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Template-Free Solution Synthesis of Sulfur Microtubules

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Nanomaterials possessing elaborate morphology (tubes, spheres, helices, etc.) attract considerable attention of researchers from different domains of chemistry.[1,2] After the pioneering works in which carbon[3] and metal halcogenide[4] nanotubes were prepared under severe reaction conditions, many soft methods were developed for producing such structures. Usually complex organic molecules are used as the structure-directing agents[5] or as building units[6] in these preparations. Nevertheless, it was shown that in some cases inorganic materials are susceptible to produce on their own complex morphologies.[7−12] Thus, particular acid−base properties of the sheets present in the structure of some niobates[7] or perovskites[8] allow them to acquire a non-zero curvature in solution. In the case of single-crystal tellurium nanotubes prepared in ethylene glycol,[9] it was clearly demonstrated that a particular shape is due to concentration depletion at the surface of seeds. It was found however that some *amorphous* materials can also form microtubules or hollow microspheres without any complex organic molecule added.[11,12] As in this case no predefined structural units such as sheets or chains can be involved in this formation, another physical mechanism accounting for the particular morphology should therefore exist. In the present work we describe the preparation conditions, composition, and some structural features of a new type of such solid−sulfur microtubules obtained in acetone solution in the presence of $(NH_4)_2Mo_2S_{12}$.

The detailed experimental procedure was as follows: 300 mg of sulfur (high purity, Merck) and 100 mg of $(NH_4)_2Mo_2S_{12}$,$2H_2O$ (ATDM, prepared according[13]) were mixed with 200 mL of acetone and heated to 50 °C under stirring. Just after the temperature was attained, the mixture was filtered into a warm recipient. (For well-defined microtubules to form, it is important to avoid a rapid precipitation during filtration.) The brown suspension obtained was allowed to cool to room temperature and after ≈15 min a light bulky precipitate began to appear. The mixture was allowed to evaporate at room temperature to half its initial volume. At this stage the suspension contains two different solid phases: flocculated microtubules in the precipitate and suspended fine particles of $MoS_{5.6}$ formed through the condensation of $(NH_4)_2Mo_2S_{12}$.[14] To separate these solids, the mixture was filtered through a Whatman 4 paper filter without sucking: the particles of molybdenum sulfide are sufficiently small to pass through the filter while the microtubules agglomerates are retained. The light brown solid obtained was dried in air at room temperature without any washing. The scanning electron micrographs were taken on a JEOL 6400F instrument. For transmission electron microscopy (Hitachi H9000NAR, operated at 300 kV) the solid was dispersed in water without previous grinding and after sonification the suspension was deposited on a carbon-coated Cu grid. The solids were characterized by X-ray diffraction (XRD) (Siemens D5000), Raman spectroscopy (Brucker IFS-100), X-ray photoelectron spectroscopy (XPS) (VG ESCALAB 200R, C 1s binding energy at 284.5 eV), and thermogravimetry analysis (TGA) (SETARAM TGA92, N_2 flow at 5 °C/min).

The SEM images of the solid (Figure 1) show the aggregates of microtubules of 5−100 μm length and 100−400 nm outer diameter. As shown by the images of the extremities and wall imperfections, the objects are hollow. Along with single well-defined tubules, some bundles can be observed in which the tubules are tightly bound or even intergrown. The TEM images (Figure 2) confirm that the microtubules are hollow and reveal that compared with the outer diameter the tube walls are thin, ca. 10 nm. No diffraction picture has been observed from the microtubule walls, which suggests that they are amorphous. Nevertheless, the XRD pattern of the solid contains some peaks of low intensity, characteristic of monoclinic sulfur (JCPDS N 34-0941), which is probably present as traces (vide infra).

