Role of Metal Co-catalyst in Semiconductor Assisted Photocatalysis. Charge Equilibration versus Plasmonic Effects

Prashant V. Kamat
University of Notre Dame
Radiation Laboratory, Departments of Chemical & Biomolecular Engineering, and Chemistry & Biochemistry, Notre Dame, Indiana 46556

Semiconductor-metal nanocomposites are effective in facilitating photocatalytic processes. The coupling of semiconductor and metal nanoparticles provides a unique pathway for the discharge of electrons at the electrolyte interface.[1-7] The recent efforts to explore plasmon resonance effect to influence charge separation efficiencies in photocatalytic systems often undermine the electron acceptor properties of metal nanoparticles.[8, 9] The results presented here demonstrate that photocatalytically deposited Ag on TiO_2 nanoparticles improve the photoelectrochemical performance of TiO_2/Ag composite by capturing the photogenerated electrons and maintaining a more negative Fermi level. The shift in the plasmon resonance of Ag shows that the charge equilibration between TiO_2 and Ag is dependent on the irradiation conditions. The charging and discharging can be reversibly modulated through on-off cycles of UV irradiation. These electron storage effects should be taken into consideration while evaluating the photocatalytic and photoelectrochemical properties of semiconductor-metal composites.

References

(1) Takai, A.; Kamat, P. V. Capture, Store and Discharge. Shuttling Photogenerated Electrons across TiO2-Silver Interface. *ACS Nano* **2011**, *4*, 7369–7376.
(2) Harris, C.; Kamat, P. V. Photocatalytic Events of CdSe Quantum Dots in Confined Media. Electrodic Behavior of Coupled Platinum Nanoparticles. *ACS Nano* **2010**, *4*, 7321–7330.
(3) Kiwi, J.; Graetzel, M. Protection, Size Factors, and Reaction Dynamics of Colloidal Redox Catalysts Mediating Light Induced Hydrogen Evolution from Water. *J. Am. Chem. Soc.* **1979**, *101*, 7214-7217.
(4) Henglein, A.; Lindig, B.; Westerhausen, J. Photochemical Electron Storage on Colloidal Metals and Hydrogen Formation by Free Radicals. *J. Phys. Chem.* **1981**, *85*, 1627-1628.
(5) Lee, P. C.; Matheson, M. S.; Meisel, D. Photogeneration of Hydrogen from Polymeric Viologen Systems. *Isr. J. Chem.* **1982**, *22*, 133-137.
(6) Matheson, M. S.; Lee, P. C.; Meisel, D.; Pelizzetti, E. Kinetics of Hydrogen Production from Methyl Viologen Radicals on Colloidal Platinum. *J. Phys. Chem.* **1983**, *87*, 394-399.
(7) Aspnes, D. E.; Heller, A. Photoelectrochemical hydrogen evolution and water- photolyzing semiconductor suspensions: Properties of platinum group metal catalyst-semiconductor contacts in air and in hydrogen. *J. Phys. Chem.* **1983**, *87*, 4919-29.
(8) Liu, Z.; Hou, W.; Pavaskar, P.; Aykol, M.; Cronin, S. B. Plasmon Resonant Enhancement of Photocatalytic Water Splitting Under Visible Illumination. *Nano Lett.* **2011**, *11*, 1111-1116.
(9) Nishijima, Y.; Ueno, K.; Yokota, Y.; Murakoshi, K.; Misawa, H. Plasmon-Assisted Photocurrent Generation from Visible to Near-Infrared Wavelength Using a Au-Nanorods/TiO_2 Electrode. *J. Phys. Chem. Lett.* **2010**, *1*, 2031-2036.

Proceedings Published 2012 by the American Chemical Society