Ambient pressure X-ray photoelectron spectroscopy with application to solar water splitting materials

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The development of ambient pressure X-ray photoelectron spectroscopy (AP-XPS) has enabled photoelectron spectroscopy experiments at elevated pressures. This has made possible quantitative, chemically specific investigations of technologically relevant surfaces and interfaces in equilibrium with realistic gas pressures. This technique has been predominantly applied using soft X-rays. However, the AP-XPS technique has recently been extended into the tender (or “hard”) X-ray regime (ambient pressure hard X-ray photoelectron spectroscopy, AP-HAXPES). AP-HAXPES provides the possibility to investigate buried interfaces, including solid – electrolyte interfaces. We have used both AP-XPS and AP-HAXPES to understand the bismuth vanadate (BiVO$_4$) – electrolyte interface used in solar water splitting devices. We have studied gas phase water adsorption onto a BiVO$_4$(010) single crystal surface at pressures up to a few Torr with soft X-ray AP-XPS. Our results indicate that the surface is significantly hydroxylated by ~0.5 Torr. Surface hydroxylation is accompanied by reduced vanadium in the surface and occupied states above the valence band maximum which are attributed to hydroxyl induced small polaron formation. We have also investigated the effects of solar illumination on BiVO$_4$ – potassium phosphate electrolyte and BiVO$_4$ – potassium borate electrolyte interfaces at open circuit potential using AP-HAXPES. Upon illumination with a solar simulator, we observe spectral changes consistent with the formation of bismuth phosphate and significant restructuring of the electrolyte near the BiVO$_4$ – potassium phosphate interface. These changes were not observed upon illuminating the BiVO$_4$ – potassium borate electrolyte interface. These results provide fundamental information about the general behaviour of water splitting photoelectrodes under illumination and insight into how the electrolyte influences device stability.