Graphene windows enable photoelectron microscopies of liquid samples.

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Nanometer-range inelastic electron mean free path (IMFP) of 10 eV-10^3 eV electrons in solids has been a basis of the superior surface sensitivity of spectromicroscopy tools such as µESCA, SPEM, PEEM, etc. However, the same efficient electron attenuation in a dense matter becomes the major experimental obstacle for studying of catalytic, electrochemical, biological and environmental interfaces / phenomena under realistic conditions using these powerful analytical methods. In response to these challenges, the evolution of the high-pressure "photon IN-electron OUT" spectromicroscopy instrumentation proceeds in two directions: (i) development of the differential pumping stages coupled with sophisticated electron optics [1] and more recently via (ii) separation of the liquids or dense gaseous environments from the standard UHV instrumentation using electron transparent membranes [2]. In the latter case, the transfer of the complexity from the analytical instrumentation to the sample stage potentially has a great advantage since it can effectively employ already existing microfabrication and lab-on-a-chip technology and standard UHV analytical equipment. Here we highlight the tested capabilities of the membrane approach and future trends.
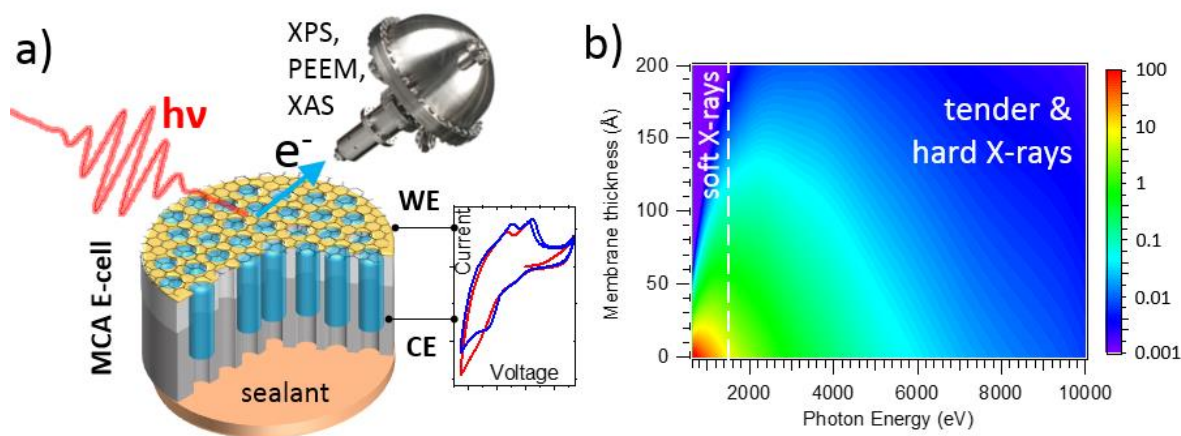

Figure. 1. a) Experimental setup for through-the-membrane spectromicroscopy in liquids using MCA platform; b) Simulated water O 1s photoelectron yield (in percent of max O 1s intensity) as a function of photon energy and membrane thickness (Adapted from [3]).

Since only micron size diameter graphene can sustain 1 Bar pressure differential, most of the current designs of the membrane-based high-pressure cells are based on multi-orifice samples or multi-channel arrays (MCA) capped with a single or bilayer graphene and coupled with an additional functionality such as electrochemical, heating/cooling and flow capabilities Fig.1a. The ability to increase the probing depth in liquids and gases to few nanometers is often an experimental need that and can be achieved by

increasing the energy of the photons and therefore the outgoing photoelectrons. However, the increase of IMFP with photon energy is largely compensated by the concomitant fast drop of the photo-absorption cross-section. Therefore, depending on the elements being probed, there exist an optimum photon range where these experiments are most feasible (Fig.1b).

Multi-orifice design of the graphene cells has additional advantages since it allows for application of high throughput combinatorial data mining algorithms such as principle component analysis, clustering, Bayesian inference methods etc. This is particularly important when multi-dimensional/ hyperspectral datasets like in PEEM are collected. Figure 2 depicts an example of the application of Bayesian Linear Unmixing (BLU) algorithm to spatiotemporal PEEM data of water under graphene being excited across O1s absorption edge.
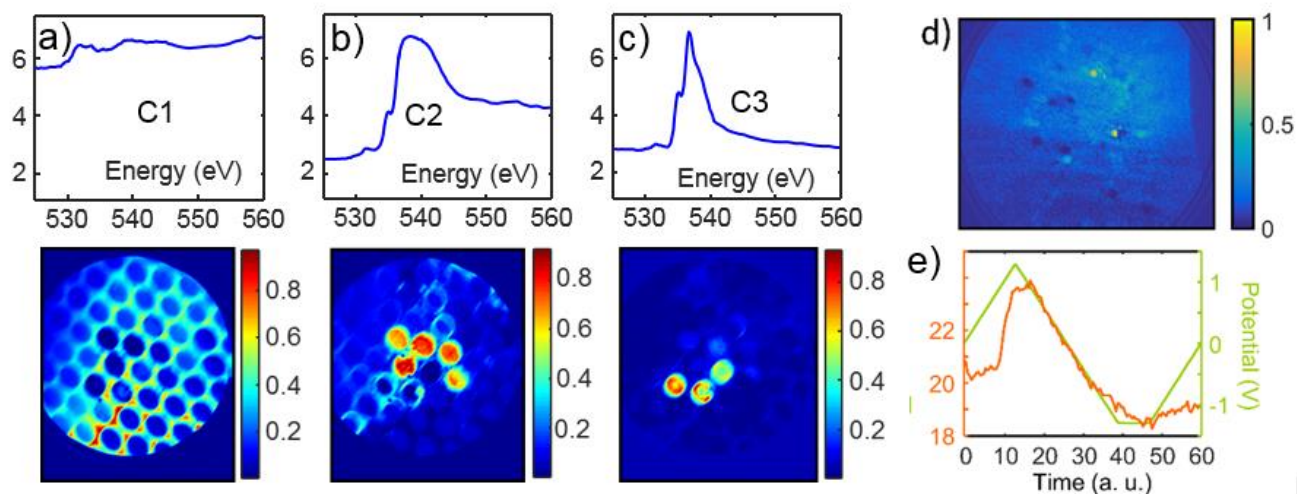

