Through Graphene and Beyond

deeper understanding via scanning transmission electron microscopy

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2D materials are produced by separating the atomic layers of van der Waals solids such that the resulting crystal sheets are very thin in comparison to their lateral dimensions. Graphite is the archetypal van der Waals solid, which can be thinned to produce graphene sheets via a variety of routes including mechanical or liquid phase exfoliation. The number of successfully isolated 2D materials has increased enormously in recent years and now includes insulators, metals and semiconductors.[1] Furthermore, by stacking different 2D crystals on top of each other with controlled thickness or twist angle it is possible to produce artificial crystals with bespoke properties.[1] This is fast establishing a new generation of optical and electronic devices with advanced functionality, often referred to as van der Waals heterostructures. For example, by sandwiching an optically active transition metal dichalcogenide layer (e.g. MoS_2), between insulating hexagonal boron nitride (hBN) tunnelling barriers and graphene electrodes, it is possible to produce light emitting diodes (LEDs) with efficiencies similar to current organic LEDs but in a structure only a few tens of atoms thick (Figure 1a) [2].

Prototyping of these van der Waals heterostructures has been achieved by mechanical exfoliation (peeling) of atomic layers from their bulk counterparts using a polymeric support layer and sequentially stacking them on top of each other.[3] Despite the inherently 'dirty' nature of this processing, surprisingly the materials produced are found to contain large areas of pristine synthetic crystal; free from contaminants at the atomic scale.[4] Improved device engineering requires a detailed knowledge of their atomic structure and the only technique capable of yielding this information is scanning transmission electron microscopy (STEM). In this talk I will demonstrate some unexpected science that has resulted from close collaboration between microscopists and 2D materials experts. I have been fortunate to have worked closely with a wide range of researchers pioneering different applications for graphene and other 2D materials.

We have worked with Material Scientists to show how cross sectional STEM analysis can be harnessed to understand the bending behaviour that underpins exfoliation in this interesting class of materials. We find that the types of defect can be predicted from just the bend angle and thickness of the materials [5]. Above a critical thickness the materials exhibit numerous twin boundaries and for large bend angles these can contain nanoscale regions of local delamination (Fig.1b). Such features are proposed to produce stress concentrations and therefore to be important in determining how easily the material can be thinned by mechanical or liquid exfoliation.

We have worked with Physicists who are incorporating lithographically etched channels and wells in to 2D material stacks. These devices provide an unrivalled means of studying gas and liquid flow through nano-sized constrictions which has revealed important understanding fundamental to understanding biological flow and gas/liquid separation [6,7]. Cross sectional STEM imaging has been vital to the successful realisation of this technology by providing the only method able to reveal when few-atom high channels have been successfully realised. We show that this platform can also be used to enhance STEM imaging capabilities - allowing the real time studies of reactions in liquid environments with unprecedented spatial resolution and spectroscopic capabilities [8].

We are also working with scientists trying to harness the exciting properties achievable in 2D materials that are unstable in air (magnetism, superconductivity, THz communications, sensing). The potential of these air sensitive 2D layers (black phosphorus, $NbSe_2$, $CrBr_3$, InSe and GaSe) can be realised by peeling the layers in an inert atmosphere and encapsulating with another stable 2D crystal like graphene or hBN [3,9-11]. In addition, such encapsulation provides a powerful means of studying point defects and defect dynamics in such materials (Fig. 1c) [12,13] and can even be harnessed to enable device miniaturisation via a novel resist-free lithographic patterning approach [14],

