Template conversion of MoO$_3$ to MoS$_2$ nanoribbons: synthesis and electrochemical properties†

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Hydrothermally synthesized $\alpha$-MoO$_3$ nanoribbons were converted to MoS$_2$ whilst retaining the same morphology by a solid–gas reaction at 800 °C in a H$_2$S/H$_2$/N$_2$ atmosphere. In order to keep the nanoribbon morphology from the oxide in the sulfide, it was crucial to have a H$_2$S stream during the whole heating process. Thereby, the first layer of sulfide is formed as soon as the oxide is activated avoiding coalescence of the nanoribbons. Afterwards, the sulfidization takes place from the outer shell to the inner core of the nanoparticles. Both $\alpha$-MoO$_3$ and MoS$_2$-NRs were investigated for the electrochemical intercalation of lithium-ions. The electrochemical insertion and removal of lithium in the molybdenum oxide are accompanied by a change of color, which was measured by in situ UV-Vis. Spectroelectrochemical experiments showed a distinguished electrochromic behavior with a significant potential-dependent change in absorbance at 660 nm upon Li$^+$ insertion. Analysis of in situ voltammetry revealed the presence of three active sites for lithium insertion in the MoO$_3$–NRs, which are accompanied by only two chromophores in the same potential range. Voltammetric measurements of the MoS$_2$ nanoribbons presented a reversible reduction of MoS$_2$ to Li$_x$MoS$_2$ followed by Mo and Li$_2$S, which can be further reduced to Li and S at more negative potentials. Such sulfide materials are highly promising for lithium batteries. This template synthesis is a simple method to obtain high purity MoS$_2$ nanoparticles with a controlled morphology of nanoribbons.

1 Introduction

Materials with the capacity of simultaneously changing the electrical and optical properties upon insertion or removal of ions are known as electrochromic materials. These materials have promising applications such as electrochromic windows, lithium-ion batteries, catalysis and sensors.†,‡ For instance, tungsten oxides have been widely investigated for their electrochromic properties.† Likewise, molybdenum oxides also show pronounced electrochemical† and electrochromic properties.† Orthorhombic $\alpha$-MoO$_3$, for example, consists of a layered structure of covalently bonded MoO$_6$ octahedra connected at the edges and corners forming channels,§ which allow the intercalation of ions to form molybdenum bronzes $\mathrm{M}_x \text{MoO}_3$ (M = H$^+$, Li$^+$, Na$^+$, K$^+$, Mg$^{2+}$).‡ This ion insertion in the $\alpha$-MoO$_3$ channels is accompanied by a change in coloration from pale to dark-blue.† Nanstructured $\alpha$-MoO$_3$ with morphologies such as nanoparticles§ and nanorods‖ are expected to have an improved electrochromic response due to their smaller diffusion path§ and increased surface area.‡

Molybdenum sulfides have been noted for their superior performance for energy storage applications such as lithium-ion batteries (LIB).§,‖–‡‖ Different nanostructures including nanorods‖ and single layered MoS$_2$ (ref. 16) have been investigated with respect to their electrochemical properties. Therefore, several attempts of preparing uniform MoO$_3$ nanorods as precursors for MoS$_2$ with the same morphology have been reported.‖,‖–‖

One of the methods to prepare nanostructured MoS$_2$ is the solid–gas reaction of bulk $\alpha$-MoO$_3$ in an H$_2$S/H$_2$/N$_2$ atmosphere at 800 °C.‡ The oxide nanoparticles are formed in situ in the gas phase and the oxide-to-sulfide reaction takes place from the outer layer to the inner core of the oxide nanoparticles.‖ Consequently, the size and shape of the oxide normally determine the morphology of the final sulfide materials.‖–‖‡ Hence, oxide nanorods usually generate sulfide nanotubes (NT) whereas spherical nanoparticles generate
inorganic fullerene-like (IF) MoS₂. Nevertheless, because the preparation of the molybdenum oxide nanoparticle takes place in the gas-phase at 800 °C, it is rather challenging to control the morphology of the oxide and consequently, that of the sulfide. Thus, for most of the solid–gas preparation methods described so far, a mixture of nanotubes and spherical fullerene-like MoS₂ nanoparticles is obtained.

