Layer-by-Layer Assembly of Molecular Photoelectrodes on Conductive Oxides

Scientific Achievement

A layer-by-layer methodology was utilized to spatially arrange redox and/or chromophoric molecular components on an ITO surface. We report that mesoporous thin films of conductive indium-doped tin oxide (ITO) nanocrystallites support long-lived charge separation with first-order (k = 1.5 s^{-1}) recombination kinetics. Monochromatic steady-state light excitation resulted in sustained photoelectrochemical water splitting.

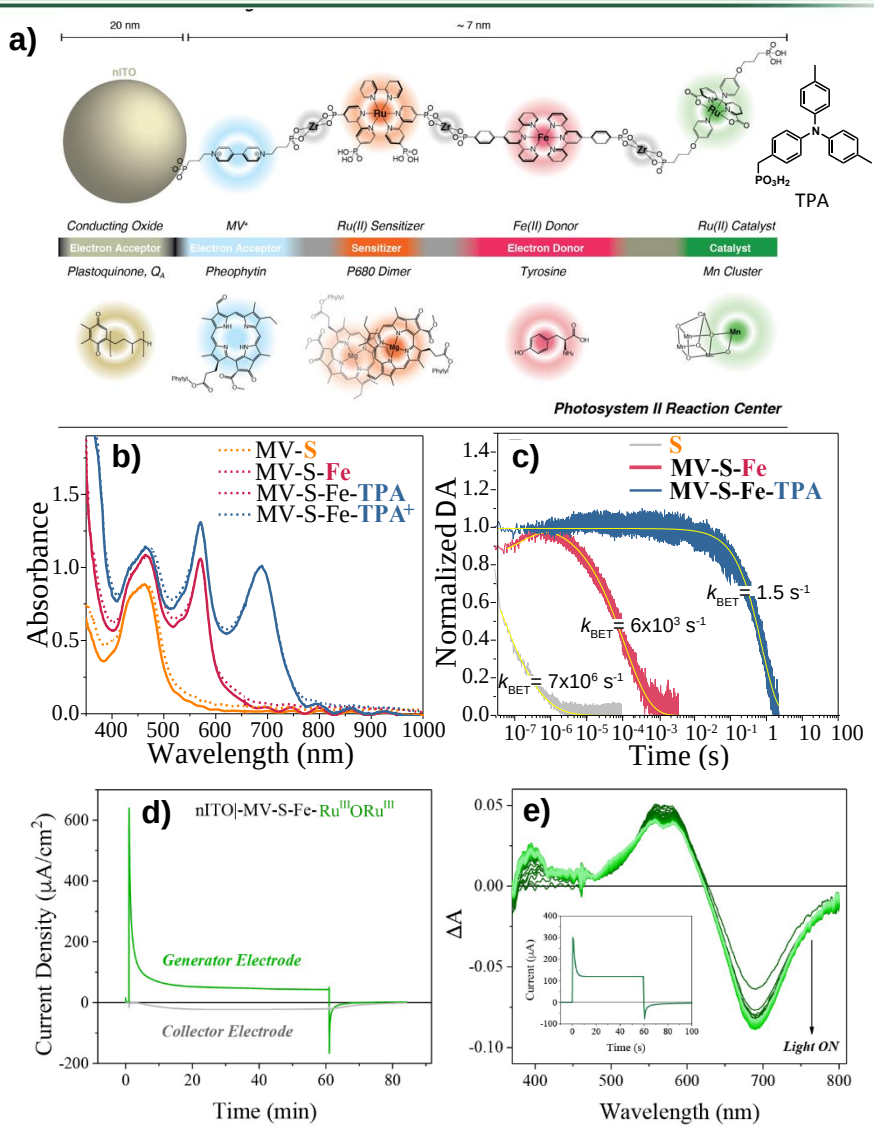
Significance and Impact

A conductive photoanode that incorporates an electron acceptor, a sensitizer, an electron donor, and a water oxidation catalyst (or a TPA donor) in a single molecular assembly, with similarities to photosystem II, is described. The data provide a first example of long-lived charge separation and water oxidation at a conductive oxide interface. Steady-state light excitation at 440 nm resulted in photoelectrochemical water splitting with a per-photon absorbed efficiency of 2.3% at V_{app} = 0.5 V vs NHE.

Research Details

- An electron acceptor (MV), sensitizer (Ru), primary electron donor (Fe) and catalyst (Ru) (or secondary electron donor (TPA)) were assembled through layer-by-layer deposition with zirconia bridges.
- A 1:1:1 stoichiometry was achieved
- The rate constant for unwanted charge recombination decreased with each additional layer.
- With TPA donors, the recombination kinetics were first-order (k = 1.5 s^{-1}).
- Sustained water oxidation with a per-photon absorbed efficiency of 2.3% was quantified with blue light excitation and a 0.5 V vs NHE applied potential.

1. R. N. Sampaio,# L. Troian-Gautier,# G. J. Meyer, ACIE, **2018**, *130*, 15616-15620
2. D. Wang,# R. N. Sampaio,# L. Troian-Gautier, S. Marquard, B. H. Farnum, B. D. Sherman, M. V. Sheridan, C. J. Dares, G. J. Meyer, T. J. Meyer, Submitted



Work was performed at the University of North Carolina at Chapel Hill

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