

Large-scale Synthesis of Crystalline Tellurium Nanowires with Controlled-Diameters via a Hydrothermal-reduction Process

Liqiang Xu,^{†,††} Yanwei Ding,[†] Guangcheng Xi,^{††} Wanqun Zhang,^{††} Yiya Peng,^{††} Weichao Yu,^{††} and Yitai Qian^{*,†,††}

[†]Structure Research Laboratory, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China

^{††}Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China

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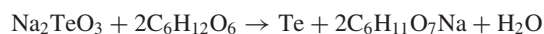
Single crystalline Te nanowires with diameters ranging from a few nanometers to ≈ 30 nm and lengths ranging from hundreds of nanometers to several micrometers were produced with a yield of $\approx 95\%$ via a hydrothermal-reduction process using Na_2TeO_3 and glucose as reactants and sodium dodecyl benzene-sulfonate (SDBS) as surfactant at 180°C .

Tellurium is a narrow bandgap semiconductor with a highly anisotropic crystal structure consisting of helical chains of covalently bound atoms. It has many interesting properties such as photoconductivity, thermoelectricity, catalytic activity toward hydration or oxidation reactions, and high piezoelectricity, as well as nonlinear optical properties.^{1,2} Many approaches including high-temperature and high-pressure injection,³ γ radiation,⁴ refluxing,⁵ solution-phase and self-seeding,⁶ electrochemical and electrophoretic deposition,⁷ chemical vapor deposition,⁸ hydrothermal,^{9,10} and microwave method¹¹ have been developed to synthesize nanocrystalline tellurium with diversified morphologies such as rod-like, needle-like, wire-like, tube-like, and belt-like.

Recently, one-dimensional (1D) nanowires have received extensive attention because of their potential applications in various fields such as in improving optoelectronic devices,¹² data-storage,¹³ biochemical and chemical sensors,¹⁴ and as the necessary functional components and interconnects in building nanocircuitry.^{12,15} Controlling the diameter and length of 1D objects is a challenging goal of contemporary materials science.¹⁶ The controlled synthesis of 1D Te nanowires should be able to bring in new types of applications or to enhance the performance of the currently existing devices as a result of quantum-sized effects. Very recently, Te nanowires with diameters range of ≈ 25 – 100 nm have been prepared by reducing Na_2TeO_3 with $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ in a mixed ethanol and water solution.¹⁰ As $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ and glucose are common strong and weak reducing agents in aqueous solution, respectively, the curiosity to explore whether glucose could act as a more effective reducing agent in the synthesis of Te nanowires has inspired us to carry out this experiment. And the experimental results demonstrate that Te nanowires with high aspect ratios and controlled-diameters could be produced in good yield via a one-step hydrothermal-reduction process by reducing Na_2TeO_3 with glucose in the presence of SDBS, in addition, these Te nanowires are single crystalline with diameters ranging from a few nanometers to ≈ 30 nm and lengths ranging from hundreds of nanometers to several micrometers.

In a typical procedure, 0.6-g Na_2TeO_3 , 1.0-g glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) and 0.1-g SDBS were added into a 60-mL Teflon-lined stainless-steel autoclave. Then filled with water up to

90% of the total volume and agitated until the reactants were dissolved. The autoclave was sealed and heated from 20 to 180°C within 30 min, then maintained at 180°C for 1–12 h. After it was allowed to cool to room temperature, the solid precipitates in the autoclave were filtered off and washed with distilled water and absolute ethanol for several times. After that, the resulting products were dried in a vacuum at 50°C for 4 h and were collected for characterization. The overall reaction of this experiment could be described as below:



The morphology and structure of the as-obtained products were examined with field emission scanning electron microscopy (FSEM, JEOL JSM-6300F), transmission electron microscopy (TEM, HITACHI 800), and high-resolution TEM (HRTEM, JEOL 2010 of 200 kV). The powder X-ray diffraction pattern (XRD) of the product was recorded on a MXPAPHF (Japan) X-ray diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$). The samples used for characterization were ultrasonicated before TEM and HRTEM analyses.

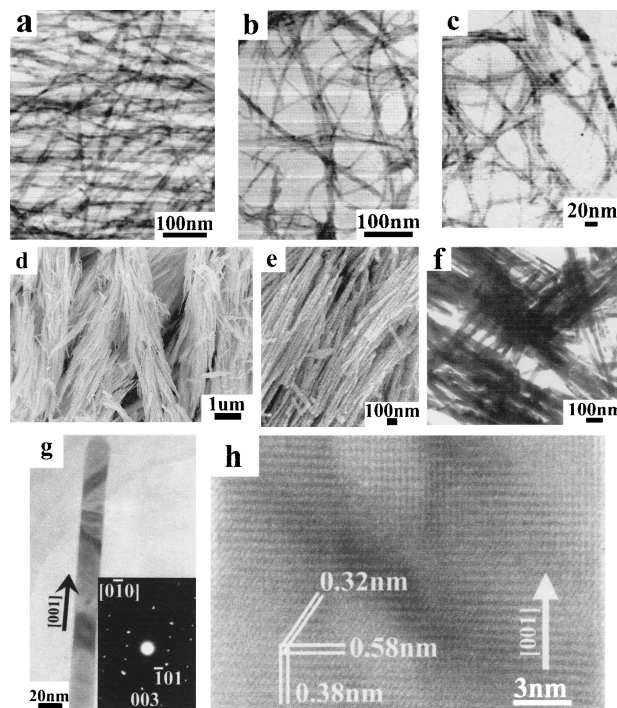


Figure 1. Typical TEM, FSEM and HRTEM images of the products obtained at 180°C for different time. (a) for 1 h. (b) and (c) for 2 h. (d), (e), and (f) for 12 h. (g) A single Te nanowire, inset is its SAED pattern. (h) A part of the HRTEM image of (g).

