

## Synthesis of Uniform CoTe and NiTe Semiconductor Nanocluster Wires through a Novel Coreduction Method

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A novel coreduction method was developed to synthesize uniform one-dimensional CoTe and NiTe nanocluster wires. In the synthesis, soluble  $\text{Na}_2\text{TeO}_3$  was used to supply a highly reactive Te source and  $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$  was used both as reducing agent and as complexing agent. The as-prepared samples were characterized by XRD, TEM, and HRTEM. The probable formation mechanism of the nanowires is discussed.

Semiconducting tellurides are being actively researched due to their distinctive properties and now are widely used in material fields. For example,  $\text{Bi}_2\text{Te}_3$ -based compounds have become major components of the thermoelectric industry,<sup>1</sup>  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  is extensively investigated for fabricating IR detector arrays,<sup>2</sup> and CdTe is a promising material for electronic and optical devices.<sup>3</sup> Recently, a large magnetoresistance (MR) effect was also found in tellurides ( $\text{Ag}_2\text{-Te}$ ).<sup>4</sup> Herein, a new type of CoTe and NiTe nanocluster wires (consisting of CoTe and NiTe nanoclusters) is reported. We choose CoTe and NiTe just because they are typical magnetic semiconductors, which have attracted great interest in current research for their distinctive electrical transport properties.

Although many nanorods and nanowires of oxides, sulfides, and selenides<sup>5–8</sup> have been synthesized, up to now, comparatively few studies of telluride nanowires have been reported. The traditional method used to prepare tellurides is the direct combination of the elements in evacuated silica tubes at very high temperature (about 1000 °C).<sup>9</sup> MOCVD (metalorganic vapor chemical deposition)<sup>10</sup> and molecular

precursor methods<sup>11</sup> are usually used for films and coating. Solvothermal methods<sup>12</sup> can also be used to produce tellurides, in which commercial Te powder will combine with metal salts in ethylenediamine medium. However, none of them can produce 1-D telluride nanowires. Recently, Sander<sup>13</sup> et al. have reported an electrodeposition method to  $\text{Bi}_2\text{Te}_3$  nanowires by using porous anodic alumina templates. On the basis of the syntheses of selenides in our former work,<sup>8,14</sup> we developed a novel coreduction method to CoTe and NiTe nanocluster wires. By using the in situ produced highly reactive Te and Co (or Ni), CoTe and NiTe nanocluster wires were successfully synthesized on the basis of complex reaction at 140 °C. It is worthy to note that, as a kind of low-dimensional assembly of nanoparticles, nanocluster wire has potential applications and is becoming of increasing interest because it behaves as quantum dots.<sup>15</sup>

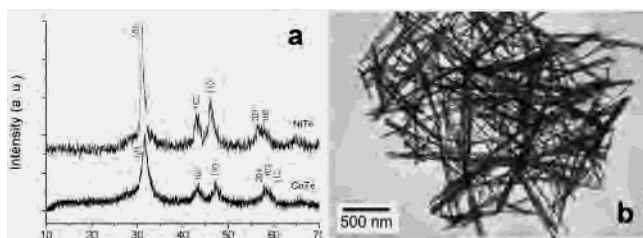
$\text{CoSO}_4\cdot 7\text{H}_2\text{O}$  (1.4 g, 0.005 mol) or  $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$  (1.19 g, 0.005 mol) was put into a Teflon-lined autoclave of 100 mL capacity and dissolved in 50 mL of deionized water. The 1.11 g (0.005 mol) of  $\text{Na}_2\text{TeO}_3$  was added into the autoclave, and a precipitation of  $\text{CoTeO}_3$  (or  $\text{NiTeO}_3$ ) appeared immediately. After stirring for about 10 min, 20 mL of hydrazine hydrate ( $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ ) was added, and finally the precipitate was dissolved. The autoclave was filled with deionized water up to 80% of the total volume, sealed, and heated at 140 °C for about 5 h. After that, the system was allowed to cool to room temperature naturally. Black products (the yield is about 95%) were collected by filtration, washed with deionized water and absolute ethanol, and then dried at 60 °C.

The obtained samples were characterized on a Bruker D8-advance X-ray powder diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). The size and morphology of the nanowires

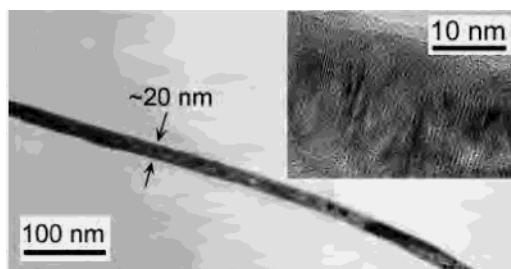
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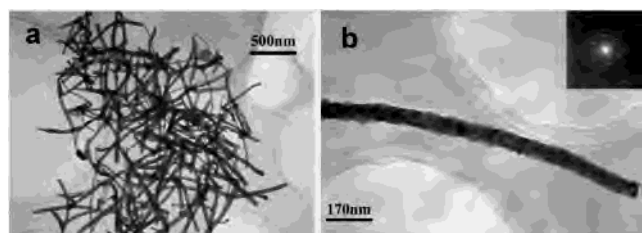
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**Figure 1.** (a) XRD patterns of CoTe and NiTe nanowires. (b) TEM image of as-prepared CoTe nanowires.



