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Preparation and Characterization of Molybdenum Particles by Reducing MoO_3 Nano-fibers

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One-dimensional nanostructures of orthorhombic molybdenum trioxide have been synthesized in the forms of fibers under hydrothermal conditions at 170–180°C. It has been found that the dimensions of the fibers are about 50 nm in thickness, 100–200 nm in width and a few tens of micrometers in length under our experimental settings. Using H_2 stream, the MoO_3 fibers prepared can be converted completely to Mo metal powders at 600°C. The original fiber-like morphology is not well-retained, but in some special cases, fiber-like morphology can be partial retained, although the aspect ratio of the oxide template is reduced upon the reduction treatment.

Keywords metal Mo powder, MoO_3, nano-fibers, reduction

New methods of making new or existing inorganic materials are always interesting and challenging for materials scientists. Development of one-dimensional (1D) materials has become a focal area in nanostructured materials research, owing to their special characteristics which differ from those of respective bulk crystals. These highly anisotropic 1D materials include elemental carbon, metals, semiconductor, alloys, sulfides, oxides, hydroxides, and so forth. Among the important layered transition metal oxides and chalcogenides have been extensively investigated.[1–5]

MoO_3 and its derivatives are widely used in industry as catalysts, display devices, sensors, smart windows, lubricants, battery electrodes. In particular, MoO_3 has been prepared into the forms of carbon-metal-oxide nanocomposites, nanotubes, and nanorods using carbon nanotubes (CNTs) as a host material or template. The MoO_3 nanofibers obtained with this novel method are up to 15 μm long with their diameters ranging from 50 to 150 nm.[6]

An efficient method to produce nanoscopic molybdenum oxide fibers was reported. The procedure is based on the intercalation of primary amines into the layered structure of molybdic acid and subsequent transformation of the lamellar molybdenum oxide–amine intermediate into the fibrous product.[7]

A simple hydrothermal method for preparation of nanostructured α-MoO_3 with morphology control on either ribbons or rods at only 140–200°C. 2H-MoS_2 nanorods indeed can be prepared from the resultant MoO_3 nanorods through sulfidation conversion.[8] Molybdenum trioxide nanobelts and microballs were prepared by oxidization of molybdenum metal in an ambient atmosphere,[9] but nano Mo metal powders prepared from MoO_3 nanorods or nanofibers have not been reported in the literatures. Here, we report the process of MoO_3 nanofiber prepared by hydrothermal method, and the nano Mo metal powder indeed can be reduced from the resultant MoO_3 nanofibers through reduction conversion by using H_2 stream.

EXPERIMENTAL

Materials Preparation

The α-MoO_3 nanofibers were synthesized by a hydrothermal route. Ammonium heptamolybdate tetrahydrate (AHM; $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$) and nitric acid were the two starting reagents. A saturated solution of precursor compound AHM was prepared at room temperature. For each run of experiment, 30.0 ml of the saturated solution was diluted with deionized water (30.0 ml) and then further acidified using the 2.2M nitric acid to a total of 70–85.0 ml in volume. The resultant solution was transparent and transferred to a Teflon-lined stainless steel autoclave and heated at 170–180°C for 40 h. The product precipitate was filtered and rinsed with deionized water, followed by drying at 62°C for 5 h. The dried sample was fibrous and pale yellowish.

The above as-grownα-MoO_3 crystals were further used as metal oxide precursors for reduction investigation. The

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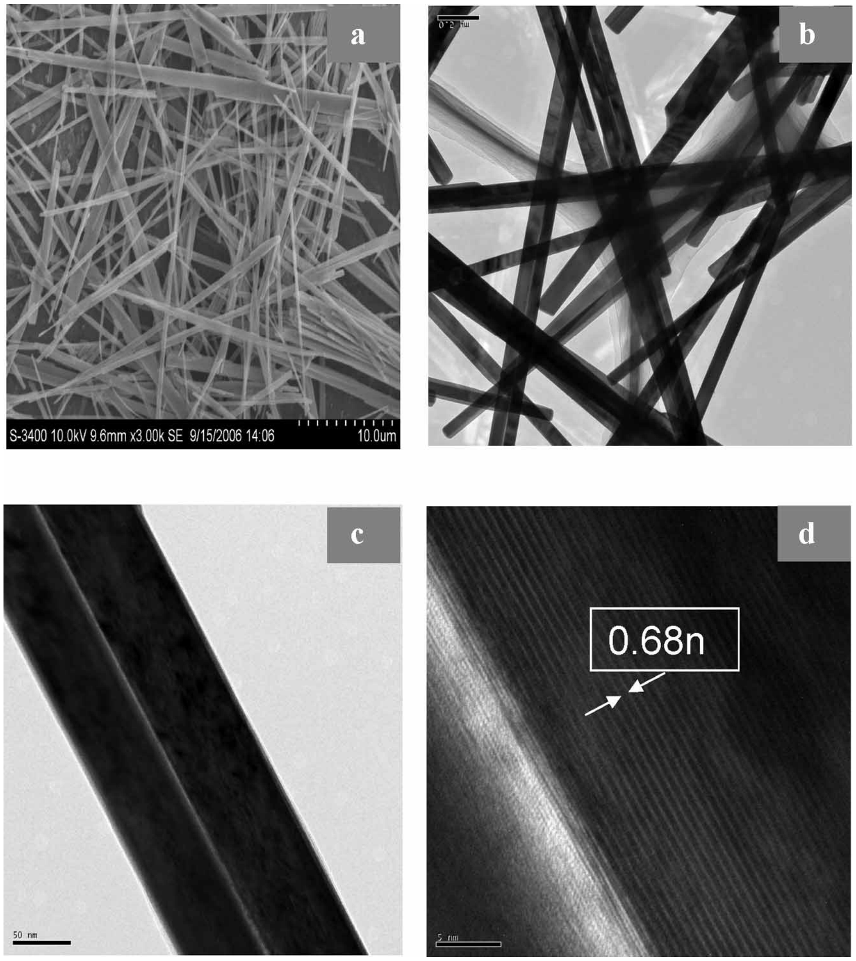

