

Final Technical Report

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Office of Basic Energy Sciences, Solar Photochemistry Program

Recipient: Board of Regents of the University of Wisconsin System

Project Title: Ultra-stable Molecule-Surface Architectures at Metal Oxides: Structure, Bonding, and Electron-transfer Processes

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3. Executive Summary:

Research funded by this project focused on the development of improved strategies for functionalization of metal oxides to enhance charge-transfer processes relevant to solar energy conversion. Initial studies included Fe_2O_3 , WO_3 , TiO_2 , SnO_2 , and ZnO as model oxide systems; these systems were chosen due to differences in metal oxidation state and chemical bonding types in these oxides. Later studies focused largely on SnO_2 and ZnO , as these materials show particularly promising surface chemistry, have high electron mobility, and can be readily grown in both spherical nanoparticles and as elongated nanorods. New molecules were synthesized that allowed the direct chemical assembly of novel nanoparticle “dyadic” structures in which two different oxide materials are chemically joined, leading to an interface that enhances the separation of charge upon illumination. We demonstrated that such junctions enhance photocatalytic efficiency using model organic compounds. A separate effort focused on novel approaches to linking dye molecules to SnO_2 and ZnO as a way to enhance solar conversion efficiency. A novel type of surface binding through a dithione compound was discovered that leads to highly stable light-absorbing interfaces on ZnO .

4. The primary goal of the project was to develop improved strategies for functionalization of metal oxides to enhance charge-transfer processes relevant to solar energy conversion. Specific goals were:

- 1) Developing methods for making high-stability interfaces between molecules and oxide semiconductors .
 - 2) Developing versatile synthetic methods that will enable the creation of complex molecular structures at metal oxides by using “click” chemistry.
 - 3) Using optical and opto-electronic measurements to understand how specific surface chemistries impact optical absorption and subsequent charge-transfer processes.
- As described below, we made substantial progress in all of these goals.

5. Summary of Project Activities:

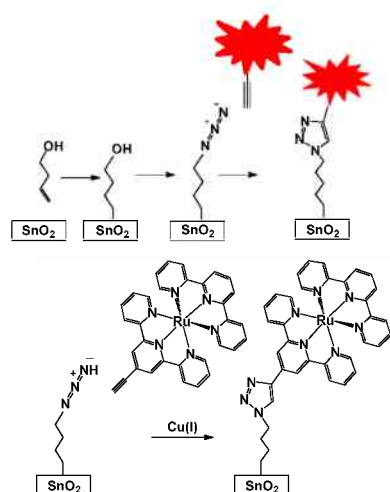
Research efforts during the project period were primarily oriented toward using molecular chemistry to improve charge transfer processes relevant to solar energy conversion. Efforts included both the development and characterization of new surface attachment chemistry with improved performance, and the use of molecular chemistry to link metal oxide with other moieties including molecules and other metal oxide nanoparticles, forming “dyadic” structures. A second major theme was to use “click”

chemistry as a modular approach to forming molecule-surface interfaces with good charge-transfer characteristics and for forming oxide-oxide dyadic nanoparticle structures.

Initial studies explored formation of molecular interfaces to several metal oxides relevant to solar energy conversion, including Fe_2O_3 , WO_3 , TiO_2 , SnO_2 , and ZnO . These model systems span oxidation states from +2 (ZnO) to +6 (WO_3) and electronic structures ranging from sp-band (ZnO and SnO_2) to those dominated by d-band bonding. Later studies were performed primarily on SnO_2 and ZnO , as these materials show particularly promising surface chemistry, have high mobility, and can be readily grown in both nanoparticle and nanorod form, thereby facilitating work with several different geometries..

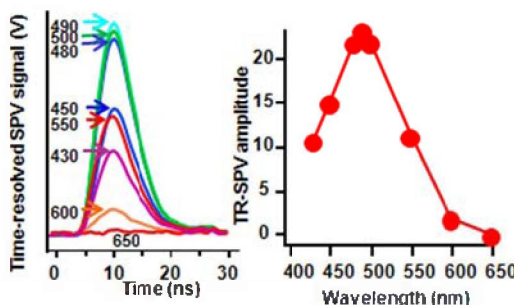
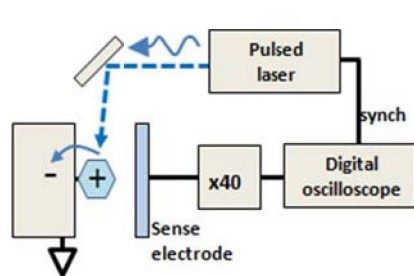
Efforts in the first year focused primarily on the development of improved strategies for functionalization of metal oxides to enhance charge-transfer processes. Our goal was to enable the creation of improved nanoparticle-molecule and nanoparticle-nanoparticle adducts using chemical assembly methods such as the azide-alkyne "click" chemistry, and to characterize the photophysical response of these resulting structures.

