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Ambient Pressure X-ray Photoelectron Spectroscopy to Characterize the Solid/Liquid Interface: Probing the Electrochemical Double Layer

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Ambient pressure X-ray photoelectron spectroscopy (APXPS) has contributed greatly to a wide range of research fields ranging from environmental science,[1] catalysis,[2] and electrochemistry[3] to name a few. The use of this technique at synchrotron facilities primarily focused on probing the solid/gas interface, however quickly advanced to the probing of liquid/vapor interfaces[4,5] and solid/liquid interfaces through an X-ray transparent window.[6-8] Most recently by combining APXPS with "Tender" X-rays (~2.5 keV to 8 keV) on beamline 9.3.1 at the Advanced Light Source in Lawrence Berkeley National Laboratory (which can generate photoelectrons with much longer inelastic mean free paths), has enabled the ability to probe the solid/liquid interface without needing a window.[9] This innovation allows to probe interfacial chemistries of electrochemically controlled solid/liquid interfaces undergoing charge transfer reactions.[9] These advancements have transitioned APXPS from a traditional surface science tool to an essential interface science technique.

Using "Tender" APXPS researchers have successfully probed the metal/liquid[9] and oxide/liquid[10] interfacial chemistry all under *operando* (under applied potentials) conditions. Going beyond chemistry, by taking advantage of XPS ability to detect potentials, researchers for the first time were able to probe potential profiles across a solid/liquid interface.[9,11,12] Results obtained so far range from the observation of band bending and flat band potential features for an oxide semiconductor/liquid interface up to the newest achievement, the probing of the electrochemical double layer (EDL) under *operando* conditions.[11]

The electrochemical double layer is present at every solid/liquid interface. As a result of the chemical/physical response to the interaction with the solid electrode, the ionic distributions in the liquid lead to the potential profile spanning between the solid electrode and the "bulk" electrolyte (where the ionic distribution and potential profile are uniform). Hermann von Helmholtz first conceived the EDL over 100 years ago, and since then many theoretical models have been created, but they have been very challenging to experimentally verify. Using "Tender" APXPS, Favaro et al have recently succeeded in directly probing the potential drop (i.e. the shape of the EDL) as well as the potential of zero charge (PZC) at the solid/liquid interface as shown in **Figure 1**.[11] This was accomplished by characterizing how the spectra full-width at half-maximum (FWHM) from the water combined with numerical simulations of the electric field as a function of applied potential. To further expand the power of this technique, a neutrally charged molecule, pyrazine was also added and characterized to validate the use of an independent probing marker that one could use to study the potential profile in the event the selected solid/liquid spectral chemical features overlapped complicating the data analysis. Conducting this experiment across various electrolyte concentrations and applied potentials they were able to demonstrate that the potential profile of the EDL does indeed follow the Gouy-Chapman-Stern model. This achievement now opens the door for many different fields of science to study the EDL in more complicated environments such as redox reactions, non-aqueous electrolytes, photoactive semiconductors, corrosion processes, geological and biological systems.

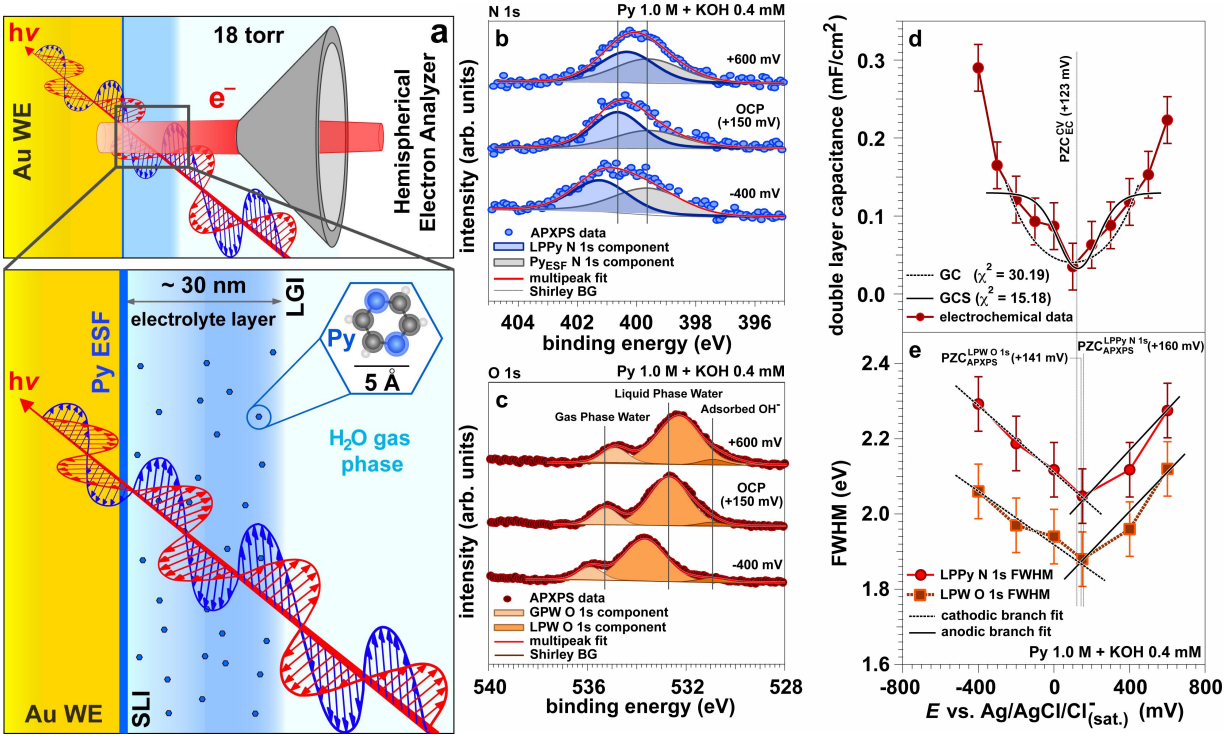

Figure 1: (**a**) EDL probing using a gold polycrystalline working electrode (WE) in KOH 0.4 mM aqueous solution (*d*EDL=15.2 nm) containing 1.0 M pyrazine (SLI, solid/liquid interface, LGI, liquid/gas interface, and Py ESF, pyrazine at the electrode surface). (**b**,**c**) Representative intensity-normalized N 1*s* and O 1*s* core-level peaks, respectively, acquired at different applied potentials to the WE (OCP, open circuit potential, LPPy, liquid phase pyrazine, GPW, gas phase water, LPW, liquid phase water, and BG, background) and (**d**) double-layer capacitance (obtained from electrochemical characterization) as a function of the applied potential. The double layer capacitance trend has been fitted within a range of 400 mV centered on the PZC, by using both Gouy–Chapman (GC) and Gouy–Chapman–Stern (GCS) models; (**e**) LPPy N 1*s* and LPW O 1*s* full-width at half-maximum (FWHM) trends as a function of the applied potential within the EDL region (CV, cyclic voltammetry, and EC, electrochemistry). The error bars were determined via repeated measurements of the FWHM of a given core level, propagated with the experimental spectral resolution. (Figures are from Nature Communications 2016[11]).

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