A novel ultrasonic-assisted solution-phase approach for the fabrication of tellurium bundles of nanowhiskers

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Abstract

An ultrasonic-assisted solution-phase approach to tellurium bundles of nanowhiskers has been successfully established. It is a convenient and efficient process for the formation of Te nanowhiskers and their simultaneous assembly into tellurium bundles without using any templates. It was found that the transformation from Te powder to Te nanowhiskers involved the reversible disproportionation of tellurium. Sonication played a critical role for the formation of the Tellurium bundles of nanowhiskers. The bandgap of the Te nanowhiskers was calculated to be about 3.8 eV based on the UV–visible spectrum. The simplicity and rapidity of the procedure, and the newly discovered uniform morphology of the products made this synthesis promising and potential for related future applications.

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1. Introduction

Nanostructures and nanomaterials, especially those of one-dimension, have been the focus of considerable interest due to their great potential for addressing some basic issues about the dependence of the properties on size confinement, as well as for applications in nanodevices [1]. And the synthesis of well-defined complex architectures based on these one-dimensional (1D) nanostructures provided the opportunity to exploit the distinctive optical and electronic properties of the discrete 1D nanostructures and the possibility to probe potential new phenomena arising from their 2D or 3D organization [2].

One of the primary hurdles in this field is to produce 1D nanostructures without the necessity for costly and complex processing. Although the solid-state materials with submicrometer or nanoscale 1D structures can be fabricated by advanced lithographic techniques [3] or via gas-phase chemical processes [4], solution-phase chemical synthesis is regarded as a more promising approach in terms of much lower cost and potential for high-volume production as well as tight dimension control. Among the solution-phase approaches that have already been reported, template directed [5] or crystal seed mediated methods [6] are most commonly employed to confine or catalyze the preferential 1D growth of various kinds of materials. However, exploring convenient and efficient solution-phase approaches to 1D structural materials without using any templates or crystal seeds still remains a great challenge.

Another major scientific challenge in 1D material research is to develop simple and efficient methods to
create the patterns of well-arranged 1D structural materials in a predictable and controllable way. One possible route is to develop suitable hierarchical assembly techniques to put 1D structural building blocks together into functional structures [2d]. The other possibility, which is more convenient and, thus, more attractive, is to form superstructural arrays through direct one-step growth processes.

Currently, trigonal tellurium (t-Te) and related materials have attracted more and more attention. Trigonal tellurium is a narrow bandgap (direct bandgap energy of 0.35 eV) semiconducting material, with a highly anisotropic crystal structure consisting of helical chains of covalently bond atoms, which are in turn bound together through van der Walls interactions into a hexagonal lattice [7]. This inherent anisotropy makes Te an ideal candidate for generating one-dimensional nanostructures without the need for templates or surfactants to induce and direct anisotropic growth. Tellurium exhibits a unique combination of many useful and interesting properties, such as photoconductivity, nonlinear optical response, high thermoelectric or piezoelectric responses, which results in their potential applications in electronic and optical electronic devices [8]. In addition, solid tellurium can be used to synthesize a wealth of functional materials, such as Bi₂Te₃, ZnTe, and CdTe [9].

Recently, some references have reported the preparation of one-dimensional tellurium nanoparticles [10–14]. For examples, Te nanotubes and nanorods were prepared through the refluxing process by the reduction of Te(VI) or Te(IV) and hydrothermal routes; A microwave-assisted ionic liquid method was also used to prepare this material.

Ultrasound wave has been extensively used to synthesize various nanostructured materials, such as metal colloids, semiconductor powders and nanorods [15–21]. During sonication, microscopic bubbles form and grow in the low pressure stage, and subsequently collapse in the high pressure stage [19,20], causing hot spots-localized regions of extremely high temperatures as high as 5000 K, and pressures of up to ~1800 atm, and cooling rates can often exceed ~10¹⁶ K s⁻¹ [15]. The energy released from this cavitation process can lead to enhanced chemical reactivities and accelerated reaction rates. Here, in our ultrasonic-assisted solution-phase approach to tellurium bundles of nanowhiskers, these hot spots could cause local fluctuation in the solubility of tellurium, and thus induced the seeding and growing of t-Te from amorphous Te.

In the present work, our research focuses on developing a new route for the large-scale transformation from commercial Te powder to bundles of t-Te nanowhiskers. In this approach, sonication was used as a driving force for the growth of t-Te nanowhiskers under ambient pressure. The procedure was fast and took no longer than 1 h to generate high-quality, uniform, crystalline nanowhiskers bundles of t-Te. Moreover, Te powder could be transformed into nanowhiskers entirely; KOH and water used in this procedure could be recycled. This is obviously a great advantage for large-scale production. This process is very convenient and efficient, free of any templates or crystal seeds, and the results are easily reproducible. It provides a novel solution-phase route that leads to the formation of 1D structural Te nanowhiskers and their simultaneous assembly into Tellurium bundles.

2. Experimental

Tellurium used was purchased from Acros Organics, and potassium hydroxide from Shanghai Chemical Reagent Co., Ltd. All of the reagents were used without further purification.

