Synthesis and chemical etching of Te/C nanocables

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Abstract. In this paper, Te/C nanocables were fabricated by a hydrothermal method in the presence of cetyltrimethylammonium bromide (CTAB). The products were characterized in detail by multiform techniques: transmission electron microscopy, X-ray diffraction, energy-dispersive X-ray analysis and Fourier transform infrared (FTIR) spectroscopy. The results showed that the products were nanocables with lengths of several microns, core about 20 nm in diameter, and a surrounding sheath of about 60–80 nm in thickness. Te/C nanocables were tailored freely by chemical etching. Carbonaceous nanotubes and Te/C nanocables with fragmentary Te core were obtained by adjusting time of chemical etching.

Keywords. Carbon; Te nanocable; heterostructure; chemical etching.

1. Introduction

Tellurium (Te) is a narrow bandgap semiconductor ($\sim$0·35 eV) that exhibits a wealth of unique useful properties, such as nonlinear optical response, photoconductivity and thermoelectric properties. These properties make it useful as an infrared photoconductive detector, piezoelectronic device, and thermoelectronic material (Xi *et al* 2005; Song *et al* 2009). The size and shape of nanostructures are two crucial factors in determining the properties of nanomaterials, and thus, the control of size and shape is of great interest (Lu *et al* 2005; Song *et al* 2007a). Recently, many methods have been developed to fabricate Te nanostructures. Mo *et al* (2002) synthesized Te nanobelts by the *in situ* disproportionation of sodium tellurite (Na_2TeO_3) in an aqueous ammonia system at 180°C. Mayers and Xia (2002) reported solution-phase synthesis approaches of tellurium nanotubes. Liu *et al* (2003, 2004) synthesized Te nanorods and nanowires by a Na_2SO_3 reducing $(NH_4)_2TeS_4$ route. Using biomolecules as structure-directing agents, He and Yu (2005) synthesized scrolled Te nanotubes.

Nanocable, a new kind of 1-D nanocomposite of nanowires (core) wrapped with one or more outer layers (shell), has emerged recently and drawn much intensive investigations. Nanocables reveal some fancy performances for their core-shell structure, so they can be used as the connection wires among high-density integrated elements, super capacitor, micro-implements and elements of micro-robot. A number of approaches, such as thermal evaporation, γ-irradiation, and templating, have been developed

to fabricate these kinds of 1-D nanocomposites (Xie *et al* 1999; Hu *et al* 2003; Jiang *et al* 2003). Iijima and his co-workers prepared coaxial three-layer nanostructures consisting of silicon carbide cores via a laser ablation route (Zhang *et al* 1997). Fang *et al* (2006) reported a CTAB-assisted hydrothermal approach to fabricate core-shell nanoparticles and nanocables with silver cores. Song *et al* (2008a) successfully prepared Se/C coaxial nanocables via one-step reduction and carbonization under mild hydrothermal condition. Zhang *et al* (2001) synthesized coaxial TiO_2/SiO_2 nanocables by using a sol–gel method with anodic alumina templates. Recently, a new method to prepare Ag/C nanocables with cross-linked structure via SDS-assisted hydrothermal route was reported by Song *et al* (2008b). In this article, we present a simple hydrothermal route for the synthesis of Te/C nanocables by using glucose as reductant and Na_2TeO_3 as tellurium source. Using the as-prepared Te/C nanocables as raw material, carbonaceous nanotubes and Te/C nanocables with fragmentary Te cores were obtained by adjusting time of chemical etching.

