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A Solution Low-Temperature Route to MoS_2 Fiber

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Layered semiconductor metal dichalcognides, MQ_2 (M=W, Mo; Q=S, Se), are anisotropic materials with trigonal primatic structure, formed by stacking sandwiches consisting of a layer of transition-metal atoms between two layers of sulfur or selenium atoms; these layers are held together by van der Waals forces. As a known compound for this structure, MoS_2 has numerous applications as a useful catalyst for an electrode in high-energy density batteries,[1] with hydrodesulfurization,[2] and as an intercalation host to form new materials.[3]

The carbon nanotube, which consists of singly or multiwalled graphite sheets, discovered by Iijima in 1991,[4] are at present in the focus of worldwide investigations because of their unique structural and physical properties,[5] which render applications as multifunctional nanodevices possible.[6] As compounds possessing graphite-analogue layered structures, layered semiconductor compounds MQ_2, which are able to form nanotubes or fullerene-type structures, have been extensively investigated by the Tenne group.[7] They have produced macroscopic quantities of fullerene-like nanotubules and negative-curvature polyhedra, or nested inorganic fullerene-like clusters, through high-temperature gas−solid reaction under a reducing gas atmosphere. Although they have extensively investigated the reaction mechanisms, they have not realized the control synthesis of the size, size distribution, and the shape of the product. Others have examined this process as well without realizing the ability to control the size and shape of the nanotubules or cluster.[8] Recently, Dorhout et al. synthesized fibers and tubules of MoS_2 within the pore of a porous aluminum oxide template by controlled thermal decomposition of an ammonium thiomolybdate precursor.[9] All these methods involved complex or high-temperature reaction, and the morphology cannot be easily controlled. So it is still a challenge to develop a simple, low-temperature method to synthesize the intriguing tubule and fiber of the layered semiconductor compounds.

Figure 1. TEM image of the sample prepared at room temperature.

A soft chemically synthetic method is a promising method for the synthesis of inorganic compounds with a tubular morphology. Recently, a solution method was extensively investigated to synthesize nanorods and nanotubules.[10] In the former case, CdE (E = S, Se, Te) nanorods have been fabricated in ethylenediamine. Ethylenediamine plays a very important role in the formation of the nanorods, which confirms that ethylenediamine is one powerful solvent for the preparation of one-dimensional inorganic compounds.

In this work, MoS_2 fiber has been synthesized through a low-temperature liquid route. At room temperature, the as-prepared product was composed of amorphous fibers. After annealing, the morphology of the product was kept and it crystallized. The products were characterized by several spectroscopic techniques.

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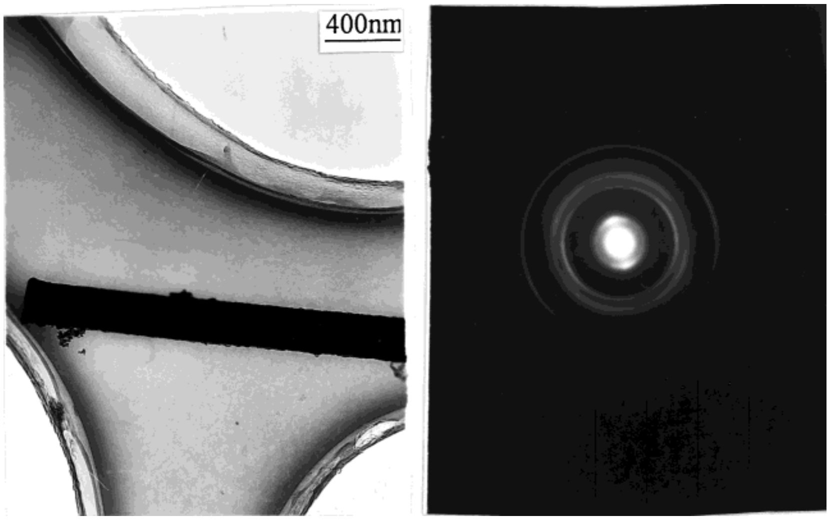

Figure 2. TEM image of the sample annealed and an electron diffraction of the fiber.