In a typical procedure, 0.1 g Te powder and 70 g KOH were put into a beaker, and then 50 mL distilled water was added. The mixture was stirred to obtain a dark purple solution, from which the redundant Te powder was centrifuged. 30 mL distilled water was added into 10 mL of this purple solution, and immediately the system was sonicated for 60 min. During the sonication, the temperature of the system increased to ~65 °C after 15 min and kept at ~75 °C after 30 min. The grayish-black floccules obtained was centrifuged from the liquid, and washed with distilled water and absolute ethanol subsequently.

Sonication was performed using a VCX 750 VibraCell high intensity ultrasonic processor (Sonics & Materials, USA) equipped with an immersion ultrasonic probe, which was made of titanium alloy Ti-6AL-4V, and with the tip diameter of 13 mm. The frequency is 20 kHz, and the net power output is 750 W. The variable power output control allows the ultrasonic vibrations at the probe tip to be set to any desired amplitude. With the amplitude control set at 100%, the amplitude at the tip with diameter of 13 mm is 124 μm. In our work, the amplitude control was set at 38%. The pulse cycle of 7 s on and 1 s off was set via the independent on/off pulser.

The X-ray diffraction (XRD) patterns of the products were recorded with a Philips X’pert X-ray diffractometer (using Cu-Kα radiation, λ = 1.5418 Å). The transmission electron microscope (TEM) images and selected area electron diffraction (SAED) patterns were obtained using a JEM-200CX (JEOL, 200 kV) TEM. The scanning electron microscope (SEM) images were obtained using a LEO-1530VT field-emission SEM. UV-vis absorption spectrum of the sample-dispersion in ethanol was recorded using a UV-3100-VIS-NIR-recording spectrophotometer.
3. Results and discussion

3.1. Characterizations

The dimensions and morphologies of the product were characterized by TEM and SEM measurements. In the typical TEM and SEM images shown in Fig. 1A and B, t-Te nanowhiskers self-assembled into bundles can obviously be observed. The Te nanowhiskers were uniform filamentary crystals with long tapered tips, and with the largest widths of ~40 nm in the middle and lengths of 400–600 nm. Fig. 1C shows a SAED pattern of a single Te nanowhisker, indicating that it is single-crystalline.

X-ray diffraction (XRD) analysis confirmed that these nanowhiskers were in the pure phase of well-crystallized elemental Te with the hexagonal structure. The XRD pattern shown in Fig. 2 was in good agreement with that reported in literature (JCPDS File No. 36-1452), and all the peaks could be indexed to Te, indicating the high purity of the product.

Optical absorption spectrum of Te was studied. The UV–visible spectrum of the Te nanowhiskers is shown in Fig. 3. A characteristic absorption band at about 250 nm was observed in the spectrum, which was in agreement with the result reported by Rao [22]. They pointed out that the characteristic absorption band of the Te nanorods and nanowires shifted from about 300 nm for the 300 nm-wide nanorods to 260 nm for the 10 nm-wide nanowires. The bandgap of the Te nanowhiskers was calculated to be about 3.8 eV, based on the electronic absorption spectrum.

3.2. Formation of t-Te nanowhiskers

The formation process of the bundles composed of Te nanowhiskers can be reasonably divided into three stages. The first step is the dissolution of the Te powder in condensed KOH solution, giving out a purple solution, which was referred to as “Te-solution” in this paper. This step is the disproportionation of Te in fact, and can be represented by the following equation:

\[
3 \text{Te} + 6 \text{KOH} \rightarrow \text{K}_2\text{TeO}_3 + 2 \text{K}_2\text{Te} + 3 \text{H}_2\text{O} \quad (1)
\]

Fig. 1. The morphology of the product (A) TEM image, (B) SEM image, and (C) SAED pattern of a single Te nanowhisker.

Fig. 2. The XRD pattern of the as-prepared Te nanowhiskers.
At the second step, when distilled water was added into this solution, the reaction was carried backward to give out amorphous Te nanoparticles, and the purple solution turned into black suspension:

\[ K_2TeO_3 + 2K_2Te + 3H_2O \rightarrow 3Te(\text{nanoparticles}) + 6KOH \]  

At the third step, sonication was used to promote the growth of the t-Te nanowhiskers from Te nanoparticles and their simultaneous assembly into bundles. At this step, the black suspension turned into grayish black floccules:

\[ \text{a-Te(nanoparticles)} \rightarrow \text{t-Te(nanowhiskers)} \]  

Fig. 4 provided a set of TEM images (A–D) and SEM image (E) corresponding to those samples obtained at different stages of the growth of t-Te nanowhiskers. Fig. 4A showed the aggregated nanoparticles obtained just before sonication; Fig. 4B, C and D showed the samples obtained after sonication for 2, 10 and 30 min, respectively, clearly indicating that all the nanowhiskers probably originated from the particles, and grew longer by continually consuming the particles; After sonication for 60 min, the t-Te nanowhiskers assembled into bundles, as shown in Fig. 1. According to the experimental results, the whole growing procedure can be described as follows: First, the aggregated spherical Te particles were obtained when the condensed
KOH solution was diluted by adding water in step 2; Second, under sonication, 1D t-Te nanowhiskers grew along with the dissolution of the amorphous Te particles, until the amorphous Te were used up. Due to the dispersion effect of the ultrasonic wave, the nanowhiskers grew uniformly. Simultaneously, these t-Te nanowhiskers assembled into bundles.

