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Aberration corrected imaging of a carbon nanotube encapsulated Lindqvist Ion and correlation with Density Functional Theory

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Abstract. 80 kV aberration-corrected transmission electron microscopy (AC-TEM) of discrete $[W_6O_{19}]^{2-}$ polyoxometalate ions mounted within double walled carbon nanotubes (DWNTs) allow high precision structural studies to be performed. W atom column separations within the octahedral W_6 tungsten template can be visualized with sufficient clarity that correlation with full-scale density functional theory (DFT) can be achieved. Calculations performed on the gas phase and DWNT-mounted $[W_6O_{19}]^{2-}$ anions show good agreement, in the latter case, with measured separations between pairs of W_2 atom columns imaged within equatorial WO_6 octahedra and single W atoms within axial WO_6 octahedra. Structural data from the tilted chiral encapsulating DWNT was also determined simultaneously with the anion structural measurements, allowing the nanotube conformation to be addressed in the DFT calculations.

1. Introduction

In tandem with the burgeoning interest in a wide diversity of nanoscale structures, associated studies into single molecules are becoming more prevalent. Advances in atomic probe-type (i.e. AFM, STM or similar) [1] and electron microscopy [2,3] atomic and molecular imaging techniques are making efficient comparison between experimentally determined discrete structures and *ab initio* or *a posteriori theory* more routine. A key aspect of these investigations is the correlation of intramolecular perturbations with effects induced by the local environment. Polyoxometalate ions (POMs) are of interest in this respect as they have an extensive structure-synthetic chemistry enabling a wide variety of ordered molecular-scale cluster anions to be produced with variable charge-ordering arrangements [4]. In the present context, they provide molecular-scale heavy atom motifs with observable symmetry than can be imaged by conventional high resolution transmission electron microscopy (HRTEM) when mounted in single or double walled carbon nanotubes (i.e. SWNTs or DWNTs) or graphene oxide [5,6]. We have previously been able to image the octahedral O_h symmetry Lindqvist $[W_6O_{19}]^{2-}$ ion in DWNTs [5] (Fig. 1(a)) by HR-TEM and have imaged the W_2 - W_2 atom column separations in the equatorial plane of the anion. A limitation of this study was that information from the corresponding axial W atom columns was blurred however a minimum requirement for an

effective comparison with theory is that at least two dimensions of the anion be resolvable. We demonstrate here that it is possible to do this for individual ions by aberration corrected transmission electron microscopy (AC-TEM) and also that we are able to obtain conformational information from the nanotube simultaneously [7]. This allows us to produce trial composite anions and nanotube conformations for investigating both structural and electronic interactions between the encapsulated anion and the nanotube using DFT.

