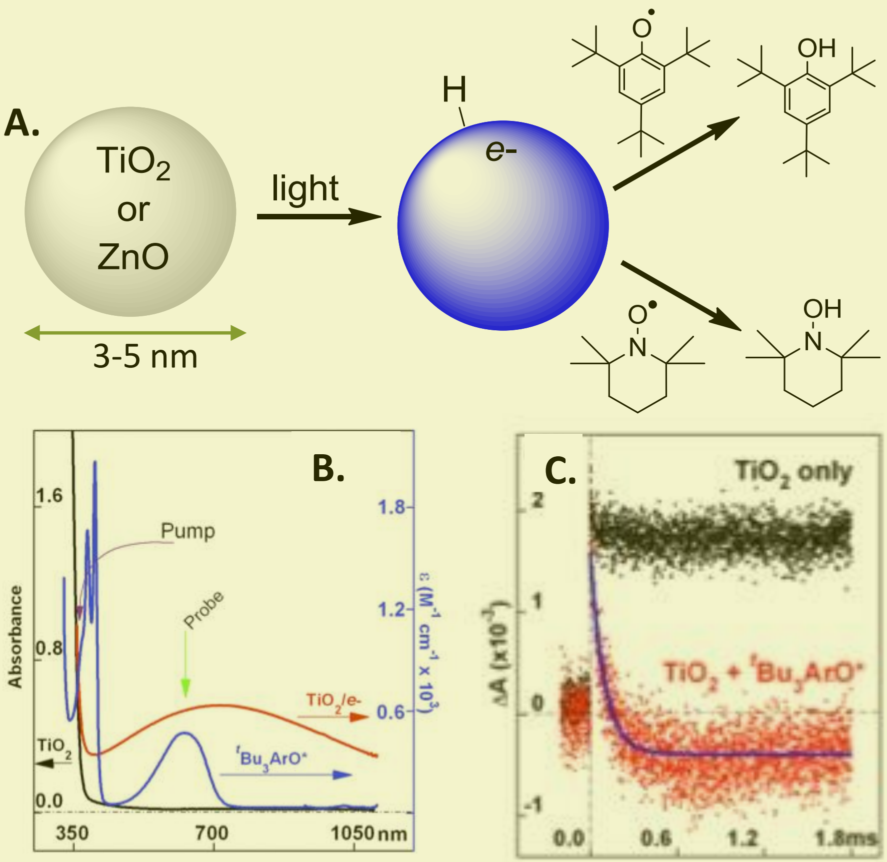
James M. Mayer, Department of Chemistry, University of Washington

The Role of Protons in Charge Transfer Reactions of Metal Oxide/Solution Interfaces



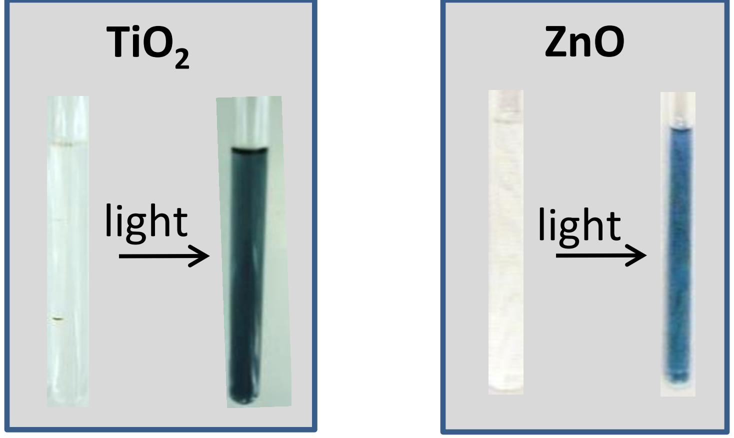
Caption: **A.** Solutions of 3-5 nm diameter particles of TiO_2 or ZnO become colored upon irradiation with ultraviolet light, indicating that electrons are being stored in the materials. These reduced particles can react to transfer both electrons and protons. **B.** Optical spectra of as-prepared TiO_2 particles (black), reduced TiO_2 (TiO_2/e^-), and ${}^tBu_3ArO^\bullet$ (blue). **C.** Laser irradiation at 355 nm ("Pump" arrow in **B**) causes changes in absorbance at the "Probe" wavelength (620 nm): black points, TiO_2 only; red points, TiO_2 + ${}^tBu_3ArO^\bullet$ with fit to second order kinetics.

