Processing and aberration-corrected imaging of inorganic two-dimensional nanostructures

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Low-dimensional nanostructured materials such as organic and inorganic nanotubes, nanowires and platelets [1-4] are potentially useful in a number of areas of nanoscience and nanotechnology due to their remarkable mechanical, electrical and thermal properties. However difficulties associated with their lack of processability have seriously hampered both. In the last few years dispersion and exfoliation methods have been developed and demonstrated to apply universally to 1D and 2D nanostructures of very diverse nature [5,7], offering a practical means of processing the nanostructures for a wide range of innovative technologies. Among the first materials to have benefitted most from these advances are carbon nanotubes [6] and more recently graphene [7]. Recently this work has been extended to boron nitride and a wide range of two-dimensional transition metal chalcogenides [8]. These are potentially important because they occur in >40 different types with a wide range of electronic properties, varying from metallic to semiconducting.

To make real applications truly feasible, however, it is crucial to fully characterize the nanostructures on the atomic scale and correlate this information with their physical and chemical properties. Advances in aberration-corrected optics in electron microscopy have revolutionised the way to characterise nano-materials, opening new frontiers for materials science. With the recent advances in nanostructure processability, electron microscopes are now revealing the structure of the individual components of nanomaterials, atom by atom [9]. Here we will present an overview of very different low-dimensional materials issues, showing what aberration-corrected electron microscopy can do to answer materials scientists' questions.

Particular emphasis will be given to the investigation of hexagonal boron nitride (hBN), molybdenum disulfide (MoS2), and tungsten disulfide (WS2) and the study of their structure, defects, stacking sequence, vacancies and low-atomic number individual adatoms. The analyses of the *h*-BN data showed that majority of nanosheets retain bulk stacking. However several of the images displayed stacking different from the bulk (Fig. 1). In Fig. 1 the 2D nanostructure appears to have locally varied stacking and displays large shear strain. Images, where variation in stacking had been observed, also displayed the presence of impurities, most likely trapped between the layers. It suggests that the presence of impurities can help to stabilize non-bulk stacking, altering physical properties of the material. Furthermore, by introducing tiny amount of NaCl into thin hBN film, we were able to show that indeed it causes changes in the stacking.

Similar, to 2D *h*-BN, images of MoS_2 and WS_2 have shown the stacking previously unobserved in the bulk (Fig. 2). This novel stacking consists of Mo/W stacked on the top each other in the consecutive layers. Since the atomic number of Mo/W is much higher than S, it means that in ADF images of 2D MoS_2/WS_2 the signal from S columns is swamped by the neighbouring Mo/W signal. As a result S columns are not properly resolved, preventing complete determination of the structure. Statistical analysis of the intensities of the potential S positions was attempted. Unfortunately, results were not fully conclusive. Finally, it must be noted that for the case of 2D WS_2 non-bulk stacking appears to be dominant.

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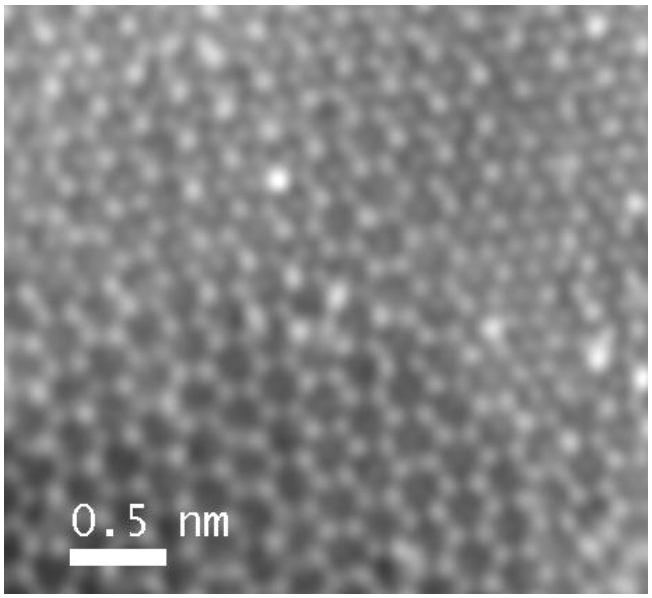

Fig. 1*. ADF STEM image of h-BN acquired using a JEM-ARM200F operated at 80 keV.*

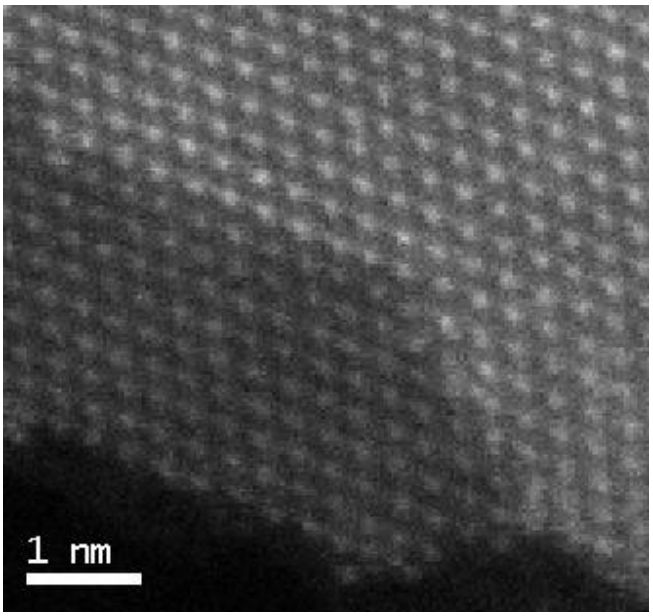

Fig. 2*. ADF STEM image of 2D MoS_2 acquired using a JEM-ARM200F operated at 80 keV. Only Mo columns are resolved.*