Preparation and Characterization of Tungsten-substituted Molybdenum Disulfide Nanorods

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The tungsten-substituted molybdenum disulfide nanorods were synthesized through a pyrolysis process. The rod-shaped trisulfide precursor was prepared using a reversed micelle based method. The tungsten-substituted molybdenum disulfide nanorods were obtained by thermal decomposition of the as-prepared precursor. Energy dispersive spectroscopy identified that the chemical composition of the final product was $Mo_{0.95}W_{0.05}S_2$. The produced nanorods were further characterized with X-ray power diffraction and transmission electron microscopy.

Since the discovery of carbon nanotube in 1991,[1] 1-D nanostructured materials such as nanotubes, nanorods, nanowires, and nanofibers have attracted wide interests because of their unique physical and chemical properties as well as their potential applications in the fields of optics, electricity, magnetics, and nanoelectronics, etc. Various types of 1-D-nanostructured materials including metals, alloys, inorganic oxides, metal chalcogendies, inorganic salts, and polymers have been reported. Recently, the synthesis of 1-D-layered sulfides has attracted special attentions. MS_2 ($M = Mo, W$) nanotubes have been synthesized by different methods.[2–7] Besides developing new synthesis strategies, there also have been attempts on substituting either the metal atoms or the chalcogens in 1-D-nanostructured metal chalcogendies by other elements in order to alter their structure, electronic behaviors and other properties.[8–10] Previous study has showed that the substitution of W for Mo in MoS_2 changed its semiconducting behavior and thermal stability.[11] The 1-D-nanostructured $Mo_{1-x}W_xS_2$ is expected to have some other different properties compared with MoS_2 and WS_2. $Mo_{1-x}W_xS_2$ nanotubes have already been successfully synthesized by pyrolyzing ammonium thiometallates in a H_2 atmosphere.[12] However, according to our best knowledge, so far there are neither reports on the method of preparing substituted metal disulfide nanorods by directly pyrolyzing the corresponding trisulfides nor reports on tungsten-substitued molybdenum disulfides nanorods.

In this letter we report the synthesis of $Mo_{1-x}W_xS_2$ nanorods using a pyrolysis method. The rod-shaped decomposition precursor $Mo_{1-x}W_xS_3$ was synthesized in reversed micelles. The reversed micelles serve as a soft template in the $Mo_{1-x}W_xS_3$ nanorods formation course. A typical experimental procedure is as follows. First, Na_2WO_4 and Na_2MoO_4 were dissolved in distilled water with a molar ratio of 17:1. The basic reversed micelle was prepared by adding appropriate amount of the above aqueous solution of inorganic salts to *n*-octane containing Gemini surfactant (12-3-12, $2Br^-$) and cosurfactant *n*-butanol. Transparent stable reversed micelles were obtained and then were put into a three-neck flask. H_2S gas was slowly bubbled through the reversed micelles from the bottom of the flask. The H_2S flow was adjusted by carefully controlling H_2S production rate. During this course the reversed micelle system was moderately stirred. The off-gas was introduced to $ZnSO_4$ solution to remove unreacted H_2S before vented into ambient atmosphere. Then diluted hydrochloric acid was gradually added to the mixtures at room temperature. A color change was observed firstly to yellow, subsequently to red, and finally to black. After aged for 6 h, the mixtures were filtered and repeatedly washed with acetone and deionized water to remove the surfactant and by-products. The final trisulfide compounds were collected and dried in a vacuum at 60 °C for 3 h.

The as-prepared trisulfides were transferred into a quartz boat. This quartz boat was put in a 15-mm inner diameter quartz tube placed in the central zone of a tubular furnace. The temperature of the furnace was set at 1173 K. The trisulfides were pyrolyzed at this temperature for 2 h. During this course inert gas (high purity N_2, 99.999%) was passed through the quartz tube to prevent the trisulfides from oxidation. The final product is gray, similar to MoS_2.

X-ray diffraction (XRD) pattern was recorded on a X'pert MPD Philips diffractometer (Cu Kα radiation, $\lambda = 0.154$ nm). The morphologies of the decomposition precursor and the final product were observed with a JEM-200CX transmission electron microscopy (TEM). Elemental analysis was performed on an energy dispersive spectroscopy (EDS) system equipped on the TEM.

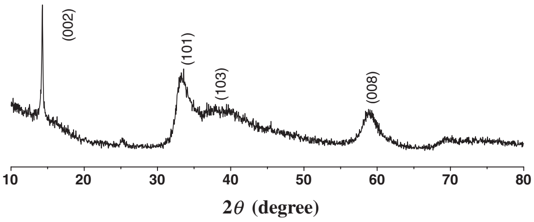

Figure 1. XRD pattern for the final products.

