Surface Grafting of Ru(II) Diazonium-Based Sensitizers on Metal Oxides Enhances Alkaline Stability for Solar Energy Conversion

Scientific Achievement

- Electrografting of ruthenium(II) sensitizers on several metal oxide surfaces was achieved and compared to structurally identical sensitizers that contained carboxylic or phosphonic acid groups.
- Electrografted sensitizers exhibited greater (photo)stability in alkaline solution with 98% of the surface coverage maintained after 24h at 1 sun illumination at pH 12. At this pH using carboxylic or phosphonic derivatives, 100% of surface coverage was lost within 1 minute.

Significance and Impact

- Sensitizers stable throughout the pH range are of paramount importance for development of Dye Sensitized Photoelectrosynthesis Cells (DSPEC).
- Water oxidation catalysis is most rapid under alkaline conditions where stable surface linkages are critically needed.

Research Details

- Electrochemical grafting in CH_3CN and water was achieved.
- Surfaces are stable up to pH 14, both in the dark and under 1 sun illumination.
- In pH 10 solution after 6 hours illumination, 98% of diazonium sensitizer remained surface anchored. By comparison, <10% phosphonic and <1% of carboxylic anchored sensitizer remained.
- Loss of N_2^+ confirmed by FTIR.
- IR and XPS data point toward bond formation between oxygen of Ti-O lattice and aryl radical generated by diazonium loss.
- Photocurrent smaller than structurally identical PO_3H_2 derivatives → Currently under investigation.

R. Bangle, R. N. Sampaio, L. Troian-Gautier, G. J. Meyer,
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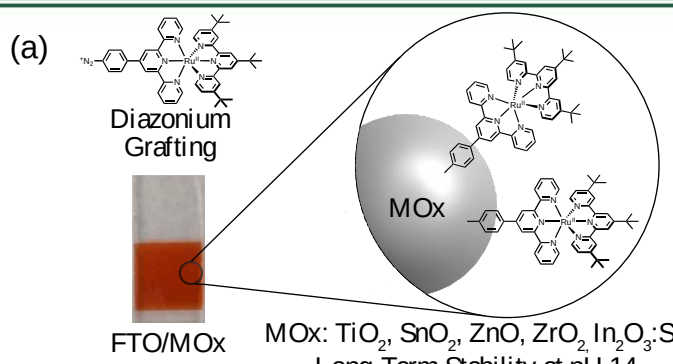

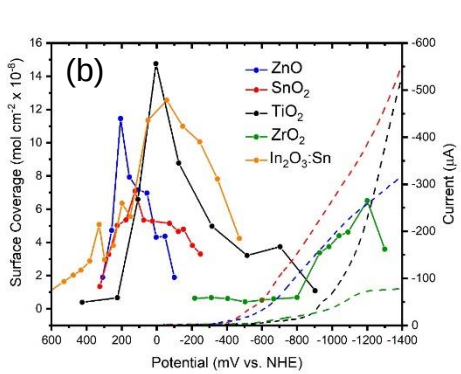

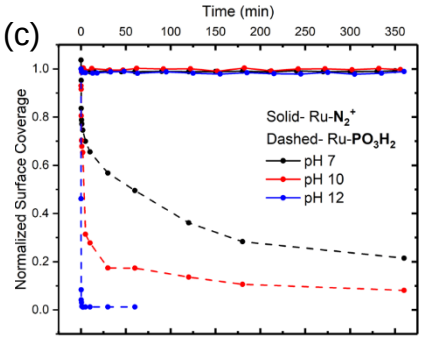

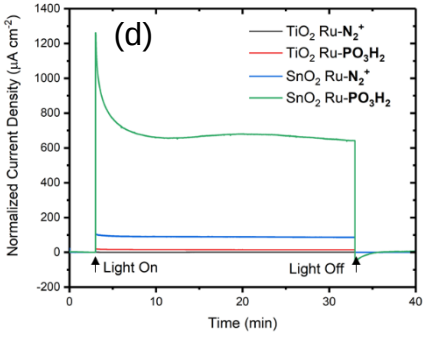

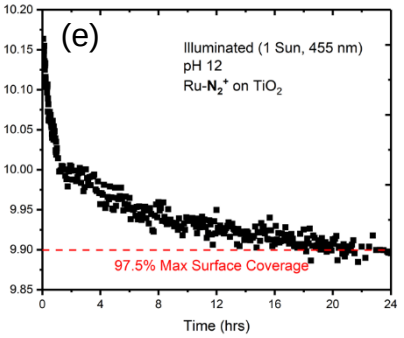

Work performed at the University of North Carolina at Chapel Hill

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