Monitoring the Interfacial Electronic Dynamics at the Semiconductor–Liquid Junction: a New Route to Interrogate Photoelectrosynthetic Reactions

Néstor Guijarro

Institute of Chemistry and Chemical Engineering, École Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland
nestor.guijarro@epfl.ch

Photoelectrochemical (PEC) water splitting, wherein high-energy charge carriers photogenerated within the semiconductor (SC) photoelectrode trigger the production of H_2 and O_2 at the aqueous interface, stands out as a tantalizing approach to store sunlight into chemical commodities. However, the conversion efficiency remains far below the expectations primarily because of the lack of information on the semiconductor–liquid junction (SCLJ), a crucial component of this tech wherein the catalytic processes occurs. A tool capable of sensing the electronic characteristics of the SCLJ would bring out the parameters constraining the performance and provide specific remedies.

Here, I will present a novel technique wherein a secondary electrical contact (EC2) deposited at the electrode–electrolyte interface allows, for the first time, direct tracking of the surface energetics and electronic dynamics at the SCLJ when operating in steady-state (SS) or time-resolved (TR) modes, respectively. When applied to standard (Pt-coated InP) or emerging SC photocathodes ($CuInGaS_2$), SS measurements revealed elusive catalytic features (surface overpotential η_R, tafel slope) whereas TR data provided unprecedented kinetic information on the surface recombination and interfacial reaction (rate constant, mechanism). All in all, this unique surface-sensitive tool identifies unambiguously the processes governing the performance while building a needed understanding on the reactive interface.