Figure 2. a)-c) BLU of PEEM hyperspectral data of liquid water behind the graphene; BLU abundance map (d) and corresponding O1s intensity evolution (e) recorded from graphene capped $CuSO_4$ 0.5 mol/L aqueous solution upon ramping of the CE potential between -1V and 1V (Adapted from [4] and [3])

BLU reveals there is a minimum of three meaningful spectral components C1-3 Fig. 2. The corresponding PEEM abundance maps are shown below the spectra. C1 corresponds to the gold-graphene interface of MCA and has a strong Au background signal with a few weak spectroscopic features at ca 533 eV due to hydrocarbon contaminations and a weak band (535 eV to 550 eV) due to intercalated interfacial water. Five water-filled channels in the abundance map Fig.2b exhibit well-documented liquid water XAS features (C2) indicating that these channels are filled with water. The unusual spectral shape recorded from the three channels C3 in the Fig. 2c reveals that there exists an additional process (temporal evolution due to water radiolysis) which convolutes with normal spectral behavior [4]. The similar algorithm can be applied to the electrochemical process depicted in the Fig. 2d, e. Here a ramping potential was applied to the bottom counter electrode CE of the MCA electrochemical cell (see Fig.1 a) while PEEM image at 540 eV was collected from the graphene (WE) capped $CuSO_4$ 0.5 mol/L aqueous solution [3].

We are currently testing the next generation of the MCA sample platform which has UHV compatible microfluidic capabilities Fig 3. The key feature of the design is very small degassing rate even if several graphene windows are disrupted during the experiment. The new device maintains UHV conditions in the vacuum chamber of the analyzer/detector without differential pumping stage.
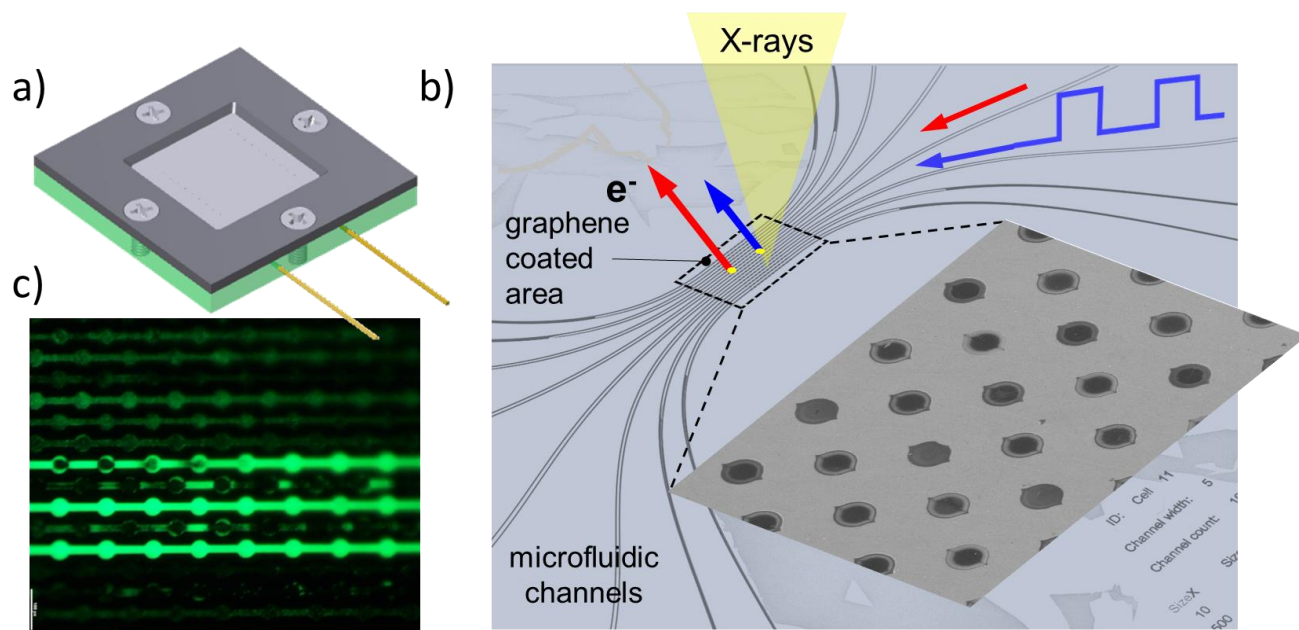
Figure 3. Fluidic multichannel graphene cell for photoelectron spectromicroscopy under UHV conditions. a) Overall design; b) SEM image of water filled micro-channels with graphene capped orifices; c) Fluidic tests with fluorescein dye.

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