Electrochemical Impacts of TiOx Shells on Rutile TiO2 Nanorods

Rutile TiO2 shows promise for being used as a photoanode semiconductor in dye-sensitized photoelectrosynthesis cells (DSPECs), devices that use sunlight to drive the production of solar fuels. The addition of a TiO2 coating or shell onto a mesoporous nanocrystalline TiO2 photoanode substrate has been shown to improve device efficiency for water oxidation, yet little is known about why this change improves the performance of DSPECs. In this research, TiOx shells were deposited using atomic layer deposition onto rutile TiO2 nanorods and the electrochemical effects of the deposition were probed to help elucidate changes to the electronic structure induced by the shell. Rutile TiO2 was found to have a monoenergetic collection of deep trap states that is positive in potential to an exponential trap distribution in the band gap below the conduction band minimum. When increasing the TiOx shell thickness, the deep trap states of rutile TiO2 shifted to more positive potentials without changing the density of these states. In addition, the band gap of the material was found to decrease as shell thickness increased as quantified using diffuse reflectance spectroscopy. These results suggest the monoenergetic deep trap state population is not related to the surface of the nanorods. From photoelectrochemical impedance spectroscopy, the calculated rates of back-electron transfer were lower for samples with a TiOx shell compared to samples of rutile TiO2 without a shell. This agrees with findings showing core-shell materials have improved photoanode efficiency, since back-electron transfer hinders efficiency.