

Molybdenum polysulfide hollow microtubules grown at room temperature from solution

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Received (in Oxford, UK) 16th February 2000, Accepted 27th April 2000

Published on the Web 23rd May 2000

Reaction of $(\text{NH}_4)_2\text{MoS}_4$ and $(\text{NH}_2\text{OH})_2\cdot\text{H}_2\text{SO}_4$ under hydrothermal conditions led to the new compound $(\text{NH}_3\text{OH})_{3.9}\text{MoS}_{4.8}$ **I**, which crystallises from acetone solution producing hollow tubules of nanoscopic size (50–500 nm diameter, 0.1–20 μm length); thermal decomposition of **I** led to the formation of highly dispersed tubular MoS_2 .

The recent discovery of hollow graphite tubules of nanometer dimensions¹ has greatly stimulated the study of nanoscopic structures. Nanotubes are envisaged for potential applications in several areas such as catalysis, composite materials and nanowires, up to artificial muscles and intramolecular junctions.² Several types of nanotubes (and generally, hollow microtubules) have been synthesised. Arc discharge or high temperature treatment of molecular precursors have been applied to elaborate the nanotubes of simple materials such as C,¹ MoS_2 ³ or BN.⁴ Fullerene-like nanoparticles and nanotubes of the MS_2 sulfides (M = Mo, W) could be obtained using high temperature reactions of the corresponding oxides with H_2S , or by means of sonoelectrochemical syntheses.⁵ Different types of nanoscopic tubules were obtained at low temperatures, using templating reactions with organic surfactants. This approach has led to hollow tubules of oxides such as SiO_2 ⁶ or V_2O_5 .⁷ Tubular MoS_2 has been prepared by decomposition of $(\text{NH}_4)_2\text{MoS}_4$ within the pores of an alumina membrane, followed by dissolution of the templating oxide in aqueous NaOH.⁸

Here, we report on a new type of inorganic hollow tube, formed at low temperature without addition of template. A newly synthesised compound $(\text{NH}_3\text{OH})_x\text{MoS}_y$, ($3 < x < 4$, $4 < y < 5$) prepared hydrothermally, led to tubules upon crystallization at room temperature.

The preparation technique was as follows. To a stainless steel vessel were added solutions of 2.8 g $(\text{NH}_4)_2\text{MoS}_4$ (ATM) in 100 ml of water and 8 g $(\text{NH}_2\text{OH})_2\cdot\text{H}_2\text{SO}_4$ dissolved in 100 ml of water. An H_2S pressure of 20 bar was then applied to the reaction mixture and after 30 min at 493 K a brown powder was filtered off, washed with distilled water and dried in air. The product was then treated with acetone in a Soxhlet apparatus for 2 h. A dark red washing solution of **I** was obtained and a brown insoluble residual **II** (ca. 1 g) was collected from the filter. The acetone solution was cooled to room temperature and evaporated in a glass vessel in air. After evaporation of the acetone, 0.7 g of light brown powder **I** was obtained.

The solids were characterised by several physico-chemical techniques, including X-ray diffraction (XRD), FTIR spectroscopy and surface area measurements. High resolution transmission electron microscopy (HREM) combined with EDX analysis was performed on a JEOL 2010 microscope. EXAFS measurements were performed at the Laboratoire d'Utilisation du Rayonnement Electromagnétique (LURE), on the XAS2 spectrometer. Measurements were carried out in transmission mode at the Mo K edge in the range 19900–21000 eV at 8 K. The EXAFS data were treated with SEDEM⁹ and FEFF¹⁰ programs. X-Ray photoelectron spectra (XPS) were measured on a VG ESCALAB 200R spectrometer using Al-K α radiation. Thermal decomposition of solids was studied using a mass-spectrometer Gas trace A instrument (FISONS Instruments).

Dispersed MoS_2 for catalytic applications is often obtained from the decomposition of ATM. To prepare dispersed MoS_2 in an aqueous medium, we studied the reactions of ATM in the presence of inorganic reducing agents, such as hydroxylamine and hydrazine.¹¹ If a solution of $(\text{NH}_2\text{OH})_2\cdot\text{H}_2\text{SO}_4$ was added at room temperature to aqueous ATM, an MoS_3 suspension was formed according to reaction (1), due to the acidic pH of the reaction medium.



