ACHIEVING SURFACE SENSITIVITY IN ULTRAFAST XUV SPECTROSCOPY

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The ability to follow electron dynamics at surfaces is necessary to identify the material properties and surface defect states, which mediate carrier lifetime and ultimately determine energy conversion efficiency. Toward this goal we have recently developed extreme ultraviolet reflection-absorption (XUV-RA) spectroscopy as a surface specific analog of XUV transient absorption. Unlike absorption measurements, which sample only the imaginary component of the refractive index, reflection measurements probe both the real and imaginary components of the material's complex refractive index. We find that the imaginary component is sensitive to the chemical state of the material as reported by the core-hole resonant spectrum while the real component is additionally sensitive to the physical morphology of the material. Using semi-empirical spectral simulations we show that XUV-RA spectroscopy retains the element and chemical state specificity of XUV absorption spectroscopy. Accordingly, this technique extends the benefits of element specific x-ray absorption spectroscopy to the study of surface electron dynamics by measuring core-hole resonances with a probe depth of less than 3 nm and a time resolution of less than 100 fs. Here we describe the application of XUV-RA spectroscopy to the study of ultrafast electron trapping and defect-mediated recombination at the surface of NiO. Direct observation of ultrafast electron trapping and subsequent recombination shows that grain boundaries rather than oxygen vacancies are responsible for fast electron-hole pair recombination. This result clarifies the design parameters for NiO water oxidation catalysts by showing that oxygen vacancies, which enhance catalytic activity, have no detrimental effect on carrier lifetime. Rather, carrier lifetime can be dramatically extended by the elimination of near-surface grain boundaries even in the presence of chemically active oxygen vacancies.