Mo$_6$S$_{4.5}$I$_{4.5}$ Nanowires: Structure Studies by HRTEM and Aberration Corrected STEM

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Abstract. The atomic structure of subnanometer diameter Mo$_6$S$_{4.5}$I$_{4.5}$ nanowires and their superlattice packing in bundles have been studied by High Resolution Transmission Electron Microscopy (HRTEM) and Aberration Corrected Scanning Transmission Electron Microscopy (STEM). The individual nanowires are best described as one-dimensional Mo-chalcogenide-halide cluster polymers, composed of Mo octahedra, surrounded by iodine atoms and connected by bridging planes of 3 sulfur atoms. The nanowires are weakly bounded together into bundles by Van der Waals forces in a trigonal packing arrangement, with a nanowire to nanowire distance of 0.96 nm.

1. Introduction
Recently one-dimensional inorganic nanowires have been receiving growing attention as a viable alternative to carbon nanotubes and nanostructured, tube-like materials in general. Good example are the Mo$_6$S$_{9-x}$I$_x$ family (1) which can easily be fabricated, dispersed and processed. In addition, uniformity in terms of diameter and electronic structure, makes Mo$_6$S$_{9-x}$I$_x$ nanowires one of the most promising one-dimensional materials. However, in spite of the rapid progress in understanding the functional properties and applications of Mo$_6$S$_{9-x}$I$_x$ nanowires, their detailed structure has so far been unknown. This is because of the inherent difficulty in determining the structure of bent and twisted bundles of weakly bound nanowires. This lack of structural information has proved to be a serious obstacle to further investigations of the fundamental properties of this important new class of materials. In the present work we report on the results of a detailed investigation of the structure of Mo$_6$S$_{9-x}$I$_x$ nanowires using two electron microscopy techniques, high resolution electron transmission microscopy (HRTEM) and scanning transmission electron microscopy (STEM) combined with crystallographic modelling and simulation processes.

2. Experimental method
Mo$_6$S$_{4.5}$I$_{4.5}$ nanowires have been obtained by direct synthesis from elemental material mixed in stoichiometrical quantities [1]. The as grown material has been purified from impurities and other unwanted phases as previously reported [2]. Solutions of the purified phase in isopropanol at a
concentration of 0.1 mg/ml have been prepared and deposited by drop casting on holey carbon grids (300 mesh) in order to perform the microscopic characterization. High resolution TEM characterization has been carried out using a JEOL-3000. Scanning transmission electron microscopy (STEM) studies have been performed using a VG HB501 instrument fitted with a Nion Cs corrector. Crystallographic modeling has been carried out on the basis of the features appearing in the HRTEM STEM images, using the software “CrystalMaker 5.2”.

3. Results and Discussion

3.1. Background
Crystallographic libraries on molybdenum chalcogenides and a combined X-ray powder diffraction - X-ray absorption fine structure (XAFS) study on Mo₆S₉₋ₓIₓ recently carried out by A. Meden et al., have been used to find the preliminary coordinates of the nanowire backbone as a starting point for our systematic electron microscopy study. The structure of the single nanowire and of the nanowire bundles proposed are shown in figure 1. The single nanowire is there described as a one-dimensional Mo-chalcogenide-halide cluster polymer, composed by Mo octahedrons surrounded by trimers of sulfur, connected by bridging planes of 3 iodine anions.

The consistently appearing features of the described model were: a) the absence or a low occupancy (below 20%) of the central face-bridging sulphur atom (shown yellow in figure 1); b) full iodine occupancy of the corner-bridging atoms (labelled B in figure 1); c) mixed occupancy of the non-bridging surface anions (A in figure 1). Single nanowires appear to prefer aggregation in hexagonal or trigonal symmetries.

3.2. Adapting the background knowledge to the experimental microscopical evidences
HRTEM and above all aberration corrected STEM have been used to make detailed refinements to the described atomic structure. The most interesting experimental evidences derive in particular from the annular dark field (ADF) STEM characterization. This technique has in fact the strong advantage to be highly sensitive to the atomic number (Z contrast), resulting in images in which composition changes are more strongly visible than in the case of HRTEM imaging. Figure 2 shows in detail two dark field images of typical Mo₆S₄.₅I₄.₅ nanowire bundles.

