

How Charge Transforms Chemical Bonds at Solid-Liquid Interfaces

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The principles that govern catalysis at solid-liquid interfaces are at the heart of energy storage technologies, enabling chemical reactions required to store energy in batteries, to release it in fuel cells, and to convert it in solar-to-fuel systems. Catalysis at this interface proceeds from the localization of charge onto surface atoms, forming catalytic intermediates. My lab leads an effort in resolving the reaction pathway from the *point of charge transfer* to the surface. The experiments merge time-resolved (optical, mid-infrared) spectroscopy with efficient pulsed excitation of photo-electrochemical O₂ evolution on a model system, the n-SrTiO₃/aqueous interface. Thus far, for the intermediates that precede the first chemical bond of the cycle (O-O), the following picture has emerged: valence band holes localize on terminating O surface sites, creating titanium oxyl (Ti-O•) radicals, and on in-plane O-sites, creating bridge (Ti-O•-Ti) radicals. Aided by theoretical calculations, the oxyl radical was detected by its unique Ti-O stretch vibration in the plane right below Ti-O•^[1] (Fig. 1), and the bridge radical by an in-plane polarized optical dipole transition^[2]. We find that the radicals are created within a couple picoseconds and are stable for microseconds. Further, these experiments demonstrate that water reorganization around the intermediates (*e.g.* aqueous solvation) is critical to stabilizing them at the surface, by the time constants with which the O-site radicals form^[2] and by the coupling of the oxyl radical's vibration to water librations^[1]. In a related system (n-GaN/aqueous interface), the presence of intermediates enhanced the mobility of charge along the surface^[3], which suggests the importance of intermediate surface hopping and the disruption of the solvation sphere to bond formation. Current work in my laboratory, which will also be discussed, focuses on the evolution of the O-site radical population on SrTiO₃ towards the O-O bond.

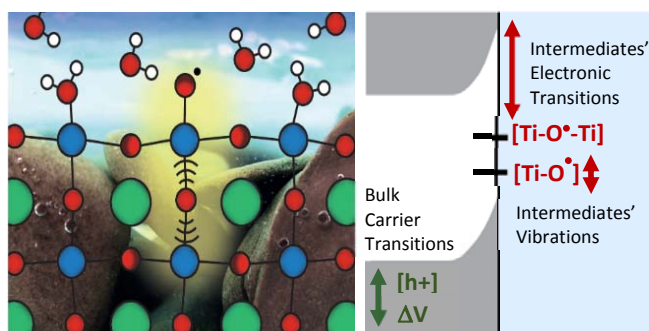


Figure 1. Formation of titanium oxyl and bridge radicals, at terminating and in-plane O-sites on the surface, respectively (red text and arrows) from valence band holes (green text and arrows) at the n-type semiconductor (SrTiO₃)/aqueous interface.

Funding: Department of Energy, Basic Energy Sciences, Chemical Sciences Division & Air Force Office of Scientific Research

References:

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