Photochemistry of Colloidal Dilute Magnetic Semiconductor Quantum Dots

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Project Summary:
Wide-bandgap semiconductors (E_g>3.0 eV) have been known for years to photocatalytically promote otherwise thermodynamically unfavorable reactions. The major drawback to these materials is that they only create photogenerated conduction band electrons (e_{CB}) and valence band holes (h_{VB}) with potentials sufficient enough to promote, for instance, the photo-splitting of water with ultraviolet photons. Doping these materials with transition metal ions has been shown to improve the photocatalytic activity toward hydrogen evolution in the case of Ni^{2+} doped ZnS bulk powders[1], supposedly from the production of the same high potential transients to promote the photochemical reaction with visible photons. Figure 1 shows the Jablonski diagram for Ni^{2+} doped into a wide-bandgap semiconductor (i.e., ZnO or ZnS), which displays a broad ligand-to-metal charge transfer transition in the visible region. Excitation into this charge transfer transition produces a delocalized carrier that can catalyze a reaction at or near the surface of the nanocrystals. Recently, nanocrystalline Ni^{2+}:ZnO and Co^{2+}:ZnO have been prepared in the Gamelin lab.[2] The reduced dimensionality drastically increases the surface-to-volume ratio of the material, which could also play an important part in enhancing the photocatalytic efficiency.

During the past year, the synthesis of Ni^{2+}:ZnO and Co^{2+}:ZnO nanocrystals has successfully been scaled-up to produce gram-scale quantities for photocatalytic experiments. Currently, the photochemical reactions that we are attempting include the photochemical water-splitting reaction and the degradation of various phenolic compounds. Future experiments at PNNL include variable wavelength excitation transient absorption spectroscopy and time-resolved emission of other transition metal doped ZnO nanocrystals.

Publications:
1. Schwartz, D.A.; Kittilstved, K.R.; Gamelin, D.R. "Above-Room-Temperature Ferromagnetic Ni^{2+}:ZnO Thin Films Prepared from Colloidal Diluted Magnetic Semiconductor Quantum Dots" *Appl. Phys. Lett.* **2003**, *submitted for publication*.

2. Kittilstved, K.R., Schwartz, D.A., Gamelin, D.R. "Synthesis and Characterization of Ni^{2+}-Doped II-VI Nanocrystals" *manuscript in preparation.*

Presentations:
Kittilstved, K.R.; Schwartz, D.A.; Joly, A.G.; Gamelin, D.R. *Classical and Dynamic Spectroscopy of Ni^{2+} in Nanoscale II-VI Semiconductor.* Nanoscale Science and Technology Workshop 2003, September 22-23 (Poster).

Research Grants:
Anticipated submittal in February 2004.

[1] Kudo, A. and Sekizawa, M. *Chem. Commun.* **2000**, 1371-1372.
[2] Schwartz, *et al*. *J. Amer. Chem. Soc.* **2003**, *125*, 13205-13218.