Chemical analysis shows that the microtubules consist mainly of sulfur: 96.1 wt % S, 2.8 wt % Mo, and 0.9 wt % C. This gives an atomic S/Mo ratio close to 100, rather unrealistic for any individual molybdenum sulfide compound. We observed also that the solid obtained almost completely dissolves in CS_2, ethanol, or acetone and we thus supposed that the microtubules walls are composed mostly of elemental sulfur. Five

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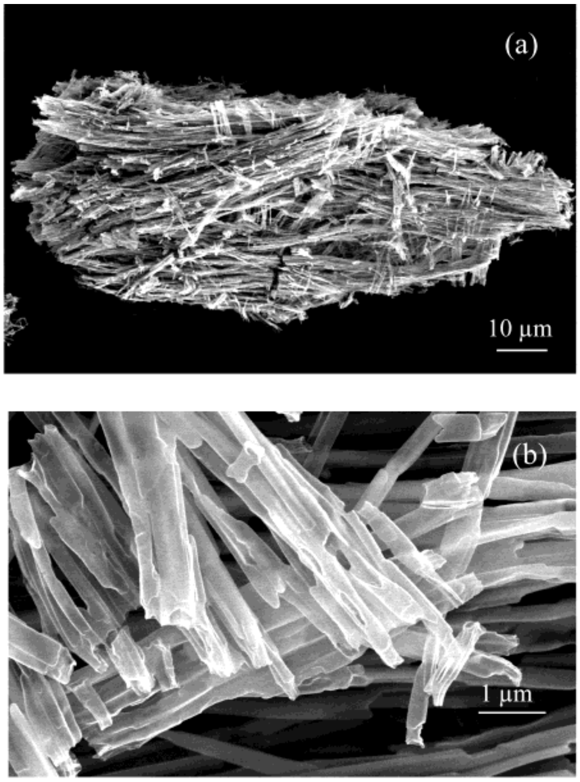

Figure 1. Low- (a) and high-magnification (b) SEM micrographs of the particle of the solid prepared in the work.

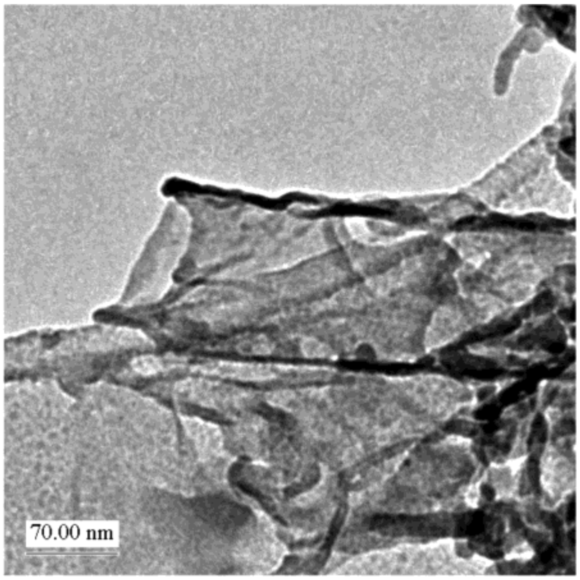

Figure 2. TEM image of a single sulfur microtubule.

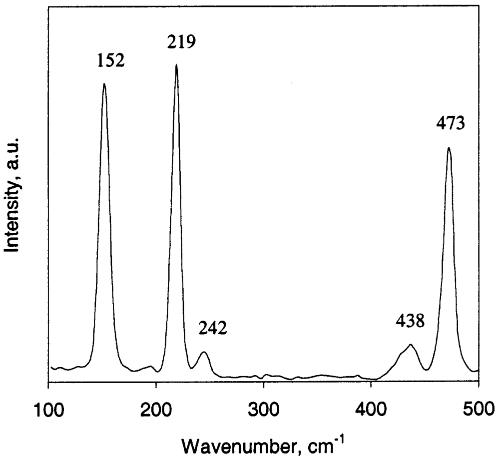

Figure 3. Raman spectrum of the microtubular solid.

