Aberration-corrected electron microscopy processing and imaging of novel organic and inorganic nanostructures

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Abstract. One dimensional nanostructures such as organic and inorganic nanotubes, nanowires and graphene have generated much excitement among materials scientists in recent years. However difficulties associated with their lack of processability have seriously hampered the number of possible applications. Poor dispersability in most common solvents and tendency to bundle forming larger aggregates has been a hurdle in the way of real exploitation. The recent development of techniques able to disperse and exfoliate these 1D objects have captured much attention, strongly re-launching these materials towards the applicative scene. It is mandatory to understand at what extent these techniques are efficient and whether the atomic structures of these nanomaterials are damaged or remain pristine after dispersion and exfoliation in liquid media. Aberration-corrected electron microscopy becomes in this context a very attractive and unique tool to investigate these structures at atomic scale.

1. Introduction

One-dimensional nanostructured materials such as organic and inorganic nanotubes[1] and nanowires[2] are potentially useful in a number of areas of nanoscience and nanotechnology due to their remarkable mechanical, electrical and thermal properties[3]. However, isolated and pure objects are rarely available to experimentalists. They tend to be produced in presence of large quantities of impurities and tend to aggregate into larger objects whose properties are generally inferior to those of isolated ones. In the last few years thermodynamic dispersion and exfoliation theories have been developed and showed to apply universally to 1D nanostructures of very diverse nature[4,5]. The first material which has benefited from these newly developed processing methods are the inorganic nanowires made up from molybdenum, sulfur and iodine (MoSI nanowires). Purification and dispersion in liquid phase media and exfoliation of the as-synthesised nanowire ropes down to single, sub-nanometer wide wires or very thin nano-sized bundles have allowed to study their previously unknown atomic structure[6-7]. Here we present an aberration-corrected scanning transmission electron microscopy (STEM) that was essential and extraordinarily suitable to pin down the extremely complicated structure of both individual nanowires and nano sized bundles of them. This was essential for unlocking the whole range of unexplored potential of these materials and render them applicable for innovative technologies. Another nanomaterial which has been at the centre of the most advanced

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nanotechnology research and that has most benefitted from a liquid phase dispersion method has been graphene. Until a few years ago the standard procedure used to make graphene was micromechanical cleavage[8], which is a very low yield production method. In order to fully exploit graphene’s outstanding properties, a mass production method was necessary and the development of a method to exfoliate cheap, commercial graphite in organic solvents down to large area single graphene flakes with high yield was one major achievement[5]. Before applying this method for real high-tech purposes it is imperative to see whether the graphene’s structure endures the exfoliation procedure. In order to do so, flakes were characterised by aberration-corrected high resolution transmission electron microscopy (HRTEM), revealing extremely high quality graphene structures.

**Experimental method**

MoSI nanowires have been obtained in the stoichiometry $\text{Mo}_6\text{S}_3\text{I}_6$ by direct synthesis from elemental material[9]. The as grown material was purified as previously reported[6], dispersed in acetone at a concentration of 0.01 mg/ml and deposited by drop casting on holey carbon grids (400 mesh). Scanning transmission electron microscopy (STEM) studies were performed using the Oxford Jeol 2200MCO instrument fitted with a Ceos Cs corrector. STEM characterisation on the nanowires was performed at 200kV. STEM simulations were performed using the Melbourne STEM program developed by L J Allen, S D Findlay and M P Oxley[10].

The commercial graphite purchased from Sigma-Aldrich (Product Number 332461) was dispersed and exfoliated in N-methylpyrrolidone (NMP) at concentration of 0.1 mg/ml as previously described (ref). The dispersion obtained was drop casted onto holey carbon grids (400 mesh size) and HRTEM performed using the Oxford Jeol 2200MCO instrument fitted with a Ceos Cs corrector, operated at 80kV.

