



One-step hydrothermal synthesis of CdTe nanowires with amorphous carbon sheaths

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ABSTRACT

CdTe nanowires with carbon sheaths were synthesized via a one-step hydrothermal process using ascorbic acid as a reducing agent and carbonization source. The average diameter of CdTe core nanowires and thickness of amorphous carbon sheaths are about 20 nm and 10 nm, respectively. During this process, carbon-coated Te nanowires were formed and then reacted with Cd^{2+} ions, resulting in the formation of carbon-coated CdTe nanowires. Additionally, the size and shape of the CdTe nanowires were determined during the initial stage of Te formation.

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1. Introduction

In recent decades, one-dimensional (1D) semiconductor nanostructures including nanowires, nanorods, and nanotubes have become the focus of research interest due to their novel properties and their potential application as building blocks for fabricating nanoscale devices [1–4].

Cadmium telluride (CdTe) has been identified as an ideal material for photovoltaic-devices [5] due to its near-infrared direct band gap (1.5 eV) and high optical absorption coefficient [6]. CdTe nanowires have been synthesized through a number of methods including self-assembly [7], electrodeposition [8], and solution-based chemical methods [9]. However, their potential drawbacks, such as the adsorption of unwanted species (e.g., water and oxygen) on the surface of the wire as well as the unnecessary charge injection into CdTe nanowires, could negatively affect device characteristics or stability [10,11]. Recent investigations of CdTe nanowires with insulating sheaths have suggested potential solutions to these limitations. Xi et al. [11] reported the preparation of metal telluride/carbon nanocables using a hydrothermal method, with the pre-synthesized Te/carbon nanocables as templates. Liang et al. [10] fabricated a coaxial silica shell on the surface of CdTe nanowires via the base-catalyzed hydrolysis of tetraethyl orthosilicate. However,

further studies on the formation mechanism of CdTe nanowires with insulating sheaths are essential to optimize their geometry and other key characteristics.

In the present work, we demonstrate a one-step hydrothermal process for synthesizing CdTe nanowires with amorphous carbon sheaths, using ascorbic acid as a reducing agent and carbonization source. The sequential mechanisms for phase formation, shape evolution, and carbon sheath coating of the CdTe nanowires were also investigated by detailed analysis of reaction times from the experimental data.

2. Experimental

Initially, 14.2 mmol of ascorbic acid ($\text{C}_6\text{H}_8\text{O}_6$) and 0.823 mmol of cetyltrimethylammonium bromide (CTAB) were dissolved in 40 mL of deionized water under mild magnetic stirring at room temperature. Next, 1.88 mmol of Na_2TeO_3 and 1.88 mmol of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ were added to the above solution in order; a white TeO_2 was precipitated immediately upon the addition of the Na_2TeO_3 . Finally, 40 mL of deionized water was added to the previous solution under continuous stirring. The final solution was transferred into a 100 mL Teflon-lined stainless steel autoclave, which was sealed and maintained at 180 °C for various reaction times (20 min, 1, 3, 6, 12, 24, and 36 h) in a preheated electric oven, then allowed to cool to room temperature. The products were collected and washed repeatedly with deionized water and ethanol, then dried at 60 °C for 12 h.

The phase of each resulting product was characterized by X-ray diffractometer (XRD, D/MAX-IIIC, Rigaku, Japan) with $\text{Cu K}\alpha$ radiation. Scanning electron microscopy (FE-SEM, S-4800, Hitachi, Japan) and transmission electron microscopy (TEM, Tecnai G2 F30, FEI

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Company, Netherland) were utilized to observe the morphology and size of the products. To analyze the sheaths on the CdTe nanowire surfaces, Raman spectra were recorded with a high-resolution dispersive Raman microscope (LabRAM HR UV/Vis/NIR, Horiba Jobin Yvon, France).

3. Results and discussion

The XRD patterns of the products synthesized at 180 °C are shown for different reaction times (20 min, 1, 6, and 36 h) in Fig. 1(a). The product reacted for 20 min is shown to exhibit an amorphous-phase. When the reaction time increased to 1 h, a pure trigonal Te (t-Te) (JCPDS No. 36-1452) phase is formed. With additional increases in the reaction time, the intensity of t-Te XRD peaks decreases, whereas that the intensity of the zinc-blende CdTe (JCPDS No. 15-0770) peaks appears and continues to increase. A pure-phase CdTe was ultimately obtained after 36 h of reaction time.

