

Biomolecule-Assisted Synthesis of Highly Ordered Snowflakelike Structures of Bismuth Sulfide Nanorods

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Biomolecules, as life's basic building blocks, have special structures and fascinating self-assembling functions. Their special properties make them templates of unmatched type for the design and synthesis of complicated structures at molecular level.¹ Thus far, many synthesis efforts have been focused on using biomolecules to template and assemble nanostructures.² With the use of DNA, polylysine, or cytochrome *c*₃, several nanowires have been obtained,³ and due to its cylindrical, double helical structure, DNA also has been confirmed to be useful in the assembly of nanoparticles to two- or three- dimensional structures⁴ and in the alignment of discrete one-dimensional (1D) nanomaterials.⁵ How to utilize biomolecules' special structures and strong assembling functions to fabricate nanocrystals of desired shape and to construct complicated superstructures from a single functional structure is very important in all of biology, chemistry, and materials science, but this approach is still in its infancy.

It has been well-known that 1D nanostructures have unique optical, magnetic, and catalytic properties and are expected to be elementary units of optoelectronic devices.⁶ The synthesis of 1D nanostructures and guiding these nanometer-scaled building blocks to ordered superstructures or complex functional architectures would offer great opportunities to explore their novel properties and lead to the construction of nanoscale devices.⁷ Porous alumina,⁸ nanotubes⁹ and patterned catalyst-limited¹⁰ growth, reverse micelles approach,¹¹ precursor decomposition route,^{12a} and room-temperature solution method¹³ have been reported for the construction of ordered and complex 1D nanostructures such as multi-armed,¹² self-sustained,¹³ and penniform¹¹ nanostructures. As a semiconductor with extensive applications, Bi₂S₃ has been paid much attention for its 1D nanostructures.¹⁴ In this communication, we propose a simple biomolecule-assisted approach for the synthesis of unusual, highly ordered snowflakelike structures that can be assembled with Bi₂S₃ nanorods under microwave-hydrothermal conditions. Glutathione (GSH) (HO₂CCH(NH₂)CH₂CH₂CONHCH(CH₂SH)CONHCH₂CO₂H), a polypeptide, is used not only as an assembling agent but also as a sulfur source. By controlling the ratio between bismuth nitrate and GSH as well as the synthetic temperature, highly ordered structures and nanowires with different lengths can be controllably synthesized.

In a typical procedure, 0.06 mmol Bi(NO₃)₃·5H₂O and 0.16 mmol GSH were mixed with 0.45 mol distilled water and sealed in a Teflon vessel of a double-walled digestion vessel. After treating at 120 °C for 1 h using a microwave digestion system, MARS-5 (CEM Corp.), the vessel was then cooled to room temperature. The product was collected, washed with distilled water and alcohol, and dried at room temperature. The obtained products were confirmed to be orthorhombic Bi₂S₃ by powder X-ray diffraction (XRD) and energy dispersive spectroscopy (EDS) (see Supporting Information, SI). No absorption peak of carboxyl could be found in infrared spectrum after the synthesis of Bi₂S₃, which suggests that the obtained product has high purity and no GSH remains in the final product.

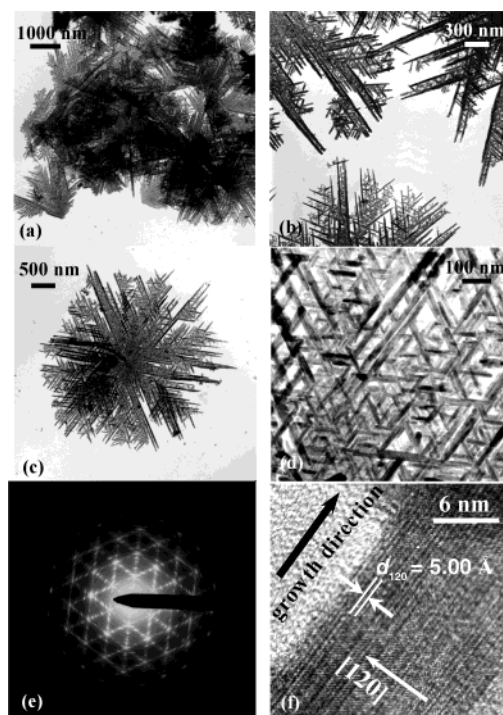


Figure 1. (a, b) Low-magnification TEM images of highly ordered snowflakelike structures; (c, d) TEM image of a single snowflakelike structure and its selected-area magnified image; (e) ED pattern of the single snowflakelike structure; (f) HRTEM image of a nanorod.