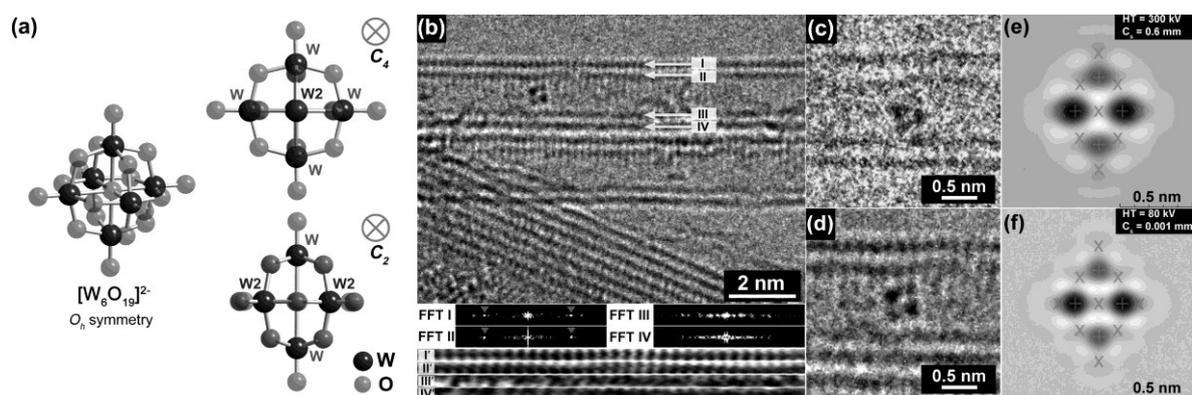


Fig. 1 a) Perspective view, C_4 projection and C_2 projection of the $[W_6O_{19}]^{2-}$ ion; b) 80 kV AC-TEM image of $[W_6O_{19}]^{2-}$ ion in a DWNT with fast fourier transforms of the two pairs of opposing walls **I-IV** (i.e. **FFT I-FFT IV**) and corresponding filtered images (i.e. **I'-IV'**) at bottom; c) & d) Details from 300 kV ($C_s = 0.6$ mm) image and 80 kV ($C_s = 0.001$ mm) image of $[W_6O_{19}]^{2-}$ ions in a DWNT. e) & f) corresponding image simulation of the $[W_6O_{19}]^{2-}$ ion, using the same imaging conditions as c) and d).

2. Experimental Details

The DWNTs used in this experiment were supplied by Carbon Nanotechnology Inc. $[nBu_4N]_2[W_6O_{19}]$ was prepared and inserted into DWNTs from an ethanolic solution. The previous 300 kV HR-TEM image of the $[nBu_4N]_2[W_6O_{19}]@DWNT$ composite was obtained on a JEOL 3000F instrument (Oxford) with an objective C_s of 0.6 mm and a 300 kV accelerating voltage [5]. 80 kV images were obtained from the freshly prepared $[nBu_4N]_2[W_6O_{19}]@DWNT$ composite in a JEOL 2010F AC-TEM (Tsukuba) equipped with a CEOS corrector for which C_s was tuned to 0.001 mm. Image simulations were performed using the multislice package SimulaTEM. Nanotube models were generated using the program Nanotube Modeler from JCrystalSoft (©2004-2011). Full scale CASTEP DFT calculations were performed using High Performance Computing (HPC) facility at the University of Nottingham.

3. Results

The previous imaging study of $[W_6O_{19}]^{2-}$ ions mounted within DWNTs [5] revealed that within sterically matched nanotubes with an innermost ~ 1.2 nm diameter SWNT the ions lie with a preferred orientation within the encapsulating cylindrical volume, specified by the van der Waals radii of the wall carbons (i.e. 0.17 nm), of diameter ca. 0.9 nm. This orientation (which is projected along the C_2 rotation axis of the anion – see Fig. 1(a)) conveniently enables W_2 - W_2 atom column pairs within the equatorial plane of the $[W_6O_{19}]^{2-}$ superoctahedron, to be directly visualised by a conventional HR-TEM with an objective lens coefficient of spherical aberration, C_s (alternatively, C_s), of 0.6 mm. Multislice image simulation studies showed that this level of aberration blurs the image contrast from the W_2 - W_2 atom column pairs once the contribution of the equatorial terminal oxygen atoms is taken into account. Additionally, image contrast from the single atom W-W pair was blurred or missing. Fig. 1(b) shows a wider field of view image of two parallel DWNTs, one empty, one containing a discrete $[W_6O_{19}]^{2-}$ anion. Comparison of a detail of the same structure anion as imaged using the 300 kV HR-TEM ($C_s = 0.6$ mm) in Fig. 1(c) with the same structure anion using the lower voltage (i.e. 80 kV) AC-TEM ($C_s = 0.001$ mm) imaging conditions in Fig. 1(d) shows the improvement in detail.