The precursor $(NH_4)_2Mo_3S_{13}$ was prepared according to the literature methods.[11] The preparation process of MoS_2 fiber was described as follows: 2 g of $(NH_4)_2Mo_3S_{13}$ was added into a 100-mL flask and then 50 mL of ethylenediamine was added into the flask. It was maintained at room temperature while stirring with a magneton stirrer for 10 h. The final solution became dark green, and the red needle-like crystal turned into black powder. The black powder was collected by filtration and characterized by infrared spectroscopy. A portion of the black powder was annealed at 400 °C under a high pure N_2 atmosphere for 3 h.

Transmission electron microscope (TEM) images were taken with a Hitachi H-800 transmission electron microscope. Figure 1 is a TEM image of a sample prepared at room temperature. It is apparent that the product prepared at room temperature was composed of fiber (Figure 1). The electron diffraction (ED) pattern shows that they are amorphous. The TEM image shown in Figure 2a is the sample after annealing. It is obvious that the morphology of the product was kept during the annealing process. A typical electron diffraction pattern of a selected region of the fiber is shown in Figure 2b, and all of the electron diffraction rings could be indexed to the pattern of $2H-MoS_2$.

X-ray diffraction (XRD) was carried out on a Japan Rigaku D/max rA rotation anode X-ray diffractometer with Ni-filtered Cu Kα radiation. The XRD pattern of the sample prepared at room temperature shows that most of the integrated intensity of the X-ray spectrum is confined to a wide peak of the amorphous material, and the (002) peak of the crystalline MoS_2 is very weak. Figure 3 shows the XRD pattern of the sample annealed; a strong (002) peak of the crystalline $2H-MoS_2$ phase predominates. The XRD pattern is consistent with the observations made by Müller[12] and indexed to a hexagonal cell with lattice parameters $a = 3.161(4)$ and $c = 12.84(6)$ Å.

The electronic states of Mo and S in the post-treatment product were determined by X-ray photoelectron spectroscopy (XPS). XPS was recorded on an ESCALAB MKII with Mg Kα as the exciting source. The XPS spectra analysis of MoS_2 fibers annealed showed (Figure 4) that there were two strong peaks at 163.20 and 230.4 eV corresponding to S(2p) and Mo(3d) binding energy, respectively. XPS showed well-defined spin-coupled Mo and S doublets at binding energies the same as those for conventional MoS_2.[13] The quantification of the peaks gives the S/Mo atomic ratio of 1.97, which is very close to the stoichiometrical MoS_2.

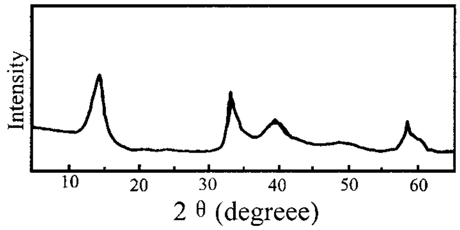

Figure 3. XRD pattern of the sample annealed.

Optical characterization of the products was performed by UV−visible absorption spectroscopy at room temperature. Ultraviolet−visible absorption spectra were collected at room temperature on a Shimadzu ultraviolet−visible absorption diode array spectrometer. The absorption spectra were shown in Figure 5. Figure 5a shows the absorption spectrum of the sample prepared at room temperature. There is no characteristic absorption of MoS_2. Figure 5b shows the absorption spectrum of the product annealed. It typically displayed a strong, broad absorption with a maximum centered at 386 nm and two weaker absorbances at 610 and 652 nm. The spectral data are similar to those of bulk MoS_2, which possesses an intense absorption in the blue region of the spectrum and weaker absorption in the red region. Our spectral data appear to be slightly shifted with respect to the data obtained by Tenne.[14] They described two peaks in the low-temperature region of the spectrum, at 616.3 and 667 nm, and a third, very broad and noisy, peak at 525 nm. The spectral signature of our fibers falls within a region bounded by bulk and nanocluster.