2. Experimental

2.1 *Synthesis of Te/C nanocables*

All chemicals were of analytical grade without further purification. Experimental details are as follows: CTAB (1 g) was dissolved in 25 mL of distilled water, followed by addition of glucose (2 g) under vigorous stirring. When the solution attained clarity, 10 mL of aqueous solution containing 0·1 g of Na_2TeO_3 was added slowly to the above solution under continuous stirring. The final solution was transferred into a
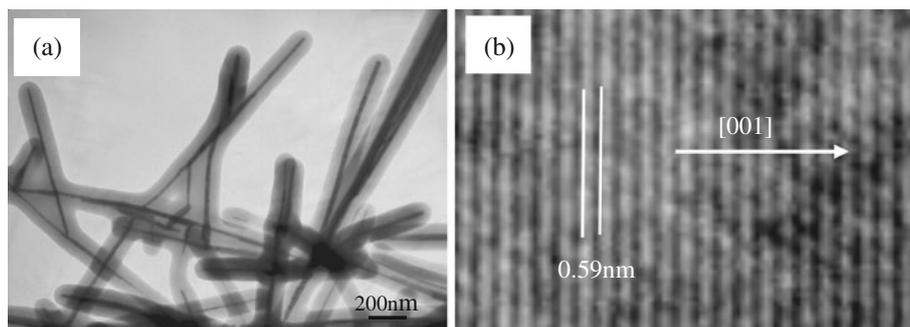
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Figure 1. (**a**) TEM and (**b**) HRTEM of Te/C nanocables.
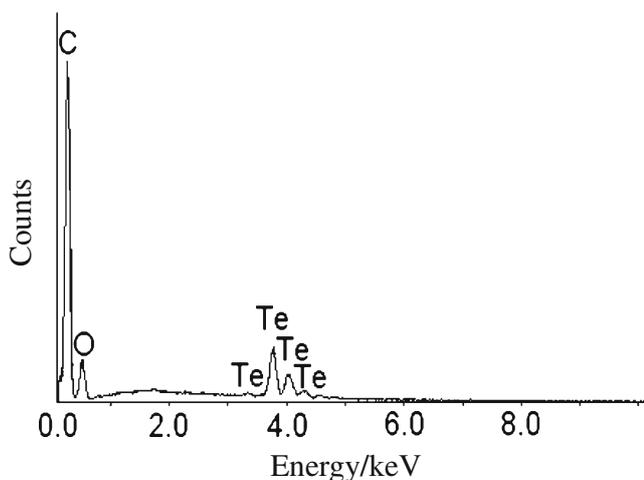

Figure 2. EDS spectrum of Te/C nanocables.

Figure 3. FTIR spectra of Te/C nanocables.

50 mL Teflon-lined stainless steel autoclave, and filled with distilled water up to 90% of the total volume. The autoclave was sealed and maintained at 190°C for 12 h. After the reactions, the autoclave was allowed to cool to room temperature naturally. Finally, the products were collected and washed with deionized water and ethanol several times and dried in air at 80°C.

2.2 *Chemical etching of Te/C nanocables*

Te/C nanocables (0·1 g) were dispersed into 25 mL of aqueous solution containing 2 mL hydrochloric acid (36·5 wt%) and 5 mL H_2O_2 (30 wt%). The above solution was kept still for 45–90 min, and then was filtered to separate the precipitates. The precipitates were washed by distilled water and anhydrous ethanol several times. Then the products were dried at 80°C for further characterization.

2.3 *Characterization*

The morphologies of the products were characterized with transmission electron microscopy (TEM, JEM200CX, 120 kV). High-resolution TEM study was carried out with a JEOL
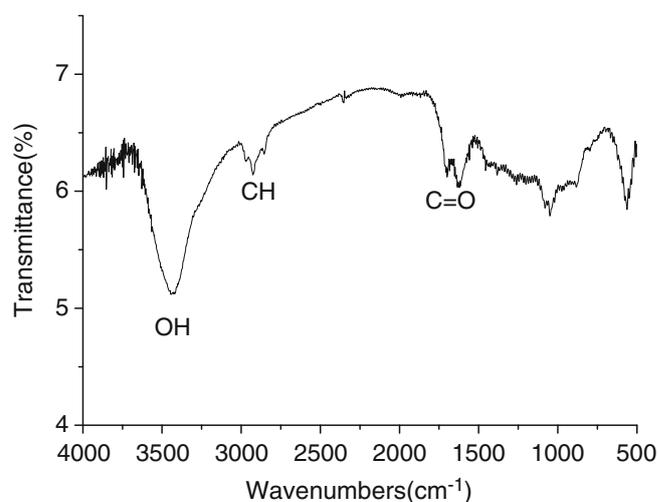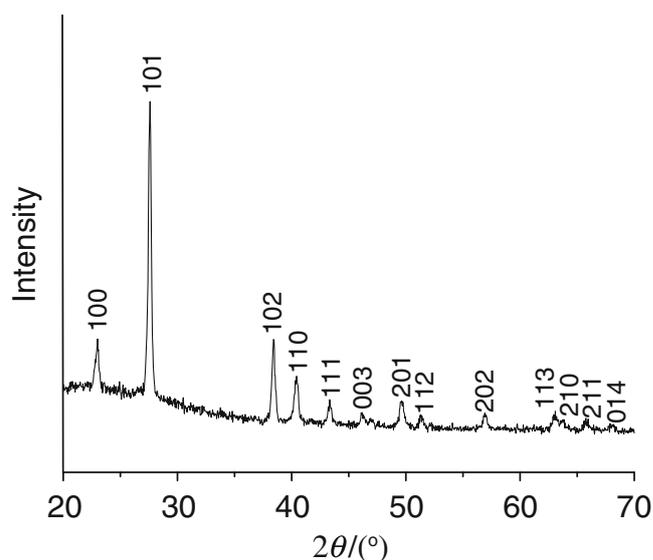

