CONTROLLING PHOTOEXCITED STATE DYNAMICS AT HEMATITE SURFACES

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Hematite is an earth abundant material that has the potential to be used as a photoanode for oxygen evolution from water using solar energy. Modifications such as surface functionalization, surface doping, use of a co-catalyst and preparation of layered heterojunctions have each been explored in an effort to increase the efficiency of the hematite electrode with varying degrees of success. However, due to the complexity of this material and the challenges associated with probing electron and hole dynamics with surface specificity and chemical state resolution, the fundamental processes governing carrier transport and trapping in surface states is still not well understood. In particular, recent transient studies carried out on hematite using extreme ultraviolet (XUV) absorption spectroscopy and XUV reflection absorption (RA) spectroscopy show key differences in the dynamics of small polaron formation in bulk hematite versus at the surface. To better understand the origin of these differences, we have functionalized hematite surfaces with a series of small organic molecules, including phenyl phosphonic acid (PPA), 4-Cyano PPA and 4-methoxy PPA. These molecularly functionalized surfaces have been characterized using x-ray photoelectron spectroscopy and sum frequency generation vibrational spectroscopy. Linear sweep voltammetry measurements is used to explore the effect of these systematic surface modifications on the photoelectrochemical efficiency of this material. To better understand the mechanism by which surface modification influences catalytic efficiency, transient XUV-RA spectroscopy is used to measure changes in the rate of small polaron formation and surface trapping in these materials. This direct observation of electron and hole dynamics in systematically modified hematite surfaces provides a better understanding of the material properties responsible for mediating energy conversion efficiency in these and related materials.