

Design of Photoelectrochemical Cells for the Splitting of Water and Production of Fuel

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The design of bioinspired schemes that couple solar energy conversion to the oxidation of water and the subsequent use of the reducing equivalents to synthesize energy-rich compounds, such as hydrogen or fuels based on reduced carbon is the main objective of our present research.^{1,2} In order to establish the design principles for a tandem, two junction (or threshold) photochemical cell, we are assembling Grätzel-type photoelectrodes that model photosystems I and II (PSI and PSII) of plants. The photoanode model of PSII will contain a mimic of the donor side (water oxidizing side) of PSII reaction centers. In PSII, tyrosine Z (Tyr_Z) mediates charge transport between the photo-oxidized primary donor (P680⁺⁺) and the oxygen-evolving complex (OEC). The oxidation of Tyr_Z by P680⁺⁺ likely occurs with the transfer of the phenolic proton to a hydrogen-bonded histidine residue (His190). This coupling of proton and redox chemistry is thought to poise the Tyr_Z oxidation potential between those of P680⁺⁺ and the OEC. We have prepared a bioinspired system (BiP-PF₁₀) consisting of a high oxidation potential porphyrin (PF₁₀, 1.59 V vs. NHE, a model of P680) that is covalently attached to a benzimidazole-phenol pair (BiP) that mimics the Tyr_Z-His190 pair in PSII. Electrochemical studies show that the phenoxyl radical/phenol couple of the model system is chemically reversible with a midpoint potential of 1.24 V vs. NHE and is therefore thermodynamically capable of water oxidation. When the BiP-PF₁₀ construct is attached to TiO₂ nanoparticles and excited with visible light, it undergoes photoinduced electron transfer. Electrons are injected into the semiconductor and the corresponding holes are localized on either the porphyrin (BiPPF₁₀⁺⁺-TiO₂⁻) or the phenol (BiP⁺⁺-PF₁₀-TiO₂⁻). EPR provides a clear spectroscopic picture of these processes.³ The photoelectrode model of PSI will be sensitized by low potential naphthalocyanines or phthalocyanines, which absorb light in the near IR region of the spectrum. Upon photoexcitation, these dyes are designed to inject electrons into semiconductors having sufficiently negative conduction bands to effectively drive the reduction of protons to hydrogen at a cathode. The semiconductor will be electrically wired to a cathode suitable for hydrogen production: either a metal electrode (Pt or Ni) or a hydrogenase-modified carbon electrode.⁴

References

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