

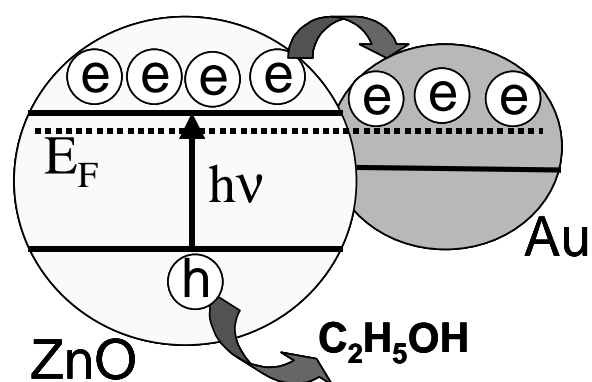
Fermi-Level Equilibration in Semiconductor-Metal Nanocomposites

Vaidyanathan Subramanian, Eduardo E. Wolf
and Prashant V. Kamat*

Radiation Laboratory and Department of
Chemical Engineering
University of Notre Dame
Notre Dame IN 46556-0579

A major limitation of achieving high photocatalytic efficiency in semiconductor nanoparticle systems is the quick recombination of charge carriers. Efforts have been made by several research groups to overcome this limitation by developing semiconductor-semiconductor and semiconductor-metal type composite nanoclusters. In our earlier work [1] we have shown that the photoelectrochemical performance of nanostructured TiO₂ films can be improved by coupling them with noble metal nanoparticles.

Photoinduced electron accumulation in ZnO nanoparticles results in the bleaching of exciton band as well as quenching of visible emission. In the absence of an electron scavenger, photogenerated electrons are stored near the conduction band edge and interact with the oxygen vacancies via nonradiative recombination process. By exposing the UV-irradiated ZnO suspension to an electron acceptor (O₂ or thionine dye) the stored electrons are discharged and the original excitonic band and the visible emission are restored. Titration of electrons stored in ZnO nanoparticles with an electron acceptor, thionine dye shows a linear relationship between stored electrons and the emission quenching. When gold colloids were added to pre-UV-irradiated ZnO colloids only partial recovery of the emission is seen. Pt colloids on the other hand caused almost complete recovery of the quenched emission as the electrons are discharged into the solution.. The charge distribution between UV-irradiated ZnO colloids and gold colloids suggests Fermi-level equilibration between the two systems. The benefits of Fermi-level equilibration on the photoelectrochemical performance of nanostructured semiconductor films modified with metal nanoparticles will be discussed.



Scheme 1. Charge distribution in semiconductor-metal composite system leads to Fermi-level equilibration

Acknowledgments: The work described herein was supported by the Office of the Basic Energy Sciences of the US Department of Energy.

References.

1. Subramanian, V.; Wolf, E.; Kamat, P. V., "Semiconductor-Metal Composite Nanostructures. To What Extent Metal Nanoparticles (Au, Pt, Ir) Improve the Photocatalytic Activity of TiO₂ Films?" *J. Phys. Chem. B*, 2001. 105, 11439-11446.