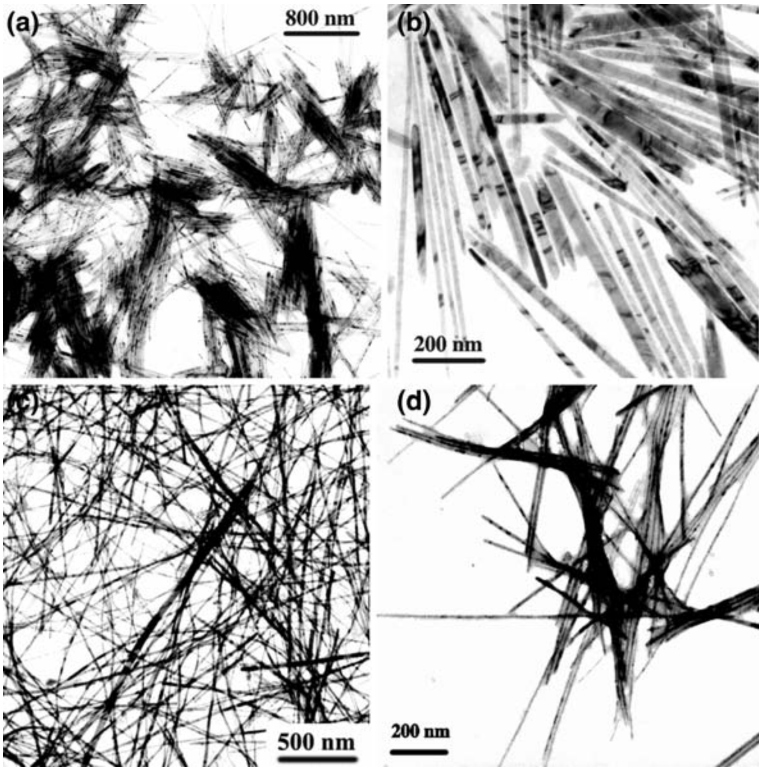


Fig. 2 (**a**, **b**) TEM images of the Te sample prepared with weight ratio between H_2TeO_4 and gluconate of 0.1 g/0.1 g; (**c**) TEM image of the Te sample prepared with weight ratio between H_2TeO_4 and gluconate of 0.2 g/0.2 g; (**d**) TEM image of the Te sample prepared with weight ratio between H_2TeO_4 and gluconate of 0.1 g/0.2 g

Sorbitol, the alcohol form of glucose, is also a coordinating reagent and has relatively strong reducing ability. In our experiments, we introduced this green chemical into the hydrothermal system to obtain elemental Se nanostructures from Na_2SeO_3. Figure 3a shows the TEM image of the sample reduced by sorbitol, confirming that the formed selenium crystallites have cylindrical wire-like morphology. The average diameter is calculated to be ~60 nm and the lengths are up to micrometers. Figure 3b shows the TEM image of a single nanowire. Its SAED pattern (Fig. 3b inset) confirms that it is of single crystal in nature. According to the diffraction dots, the nanowire might have a preferred growth direction of [001].

Polysaccharides

Polysaccharide starch is a polymer of glucose, the most abundant saccharide stored in plants, and widely used as a food source [53, 54]. This bioorganic molecule has been

