Supplementary Material (ESI) for Nanoscale

Supporting Information for:

Insights into the capping and structure of MoS_2 nanotubes as revealed by aberration-corrected STEM

by Francis Leonard Deepak, Alvaro Mayoral, Andrew J. Steveson, Sergio Mejía-Rosales, Douglas A. Blom and Miguel José-Yacamán*

MoO_3 nanobelts

In a typical synthesis, 100 mg of Mo powder was placed in a 250 mL beaker in a Petri dish with water on a magnetic stirring plate. Under light stirring, 10 mL of H_2O_2 (30 wt % in H_2O) was then added slowly. The solution rapidly turned to an orange-yellow color. After 10 minutes of continuous stirring, the clear orange solution was transferred to a Teflon container which was then loaded into an autoclave. The autoclave was heated in an oven at 180 ^oC for 12-24 hours. After this time period, the autoclave was allowed to cool and the white powder was collected and washed thrice with H_2O and ethanol and dried overnight in the oven.

Figs. 1a and b show the SEM and TEM images of the MoO_3 nanobelts synthesized using Mo powder and H_2O_2. Large yields of the as-synthesized nanobelts can be clearly seen from the images. The length of the nanobelts extends upto several tens of microns whereas the diameter of the nanobelts is in the 300-500 nm range (Fig. S1b). The selected area electron diffraction (SAED) pattern shown in Fig. S1c reveals the single crystal structure of the nanobelts with diffraction spots corresponding to (002) and (200) lattice planes of orthorhombic MoO_3 (α-MoO_3). The nanobelts grow along the <001> direction due to the intrinsic structural anisotropy and growth rate (r_{hkl}) variation in all three principal directions $r_{001} > r_{100} > r_{010}$.[1,2] The SEM-EDAX spectrum (Fig. S1d) confirms the presence of the respective elements of Mo and O as revealed by the characteristic and distinct Mo (K,L) and O (K) lines. The atomic ratio of Mo:O is found to be close to 1:3. Further evidence for the presence of only Mo and O in the nanobelts can be inferred from the elemental maps of Mo (Mo-L) and O (O-K) (Fig. S1e and f).

MoS_2 nanotubes

Fig. S2 shows the SEM image of the MoS_2 nanotubes that were obtained starting from the MoO_3 nanobelts and using a mixture of gases of H_2/H_2S at 900 °C. Copious amounts of nanotubes were obtained during the synthesis as can be seen from the images wherein the length of the nanotubes extends upto a micron.

Fig. S3a depicts the HRTEM images of well faceted MoS_2 nanotubes. The nanotube of ~ 100 nm in diameter exhibits an unusual faceted closed end. The thickness of the wall is approximately 15 nm and the nanotubes have about 15-20 layers (Fig. S3b). The individual and distinct layers are clearly differentiated in the image. The layers correspond to the d_{002} planes, with a lattice distance of 0.633 nm, as shown by the line profile in Fig. S3c. STEM-HAADF images of the MoS_2 nanotubes, obtained from a JEOL 2100F operated at 200 kV, with a probe size of 0.5 nm, are shown in Fig. S3d. A close-up view of the individual layers of the nanotubes is shown in Fig. S3e (corresponding to the region marked by the box in Fig. S3d). The fact that the nanotubes are composed of only Mo and S is revealed by the line scan analysis that was carried out along the entire diameter of the nanotube (Fig. S3f). The compositional analysis revealed a ratio of 1:2 between Mo and S, in accordance to the formation of MoS_2.

A schematic representation of the various cap formations are shown in Fig. S4. Fig. S4a shows the schematic of the sharp 90° bends of the cap with respect to the nanotube. The two variations in the conical capped nanotubes are shown in the schematics in Figs. 4b and 4c. The more facetted octagon-like capped structure is shown in the schematic of Fig. S4d.

Figure Captions

Fig. S1 (a) and (b) SEM and TEM images of the MoO_3 nanobelts synthesized from Mo powder and H_2O_2, (c) SAED pattern of α-MoO_3 taken along the [010] orientation of the crystal and indexed assuming orthorombic symmetry, (d) EDAX spectrum of the MoO_3 nanobelts and the corresponding elemental maps of Mo (L) (e) and O (K) (f).

Fig. S2 (a) and (b) SEM image of the MoS_2 nanotubes that were obtained starting from the MoO_3 nanobelts and using a mixture of gases of H_2/H_2S at 900 °C.

Fig. S3 (a) TEM image of a MoS_2 nanotube with an unusual facetted closed cap, (b) Closer look at the capped end of the nanotubes: HRTEM image of the capped edge of the MoS_2 nanotube showing showing the lattice fringes corresponding to the d_{002} layers, (c) Line profile showing the spacing of the MoS_2 layers to be 0.63 nm, (d) STEM-HAADF image of a MoS_2 nanotube, (e) A High resolution STEM image of one of the corners, marked by a square, is shown, f) A line scan analysis carried out on the nanotube shows the composition of Mo (in blue) and S (red).

