High-Potential Porphyrin Photosensitizers for Solar Water-Oxidation Catalysis

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Devising cost effective methods for efficiently capturing and storing solar energy is among the grand challenges of science (1). We are using insights from studies of natural photosynthetic systems (2) to develop bioinspired materials for photochemical water oxidation and solar fuel production. Our progress on the development of synthetic water-oxidation catalysts (3-4) and their use in materials for artificial photosynthesis (5-6) will be discussed. In order to use visible light to drive water-oxidation catalysis, we have designed high-potential porphyrin photosensitizers for functionalization of metal oxide surfaces. In these constructs, the photosensitizer efficiently absorbs visible light and uses the energy to initiate electron transfer to an attached metal oxide. The injected electrons can ultimately be used for H^+ or CO_2 reduction at a cathode while the resulting holes (sensitizer radical cations) provide the potential needed for a water-oxidation catalyst. We have prepared photoanodes consisting of a high-potential zinc *bis*-pentafluorophenyl porphyrin sensitizer ($ZnPF_{10}$) bearing linkers for functionalization of TiO_2 or SnO_2 nanoparticles. THz studies and photoelectrochemical measurements demonstrate that photoexcited $ZnPF_{10}$ is capable of injecting electrons into both the TiO_2 and SnO_2 conduction bands. Co-deposition of the photoanode with a molecular water-oxidation catalyst (IrCp*) (4) results in a marked increase in the observed photocurrent, consistent with light-induced activation of the catalyst.

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