Figure 4. XRD pattern of Te/C nanocables.

2010 microscope at an accelerating voltage of 200 kV. The composition of the products was analysed by energy dispersive X-ray detector (EDS, Thermo Noran VANTAG-ESI,

120 kV). The X-ray diffraction (XRD, Thermo ARL SCINTAG X'TRA with CuKα irradiation, $\lambda = 0.154056$ nm) was used to analyse the crystallinity of the products. IR measurement was carried out with a Nicolet Avatar 360 Fourier-transform infrared (FTIR) spectrophotometer.

3. Results and discussion

The morphologies and particle sizes of the samples were investigated by TEM. Figure 1a shows typical pattern of Te/C nanocables prepared via CTAB-assisted hydrothermal route at 190°C. TEM image shows that the products are a composite comprising of a smooth core of about 20 nm in diameter and a surrounding sheath of about 60–80 nm in thickness. HRTEM analysis provides more detailed structural information about Te core. Figure 1b is a HRTEM image taken from Te core. The observed interplanar spacing is 0.59 nm, which corresponds to the separation between [001] planes of Te. And this HRTEM image indicates that the Te core growth direction is along [001]. The EDS analysis was employed to determine composition of the products and is shown in figure 2. The EDS results confirm that the obtained nanocables composed of inner tellurium nanowires and outer carbonaceous layers.

The FTIR spectra have been used to detect the functional groups of sheaths, as shown in figure 3. The peaks around 3419 cm^{-1}, 2900 cm^{-1} and 1620 cm^{-1} are attributed to the O–H, C–H and C=O vibrations, respectively. The results show that the surface of these carbonaceous sheaths is obviously highly functionalized.

The phase and purity of the products were examined by XRD. Figure 4 displays XRD patterns of the as-prepared Te/C nanocables in the presence of CTAB at 190°C. All the diffraction peaks can be indexed to be the trigonal phase of tellurium with lattice parameters $a = 4.460$ Å and $c = 5.923$ Å, which correspond with the values in the literature (JCPDS card No. 36-1452, $a = 4.458$ Å and $c = 5.927$ Å). No other phases were detected in figure 4, which indicates that high purity of Te/C nanocables were obtained by the present synthetic method.

Figure 5 is the TEM image of the samples obtained without CTAB at 190°C. The results show that the obtained products were nanocables with crude Te core. As we know, the crystal structure of tellurium is highly anisotropic, and the
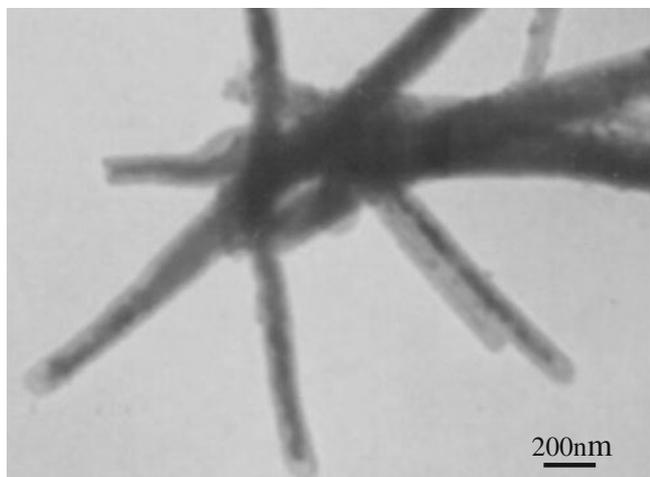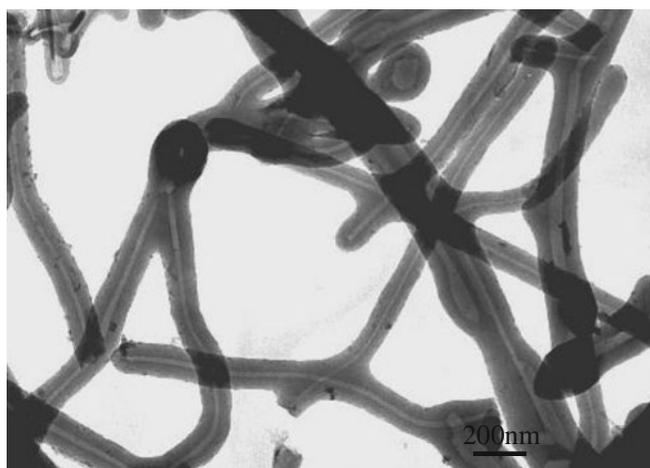