Alternatively, several attempts of preparing uniform MoO₃ nanorods as precursors for MoS₂ with the same morphology have been reported. Hydrothermal treatment of sodium molybdate or acidified ammonium heptamolybdate led to uniform MoO₃ nanorods. Thermolysis of ammonium molybdate generated a mixture of spherical and rod-shaped MoO₃. These oxide nanoparticles were converted to MoS₂ using H₂ as a reducing agent and H₂S or S²⁻ as the sulfur source. However, many of the attempts of sulfiding MoO₃ nanorods was not successful for the homogeneity of the final product, resulting in mixtures of MoO₃ nanotubes and fullerene-like nanoparticles, mixtures of MoS₂ nanorods with nanoparticles, MoS₂ nanorods with an oxide core due to incomplete sulfidization and in certain cases the sulfidization led to a complete loss of the original oxide morphology.

In this work, we contribute to the development of novel synthetic methods for the preparation of MoS₂ with a high morphological yield of nanoribbons. α-MoO₃-NR synthesized by a hydrothermal method was used as the precursor for the synthesis of MoS₂-NR at 800 °C under a stream of H₂S and H₂/ N₂ since the beginning of the heating ramp. With this strategy, we were able to retain the oxide nanoribbon morphology in the sulfide product. A mechanism for the oxide-to-sulfide conversion has been proposed. We investigated the electrochemical behavior toward lithium insertion and removal of both oxide and sulfide nanostructures and we show that the MoO₃ nanoribbons have a pronounced electrochromic behavior, whereas MoS₂ present a reversible electrochemical behavior, making the oxide and sulfide good candidates for electrochromic devices and LIBs, respectively.

2 Experimental

2.1 Preparation of MoO₃ nanoribbons

MoO₃ nanoribbons were prepared by a previously described hydrothermal method. In a typical procedure, 310 mg of previously prepared molybdic acid added to 0.7 mL of glacial acetic acid and 1.8 mL of deionized water in a 45 mL capacity Teflon-sealed stainless steel autoclave. Hydrothermal treatment was performed at 180 °C for 7 days. After cooling to room temperature, the product was filtered and washed stepwise with water, ethanol and ether. The pale-blue powder obtained was vacuum dried with a final yield of 93%.

2.2 Preparation of MoS₂ nanoribbons

The prepared MoO₃ nanoribbons were dispersed carefully in a boat quartz plate and subsequently placed in a tubular furnace. After purging with N₂ (100 mL min⁻¹), the gas stream was replaced by 5/95% H₂/N₂ (96 mL min⁻¹) and 99.9% H₂S (6 mL min⁻¹). Subsequently, the quartz tube was heated to 800 °C with a heating ramp of 30 °C min⁻¹ and kept at the final temperature for 30 min. After cooling to room temperature, a dark powder of MoS₂ was removed from the oven.

3 Results and discussion

3.1 Synthesis of molybdenum oxide and sulfide nanoribbons

3.1.1 Synthesis and structural characterization of MoO₃ nanoribbons. Molybdenum oxide obtained after a hydrothermal treatment of MoO₃·2H₂O (Fig. SI1†) show a high...
morphological yield of nanoribbons (Fig. 1a and b), with an average diameter of 150 nm and length of 3 to 8 μm (Fig. SI2†). The nanostructures have an orthorhombic α-MoO3 phase (Fig. 1c, Pbnm, ICDS 36167), which consists of corner and edge sharing MoO6 octahedra chains, forming stacked layers held together by weak van der Waals forces.32 The oxide crystals grow anisotropically, with a preferential orientation in the [010] direction,33 as seen in the intense signals for the (00l) diffraction planes.

During the hydrothermal synthesis, MoO3 nanostructures precipitate from MoO3·2H2O dissolved in acidic media, without the formation of intermediate phases.34 The complete conversion of MoO3·2H2O to α-MoO3 is supported by the TG and DSC profile (Fig. 1d). The release of adsorbed water occurs until 100 °C and the absence of any signal related to coordinated water – that should appear up to 400 °C (ref. 35) – confirms the formation of the stable orthorhombic structure.

The morphology of the MoO3 nanoribbons is quite sensitive to the annealing temperature. At around 550–600 °C the nanoribbons can collapse forming large plates.36 The DTA curve shows an endothermic wave at around 550 °C (Fig. 1c), which could be correlated with this morphology loss, also visible by Raman spectroscopy.36 The collapsing of the nanoribbons morphology is a critical point for converting the oxides to sulfides while maintaining the morphology. For a successful template sulfidization, a first outer sulfide layer must be formed below 500 °C, as it will be discussed in the following session. Sublimation of the oxide starts after 700 °C, noticed by the abrupt weight loss and the endothermic peak at 795 °C. Almost all of the oxide mass is volatilized at 850 °C.