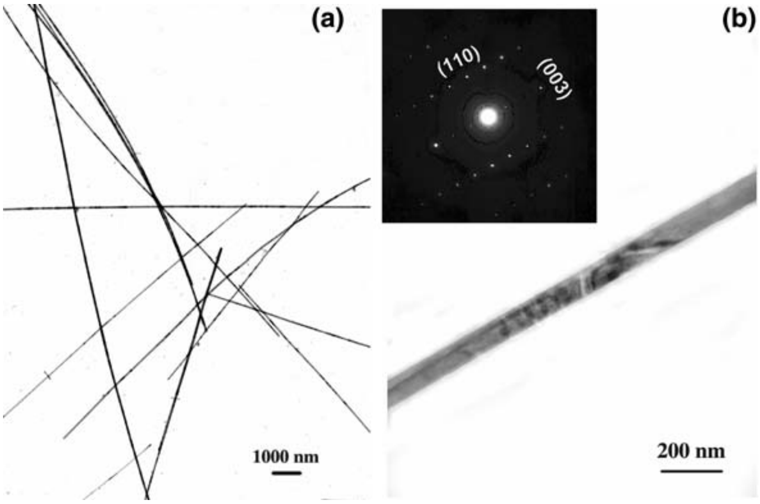


Fig. 3 TEM images and SAED pattern of Se nanowires with sorbitol as reducing agent

well studied and confirmed to have chain-like shape with hydroxyl (–OH) on surface [53, 54], which might be beneficial for the growth of 1D nanomaterials. Although starch is known as a non-reductive saccharide [53, 54], here we demonstrated that this biomolecule could also reduce $H_2TeO_4 \cdot 2H_2O$ powders to form tellurium nanowires under conventional hydrothermal conditions. Figure 4a shows a TEM image of the obtained tellurium, from which it can be clearly seen that the obtained samples have wire-like morphology with high yield. The average diameter of these nanowires is of ~25 nm and lengths are up to 10 μm. This result confirms that crystalline tellurium nanowires could be synthesized in a large scale by using starch as reducing agent.

Cellulose is the single most abundant organic molecule in the biosphere, and yet the most profligately wasted natural polymer. Like starch, cellulose is a polysaccharide with glucose as its monomer. In our experiments, we also used it to synthesize selenium nanocrystals under hydrothermal conditions. Figure 4b shows a TEM image of the product with cellulose and Na_2SeO_3 as reactants, confirming the formation of 1D Se nanostructures. The bending of these 1D nanostructures (TEM image of a single 1D nanostructure shown in Fig. 4b inset) indicates that they are of belt-like (ribbon-like) morphology. The widths of these nanobelts are not quite uniform ranging from 200 to 1,500 nm and their lengths are up to tens of micrometers. The thicknesses of these nanobelts are about tens of nanometers. The surfaces of two sides of nanobelts are not smooth and have saw-like structures. This synthetic reaction was carried out in solution at low temperature under simple hydrothermal conditions, which is quite different from the previous high temperature evaporation/reaction processes for nanobelts and might bring a new, mild, and economical concept for the synthesis and construction of nanobelts.

Amino acids and their polymers, peptide and protein

Amino acids, peptides, and proteins are the "building blocks" of the body. All of these biomolecules have several functional groups, such as carboxyl and amine, which could chelate with metal ions to form special complexes and then might direct the growth of the inorganic materials. Herein we report the synthesis of several 1D nanostructures of semiconductor sulfide and oxide with the assistance of amino acids and their polymers under conventional- or microwave-hydrothermal conditions.

Amino acids

Amino acids have both an acidic group, in the carboxylic acid –COOH, and a basic group, in the amine $-NH_2$. These functional groups have strong coordination ability toward the metal ions, and might provide reaction sites by coordinating with metal ions to confine the growth of 1D nanostructures. Figure 5a displays the SEM image of the sample prepared with $PbCl_2$ and thiourea as reactants and aspartic acid as an additive under conventional hydrothermal conditions. It can be clearly seen that the obtained sample has a multi-armed horn-like structure formed by nanorods. The average width and length of the horn-like structures can be calculated to be ~2 and ~5 μm, respectively. The detailed structure (as shown in Fig. 5b with a higher magnification) can be described as many multi-armed nanorod-based structures arranged along a line and in parallel to each other. The diameters of the nanorods are about 100–200 nm and their lengths are up to ~2 μm. Figure 5c shows the TEM image of a small horn-like structure. Form the image, it can be seen that many short nanorods are grown from a center line and are