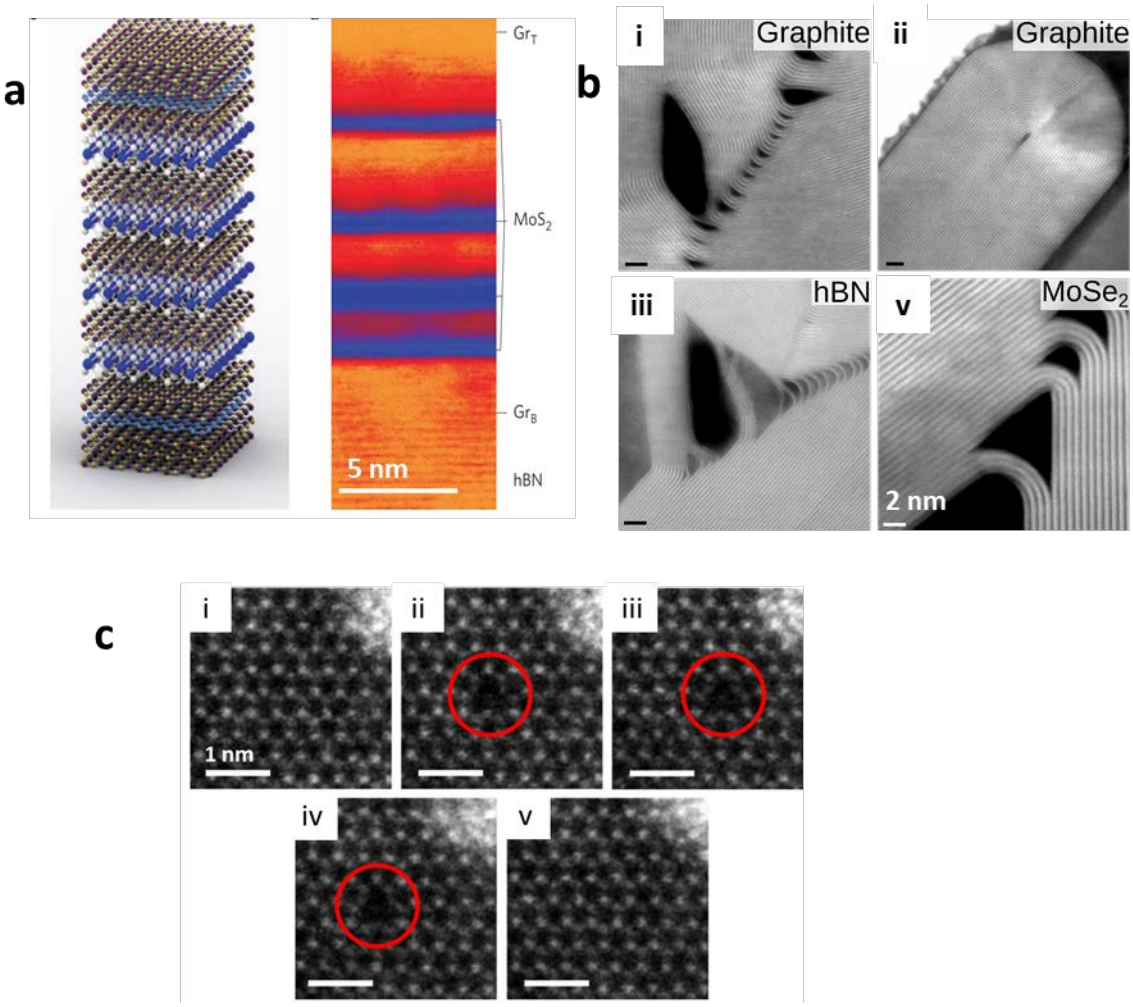

Figure 1: STEM imaging of 2D materials and van der Waals materials, (a) LED device cross sectional image and schematic (*reproduced with permission from F. Withers et al. Nat. Mat., 14, 301–306 (2015)*), (b) Defects induced by mechanical deformation in Van der Waals materials (reproduced with permission from *A P Rooney et al. Nat. Comm. 9, 35 (2018)*), and (c) plan view imaging of defect dynamics in monolayer InSe (reproduced with permission from *D. G. Hopkinson et al, ACS Nano, (2019).*

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