Controlled Synthesis of Se/Te Alloy and Te Nanowires†

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Se/Te alloy and Te nanowires (NWs) with different morphologies were synthesized through a novel, controllable solution-phase method. Sodium dodecylbenzene sulfonate was employed as a surfactant to control the reaction rate in the synthesis. Through reaction process dynamics control, both “bending” and “V-shaped” Se/Te alloy NWs were controllably produced. The phase structures and morphologies of the Se/Te and Te products were investigated with XRD, TEM, and HRTEM. The formation mechanisms of the NWs were investigated on the basis of the experimental results. The significance of these results lies in the important implications concerning the potential use of these NWs materials for nanoscale electronic devices.

Key words: Se/Te alloy, “V-shaped” structure, Nanowires

I. INTRODUCTION

One-dimensional (1D) nanostructures, including nanowires (NWs), nano-belts, nanorods, and nanotubes, have received considerable attention in recent years due to their novel electronic properties and potential applications in nanoscale electronic or electromechanical devices [1-5]. Semiconductor NWs, for example, have been found to have a number of potential roles for their basic functions in fabricating nanoscale electronic or optoelectronic devices [6-11]. As group VI elemental semiconductors Se, Te, and their alloys have many interesting properties such as a relatively low melting point, high photoconductivity, catalytic activity in hydrolysis and oxidation reactions, and high piezoelectric, thermoelectric, and nonlinear optical responses [12]. Furthermore, these two elements can also react with many other substances to form a range of technologically important materials such as CdSe, CdTe, and ZnTe [13]. In the case of Se/Te alloy, there is the exhibition of an unusual temperature dependence of electrical resistivity [14]. The magnetoresistance (MR) has also been found to be highly sensitive to the composition and may exhibit both positive and negative MR behavior [14]. It is reasonable to expect that the availability of these materials in the form of NWs may provide new opportunities to fabricate many important semiconductor materials or nanoscale functional devices that will exploit these interesting properties. To date, Se NWs [15-17], Te NWs [18-21] and Se/Te [22] alloy nanorods/NWs have been prepared successfully by chemical solution processes. Qi et al. have reported the synthesis of single selenium nanotubes by the dismutation of Na$_2$SeO$_3$ under acidic conditions in micelle solutions of the surfactant poly(oxyethylene dodecyl ether) [23]. The growth direction of 1D nanostructures of these materials has been confirmed to be along the c-axis, i.e., in the direction parallel to the helical chains of Se, Te, or Se-Te atoms in the trigonal structure.

As an anion surfactant, sodium dodecylbenzene sulfonate (C$_{12}$H$_{25}$SO$_4$Na, SDBS) has been widely used to successfully prepare a variety of nano-materials, such as Au [24], Co(O$_3$PC$_6$H$_5$)$_3$H$_2$O [25], Co$_3$O$_4$ [26] nanoparticles and mesostructured vanadium-magnesium oxides [27]. We are also capable of controlling the lateral dimensions of Se/Te alloy NWs by changing the concentration of SDBS in the solution to values different with that of our previous work [28]. In this work, we present new and simple methods for the fabrication of Se/Te NWs with different morphologies and self-assembled Te NWs. For the first time we have fabricated Se/Te NWs with a V-shaped morphology in the presence of SDBS surfactant by using short Te nanorods as crystalline seeds. We prove here that such a method is a highly effective synthesis protocol to produce 1D nanostructures of Se/Te alloy NWs with different morphologies. Because of the mild reaction conditions and easily controllable synthesis, this method can be used in large-scale production of Te and Se/Te NW materials.

II. EXPERIMENTS

A. Materials

Selenious acid (H$_2$SeO$_3$, 99.999%) and orthotelluric acid (H$_4$TeO$_6$, 99.999%) were purchased from Aldrich (Milwaukee, WI), hydrazine (N$_2$H$_4$, 98%) and sodium dodecylbenzene sulfonate (C$_{12}$H$_{25}$SO$_4$Na, SDBS) were bought from Fisher Chemical Corporation. They were prepared as stock solutions by diluting with 18 MΩ wa-

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ter (E-Pure, Dubuque, IA), or by ethylene glycol (EG, HOC2H4OH, 99.8%, Fisher). All chemicals were used without any further purification.

B. Preparation of Se/Te alloy NWs with different morphology

The Se/Te alloy NWs with bending and V-shaped morphologies were prepared following two different procedures employing the same solvent and chemicals. Selenious acid and orthotelluric acid were reduced with hydrazine in water refluxed at temperatures in the range of 90-100 °C. In general, the reactants were stirred and heated until the initial reduction was complete (about 10 min). Reaction mixtures were cooled to room temperature and allowed to age in the dark for several days. One to several drops of the resulting solution were then put onto a Cu grid for electron microscopy characterization. It is well known that the growth of t-Se and t-Te nanostructures is quite different. Some Te tends to form a trigonal structure when the reaction is refluxed in water at temperatures of around 100 °C while almost no t-Se is obtained after the reaction is quenched to room temperature in an ice bath [15]. The α-Se or α-Te colloids slowly dissolved into the solution and grew into NWs on the seeds of t-Te nanocrystallites. The detailed procedures for two different procedures are described below.

