Layer-by-Layer Self-Assembly of Polychromophore and Molecular Water Oxidation Catalyst for Solar Fuel Conversion

Scientific Achievement

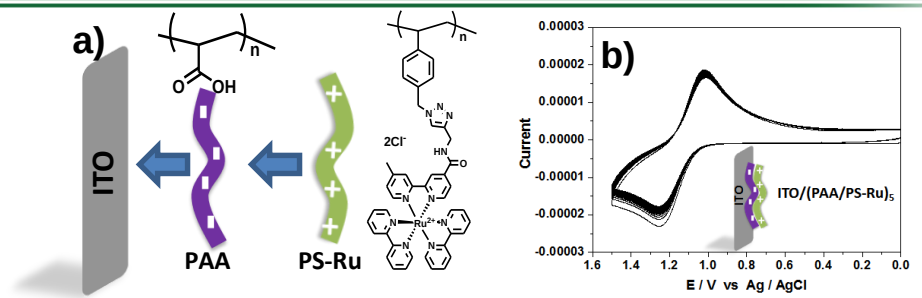
- **Polyelectrolyte Layer-by-Layer (LbL) self-assembly of a polychromophore (PS-Ru) and a water oxidation catalyst (WOC) is used to fabricate chromophore/catalyst films.**
- **Photoelectrochemical response of LbL assembly films on ITO substrates confirms catalytic activity of WOC in the presence of the polychromophore.**

Significance and Impact

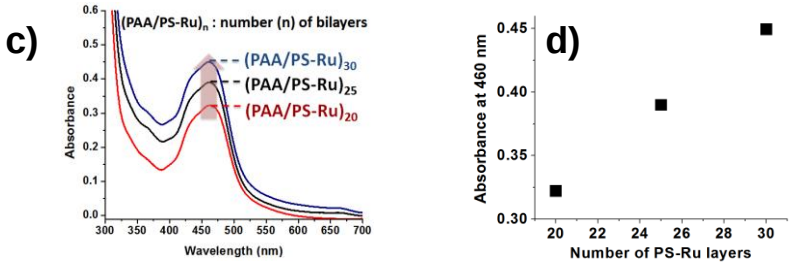
Layer-by-Layer technique is facile and allows rapid construction of a variety of polychromophore/catalyst assemblies atop conducting and semi-conductor substrates. Technique easily extends to other oxidation and reduction catalyst systems and planar and nano-structured substrates.

Research Details

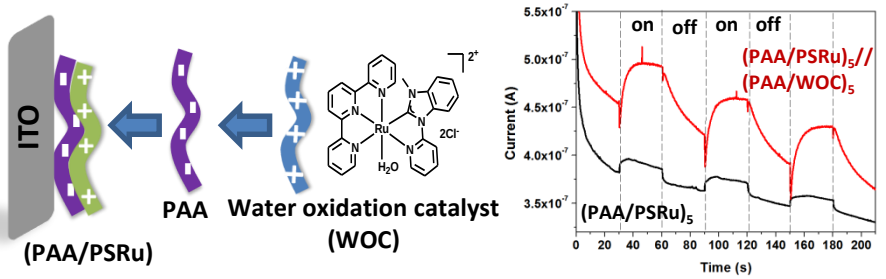
- Polychromophores and a water oxidation catalyst as positively charged species are alternately deposited with a polyacrylic acid (PAA) polyanion layer driven by electrostatic forces.
- Cyclic voltammetry and UV-visible absorption reveal that the bilayer deposition process gives linear film deposition on ITO glass substrates. Films are stable in aqueous solution at low and high pH.
- Transient photocurrent response shows that at 0.7 V vs. Ag/AgCl applied potential the ITO//$(PAA/PSRu)_5$//$(PAA/WOC)_5$ assembly gives an increased photocurrent compared to the reference ITO//(PAA/PS-Ru) assembly lacking the water oxidation catalyst.
- Work in progress seeks to explore the photoelectrochemistry on TiO_2/nano-ITO core-shell substrates



ITO: Indium Tin Oxide, PAA: Polyacrylic acid, PS-Ru: Polystyrene-based Ru chromophore.



(a) LbL assembly of ITO//$(PAA/PS-Ru)_n$. (b) Cyclic voltammetry of ITO/$(PAA/PS-Ru)_5$ film in 0.1 M $HClO_4$ aqueous solution at 100 mV/S scan rate. (c) UV/vis spectra of assembled multilayer films as a function of the number of bilayers. (d) Linear deposition pattern at 460 nm with respect to the amount of polymer deposited per bilayer combination.



(Left) LbL assembly of ITO//(PAA/PSRu)//(PAA/WOC). (Right) Transient photocurrent response of ITO//$(PAA/PSRu)_5$//$(PAA/WOC)_5$ and ITO//$(PAA/PSRu)_5$ (light intensity 100 mW/cm^2, applied bias 0.7 V).

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Work was performed at the University of Florida and at UNC Chapel Hill

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