Multi-scale Modeling of Molecule-Surface Interactions for Improved Charge Transfer across Photoelectrochemical Interfaces

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The design of efficient, stable photoelectrochemical devices requires the use of complex heterojunctions composed of semiconducting, protective, and catalytic layers. Understanding the nature of charge transport across these interfaces is challenging, due to the complexity of the interfaces and possibility of competing charge transfer mechanisms. We present our recently developed multiscale approach that combines first-principles density functional theory (DFT) and solid-state drift/diffusion device scale modeling to give insights into the nature of charge transport across photoelectrode interfaces [1-3], Fig. 1. DFT is used to estimate the surface dipole induced by the functionalization, and the device software wxAMPS is used to predict experimentally measurable features such as the JV curve and the open-circuit voltage. Using this approach, we are able to identify the mechanism of hole transfer across *n*-Si(111)–*R*|TiO2 photoanodes where −*R* is a series of mixed aryl/methyl monolayers containing an increasing number of methoxy units (mono, di, and tri). In collaboration with experiment, we find that hole transport is limited at the *n*-Si(111)–*R*|TiO2interface and occurs by two processes—*thermionic emission* and/or *intraband tunneling*—where the interplay between them is regulated by the interfacial molecular dipole. Finally we will highlight how molecule/surface interactions can be used to model doped silicon slabs at experimental doping densities in a computationally tractable manner.

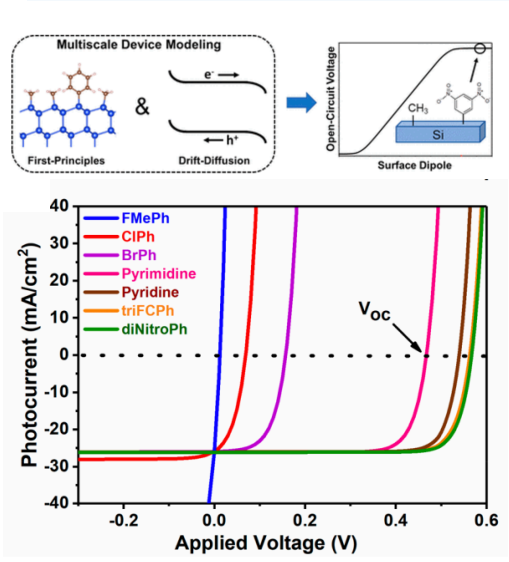

Figure 1. Multiscale approach combining first-principles methods and solid state drift/diffusion modeling.

[1] Kara Kearney*, Ashwathi Iyer*, Angus Rockett, Aleksandar Staykov, Elif Ertekin. "Multiscale Computational Design of Functionalized Photocathodes for H2 Generation", Journal of the American Chemical Society DOI: 10.1021/jacs.7b10373 (2018). (*equal contribution)

[2] Ashwathi Iyer, Kara Kearney, Shohei Wakayama, Hirotoshi Odoi, Elif Ertekin. "Design strategy for the Molecular Functionalization of Semiconductor Photoelectrodes: A Case Study of p-Si(111) Photocathodes for H_2 Generation", Langmuir (2018). DOI: 10.1021/acs.langmuir.7b03948

[3] Ryan T. Pekarek, Kara Kearney, Benjamin M. Simon, Elif Ertekin, Angus A. Rockett, and Michael J. Rose. "Identifying Charge Transfer Mechanisms across Semiconductor Heterostructures via Surface Dipole Modulation and Multiscale Modeling", J. Am. Chem. Soc. (2018). DOI: 10.1021/jacs.8b05057

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