Fig. 1(b) shows SEM micrographs of the products synthesized at 180 °C for the various reaction times (20 min, 1, 6, and 36 h). The

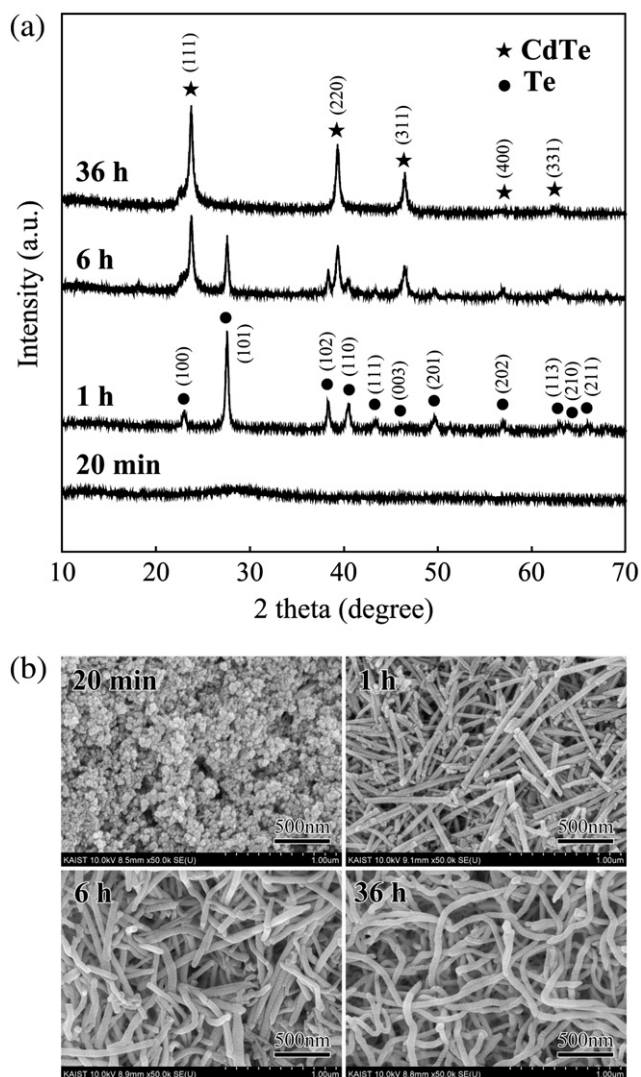


Fig. 1. (a) XRD patterns and (b) SEM micrographs of the products hydrothermally reacted at 180 °C for 20 min, 1, 6, and 36 h.

amorphous product reacted for 20 min consists of nanoparticles with an average size of a few nanometers. The t-Te products synthesized at the reaction time of 1 h exhibit straight nanowires with diameters of 20–30 nm and lengths of few micrometers. As the reaction time approaches 36 h, the final CdTe nanowire products have greater average diameters of 40–50 nm and a more winding shape compared to the diameters and shapes of the t-Te nanowires. The above XRD patterns and SEM micrographs clearly reveal that the formation of CdTe nanowires is achieved through the sequential steps of straight t-Te nanowire formation followed by transition to CdTe nanowires with winding shape.

The TEM, HRTEM micrographs, electron diffraction patterns, and Raman spectra of the products prepared at 180 °C for different reaction times (20 min, 1, 6, and 36 h) are displayed in Fig. 2. These results clearly demonstrate the mechanism of the phase formation and shape construction for the synthesized products as a function of reaction time. The TEM and HRTEM micrographs for the samples show the evolution of shape from nanoparticles to nanowires with increasing reaction time, which is in agreement with the SEM results in Fig. 1(b). Meanwhile, the obvious contrast between the inner and outer regions of the wires demonstrates a core-shell structure for the samples reacted for 6 h and above, which shows crystalline core nanowires coated uniformly with amorphous sheaths. The HRTEM micrograph and electron diffraction pattern for the core region of the sample reacted for 6 h clearly demonstrates a mixture of t-Te and zinc-blende CdTe, which reflects an intermediate state of phase transition. The calculated interplane distances perpendicular to the axial direction of the core nanowires in regions 1 and 2 are about 0.5833 and 0.378 nm, corresponding to the d-spacing of (001) planes of t-Te and (111) planes of zinc-blende CdTe, respectively. These TEM analyses are in agreement with the phase transitions observed by XRD investigation (Fig. 1(a)). Raman spectroscopy was also applied to reveal the composition of the amorphous sheaths. The resulting Raman spectra show two distinct peaks around 1346 (D band) and 1594 cm^{-1} (G band) for the samples reacted for 6 h and above, which are not observed in Raman spectra of the products prepared for 20 min and 1 h. The D band results from a disorder-induced band due to the double-resonance effect, and the G band is attributed to in-plane vibrations of graphitic carbon [12]. These results verify that the sheaths are composed of amorphous carbon. The sheath thickness also increases as reaction time increases to 36 h, in proportion to the intensity increase of the D and G bands in the Raman spectra.

