Fabrication of Single-crystalline MoO_3 Nanobelts by Using Carbons

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Single-crystalline MoO_3 nanobelts were formed by calcination of physical mixtures of carbon nanofibers and $H_3(PMo_{12}O_{40})$ under air at 873 K. In contrast, single-crystalline MoO_3 with long wire structure were formed by calcination of physical mixtures of carbon nanofibers and $H_4[Si(Mo_3O_{10})_4]$.

One-dimensional nanostructured materials such as nanowires and nanotubes are drawing attention due to their specific physical, electrical, and chemical properties.[1] Recently, metal-oxide nanobelts (ZnO, SnO_2, Ga_2O_3, In_2O_3, and CdO) were synthesized by evaporation of the corresponding metal-oxide powder at high temperatures.[2] The shape of nanobelt is long plate-like crystalline as the name implies. Some applications of metal-oxide nanobelts have been proposed, for example, SnO_2 nanobelts can be utilized as photochemical sensor for NO_2 at room temperature.[3] In this study, MoO_3 nanobelts were prepared through the simple method. MoO_3 nanobelts can be synthesized by calcination of $H_3(PMo_{12}O_{40})$ and carbons.

Carbon nanofibers (home-made), graphite (from Wako Pure Chemical Industries), and graphitized carbon fibers (from Asahi Kasei Corporation) were used as carbonaceous materials for the synthesis of MoO_3 nanobelts. Carbon nanofibers are denoted as CNF, hereafter. CNF were prepared by methane decomposition over Ni/SiO_2 catalysts at 823 K.[4] $H_3(PMo_{12}O_{40})$ was used as a source of MoO_3. Carbons and $H_3(PMo_{12}O_{40})$ were physically mixed by an agate mortar. The weight ratio of $H_3(PMo_{12}O_{40})$ to carbon was adjusted to 1:1. The physical mixtures in alumina crucible were calcined under air at 873 K for 5 h, to form pale yellow powder. According to XRD patterns of calcined samples (see Supporting Information), all the diffraction lines were assignable to orthorhombic molybdenum trioxide (α-MoO_3). No diffraction line due to carbons or $H_3(PMo_{12}O_{40})$ was observed. Figure 1 shows SEM and TEM images of MoO_3 formed by calcination of $H_3(PMo_{12}O_{40})$ and CNF. SEM image (a) indicated that formed MoO_3 was of plate-like structure. The length of MoO_3 was several micrometers, and their width was 200–400 nm. Most of MoO_3 observed in SEM images were of plate-like structures. TEM image (b) clearly showed that MoO_3 had plate-like structure (the thickness is ca. 50 nm). Results in Figure 1 suggested that MoO_3 nanobelts were formed by calcination of $H_3(PMo_{12}O_{40})$ and CNF. According to EDX analysis, MoO_3 nanobelts were consisted of Mo and O. P contained in $H_3(PMo_{12}O_{40})$ would be removed as H_3PO_4 during calcination ($H_3(PMo_{12}O_{40}) \rightarrow 12MoO_3 + H_3PO_4$). Electron diffraction pattern of MoO_3 nanobelts indicated the formation of single-crystalline MoO_3 (the inset of Figure 1b). In addition, similar MoO_3 nanobelts were formed by using graphite and graphitized carbon fibers instead of CNF. In previous studies, MoO_3 nanobelts have been fabricated on a mirror-polished silicon (100) wafer through the heat treatment of a Mo foil in air at 1123 K,[5] or by the hydrothermal reaction of Na_2MoO_4 with perchloric acid in a stainless autoclave at 413 K for 24 h, followed by the filtration, washing and drying.[6] Compared to these previous methods, our fabrication method of MoO_3 nanobelts is much simpler. MoO_3 nanobelts could be easily formed with a high yield through our method.