The morphology and structure of the products have been investigated by transmission electron microscopy (TEM). The low-magnification TEM images (Figure 1a, b) display many snowflakelike structures, which are typical of this product. Indeed, the yield of these structures is very high, and almost all of the crystals have highly ordered structures (above 90%). Panels c and d of Figure 1 are TEM images with relatively high magnification, showing a whole ordered structure and its selected-area magnification. It can be seen that the flake is formed by both short and relatively long nanorods. The long nanorods are radially grown 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 average diameter of the short nanorods is about 15 nm, which is narrower than that of the long nanorods (about 27 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 snowflake structures are elevated intersection structures, and the thickness seems to be about several hundred nanometers. The electron diffraction (ED) pattern of the snowflakelike particle (Figure 1e)

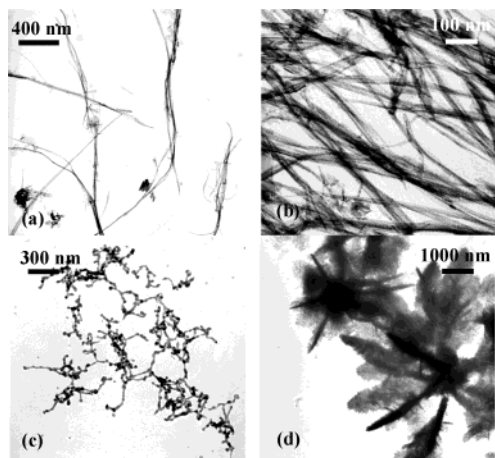


Figure 2. TEM images of the samples prepared with different conditions: (a, b) changing $\text{Bi}(\text{NO}_3)_3/\text{GSH}$ molar ratio to 2.2, (c) changing the temperature to 80 °C, (d) changing the temperature to 160 °C

displays six strong ordered electron diffraction spots and many linearly arranged spots, similar to single-crystal-like diffraction spots, which means these nanorods have high crystallinity and preferred growth direction and are organized to form a specially ordered hexagonal-symmetry structure. The six strong hexagonal electron diffraction spots are calculated to have a d spacing of 2.00 Å, which might be from the periodic crystal planes of (002) of hexagonally arranged Bi_2S_3 single crystal nanorods. This suggests that these nanorods might have [001] growth direction. The linearly arranged electron diffraction spots are approximately calculated to have d spacings of 5.60, 5.00, 3.96, 3.55, 2.50, 1.76 Å, etc. and might be from (020), (120), (220), (130), (240), (620), etc. crystal planes, which are perpendicular to (002) crystal planes. Figure 1f shows a high-resolution TEM (HRTEM) image of a nanorod, further confirming our suggestions on the structure. The crystal planes, parallel to the rod axis, have the spacing of about 5.00 Å, which corresponds to that of (120) planes. This result indicates that the nanorod might have [001] directional preferred growth, in agreement with the ED result.

In our experiments, the formation of these highly ordered snowflake-like structures is no doubt relevant to the coordination interaction between bismuth ions and GSH. The molar ratio between $\text{Bi}(\text{NO}_3)_3$ and GSH ($\text{Bi}^{3+}/\text{GSH}$) determines the product's final morphology and structure, but without changing the product's crystal phase, which could be confirmed by XRD pattern of the product prepared under high $\text{Bi}^{3+}/\text{GSH}$ of 2.2 (see SI). An appropriate ratio of $\text{Bi}^{3+}/\text{GSH}$ is critical to the construction of superstructures. With the decrease of GSH relative concentration, the products' structures change from snowflake structures to spindle structures to nanorods (see TEM images in SI) and then finally to long Bi_2S_3 nanowires. Panels a and b of Figure 2 are the TEM images of the sample synthesized with $\text{Bi}^{3+}/\text{GSH}$ of 2.2, showing that the product consists of nanowires with diameters of about 15 nm and lengths up to several micrometers. Thus, this method also provides an efficient way for the synthesis of nanowires with controllable axis ratio. In addition, the synthetic temperature would also affect the product's morphology and assembly behavior. At lower temperature, the products consist of particle nanowires (Figure 2c) with a uniform diameter of about 24 nm, while at higher temperature, the particles have flowerlike structures (Figure 2d), similar to snowflake-like structures but with lower order.

In summary, a simple procedure based on a biomolecule-assisted technique has been developed to spontaneously crystallize Bi_2S_3 nanorods into highly ordered snowflake-like superstructures in high yield under microwave-hydrothermal¹⁵ conditions. By controlling the synthesis conditions, other kinds of 1D nanomaterials were prepared. In principle this approach has promise for extension to topologically more intricate structures, in addition to the generation of other 1D materials.

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Supporting Information Available: XRD pattern, EDS spectrum of the snowflake-like structures, XRD pattern of the product prepared under high molar ratio, 2.2, of $\text{Bi}(\text{NO}_3)_3$ to GSH, TEM images of spindle structures and nanorods (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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