Transition Metal Doped ZnO Semiconductor Nanoparticles: Synthesis and Characterization of Electronic Structure

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Project Summary:

Recent discoveries of ferromagnetic behavior in certain diluted magnetic semiconductors (DMSs) have led to increased interest in the development and studies of these materials. Development of room temperature ferromagnetic materials will be essential for spintronics technology. Despite further reports of ferromagnetic DMSs, including Co^{2+}:ZnO thin films, little is understood about the origin of these ferromagnetic interactions. In addition, no work has been done on ZnO DMS quantum dots (DMS-QDs). This work focuses on the synthesis of ZnO DMS-QDs from solution, and the investigation into their electronic structure and magnetic properties using electronic absorption, magnetic circular dichroism (MCD), and electron paramagnetic resonance (EPR) spectroscopies. These studies will give detailed insights into the strength and type of exchange interactions that occur, offering new data on the origins of ferromagnetism and other magneto-optical properties in oxide diluted magnetic semiconductor quantum dots.

Synthesis of colloidal Co^{2+}:ZnO DMS-QDs was achieved by addition of LiOH base to a solution of $ZnAc_2$ and $CoAc_2$ in ethanol, forming colloidal Co^{2+}:ZnO through hydrolysis and condensation. Although Co^{2+} was shown to be incorporated into the nanocrystal during growth, due to the high surface-to-volume ratio of nanocrystals, a fraction of the Co^{2+} ions will be bound to the nanocrystal surface. Complete internally doped Co^{2+} was produced with the isocrystalline core/shell (ICS) method, where a pure ZnO shell is grown around the core Co^{2+}:ZnO.

The ground state electronic structure of the Co^{2+} in ZnO was probed using X-band Electron Paramagnetic Resonance (EPR) spectroscopy at liquid Helium temperatures performed at PNNL. The g-values obtained from EPR (Figure 1), which define the magnetization behavior of the Co^{2+} ground state, match those previously reported for bulk Co^{2+}:ZnO. This confirms the samples are of high quality, and allows the magnetization behavior for Co^{2+}:ZnO QDs to be mapped out.

The sp-d exchange between the dopant ion and the semiconductor bands, required for DMSs, was observed by magnetization of the band gap seen by MCD spectroscopy (Figure 2). This exchange is thought to be responsible for ferromagnetic behavior in DMSs. In addition, ferromagnetism of these nanocrystals can be achieved by allowing them to agglomerate when dried from solution, reproducing the magnetic ordering previously only seen in thin films. Future work involves continued investigation into the origins of ferromagnetism in the DMSs, and the quantum confined effects on the optical and magnetic properties.

Publications, Presentations and Proposals:

1. P. V. Radovanovic, Nick S. Norberg, K. E. McNally, D. R. Gamelin, *J. Am. Chem. Soc.*, (2002) **124**, 15192.

Figures:

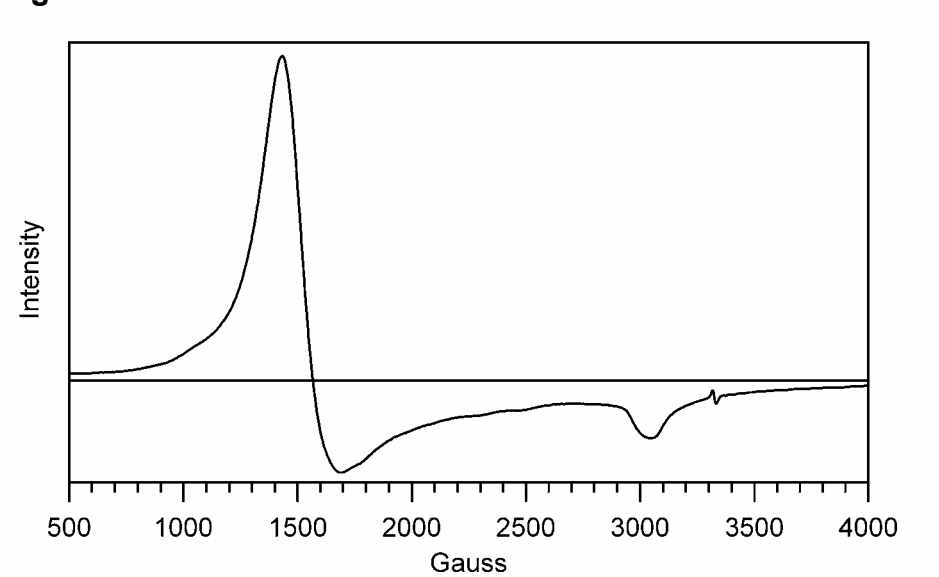

Figure 1. 6K electron paramagnetic resonance spectroscopy of 0.5 % Co^{2+}:ZnO nanocrystal powder.

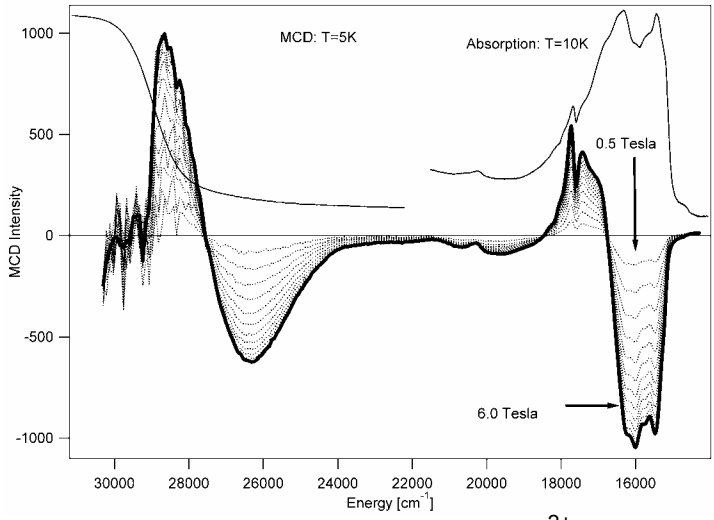

Figure 2. 5K MCD spectra of 3.6% Co^{2+}:ZnO with 10K electronic absorption of the ligand field region and 300K absorption of the bandgap region. MCD measurements were taken at 0.5 Tesla increments.