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Low-temperature synthesis of morphology controlled metastable hexagonal molybdenum trioxide (MoO_3)

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ABSTRACT

We demonstrate a simple low-temperature chemical method to produce metastable hexagonal MoO_3 phase nanorods. The structure, chemical purity, thermal stability and optical properties of hexagonal MoO_3 are reported. Our results provide a more direct method to produce high quality and stable hexagonal MoO_3, which exhibits phase stability up to 400 °C at which point an irreversible phase transition occurs to form orthorhombic MoO_3.

Transition metal oxides are of great importance due to their potential applications in heterogeneous catalysis, optoelectronics, microelectronics, energy storage and conversion, magneto-electronics, and electrochemical science and technology [1–10]. Molybdenum trioxide (MoO_3) has been explored recently, for its interesting properties, and its potential in scientific and technological applications [3–10]. By virtue of its layered structure, chemical stability, and electrochemical activity, MoO_3 finds application as a cathode material in high-energy density solid state microbatteries [4]. Inherent chromogenic properties makes MoO_3 useful in the fabrication and development of electrochromics, electronic information displays, and optical memory devices [3–8]. In addition, MoO_3 finds application in sensor device technology, as it exhibits changes in its surface conductivity when exposed to different chemical environments [9,10]. In all present and future applications, the controlled growth, structure, and electronic properties of MoO_3 are highly important.

Recently, several research efforts have been focused on the synthesis and characterization of MoO_3 low-dimensional structures [4–13]. In particular, these include two-dimensional (2D) and one-dimensional (1D) structures such as ultra thin-films, nanorods, nano-belts, and nano-fibers, which, due to their dimensions, exhibit characteristics quite different from the bulk properties of the materials. It is well known that the particular phase of nanostructured Mo oxide is highly dependent on the synthetic procedure and growth conditions. The obvious reason is that MoO_3 exhibits several polymorphs [14]: the α-phase (space group *Pbmn*) is stable under normal conditions; the β-phase ($P2_1/c$) is a metastable polymorph; MoO_3-II ($P2_1/m$) is a metastable high-pressure phase; and the hexagonal phase h-MoO_3. Most of the chemical/physical synthetic procedures adopted to date for the synthesis of micro and nano MoO_3 result in the formation of either the α-phase or the β-phase, or a mixture of both [4–13,15]. The structural chemistry and properties of orthorhombic (α-type) and monoclinic (β-type) of MoO_3 were,

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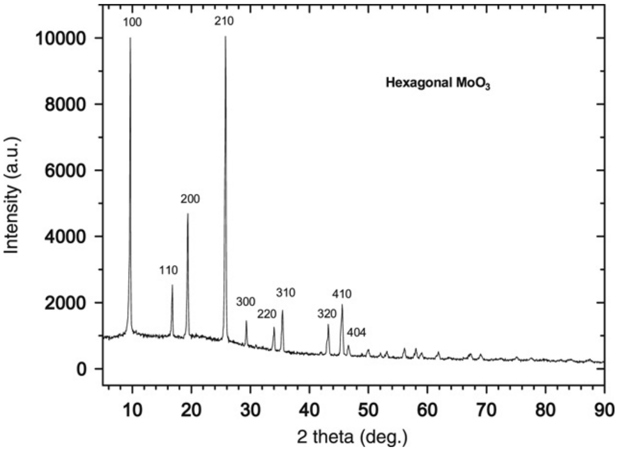

Fig. 1. XRD pattern of *h*-MoO_3 rods.

therefore, thoroughly investigated [4–13,15,16]. However, the metastable hexagonal MoO_3 phase has not been explored much. The number of successful efforts to synthesize *h*-MoO_3 have been very limited, partly due to the complications in stabilizing this metastable phase as compared to the thermodynamically stable α-MoO_3. As such, the physicochemical properties of the metastable *h*-MoO_3 phase are largely unknown, in spite of the fact that metastable structures often demonstrate new or enhanced activity when compared to thermodynamically stable phases. Very few reports on the synthesis of this metastable phase claim that well-crystallized *h*-MoO_3 can be obtained, and they employ chemical routes that require either high processing temperatures or prolonged processing time [16–18]. Here, in this report, we demonstrate a simple chemical method to produce high-quality, chemically and structurally stable, highly crystalline *h*-MoO_3 nanorods with controlled morphology and without involving either high temperature or prolonged processing time. The impetus for this work is to make use of the metastable *h*-MoO_3 phase for electrochemical applications, particularly in lithium batteries and chemical sensors. In this paper, we report, for the first time, the crystal structure, morphology, and optical properties of hexagonal phase MoO_3 nanorods prepared by a simple chemical precipitation route using ammonium paramolybdate.

