Controlling Electron Dynamics at Semiconductor Surfaces by Molecular Functionalization Probed by XUV Reflection-Absorption Spectroscopy

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Directly observing electron dynamics at surfaces is required to understand the material properties that govern efficient energy conversion as well as ultrafast information processing. To enable this, Extreme Ultraviolet Reflection-Absorption (XUV-RA) spectroscopy combines the benefits of traditional X-ray absorption, such as element, oxidation, and spin state resolution, with surface sensitivity and ultrafast time resolution.

Using XUV-RA spectroscopy, we measure electron dynamics in hematite (α-Fe_2O_3) with a probe depth of less than 3 nm equating to roughly two atomic layers of the 0001 surface. This provides comparison of rates of electron self-trapping at a hematite surface with the equivalent process in the bulk material. Results show that the electron trapping rate is approximately three times slower at the surface and this difference is driven primarily by the greater lattice reorganization energy associated with small polaron formation at the surface compared to bulk.

In an effort to improve polaronic transport at interfaces, hematite surfaces were covalently functionalized with small molecules (phenylphonic acid and substituted derivatives) to create a tunable interfacial dipole moment. XUV-RA spectroscopy shows that this approach provides systematic control of the rates for electron self-trapping offering the possibility for design of photocatalytic interfaces with enhanced carrier transport based on earth abundant materials.

We are now extending these studies to CuO and Cu_2O surfaces. Importantly, Cu oxides can be electrochemically deposited in the presence of a chiral ligand, which leads to templating of the deposited film. This produces to a chiral semiconductor interface, where the chirality persists even after thermal removal of the templating molecule. XUV-RA spectroscopy of this material will soon provide measurements of spin polarized electron dynamics at these chiral interfaces, an important step toward understanding spin selective photocatalysis at semiconductor surfaces.