Both Raman and infrared spectra (Fig. 2) show characteristic stretching modes of the crystalline orthorhombic α-MoO3.36–41 α-MoO3 consists of distorted MoO6 octahedra with the Mo–O bond length varying between 167 and 233 pm.38 The oxygen atoms in the MoO6 octahedra can be divided into three types: (i) terminal Mo–O from unshared oxygen, (ii) Mo2–O edge-shared oxygen in common with two or three octahedra, i.e. bound to two metal atoms and (iii) Mo3–O, an oxygen atom bound to 3 metals.40,41 These three stretching modes are observed in both Raman and IR spectra (Fig. 2) at (i) 996, (ii) 826 and (iii) 667 cm⁻¹,42 and (i) 998, (ii) 868 and (iii) 560 cm⁻¹,40 respectively.

3.1.2 Template conversion of MoO3 to MoS2. MoS2 samples were prepared from the synthesized MoO3 nanoribbons by a solid–gas reaction. MoO3 nanoribbons were used as prepared and heated up to 800 °C (30 °C min⁻¹) for 30 min under a stream of 5% H2/95% N2 and H2S. SEM images of the black powder produced (Fig. 3a and b) show that the nanoribbon morphology of the oxide precursor is retained in the final product. The XRD pattern (Fig. 3c) resembles the characteristic reflections for 2H–MoS2 (hexagonal MoS2, space group P63/mmc).
MoS₂ inorganic fullerenes (IF) and/or nanotubes (NT). Accord-

no bands of MoO₂ or MoO₃ were observed, consistently with the

converted to sul-

403 cm⁻¹ under N₂ atmosphere generating oxide nanoparticles (5

nm). Subsequently, the oxide vapor is reduced to MoO₃

described in the literature

ing to this mechanism, the size and shape of the original oxide

sul-

ation of the oxide and formation of MoS₂. The in-plane displacement E₁

2g of Mo

–MoO₃ are observed, con-

second order zone-edge phonon 2LA(M) of MoS₂.

The mechanism of sul-

a preferred orientation of the nanostructures. No reflexes

related to the MoO₂ or α-MoO₃ are observed, confirming the

complete sulfidization of the oxide and formation of MoS₂.

Raman spectra of nanoribbons, nanotubes and bulk MoS₂

(ref. 43) showed that the nanoribbon Raman bands are shifted
downward and more similar to the spectrum of the bulk sulfide

when compared to the Raman spectrum of MoS₂ nanotubes.
The wavenumbers, as well as the band relative intensities for the

Raman spectrum of the prepared material (Fig. 3c) are

consistent with the spectrum reported for MoS₂ nanoribbons.⁴³

The in-plane displacement E₂³g of Mo–S is observed at 375 cm⁻¹

whereas the out-of-plane A₁g has a very intense band at

403 cm⁻¹.⁴⁴ The weak band at 450 cm⁻¹ corresponds to the

second order zone-edge phonon 2LA(M) of MoS₂.⁴⁴ ⁴⁵ Moreover,

no bands of MoO₂ or MoO₃ were observed, consistently with the

XRD observations.

The mechanism of sulfidization of MoO₃ to MoS₂-IF and -NT

described in the literature⁴⁴⁷ consists of a gas-phase reaction

involving three steps: firstly MoO₃ powder is sublimed at 800 °C

under N₂ atmosphere generating oxide nanoparticles (5–300

nm). Subsequently, the oxide vapor is reduced to MoO₃₋ₓ under

a flow of 5% H₂/95% N₂ at 820 °C. Finally, the sub-oxide is

converted to sulfide upon a stream of H₂S at 840 °C, generating

MoS₂ inorganic fullerenes (IF) and/or nanotubes (NT). Accord-

ing to this mechanism, the size and shape of the original oxide

nanoparticle is maintained after the conversion to the

sulfide.⁵⁵ ⁵⁶ Yet, as this method for the preparation of the oxide

nanoparticle takes place in the gas-phase, it is rather difficult to

to control the morphology of the oxide and consequently of the

sulfide. Hence, a mixture of IF and NT-MoS₂ is obtained.

In this work, we suggest a new synthetic approach for

preparing MoS₂ with nanoribbon morphology. It involves first

preparing the precursor material – molybdenum oxide – already

with the desired final morphology of nanoribbons. Then, we

provide a sulfur source for the conversion of MoO₃ to MoS₂ from

a stream of H₂S, and we thermally treat the material heating

from room temperature up to 800 °C. By streaming H₂S from

the beginning of the heating ramp, the collapsing of the MoO₃-

NR is successfully avoided and MoS₂ with nanoribbons morphology is obtained (Fig. 4). The formation of an outer-shell

of MoS₂ onto the MoO₃-NR is likely to be formed immediately
during heating of the oxide and hinders the coalescence – at

500 °C (ref. 36) – and the sublimation of the oxide nanoparticle.