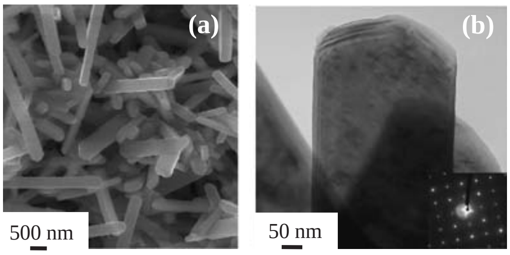

Figure 1. (a) is SEM, and (b) is TEM images of MoO_3 nanobelts.

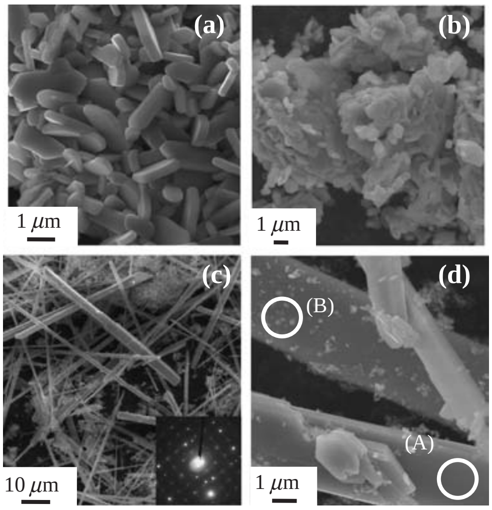

Figure 2. (a) SEM image of MoO_3 formed by the calcination of $H_3(PMo_{12}O_{40})$. (b) SEM image of MoO_3 formed by the calcination of the mixture of $(NH_4)_6Mo_7O_{24}$ and CNF. (c) and (d) SEM images of MoO_3 formed by the calcination of the mixture of $H_4[Si(Mo_3O_{10})_4]$ and CNF.

In order to confirm the role of carbons on the preparation of MoO_3 nanobelts, MoO_3 was synthesized by calcination of only $H_3(PMo_{12}O_{40})$ at 873 K for 5 h. Figure 2a shows SEM image of MoO_3 thus formed. As shown in this image, plate-like MoO_3 with a low aspect ratio (length, $<2\,\mu m$; width, ca. $1\,\mu m$; and thickness, 300–500 nm) was formed. This result strongly suggests that carbons are indispensable for preparing MoO_3 nanobelts. Subsequently, the effect of MoO_3 precursors on the shapes of formed MoO_3 was examined. Figure 2b shows SEM image of MoO_3 formed by calcination of a physical mixture of $(NH_4)_6Mo_7O_{24}$ and CNF. Obviously, SEM image (b) indicated the formation of a large block of MoO_3, that is, MoO_3 nanobelts were not formed. Therefore, it is considered that the kind of MoO_3 precursors affects the shape of MoO_3 formed by the calcination with carbons. Figures 2c and 2d show SEM images of MoO_3 formed by calcination of $H_4[Si(Mo_3O_{10})_4]$ and CNF. SEM image (c) indicated the formation of MoO_3 with long wire structure (the length was several tens micrometers). Electron difffraciton pattern shown in the inset of Figure 2c suggested that formed MoO_3 wires were composed of single-crystalline. SEM image (d) showed that small particles were present on some MoO_3 wires. According to EDX analysis, long wires without particles (for example, white circle (A) in SEM image (d)) were consisted of Mo and O. In contrast, EDX analysis of wires with a lot of particles (for example, white circle (B) in SEM image (d)) showed the presence of Mo, Si, and O, indicating that Si atoms in $H_4[Si(Mo_3O_{16})_4]$ would be present as SiO_2 particles on MoO_3 wires. The results in Figures 1 and 2 indicate that the shapes of formed MoO_3 are strongly dependent on the kinds of starting materials.

