**ZnO nanocrystal facet-dependence of Au photodeposition and catalytic activity**

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**Introduction**

The photochemical reduction of gold on four differently-shaped zinc oxide colloids, hexagonal-based nanocones, nanorods, nanobullets, and nanoplates, was investigated to understand the ZnO crystal facet-dependence of photodeposition. The colloidal ZnO nanoparticles (NPs) were approximately the same size and synthesized without the use of strong-binding, capping agents. Au-ZnO NP hybrids were made from these samples by photoreducing AuCl2- onto the ZnO NPs during exposure to UV illumination at 370nm. The solvent system, irradiation exposure time, and dissolved oxygen content in the solvent were modified to generate changes in the pattern of Au NP photoreduction onto the ZnO shapes. Photodeposition was found to be controlled by a combination of the charge distribution (that determined the electron transfer kinetics) at the ZnO NP – solution interface and how the free energy for nucleation depended on the zinc oxide NP shape. Defect sites and dangling bonds on ZnO are considered significant factors when a weak capping ligand is present. The relative surface area of exposed high-energy facets of the ZnO NPs had a dramatic effect on the energy barrier to Au NP nucleations on the zinc oxide surfaces, with the established facet-dependent order of The photocatalytic activity of the different gold-zinc oxide hybrid NPs were tested by degrading toluidine blue dye in aqueous conditions. The Au-ZnO hybrid NPs photoactivity was significantly greater than that of pure, ZnO NPs, which was attributed to improved separation of charge and reduced electron-hole recombination rate. Scavengers were added to control samples to determine the dominant mechanism of dye-degradation, which was found to be by hydroxyl radicals generated through oxidative pathways.

**Methods**

A variety of ZnO shapes were produced using the synthesis method described by Chang and Waclawik1. This is a non-hydrolytic aminolysis reaction where the temperature, reaction time, the concentration and time of insertion of the capping agent can be adjusted to produce good yields of hexagonal ZnO rods, plates, bullets or cones. Reactions were conducted under N2 atmosphere.

**Conclusions**

Deposition of Au NPs on the ZnO nanocrystals significantly increases photocatalytic activity, with the greatest improvement noted for the synthesized nanorods, which are most dominated by stable ZnO [1010] facets. Enhanced charge separation and prevention of electron-hole recombination imparted by addition of Au NPs to the ZnO surfaces was most beneficial for ZnO nanocrystal shapes with low-energy facets.

**References**

1. Chang, J. & Waclawik, E. R. (2012). *Facet-controlled Self-assembly of ZnO Nanocrystals by Non-Hydrolytic Aminolysis and their Photodegradation Activities*. Chryst. Eng. Comm., 14, 4041-4048.

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