However, under the mild hydrothermal conditions used (20 bar H_2S , 493 K, 30 min), MoS_3 reacted further to give a dark brown solid **I** which was insoluble in water but partially soluble in acetone. According to chemical analysis, solid **I** had composition $(\text{NH}_3\text{OH})_{3.9}\text{MoS}_{4.8}$, close to the idealised formula $(\text{NH}_3\text{OH})_4\text{MoS}_5$.

The insoluble brown residual **II** had chemical composition $\text{MoS}_{7.88}$, close to the MoS_8 stoichiometry. The amounts of nitrogen and oxygen in solid **II** were < 0.5%.

Scanning electron microscopy revealed that **I** consists mostly of hollow tubes of different diameters and lengths. The external diameter of tubules varied from 50 to 500 nm whereas the length was between 0.1 and 20 μm . Some irregular spherical agglomerates were also observed. Transmission electron microscopy (Fig. 1) showed that the tubes are hollow, with straight walls. Electron diffraction did not reveal any crystal ordering in the tubules or spherical agglomerates.

Solid **II** consisted of shapeless agglomerates and was XRD amorphous but was fairly homogeneous according to HREM

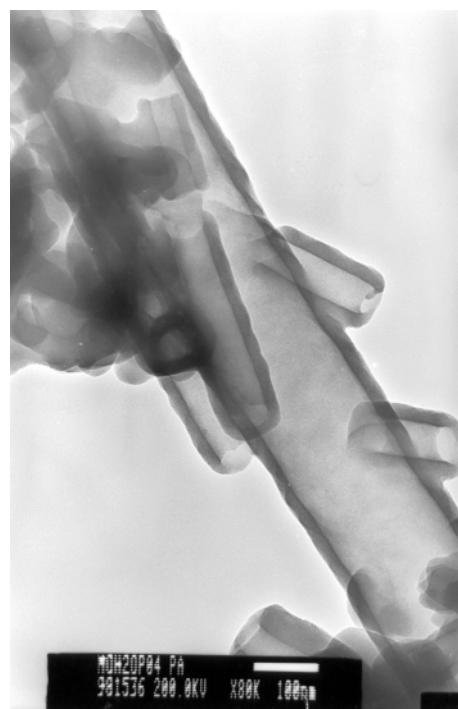


Fig. 1 Transmission electron micrograph of tubules of solid **I**.

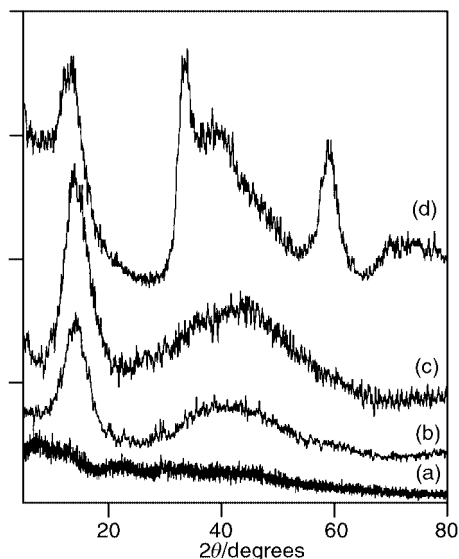


Fig. 2 Powder XRD patterns of (a) solid **I**, (b) solid **II**, (c) reference MoS₃ and (d) MoS₂ obtained from decomposition of **I** at 823 K.

and EDX studies. Formation of **II** has been observed under different reaction conditions. A solid of composition MoS_{7.6} was obtained at 1 bar of H₂S and 373 K (in this case an acetone-soluble product was not formed). We suggest therefore that solid **II** is a distinct compound close to the MoS₈ composition.

The preparation of microtubules **I** was reproduced under various reaction conditions. For example, at 473 K and for a reaction time of 1 h, a solid of composition (NH₃OH)_{3.4}MoS_{4.7} was obtained, in somewhat lower yield and with a decreased but still high number of tubules. Tubules **I** could be repeatedly redissolved in acetone and reprecipitated by slow evaporation, either at ambient conditions or at 313 K.

The role of hydroxylamine in the synthesis is, as yet, not clear but is certainly important, since without addition of hydroxylamine only poorly crystallised MoS₂ was obtained under the same reaction conditions. Our attempts to prepare single crystals of **I** suitable for structure determination, *via* crystallisation from alcohols or methylformamide were not successful.

