Direct synthesis of MoS$_2$ or MoO$_3$ via thermolysis of a dialkyl dithiocarbamato molybdenum(IV) complex†

Niting Zeng, a David G. Hopkinson, b Ben F. Spencer, b Simon G. McAdams, a Aleksander A. Tedstone, b Sarah J. Haigh a and David J. Lewis a

We have been interested in thin film deposition of MoS$_2$ by use of single source precursors. For example, tetrais[N,N-diethyldithiocarbamato)molybdenum(IV)] (Mo(DTC)$_4$, Scheme 1) can be used in combination with other metal dithiocarbamate complexes to produce doped MoS$_2$ via aerosol-assisted chemical vapour deposition (AACVD). 29 Molybdenum dithiocarbamate (MoDTC) has also been used as a lubricant additive which has been widely investigated for its decomposition mechanism to molybdenum sulfide species in tribology; 30,31 MoS$_2$ and MoO$_3$ are reported as two major products in tribological experiments, whilst another study recently revealed that MoS$_2$, FeMoO$_4$ and MoO$_3$ (where $x > 2$) are the dominant species formed under certain conditions. 32

Here we report the direct synthesis of either 2H-MoS$_2$ or $\alpha$-MoO$_3$ from a single molecular precursor, with the reaction product controlled by choice of processing conditions. Mo(DTC)$_4$ was produced as per Lewis et al. 29 The growth of 2H-MoS$_2$ was achieved via thermolysis of Mo(DTC)$_4$ in argon whilst bulk $\alpha$-MoO$_3$ was formed by the same reaction but in air. The characterisation performed shows that the 2H-MoS$_2$ powder produced is free-standing and nanostructured whilst polycrystalline $\alpha$-MoO$_3$ is produced in air. The low temperature (450 °C) combined with the short processing time for both routes (1 h) represents a new soft synthetic pathway toward these important functional inorganic materials (Scheme 1).

Raman spectra (Fig. 1) indicate that the reaction under argon produces MoS$_2$ with the in-plane mode E$_{2g}$ observed at 380 cm$^{-1}$ and the out-of-plane mode A$_{1g}$ located at 403 cm$^{-1}$ ($\Delta \nu = 23$ cm$^{-1}$). 3 The softening of the two modes together with the broadening of peaks may be caused by phonon confinement, 33 which suggested that the material was few-layer. For reaction in air, MoO$_3$ is formed with lattice modes below

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[a] School of Materials, University of Manchester, Oxford Road, M13 9PL, UK.
E-mail: david.lewis-4@manchester.ac.uk

[b] School of Chemistry, University of Manchester, Oxford Road, M13 9PL, UK

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c8cc08932a
200 cm$^{-1}$, deformation modes between 450 cm$^{-1}$ and 200 cm$^{-1}$ and stretching modes above 450 cm$^{-1}$. The peaks at 112 cm$^{-1}$ ($B_{2g}$, $B_{3g}$), 125 cm$^{-1}$ and 153 cm$^{-1}$ ($A_{2u}$, $B_{1g}$) represent vibrations of the main chains of Mo atoms, and the peaks at 280, 289 cm$^{-1}$ ($B_{2g}$, $B_{1g}$) are assigned to the wagging vibrational mode of pendant oxygens. The characteristic peaks at 664 cm$^{-1}$ ($B_{2g}$, $B_{3g}$), 817 cm$^{-1}$ ($A_{g}$, $B_{1g}$) and 993 cm$^{-1}$ ($A_{g}$, $B_{1g}$) are associated with the symmetric and asymmetric stretching modes of $\alpha$-MoO$_3$.

