Photochemistry of a Diluted Magnetic Semiconductor Quantum Dot: A Possible Photocatalyst for Water-Splitting

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Project Summary:

Nanoscale photocatalysts have attracted much attention due to their high surface area to volume ratios. Photocatalytic water-splitting materials with nanometer dimensions are likewise generating intense interest due to this inherent feature. Furthermore, this research is appealing due to the realized use of hydrogen as a clean source of fuel for future fuel technologies. We proposed to investigate the photophysical and photochemical properties of nanoscale Ni^{2+}:ZnS, where the bulk material demonstrated photocatalytic hydrogen evolution under visible-light from aqueous solutions. This will be accomplished by preparing nanocrystalline Ni^{2+}:ZnS and using both classical and ultrafast spectroscopic methods to obtain an understanding of the dynamic electronic processes that can be related to the photocatalytic water-splitting activity.

During the past year much progress in the preparation of high-quality internally doped Ni^{2+}:ZnS (see Fig. 1) has been made in our laboratories, as well as the synthesis of another prospective photocatalytic material, Ni^{2+}:ZnO. Initial transient absorption experiments performed at PNNL on these Ni^{2+} doped wide-gap semiconductors exhibit a difference in the transient lifetimes versus the undoped semiconductors and the solvent. The transient signal (see Fig. 2) for Ni^{2+}:ZnO has been assigned as an excited state absorption process due to the fact that both pure ZnO and toluene give similar signals Bleaching of the LMCT transition at the same energy as the pump beam is ruled out from observing a positive signal when viewed on the oscilloscope. Further experiments with varying the Ni^{2+} concentration and changing the pump wavelength will be performed to gain even more insight into the process giving the enhanced transient absorption and longer transient lifetimes in the doped system compared to the undoped material.

The photochemistry of these nanoparticles, as well as Ni^{2+}:ZnO, has not been previously studied and more efforts to study the photocatalytic activity of these materials will be explored in the near future. Specifically, the water splitting activity of these materials will be determined using pure water and aqueous solutions. Characterization of any evolved hydrogen and/or oxygen will be analyzed using gas chromatography. The photochemistry in the Mg^{2+} co-doped Ni^{2+}:ZnO nanoparticles will also be explored, since the widened the band gap of these materials should raise the potentials of the photogenerated hole and electron.

Selected Figures:

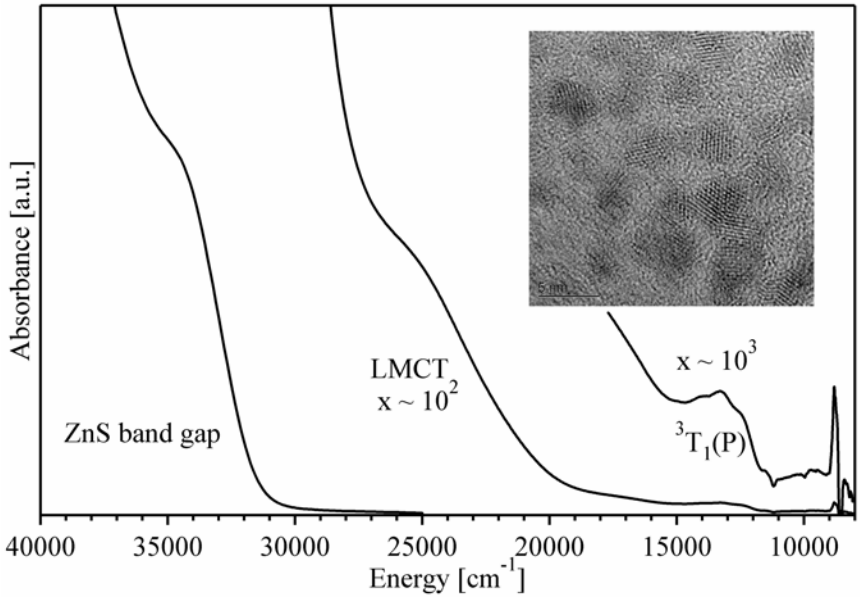

Figure 1: Electronic absorption spectra of a high-quality Ni^{2+}:ZnS nanoparticles with a ZnS shell resuspended in pyridine. Ligand field spectroscopy confirm internally doped tetrahedral Ni^{2+} speciation. High-resolution TEM image of Ni^{2+}:ZnS nanoparticles taken at PNNL with the assistance of Dr. Chongmin Wang are also shown in the inset. Electronic absorption of the ZnS band gap correlates to an estimated particle diameter of ca. 3.2 nm and the TEM image confirms that estimate. Lattice fringes confirm crystallinity in the samples.

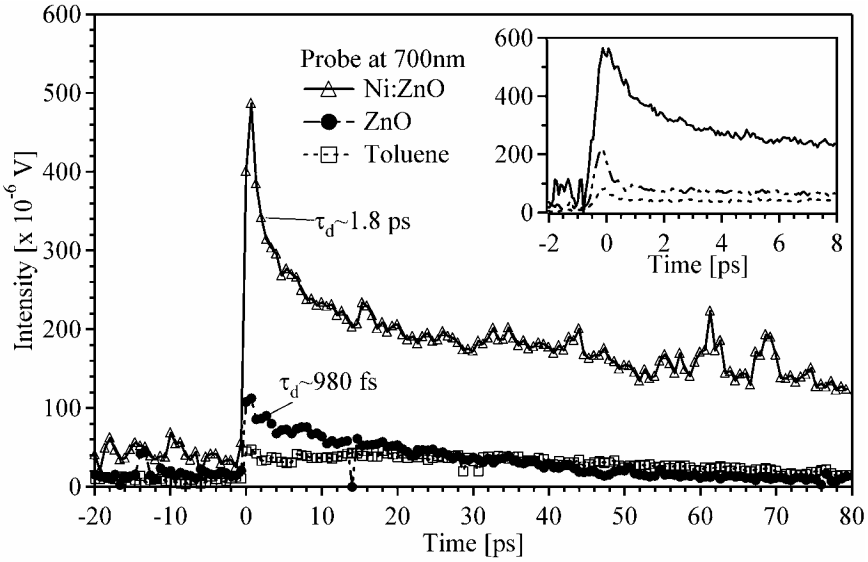

Figure 2: Transient absorption traces for Ni^{2+}:ZnO, ZnO and toluene using a 400 nm excitation pulse and 700 nm probe pulse. Traces are scaled to equivalent optical densities of the bandgap absorption in Ni^{2+}:ZnO and ZnO quantum dots. Short time-scale transient decay profile is shown in the inset.