**Results and Discussion**

1.1 $\text{Mo}_6\text{S}_3\text{I}_6$ nanowires

Crystallographic libraries on molybdenum chalcogenides and a combined X-ray powder diffraction (XRD) and X-ray absorption fine structure (XAFS) study on $\text{Mo}_6\text{S}_3\text{I}_6$ carried out by A. Meden and co-workers[11] were used to get preliminary structural information as a starting point for our systematic electron microscopy study. The predicted structure is shown in Figure 1a. In this model the hollow striped spheres represent Mo atoms, arranged in octahedral symmetry; the grey and black spheres represent instead two structural positions, peripheral (P) and linkage (L) sites respectively. XRD and XAFS were able to accurately determine the positions of the molybdenum octahedra and of both P and L sites but could not determine their occupancy in terms of sulfur or iodine atoms. Space groups of hexagonal-lattice $\text{P}6_3$ or trigonal lattice $\text{R}-3$ were suggested to describe the packing. Occupation of the L sites by iodine atoms was suggested.

![Figure 1](image_url)

**Figure 1.** a)The nanowire atomic structure as determined by XRD and XAFS [11]. Hollow striped, grey and black spheres represent Mo atoms, and Peripheral and Linkage sites respectively; b) ADF STEM image of a nanowire bundle cross section
Aberration corrected HAADF STEM was used to make detailed refinements to the suggested atomic structure. Making use of high angles of electron scattering, HAADF STEM is strongly dependent on atomic number (Z-contrast) and becomes an attractive methodology to detect the different atomic species in the structure of the nanowires. The heavy iodine atoms become with this technique particularly detectable. Figure 1b shows a cross section of a nanowire bundle confirming an hexagonal close packing with a nanowire-to-nanowire distance of 0.96nm. Representative images of the three different high symmetry projections are shown in Figure 2a,b,c. The fact that three different image types were observed for the three high symmetry directions immediately suggests deviations from the previously predicted structure (both R-3 and P63 possess rotational symmetries and that would lead to identical projections for the three high symmetry directions). These three patterns can only be reproduced if iodine is allocated to the P sites and the sulfur atoms in the L sites respectively. ADF simulations, obtained using allocation of the I in the P sites and S atoms in the L sites, are shown for a nanowire bundle from the three high-symmetry directions, α, β, and X. The out-of-phase zig-zag pattern appearing in figure 2a can only be obtained for a nanowire bundle configuration P-1.

![Figure 2. a-b-c) Experimental ADF STEM images of nanowire bundles viewed along the three high-symmetry directions shown as α (A), β (B), and X(C); d-e-f) Simulated ADF images obtained using a P1' structure and sulfur in the L sites.](image)

1.2 Graphene

Methods recently developed to obtain individual carbon nanotubes suspended in liquids[5] were used to disperse and exfoliate commercial graphite into single graphene flakes. According to these studies, 1D nanomaterials disperse well into solvents whose surface energy matches theirs. The key question was to understand whether this dispersion method was giving dispersed graphite or suspended graphene. Shown in figure 3a is a bright field TEM images of an object typically observed. Statistical analysis show that Figure 3a is representative of about 80% of the material deposited on the TEM grid. Electron diffraction was used to confirm the presence of monolayers. The two insets show in fact
selected area diffraction patterns acquired from the two different areas indicated by the two arrows respectively. The main difference between the two diffraction patterns is that for the multi-layer (lower inset), the {2110} spots appear to be more intense relative to the {1100} spots. The large flake over the grid’s hole is therefore certainly a monolayer. Aberration-corrected HRTEM was carried out to investigate whether the exfoliation technique was introducing structural defects. Figure 3a shows a typical, unfiltered HRTEM image of a flake over a grid’s hole, that elegantly proves the non-destructive nature of this exfoliation technique.

![Figure 3](image)

**Figure 3.** a) a Bright field TEM image of a typical graphene flakes found on the TEM grid after liquid phase dispersion. The insets show electron diffraction patterns relative to the two selected area. The upper diffraction pattern corresponds to a monolayer, while the lower one to a multi-layer; b) Aberration-corrected HRTEM image of an area over a grid’s hole.

**Results and Discussion**

We have developed a method to disperse, exfoliate and process organic and inorganic 1D-nanostructures, such as inorganic nanowires made of Molybdenum, Sulfur and Iodine and graphene. To make real applications feasible it is crucial to fully characterize their structure down to atomic resolution and correlate this to their actual physical and chemical properties. Advances in aberration-corrected optics in electron microscopy have revolutionised methods of characterising nano-materials, and have opened new frontiers for materials science. Here we have presented an overview of a variety of low-dimensional materials issues, showing what aberration-corrected electron microscopy can do for material scientists.

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