Fig. S4 (a)–(d) Schematic models showing the different caps observed in the present study, (a) Nanotube with a flat cap structure, (b) and (c) Variations of the conical caps, (d) Nanotube with a half-octagon cap.

References

1 H. C. Zeng, *Inorg. Chem.*, 1998, **37**, 1967–1973.

2 H. C. Zeng, C. W. Sheu and C. H. Hia, *Chem. Mater.*, 1998, **10**, 974–979.

Fig. S1

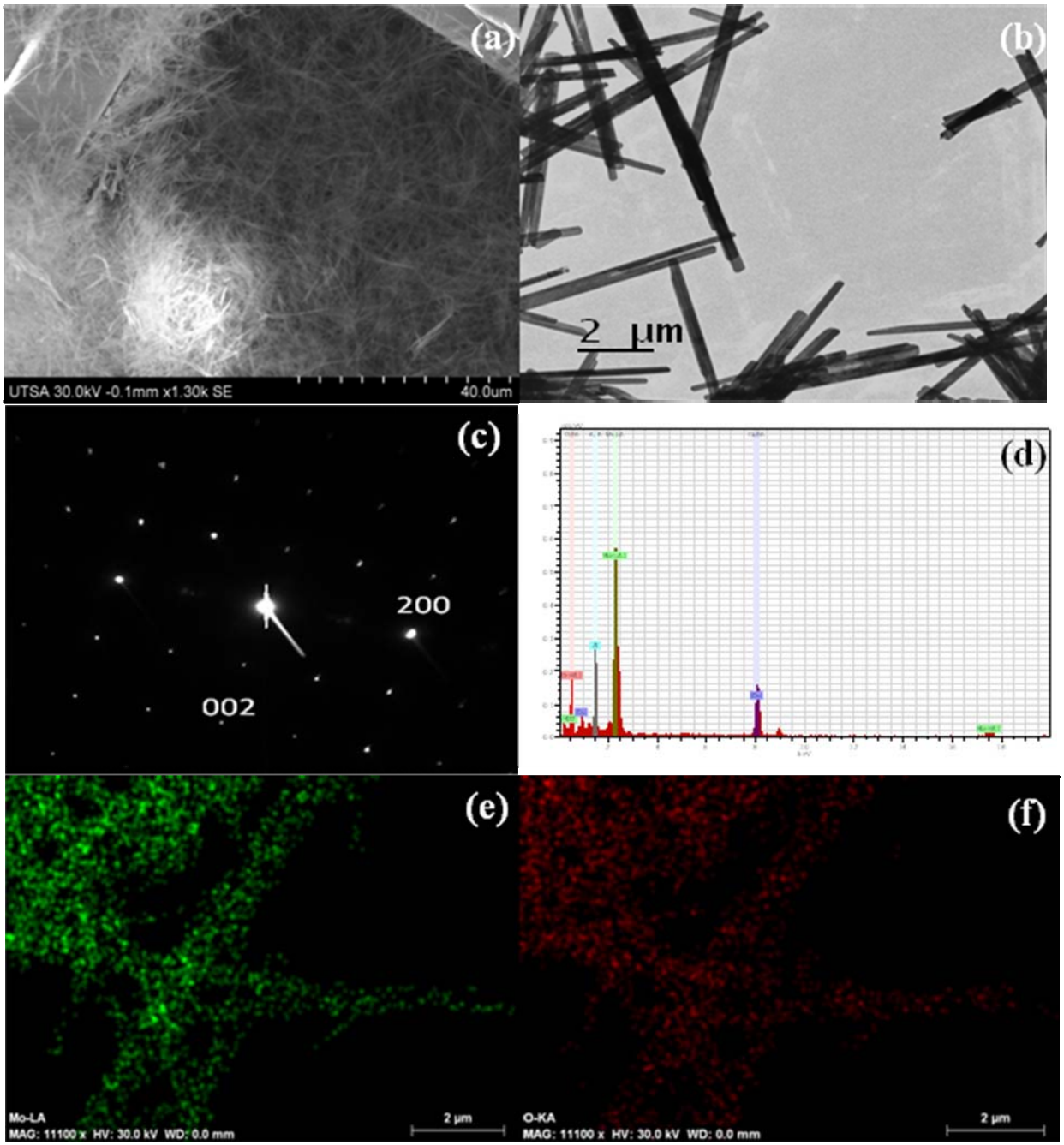

Fig. S2

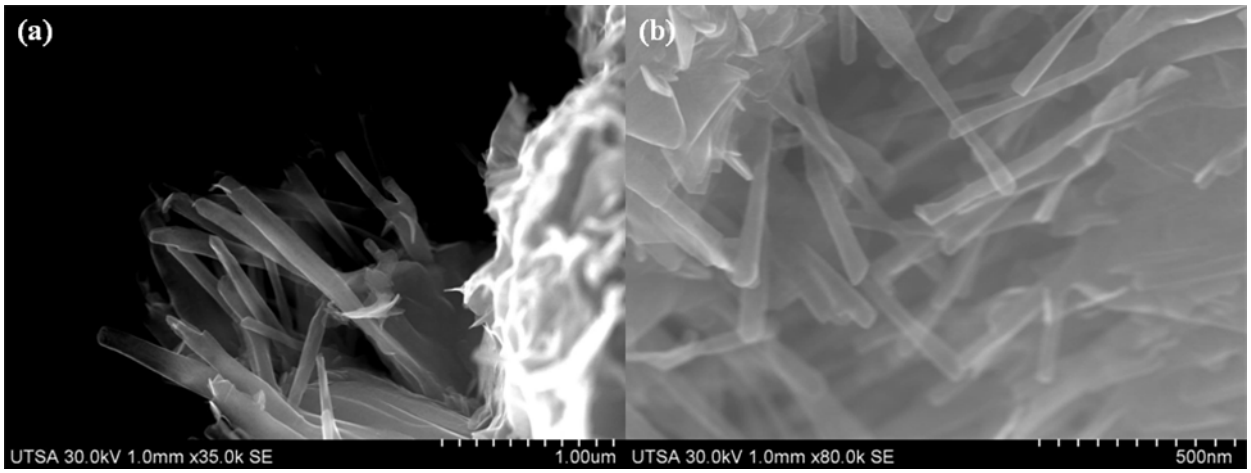

Fig. S3

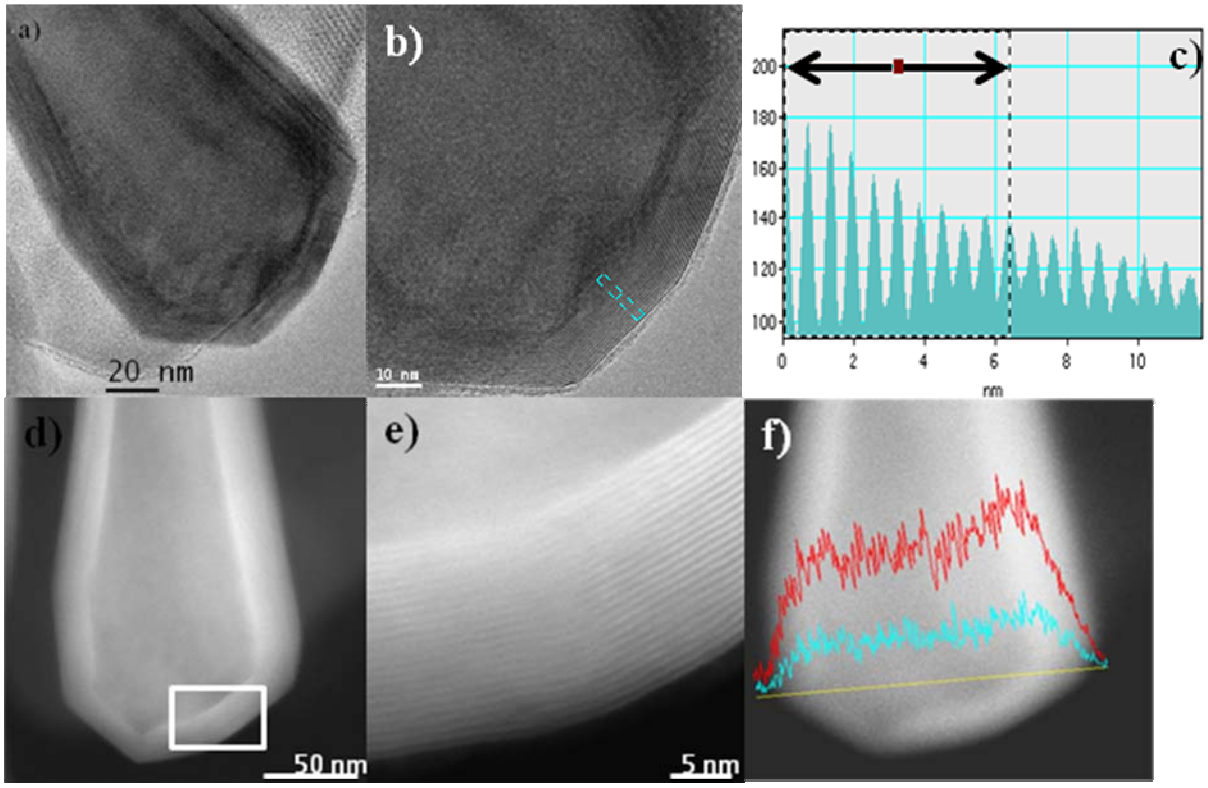

Fig. S4