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Communications

Amino Acids Controlled Growth of Shuttle-Like Scrolled Tellurium Nanotubes and Nanowires with Sharp Tips

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Organic molecules play a great role in adsorption of inorganic elements on special carriers and shaping inorganic crystals;[1] especially, biologic ones with specific functional groups have significant influence on the growth of inorganic crystals.[2,3] Amino acids, a most important kind of biomolecule, which construct proteins, have a very important effect on the human tissue development process.[4−6] Therefore they have attracted much interest from biologists, as well as from chemists. However, to the best of our knowledge, it is rarely reported that they are utilized to control inorganic crystal growth,[7] especially as a crystal growth modifier for semiconductors.

Tellurium was widely studied as a narrow band gap semiconductor in recent decades, and anisotropic two-dimensional ellipsoidal tellurium was considered as a very promising photonic crystal.[8] One-dimensional structures of elemental tellurium were prepared through several distinct routes, in which reduction of telluride of higher valence to element is a general solution method. Tellurium nanotubes were synthesized by a polyol process in which ethylene glycol was used as solvents and a reducing reagent.[9] Aqueous ammonia was also applied to form tellurium nanotubes.[10] Under high alkaline solution, rigid tellurium nanotubes were synthesized in hydrazine by a solvothermal method.[11] Gautam et al. reported a hydrothermal route to prepare Y-junction nanowires in the presence of a strong reducing reagent, $NaBH_4$.[12] Recently, a biomolecule called alginic acid, a straight-chain polyuronic acid made of monosaccharide units, was used for the synthesis of Te nanowires.[13]

In this communication, several amino acids with different functionalities and structural conformation have been first applied to illustrate how they can influence the crystal growth of Te. Serine, lysine, and histidine have been used as additives in this study. Either shuttle-like scrolled nanotubes with flexible sharp tips or nanowires with very sharp ends can be selectively synthesized.

All chemicals used were analytical grade. In a typical synthesis, 0.01 mmol sodium telluride (analytic grade) was

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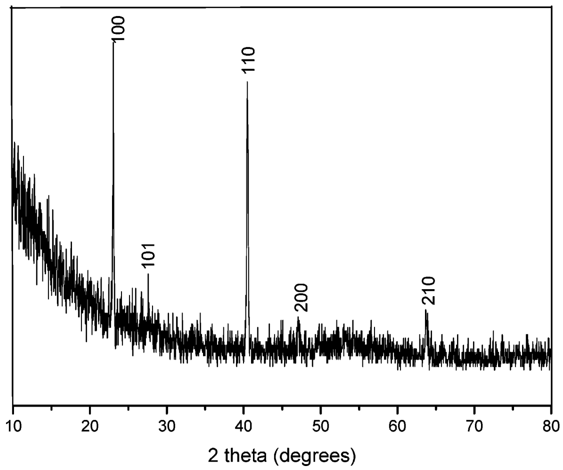

Figure 1. XRD pattern of shuttle-like scrolled nanotubes of single crystal tellurium in the presence of serine after reaction at 160 °C for 24 h.

dissolved in 25 mL of deionized water, then, 2 mmol amino acid was dissolved into the solution. After being vigorously stirred for half an hour, the mixed solution was put into a Teflon lined autoclave of 30-mL capacity and heated to 160 °C for different reaction time. Silver tint floccules were obtained finally. These products were washed several times by deionized water and pure ethanol, respectively, to remove organic remainder and inorganic ions.

The samples were characterized by X-ray diffraction pattern (XRD), which was recorded on a MAC Science Co. Ltd. MXP 18 AHF X-ray diffractometer with monochromatized Cu Kα radiation ($\lambda = 1.54$ Å), transmission electron microscopy (TEM), and high-resolution transmission electron microscopy (HRTEM), which were performed on a Hitachi (Tokyo, Japan) H-800 transmission electron microscope (TEM) at an accelerating voltage of 200 kV, and a JEOL-2010 high-resolution transmission electron microscopy (HR-TEM), also at 200 kV, respectively. Scanning electron microscope (SEM) measurements were carried out with a field-emission microscope (JEOL, 7500B) operated at an acceleration voltage of 10 kV.

Figure 1 shows that the product obtained in serine is well-crystallized trigonal tellurium. All the diffraction peaks can be indexed as a trigonal tellurium phase with calculated lattice constants $a = 4.46$ Å and $c = 5.83$ Å, which are consistent with the standard literature values (JCPDS 36-1452).