Synthesis of Se/Te alloy NWs begins with the addition of 2 mmol selenious acid, 2 mmol orthotelluric acid, and 0.5 g SDBS to 100 mL pure water. The solution is then refluxed for 1 h until a clear solution was obtained. Next, the resulting solution was heated to 95 °C at a heating rate of 10 °C/min in an argon atmosphere. After 30 min, 1.5 mL of hydrazine was quickly injected into the solution through a syringe and the solution turned black immediately. The solution was kept at 95 °C for another 15 min and then moved to an ice bath to quench the reaction to 0 °C. The resulting solution was stirred for four days until all the α-Se colloids dissolved into the solution and grew into NWs on the seeds of t-Te nanocrystallites.

Synthesis of bending Se/Te alloy NWs with the V-shaped morphology begins with the addition of 2 mmol orthotelluric acid and 0.5 g SDBS to 100 mL pure water. This solution was then refluxed for 1 h until a clear solution was obtained. Next, the resulting solution was heated up to 95 °C at a heating rate of 10 °C/min in an argon atmosphere. After 30 min, 1.5 mL of hydrazine was quickly injected into the solution through a syringe and the solution turned black immediately. The solution was kept at 95 °C for another 15 min and then moved to an ice bath to quench the reaction to 0 °C. The resulting solution was stirred for four days until all the α-Se colloids dissolved into the solution and grew into NWs on the seeds of t-Te nanocrystallites.

C. Preparation of Te NWs with different solvent

The t-Te nanostructures were prepared in two different solvent systems that include water and EG. Orthotelluric acid was reduced by hydrazine in these solvents and refluxed at 90 and 190 °C. The preparation process of t-Te NWs in water was similar to the synthesis of the Se/Te alloy NWs minus the use of any selenious acid. We also prepared Te NWs without using any surfactant by using EG as the solvent. A detailed preparation process can be found [19]. In a typical preparation process, pure ethylene glycol and 6 mmol orthotelluric acid was added to 10 mL of anhydrous EG and heated to 190 °C in a round bottom flask in an oil bath for temperature regulation, fitted with a condenser, and stirred magnetically. A hydrazine solution (2 mL) was rapidly added under constant magnetic stirring. The total reaction time was controlled to be several minutes.

III. RESULTS AND DISCUSSION

Figure 1(a) shows the TEM image of a typical, as-synthesized Se/Te NW. The TEM image indicates the uniformity along the lateral dimensions (about 8 nm thickness), the bending morphology (as opposed to straight Se/Te NWs obtained without using any surfactants [22], and the large quantity that we could routinely achieve for this system. In our previous work, we had concluded that in the case of Se/Te alloy NWs synthesized by injecting hydrazine into the selenious acid and orthotelluric acid hybrid solution, the atomic ratio of Se to Te is nearly 1:1. This value is close to the molar feed ratio of the selenious and orthotelluric acids in the reaction mixture [28]. In addition, self-assembled, uniform Te in large quantities was obtained using the same synthesis process (Fig.1(b)). Figure 1(c) gives a TEM image of NWs displaying a very different morphology. These Se/Te NWs were synthesized by using very short trigonal Te rods as crystalline seeds (the inset shows the TEM image of Te nanorods and nanoparticles before adding the selenious acid solution). The NWs indicate a uniform V-shaped morphology with each segment about 200 nm in length and 8 nm in diameter. It is interesting that each segment is very straight, quite different from the bending structure shown in Fig.1(a). The single-crystallinity and structural integrity of the bending Te/Se NWs are further demonstrated by the high-resolution transmission electron microscope (HRTEM).
FIG. 1 TEM images of bending Se/Te (a), Te (b), V shape Se/Te NWs (c), and their corresponding HRTEM image (d), (e), and (f).

FIG. 2 TEM images of V-shape Se-Te alloy NWs with different Se:Te ratio, (a) 1:2, (b) 1:1, (c) 2:1.

image of the wire edge (Fig.1(d)), which is basically the same as the HRTEM image obtained from the other part of the wire, further suggesting a single crystalline structure like that of the bending Se/Te NWs. The figure shows well-resolved lattice fringes in the (001) planes of the trigonal Se/Te lattice, with an interplane spacing of 5.3 Å. We also investigated the structure of Te NWs by HRTEM. Shown in Fig.1(f) is the HRTEM image of a Te NW. High resolution TEM images further confirm that the Te NW is single crystalline with infinite helical chains of tellurium atoms parallel to the c-axis. In Fig.1(f) is the HRTEM image of a V-shaped Se/Te NW obtained by focusing the electron beam on the middle part of the NW. These figures show well-resolved lattice fringes of a trigonal Se/Te lattice, with the interplane spacing of 5.0 Å, indicating the single crystalline structure of the Se/Te NWs.