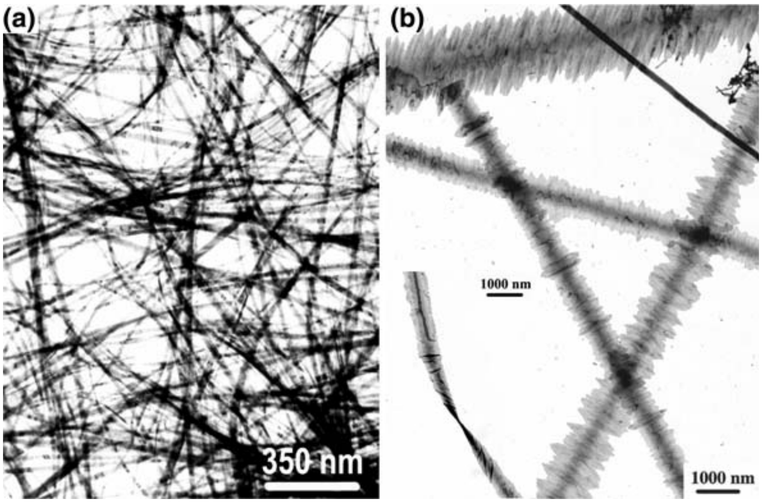


Fig. 4 (**a**) TEM image of the Te nanowires with starch as reducing agent; (**b**) TEM images of the Se nanobelts with cellulose as reducing agent

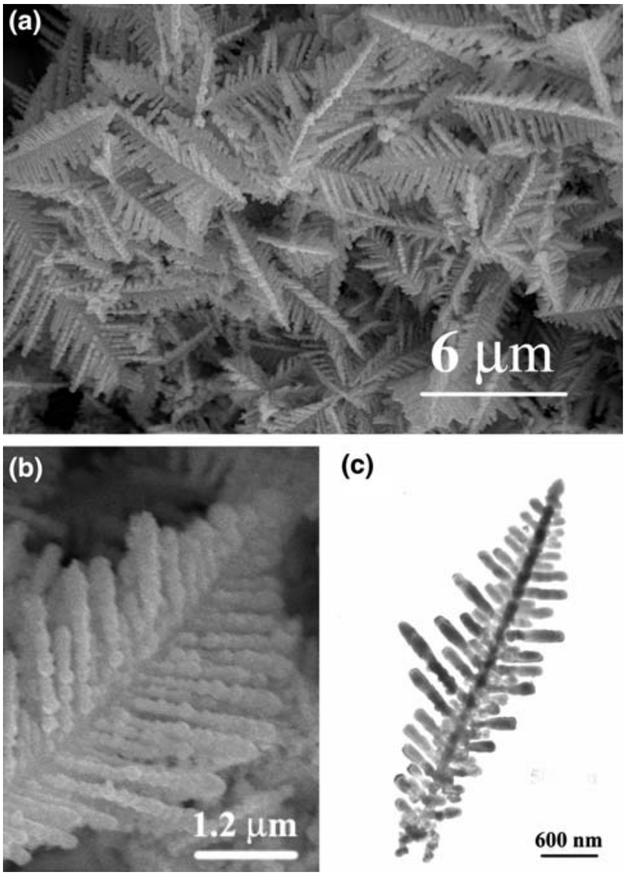


Fig. 5 SEM and TEM images of PbS sample prepared with aspartic acid as additive

separate but parallel to each other, which are consistent with the result from SEM observations.

By simply replacing aspartic acid with serine, the nanorod-based structures could be controlled to be more complicated architectures. Figure 6a displays an SEM image of the sample prepared with $PbCl_2$ and thiourea as reactants and serine as an additive under conventional hydrothermal conditions, from which it can be seen that the obtained sample shows bi-pyramid-like structures. This bi-pyramid-like structure is assembled from several horn-like structures (horns), usually six horns to form a bi-pyramid-like structure. Viewed from different directions, the bi-pyramid-like structure can appear in two forms, the co-point bi-prism-like structure and co-face bi-pyramid-like structure, as shown in Fig. 6b and c, respectively. The sizes of the bi-pyramid-like structures are about ~8 µm on an average. The diameters of the horns are about ~2.5 µm and the lengths are about ~5 µm. Every horn-like structure is formed by parallelly arranged short nanorods, similar to the structure obtained with aspartic acid as additive. The smallest building units, nanorods, are about 150 nm in width and 1.5 µm in length. Figure 6d shows a TEM image of a co-face bi-pyramid-like structure. Six horn-like structures are orderly arranged from a center point in 3D space. The size of the complex structure and the diameter and length of the smallest building unit are consistent with the results from SEM investigations.