Figure 1a shows the TEM image of the curving Te nanowires with diameters of only a few nanometers obtained at 180 °C for 1 h. When the reaction time was prolonged to 2 h, flexible Te nanowires with diameters of up to ≈ 15 nm were produced (Figures 1b and 1c). Figures 1d–1h show representative FSEM, TEM, and HRTEM images of the Te nanowires produced in high yield at 180 °C for 12 h with uniform diameters in the range of ≈ 10 –30 nm and lengths ranging from hundreds of nanometers to several micrometers. It is interesting that all the Te nanowires are straight and aligned to form nanowire bundles. An individual Te nanowire with a diameter of 20 nm is presented in Figure 1g, which indicates its uniformity in diameter along the entire longitude, and its SAED pattern inset in Figure 1g (with a zone axis of [010]) reveals its single crystal nature. A part of the HRTEM image of the same Te nanowire (Figure 1g) is shown in Figure 1h, which displays three set of distinct lattice spacing of 0.58, 0.38, and 0.32 nm that correspond to the (001), (100), and (101) planes of hexagonal tellurium, respectively. The result of the HRTEM image coincides with that of the SAED pattern further demonstrate its single-crystal structure with [001] orientation. SAED and HRTEM analyses of other randomly selected Te nanowires gave the same result. It is also observed that large part of the as-obtained nanowires are structurally uniform and free of dislocation or other planar defects, which might make this 1D nanostructures particularly useful in the fabrication of electronic, optical, or electromechanical devices.

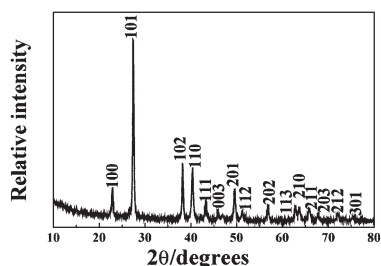


Figure 2. XRD pattern of the sample obtained at 180 °C for 12 h.

Figure 2 shows the XRD pattern of the products obtained at 180 °C for 12 h, all the reflection peaks in the figure could be indexed as hexagonal Te with calculated lattice parameters $a = 4.46$ Å, $b = 5.92$ Å, which agree well with that of JCPDS (36-1452), and the calculated average diameter of Te nanowires (≈ 25 nm) is also consistent with that of SEM and TEM observations. While the relative peak intensity of 100 and 110 were bigger than those of ordinary Te particles, which also reveals the preferential growth of Te nanowires along [001] direction.^{17,18}

Besides the reaction time, it is found that the temperature, surfactant and solvent also play important roles on the formation

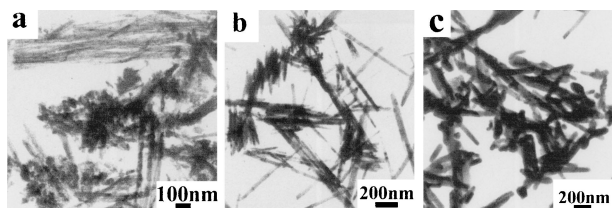


Figure 3. Typical TEM images of the products obtained at different conditions for 12 h. (a) 160 °C. (b) without using surfactant. (c) using CTAB as surfactant.

of Te nanowires, for example, when the reaction was fixed at 160 °C for 12 h, the products are composed of Te nanoparticles (or colloids), nanorods and nanowires (Figure 3a); If SDBS was absent, Te nanorods and nanowires with diameters in the range of ≈ 15 –50 nm are observed (Figure 3b). Figure 3c shows TEM image of the sample produced using cetyltrimethylammonium bromide (CTAB) as surfactant, which is mainly composed of Te nanorods and nanoparticles; If the solvent was replaced by ethylene glycol (EG), or the mixture of water and EG, only Te nanorods could be obtained.

On the basis of the experimental results, a possible formation mechanism of the Te nanowire bundles is described as follows: Te nanoparticles (or colloids) are formed at first by reductive reaction below 160 °C, with the increasing temperature and through the adsorption and desorption of SDBS, they may combine with each other at one orientation along special lattice face and form rod-like particles. The rod-like particles tend to form aligned-nanorod bundles owing to the diffusion-control growth with the assistant of SDBS,¹⁹ and these aligned-nanorod bundles may then serve as initial template for the growth of aligned-nanowire bundles. With the prolongation of reaction time, Te nanowire bundles are formed by further longitudinal and lateral growth and crystallization process.

In summary, a convenient hydrothermal-reduction route using Na_2TeO_3 and glucose as reactants and SDBS as surfactant at 180 °C has been successfully developed to synthesize Te nanowires in high yield ($\approx 95\%$) with confined diameters and with high aspect ratios. The availability of these large-quantity and high-quality Te nanowires is expected to enable fascinating opportunities in nanometer scale science and technology.

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