The changes in core nanowire diameter and carbon sheath thickness, after the formation of t-Te nanowires as a function of reaction time (1, 3, 6, 12, 24, and 36 h), are shown in Fig. 3. The core nanowire diameter is stable at 20 nm from the initial stage of t-Te formation through the completion of CdTe formation (Fig. 3(a)). However, the presence of amorphous carbon sheaths on the nanowires was not observed for the initial stage of t-Te nanowire formation, but appeared during the intermediate stage (mixture of t-Te and CdTe) and remained through the final stage (completely CdTe). The thickness of the amorphous carbon sheaths increases up to, and stabilizes at, approximately 10 nm (Fig. 3(b)). These results suggest that the core diameter of the final CdTe nanowires is previously determined at an initial stage of t-Te nanowire formation, and that the formation of amorphous carbon sheaths starts with the phase transition from t-Te to CdTe.

Based on the above experimental results, the phase and shape evolution of amorphous carbon-coated CdTe nanowires could be summarized as follows. When the hydrothermal reaction starts, the straight t-Te nanowire shape is created by 'solid-solution-solid transformation' [13]. In this process, the growth into t-Te nanowires is associated with the highly anisotropic inherent structure of Te, causing it to crystallize along the *c*-axis [14]. As the reaction proceeds, the polymerization and carbonization of the ascorbic acid