Hexagonal MoO_3 nanorod samples were prepared via the precipitation of molybdenum oxide from an ammonium paramolybdate solution, by the addition of nitric acid. After dissolving 0.1 g of reagent-grade ammonium paramolybdate, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, in distilled water, 5.0 mL of concentrated nitric acid was added and mixed, and the reaction was held at 85 °C for 1 h. The resultant crystals were separated and washed with distilled water until the pH of the wash water was 6. The precipitate was dried in air at 21 °C. The samples obtained were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), x-ray microanalysis, optical absorption in the UV–vis–NIR region, and differential thermal analysis (DTA) to study the microstructure, optical properties, and thermal stability of the grown materials.

The XRD pattern of the sample obtained in this work is shown in Fig. 1. It is evident that the material synthesized using present approach is well-crystallized and single phase. All of the observed peaks can be indexed in hexagonal symmetry, with interplanar spacings reported for the hexagonal molybdenum oxide [14]. The interplanar spacings (not listed) obtained from the XRD data are in excellent agreement with those reported for hexagonal phase MoO_3 [14].

The scanning electron microscopy (SEM) data of *h*-MoO_3 samples are shown in Fig. 2. The SEM images, which are obtained in ultra-high resolution mode, show a rod-like morphology. The nano-rod *h*-MoO_3 crystals have the shape of straight hexagonal rods (Fig. 2a, b). It is important to recognize that the estimated aspect ratio (length/diameter) is about 60, which is three orders of magnitude higher than the value obtained by Song et al. [18] for a hexagonal MoO_3 prepared using a temperature of 300 °C. The projection (Fig. 2a) and side view (Fig. 2b) of the *h*-MoO_3 sample also makes it clear that the crystals grow uniformly with a rod-shaped morphology. Note that nanocrystals are well-faceted (Fig. 2a). The agglomeration of nanocrystals into "sea-urchin" shaped clusters is observed (insert in Fig. 2b) when the mother liquor containing *h*-MoO_3 particles was boiled with either silicon or carbon substrate. Attempts to reduce the size of hexagonal rods by terminating the chemical reaction, either by reducing the precipitation time or by lowering the crystallization temperature to 0–5 °C, were not successful. In addition, such attempts resulted in the formation of poorly faceted and irregular crystals.

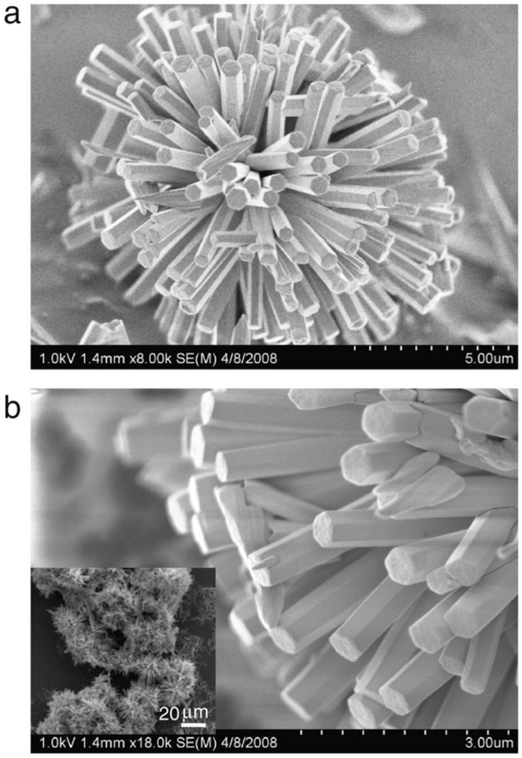

Fig. 2. SEM data of *h*-MoO_3 rods. The images shown are obtained with: (a) projected view and (b) side view of *h*-MoO_3 rods. Insert in (b) shows the "sea-urchin" shaped clustering of *h*-MoO_3 rods on silicon substrate.

The electron-beam generated x-ray elemental mapping data of *h*-MoO_3 sample is shown in Fig. 3. The x-ray microanalysis indicates a high chemical quality of the hexagonal MoO_3 nanorods. It is well-known that the x-rays generated are characteristic of the atoms [19]. Therefore, the detection of x-rays emitted from the sample as a result of sample-electron beam interaction provides the identification of the atoms present in the crystal [19]. The emitted x-ray peaks detected are only from Mo and O with an estimated O to Mo ratio of 3.03 ± 0.05. No other elements were detected, which is a sign of high purity MoO_3 without any elemental impurities incorporated from chemical processing or post-preparation handling. The chemical stoichiometry and absence of impurities was also confirmed by X-ray photoemission measurements, which also indicate the existence of Mo in its highest chemical valence sate of Mo^{6+} (not shown). Furthermore, a one-to-one correspondence in the x-ray mapping images of Mo and O (Fig. 3b and c) indicate the chemical homogeneity of the *h*-MoO_3.