In order to investigate the effect of Se quantity on the morphology of V-shaped Se/Te NWs, the quantity of Te was fixed by using 2 mmol orthotelluric acid in all reactions while changing the quantity of selenious acid. Shown in Fig.2 are the TEM images of V shape Se/Te NWs synthesized with different amounts of selenious acid added in (the molar ratio of Se to Te was adjusted to 0.5:1, 1:1, and 2:1 respectively). We found that all the NWs exhibited the V-shaped structure. The morphology of V-shaped Se/Te NWs tend to be more homogeneous with decreasing Se content.

Figure 3 shows the XRD patterns of the as-synthesized sample of Se/Te NWs prepared by injection of hydrazine into selenious acid (H₂SeO₃, 99.999%) and orthotelluric acid (with atomic ratio Se:Te=1:1) (other V-shaped Se/Te NWs have similar XRD patterns) and pure Te NWs prepared by hydrazine reduction with 0.5% SDBS as the surfactant. The main diffraction peaks can be assigned to the (100), (101), (110/102), (111), (200), (202), (210), and (201/003) peaks of Se/Te and the (100), (101), (102), (201), (112), (111), (040), (003), (103), (113), (210), (301), and (114) peaks of Te NWs. No peaks corresponding to impurities were detected, implying the synthesis of high purity Te/Se products and indicating that these alloy wires had crystallized into a trigonal lattice.

As for the growth mechanism of Se/Te and Te
NWs prepared with SDBS as the surfactant, the solid-solution-solid transformation, the anisotropic nature of the building blocks along the [001] direction of nanocrystalline Se/Te and Te, and the surfactant-assisted preferentially unidirectional growth mechanism could be key factors in the formation of Se/Te and Te NWs. The morphology of the final product was largely determined by the anisotropic nature of the building blocks, that is, the 1D characteristics of the infinite, helical chains of Se or Te in the crystalline phase, which had been confirmed by our previous work [28] and other research group’s work [16]. In order to find out the possible mechanism for formation of V-shaped Se/Te NWs, we used EDS to investigate the Se and Te content in different parts of the samples (as shown in Fig. 4). As shown in Table I, the atomic percentage of Te is higher than that of Se in the middle part of the NWs. The content of Te decreases almost linearly from the middle part to the end of the V-shaped Se/Te NW (the Te content in 2a, 3a, 4a is similar to those of 2b, 3b, 4b). 57% content of Te was obtained in the middle part of the V-shaped Se/Te NW. This implies that the growth of V-shaped Se/Te NWs took place beginning from the middle part. The mechanism sketched in Fig. 5 is a possible mechanism for V-shaped Se/Te NW growth and is consistent with our visual observations. Upon injecting hydrazine into a solution containing orthotelluric acid, the clear mixture immediately turned to black, indicating the formation of spherical colloids of α-Te and t-Te with excess hydrazine. With the presence of SDBS surfactant, the growth of different planes of t-Te is largely confined. We speculate that the sidewalls are almost completely passivated by SDBS while the axial growth planes ([001] direction) are only partially passivated by SDBS. The growth of V-shaped Se/Te NWs may be due to the following three main results: (i) Se and Te will compete with each other to attack the ends of a Te nanowire. (ii) Surface tension formed by the atom size changes from Te to Se will alter the nanowire growth direction in order to relax the energy. (iii) The trigonal structure is the lowest energy state in the case of Se or Te and both tend to form trigonal single crystals in this case (Fig. 5(f)).

IV. CONCLUSION

We have demonstrated a simple approach on large-scale synthesis of single-crystalline NWs of Se/Te alloys and Te. Se/Te NWs with bending and V shape structure were synthesized by using different synthesis method. Self assemble of Te NWs were also obtained when using SDBS as surfactant. As the elemental composition of these nanorods is basically the same as that of the feeding ratio, the present method will provide a simple and practical way of preparing nanorods of Se/Te alloys with controllable and tunable compositions and properties. All these results indicate that these NWs may be used as functional components for fabricating drop by drop into a solution containing α-Te and t-Te with excess hydrazine. With the presence of SDBS surfactant, the growth of different planes of t-Te is largely confined. We speculate that the sidewalls are almost completely passivated by SDBS while the axial growth planes ([001] direction) are only partially passivated by SDBS. The growth of V-shaped Se/Te NWs may be due to the following three main results: (i) Se and Te will compete with each other to attack the ends of a Te nanowire. (ii) Surface tension formed by the atom size changes from Te to Se will alter the nanowire growth direction in order to relax the energy. (iii) The trigonal structure is the lowest energy state in the case of Se or Te and both tend to form trigonal single crystals in this case (Fig. 5(f)).

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FIG. 5 Schematic illustration of a plausible mechanism for the formation of V shape Se/Te NWs (a), (b) Reduction of orthotelluric acids with excess hydrazine at the set-point temperature in an aqueous medium generates monodispersed spherical colloids of α-Te and t-Te that are ∼10 nm in diameter, (c) Formation of very short t-Te nanorods, (d) Formation of α-Se when selenious acid was added drop by drop into the solution containing excess hydrazine, (e) α-Se and α-Te were absorbed on the surface of t-Te nanorods and growth, (f) V shape Se/Te NWs formation.

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