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LETTER TO THE EDITOR

Preparation of MoO_3 nanostructures and their optical properties

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Abstract

In this letter we report the synthesis of nanostructures of molybdenum trioxides by directly oxidizing a spiral coil of molybdenum, at ambient atmosphere, by passing a current through the coil. The advantage of this approach is that the temperature of the substrate is low (normally below 200 °C), and that the nanostructures to be formed could be chosen, via controlling the current or, equivalently, the temperature of the coil. We show that, by adjusting the current through the coil, α-MoO_3 lamellas with a thickness of ~20–50 nm, and β-MoO_3 spheres of diameters down to nanometre scale can be synthesized at ambient atmosphere. These nanostructures exhibit a large optical band gap of ~3.05 eV, and room-temperature photoluminescence at ~395 nm. This study provides a simple, controllable way of fabricating metal oxide nanostructures of interest.

Transition metal oxides comprise a large family of materials exhibiting a variety of interesting properties that are attractive for applications in lithium-ion batteries [1, 2], catalysts [3], electrochromic materials [4, 5], sensors [6, 7], etc. Among the transition metal oxides, MoO_3, due to its excellent optical and electronic properties, has become a promising material for applications in electrochromic systems ranging from microbatteries [8] and gas sensing [9] to devices for information displays [10, 11]. As many properties of nanosized transition metal oxides are distinct from their bulk forms, the synthesis, structure characterization and properties evaluation of these nanostructures have thus become the focus of research in recent years.

Currently, there are several approaches available for preparing MoO_3 film with either an amorphous or a polycrystalline structure, e.g., sputtering [4], chemical vapour deposition

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(CVD) [12, 13], electro-deposition [14] and flash evaporation [15, 16]. To fabricate nanoscopic MoO_3, methods like template-directed reaction of molybdic acid and the subsequent leaching process [17], and templating against carbon nanotubes [18] have previously been attempted. These complicated approaches, however, are not able to bring growth of nanoscopic MoO_3 structures on planar substrates, which is a necessity for applications in real devices. Therefore, new methodologies are demanded for the synthesis of nanostructured MoO_3.

Here, we report the synthesis of MoO_3 nanostructures by thermally oxidizing a molybdenum spiral coil at ambient atmosphere. Via adjusting the current passing through the coil or, equivalently, the temperature of the coil, nanostructures of MoO_3, i.e., α-MoO_3 lamellas, a mixture of α-MoO_3 lamellas plus β-MoO_3 nanospheres and β-MoO_3 nanospheres can be synthesized in sequence as the temperature increases. Thus this study provides a simple way for selecting the nanostructures of MoO_3 to be formed.

A spiral coil ($\sim$2 cm in diameter and $\sim$10 cm long) made from a molybdenum wire with a purity of 99.9%, was connected to two copper electrodes in a vacuum chamber. A voltage was applied to the two electrodes at ambient atmosphere to pass a current through the coil. The current was controlled via adjusting the voltage applied. A Si(001) substrate was supersonically cleaned in acetone, alcohol and deionized water baths, and was fixed on a substrate holder $\sim$5 cm above the coil. Due to the oxidization of the molybdenum coil, nanostructures of molybdenum oxides were deposited on the substrate. The temperature of the coil was monitored using a WFH-655 fibre-optic infrared thermometer. The temperature of the silicon substrate was measured by a thermal couple, and was found to be below 200 °C within a typical deposition time of $\sim$1 min. The growth morphology, the structure and the optical properties of molybdenum oxide nanostructures deposited on the silicon substrates were examined and investigated using a scanning electron microscope (SEM), a transmission electron microscope (TEM), x-ray diffraction, micro-Raman spectroscopy and photoluminescence measurements, respectively.

To investigate the effect of the temperature of the Mo spiral coil on the formation of the nanostructures, three currents, i.e., $\sim$25, $\sim$50 and $\sim$75 A were passed through the Mo coil, corresponding to temperatures of $\sim$700, $\sim$1000 and $\sim$1300 °C, respectively, monitored by the fibre-optic infrared thermometer. Figures 1(a)–(f) show the SEM micrographs and corresponding Raman spectra of nanostructures deposited on the Si(001) substrate, at currents of $\sim$25, 50 and 75 A, respectively. The SEM images were taken using a JSM-6301F SEM working at 20 kV. One sees that different nanostructures of molybdenum oxide were formed at three currents: at $\sim$25 A, lamellas were formed; at $\sim$50 A, a mixture of lamellas and spheres were formed; at $\sim$75 A, only spheres were formed. The lamellas are typically several micrometres long and sub-micrometre wide. Their thickness, as shown by the arrows in figure 1(c), is $\sim$ several tens of nanometres. One may notice that the lamellas are so thin that they are transparent to the 20 keV electrons, i.e., those spheres and lamellas beneath can be clearly seen from the image. The diameter of the spheres ranges from several tens to several hundreds of nanometres.