Peptide Glutathione

Glutathione ($HO_2CCH(NH_2)CH_2CH_2CONHCH(CH_2SH)$–$CONHCH_2CO_2H$), is a tripeptide and can be used not only as a sulfur source but also as an assembling agent to form highly ordered snowflake-like structures of Bi_2S_3 nanorods. The reaction is carried out under microwave-assisted hydrothermal condition with $Bi(NO_3)_3{\cdot}5H_2O$ and GSH as reactants. The morphology and structure of the products have been investigated by TEM. Figure 7a displays a typical TEM image of the sample, showing that almost all of the crystals have ordered snowflake-like structures. The yield of these structures is very high (>90%). Figure 7b shows a whole ordered snowflake-like structure with relatively high magnification. It can be clearly seen that the snowflake architecture is built by both short and relatively long nanorods. The long nanorods radially grew from the center to form hexagonally ordered structures and on these long nanorods several short nanorods grew from one center and aligned in an orderly fashion, which forms an unusual but highly ordered hexagonal structure, like snowflakes in nature. The diameters of the long nanorods are uniform with an average diameter of about 27 nm, which is relatively wider than that of the short nanorods (the average diameter is about 15 nm). The length of the short nanorods is about dozens of nanometers, while that of the long nanorods is up to micrometers, which means that the ordered structures can be extended up to several micrometers. The ED pattern of the snowflake-like particle (Fig. 7c) displays highly ordered diffraction spots, confirming that these nanorods have high crystallinity and preferred growth direction and are organized to form a specially ordered hexagonal-symmetry structure which expands to the whole snowflake-like particle. Figure 7d shows an HRTEM image of a nanorod, further confirming our suggestions on the high crystallinity and the structure of these nanorods. The interplanar spacing, parallel to the rod axis of Bi_2S_3 nanorods, is about 0.398 nm, which corresponds to the *c*-axis of the orthorhombic structure. This result indicates that these nanorods have the [001] directional preferred growth, in agreement with the ED result. Infrared spectrum of the sample (not shown) shows that no absorption peaks of carboxyl groups could be found after the synthesis of Bi_2S_3, which suggests that the obtained product has high purity and no GSH remains in