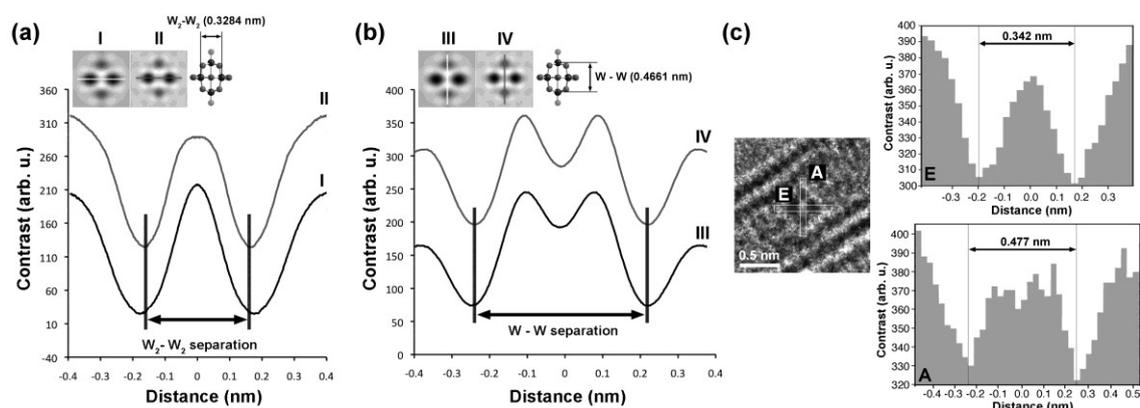


Fig. 2 a) Line profiles through simulated equatorial W_2-W_2 atom column pairs (I 300 kV, $C_s = 0.6$ mm; II 80 kV, $C_s = 0.001$ mm); b) as for a) but for line profiles through W-W atom column pair (I 300 kV, $C_s = 0.6$ mm; II 80 kV, $C_s = 0.001$ mm). c) (left) 80 kV image ($C_s = 0.001$ mm) of the $[W_6O_{19}]^{2-}$ ion from Figs. 1(b) and (d). (right) Experimental line profiles E and A through W_2-W_2 atom column pair and W-W atom column pair respectively.

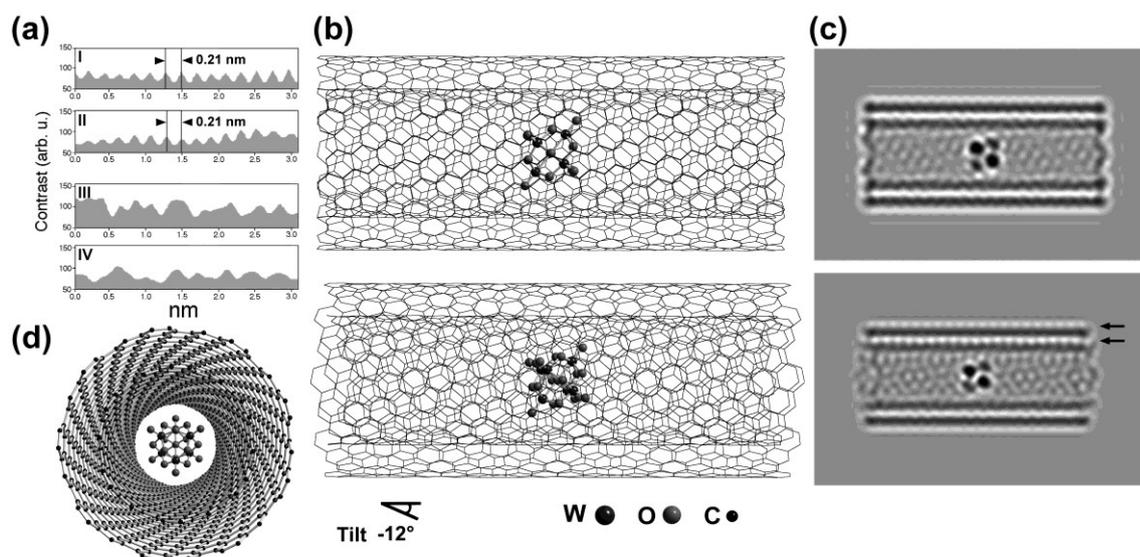


Fig. 3 a) Line profiles I-IV obtained through the four filtered images I'-IV' in the bottom part of Fig. 1(b). The upper two walls have a periodicity of ca. 0.21 nm whereas the lower walls are aperiodic. b) Models corresponding to a $[W_6O_{19}]^{2-}@(12,6)@(18,9)$ DWNT. The top model is untilted and the bottom model tilted 12° out of plane. c) Multislice image simulations from the two configurations in Fig. 4(b). Only the bottom simulation exhibits wall carbon spacings on the uppermost two walls. d) Perspective end-on model of the $[W_6O_{19}]^{2-}@(12,6)@(18,9)$ DWNT in Fig. 2(b).