**Figure 2.** TEM and HRTEM image of one individual CoTe nanowire.



**Figure 3.** TEM images of (a) NiTe nanowires and (b) one individual nanowire.

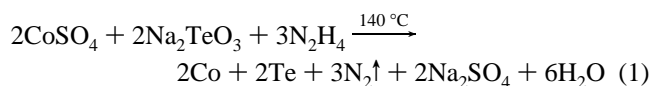
were determined at 200 kV by a Hitachi H-800 transmission electron microscope (TEM) and a JEOL JEM-2010F high-resolution transmission electron microscope.

Figure 1a shows the typical XRD patterns of CoTe and NiTe nanocluster wires. The two as-prepared samples are pure phase with NiAs structure. All the reflections can be indexed to hexagonal CoTe ( $a = 3.893 \text{ \AA}$  and  $c = 5.375 \text{ \AA}$ , the (201), (103), and (112) peaks are overlapped to form a broad peak) or hexagonal NiTe ( $a = 3.9293 \text{ \AA}$  and  $c = 5.3657 \text{ \AA}$ ). The broad peaks indicate the fine average size of products.

TEM measurement of CoTe (Figure 1b) indicates that the average length of these nanowires is about  $2 \mu\text{m}$ , with the diameters ranging from 10 nm to 30 nm. Figure 2 shows a typical individual nanowire with the diameter of  $\sim 20 \text{ nm}$ . Figure 3a shows the nanowires of NiTe. Their lengths range from 500 nm to about  $2 \mu\text{m}$ . The diameter of a typical individual nanowire is about 70 nm (Figure 3b). Unlike the appearance of single crystallized nanowires, many black clusters can be found in both CoTe and NiTe nanowires (Figures 1b, 2, 3). In the inset HRTEM image (Figure 2) of one CoTe nanowire, we can clearly see that a bunch of nanoclusters, which have discontinuous lattice fringes, are embedded in the middle of the nanowire and welded by amorphous substance. It is difficult to calculate the interplane distances and estimate the accurate size of these nanoclusters. Almost all of the lattice fringes are perpendicular (or approximately perpendicular) to the long axes of nanowire.

These specific oriented lattice fringes indicate that there is a predominant direction during the growth of CoTe in the solution. From the inset ED pattern (in Figure 3b) of NiTe, it can be considered that NiTe nanowires are also composed of micro NiTe nanoclusters.

Compared to the reported synthetic methods of tellurides, the most innovative place in our experiments is the use of  $\text{Na}_2\text{TeO}_3$  to supply a highly reactive Te source.  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$  is used both as reducing agent and as complexing agent, which helps to form a uniform and transparent aqueous solution before reaction. The reaction to form CoTe (similar to NiTe) can be formulated as the following equations:



Soluble  $\text{Na}_2\text{TeO}_3$  will first dissociate in water into  $\text{TeO}_3^{2-}$  and  $\text{Na}^+$ , and then react with  $\text{Co}^{2+}$  to form  $\text{CoTeO}_3$  precipitation. When  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$  is added,  $\text{CoTeO}_3$  precipitation is dissolved by the formation of  $\text{Co}^{2+} - \text{N}_2\text{H}_4$  complex ion (and dissociative  $\text{TeO}_3^{2-}$  is formed again), which provides an ideal environment for the growth of CoTe nanowires. At  $140^\circ\text{C}$ ,  $\text{TeO}_3^{2-}$  can easily be reduced by hydrazine to  $\text{Te}^{8,14}$  and at the same time  $\text{Co}^{2+}$  can also be reduced to Co (eq 1).<sup>16</sup> These newly produced Te and Co are highly reactive, and they will react with each other to form the CoTe product (eq 2). We call this process a hydrothermal coreduction routine.<sup>17</sup> Another possible routine is that the newly produced Te will be reduced further to  $\text{Te}^{2-}$ ,<sup>18</sup> and then  $\text{Te}^{2-}$  reacts with  $\text{Co}^{2+} - \text{N}_2\text{H}_4$  to form the product. Because of these highly reactive Te and/or Co sources, the whole reaction rate is expedited and a higher concentration of CoTe monomer (single CoTe molecule before its nucleation and growth) will form, which may cause the fast growth along the predominant direction to form nanowires.<sup>19</sup> To substantiate our hypothesis, we performed control experiments. When commercial Te powder instead of  $\text{Na}_2\text{TeO}_3$  was used as reactant in our experiments, no CoTe or NiTe product (we obtained only  $\text{Co}(\text{OH})_2$ ,  $\text{Ni}(\text{OH})_2$ , and unreacted Te) could be obtained.

This coreduction method to CoTe and NiTe nanowires surely can be used to synthesize other 1-D tellurides. It will have potential applications in fabricating diluted magnetic semiconductors and other advanced materials.

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