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Combinatorial Microscopy in Liquids with Low Energy Electrons

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The modern ambient pressure or in-liquid electron microscopy of energy and catalysis related materials is based on microfluidic/closed cells equipped with a few tens of nanometers thick Si_3N_4 (or SiO_2) windows that are highly transparent for high energy (>100 keV) electrons [1]. Scanning electron microscopy (SEM) with true secondary electrons, Low Voltage SEM [2] or Photoemission Electron Microscopy (PEEM) [3] rely on detection of slow electrons emitted from very few surface layers and therefore have unique surface sensitive contrast mechanisms. However, ca. 1 nm to 3 nm short electron mean free path of the low energy elections in condensed matter makes it impossible to apply these powerful techniques to probe liquid-solid or gas-solid interfaces using the standard Si_3N_4 membranes. We have recently shown, that this restriction can be lifted by filling of graphene-based membranes as electron transparent molecularly-impermeable windows separating the liquid (or gaseous) sample from the high vacuum of the microscope [4, 5].

In this report we make one step further and design a novel graphene based micro-fabricated sample platform, which comprises millions of identical graphene-capped liquid-filled micro volumes. This platform, in combination with full field hyperspectral PEEM or scanning electron imaging, allows for both high resolution examination of individual channels, and global high-throughput screening of real-time processes taking place at the graphene–liquid interfaces [6]. Figure 1a depicts the principle design of the graphene-capped multi-channel liquid sample array (MCA). The spatially coded filling of 3 different analytes into MCA (Fig. 1b) allows for prompt combinatorial screening of different liquid-solid interfaces under the same imaging conditions (Fig. 1c). Discrimination between different analytes is possible via histogram analysis, with the difference between the MCA frame peak and liquid-filled cells peaks being specific to the analyte.

MCA structure is ideally suitable for large-scale data mining and pattern recognition algorithms. We were able to interpret spectro-temporal and spatiotemporal evolutions of X-ray absorption spectra (XAS) at solid-liquid interfaces. Visualization and analysis of the 3-dimensional PEEM dataset (electron total yield intensity as a function of excitation energy and x-y coordinates) was performed using clustering and spectral unmixing algorithms such as Bayesian Linear Unmixing (BLU) algorithm [7,6]. The optimal number of BLU deduced behaviors present in the dataset was found to be four which abundance maps and endmember spectra are shown in Figure 2a-e. Component (i) is behavior of empty channels with very low spectral intensity, nearly energy-independent. Component (ii) is the MCA frame behavior, which shows high intensity due to gold coating signal amplification. Component (iii) map pinpoints water-filled channels, and its spectrum has well-defined water XAS features and a small carbon peak. Component (iv) map highlights 3 cells in which water was significantly affected by radiolysis process as spectra were recorded. K-means clustering correctly identified localization of these 4 spectral behaviors (Fig.

2g, h): empty cells (cluster 3), MCA frame with small amount of water trapped beneath the graphene (cluster 1), MCA frame with large amounts of water (cluster 4) and water-filled cells (cluster 2). To investigate individual behaviors, was used. Thus, the combination of the MCA platform with BLU algorithm allowed us to extract complex behaviors from a multidimensional dataset and assign clear physical meaning to them.

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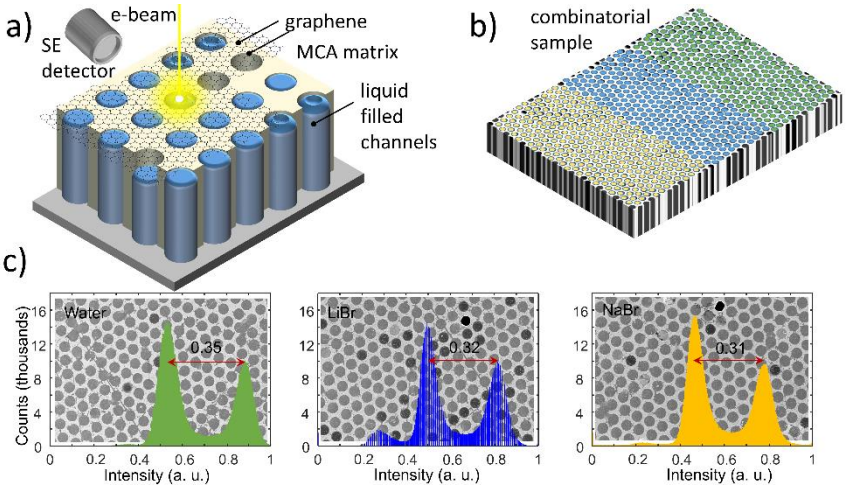

Figure 1. Combinatorial approach with MCA: a) SEM setup, b) MCA combinatorial sample, c) SEM images and histograms of MCA filled with: water, and 1M solutions of LiBr and NaBr.

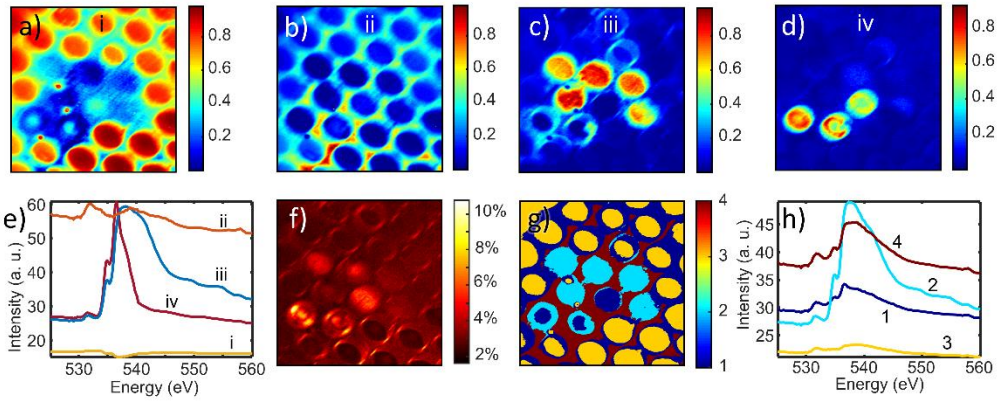

Figure 2. PEEM dataset: a)-d) four BLU abundance maps and e) corresponding BLU endmembers; f) BLU error map; g) k-means clustering map and h) mean spectra corresponding to 4 clusters of map g).

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