The powder XRD pattern of **I** [Fig. 2(a)] showed only a broad peak, corresponding to an interplanar distance of *ca.* 1.08 nm. Solid **II** [Fig. 2(b)] was also XRD amorphous, with broad maxima close to those of the MoS₃ reference sample [Fig. 2(c)].

In the IR spectrum of **I**, intense absorptions at 499 and 350 cm⁻¹ were observed, characteristic for Mo–S bonds.¹² The IR spectrum of **II** showed the same Mo–S features, and a broad peak at *ca.* 520 cm⁻¹ attributed to S–S stretching vibrations. Comparison of the IR spectra suggests that **II** contains many S–S bonds whereas they are absent in **I**.

XPS binding energies were studied at the Mo 3d and S 2p levels (C 1s reference binding energy = 284.5 eV). The binding energies are estimated at an accuracy of *ca.* 0.2 eV. Single molybdenum species were observed in both **I** and **II**. The Mo 3d_{5/2} binding energies in **I** and **II** were 229.8 and 229.1, respectively, suggesting that in **I** the electron density on Mo is lower, than in **II**. The sulfur S 2p binding energies are 163.2 and 162.8 eV for **I** and **II**, at the positions of ionic (sulfoxide) sulfur¹³ and terminal bidentate S₂²⁻ species, respectively.¹⁴ Both changes of molybdenum and sulfur signals from **I** to **II** correspond to the removal of S–S bridges with simultaneous formation of terminal Mo–S species, in which sulfur is probably coordinated to nitrogen or oxygen.

Results of EXAFS studies of **I** and **II** are listed in Table 1 and compared to the literature data on Mo coordination in some reference compounds. For the EXAFS fit for **I** and **II**, the energy shift ΔE_0 was 4 eV for the Mo–S and 9 eV for the Mo–Mo shell. Debye–Waller factors for both shells were in the range *ca.* 2.10–5 nm². According to the EXAFS fitting results, molybde-

Table 1 EXAFS fitting results of molybdenum coordination in **I** and **II** as well as for some reference sulfide compounds

Sample (state ^a)	Mo–S	N(S)	Mo–Mo	N(Mo)	Ref.
I (am)	2.33	1.3	3.05	1.08	—
	2.49	3.8			
II (am)	2.40	4.1	2.75	0.92	—
	2.48	4.5			
MoS ₃ (am)	2.43	6	2.75	1	15
MoS _{4.7} (am)	2.44	7.33	2.78	1.33	15
MoS ₃ (am)	2.44	5.5	2.75	1–2	16
(NH ₄) ₂ Mo ₂ S ₁₂ ·2H ₂ O (cr)	2.38–2.5	8	2.82	1	17

^a am = Amorphous, cr = crystalline.

num has approximately the same number (*N*) of S and Mo neighbours in **I** as in MoS₃, but a considerably longer Mo–Mo distance. By contrast, a short Mo–Mo distance was observed in **II**, but the number of S neighbours is significantly higher than in MoS₃, and even higher than that in MoS_{4.7}.¹⁵

Both **I** and **II** are chemically derived from MoS₃ (which itself possesses a poorly organized, probably chainlike structure). It can be suggested that **I** and **II** are formed by addition of sulfide ions or of zerovalent sulfur to the MoS₃ chains, giving, respectively, MoS₅²⁻ (solid **I**) or MoS₈ (solid **II**). Since **I** is soluble in acetone it is probably oligomeric with short chains, whereas **II** is insoluble in any solvent, which suggests a three-dimensional or chainlike structure. The reason why a tubular morphology is adopted by **I** is not yet understood and the reaction mechanism requires further clarification.

Heating compound **I** under an inert gas flow at 823 K leads to its decomposition with formation of pure MoS₂ [Fig. 2(d)]. Decomposition of **I** was monitored by mass spectrometry which established a multistep process with formation of water and ammonia at *ca.* 435 K, and water and nitrogen at 683 K. According to thermogravimetric analysis, the mass loss at 823 K was 64%, whereas the calculated value for (NH₃OH)₄MoS₅ decomposition to MoS₂ is 59%. The MoS₂ obtained from **I** showed a specific surface area of 65 m² g⁻¹ with retention of the same tubular morphology as the precursor. The synthesis reported here provides therefore a route to large scale production of hollow microtubules of the technologically very important MoS₂.

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