

Liquid-Phase STEM-EDS in Graphene and Silicon Nitride Cells

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Liquid-phase transmission electron microscopy (LP-TEM) has come to the fore as a method for the characterization of dynamic processes in wet environments with high spatial and temporal resolution, allowing insight that cannot be obtained with any other technique[1]. Liquid cells based on both silicon nitride and graphene windows have been used to study the physical structure of nanomaterials in liquids using conventional TEM and scanning TEM (STEM). Combining imaging with electron-energy loss and energy dispersive X-ray spectroscopies (EELS and EDS respectively) provides a method to analyze the nanoscale chemistry of such structures [2, 3], but quantitative elemental analysis in liquids is challenging due to the difficulty of accounting for unwanted electron scattering in the liquid and windows.

LP-STEM EELS and EDS provide a means to study the physical and chemical properties of the liquid layer, giving insight into local thickness variations, solution chemistry and effects resulting from the electron beam's interaction with the liquid[4]–[6]. By accurate measurement of these parameters it should be possible to account for the artefacts they produce in both imaging and spectroscopy techniques in order to achieve meaningful quantitative information[7]. For LP-STEM EDS, it is also necessary to consider the risk of X-rays being shadowed by the in situ holder geometry, though significant improvements have been made by modification of liquid cell holder designs [8].

Graphene based liquid cells have advantages over SiN holders for EDS spectrum imaging as they are mounted on standard TEM specimen holder, thus shadowing is minimized and the efficiency of EDS for a given electron fluence is high. In addition, thin (30 nm) liquid layers are achievable allowing high spatial-resolution spectrum imaging to be performed. We recently reported EDS resolution on the order of a nanometer, an order of magnitude increase compared to earlier studies involving LP-STEM-EDS, and demonstrated elemental mapping of core-shell nanoparticles in water [5]. The approach utilized novel LP-TEM cells based on graphene-boron nitride heterostructures, which we refer to as engineered graphene liquid cells (EGLCs) [5]. These EGLCs consist of graphene windows either side of a hexagonal boron nitride (hBN) spacer. Wells etched in the hBN contain thin liquid layers with defined volumes. Atomic force spectroscopy (AFM), EDS and EELS have been used to confirm the presence of water and show EGLCs are robust to vacuum cycling.

Building on this, we have studied the effects of the liquid layer, cell windows and holder geometry on EDS acquisition using graphene liquid cells and silicon nitride e-chips with a Protochips Poseidon Select holder. By comparison of specimens characterized in both wet and dry environments within the cell, as well as ex situ results, we define a means to determining relative thickness of the liquid layer using EDS and confirm these measurements with EELS. Knowledge of the liquid layer allows its presence to be accurately compensated providing a route to quantitative EDS analysis at electron fluences appropriate for LP-TEM/STEM. Our analysis includes accounting for shadowing by the holder and the presence of

large backgrounds due to the membrane and liquid layer bowing. Ultimately we extend this technique to map multi-elemental nanoparticles in liquid and correlate our results with ex situ experiments, illustrating the feasibility of quantitative EDS in wet environments[9].

References:

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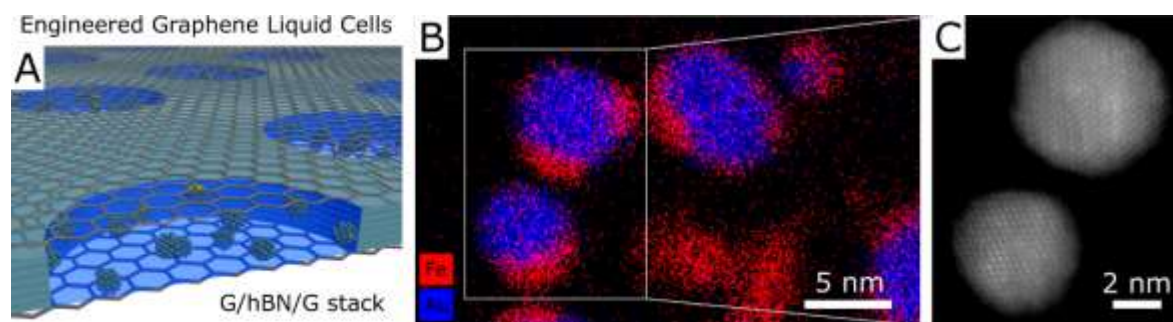


Figure 1. A. Illustration of an EGLC, B. STEM-EDS map of Au Fe nanoparticles acquired at 80 kV with total fluence: $5.2 \times 10^7 \text{ e}^-/\text{\AA}^2$, C. High-angle annular dark field (HAADF) STEM micrograph of indicated Au particles with no clearly visible Fe.

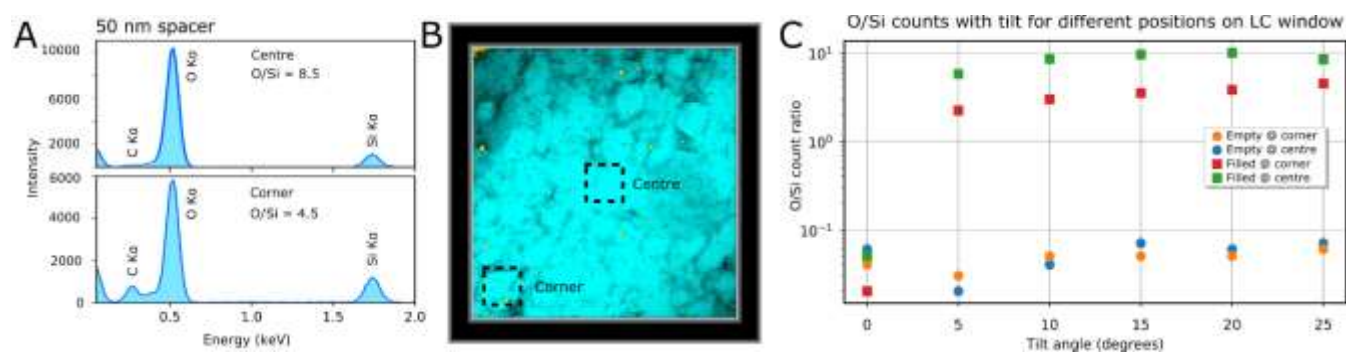


Figure 2. An EDS spectra from two lateral positions (indicated in B) on a liquid cell window. The higher $O_{K\alpha}/Si_{K\alpha}$ at the center of the windows is due to bowing of the windows. B. False-colored HAADF (yellow Au nanoparticles, blue background), C. Plot showing increase in $O_{K\alpha}/Si_{K\alpha}$ with tilt due to decreased shadowing. Silicon counts have been normalized to account for the effective window thickness increasing with tilt, oxygen counts are as acquired.