In-situ exploration of the solid/liquid interface via XPS

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Understanding of the solid/liquid interface is critical in applications such as catalysis, batteries and solar water splitting to name but a few choice topics. X-ray photoelectron spectroscopy (XPS) is an ideal technique to study surface and interface chemical reactions of thin (~5 to 10 nm) solid films owing to the elemental and rich chemical information obtainable from the technique. Historically, the vast majority of XPS analysis has focused on solid, low vapour pressure, materials. This is due to the high vacuum restrictions imposed by the technique however; near ambient pressure XPS (NAP-XPS) has emerged as a useful technique to study high vapour pressure samples up to typical working pressures of about 15 mbar. This vapour pressure regime aligns strongly with the vapour pressure of water, thereby enabling direct analysis of liquid water layers to be performed. While the technological ability to study liquid water is realised, further challenges remain in the study of the solid/liquid interface, mainly in relation to the surface sensitive nature of NAP-XPS. The limited escape depth of the photoelectrons imposes restrictions on solid/liquid experiments, forcing users to study this critical interface either through a thin solid membrane which sits above a bulk liquid layer or by forming an ultra-thin wetting layer of liquid above a solid surface.

The work presented here details a novel methodology of forming ultra-thin wetting layers of liquid on a solid surface during NAP-XPS analysis, known as the "Offset Droplet Method". This technique has been demonstrated both at a synchrotron beamline and within conventional lab based NAP-XPS systems, extending this cutting edge ability to be made available to a wide audience of researchers. The ability to control the thickness of the wetting layer above the solid surface in the 0 to 18 nm range is achievable with demonstrated ultra-clean interfaces of no detectible carbon present. Further still, we demonstrate the ability to electrically polarise the wetting layer, thereby allowing operando study of the solid/liquid interface. A number of solid/liquid interface combinations have been studied including water/TiO2 for photo-degradation of organic species and H2SO4/Pt for oxygen reduction reaction during electrical polarisation. Additionally, the knowledge and understanding accrued during development of the Offset droplet technique as enabled further lines of in-situ solid/liquid analysis such as vacuum water contact angle (WCA) measurements of UHV prepared surfaces, with the ability to correlate surface chemistry and WCA of pristine material surfaces.