Fig.2 clearly reveals various regions of interest, characterized by distinct geometrical motifs, differentiated by aspect (diagonal, perpendicular or parallel lines respect to the nanowire axis), spacings and angles. Those patterns can be related to the fact that the nanowire bundles do no not sit on the grid showing always the same crystallographic face; moreover, as these systems possess very low sheer modulus, a twisting process along the axis of the same nanowire bundle may occur as showed in figure 2a. This therefore produces different projections. In table 1 we report the exact dimensions (angles and spacings) of the 7 fringe patterns observed in more than 200 HRTEM and STEM pictures.
Table 1

|         | Angles respect to the nanowire longitudinal axis (°) | Spacing (nm) |
|---------|------------------------------------------------------|--------------|
| 1       | 0                                                    | 0.84 ± 0.04  |
| 2       | 0                                                    | 0.175 ± 0.015|
| 3       | 146.86                                              | 0.205 ± 0.019|
| 4       | 128.89                                              | 0.237 ± 0.021|
| 5       | 123.17                                              | 0.158 ± 0.027|
| 6       | 119                                                 | 0.15 ± 0.014 |
| 7       | 90                                                   | 0.207 ± 0.02  |

In order to refine the Mo$_6$S$_4$I$_4$ nanowire structure and get information about the superlattice packing in bundles, models having always the same stoichiometry but with different distribution of atomic occupancies have been simulated. Accepting Meden et al.’s molybdenum octahedral configuration, the research has been extended to the 14 most probable surrounding atomic environments, involving different allocation of sulfur and iodine around the molybdenum backbone; the superlattice study has been extended to the two most probable space groups indicated by the XRD and XAFS studies [3], the hexagonal P$_{63}$ (nr. 173) and the trigonal with rhombohedral lattice R-3 (nr. 148). In figure 3 we report the Mo$_6$S$_4$I$_4$ nanowire unit cell that we propose as the most likely to be the correct one, since it is so far the only one to give perfect agreement to the patterns and angles observed at the electron microscopes. The backbone of the unit cell is again mainly defined by the octahedral molybdenum structures (in red in figure 3) but this time sulfur atoms form trimers in the linking plane; the two central layers result to have mixed occupancy; iodine trimers are bonded to the first and last layers of molybdenum. The total numbers of atom in the unit cell results to be 30 (12 Mo, 9 I and 9 S).

Finally in table 2 we present four of the seven bundle orientations (those ones related to the patterns in fig. 2) able to explain the crystallographic features evidenced by electron microscopy. The trigonal symmetry group R-3 successfully explains 7 fringe patterns (table 1) on 7, while the hexagonal P$_{63}$ is in agreement with only 4 of them.
Table 2

| Image | Front view of the bundle | Side view of the bundle in the 2-1-0 direction |
|-------|--------------------------|-----------------------------------------------|
| 2a    | ![Image Front view of the bundle](image1) | ![Side view of the bundle in the 2-1-0 direction](image2) |
| 2a    | ![Image Front view of the bundle](image3) | ![Side view of the bundle in the 2-1-0 direction](image4) |
| 2b    | ![Image Front view of the bundle](image5) | ![Side view of the bundle in the 2-1-0 direction](image6) |
| 2c    | ![Image Front view of the bundle](image7) | ![Side view of the bundle in the 2-1-0 direction](image8) |

4. Conclusion

HRTEM and STEM, supported by XRD and XAFS characterizations, and combined with crystallographic modelling and simulation processes, have been used to study the structure of Mo$_6$S$_{4.5}$I$_{4.5}$ nanowires and the way they pack in bundles. The single nanowire can be described as a one-dimensional Mo-chalcogenide-halide cluster polymer, composed by Mo octahedrons surrounded by trimers of iodine, connected by bridging planes of 3 sulfur atoms. Superlattice structures, such as the nanowire bundles, can be described by the trigonal space group R-3 (nr. 148).

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