In situ characterisation of dynamic nanoscale processes both in and on two-dimensional materials

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The advent of in situ techniques for transmission electron microscopy (TEM) has brought new perspectives to the characterisation of functional nanomaterials. In situ TEM facilitates the collection of high-resolution structural and compositional information during controlled stimulus (heating/biasing/mechanical), or under specific environmental conditions (liquid/gas), and thus offers a route to understanding the behaviour of materials under operating and/or transformational conditions [1].

In this work, we present several in situ TEM experiments involving graphene, hexagonal boron nitride (hBN) and molybdenum disulfide (MoS_2), demonstrating that these two-dimensional materials can be used both as the subject of interest and as a platform for investigating other chemical processes using in situ TEM.

Firstly, we present a recent development in liquid-phase (LP) TEM technology: a two-dimensional heterostructure mixing cell (2DMC) that facilitates mixing of two solutions within the electron microscope via a beam-induced trigger. The 2DMC design is based on engineered graphene liquid cells (EGLC), where an etched hBN spacer is used to form liquid compartments of fixed dimensions and graphene used to seal the filled cells [2]. The mixing cell consists of two vertically stacked EGLC, but with only the outer face of each component sealed by a sheet of few-layer graphene. A single MoS_2 crystal (mono- or bilayer) is then used to seal the interior hBN-hBN interface, separating the solutions loaded into each half of the cell, as in the figure below [3].

Once in the microscope column, controlled delivery of a high electron dose to a 5×5 nm^2 is used to instigate crack propagation across the MoS_2, resulting in widespread mixing across an individual cell and initiation of the chemical reaction. Using this mechanism, we characterise the hotly-debated reaction pathway of calcium carbonate formation, from the early stages of non-classical nucleation to the final aggregation of amorphous precursors to form crystalline calcite [3].

Furthermore, the unique 2DMC geometry is not limited to observation of chemical reactions but can utilised in a range of possible experiments. To demonstrate this, we present a similar experimental set-up where the MoS_2 is fully submerged in liquid but, in this case, acts as a substrate for single metal atoms, which allows us to investigate the effects of solvation on a single-atom catalyst system with unprecedented spatial resolution. We propose that the various components (window, separation membrane and spacer) could be swapped for other nanomaterials to achieve the desired experimental conditions and thus expand the applicability of 2DMC to range of potential in situ studies.

In addition to LP-TEM experiments involving two-dimensional materials, we also present

preliminary findings regarding the deintercalation of mechanism K-doped MoS_2 using correlated electron diffraction and energy dispersive X-ray spectroscopy (EDS). Based on structural changes that occur during in situ heating, we identify notable structural transformation stages that correspond to ordered planes of K atoms vacating the MoS_2 host lattice. We then combine knowledge of these phases with systematic EDS analysis to measure the dependence of deintercalation rate on temperature and propose an empirical model that suggests the process occurs according to first order reaction kinetics.

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[2] D.J. Kelly *et al.*, *Nano Lett.*, **18**, 2, pp. 1168–1174 (2018)
[3] D.J. Kelly, N. Clark, M. Zhou, D. Gebauer, R.V. Gorbachev, and S.J. Haigh, *Adv. Mater.*, (2021)

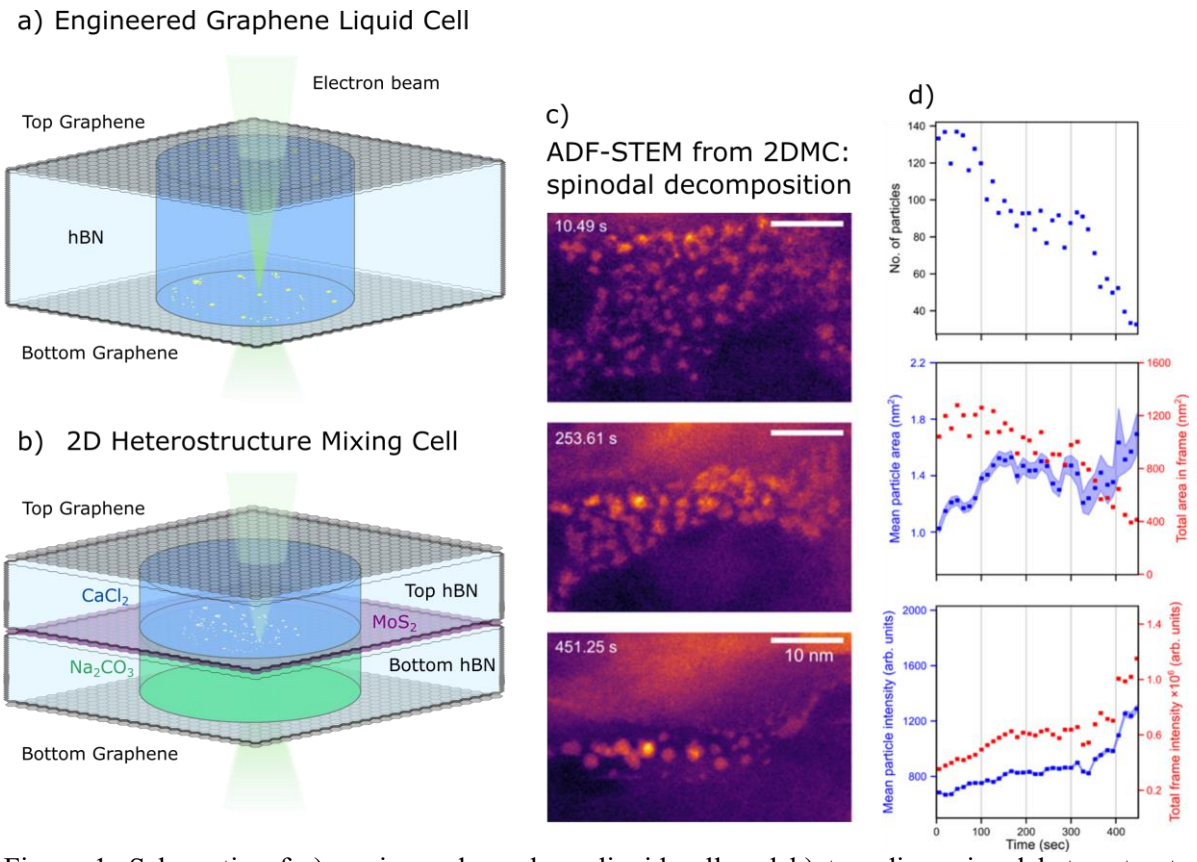

Figure 1: Schematic of a) engineered graphene liquid cell and b) two-dimensional heterostructure mixing cell, each with annotated components. c) Annular dark field scanning transmission electron micrograph series showing $CaCO_3$ formation. d) Size, morphology and density analysis of species visible in c)