Fig. 6 SEM and TEM images of PbS sample prepared with serine as additive

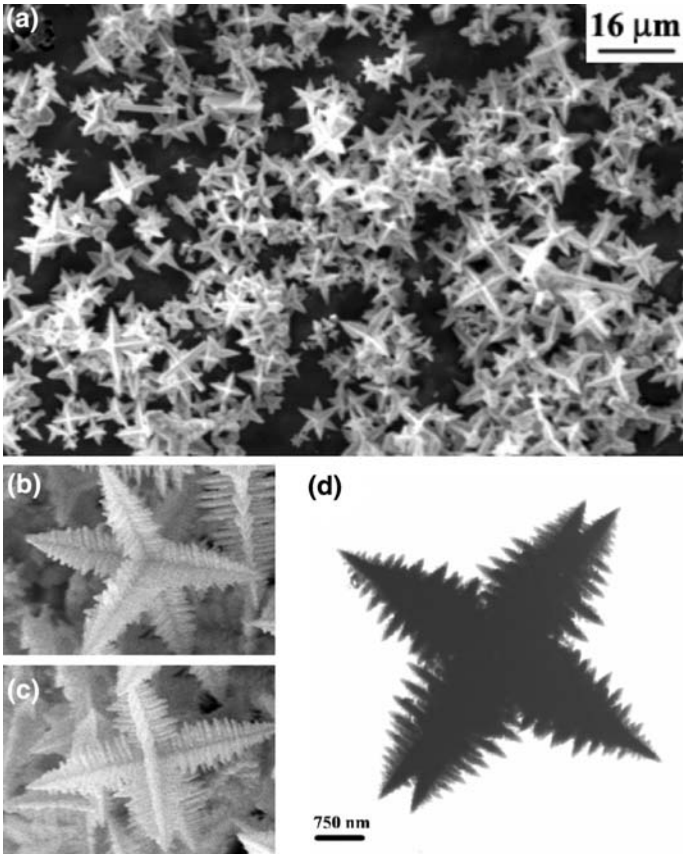
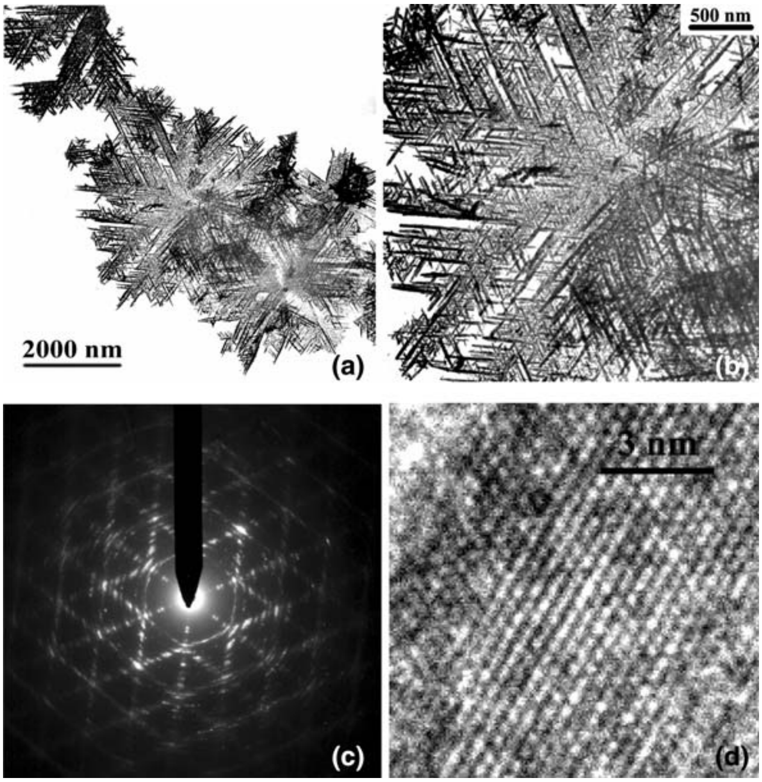


Fig. 7 TEM, HRTEM images, and SAED pattern of Bi_2S_3 snowflake-like structure prepared with assistance of GSH



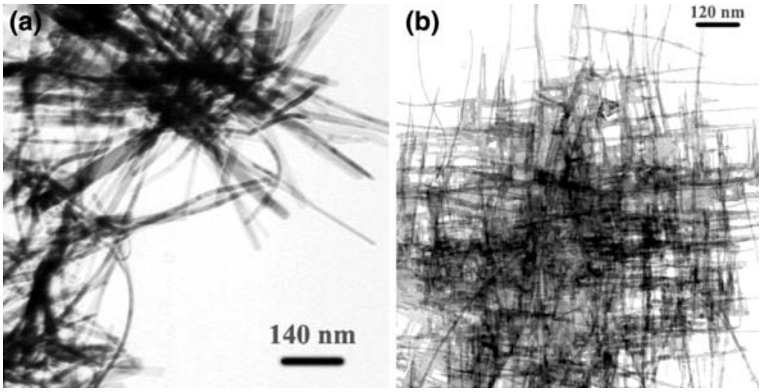


Fig. 8 (**a**) TEM image of Bi_2S_3 nanowires prepared with lysozyme as additive; (**b**) TEM image of Bi_2O_3 nanowires prepared with lysozyme as additive

