Effect of High Magnetic Field on the Fabrication of One-dimensional Tellurium Microstructures via a Solvothermal Treatment

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The magnetic-field-assisted solvothermal approach has been used in the shape-controlled growth of Te microcrystals. By applying a high magnetic field to the reaction system, the shape of obtained Te microcrystals could be changed greatly. Various techniques such as X-ray diffraction and scanning electron microscopy have been used to characterize the obtained products. The results show that the magnetic field plays a key role in the growth behavior of Te microcrystals. The possible cause of magnetic field effects is discussed.

As a narrow band gap semiconductor, tellurium exhibits many interesting chemical and physical properties including photoconductivity and catalytic activity as well as piezoelectric, thermoelectric, and nonliner optical response.[1] Due to its anisotropic crystal structure, tellurium would be expected to have a tendency to form one-dimensional (1D) structure. Many methodologies have been developed for the fabrication of elemental tellurium 1D structures, such as physical vapor deposition,[2] solution-phase reduction,[3] hydrothermal,[4] solvothermal,[5] and microwave routes.[6]

Recently, magnetic fields have been adopted to assemble fine magnetic particles into 1D, 2D, and 3D structures.[7] In addition, magnetic-field-assisted hydrothermal processes have proven to be an effective route to obtain Fe_3O_4 nanorods and nanowires.[8] Under such magnetic fields, anisotropic growth is enhanced, and the morphological symmetry disappears. Time-varied magnetic fields could also be used for fibrous aggregation of Fe_3O_4 magnetic nanoparticles.[9] Meanwhile, other magnetic-field-assisted routes have also been applied to the fabrication of 1D Fe_3O_4 nanostructures[10] and $CoPt_3$ nanostructures.[11] Furthermore, with the appearance of superconducting technology, a high magnetic field which is more than 1 T can be obtained easily, which could open a possible way to control the shape of nonmagnetic materials. After applying a high magnetic field of 10 T to the dissociation of mesitylene, the magnetic field directs the interaction between fine particles, leading to the formation of carbon filaments.[12] Doping carbon nanotubes into polymer under a 10 T magnetic field, the aligned nanotubes in polymer matrix can be obtained.[13]

While these papers were mostly focused on magnetic and paramagnetic materials, there are few reports about diamagnetic material growth under a magnetic field. Only we have reported a production of bismuth nanowires under 8 T magnetic fields previously.[14] So in this paper, the notion of magnetic-field-assistance is introduced into the solvothermal process for the fabrication of tellurium microcrystals. We found that the shape of tellurium microcrystals depended on the strength of magnetic field. The possible reason of the magnetic field effect is discussed.

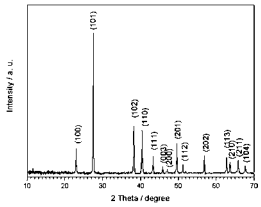

Figure 1. XRD pattern of a sample prepared via a solvothermal route at 210 °C.

In a typical preparation, 0.36 g of sodium tellurite (Na_2TeO_3) and 16 mL of ethylene glycol (EG) were put into a beaker with a capacity of 50 mL. The solution was then stirred vigorously for 30 min. Finally, a transparent colorless solution was obtained. Then this solution was transferred into a Teflon-lined autoclave of 20-mL capacity. The autoclave was sealed, transferred into a magnetic field with a strength from 1 to 12 T, and maintained at 210 °C for 24 h, followed by cooling to room temperature on standing. The obtained products were centrifuged at 4000 rpm for 10 min, washed several times with distilled water and ethanol, and finally dried in vacuum at 60 °C for 2 h.

The XRD pattern of the products obtained via this simple solvothermal route is shown in Figure 1. All of the reflections of the XRD pattern in Figure 1 can be readily indexed to a pure hexagonal phase [space group: $P3_121$ (152)] of Te with lattice constants $a = 0.4474$ nm and $c = 0.59224$ nm, compatible with the literature values of $a = 0.44579$ nm and $c = 0.5927$ nm (JCPDS 36-1452). This XRD pattern indicates that pure Te products were obtained under current conditions.