X-ray powder diffraction (XRPD) was used to investigate the crystallographic structure of the materials produced. The diffraction pattern in argon is non-identical compared to standard 2H-MoS$_2$ (JCPDS No. 37-1492). Peaks corresponding to the (101) and (110) planes of MoS$_2$ are relatively intense whereas the peaks corresponding to the (002) and (103) planes are extremely broadened (Fig. 2). A preferred orientation in the (101) and (110) planes is evinced by the pattern, which suggests MoS$_2$ crystallites may grow laterally during the thermolysis process. The reflection of the (002) plane is very weak, indicating a reduced amount of bulk character in the [00l] direction. This indicated again that potentially sheets of nanoscale thickness of MoS$_2$ were produced from this reaction pathway. The XRPD diffraction pattern of the product of the decomposition of Mo(DTC)$_4$ in air at 450 °C matches well with orthorhombic $\alpha$-MoO$_3$ (JCPDS No. 05-0508, Fig. 2). Strong intensities are noticed for the (110), (021) and (002) reflections, which indicates preferred growth orientations along these planes. No reflections assigned to MoO$_2$ or Mo$_4$O$_{11}$ are observed, which indicates high-purity $\alpha$-MoO$_3$ is formed in this reaction.

X-ray photoelectron spectroscopy (XPS) was used to characterise the chemical information and changes occurring at the surface of the materials. A neutraliser was used to remove differential charging occurring to the powders under the X-ray beam, and binding energy scale calibration was performed using the C 1s photoelectron peak at 284.8 eV. The Mo 3d spectrum under argon (Fig. 3a) is fit with three chemical species with binding energies of 228.9, 230.0 and 232.5 eV and are associated with Mo$^{4+}$ (MoS$_2$), Mo$^{5+}$ and Mo$^{6+}$ (MoO$_3$) respectively. This is in good agreement with Raman results; MoS$_2$ is the dominant material formed from reaction under argon with oxidation occurring at the surface (sampling depth for Al K$_\alpha$ is ca. 6 nm). The Mo 3d spectrum also contains the broad S 2s photoelectron peak at 226.6 eV which is suggestive of the 2H-phase for MoS$_2$ consistent with diffraction results. The S 2p spectrum also shows three chemical species, consistent with the Mo spectrum, with S 2p$_{3/2}$ binding energy positions at 161.6, 162.8 and 168.4 eV (Fig. 3b), associated with S$^{2-}$, (MoS$_2$), S$^{4-}$ and S$^{6+}$ (sulfate) respectively, which are again consistent with MoS$_2$ reported in the literature and exhibiting some surface oxidation. The ratio of Mo : S (excluding the oxidized species in the spectra, and adjusted to the relative sensitivity factor each elemental core level) is calculated as 1 : 2.1, indicating stoichiometric MoS$_2$.

For the reaction in air, the Mo 3d spectrum is adequately fit with one chemical species with a Mo 3d$_{5/2}$ binding energy
produced, which was confirmed by the broadening of both Raman peaks and XRPD reflections. XRPD further indicates very small polycrystalline sheets formed directly from the reaction which matches with both TEM and SAED results. Based on the thermogravimetric analysis (TGA) data published previously for Mo(DTC)₄ under argon the reaction proceeds by loss of the organic parts of the molecule as gaseous species to form amorphous Mo₅S₃, followed by formation of crystalline 2H-MoS₂.⁴⁴ In air, these steps are probably followed by a rapid replacement of sulfur by atmospheric oxygen to form MoO₃, or by oxidation of the Mo₅S₃ intermediates to MoO₄ species followed by formation of MoO₃.⁴⁴

We conclude that the production of high-purity MoS₂ or MoO₃ is achievable by this method with potential scalability embedded. By using various combinations of precursors (of which for metal dithiocarbamates⁴⁵ and metal xanthates⁴⁶ there are many) we should be able to produce large amounts of doped metal oxide and chalcogenide materials for various applications including catalysis, tribology and dilute magnetic semiconductor materials for spintronics. As these are layered structures we might also be able to exfoliate them to the two-dimensional limit to produce bespoke metal oxide and chalcogenide 2D materials. We are currently exploring these possibilities in our laboratory. This approach has already proven to be successful for producing synthetic layered main group sulfides and 2D derivatives thereof.⁴⁷

DJL and NZ would like to thank the University of Manchester Research Impact Donor Scholarship for funding this study. SGMcA is funded by an EPSRC doctoral prize. DGH is funded by the EPSRC Centre for Doctoral Training in the Science and Applications of Graphene and Related Nanomaterials (GrapheneNOWNANO, EP/L01548X/1).

Conflicts of interest

There are no conflicts to declare.

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