

## **Pair Distribution Function Analyses of Ultrathin-Films and Molecular Catalysts at Electrode and Functional Interfaces**

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A key challenge for the design of efficient photoelectrochemical devices that employ nanoscaled interfacial designs for solar and electrochemical energy conversion lies in resolving atomic structures and dynamics at the active interfaces, and relating these to the complex cascade of events which includes charge injection, accumulation, and multi-step energy conversion and catalysis. Our research programs have been developing in-situ, time-resolved X-ray techniques aimed at the resolution of atomic scale structures that underlie interfacial charge transfer and photo-driven water-splitting catalysis under conditions relevant to photoelectrochemical function for both interfacial thin-films and molecular photosensitizers and catalysts bound to semiconductor surfaces.

This presentation will show how high energy (>50 keV) X-ray scattering and pair distribution function (PDF) analysis provides atomic structure characterization that usefully complements electronic structure characterization derived from a combination of soft X-ray absorption (XAS), resonant X-ray emission (RXES), resonant inelastic X-ray scattering (RIXS) techniques for structure-function analysis of transition metal semi-conductor and catalyst thin films. Microporous high surface area electrodes were designed that allowed PDF analysis to be accomplished 0.2 Å spatial resolution for amorphous transition metal oxide thin films having thickness of down to 60 nm. The combined electronic and structural analyses demonstrate that hole transfer to catalytic sites in amorphous cobalt oxide thin films is the rate-limiting step for electrochemical water-splitting rather than the multi-step catalytic events themselves. The macroscopic catalytic properties of the thin films were found to be correlated to the electronic structures measured at the atomic scale for the metal-oxo cluster domains. These results show the interplay between intrinsic catalytic activity and charge transport properties of semiconductor thin-film catalysts.

We have extended this approach by the development of nanoporous electrode architectures which enable the use of combined PDF and X-ray spectroscopy analyses to resolve differences in coordination structures for molecular photosensitizers and catalysts in solution and when bound to semiconductor oxide surfaces. Measurements on ruthenium photosensitizer complexes bound to the TiO<sub>2</sub> surface resolve distortions in the surface-coordinating ligand structures. On-going work is investigating the correlation between ligand structural distortion and the metal-to-ligand charge-transfer (MLCT) states with ultrafast interfacial charge injection function.