Importance of Specific Interactions between Noble Metal and Metal Oxide Nanostructures in Efficient Electro(photo)catalysis

Pawel J. Kulesza

Faculty of Chemistry, University of Warsaw, Pasteura 1, PL-02-093 Warsaw, Poland
*pkulesza@chem.uw.edu.pl

Of particular interest to the preparation of advanced catalytic materials is efficient utilization of carbon nanostructures and noble metal nanoparticles, their stabilization and intentional activation, as well as organization into two-dimensional arrays, ultra-thin films or three-dimensional networks (e.g. through sequential attraction) on electrode surfaces. They can form nanosized materials with well-defined composition, structure and thickness that exhibit electrocatalytic properties toward oxidation of methanol, ethanol or dimethyl ether. We explore here the ability of inorganic structures to stabilize and derivatize metal and carbon nanostructures. Here certain nanostructured inorganic oxides (e.g. WO₃, MoO₃, TiO₂, ZrO₂, V₂O₅, and CeO₂) and polyoxometallates of molybdenum or tungsten influence supported metal centers in ways other than simple dispersion over electrode area. Evidence is presented that the support can modify activity (presumably electronic nature) of catalytic metal nanoparticles thus affecting their chemisorptive and catalytic properties. Metal oxide nanospecies can generate –OH groups at low potentials that induce oxidation of passivating CO adsorbates (e.g. on Pt); they can potentially break C-H or C-O bonds (e.g. by hydrogen tungsten oxide bronzes); and they can possibly weaken C-C bonds during ethanol oxidation (e.g. through changes of the electronic properties of Pt).

Our research interests also concern development of systems for reduction of carbon dioxide. For example, instead of conventional Pd nanoparticles, nanosized Pd immobilized within tridentate Schiff-base ligands of the supramolecular complex, [Pd(C₁₄H₁₂N₂O₃)Cl₂·MeOH]₂⁺, as capping agents, to enhance photocurrents generated by mesoporous tungsten trioxide, WO₃, photoanodes irradiated with visible light in aqueous solutions. To demonstrate generation of localized surface plasmons, we have performed measurements using scanning near-field optical microscope (SNOM). The mechanism for the interaction between the gold plasmons and the semiconductor is complex but sound.

We will also show that nano-electrocatalytic systems are of importance to the development of the effectively operating iodine-based charge relays in dye sensitized solar cells and in molecular electronic (charge storage) devices.