Nanometre Resolution STEM-EDX Spectrum Imaging in Liquids using Engineered Graphene Cells

Kelly, D.[1], Zhou, M.[2,3], Clark, N.[1,3], Hamer, M.J.[4,3], Lewis, E.A.[5], Rakowski, A.M.[5,3], Gorbachev, R.V.[2,3] and Haigh, S.J.[6]

[1] School of Materials, University of Manchester, United Kingdom, [2] School of Physics and Astronomy, University of Manchester, United Kingdom, [3] National Graphene Institute, University of Manchester, United Kingdom, [4] School of Physics and Astronomy, United Kingdom, [5] School of Materials, United Kingdom, [6] School of Materials, The University of Manchester, United Kingdom

High-resolution imaging of liquid samples using (scanning) transmission electron microscopy ((S)TEM) has become feasible due to advancements in microfabrication infrastructure. Specialised liquid cell holders make use of silicon nitride windows to isolate the liquid from the high vacuum of the microscope, while allowing transmission of the electron beam with minimal scattering. Graphene has been demonstrated as a superior window material, being one atomic layer in thickness, impermeable to liquids, and having high mechanical strength and flexibility. Liquid cells based on graphene have been shown to be capable of unrivaled atomic resolution imaging of nanoparticles in liquid,[1] however their widespread use has been limited, perhaps due to difficulties controlling the volume of liquid in the cell.

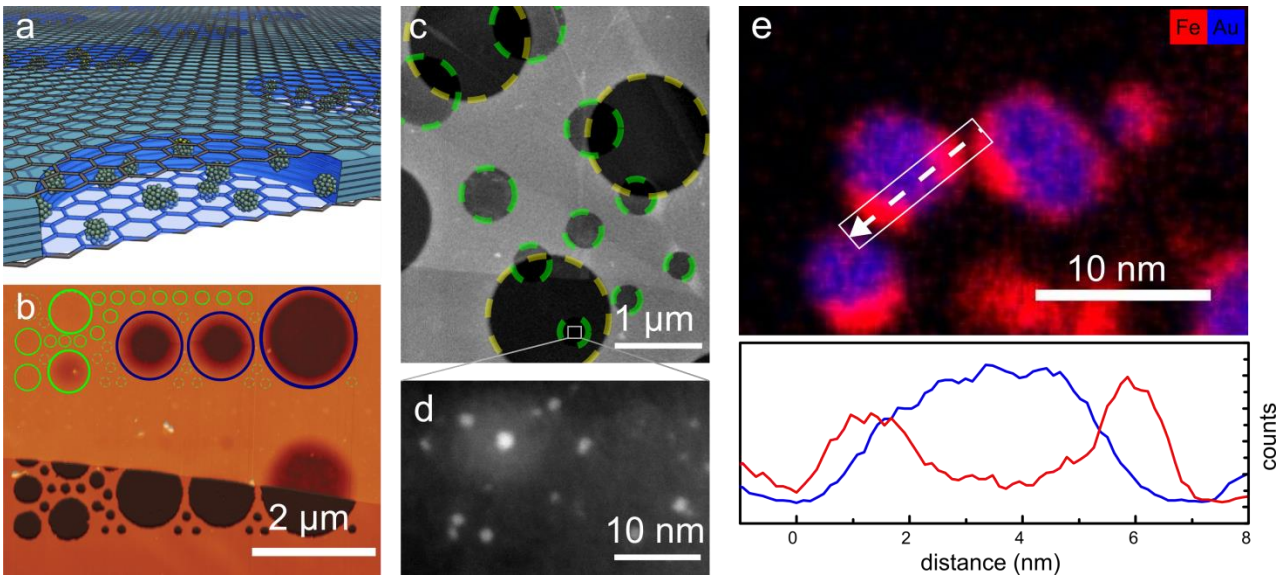

Figure 1: (a) Illustrative cross-section of EGLC (not to scale). (b) Atomic force microscopy mapping of filled (green) and partially filled (blue) wells in an EGLC (edge of the top graphene sheet is seen across the lower part of the image). (c) Low magnification HAADF-STEM image of EGLC on a TEM support with liquid wells outlined in green and support holes in yellow. (d) HAADF-STEM of nanoparticles in the EGLC (e) EDX map of iron deposited on gold nanoparticle facets, with line-scan extracted. Adapted with permission from D.J. Kelly et al., *Nano letters* (2018). Copyright 2018, American Chemical Society.

In this work, we present a novel liquid cell design for TEM based on a 2D heterostructure platform.[2] Liquid is contained in cylindrical wells that are patterned in a hexagonal boron nitride (hBN) flake, which is sealed on both sides by few layer graphene sheets, and mounted on a standard TEM support grid (Figure 1a). The resulting engineered graphene liquid cell (EGLC) contains thin liquid layers of controlled volumes, dictated by the hBN spacer dimensions, and is robust to vacuum cycling due to the hermetic seal formed by graphene on atomically flat hBN.[2]

The utility of this EGLC is demonstrated by studying the dynamic growth of ultra-small metallic nanoparticles in liquid, grown by beam-induced reduction from a salt solution, and comparing their behaviour to a model for 2D Brownian motion.[2] We also show that energy dispersive X-ray (EDX) spectrum imaging can be performed in these liquid cells with nanometre-resolution elemental mapping (Figure 1e), an order of magnitude improvement on that recorded for conventional liquid cell holders[3]. Complementary electron energy loss spectroscopy (EELS) has confirmed the presence of water in filled cells via thickness measurements and from mapping of the oxygen K-edge.

(1) Yuk, J. M.; Park, J.; Ercius, P.; Kim, K.; Hellebusch, D. J.; Crommie, M. F.; Lee, J. Y.; Zettl, A.; Alivisatos, A. P. *Science (80-.).* **2012**, *335* (6077), 61 - 64.

(2) Kelly, D. J.; Zhou, M.; Clark, N.; Hamer, M. J.; Lewis, E. A.; Rakowski, A. M.; Haigh, S. J.; Gorbachev, R. V. *Nano Lett.* **2018**, acs.nanolett.7b04713.

(3) Lewis, E. A.; Haigh, S. J.; Slater, T. J. A.; He, Z.; Kulzick, M. A.; Burke, M. G.; Zaluzec, N. J. *Chem. Commun.* **2014**, *50* (70), 10019 - 10022.

The authors acknowledge funding support from the Engineering and Physical Sciences Research Council, (EPSRC) UK, Defense Threat Reduction Agency (DTRA), the Royal Society University Fellowship Scheme, and the European Research Council (ERC).