Unexpected Dynamics at a Photoelectrode Interface

Scientific Achievement

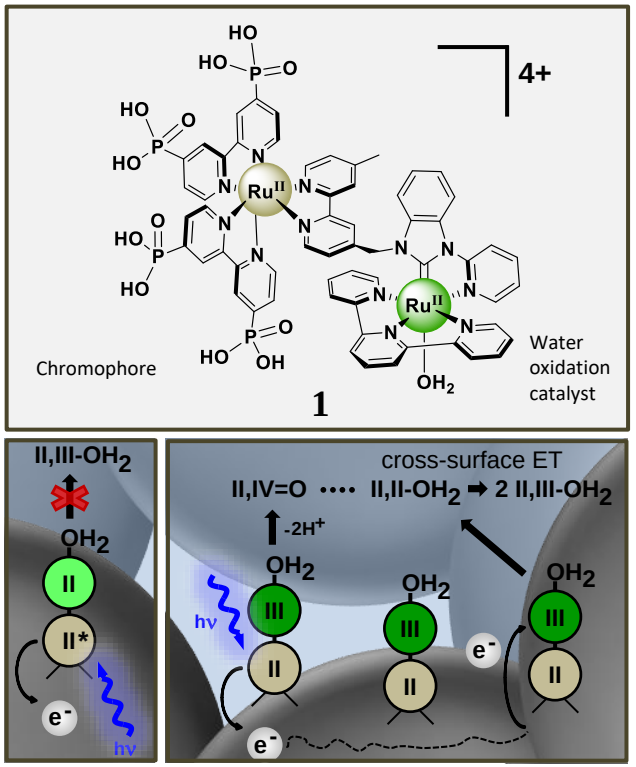
Found that the first photo-activation step in a water oxidation photoelectrode can be prohibited by the electrolyte and the second photo-activation step can be inhibited by cross-surface redox chemistry.

Significance and Impact

May be important design considerations in the development of high-efficiency dye-sensitized photoelectrosynthesis electrodes to avoid competitive side-reactions.

Research Details

- In hybrid molecule-semiconductor photoelectrodes designed for water oxidation to produce O_2 and H^+, four photon-driven steps are required to complete the reaction, although mechanistic insights are lacking.
- A detailed set of transient absorption experiments, and related spectroelectrochemistry, of the first two photo-activation steps for **1** surface-bound to TiO_2 show that the interfacial dynamics are impacted by the electrolyte, and by cross-surface electron transfer and redox reactions.



Upper : Structure of phosphonate-derivatized chromophore–water oxidation catalyst assembly, **1**.

Lower Left : Cartoon depicting events initiated by light absorption of a ground-state (II-II) assembly adsorbed to TiO_2 (gray spheres) in 0.1 M HPF_6.

Lower Right : Cartoon depicting events initiated by shining light on TiO_2-bound, II-III assemblies in a variety of acidic aqueous solutions.

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