the final product. During the synthesis process, the microwave irradiation was applied as a heating method to raise the system temperature through the interactions between the microwave energy and the individual polar molecules. However, it is not the only heating method to obtain the final interesting products. When conventional oven heating is applied, Bi_2S_3 nanomaterials with similar structures can be synthesized but the reaction time is much longer. This result suggests that compared to the conventional heating method, the microwave irradiation is an efficient heating method for materials synthesis, but not a crucial factor for the final structures. It is believed that the addition of the bio-molecules play decisive role on the final structure of the 1D structures.

Protein Lysozyme

Lysozyme is a protein with relatively high stability and responsible for breaking down the polysaccharide walls of many kinds of bacteria [53]. It has also been confirmed that it has chelating interactions with metal ions [55, 56]. So it is reasonable to expect the morphology-directing function of protein lysozyme in the formation of 1D inorganic nanomaterials. Figure 8a is a TEM image of the obtained bismuth sulfide sample, prepared under conventional–hydrothermal conditions with $Bi(NO_3)_3{\cdot}5H_2O$, thiourea and lysozyme as reactants, which clearly shows that the obtained crystallites have a wire-like morphology. The diameters are in the range of 10–50 nm and lengths are up to micrometers. Moreover, the morphology controlling function of lysozyme can be extended to the synthesis of bismuth oxide nanowires. Figure 8b shows the TEM image of the bismuth oxide sample prepared without the addition of thiourea and with the addition of lysozyme of 0.1 g. It can be seen that the obtained bismuth oxide also has wire-like morphology. These bismuth oxide nanowires intertwine with each other and have an average diameter of $\sim$8 nm with lengths of up to several micrometers.

Conclusion

In this paper, biomolecule-assisted approach has been employed to synthesize several 1D nanorods/nanowires/nanobelts and assemblies of inorganic materials under conventional- or microwave-hydrothermal conditions. Two classes of biomolecules have been investigated. One is sugars and their derivatives, and the other is amino acids and their polymers peptide and protein. With the assistance of sugars and their derivatives, different kinds of 1D elemental tellurium (Te) and selenium (Se) nanostructures with different sizes and morphologies have been obtained. With the assistance of amino acids such as aspartic acid and serine, multi-arm horn-like and bi-pyramid-like architectures of complex PbS nanorod-based structures have been realized under conventional hydrothermal conditions, respectively. Glutathione, a polypeptide, can be used not only as a sulfur source but also as an assembling agent for the synthesis of an unusual, highly ordered snowflake-like structure that is assembled with Bi_2S_3 nanorods under microwave-assisted hydrothermal conditions. Lysozyme, a protein, has also been found to be a new morphology-directing agent to direct the growth of single-crystal bismuth sulfide and oxide nanowires. Although the exact mechanism of the reactions is difficult to know, it is no doubt that the used bio-molecules have played an important role in the formation of the 1D nanostructures. The used biomolecules, irrespective of whether they are sugars or protein, peptide and amino acids, have several functional groups, such as –OH, $-NH_2$, and –COOH, which have strong coordination ability toward the inorganic ions. They also have special structures, such as chained-shape of the polysaccharide. During the syntheses of the 1D nanostructures, these bio-molecules might react with inorganic species through the functional groups to form special intermediates, and then direct the growth and/or the assembly of the 1D nanostructures by their special structures. For example, starch molecules have been reported to be chain-shaped structures with many hydroxyl (–OH) groups on their surfaces [53, 54]. During the synthesis of Te nanowires, these –OH groups might react with TeO_4^{2-} groups through hydrogen bonds to form chain-shaped intermediate compounds. Thus, the long chains of starch could serve as a directing template for the growth of tellurium nanowires. This biomolecule-assisted method enlarges the application of biomolecules to the green synthesis of low-dimensional nanostructures and would have promise for extension to topologically more intricate structures, in addition to the generation of other 1D nanomaterials.

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