

Interfacial Dynamics of Hematite Photoanode – an *in situ* Spectroelectrochemical Study

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Understanding the interface at the semiconductor-liquid junction (SCLJ) is a key step in optimization of solar energy conversion devices. Here we provide an extensive characterization on how the pH controls the semiconductor-liquid interfacial properties, viz. energetics across the interface together with the kinetics of charge transfer and recombination, in nanostructured hematite photoanode. To do so, a complementary set of *in situ* spectroelectrochemistry techniques including photoelectrochemical impedance spectroscopy (PEIS), intensity-modulated photovoltage/photocurrent spectroscopy (IMVS/IMPS) and ultraviolet-visible spectroelectrochemistry were implemented. With the help of these techniques, we could quantitatively access the information of density of surface states (DOS), degree of Fermi level pinning, charge transfer/recombination kinetics, carrier lifetime and high-valent Fe absorbance over a large range of pH and applied potential. We hope these findings will provide a better understanding on the electrochemical characteristics at the SCLJ and on the nature and role of the surface states, establishing a precise roadmap to engineer the interface and optimize the performance of the PEC devices.