Modular approach to photo-active interfaces for solar conversion: Click chemistry on metal oxides



We succeeded in enabling click chemistry on SnO_2 and other metal oxides by leveraging our prior work on photochemical grafting of alkenes as the initial step in metal oxide surface functionalization. We first grafted a short-chain alcohol (butanol) to the surface and then converted this to a surface-bound azide group with one intermediate step. The resulting azide-modified surface can be easily linked to a wide range of electrochemically and photoelectrochemically active groups and also provides a pathway to nanoparticle-nanoparticle adducts. As test systems we used a ferrocene derivative (to test thermal electron transfer rate) and the $\text{Ru}(\text{tpy})_2$ complex illustrated at left (to test highly electrochemical response at high potentials and the photoelectrochemical response on faster time scales). The $\text{Ru}(\text{tpy})_2$ molecule is representative of a broader class of molecules that can act as light-harvesting molecules, and derivatives of this structure are

known catalysts for CO_2 reduction and water oxidation. To test the photophysical properties of the surface-linked molecules we used time-resolved surface photovoltage (TR-SPV) measurements. TR-SPV is an excellent technique for examining charge transfer at surfaces because it does not require a physical contact to the face of the sample. Using TR-SPV we mapped out the wavelength-dependent charge-transfer efficiency of $\text{Ru}(\text{tpy})_2$ on SnO_2 nanoparticle films. The middle panel below shows the time



response at different wavelengths, and the adjacent plot shows the TR-SPV amplitude vs. wavelength representing charge-transfer efficiency vs. wavelength. This corresponds closely

to the absorption spectrum measured in transmission mode. The temporal response (middle panel) corresponds to a ~ 2 ns decay constant and is close to the limit of our existing laser system.

The important result from this work is to demonstrate a highly modular and general method for linking light-harvesting molecules and/or photocatalysts to metal oxide surfaces, and to demonstrate that this approach yields adducts that are able to transfer charge on the fastest time scales we can measure.

Chemical assembly of photoelectrochemically active nanoparticle-nanoparticle heterojunctions: With this protocol worked out for molecular systems, we explored whether it could be used to form

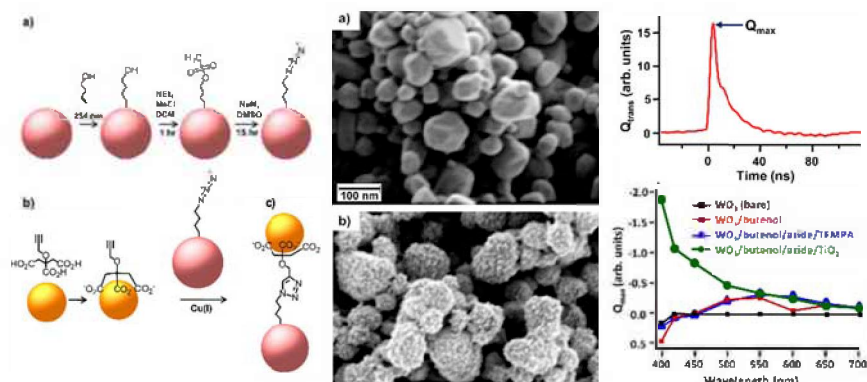


Fig. 3 Chemically assembled nanoparticle heterojunctions using "click" chemistry. Left: overall chemical scheme for forming WO_3 - TiO_2 adducts. Middle: SEM images of WO_3 film before and after "click" reaction. Right: Time-resolved SPV measurements showing charge transfer vs. time and the maximum charge transfer as a function of wavelength.

heterojunctions between two different oxide nanoparticles, forming oxide-oxide heterojunctions. In our first studies we used WO_3 - TiO_2 heterojunctions. WO_3 is particularly difficult to functionalize because its strong negative charge makes other common functionalization strategies ineffective; however, the photochemical grafting process works very well, allowing us to form azide-

terminated WO_3 using a mesyl intermediate as depicted below. Using butenol, we used the CuAAC chemistry to link TiO_2 nanoparticles to the WO_3 surfaces. SEM images show a beautiful, conformal coating of 6 nm-diameter TiO_2 nanoparticles coating the entire WO_3 surface. We performed time-resolved surface photovoltage measurements to characterize the charge-transfer properties, and used photooxidation of methylene blue to demonstrate that the addition of the TiO_2 nanoparticles to the nanocrystalline TiO_2 film increased the photocatalytic activity. The importance of this study is that it establishes the idea of robust *chemical* assembly of nanoparticle-nanoparticle heterojunctions with enhanced charge-transfer properties.