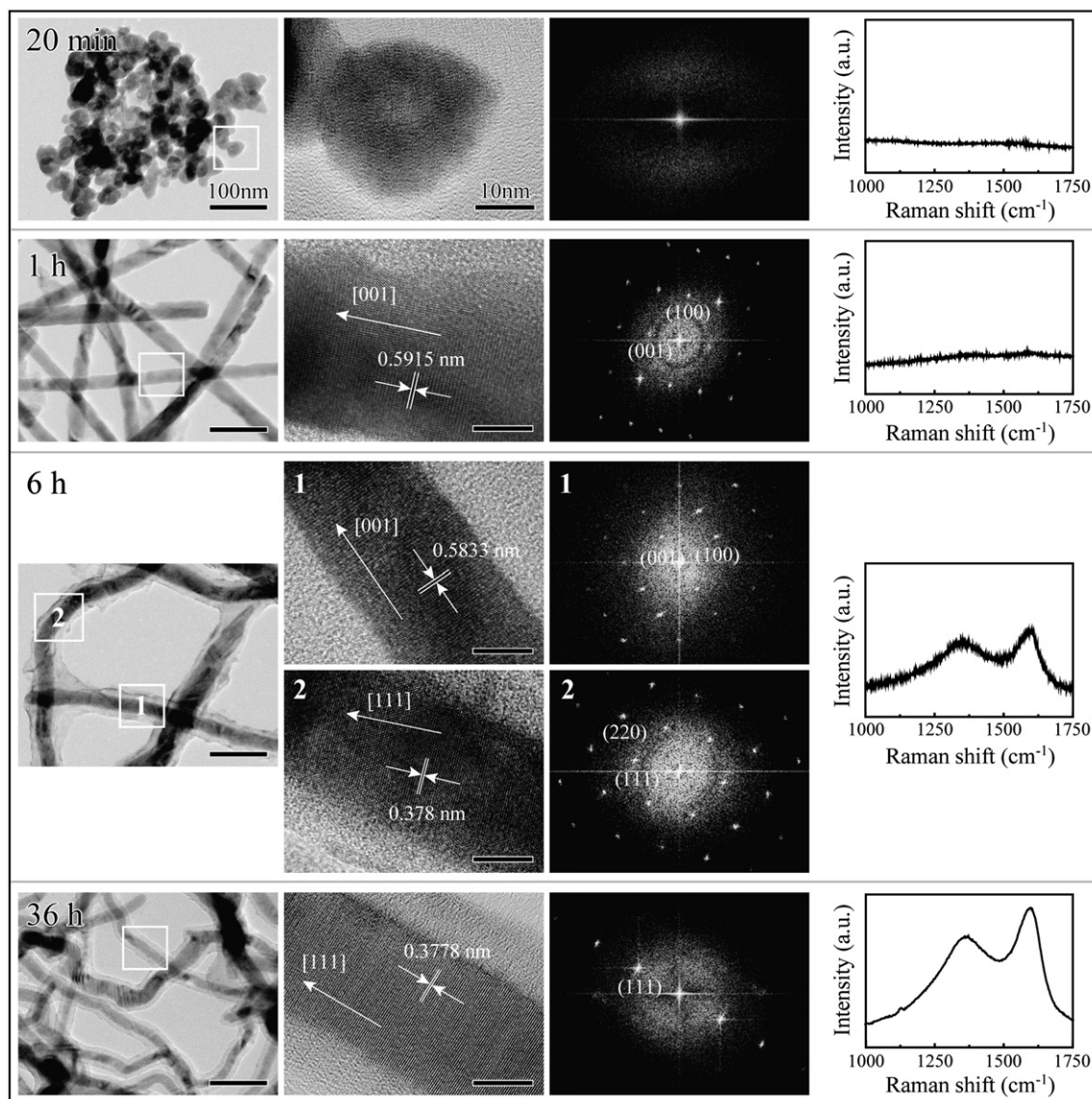


Fig. 2. TEM, HRTEM micrographs, the corresponding electron diffraction patterns, and Raman spectra of the products hydrothermally reacted at 180 °C for 20 min, 1, 6, and 36 h.

take place. As a result, amorphous carbon sheaths are formed on the surface of the initially grown Te nanowires. At the same time, Cd^{2+} ions diffuse into the carbon sheaths and react with Te nanowires, which results in the formation of CdTe nanowires. This reaction mechanism is well supported by the standard electrode potentials of Cd^{2+}/Cd and $\text{C}_6\text{H}_6\text{O}_6/\text{C}_6\text{H}_8\text{O}_6$ (-0.403 [11] and $+0.06$ V [15], respectively), which are evidence for the direct reaction between Cd^{2+} ions and Te nanowires without a reduction step to Cd atoms. During this reaction, the straight form t-Te nanowires transforms to amorphous carbon-coated CdTe nanowires with a winding shape.

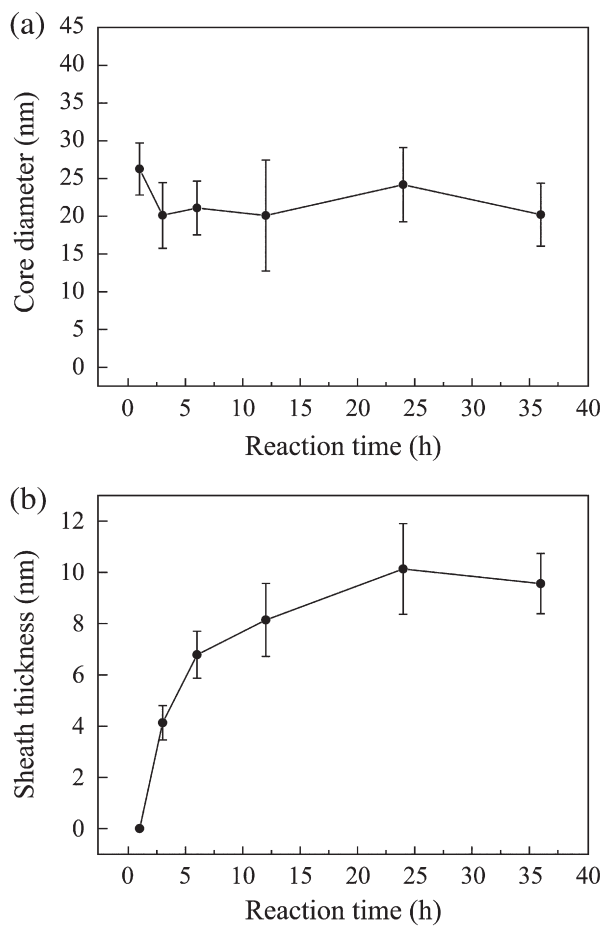
4. Conclusion

The CdTe nanowires with amorphous carbon sheaths were successfully synthesized via a one-step hydrothermal process, using ascorbic acid as a reducing agent and carbon source. Thus, the formation process of amorphous carbon-coated CdTe nanowires involves four distinctive stages: (1) the formation of straight shaped

t-Te nanowires via ‘solid–solution–solid transformation’; (2) induction of amorphous carbon coating on the t-Te nanowire surfaces by polymerization and carbonization of the ascorbic acid; (3) simultaneously, the diffusion of Cd^{2+} ions into the carbon sheaths; and (4) the formation of CdTe nanowires with carbon sheaths and winding geometry through the reaction between Cd^{2+} ions and Te nanowires. The diameter of the CdTe nanowires is determined at the initial stage of t-Te nanowire formation.

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Fig. 3. Change in (a) diameter of core nanowires and (b) thickness of carbon sheaths as a function of the reaction time (1, 3, 6, 12, 24, and 36 h) after the formation of t-Te nanowires.