FIG. 1. The SEM and HRTEM of MoO_3 nanofibers: (a) SEM 3000X; (b) HERTEM 50000X; (c) 200000X; and (d) 2000000X.

reactions were carried out in a tubular quartz reactor at 400–600°C using H_2 stream under normal atmospheric pressure.

Materials Characterization

Crystallographic information of samples including reduced ones was investigated with X-ray diffraction (XRD; Shimadzu XRD-6000, Cu $K\alpha$, $\lambda = 1.5406$ Å). Crystal sizes and the morphology of crystal samples was examined before and after the reduction reactions with scanning electron microscopy (SEM, JSM-5600LV, 15 kV).

High-resolution analytical transmission electron microscopy (TEM, JEM-2010, 200 kV) was also used to examine crystalline α-MoO_3 and its reduced products. The specimens for

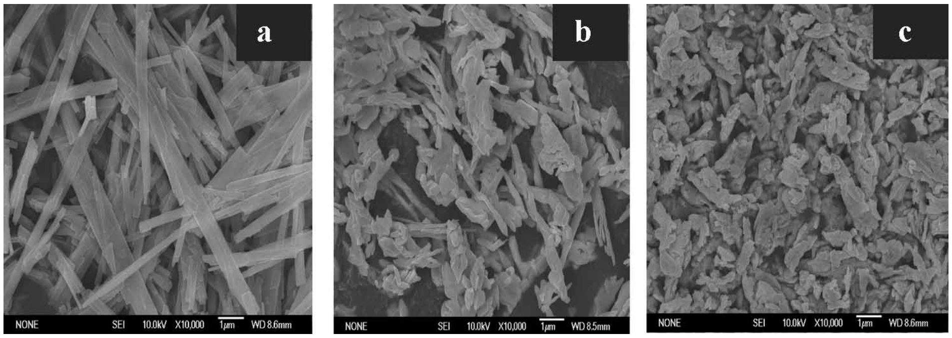

FIG. 2. SEM of MoO_3 nanofibers reduced at different temperatures: (a) Before reduced; (b) 530°C for 1 h; and (c) 600°C for 1 h.

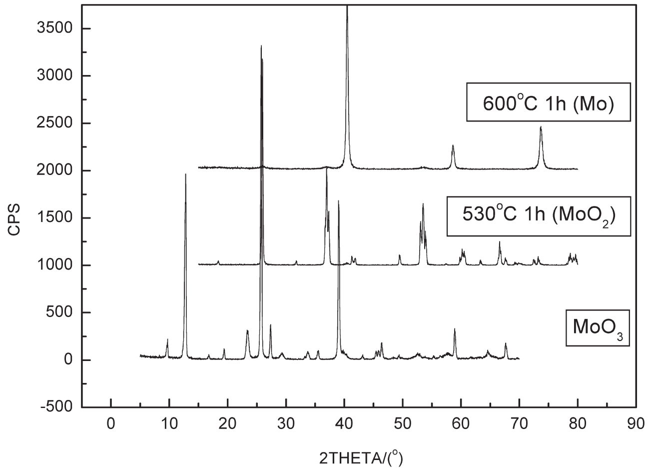

FIG. 3. XRD patterns of MoO_3 nanofibers reduced at different temperatures.

TEM imaging study were prepared by suspending solid samples in acetone.

RESULTS AND DISCUSSION

The morphology investigations were characterized with SEM and HRTEM. A SEM image of a typical product (Figure 1a) showed the sample as an entirely fiber-like structure with a width of about 50 to 200 nm, and a length of about a few tens microns. Nearly rectangle-like cross section of the nanofibers could be seen from the images. HRTEM image of an individual nanofiber (Figures 1b–d) provided further insight into the structure of these products. HRTEM images recorded perpendicular to the growth axis of the single nanofibers could be attributed to the [010] of orthorhombic MoO_3, and suggested that the nanofibers grew along the [001] direction.