3.3. The influence of sonication on the growth of t-Te nanowhiskers

In order to investigate the effect of the sonication on the growth of the t-Te nanowhiskers, several comparative experiments were carried out.

When the sonication was replaced by stirring for 1 h at room temperature, the great majority of the products obtained were spherical particles from 20 to 100 nm in diameter with a few nanowhiskers among them, as shown in Fig. 5A. When the system was stirred at \( \approx 100 ^\circ C \) in an oil-bath, the result was similar to that at room temperature. When the Te-suspension obtained at the second step was aged without sonication or after sonication for only 2 min, it was found that nanorods grew slowly. Fig. 5B shows the TEM image of the mixture of nanoparticles and nanorods obtained after ageing for 40 h, which were somewhat crystalline as the SAED pattern (inset of Fig. 5B) implies. This suggested that the growth of 1D Te nanowhiskers be very slow without a proper driving force, although the tendency of this growth was strong due to the inherent anisotropy of Te.

When microwave irradiation was used to replace the sonication, some difference was observed. Fig. 5C ~ D are the TEM images corresponding to the samples obtained after microwave heating for 10 and 30 min. These images clearly show that the small spherical particles with size of tens of nanometers can connected with each other to make chains, and then grow into small rods. These small rods grew bigger subsequently by consuming particles attached to them. After microwave irradiation for 30 min, rods with various sizes from tens of nanometers to hundreds of nanometers in width were obtained, but some particles among them were still observed. The SAED pattern (inset of Fig. 5D) corresponding to one rod indicates that the rods can grow into single crystals.

These results confirmed that Te particles formed in reaction (2) had a strong tendency to grow into 1D nanostructures due to its highly anisotropic crystal structure. However, to prepare Te with uniform 1D nanostructure rapidly needs a proper driving force. Under stirring or just ageing, the grow procedure was very slow. Microwave irradiation promoted the growth of 1D Te nanorods, but the products were bigger and less uniform than those obtained under sonication. Sonication is the better way here to prepare uniform Te nanowhiskers rapidly. During sonication, both localized transient high pressures and temperatures were produced. These

Fig. 5. TEM images corresponding to the samples obtained after (A) stirring for 1 h; (B) ageing for 40 h; and after microwave irradiation for (C) 10 min and (D) 30 min. The insets are the SAED patterns of the corresponding samples.
hot spots played important roles in the growth of bundles of 1D Te nanowhiskers. First, they presented a much more rapid and simultaneous nucleation of the t-Te on the surface of amorphous Te particle [23]. Second, they could cause local fluctuation in the solubility of tellurium, and thus induced the preferential growing of 1D t-Te at the expense of the amorphous Te in a process similar to Ostwald ripening [23]. Third, they could also induce the self-assembly of the 1D t-Te nanowhiskers into bundles to decrease the surface energy. Sonication provided a uniform environment for the nucleation and growing of Te, which was very important to the final formation of uniform and regular 1D nanowhiskers.

3.4. Influence of solvents on the fabrication of t-Te nanowhiskers

In order to investigate the effect of different solvents on the fabrication of t-Te nanowhiskers, some other solvents were used to replace water in the formation of Te nanowhiskers. Because KOH has small solubility in ethanol and ethylene glycol (EG) compared with water, less Te could dissolve in solution. Therefore, ethanol and EG were not proper solvents in this route. However, we can use some solvents to dilute the aqueous Te-solution in step 2. When EG was used to dilute the Te-solution, spherical nanoparticles generated initially grew slowly into nanorods with widths of 50–150 nm and lengths of 200–800 nm, as shown in Fig. 6A and B. This indicated that the media influenced the morphology of Te. This may be attributed reasonably to the influence of the viscosity and other properties of media on the growth of Te crystals.

4. Conclusions

Taking advantage of the reversible disproportionation of Te, we firstly dissolved Te powder in condensed basic media, and subsequently, by adding water to dilute the alkaline solution to obtain Te nanoparticles. Then, with the assistance of sonication, these Te nanoparticles grew into the 1D Te nanowhiskers. The obtained t-Te nanowhiskers were uniform, with width of ~40 nm, and length of 400–600 nm, and they could assemble into bundles through prolonged sonication. This technique may be potentially extended to generate 1D nanostructures of other materials in proper solvent. This synthesis is very simple and can be conveniently scaled up, Te powder can be transformed into nanowhiskers entirely, the reagents such as KOH and water are cheap and can be recycled, and it is fast and clean. All these advantages make this synthesis promising and potential for industrialization.

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