The intensities of 100 and 110 peaks are especially higher than others, implying possible preferential orientation growth of the crystals. The SEM image in Figure 2a shows uniform shuttle-like nanotubes of tellurium. The high-magnification SEM image in Figure 2b clearly shows that those shuttle-like nanotubes were scrolled and rather flexible. The ends of these scrolled nanotubes seem extremely like sleeve-fish tails. The arrows indicate the tube-like structures and their scrolling edges. The typical scrolled nanotubes are shown in Figure 2c. Selected electron diffraction pattern taken on a single nanotube indicates the single-crystal nature (Figure 2d).

A HRTEM image in Figure 3c was taken from the selected area marked in Figure 3a, showing lattice spacings of ca. 5.82 and 2.24 Å, respectively, corresponding to the lattice spacings of the (001) planes and (110) planes for tetragonal tellurium. Figure 3b shows the corresponding ED pattern of the tube, which was obtained by focusing the electron beam along the [1$\bar{1}$0] axis. The HRTEM image and electron diffraction pattern demonstrated that the scrolled nanotube was single crystalline and grew along the [001] direction.

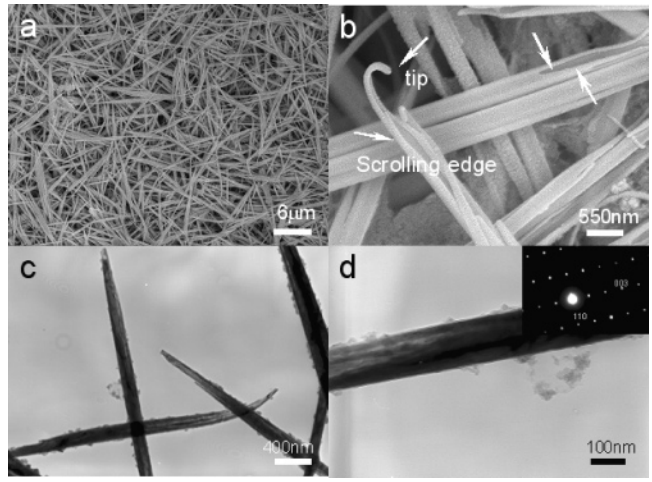

Figure 2. SEM and TEM images of the nanotubes: (a) a general view of shuttle-like scrolled nanotubes of tellurium; (b) a high magnification image (white arrows indicate the flexible tips and the scrolling edges); (c) a typical TEM image of the scrolled nanotubes; (d) a typical nanotube and the electron diffraction pattern taken on it along the [1$\bar{1}$0] axis.

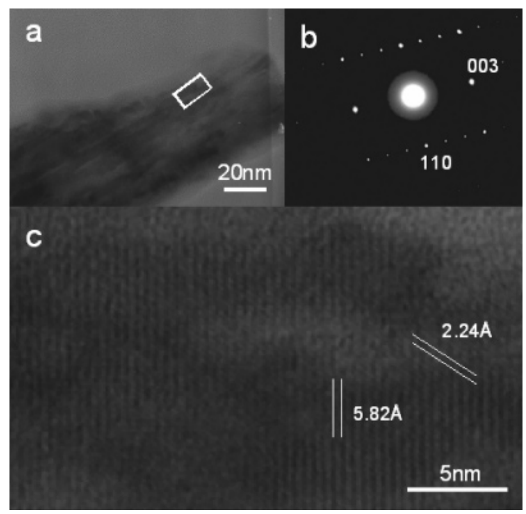

Figure 3. High-resolution TEM images (HRTEM) and electron diffraction pattern taken on a singe nanotube: (a) HRTEM image showing the tip of a scrolled nanotube; (b) ED pattern taken on the tip of the scrolled nanotube (electron beam was focused along [1$\bar{1}$0] axis); (c) a lattice-resolved HRTEM image showing lattice spacings of 5.82 and 2.24 Å were observed, respectively.

Generally, the crystals possessing layer structures are inclined to form nanotubes or fullerene-type structures.[14] Trigonal tellurium has a 3_1 helical-chain structure. It will tend to grow into one-dimensional structures inherently. Unlike the formation mechanism of tellurium nanotube reported before,[9−11] the shuttle-like scrolled nanotubes are probably formed based on a scrolling-mechanism which we will discuss below.