X-ray diffraction showed that samples consisted only of strongly oriented orthorhombic α-MoO_3 ($a = 1.385$ nm, $b = 0.3696$ nm, $c = 0.3966$ nm, JCPDS 89–7112). It can be observed in Figure 3. All the strong diffraction peaks correspond to (h00) reflections.

The crystal growth process of MoO_3 under hydrothermal conditions could be explained according to literatures.[8–10]

The MoO_3 nanofibers were reduced at different temperatures under H_2 stream atmosphere. From Figure 3, the XRD patterns indicated that MoO_3 nano fibers could be reduced as MoO_2 at 530°C for 1 hour, the materials had a pure phase of MoO_2. That means the MoO_3 nanofibers have been reduced as MoO_2 completely at 530°C. Corresponding to Figure 2a and Figure 2b, the morphology of the MoO_3 nanofibers have been changed, the fibers-like morphology was partial retained.

Figure 3c showed that the MoO_3 nanofibers had been reduced as Mo powders completely when the reduced temperature was increased to 600°C, corresponding Figure 2c, the morphology of Mo powders is not fibers-like, most of metal Mo powders are irregular shape, neither the ball-like, nor fibers-like.

But in some cases, the nanofiber-like shape of MoO_3 was retained, and the result could be seen in Figure 4. From Figure 4b, it could be found that needle-like metal Mo powder was formed. The reason of forming needle-like metal Mo powder could be explained that the MoO_3 nanofiber was restricted in a free space, with no other MoO_3 nanofiber contact with each other, although orthorhombic crystal structure of MoO_3 changed as FCC crystal structure of metal Mo, no other metal Mo particles to combine with, so the nanofibers-like shape was retained.

According to the reason mentioned above, we using small bulk (about 2–3 mm) MoO_3 nanofiber as raw materials instead of the MoO_3 nanofibers powders. The small bulk MoO_3 was reduced at 600°C for 1 h, XRD indicated that MoO_3 had been completely changed as metal Mo powder. SEM results are shown in Figure 5. Much more needle-like metal Mo powders were formed. It means nanofiber-like MoO_3 could be reduced as needle-like metal Mo powder in some special cases.

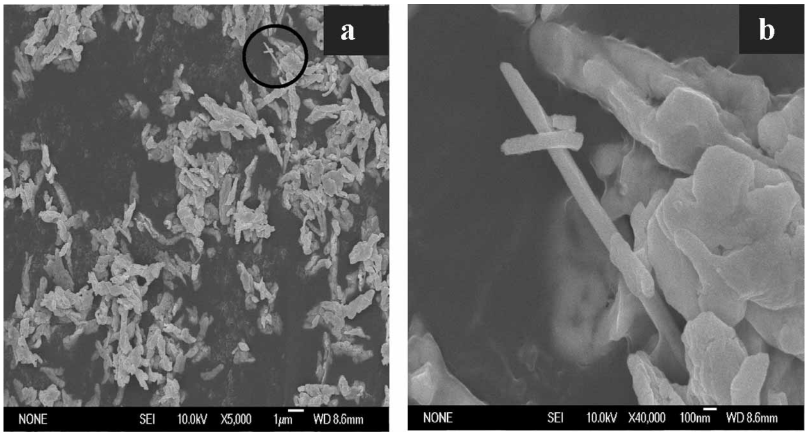

FIG. 4. SEM of Mo powder reduced from MoO_3 nanofibers: (a) 5000X; and (b) amplifying (a).

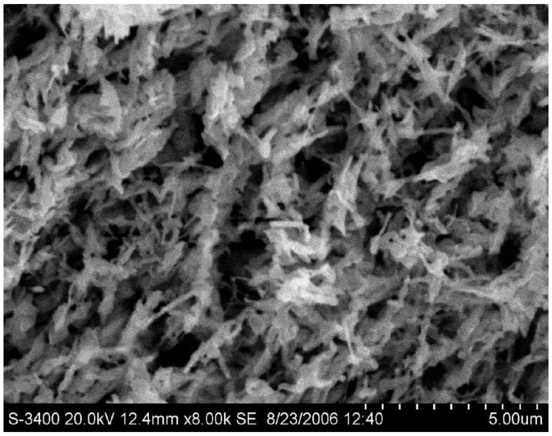

FIG. 5. SEM of Mo powders with partial needle like morphology.

CONCLUSION

One-dimensional nanostructures of orthorhombic molybdenum trioxide have been synthesized in the forms of fibers under hydrothermal conditions. The dimensions of the fibers are about 50 nm in thickness, 100–200 nm in width and a few tenths of micrometers in length under our experimental settings.

The MoO_3 fibers prepared can be converted completely to Mo metal powders at 600°C by ussing H_2 stream. The original fiber-like morphology is not well-retained, but in some special cases, fiber-like morphology can be partial retained, although the aspect ratio of the oxide template is reduced upon the reduction treatment.

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