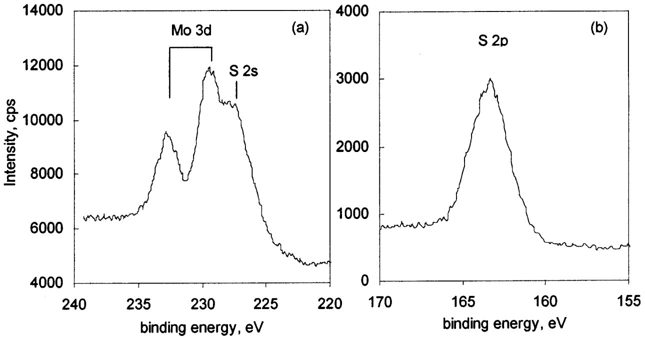

Figure 4. X-ray photoelectron spectra: (a) Mo 3d and (b) S 2p of sulfur microtubules.

well-defined peaks at 152, 219, 242, 438, and 473 cm^{-1} were observed in the Raman spectrum of our sample (Figure 3). The peak positions are close to those reported previously as Raman active S_8 ring fundamental vibrations.[15] As the peaks characteristic of $(-S-)_n$ chains (273, 416, and 456 cm^{-1} [16]) are absent, it can be concluded that the solids obtained in our work consist mostly of S_8 molecules. The uniform mass loss observed on the TGA curve corresponds to sulfur evaporation and the small feature observed at ca. 430 °C to decomposition of minority molybdenum sulfide species with the formation of the most stable form, MoS_2.

The XPS spectrum of the tubular solid (Figure 4) reveals the $Mo3d_{5/2}$ binding energy (229.3 eV), which is typical for sulfur-reach molybdenum sulfides (for example, 229.1 eV for MoS_3, 229.0 eV for $(NH_4)_2Mo_3S_{13}$[17]). The width of the S 2p peak (fwhm = 3.2 eV) is indicative of the presence of different forms of sulfur, its position (163.3 eV) allowing the conclustion that both elemental sulfur (164.0 eV[18]) and various S_2^{2-} species (161.6–163.0 eV[17]) are present on the surface of the sample. The atomic S/Mo ratio determined from the XPS spectra (6.7) is significantly lower than the bulk ratio, which means that the composition of the microtubules is not uniform and the surface layer of the particles consists mainly of Mo-containing species.

We have found previously that the tubular, vesicle-like, and sponge-like particles of Mo oxysulfides can be obtained in a similar system (ATDM in acetone solution) but under different reaction conditions.[19] It was shown that the formation of these patterns can be related to the presence of oligomeric species formed from $Mo_2S_{12}^{2-}$ anions and comprising the counterparts with different polarities. The particular structure of these oligomeric species makes their behavior in solution similar to that of organic surfactant molecules. We suppose that similar oligomeric species formed from $(NH_4)_2Mo_2S_{12}$ in the

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present study and play a key role in the morphogenesis of the microtubules. The sulfur molecules can be incorporated in less polar domains of aggregates formed by thiomolybdate oligomeric species similarly to nonpolar organic molecules, which can be solubilizied in the hydrophobic domain of surfactant-formed structures. The fact that the microtubule walls are amorphous means that the sulfur molecules are really engaged in some interactions, as otherwise they would produce crystals on cooling. This assumption accounts also for the surface enrichment of the tubules with Mo: as in the case of organic systems the nonpolar molecules (S_8 in our case) are located in the interior (less polar domain) of the aggregates, the interface with the solvent being constituted by more polar counterparts of Mo-containing species.

In conclusion, amorphous sulfur microtubules ($L = 5-100\ \mu m$, $d = 100-400$ nm) can be prepared in acetone solution in the presence of $(NH_4)_2Mo_2S_{12}$ without any organic structure-directing agent. It is supposed that the interaction between S_8 molecules and condensation products of molybdenum thioanions plays a key role in the formation of the tubular particles.

Supporting Information Available: XRD pattern and TGA curve of the tubular solid prepared in the work (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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