Structural transformation of MoO$_3$ nanobelts into MoS$_2$ nanotubes

Francis Leonard Deepak · Alvaro Mayoral · Miguel Jose Yacaman

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Abstract The structural transformation of MoO$_3$ nanobelts into MoS$_2$ nanotubes using a simple sulfur source has been reported. This transformation has been extensively investigated using electron microscopic and spectroscopic techniques including scanning electron microscopy (SEM), transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), electron diffraction (ED), and energy-dispersive X-ray analysis (SEM-EDAX and TEM-EDX). The method described in this report will serve as a generic route for the transformation of other oxide nanostructures into the chalcogenide nanostructures.

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1 Introduction

One-dimensional nanostructures, such as nanotubes, nanowires, and nanobelts, constitute an important and outstanding set of nanomaterials with new emerging applications [1, 2]. These nanomaterials can be prepared by a variety of low temperature routes including solvothermal and hydrothermal methods as well as by high-temperature synthesis, such as physical vapor deposition, thermal evaporation, and laser ablation. Various nanomaterials of transition metal oxides, sulfides, nitrides, and carbides have been suitably prepared for various applications by these methods [3–7]. Of the various afore mentioned materials MoO$_3$ is particularly attractive among the transition-metal oxides due to its unusual chemistry produced by the multiple valence states. There are two basic polytypes of MoO$_3$. The first one, orthorhombic MoO$_3$ (α-type), is a thermodynamically stable phase, and the second one, metastable monoclinic MoO$_3$ (β-type), has a ReO$_3$-type structure. The most important structure characteristic of α-MoO$_3$ is its structural anisotropy where highly asymmetrical MoO$_6$ octahedra are interconnected with their edges along [001] direction and interlinked with their corners along [100], resulting in the so-called double-layer planar structure. An alternate stack of these double-layered sheets along [010] will lead to the formation of α-MoO$_3$, where van der Waals interactions are the major binding means among the piled sheets. Nanostructured molybdenum oxide with high activity can be used in a wide variety of applications, such as cathodes in rechargeable batteries, field-emission devices, solid lubricants, superconductors, thermoelectric materials, and electrochromic devices [8–10]. In contrast to the structure of MoO$_3$, MoS$_2$ is a quasi-two-dimensional (2D) compound. Atoms within a layer are bound by strong covalent forces, while individual layers are held together by van der Waals (vdW) interactions. The stacking sequence of the layers can lead to the formation of either a hexagonal polymorph with two layers in the unit cell (2H), rhombohedral with three layers (3R), or trigonal with one layer (1T).

We have been able to successfully synthesize MoO$_3$ nanobelts by a simple thermal evaporation process and have transformed them into MoS$_2$ nanotubes using a sulfur source, namely thiourea. Thus in the present report thiourea serves as the sulfur source wherein an in-situ reduction-sulfidization environment is generated and facilitated the
transformation of the MoO$_3$ nanobelts into the MoS$_2$ nanotubes. The entire process is extremely facile and large quantities of the desired MoS$_2$ nanotubes can be easily obtained. The method employed in the present case will serve to address various important applications of MoS$_2$ nanotubes, like their use in field emission, hydrogen storage, and catalysis [5–7]. Furthermore this general route will enable transformation of a variety of nanomaterials into well-defined nanostructures for various useful applications.

2 Materials and methods

2.1 Synthesis of the MoO$_3$ nanobelts by thermal evaporation

The synthesis of the MoO$_3$ nanobelts was carried out as follows: About 0.6 g of MoO$_3$ (mpt = 795°C) was taken in an alumina boat. This boat was placed in an alumina tube at the heating zone of the horizontal furnace and heated to 1000°C in flowing N$_2$ (Flow Rate = 150–200 cc/min) (Fig. 1a). Previously cleaned silicon substrates were placed at regular intervals in the outlet region of the alumina tube to collect the as-deposited product obtained during the course of the reaction. The reaction was carried out for 1 h after which it was gradually cooled down to room temperature in flowing N$_2$. At the end of the reaction the grey colored powder was obtained (MoS$_2$ nanotubes) and collected from the Si substrates was used for further analysis.

2.2 Conversion of the MoO$_3$ nanobelts into MoS$_2$ nanotubes

The synthesis of the MoS$_2$ nanotubes was carried out as follows: The substrates containing the MoO$_3$ nanobelts were placed at the hot zone of the furnace and 1 g of thiourea (CS$_2$N$_2$H$_4$, mpt = 170–176°C) taken in an alumina boat was placed at the upstream of the furnace and heated to 1000°C in flowing N$_2$ (Flow Rate = 100–150 cc/min) (Fig. 1b). The reaction was carried out for 1 h after which it was gradually cooled down to room temperature in flowing N$_2$. At the end of the reaction the grey colored powder was obtained (MoS$_2$ nanotubes) and collected from the Si substrates was used for further analysis.

2.3 Characterization

Scanning electron microscopy (SEM) was performed in a FEG Hitachi S-5500 ultrahigh-resolution electron microscope (0.4 nm at 30 kV) with BF/DF Duo-STEM detector. Transmission electron microscopy (TEM), selected-area electron diffraction (SAED), and weak-beam dark-field (WBDF) analysis were performed using a JEOL 1230 TEM operating at 100 kV and a Tecnai 20 TEM equipped with Schottky-type field-emission gun, ultrahigh-resolution pole piece (Cs = 0.5 mm), and a scanning transmission electron microscope (STEM) unit with high-angle annular dark-field (HAADF) detector operating at 200 kV. For TEM analysis the samples were dispersed in ETOH, sonicated for a minute and placed on a holey carbon-coated copper grid.

3 Results and discussion

Shown in Figs. 2a and b are the SEM images of the MoO$_3$ nanobelts synthesized by the thermal evaporation of MoO$_3$ powder. The nanobelts have a diameter ranging from 200–4000 nm and have lengths extending up to several tens of microns. The arrow in Fig. 2a depicts the curled-up nanobelts apart from the straighter ones seen uniformly throughout. A closer look reveals the presence of buckling in the nanobelts (marked with white arrows, Fig. 2b) under the electron beam. However, the presence of long straight nanobelts (diameter = 4 µm) are also seen uniformly as revealed in the same figure (marked by black arrows, Fig. 2b). The presence of the respective elements of Mo and O is...