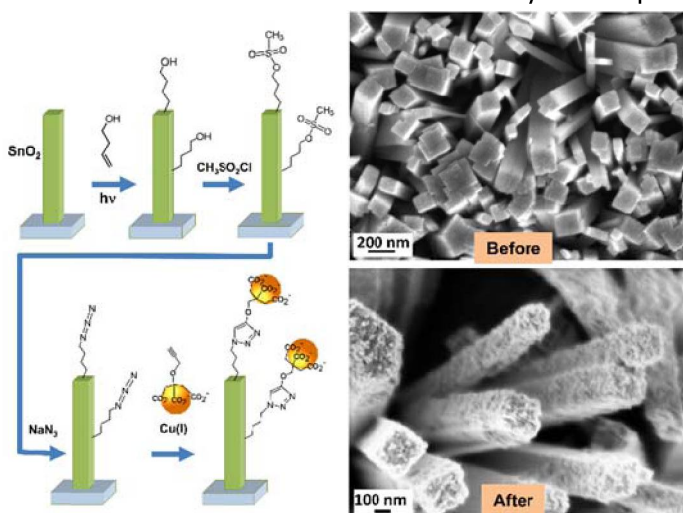


Fig. 4. Assembly of SnO_2 nanorod - TiO_2 nanoparticle junctions.

Photoelectrochemically active nanorod-nanoparticle junctions on high-mobility oxide nanorods: SnO_2 and ZnO are potentially attractive materials for photoelectrochemical charge-transfer because of their high mobility and because both can be grown as high-quality nanorods that expose well-defined crystal faces. We modified literature methods to enable growth of high-quality SnO_2 nanorods by

hydrothermal growth and demonstrated the use of “click” chemistry to chemically assemble nanoparticle-nanorod heterojunctions, using TiO_2 as a model system. Results were also obtained using Fe_2O_3 nanoparticles on SnO_2 nanorods, although with lower density. We characterized the photoelectrochemical response using time-resolved surface photovoltage measurements.

Molecule-ZnO Interfaces -- Controlling Interfacial roughness: ZnO has historically been a difficult surface to functionalize because of its susceptibility to roughening and etching. We demonstrated that

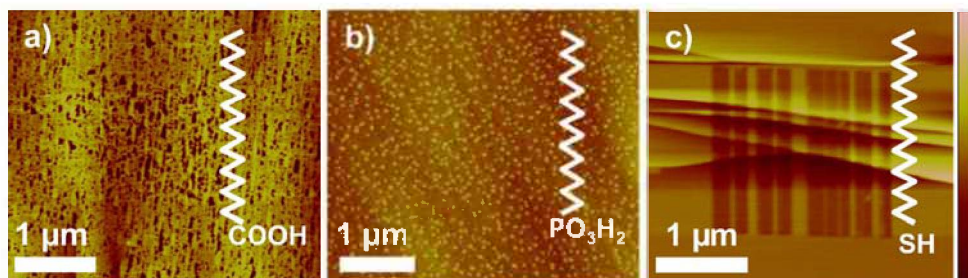


Fig. 5 Atomic force microscope images of ZnO(10-10) surfaces with grafted alkanes. The alkanethiols (right) form smooth homogeneous layers with AFM “scratching” experiments revealing a thickness of a single monolayer

while carboxylic acids and phosphonic acids etch the surface and/or produce strongly heterogeneous surfaces, *thiol* linkages form very smooth, conformal monolayers. AFM

imaging and “scratching” experiments were used to characterize the nano-scale thickness and uniformity of the molecular layers. We used Mott-Shottky analysis to characterize the electronic structure and determine how functionalization with molecular layers impacted the surface traps and the space-charge layer.

“On-surface” formation of heteroleptic charge-transferring coordination complexes: Based on the results immediately above, we obtained 4,4'-dithio-(2,2'-bipyridyl), grafted it to ZnO nanorods, and then exposed it to $[\text{Ru}(4,4'\text{-dicarboxylato-2,2'-bipyridyl})\text{Cl}_2]^{2+}$ in order to form the resulting complex via “on-surface” assembly. While this work is ongoing, initial results using this new on-surface assembly method have been highly successful. XPS results indicate formation of the dichloro complex depicted below. Visual inspection of the surfaces shows a deep red color and measurements of photovoltaic efficiency show efficiencies approaching 0.5%.