An indication of the improvement in information in the AC-TEM images can be made using line profiles through W_2-W_2 and W-W atom column pairs in multislice image simulations for both cases (i.e. Figs. 1(e) and (f)) as shown by the extracted equatorial and axial profiles (i.e. Figs. 2(a) and (b)). As noted previously, there is a $\sim 5\%$ distortion in the W_2-W_2 column separation for the more aberrated case partly due to higher C_s but also to the smearing contribution of the O_3 columns on the anion periphery [5]. This distortion is reproduced in Fig. 2(a) in which the troughs of profile I corresponding to the W_2 columns are displaced $\sim 5\%$ with respect their expected positions. Profile II in Fig. 2(a) corresponds to the simulated W_2-W_2 atom column pairs for the AC-TEM but with $C_s = 0.001$ mm. In this case, the troughs are displaced $\sim 1\%$, reflecting a greater confidence in the new measurements. According to profiles III and IV in Fig. 2(b), there is little distortion of the axial W-W columns in

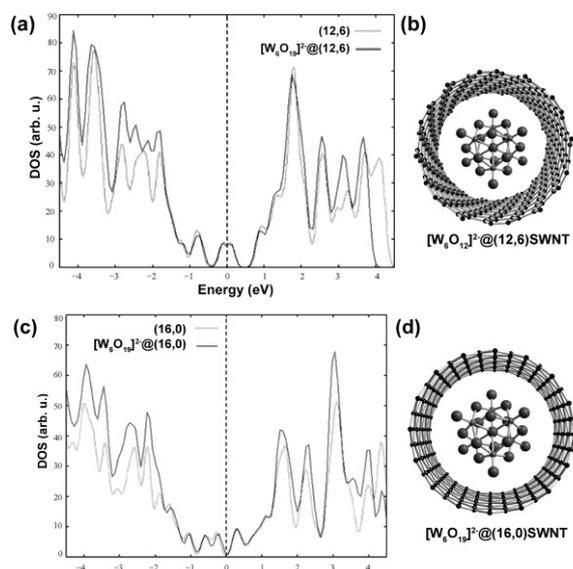


Fig. 4 a) DOS plots for metallic $[W_6O_{19}]^{2-}@ (12,6)$ composite. b) Optimised structure of $[W_6O_{19}]^{2-}@ (12,6)$ SWNT. c) and d) DOS plot and optimized structure for semiconducting $[W_6O_{19}]^{2-}@ (16,0)$ SWNT.

either the 300 kV or 80 kV images but the image contrast from the 300 kV image (Fig. 1(c)) is too noisy to produce a reliable measurement. In Fig. 2(c) we see that it is possible to measure the atom column spacings for both equatorial W_2 - W_2 and axial W-W separations for the 80 kV case (i.e. 0.342 and 0.477 nm respectively, precision ± 0.026 nm). Additionally we have also been able to resolve the wall carbon spacings on one side of the DWNT (Figs. 1(b) and (d)). Line profiles through all four walls (Fig. 3(a)) show that the top walls have an average periodicity of 0.21 nm whereas the bottom walls are aperiodic. Observation of wall carbon spacings on one side the DWNT indicates that it is chiral and tilted (Figs. 3(b) and (c)).

Reliable comparisons can now be made between the observed measurements and optimised structure models of $[W_6O_{19}]^{2-}@DWNT$ composites produced by DFT (in practice the innermost SWNT is only considered). In the first instance, we can differentiate optimised models produced for metallic $[W_6O_{19}]^{2-}@ (12,6)$ (Fig. 4(a) and (b)) and semiconducting $[W_6O_{19}]^{2-}@ (16,0)$ composites (Figs. 4(c) and (d)) The densities of states (DOS) plot in Fig. 4(a) is evidently more appropriate for comparison with the experimental case. We can

also now compare both experimentally determined and DFT-optimised equatorial W_2 - W_2 and axial W-W separations. The experimental measurements for the equatorial and axial separations (i.e. 0.342 and 0.477 nm, see above) compare reasonably with the corresponding DFT optimised gas phase separations (i.e. 0.333 and 0.471 nm, respectively) and optimised $[W_6O_{19}]^{2-}@ (12,6)$ SWNT separations (i.e. 0.331 and 0.471 nm, respectively) [7].

4. Conclusions

High quality structural detail can be obtained by AC-TEM at 80 kV from DWNT-encapsulated $[W_6O_{19}]^{2-}$ ions. The obtained structural information compares favourably that obtained from DFT and the enhanced resolution also allows for conformational information from the DWNT to be included.

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