In response to the raising global energy demand, photoelectrochemical (PEC) solar fuel production provides opportunities for the efficient harnessing of abundant solar energy. The photogenerated minority carriers are driven to the semiconductor-liquid interface for carrying out redox reactions, consequently storing photon energy into chemical bonds. The events governing overall photon-to-fuel conversion efficiency in semiconductor photoelectrodes include light absorption, bulk transport, charge separation, and heterogeneous charge transfer. In the first part of this talk I will present my doctoral research, which utilizes time-resolved X-ray spectroscopic technique to study excited-state dynamics in transition metal oxides. Because X-ray absorption promotes an electron from a localized core level to a delocalized and unoccupied valence level, this emerging technique is capable of providing information that is specific to elements and oxidation states, with femtosecond temporal resolution. The second part of my talk will focus on copper vanadate, a group of ternary oxides that are suitable for photo-driven water oxidation. By comparing key PEC functional characteristics across several different copper vanadate compounds with varying Cu:V ratios, the roles played by each metal element in a photoelectrode can be disentangled. Achieving a balance between bulk properties, such as bandgap and carrier diffusion length, and surface catalytic activity for the desired chemical reactions is proven to be imperative for designing a high-performing solar fuel production system.

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