The XRD pattern of the final products in the 2θ range of 10–80° is shown in Figure 1. The characteristic peaks in the diffraction diagram were indexed and the corresponding values of the inter-planar distance *d* were calculated and compared with the standard *d* values of 2H-MoS_2 (JCPDS File No. 24-513). Despite broadened, the diffraction pattern and the corresponding *d* values resemble those of 2H-MoS_2. It means that even upon tungsten substitution in MoS_2, the arrangements of Mo and S atoms remained basically the same as in pure host 2H-MoS_2. This is in good agreement with the XRD research of bulk tungsten-substituted molybdenum disulfide reported in the literature.[11] It is also evident from the diffractogram that the 002 peak is of maximum intensity while the intensities of other peaks such as 101, 103, and 008 reflections are relatively weak, indicating thereby a strong orientation with stacking of the planes along the *c* axis. Figure 2a is a typical TEM image of the precursor $Mo_{1-x}W_xS_3$ nanorods prepared in reversed micelles. Figure 2b is a general overview of a low-magnification TEM image of the as-prepared

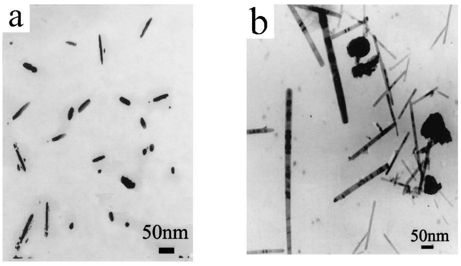

Figure 2. TEM image of (a) the precursor $Mo_{1-x}W_xS_3$ nanorods prepared in reversed micelles and (b) the $Mo_{1-x}W_xS_2$ nanorods.

final products. It reveals that most of the products are straight nanorods with the diameter around 20–50 nm. However, the length of the nanorods is not uniform. The length of majority nanorods is about a few hundred nm while the maximal length could exceed 1 μ. Further observation finds that some nanorods have perfect end-cap, similar to those commonly found in carbon nanotubes and $Mo_{1-x}W_xS_2$ nanotubes. Except nanorods, there are only trivial tube-like and fullerene-like structures. Layer fringes are visible along the axis of the nanorods on close inspection.

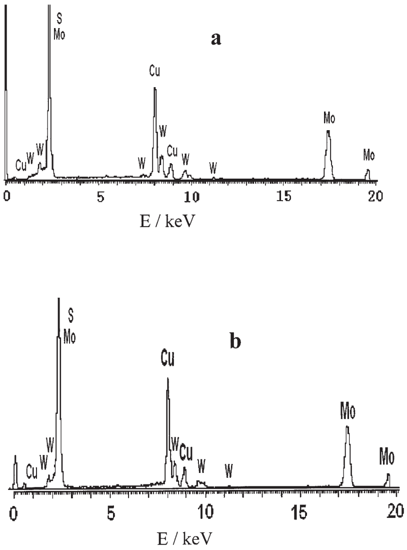

Figure 3. EDS's of (a) $Mo_{1-x}W_xS_3$ nanorods and (b) $Mo_{1-x}W_xS_2$ nanorods.

The EDS's of the precursor and the product nanorods are shown in Figure 3. According to the EDS analysis the chemical compositions of the precursor and the final product are $Mo_{0.95}W_{0.05}S_3$ and $Mo_{0.95}W_{0.05}S_2$, respectively.

On the basis of the reaction mechanism proposed by Manashi Nath[12] and our experience on preparing molybdenum and tungsten compounds, the reaction involved in the formation of disulfide is believed to be

$$(1-x)Na_2MoO_3 + x\ Na_2WO_3 + H_2S \rightarrow Na_2Mo_{1-x}W_xS_4 + H_2O$$

$$Na_2Mo_{1-x}W_xS_4 + 2HCl \rightarrow Mo_{1-x}W_xS_3 + 2NaCl + H_2S \uparrow$$

$$\text{(in reversed micelles)}$$

$$Mo_{1-x}W_xS_3 \rightarrow Mo_{1-x}W_xS_2 + S$$

In order to find the influence of precursor morphology on the morphology of final product, $Mo_{1-x}W_xS_3$ with different morphologies were prepared by different methods. Preliminary studies found that if the decomposed precursor $Mo_{1-x}W_xS_3$ was prepared just in solution, without using reversed micelles to control its morphology, no rod-like but only bulk $Mo_{1-x}W_xS_2$ could be obtained. Figure 4 shows the typical morphology of $Mo_{1-x}W_xS_2$ prepared without using reversed micelles to control its precursor shape. By varying the reaction temperature, surfactant concentration, salt concentration, and mole ratio of water to surfactant (ω_0), we also prepared nano-$Mo_{1-x}W_xS_3$ precursors with different shapes in reversed micelles. It was found the $Mo_{1-x}W_xS_2$ nanorods were more likely produced when the precursor had rod-like shape. It suggested that the precursor shape would greatly influence the morphology of final product for this preparation method. Probably it is because that the conversion from $Mo_{1-x}W_xS_3$ to $Mo_{1-x}W_xS_2$ is a template-directed process in this particular case. In addition, it was found that the pyrolysis conditions also have influence on the morphology of final product. For instance, the calefactive rate should be kept in less than 5 K per minute in the temperature-increasing course to ensure a controlled growth of nanorods. Further work is currently in progress.

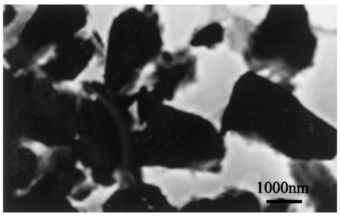

Figure 4. A typical morphology of $Mo_{1-x}W_xS_2$ prepared without using reverse micelles to control its precursor shape.

In summary, we have successfully prepared tungsten-substituted molybdenum disulfide nanorods by thermal decomposing the corresponding rod-like trisulfide precursor in N_2 atmosphere. The XRD and EDS analyses validate the product $Mo_{1-x}W_xS_2$ as well as the feasibility of this synthesis route. The work may enlighten a potential route for mass production of 1-D-structured substituted metal chalcogenides.

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