Subsequently, in order to investigate the growth process of MoO_3 nanobelts, further experiments were performed as follows. A physical mixture (50 mg) of CNF and $H_3(PMo_{12}O_{40})$ was put in a conventional gas-flow system at atmospheric pressure, and mixed gases of O_2 and He (flow rate of $O_2 = 20\,mL\,min^{-1}$, flow rate of He $= 80\,mL\,min^{-1}$) were passed over the physical mixtures. We considered that this oxidation condition was almost the same as the condition of calcination under air, because partial pressure of O_2 was the same as that of air and flow rate of mixed gases was high enough. The temperature at the reactor was increased linearly with time to 873 K at a rate of $5.5\,K\,min^{-1}$. The reactor was rapidly cooled to room temperature once the temperature at the reactor reached to 873 K. On the basis of the change in weight of the samples, ca. 40% of CNF were estimated to be oxidized into CO_2 and CO, indicating that CNF were not removed completely through the oxidation treatment. Figure 3 shows SEM images of the mixture of $H_3(PMo_{12}O_{40})$ and CNF before and after the oxidation treatment. SEM image (a) showed that $H_3(PMo_{12}O_{40})$ and CNF seemed to be well mixed before the oxidation. Bent CNF of 40–100 nm in diameter and large particle of $H_3(PMo_{12}O_{40})$ were observed. SEM image (b) showed that several MoO_3 nanobelts were formed from a block. The XRD pattern of the samples after oxidation indicated the presence of α-MoO_3 and carbons. It was reported that $H_3(PMo_{12}O_{40})$ was decomposed into MoO_3 at 623 K.[7] Therefore, in this case, $H_3(PMo_{12}O_{40})$ must be transformed into α-MoO_3 when the temperature at the reactor reached to 873 K. In addition, MoO_3 need to be liquefied during the formation of nanobelts, because it is difficult to grow long nanobelts from the solid. However, the melting point of MoO_3 (1068 K) is higher than the oxidation temperature (873 K). By the way, some one-dimensional materials have been prepared by using carbons. In these studies, carbons were proposed to work as reductants to form precursors with low melting point. For example, Ga_2O_3 nanowires were fabricated by heat treatment of Ga_2O_3 powder with carbon nanotubes at 1373 K.[8] Ga_2O_3 powder was reduced into Ga_2O and Ga by carbon nanotubes. Ga_2O and Ga vapors were carried to the outlet of reactor on Ar stream, and grew as nanowires on the basis of vapor–solid mechanism. Generally, nano-scale materials are deposited at the exit of reactor when they grow based on vapor–solid mechanism. However, in the present case, MoO_3 nanobelt was formed in alumina crucible put at the center of reactor. Therefore, we considered that MoO_3 nanobelt did not be formed according to vapor–solid mechanism.

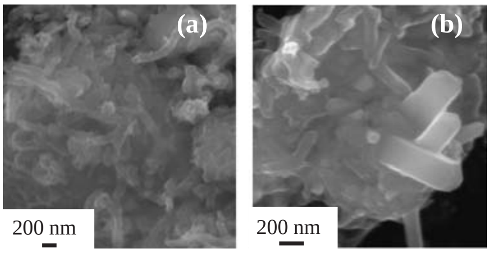

Figure 3. SEM images of the mixture of $H_3(PMo_{12}O_{40})$ and CNF (a) before and (b) after the oxidation with oxygen.

The possible role of carbons is the additional heat source, because the oxidation of carbons with oxygen is an exothermal reaction. If the additional heat was supplied during the preparation of MoO_3 nanobelts, MoO_3 was liquefied. The liquefied MoO_3 would grow as MoO_3 nanobelts on the basis of melt growth mechanism. If MoO_3 nanobelts grow according to above mechanism, MoO_3 nanobelts should be formed by the calcination of MoO_3 and CNF. However, MoO_3 nanobelts were not formed by the calcination of physical mixture of MoO_3 and CNF at 873 K for 5 h. Therefore, it is considered that $H_3(PMo_{12}O_{40})$ is indispensable for the formation of MoO_3 nanobelts. However, the detailed role of $H_3(PMo_{12}O_{40})$ cannot be explained at the present stage.

In summary, single-crystalline MoO_3 nanobelts were formed by calcination of a physical mixture of carbons and $H_3(PMo_{12}O_{40})$ at 873 K. The presence of carbons and $H_3(PMo_{12}O_{40})$ were indispensable for the fabrication of MoO_3 nanobelts.

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