The structure of these nanostructures was characterized with a micro-Raman spectrometer using a 514.5 nm Ar^+ laser. The peaks in figures 1(b) and (f) are readily indexed to α-MoO_3 of an orthorhombic structure and β-MoO_3 of a monoclinic structure, respectively [19, 20]. Note that the peak at $\sim$941 cm^{-1} in figure 1(f) is from the silicon substrate. XRD analysis of two samples (not shown) also confirmed the results given by the Raman analysis. Figure 1(d) shows, as one sees clearly, a spectrum of a mixture of α-MoO_3 and β-MoO_3. Comparing figures 1(a), (c) and (e), the lamellas in figure 1(c) should be α-MoO_3, and the spheres should be β-MoO_3. To confirm this, the deposits were mechanically removed from the substrate into alcohol by supersonic shaking, and dispersed onto another silicon substrate for micro-Raman analysis.

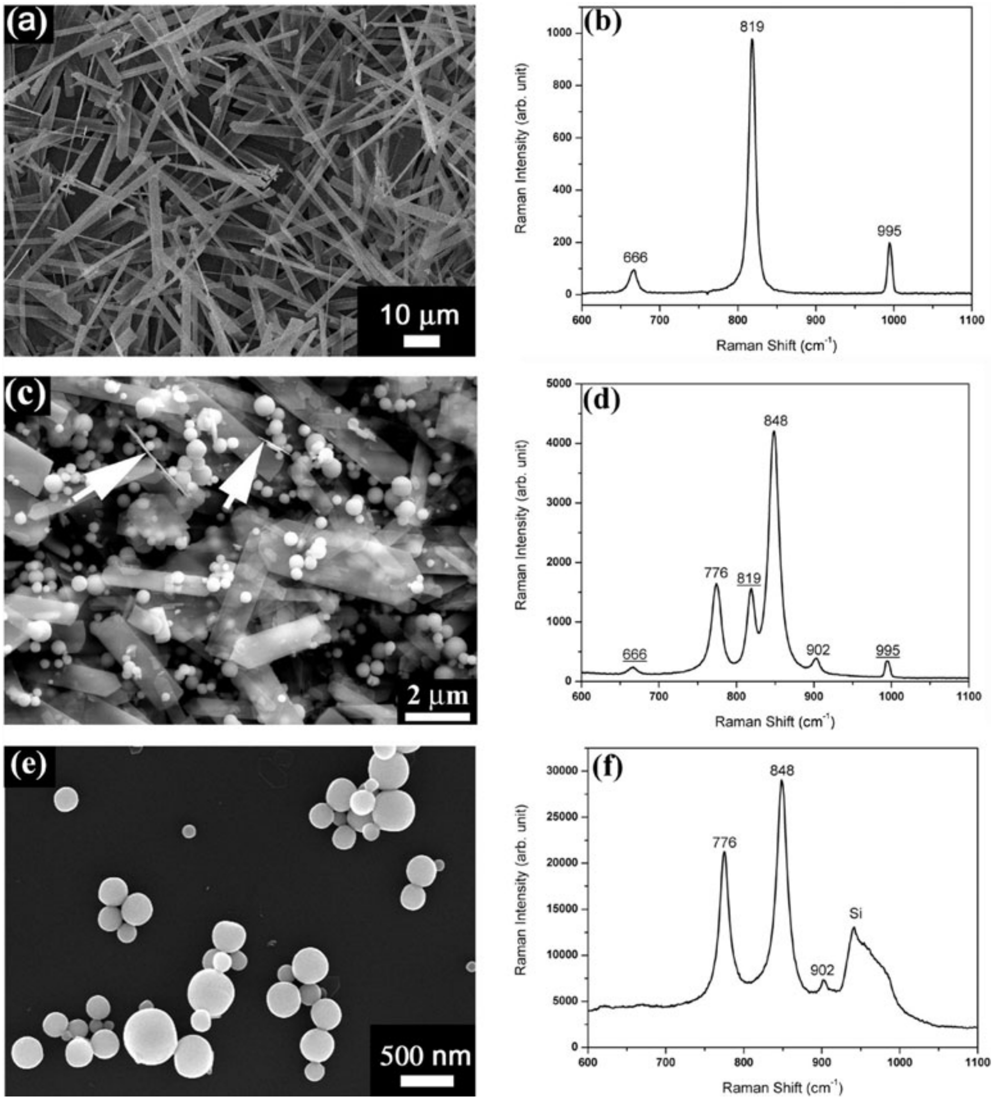

Figure 1. Morphologies and Raman spectra of molybdenum trioxides deposited on Si(001) substrates by passing different currents through a Mo spiral coil: (a) and (b) α-MoO$_3$ lamellas formed at ~25 A; (c) and (d) a mixture of α-MoO$_3$ lamellas and β-MoO$_3$ nanospheres formed at ~50 A; (e) and (f) β-MoO$_3$ nanospheres formed at ~75 A, respectively. The numbers underlined in figure 1(d) indicate peaks of α-MoO$_3$.

In this way one can distinguish using a microscope the lamellas and nanospheres, and thus obtain Raman spectra from the lamellas or nanospheres only. The spectra obtained indicate clearly that the lamellas in figure 1(c) are α-MoO$_3$ and the spheres are β-MoO$_3$. Therefore, by thermally oxidizing a molybdenum spiral coil, one could synthesize either α-MoO$_3$ lamellas or β-MoO$_3$ nanospheres via controlling the current passing through the coil or, equivalently, the temperature of the coil.

The structure of individual lamellas and nanospheres was also investigated by TEM and HRTEM analysis. Figures 2(a) and (b) shows bright field images, corresponding selected area

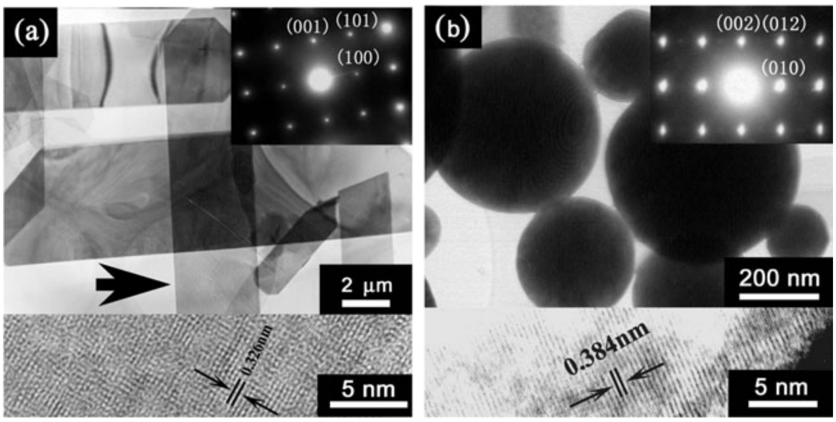