The shape evolution process was followed by examining the intermediate products obtained after different reaction

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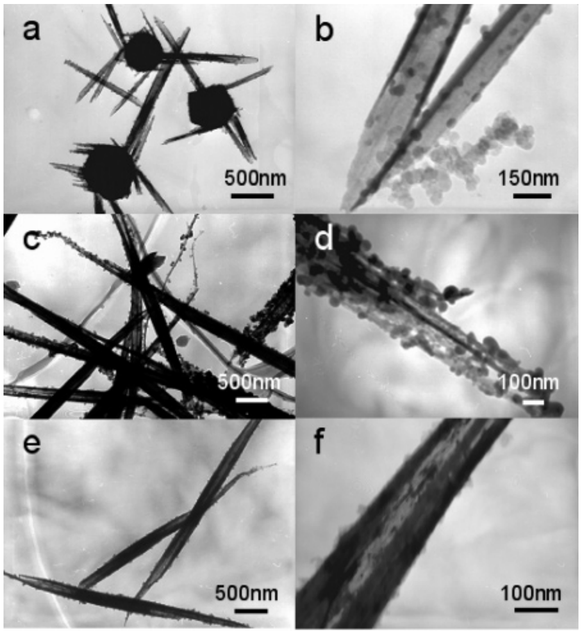


Figure 4. TEM images of the products obtained at different stages: (a) and (b) 2 h; (c) and (d) 4 h; (e) and (f) 12 h.

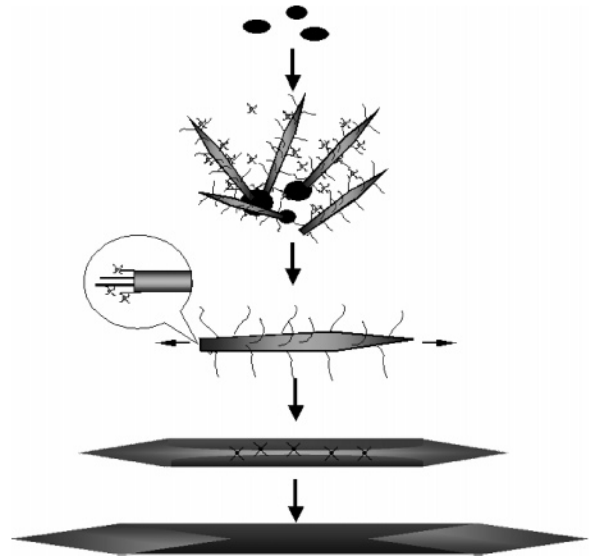


Figure 5. Proposed growth mechanism for the formation of shuttle-like scrolled nanotubes using serine as additive.

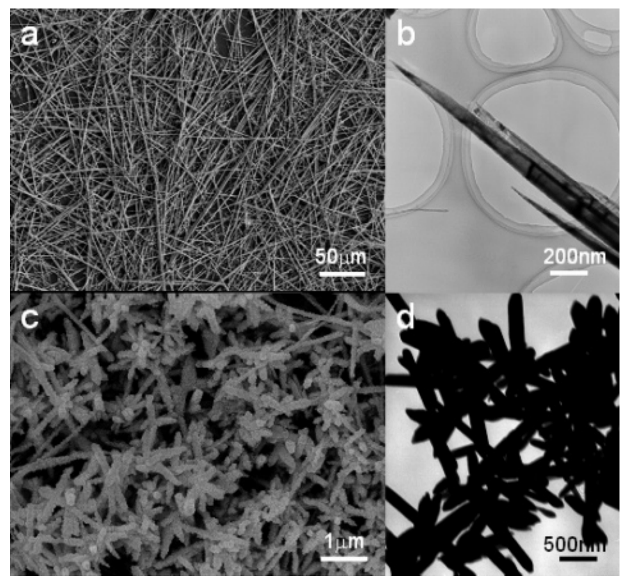
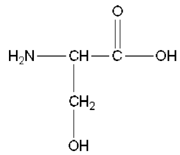
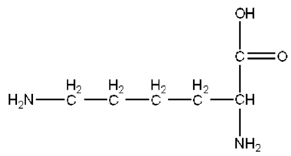
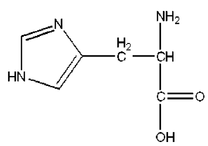


Figure 6. SEM and TEM images of the morphologies of tellurium crystals in the presence of different amino acids: (a) and (b) superlong rigid nanowires with sharp ends synthesized in the presence of lysine; (c) and (d) dendritic crystals obtained in the presence of histidine which contains a penta-ring.