Experiments performed with an H₂S stream that starts only

when the heating treatment reaches 400 °C exhibited loss of nanoribbon morphology (Fig. S1†), similarly to the results

reported elsewhere for sulfidization of MoO₃ nanoribbons under H₂S.⁶⁶ Our results suggest that the reaction takes place from the outer shell to the inner core of the nanoparticle. The reaction is limited by the slow diffusion of H₂S into the oxide core⁷⁷ and the nanoribbon morphology of the oxide precursor is well main-
tained in the final sulfide (Fig. 4). MoS₂ nanoparticles obtained

have 1D morphology, with 200 nm diameter and up to several

μm lengths. The obtained 1D-MoS₂ have no oxide or hollow

core, different from the reports where nanotubes⁷⁷ ⁷⁸ or nanorods with an oxide core³³ were produced from the sulfidization of molybdenum oxide nanorods.

3.2 Electrochemical characterization of nanoribbons

3.2.1 Spectroelectrochemistry of MoO₃-NRs. α-MoO₃ has a

layered structure⁶² with intercalation sites for cations, such as

H⁺, Li⁺, Na⁺ and Mg²⁺. Here, we studied the electrochemical intercalation of Li⁺ ions in the α-MoO₃ structure by cyclic vol-
tammetry (CV) using a thin film of MoO₃ nanoribbons on ITO in a LiClO₄ in propylene carbonate (PC) solution.

Starting at open circuit potential (+0.4 V) with a negative

sweep direction, three well-defined reduction peaks are observed

at ~0.25, ~0.37 and ~0.65 V vs. Ag/Ag⁺ (Fig. 5a). These

cathodic peaks are characteristics for Li⁺ intercalation into the

molybdenum oxide structure, forming molybdenum bronze

(Li,MoO₃).⁶ In the anodic scan, de-intercalation of lithium is

identified by the oxidation wave at ~0.3 V, followed by two small

anodic peaks at ~0.1 and +0.05 V vs. Ag/Ag⁺. Multiple reduction

peaks in α-MoO₃ films are attributed to the insertion of Li⁺ in

distinct energetic sites from the oxide structure.⁶⁴ ⁶⁵ However,

part of the inserted Li⁺ ions can be trapped into the cavities of

the layered structure⁶ and, consequently, the intercalation/de-

intercalation redox reaction is not fully reversible.⁷ In this

case, the current diminishes in the subsequent voltammetric cycles, as observed from the first to the third cycles (Fig. 5a). The
coulombic efficiency is also quite low: 85, 70 and 52% from the first to the third voltammetric cycle, respectively. The back-
ground CV of an ITO film without MoO₃ shows that the electro-
decomposition of the PC electrolyte in this potential region is minimal. Thus, the low efficiency should be mostly attributed to the irreversible formation of bronzes such as Li$_x$Mo$_{IV-VI}$O$_3$.

This irreversible intercalation can be even more drastic with ions larger than Li$^+$ such as Mg$^{2+}$. Voltammetric experiments in a PC solution containing MgClO$_4$ (Fig. SI3†) showed that the insertion of Mg$^{2+}$ is totally irreversible with no anodic peaks at all, due to the entrapment of Mg$^{2+}$ ions within the oxide interlayer space.\(^6\)

The electrochemical insertion of Li$^+$ with the formation of Li$_x$MoO$_3$ bronzes (eqn (1)) is accompanied by a change in coloration from pale-blue MoO$_3$ to dark-blue Li$_x$MoO$_3$.\(^1\) The absorbance change in the visible region was monitored as a function of the applied potential (Fig. 5b). When stepping the potential down, from +0.4 to −0.7 V, a significant increase in absorbance is observed. This absorbance change is corresponding to the change of color in the oxide from pale to dark blue. Moreover, as already pointed out that the electrochemical lithium insertion is not totally reversible, the absorbance change is consistently not completely reversible when stepping back to the initial potential (+0.4 V).

\[
\text{MoO}_3 + x\text{Li}^+ + xe^- \rightarrow \text{Li}_x\text{MoO}_3
\]