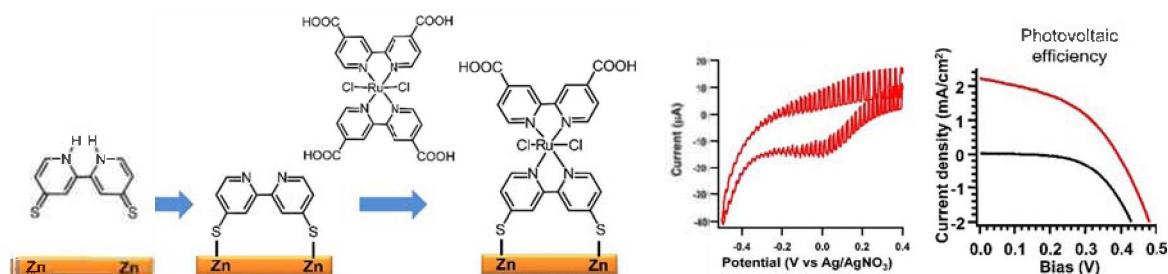


Fig. 6 Interaction of ZnO surface with dithione ligand and subsequent “on-surface” assembly of heteroleptic Ru coordination complex. The graphs at center shows a photocurrent-based cyclic voltammogram and the graph at far right shows current-voltage characteristics in the light (red) and in the dark (black) using a 1 sun AM1.5 solar simulator with I^-/I_3^- redox couple.

“On-surface” assembly of charge-transferring coordination complexes on SnO_2 surfaces: Approaches similar to those described immediately above were also used to form Ru-based dyes directed on SnO_2 surfaces. We investigated three different initial ligands, including the iodoaryl compound (1), iodobenzyl compound (2), and the thiol (which has a dithione resonance structure) (3). We showed that initial grafting of these compounds, followed by exposure to the photolabile $\text{Ru}(\text{bpy})_2(\text{CH}_3\text{CH})_2$ compound, led to the formation of the surface-bound Ru complexes shown in panel (c) below. We found that these complexes could be re-generated in situ. All three complexes exhibited good photoactivity and were able to inject electrons into the underlying SnO_2 material.