Figure 2 showed the SEM images of representative samples prepared under different reaction conditions, which clearly revealed the effect of magnetic field on the growth of 1D tellurium microstructures. Without a magnetic field, lots of Te microrods were obtained. High-magnification SEM images demonstrated that the hexagonal microrods were about 2 μm in diagonal and length between 10 and 20 μm, as shown in Figure 2a and Figure S1.[17] Obviously, the morphology changed when a high magnetic field of 12 T was applied. These microrods were about 2 μm in diameter and length from 40 to 120 μm. The length of Te microrods was much longer than that obtained without a magnetic field. The yield of these longer microrods under this condition was up to 80%.

In order to find the effect of a magnetic field on the fabrication of 1D tellurium microstructures, magnetic fields with different strength were applied to the solvothermal treatment systems. The corresponding SEM images are shown in Figure 3. When 1 T magnetic field was applied to this reaction, there were no obvious shape changes. The obtained tellurium microrods hold almost the same size and length as that shown in Figure 2a. In-

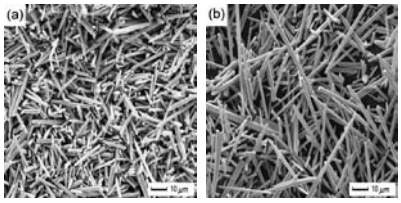

Figure 2. FESEM images of a sample prepared via a solvothermal route at 210 °C: (a) without magnetic field; (b) with a 12 T magnetic field.

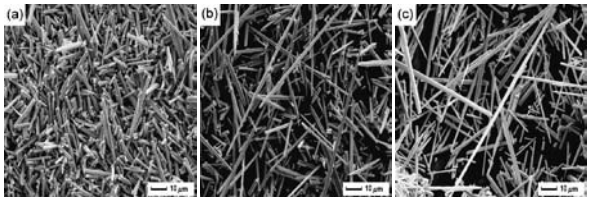

Figure 3. SEM images of samples obtained in different magnetic fields: (a) 1, (b) 4, and (c) 8 T.

creasing the strength to 4 T, some microrods with longer length could be observed. The length could be up to about 100 μm (Figure 3b). Once the strength reached 8 T, microrods with longer length could be also found, and the yield of these longer microrods was increased further, which are shown in Figure 3c. The results show that the external magnetic field could be responsible for the change of the length of Te microrods.

Based on the SEM observation, it was clearly found that the morphological evolution was dependent with the magnetic field. In order to understand the effect of the magnetic field, it was necessary to investigate the growth process of the Te microstructures under these conditions. Due to the redox potential of Te^{IV}, Na_2TeO_3 could be directly reduced by EG without adding any reduction. In the whole process of reaction, ethylene glycol served as both solvent and reducting agent.[15] The chemical reaction we employed for the fabrication of tellurium microrods may be formulated as

$$Na_2TeO_3 + 2EG \rightarrow Te + 2CH_3COONa + 3H_2O \quad (1)$$

So in the synthesis process, the tellurium proceeded directly to the trigonal phase (t-Te), which was similar to that in ref 3. These crystals would rapidly grow into rod-like crystals along the *c* axis owing to their highly anisotropic crystal structure, as can be found in Figure 2a and Figure S1. When the magnetic field was applied to the reaction system, the growth environment changed to some extent. Magnetic field has an effect on the process of nucleation and growth. It is well known that in the growth of rod-like tellurium crystals t-Te[3] severs as the nucleus. As can be observed from the above SEM images, the diameter of tellurium microrods obtained with or without a magnetic field was almost the same. It might mean that the effect of magnetic field on nucleation was insignificant. During the subsequent solvothermal process, the magnetic field affects the growth of tellurium microrods. In the previous papers,[8,16] the authors held the opinion that magnetic field affects the surface energies, so the growth along certain directions is changed. In our work, we suppose that when the reaction proceeds in a magnetic field, the crystal surface energies change to some extent and that the growth under a magnetic field is different from that without magnetic field. Especially under a higher magnetic field, the crystal surface energies change more obviously, so a much more rapid growth rate would appear, and more microrods with length from 40 to 120 μm may be observed. Microrod yield in 12 T was up to 80%.

In summary, the morphologies of tellurium crystals from a solvothermal process with or without a magnetic field have been investigated. It seems to suggest that the external high magnetic field can significantly influence the growth behavior of Te microcrystals, possibly increasing the growth rate in one direction. This method could be also applied to 1D growth of other nonmagnetic materials, and related work is under way.

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