Figure 2. TEM and HRTEM characterization of (a) α-MoO$_3$ lamellas and (b) β-MoO$_3$ nanospheres. The insets of the two images are the corresponding SAD patterns. The arrow in (a) points to the lamella from which the SAD pattern was taken.

diffraction (SAD) patterns and typical HRTEM images of the α-MoO$_3$ lamellas and β-MoO$_3$ nanospheres, respectively. The images and SAD patterns were taken with a JEM-2010F TEM working at 200 kV. The lamellas, as can be seen from the figure, are single crystalline, several micrometres long and sub-micrometre wide. From the indexing results of the SAD pattern (taken from the lamella indicated by the arrow in figure 2(a)) we note that the incident electron beam is along the $\langle 010\rangle$ and the growth direction of the lamellas is along the $\langle 100\rangle$ of α-MoO$_3$. The β-MoO$_3$ spheres, as shown by figure 2(b), are of diameters varying from several tens to several hundreds of nanometres, and are also single crystalline.

The optical properties of α-MoO$_3$ lamellas and β-MoO$_3$ nanospheres were evaluated by measuring their optical transmission in the range of ultraviolet to visible using a MPM-800 microscopic photometer, and the photoluminescence spectra with a M-4500 photoluminescence spectrometer. α-MoO$_3$ lamellas and β-MoO$_3$ nanospheres show similar optical properties. Figure 3 is a typical optical transmission spectrum of α-MoO$_3$ lamellas. The optical band gap of the lamellas can be obtained from the data at the absorption edge using the relationship of $(\alpha h\nu)^{1/2} = A(h\nu - E_g)$, where A is a constant, α is the absorption coefficient, $h\nu$ is the photo energy and E_g is the optical band gap, respectively [21, 22]. To determine E_g, $(\alpha h\nu)^{1/2}$ is plotted as a function of photon energy $h\nu$ using the data at the absorption edge, i.e., $\alpha > 10^{-4}$ cm^{-1} [22]. Extrapolating linearly to $(\alpha h\nu)^{1/2} = 0$, E_g of the lamellas was estimated to be 3.05 eV, which is a little larger than that of the bulk state of 2.9 eV [21].