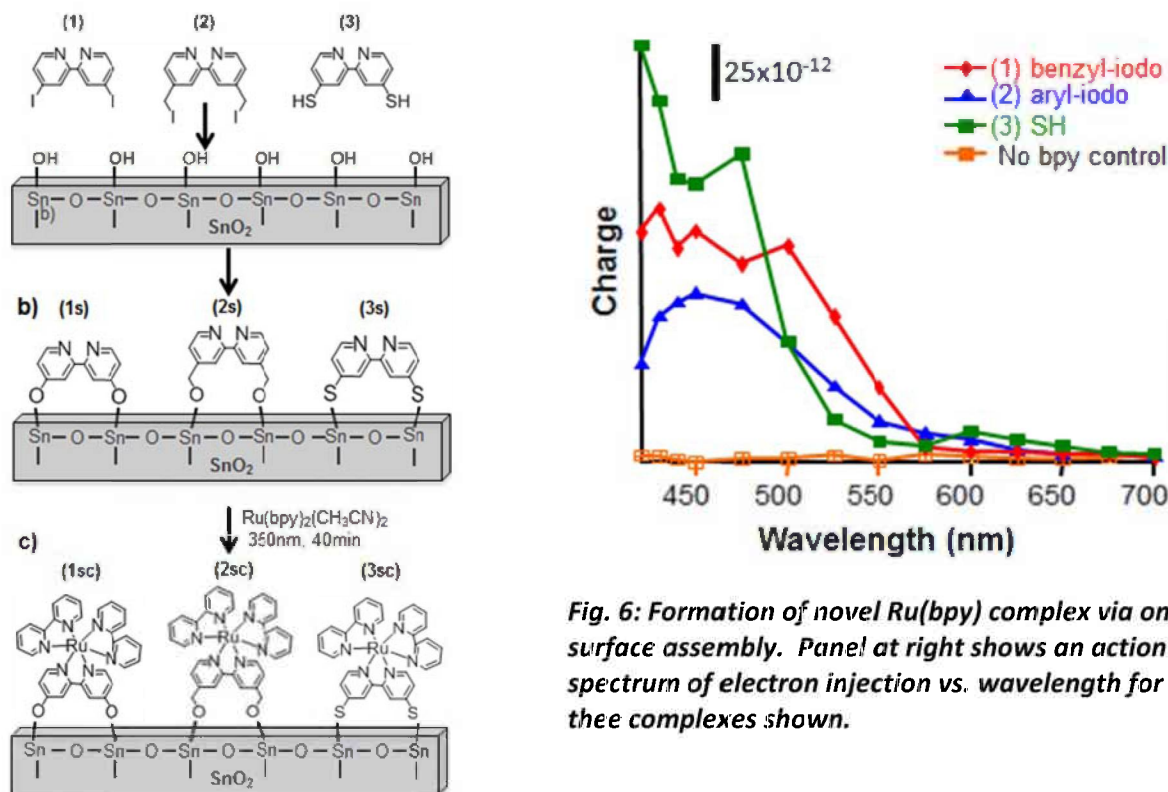


Fig. 6: Formation of novel $\text{Ru}(\text{bpy})$ complex via on-surface assembly. Panel at right shows an action spectrum of electron injection vs. wavelength for the three complexes shown.

6. Products: Publications acknowledging DOE Support:

Rose E. Ruther, Matthew L. Rigsby, James B. Gerken, Stephanie R. Hogendoorn, Elizabeth C. Landis, Shannon S. Stahl, and Robert J. Hamers, “Highly stable redox-active molecular layers by covalent grafting to conductive diamond”, *J. Am. Chem. Soc.* **2011**, *133*, 5692 .

James B. Gerken, Elizabeth Landis, Robert J. Hamers, Shannon S. Stahl, “Fluoride-modulated cobalt catalysts for electrochemical oxidation of water under non-alkaline conditions”, *ChemSusChem* **2010**, *3*, 1176.

Michelle C. Benson, Rose E. Ruther, James B. Gerken, Matthew L. Rigsby, Lee M. Bishop, Yizheng Tan, Shannon S. Stahl, and Robert J. Hamers, Modular “Click” Chemistry for Electrochemically and

Photoelectrochemically Active Molecular Interfaces to Tin Oxide Surfaces , ACS Applied Materials and Interfaces, 2011, **3**, 3110-3119 DOI: 10.1021/am200615r

Lee M. Bishop, Joseph C. Yeager, Xin Chen, Jamie N. Wheeler, Marco D. Torelli, Michelle C. Benson, Steven D. Burke, Joel A. Pedersen, and Robert J. Hamers, "A citric acid-derived ligand for modular functionalization of metal oxide surfaces via "click" chemistry", Langmuir, **2012**, 28, 1322-1329.

Allison C. Cardiel, Michelle C. Benson, Lee M. Bishop, Kacie M. Louis, Joseph C. Yeager, Yizheng Tan, and Robert J. Hamers, "Chemically Directed Assembly of Photoactive Metal Oxide Nanoparticle Heterojunctions via the Copper-Catalyzed Azide–Alkyne Cycloaddition "Click" Reaction", ACS Nano **2012**, 6, 310-318.

Ruben Gonzalez-Moreno, Peter L. Cook, Ioannis Zegkinoglou, Xiaosong Liu, Phillip S. Johnson Wanli Yang, Rose E. Ruther, Robert J. Hamers, Ramon Tena-Zaera, Franz J. Himpsel, Enrique Ortega, Celia Rogera, "Attachment of Protoporphyrin Dyes to Nanostructured ZnO Surfaces: Characterization by Near Edge X-ray Absorption Fine Structure Spectroscopy", Journal of Physical Chemistry C, **2011**, 115, 18195-1820.

Sohil Shah, Michelle C. Benson, Lee M. Bishop, Alex M. Huhn, Rose E. Ruther, Joseph C. Yeager, and Robert J. Hamers, "Chemically assembled heterojunctions of SnO₂ nanorods with TiO₂ nanoparticles via "click" chemistry" Journal of Materials Chemistry, **2012**, 22, 11561-11567.

Jixin Chen, Rose E. Ruther, Yizheng Tan, Lee M. Bishop, Robert J. Hamers, "Molecular Adsorption on ZnO(10-10) Single Crystal Surfaces: Morphology and Charge Transfer", Langmuir, **2013**, 241, 311-319.

Manuscripts in preparation (to be submitted, with recognition of DOE support)

Becca A. Putans, Lee M. Bishop, and Robert J. Hamers, Formation of regenerable light-harvesting complexes on SnO₂ nanocrystalline films via "on-surface" assembly

Jixin Chen, Rebecca Putans, Yizheng Tan, Rose E. Ruther, Joseph C. Yeager, Shu Yao, Robert J. Hamers, Surface-Directed Assembly of Heteroleptic Ruthenium Dyes on ZnO via Bipyridine Dithione Ligands