Tunable Magnetic Exchange Interactions in Manganese-doped "Inverted" ZnSe/CdSe Nanocrystals

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Magnetic doping of semiconductor nanostructures is actively pursued for applications in magnetic memory and spin-based electronics. Central to these efforts is a drive to control the interaction strength between carriers (electrons and holes) and the embedded magnetic atoms. Traditionally, embedding paramagnetic atoms into low-dimensional semiconductor structures requires molecular-beam epitaxy or chemical vapor deposition techniques. There now exists a rich variety of 'diluted magnetic semiconductor' (DMS) quantum wells, superlattices, and hetero-interfaces, with recent work demonstrating magnetic doping of epitaxially-grown 'zero-dimensional' quantum dots. In parallel however, advances in colloidal chemistry have recently allowed magnetic doping of semiconductor nanocrystals (NCs), providing an alternative and potentially lower-cost route towards magnetically active quantum dots. With a view towards enhancing carrier-paramagnetic ion spin interactions, colloidal NCs typically generate stronger spatial confinement of electronic wavefunctions compared to their epitaxial counterparts, which is thought to enhance *sp-d* exchange coupling even for a single magnetic dopant atom.

While magnetically-doped monocomponent NCs are well established, wavefunction engineering using magnetic multi-component colloidal *heterostructures* has not been extensively explored. One new class of NC heterostructure that holds promise for tuning *sp-d* exchange interactions are 'inverted' core-shell designs, wherein wide-gap semiconductor cores are overcoated with narrower-gap shells. With increasing shell thickness, the electron and hole envelope wavefunctions, $\Psi_{e,h}(\mathbf{r})$, migrate towards the NC periphery (albeit at different rates), thus tuning their overlap with magnetic atoms embedded, for example, in the core alone. In this work, we investigate precisely this type of wavefunction engineering and exchange interaction control using 'inverted' ZnSe/CdSe core/shell NCs whose cores are doped with paramagnetic, spin-$\frac{5}{2}$ Mn^{2+} ions (see Fig. 1). Magnetic circular dichroism (MCD) spectroscopy at the NC absorption edge reveals a giant *sp-d* exchange interaction that *inverts sign* with increasing shell thickness, suggesting a confinement-induced sign inversion of the electron-Mn^{2+} exchange constant, α, accompanied by significant reduction of the hole-Mn^{2+} overlap due to wavefunction engineering.

We have demonstrated a widely tunable magnetic *sp-d* exchange interaction between electron-hole excitations (excitons) and paramagnetic manganese ions using 'inverted' core-shell nanocrystals composed of Mn^{2+}-doped ZnSe cores overcoated with undoped shells of narrower-gap CdSe. Magnetic circular dichroism studies reveal giant Zeeman spin splittings of the band-edge exciton that, surprisingly, are tunable in both magnitude *and sign*. Effective exciton g-factors are controllably tuned from -200 to +30 solely by increasing the CdSe shell thickness, demonstrating that strong quantum confinement and wavefunction engineering in heterostructured nanocrystal materials can be utilized to manipulate carrier-Mn^{2+} wavefunction overlap *and* the *sp-d* exchange parameters themselves.

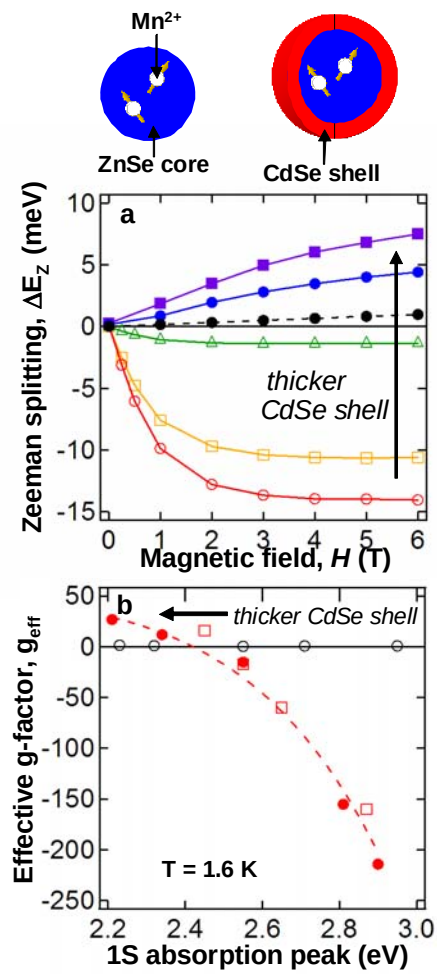

Figure 1. Mn-doped ZnSe cores, overcoated with CdSe shells of thickness *h*. b) Zeeman splitting of dots with increasing *h*. Note sign inversion when *h*>2 A c) Effective exciton

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[1] D. A. Bussian, S. A. Crooker, M. Yin, M. Brynda, Al. L. Efros, and V. I. Klimov, Nature Materials 8, 35 (2009).