Figure 5. TEM image of sample obtained without CTAB.

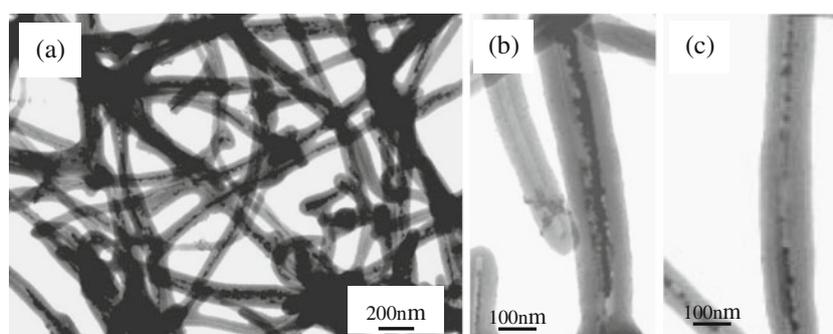**Figure 6.** TEM image of carbonaceous nanotubes obtained by chemical etching of Te/C nanocables.

Figure 7. TEM images of Te/C nanocables by partial chemical etching.

formation of 1D nanostructure first needs anisotropy during the growing process of nanoparticles. The selective interaction of the capping molecules on the facets of the first-formed nanoparticles is crucial to the anisotropic growth of nanostructures (Song *et al* 2007b). According to the results, a possible formation mechanism of Te nanocables has been proposed. In our experiments, the presence of CTAB would help to enhance the anisotropy of tellurium and cause the formation of uniform 1-D structures. As is known to all, glucose is a typical soft reducer. The glucose solution is heated in the autoclaves to 160–180°C, which is higher than the normal glycosidation temperature, and will lead to aromatization and carbonization. Based on above theories, we can conjecture that the formation process of Te/C nanocables may undergo the following procedures: first, TeO_3^{2-} is deoxidized by glucose with the assistance of CTAB, and then Te nanowires core forms at earliest; along with hydrothermal reaction continuing, glucose in the system carbonizes to amorphous carbon, and an amorphous carbon layer coats on Te nanowires surface and results in the formation of Te/C nanocables.

Figure 6 shows the TEM images of the products obtained after chemical etching for 90 min. Large numbers of amorphous carbonaceous nanotubes can be obtained from Te/C nanocables. Te can be dissolved by the solution of H_2O_2 and form TeO_3^{2-}. Because the tips of the Te/C nanocables are close (figure 1), it can be concluded that the carbonaceous layers of nanocables have a good permeation capability. H^+ ions and H_2O_2 molecules can easily be diffused into nanocables. With longer time diffusion and dissolution process, the Te core can be completely consumed. Because this etching was operated at room temperature, these carbonaceous nanotubes kept the original frame of the Te/C nanocables. When the chemical etching time was shortened to 45 min, as shown in figure 7, it could be found that the nanowire core of nanocables was partially etched. The results show that the Te cores are composed of remnants of crude nanowires and discontinuous nanoparticles (figures 7b,c).

4. Conclusions

In conclusion, Te/C nanocables have been successfully synthesized by a simple hydrothermal method. The Te/C nanocables are a composite comprising of a smooth core of about 20 nm in diameter and asurrounding sheath of about 60–80 nm in thickness. Carbonaceous nanotubes and Te/C nanocables with fragmentary Te core were obtained by adjusting time of chemical etching. These carbonaceous nanotubes kept the lengths of the original Te/C nanocables and the sizes of the shell.

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