

## Hybrid Inorganic Catalytic Materials for Electrochemical and Photoelectrochemical Generation of Fuels, Energy Conversion and Storage

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Our research interests aim at establishing structure/property relations leading to rational designs of functionalized materials for efficient electrocatalysis and electrochemical energy conversion and storage.

Electroreduction of carbon dioxide to simple organic fuels and chemicals is a topic of growing scientific and technological interest. The reaction provides means for both reducing emissions of  $CO_2$  into atmosphere and storing renewable energy. The presentation will address low-temperature  $CO_2$ -conversion processes based on electrocatalytic and photoelectrochemical approaches. Among important issues are choice of the catalytic or semiconducting materials, their morphology and operating conditions including temperature, solvent, electrolyte, pH etc. There is a need to improve the reaction dynamics and selectivity toward specific products. In practical electrolysis cells, the  $CO_2$ -reduction (at cathode) is accompanied by water oxidation (at anode or photoanode).

Recently, we have concentrated on the development of hybrid materials by utilizing combination of metal oxide semiconductors thus capable of effective photoelectrochemical reduction of carbon dioxide. For example, the combination of conducting polymers, or titanium (IV) oxide, and copper (I) oxide has been considered before and after sunlight illumination. Application of the hybrid system composed of both above-mentioned oxides resulted in high current densities originating from photoelectrochemical reduction of carbon dioxide mostly to methanol (CH<sub>3</sub>OH) as demonstrated upon identification of final products. Among important issue is intentional stabilization, activation, and functionalization of the mixed-metal-oxide-based photoelectrochemcal interface toward better long-term performance and selectivity production of small organic molecules (C1-C4) and other chemicals. In this respect, ultra-thin films of conducting polymers (simple or polyoxometallate-derivatized) and supramolecular complexes (with nitrogen containing ligands and certain transition metal sites), sub-monolayers of metals (Cu, Au), networks of noble metal (Au, Ag) nanoparticles or layers of robust bacterial biofilms have been considered.

The potential materials for charge storage applications (e.g. in high-power battery capacitor-type devices) are expected to contain three-dimensionally distributed highly concentrated redox centers between which fast electron transfers is feasible. Applicable materials also must host mobile counter-ions capable of providing charge balance during electron transfers. The emphasis is on the elements of dynamics for the efficient delivery of charge and on reactivity of the "redox conducting" materials.

We also consider nanoelectrocatalytic systems permitting effective operation of the iodine-based charge relays in dye sensitized solar cells. The ability of palladium or platinum nanostructures to induce splitting of I-I bonds in the iodine (triiodide) molecules is explored here to enhance electron transfers in the triiodide/iodide-containing 1,3-dialkylimidazolium room-temperature ionic liquids.

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