Magnetic Nanocrystals: Synthesis and Study of ZnO and GaN diluted magnetic semiconductors

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Diluted Magnetic Semiconductors (DMSs) are currently attracting intense interest in the emerging field of spin-based electronics, or "spintronics". The broad objective of this field is to control electron spins, in addition to charges, in order to transmit information and provide new functionality to semiconductor devices. However, obtaining above room temperature ferromagnetic ordering in these DMSs, essential for their use in spintronics technology, has been an experimental challenge, with many materials exhibiting Curie temperatures (T_c) well below room temperature. Several theoretical studies have focused on II-VI and III-V semiconductor DMSs, and have proposed ZnO may be an ideal candidate for providing high temperature ferromagnetism. This work presents a chemical approach to the synthesis of Co^{2+}:ZnO and Ni^{2+}:ZnO nanocrystals. With the robustness, optical transparency, and unique magnetic properties of ZnO DMSs, this synthetic route may offer opportunities towards the development of novel nanoscale devices.

Synthesis of colloidal TM^{2+}:ZnO nanocrystals was previously reported[1] from our lab using ethanol as the primary solvent. We have recently developed a better approach towards the synthesis of high quality TM^{2+}:ZnO colloidal nanocrystals[2], where an ethanolic solution of $N(Me)_4OH$ is added dropwise to a stirring DMSO solution of $Co(OAc)_2$ or $Ni(ClO_4)_2$, yielding relatively monodisperse, colloidal nanocrystals. Homogeneous speciation of the dopant ion in the ZnO nanocrystals was achieved either by growing a ZnO shell around the ZnO core (iso-crystalline core/shell method or ICS as previously reported[1]), or by treating the nanocrystals in a 180 C solution of tri-octylphosphine oxide (TOPO). The TOPO strips off the TM^{2+} from the ZnO surface, leaving purely internally doped Co^{2+}:ZnO or Ni^{2+}:ZnO nanocrystals. Ligand-field electronic absorption spectroscopy confirms the homogeneous speciation of the TOPO-treated particles. TEM of these particles show relatively monodisperse nanocrystals with electron diffraction matching that for wurtzite ZnO (Figure 1).

When Co^{2+}:ZnO nanocrystals were prepared from DMSO, followed by the ICS method (ensuring only internal dopants), and allowed to slowly aggregate from colloidal solution, ferromagnetic ordering was observed by a SQUID magnetometer (Figure 2). The coercivity and remanence both indicate the Curie temperature is well above room temperature. Although high T_c ferromagnetism has been observed on Co^{2+}:ZnO samples prepared through high vacuum deposition routes, observations of Co metal in some samples have raised questions on whether this ferromagnetism is intrinsic to Co^{2+}:ZnO, or arises from impurity phases. Due to the low temperature and chemically controlled synthesis of this material, these data demonstrate intrinsic ferromagnetism in Co^{2+}:ZnO.

Further work is in progress on the synthesis and magnetic properties of ZnO DMSs.

References:

1. P. V. Radovanovic, N. S. Norberg, K. E. McNally, D. R. Gamelin, *J. Am. Chem. Soc.*, **124**, 15192 (2002).
2. Schwartz, Dana A.; Norberg, Nick S.; Nguyen, Quyen P.; Parker, Jason M.; Gamelin, Daniel R. *J. Am. Chem. Soc.*, **125**, 13205 (2003).

Figures:

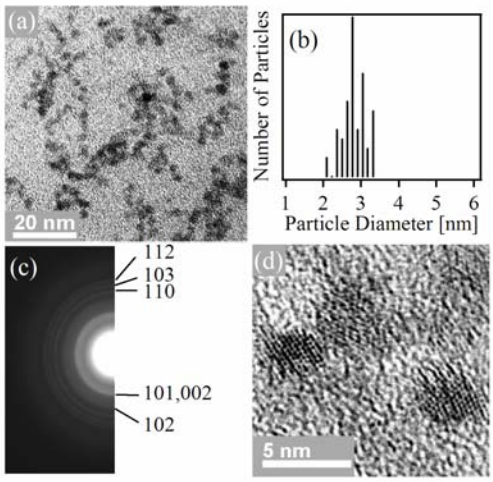

Figure 1. TEM data for 5% Co^{2+}:ZnO nanocrystals prepared in DMSO. (a) Low-resolution TEM image. (b) Histogram computed for ~100 nanocrystals showing an average particle diameter of 2.9 ± 0.3 nm. (c) Wide-area electron diffraction image. (d) High-resolution TEM image.

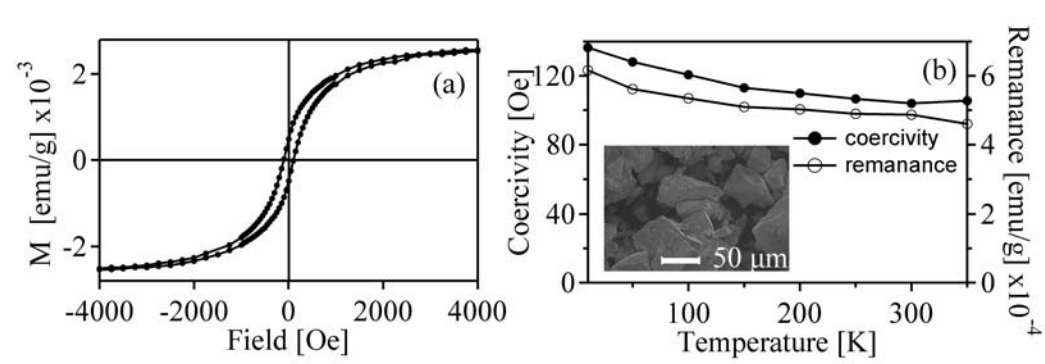

Figure 2. (a) 300K magnetic hysteresis loop and (b) hysteresis coercivity and remanance temperature dependence collected on a powder sample of 3.6% Co^{2+}:ZnO DMS-QD aggregates (inset).

Publications, Presentations and Proposals:

- "Magnetic Quantum Dots: Synthesis, Spectroscopy, and Magnetism of Co2+- and Ni2+-Doped ZnO Nanocrystals." Schwartz, Dana A.; Norberg, Nick S.; Nguyen, Quyen P.; Parker, Jason M.; Gamelin, Daniel R. *J. Am. Chem. Soc.*, **125**, 13205 (2003).
- "Magneto-optical and Magnetic Studies of Diluted Magnetic Semiconductor Nanocrystals." Norberg, Nick S.; Radovanovic, Pavle V.; Schwartz, Dana A.; Amonette, James E.; Gamelin, Daniel R., Third Annual Nanoscale Science and Technology Workshop, University of Washington, Seattle, Washington, September 2003 (poster presented).
- Norberg, Nick S.; Kittilsvted, Kevin; Gamelin, Daniel R., (manuscript in preparation).

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In preparation.