Protein-assisted synthesis of single-crystal nanowires of bismuth compounds†

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Lysozyme, a protein, has been found to be a new morphology-directing agent and a simple and mild bio-molecule assisted method has been proposed for the synthesis of single-crystal bismuth sulfide and oxide nanowires.

One-dimensional (1D) nanomaterials have been touted to be important for applications of electrical transport, optical phenomena, and as functional units in nanocircuitry.[1–3] Pursuit of methods for the synthesis of semiconducting and metallic nanowires has yielded strategies including vapor liquid solid (VLS) growth,[4] hydrothermal and solvothermal routes,[5] hard template directing technique[6] and surfactant-assisted approach.[7] Although each method developed for the production of nanowires has had success in achieving high-quality materials, developing simple and effective methods for the fabrication of 1D systems remains a challenge to materials chemists.

Bismuth sulfide has a complicated structure, arranged by chain-like structure in two different ways.[8] As a semiconductor with wide applications in various devices, it has attracted much attention based on its 1D nanostructure and bismuth sulfide nanowires have been synthesized by many methods.[9,10] Bulk bismuth oxide itself is an excellent opto-electronic material and catalyst and has also been extensively used as an effective component in third-order nonlinear optical glasses, cataphoresis and medical products.[11–13] Recently it has been confirmed that the nonlinear susceptibility of bismuth oxide nanoparticles is 100 times larger than that of bulk bismuth oxide.[14] The availability of bismuth oxide nanowires might be able to bring new types of applications and/or to enhance the performance of the currently existing devices. However, so far to the best of our knowledge, no bismuth oxide nanowires have been reported.

Biomolecules, such as proteins, peptides and single-stranded DNA, are some of the most underused, yet powerful and versatile building blocks.[15–17] Their molecular recognition properties are unmatched by conventional synthetic analogues.[18] So far, many smart inorganic materials have been prepared, such as virus-based synthesis of magnetic and semiconducting nanowires,[19] bacterial S-layers as template for the synthesis of CdS superlattices,[20] DNA-assisted synthesis of Au particle nanowires,[21] and biotemplate synthesis of metal nanowires.[22] Fully investigating and exploiting these selective biomolecules might be of great importance in the development of novel materials, especially in the areas of medicine and nanotechnology.[23,24]

Lysozyme is a protein with relatively high stability and is responsible for breaking down the polysaccharide walls of many types of bacteria.[25] Furthermore it has also been confirmed that it shows chelating interactions with metal ions.[26,27] Thus it is reasonable to expect the morphology-directing function of protein lysozyme in the formation of 1D inorganic nanomaterials. However, it has not so far found application in the synthesis of nanomaterials. Herein we report a simple lysozyme-assisted method for the synthesis of single-crystal bismuth sulfide and oxide nanowires.

Pure and crystalline bismuth sulfide could be synthesized from $Bi(NO_3)_3{\cdot}5H_2O$, thiourea and lysozyme as reactants at 160 °C under hydrothermal conditions, as confirmed by its X-ray diffraction (XRD) pattern (see ESI† for experimental details and XRD). Fig. 1(a) and (b) show transmission electron microscope (TEM) images of the obtained bismuth sulfide sample, which clearly show that the crystallites have a wire-like morphology. The diameters are in the range of 10–50 nm and lengths are up to micrometers (see ESI† for further TEM images). Its selected area electron diffraction (SAED) pattern (Fig. 1(a), inset) displays several diffraction rings, which could be indexed as the orthorhombic phase of bismuth sulfide in agreement with XRD. Besides nanowire aggregates, single nanowires have also been observed. Fig. 1(c) displays the TEM image of one nanowire with

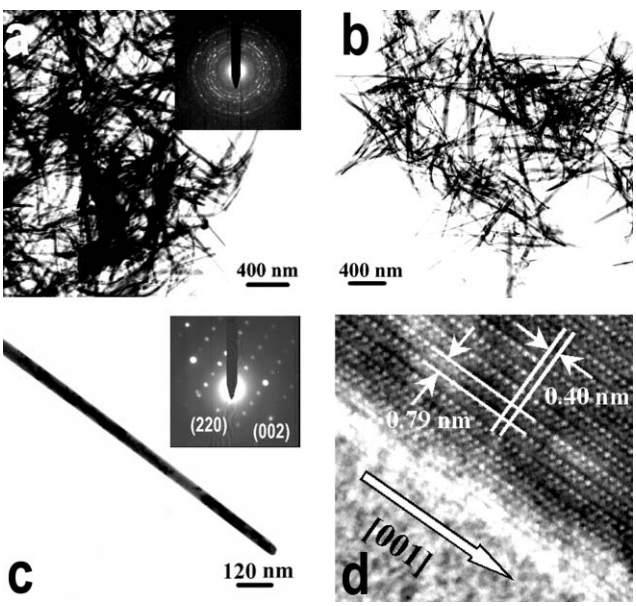

Fig. 1 TEM images, SAED patterns and HRTEM image of the obtained bismuth sulfide sample.