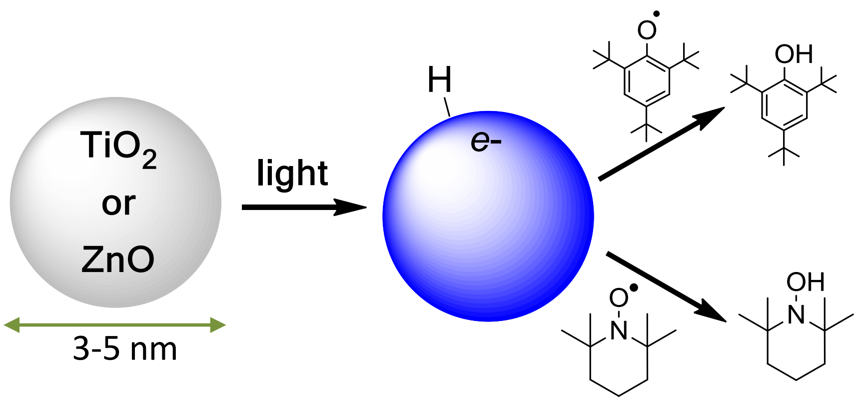
Credit: Joel Schrauben and Carolyn Valdez

Background: Underlying the reactions in next-generation solar cells, lithium ion batteries, and photocatalytic wastewater remediation are oxidation and reduction processes at metal oxide materials. Most studies of these materials have focused only on the movement of electrons, and utilized the electronic "band structure" model of bulk solids. However, this does not easily connect with the chemical reactions that occur at the surface of the material.

Results: We have shown that electron transfer at the metal-oxide/ solution interface can be coupled to proton movement. In these simple experiments, reduced zinc oxide or titanium dioxide particles were reacted with organic oxyl radicals. The radicals specifically abstract hydrogen atoms, that is $e^- + H^+$. The laser-flash kinetics experiments illustrated at left indicate that this is a facile process. This finding represents a new perspective in this well-established field.

Impact and Benefits: Oxidation and reduction processes at metal oxide surfaces are crucial to photocatalysis and emerging solar energy conversion processes. The finding of coupled movement of electrons and protons in these systems provides new understanding which should help in the design of more efficient systems. Coupling electron and proton transfers could help to reduce the energy barriers for technologically relevant chemical reactions.





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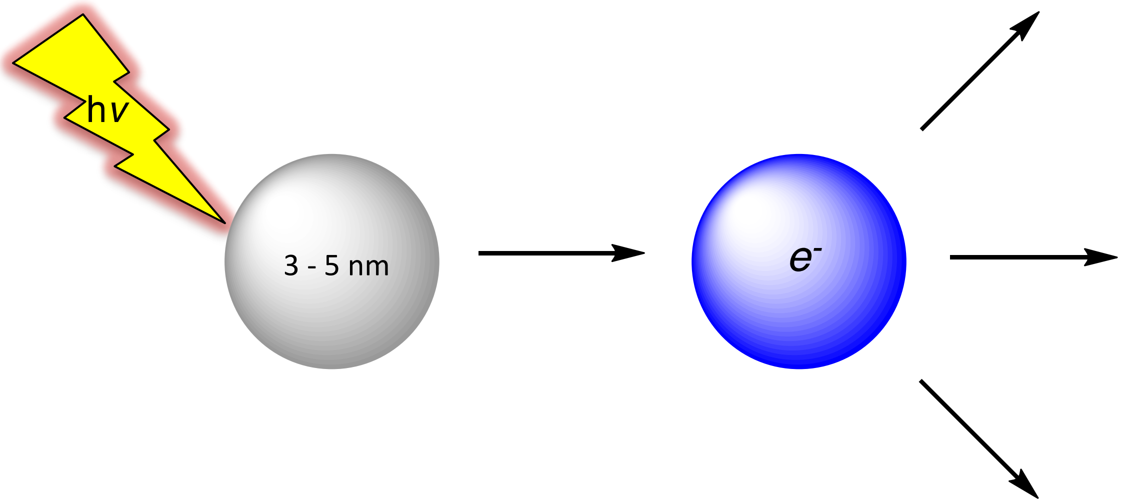

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