Figure 4 is a photoluminescence spectrum of β-MoO$_3$ nanospheres excited with a 250 nm laser at room temperature. One observes that there is a broad peak centred at $\sim$395 nm in the emission spectrum, according to a band transition energy of $\sim$4.15 eV, which might be attributed, in the crystal field model, to the Mo^{5+} d$_{xy}$–d$_{yz}$ band transition of a heavily distorted polyhedron in an octahedral crystal field [23]. The enlarged band energy from that reported (3.88 eV) might be ascribed to the reduced dimension of these nanostructured materials. The rather large gap between the two bands demonstrates strong electron–lattice coupling interaction.

In conclusion, we show that the simple thermal oxidation approach is capable of producing a variety of nanostructures, e.g., lamellas and nanospheres, and a variety of molybdenum trioxides, possessing excellent optical properties. The α-MoO$_3$ lamellas and β-MoO$_3$

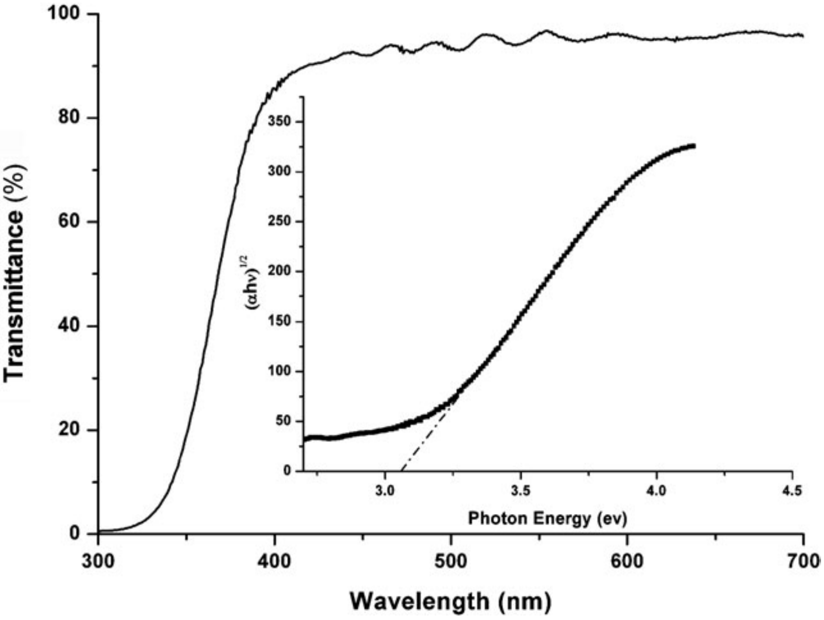

Figure 3. The optical transmission spectrum of α-MoO_3 lamellas in the UV to visible range. The nset is a plot with data at the absorption edge, from which the optical band gap can be derived.

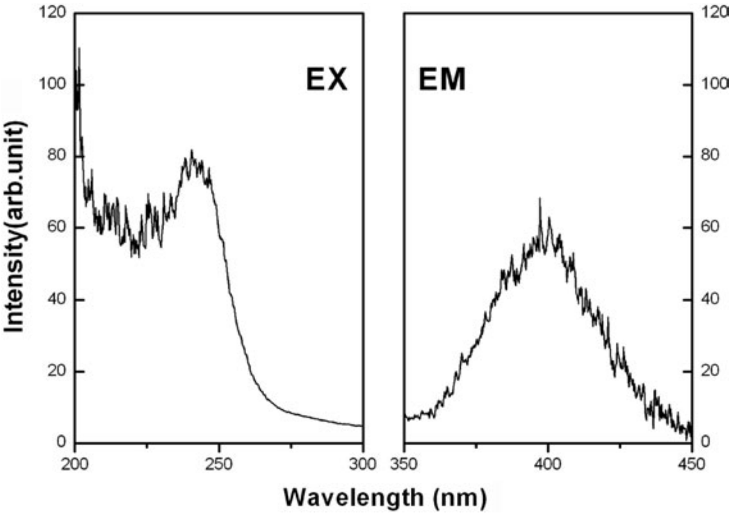

Figure 4. The room-temperature excitation spectrum (left) and the photoluminescence emission spectrum (right) of β-MoO_3 nanospheres.

nanospheres have an optical band gap of ~3.05 eV, which is greater than that of the bulk state materials, and exhibit room-temperature photoluminescence at ~395 nm.

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