time. After reaction for 2 h, black gray floccules were yielded and its XRD pattern is identical to that for trigonal tellurium while it shows amorphous peaks at 2θ of around 55°, indicating that the product is a mixture of crystallized *t*-tellurium and amorphous tellurium as confirmed by further electron diffraction analysis (Supporting Information Figures S1 and S2). The TEM image shown in Figure 4a confirmed that newly born bamboo leaf like nanostructures were living on the aggregated amorphous particles and grew further at the consumption of them. Furthermore, a lot of tiny amorphous nanoparticles are attached on the surface of the nanotubes. An enlarged TEM image in Figure 4b suggested that hypogenetic scrolls of trigonal tellurium were formed very quickly from bamboo leaf like structures even after the reaction for 2 h, which could be formed based on a rolling mechanism. After 4 h, the hypogenetic scrolls of trigonal tellurium were formed and the larger amorphous aggregates disappeared (Figure 4c). With time prolonging, the hypogenetic tubular scrolls became longer and curled depending on the growing rate of the inert nanowires along their growth direction by continuously consuming the amorphous particles. After reaction for 12 h, most of these hypogenetic tubular structures turned to be intact as shown in Figure 4e and f. Finally, the structure evolves into a smooth shuttle-like nanotube with two ends open.

The formation process of the scrolled nanotubes in the presence of serine is proposed schematically in Figure 5. At the beginning, amorphous tellurium particles were yielded, and then bamboo leaf like nanostructures were born on the surface of as-yielded amorphous aggregates under the effect of functionalities of peripheral serine. Not nanorods but thinner nanofilms growing on the surface of amorphous particles may be attributed to the alcohol groups of serine compared with other side groups of adopted amino acids. Influenced by surface tension which could be modified by serine, these nanofilms turn to curl in some degree at the beginning. As they grew, increasing diameter of the nanotubes was restricted by the initial diameter of the hypogenetic tubular structures formed on the near-spherical amorphous aggregates. After peeling off from an amorphous matrix, an individual nanotube will further grow along with the Ostwald ripening process, resulting in the formation of scrolled nanotubes with smoother surface in the later stage. Further adsorption of amorphous nanoparticles on the backbone of the tubular structures leads to epitaxial layer growing, which could be induced by the interaction of alcohol groups and carboxyl ones of two adjacent amino acid molecules. These extended layers rolled not only under gravity in the absence of backbones, but also with the charge influence of hydroxyl groups on the surface of internal and external surface of the layer. The rolling layers of both sides join first nearly at the middle part of the whole structure, finally resulting in the formation of shuttle-like nanotubes (Figure 2b).

Table 1. Morphologies of the *t*-Te Crystals Obtained in the Presence of Different Aminoacids with Different Functionalities and Structural Conformation

amino acid	structure	morphology
serine		scrolled nanotubes
lysine		nanowires with two sharp ends
histidine		dendritic crystals

To understand whether other functional groups such as $-NH_2$ and $-COOH$, and their synergistic effects, and the structural conformation can influence the morphology of *t*-Te crystals, different amino acids (lysine and histidine) were also tested. The results demonstrated that an amino acid with one extra amino group yielded superlong rigid nanowires with sharp ends, with length reaching more than 100 μm and a uniform diameter of 150 nm as shown in Figure 6. A similar product is synthesized in the presence of phenylalanine or cystine (Supporting Information Figure S3). The sharp end of the nanowires in the presence of lysine is similar to that obtained in ethylene glycol media by a polyol process reported by Xia et al.[15] The similar structures can even be synthesized by addition of a basic amino acid, i.e., glycine (Supporting Information Figure S4). Such similarity suggests that the basic groups of all amino acids mainly attributed to the formation of nanowires with two sharp ends. In contrast, the presence of another amino acid, histidine, containing a penta-ring, one carboxyl, and one amino group, yielded dendritic crystals of tellurium made of branched shorter nanorods as shown in Figure 6c and d. The results suggest that the formation of branched structures made of nanorods could be related to the molecular conformation of the amino acid, even though they are of similar functional groups (Table 1). Here, the functional hydroxyl group is believed to play a key role in the formation of longer one-dimensional Te nanostructures as found in ethylene glycol media.[15]

In conclusion, simple amino acids with different functionalities and structural conformation have been used as good crystal growth modifiers for controlled growth of tellurium crystals by a hydrothermal approach. Shuttle-like scrolled nanotubes with two sharp and flexible tails and nanowires with very sharp tips can be selectively synthesized by use of serine and lysine as additives. In contrast, histidine can induce the formation of dendritic structures made of shorter nanorods. The results demonstrate that the choice of an amino acid with a suitable combination of functional groups such as $-NH_2$, $-COOH$, and $-OH$ can induce the formation of different tellurium nanostructures by a facile hydrothermal approach. Further studies are underway to examine the flexibilities and capabilities of this approach.

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Supporting Information Available: XRD pattern and TEM and SEM images of the product (pdf). This material is available free of charge via the Internet at http://pubs.acs.org.

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