The transmittance change at a single wavelength (660 nm) was monitored simultaneously with cyclic voltammetry (Fig. 4). I/E (Fig. 6a) and A/E (Fig. 6b) potentiodynamic profiles of a MoO$_3$ film were started at +0.8 V with a negative sweep direction. A remarkable increase in absorption is observed at potentials more negative than −0.1 V (Fig. 6b). Scanning back to positive potentials causes the absorption to decrease, yet not to the starting point. This hysteresis can be correlated with an irreversible lattice expansion during insertion and kinetically slow de-intercalation of lithium during bleaching.\(^7\)

The differential curve of absorbance versus potential (dA/dE vs. E, Fig. 6c) shows two changes of optical density with potential, which take place simultaneously with two of the three cathodic peaks. The simultaneous coloration and electrochemical change, occurring at the same rate, indicate the
presence of two chromogenic species in the molybdenum oxide, which are correlated to the intercalation of Li\(^+\) at a different energetic interlayer spacing of the MoO\(_6\) octahedron layers. As for the oxidation, only one chromogenic process is observed in the differential spectrum, which superposes the main oxidation wave at +0.35 V.

3.2.2 Electrochemical lithium intercalation in MoS\(_2\)-NRs. MoS\(_2\) has been investigated for its superior properties as an electrode for lithium-ion batteries. Here, the voltammetric behavior of the synthesized MoS\(_2\)-NR was investigated in a 1 mol L\(^{-1}\) LiTFSI/PC solution. Because this material showed sensitiveness to humidity, the electrochemical measurements of the sulfide were performed in an argon-filled glove box.

The CV of the MoS\(_2\)-NR (Fig. 7) starting at +1.2 V with a cathodic scan direction, shows two cathodic peaks rising at +0.7 and +0.3 V. On the anodic scan, two well-defined oxidation peaks are observed at +0.4 and +0.7 V, followed by a broad wave from +1.3 to +2.5 V centered at ca. +1.5 V. The coulombic efficiency of the lithium insertion/de-insertion is 95.5% (whole anodic over cathodic charge), which is considerably higher than that observed for lithium intercalation/de-intercalation in the molybdenum oxide (85%).

The electrochemical lithium insertion in MoS\(_2\)-NRs is consistent with the CVs described in the literature for MoS\(_2\) with different morphologies: nanorods,\(^{15}\) nanoflakes,\(^{49}\) nanoflowers,\(^{50,51}\) MoS\(_2\)/graphene composites,\(^{52,53}\) mesoporous MoS\(_2\) (ref. 54) and commercial bulk MoS\(_2\).\(^{14}\) The first cathodic peak at +0.7 V is attributed to the Li\(^+\) insertion in the interlayer sites of MoS\(_2\) forming Li\(_x\)MoS\(_2\),\(^{15}\) with the correspondent dislodging at +0.7 V.\(^{15}\) The second and more negative peak at +0.3 V can be attributed to the formation of Mo and Li\(_2\)S from Li\(_x\)MoS\(_2\), as suggested from in situ XRD of bulk MoS\(_2\) in 1 mol L\(^{-1}\) LiPF\(_6\) 1:1 ethylene carbonate: dimethyl carbonate,\(^{44}\) with the correspondent anodic process taking place at +0.4 V. The small cathodic wave at +0.2 V could be attributed to the more negative reduction of Li\(_2\)S to Li and S.\(^{15}\)
4 Conclusions

z-MoO₃ nanoribbons with high purity of phase and morphology were prepared by a hydrothermal method from MoO₃·2H₂O. The molybdenum oxide was converted into MoS₂ retaining the same nanoribbons morphology by solid–gas reaction with H₂ and H₂S. Streaming H₂S from the beginning of the thermal treatment was a key factor in maintaining the nanoribbons morphology from the oxide in the final MoS₂ product. A protective MoS₂ outer layer is formed in the oxide preventing the collapsing of the nanoribbons morphology. MoO₃ nanoribbons showed distinct electrochromic performance for Li⁺ insertion, changing coloration from pale to dark blue upon changing the potential negatively. Spectroelectrochemical measurements with a laser in 660 nm showed the presence of two chromophores correspondent to three cathodic peaks and a hysteresis in absorption as well as in the charge consumed is observed. The voltammetric behavior of MoS₂ shows that lithium can be intercalated within the interlayer spacing this material forming LiₓMoS₂, which can be removed in the anodic scan. This template synthesis is a simple method to obtain MoS₂ nanoribbons with a controlled morphology (100% of nanoribbons).

Conflicts of interest

The authors declare no conflicts of interest.

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