Probing the TiO$_2$/Liquid Interface of a Photoelectrochemical Cell by X-Ray Photoelectron Spectroscopy — •Michael F. Lichterman$^{1,2}$, Matthias H. Richter$^{1,2,7}$, Shu Hu$^{1,2}$, Ethan J. Crumlin$^3$, Stephanus Axnanda$^3$, Marco Favaro$^{3,4}$, Walter Drisdell$^{3,4}$, Zahid Hussain$^3$, Bruce S. Brunschwig$^1$, Zhi Liu$^{3,5,6}$, Nathan S. Lewis$^{1,2}$, and Hans-Joachim Lewerenz$^{1,2}$ — $^1$Caltech, Pasadena, USA. — $^2$JCAP, Pasadena, USA. — $^3$LBNL, Berkeley, USA. — $^4$JCAP, Berkeley, USA. — $^5$Chinese Academy of Sciences, China. — $^6$ShanghaiTech University, China. — $^7$BTU C-S, Cottbus, Germany.

Amorphous TiO$_2$ coatings can stabilize semiconductor photoanodes such as Si, GaAs, and GaP that are otherwise unstable in aqueous media [1]. Using tender X-rays with their substantially increased inelastic mean free scattering length of photoelectrons and using the classical three-electrode potentiostatic arrangement allows one to follow of the influence of the applied potentials on the semiconductor electrode energetics such as band bending and band edge shifts directly [2, 3]. The observed shifts in binding energy with respect to the applied potential have directly revealed rectifying junction behavior on semiconducting samples. Accumulation, depletion and Fermi level pinning were observed. Additionally, the non-linear response of the core level binding energies to changes in the applied electrode potential has revealed the influence of defect-derived electronic states on the Galvani potential across the complete cell. [1] Science 344 (2014) 1005; [2] Sci Rep 5 (2015) 9788; [3] Ener & Env Sci 8 (2015) 2409