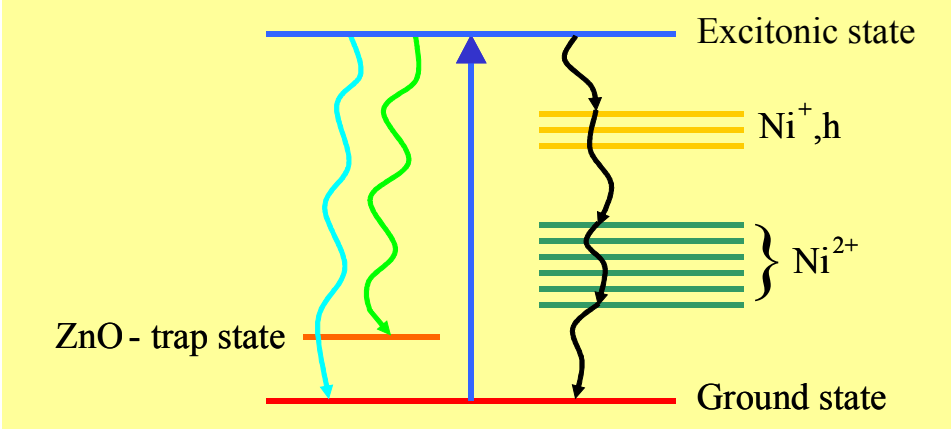

Figure 1. Jablonski diagram of the possible pathways for relaxation of an exciton excited from the ground state of the Ni^{2+}-doped wide-gap semiconductor to the excitonic state at room temperature. Non-radiative pathways are shown as black curved lines, while the radiative pathways are shown as colored straight lines, where the length of the lines are roughly proportional to the energy of the emitted photons.

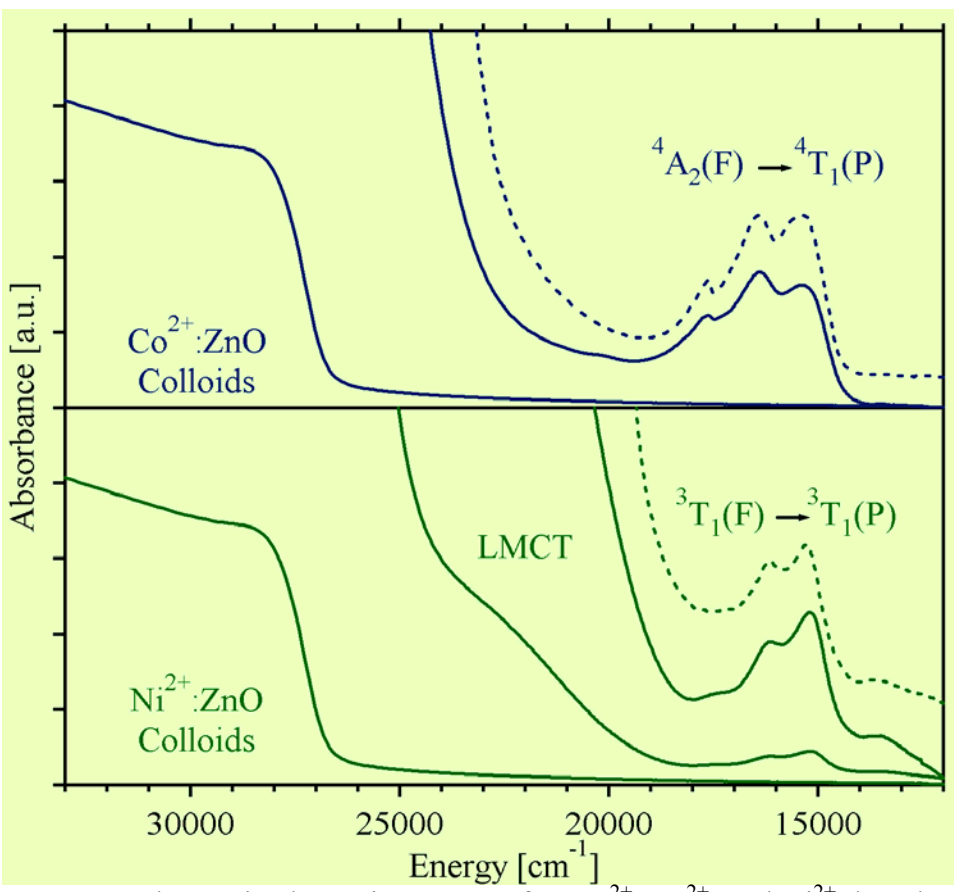

Figure 2. Electronic absorption spectra for Mn^{2+}, Co^{2+}, and Ni^{2+} doped ZnO colloids. The broad valence band (ligand) to metal charge transfer transition is observed Ni^{2+}:ZnO. The charge transfer transition is occluded by the bandgap transition in Co^{2+}:ZnO, but the onset has been observed in the magnetic circular dichroism spectrum. The spin-allowed ligand field transitions in Co^{2+} and Ni^{2+}:ZnO are readily assigned as substitutional dopants in a pseudotetrahedral environment inside the ZnO lattice.