Materials Science and Engineering Doctoral Defense

Probing atomic, electronic, and optical structures of nanoparticle photocatalysts using fast electrons

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abstract

Photocatalytic water splitting has been proposed as a promising way of generating carbon-neutral fuels from sunlight and water. In one approach, water decomposition is enabled by the use of functionalized nano-particulate photocatalyst composites. The atomic structures of the photocatalysts dictate their electronic and photonic structures, which are controlled by synthesis methods and may alter under reaction conditions. Characterizing these structures, especially the ones associated with photocatalysts' surfaces, is essential because they determine the efficiencies of various reaction steps involved in photocatalytic water splitting. Due to its superior spatial resolution, (scanning) transmission electron microscopy (STEM/TEM), which includes various imaging and spectroscopic techniques, is a suitable tool for probing materials' local atomic, electronic and optical structures. In this work, techniques specific for the study of photocatalysts are developed using model systems.Nano-level structure-reactivity relationships as well as deactivation mechanisms of Ni core-NiO shell co-catalysts loaded on Ta2O5 particles are studied using an aberration-corrected TEM. It is revealed that nanometer changes in the shell thickness lead to significant changes in the H2 production. Also, deactivation of this system is found to be related to a photo-driven process results in the loss of the Ni core.In addition, a special form of monochromated electron energy-loss spectroscopy (EELS), the so-called aloof beam EELS, is used to probe surface electronic states as well as light-particle interactions from model oxide nanoparticles. Surface states associated with hydrate species are analyzed using spectral simulations based on a dielectric theory and a density of states model. Geometry-induced optical-frequency resonant modes are excited using fast electrons in catalytically relevant oxides. Combing the spectral features detected in experiments with classical electrodynamics simulations, the underlying physics involved in this excitation process and the various influencing factors of the modes are investigated. Finally, an in situ light illumination system is developed for an aberration-corrected environmental TEM to enable direct observation of atomic structural transformations of model photocatalysts while they are exposed to near reaction conditions.

November 21, 2017; 9:30 AM; ERC 593