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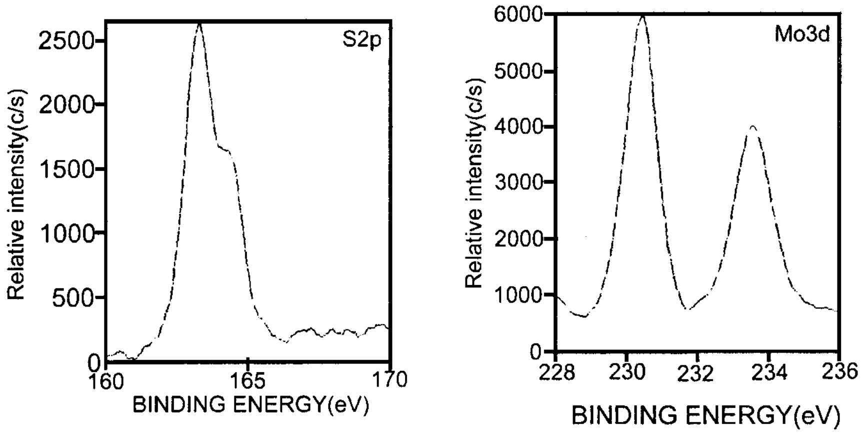

Figure 4. XPS analysis of the sample annealed.

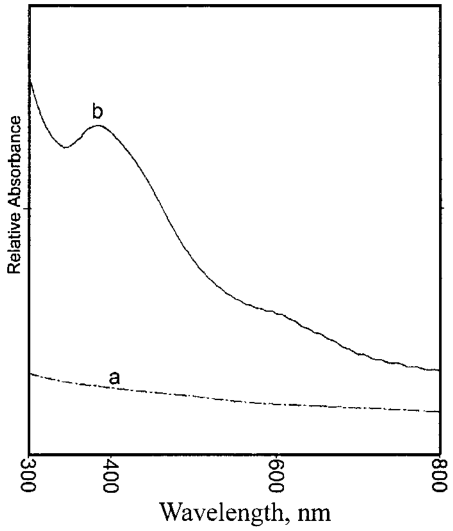

Figure 5. Optical absorption spectra of the samples: (a) prepared at room temperature; (b) annealed at 400 °C.

To investigate the influence of the solvent, the precursor $(NH_4)_2Mo_3S_{13}$ was directly annealed at the same temperatures under a N_2 atmosphere. The XRD patterns of the product displayed sharp peaks, which could be refined to the MoS_2 phase. The TEM image of the product shows that the MoS_2 product was composed of spherical particles. Therefore, enthylenediamine is the key factor for synthesizing MoS_2 fiber. On the basis of the above results, we proposed the following mechanism for the formation of the fiber. The crystal of $(NH_4)_2[Mo_3S_{13}]$ has been found to contain crystal water. The crystal structure shows the cell of $(NH_4)_2[Mo_3S_{13}]$ containing zig-zag chains of H_2O molecules and NH_4^+ cation, which are approximately perpendicular to the mean plane through the $[Mo_3S_{13}]^{2-}$ anion.[15] When the needlelike precursor was dissolved in enthylenediamine, enthylenediamine gradually took the place of H_2O molecules and NH_4^+ cation in the precursor and connected the anions to form a fiber structure. The FT-IR spectrum showed that there existed enthylenediamine in the product obtained at room temperature. During the process of annealing, enthylenediamine and the superfluous sulfur were removed and MoS_2 fiber was obtained. While the precursor was directly annealed, without enthylenediamine to connect the anions, the zig-zag chain was destroyed with loss of the water and NH_4^+ cation during the annealing process. A spherical particle was formed.

In conclusion, this work describes a simple solution method to prepare MoS_2 fiber. MoS_2 fiber had been fabricated through a solution room-temperature route. And the products were investigated by TEM, XRD, XPS, and UV−vis techniques. A mechanism of the formation of the fiber was proposed. This method may be used to fabricate other one-dimensional inorganic compounds.

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