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# Dynamic Atomic Behaviour, Ion Exchange and Chemical Synthesis Studied Using our Liquid Cell 2D Material Heterostructures and Scanning Transmission Electron Microscopy

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Materials' phase transformations involving liquid precursors or products have traditionally been more even challenging to study in the transmission electron microscope (TEM) than phase transformations involving purely solid materials. This presentation will illustrate two approaches to study phase transformations involving liquids.

This talk will present recent work showing how our TEM liquid cell platform, based on wells and channels etched into a two dimensional (2D) heterostructure stack,[1-3] can be used to directly image both adatom motion and chemical synthesis in liquids. Our liquid cells uniquely contain two separate sets of liquid wells separated by a 2D $MoS_2$ monolayer separation membrane. We demonstrate scanning transmission electron microscopy imaging of the earliest stages of chemical synthesis, achieved by fracturing the separation membrane with the focused electron probe to initiate the mixing of liquids in the upper and lower wells and the beginning of the reaction. To demonstrate this technology we have investigated the synthesis of calcium carbonate achieved through the mixing of aqueous calcium chloride, in the upper liquid wells with an aqueous solution of sodium carbonate in the lower liquid wells.[4] This process is key to the growth of many marine organisms as well as being used in a huge range of chemical processes, but how calcium carbonate forms during this reaction is complex and hotly debated among experts. Using in situ atomic resolution imaging and elemental analysis we find that unlike traditional crystal growth which starts from a tiny solid particle, the first signs of a reaction are is not a solid but a denser Ca rich liquid phase, which gradually solidifies and coarsens. By minimizing electron beam effects we are able to propagate the synthesis reaction so as to form fully crystalline particles. These results provide the first dynamic evidence of a recently proposed liquid-liquid synthesis mechanism.[4]

I will also demonstrate how we have used a snap-shot approach and low dose STEM annular dark field and annular bright field imaging to investigate ion exchange in atomically thin clays and micas.[5] These materials are highly sensitive to electron beam effects so typically only allow 1-2 atomic resolution images to be acquired before the structure is completely destroyed. We studied large (up to 10 μm diameter) few layer flakes of vermiculite, biotite and muscovite. We found that in vermiculite clay samples, consisting of stacked 2D aluminosilicate layers, the speed of ion exchange in the 2D interlayer space is many orders of magnitude faster for few-layer thick samples than for bulk powder specimens. The greatest differences were seen for samples that consist of just 2 aluminosilicate layers (bilayers) with the interlayer diffusion rates converging to the bulk behavior for thicknesses of ~6 layers [5]. By studying >60 samples of different thickness we find a quantitative thickness dependency which can be explained by reduced cumulative interlayer forces. These are observable from measurements of the

slightly increased swelling measured in atomically thin samples, and particularly in bilayers via liquid phase atomic force microscopy. These atomic scale observations have been exploited to produce membranes composed of few-layer vermiculite which demonstrate ion exchange in minutes compared to the days needed for bulk samples, suggesting their potential use for optimization of membrane applications [6]. We also observe ion exchange islands are formed in the twisted interlayer space for biotite samples [5], with potential application in novel quantum systems where the band structure is seen to depend on local phase transformations in 2D materials twisted to small angles [7].

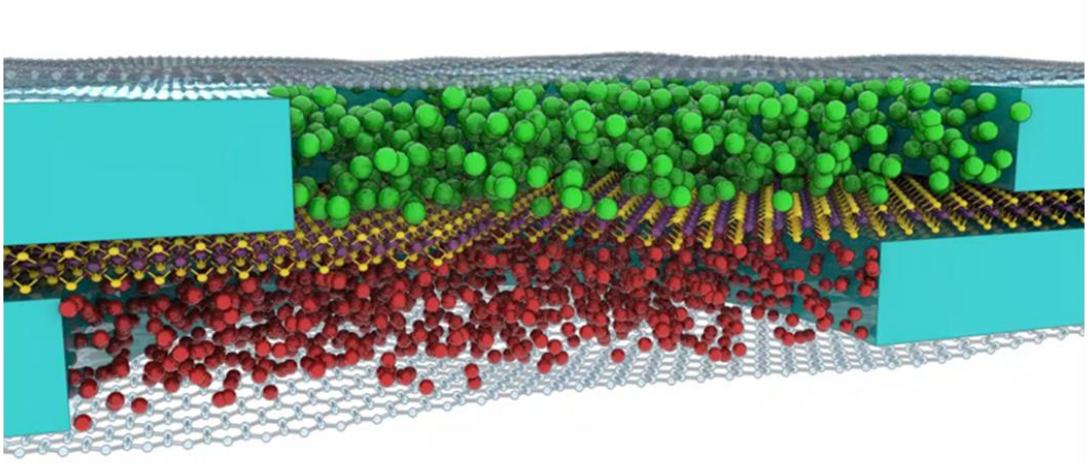

**Figure 1.** Schematic Illustration of the double-liquid well structure and $MoS_2$ separation membrane in our 2D heterostructures. Reproduced with permission from Kelly et al. [4]

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