† Electronic supplementary information (ESI) available: XRD pattern, TEM images. See http://www.rsc.org/suppdata/cc/b4/b413584a/

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its corresponding SAED pattern (inset). The two diffraction spots perpendicular to each other in the SAED pattern could be indexed to (002) and (220), respectively, which indicates that the nanowire is a single crystal and has a preferred growth direction of [001]. The single-crystal nature of the obtained nanowires is different from those using bio-molecules as templates for particle assembled nanowires. A high-resolution transmission electron microscope (HRTEM) image (Fig. 1(d)) directly confirms that the nanowires are single crystals with high crystallinity. The crystal planes, perpendicular and parallel to the wire axis, have spacings of about 0.40 and 0.79 nm, which correspond to those of (001) and (110) planes, respectively. This result indicates that the nanowires might have [001] directional preferred growth, in agreement with the SAED result.

Although the exact mechanism of the 1D growth is unclear, we believe the formation of single-crystal 1D nanostructures is relevant to the coordination interaction between inorganic ions and bio-molecules. Bi(III) could easily react with many inorganic negative ions and organic compounds. Previous literature has reported that bismuth ions could react with amino acids with amino- and thiol-groups to form complexes.[28] Lysozyme is a protein formed by amino acids containing nitrogen and sulfur atoms. Thus it is reasonable to expect that lysozyme could coordinate with bismuth ions to form an intermediate complex, which might benefit the 1D growth of the final product. In our experiments, the reaction to form bismuth sulfide does not occur initially when the several reagents are mixed. The added lysozyme could react with Bi(III) to form an intermediate compound and with the increase of temperature and pressure it could react with hydrogen sulfide from the decomposition of thiourea to form bismuth sulfide. Without the addition of lysozyme, the obtained sample contains irregular shapes with a large range in size distribution. An appropriate ratio between bismuth ion and lysozyme is important to the formation of nanowires. At a lower bismuth ion concentration, the obtained bismuth sulfide grains have a spherical structure formed by short, film-like rods (rod-like shape but formed by the rotation of thin films; see ESI for TEM image†). With the increase of the bismuth ion concentration, these short film-like rods change to be separated rods and then the length of these 1D nanostructures increases gradually. This result means that high lysozyme concentration is not beneficial to the formation of nanowires. This may be because at a relatively high bio-molecule concentration, the bio-molecules might have stronger assembly activity rather than morphology directing function.[29] To further confirm this suggestion, we kept the concentration of bismuth ion constant, but increased the concentration of lysozyme and we found that the length of the obtained 1D bismuth sulfide nanostructures decreases and the formed nanorods have a tendency to aggregate gradually (see ESI† for TEM image).

Moreover, the morphology controlling function of lysozyme can be extended to the synthesis of bismuth oxide nanowires. Fig. 2(a) and (b) show the TEM images and SAED pattern of the bismuth oxide sample prepared without the addition of thiourea and with the addition of 0.1 g lysozyme. It can be seen that the obtained bismuth oxide also has high crystallinity and wire-like morphology with an average diameter of $\sim$8 nm and lengths up to several micrometers. Fig. 2(c) and (d) display a HRTEM image and a selected area magnified HRTEM image of nanowires. The crystal planes perpendicular to the long axis of the nanowire have a

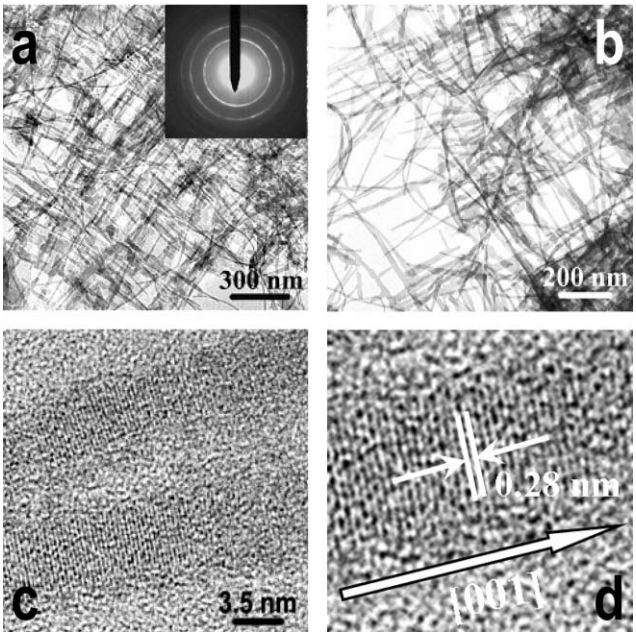

Fig. 2 TEM images, SAED pattern and HRTEM images of the obtained bismuth oxide sample.

spacing of 0.28 nm, which is consistent with those of (002) crystal planes. This means that the nanowire is apparently growing in a preferred direction of [001].

In summary, we report a simple method for the synthesis of bismuth sulfide and oxide nanowires with the first use of protein lysozyme as a morphology controlling agent. The obtained bismuth sulfide and oxide nanowires have single-crystal nature, which is different from particle-assembled nanowires using templates such as DNA. The use of protein lysozyme directs the 1D growth of nanowires of bismuth compounds and this might be extended to nanowires of other compounds.

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