Evidence for Ligand-Induced Paramagnetism in CdSe Quantum Dots

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The appearance of magnetism in otherwise nonmagnetic materials has recently been reported for a number of nanoscale systems. Coupled with the size-dependent optical and electronic properties of the nanocrystalline materials, this magnetic behavior opens the possibility for an extended range of technological applications. Thus, identifying the origin of the magnetism is an extremely important goal, yet this remains the subject of some controversy in the literature. For instance, two previous studies have shown that Au, a 5d[9] metal, exhibits ferromagnetic behavior in the nanocrystalline form,[1,2] but the respective authors propose conflicting mechanisms. Meanwhile, a recent observation of magnetization in PbSe quantum dots (QDs) suggests that the magnetism is intrinsic to the QD and not due to a surface effect.[3] More recently, induced magnetism has been reported for CdSe QDs[4−6] and attributed to a variety of sources, including the existence of dangling bonds,[4] induction by surface ligands,[5] and even defects in the CdSe particles.[6] Adding more complexity to these observations is the fact that none of these studies systemically investigated both size and surface-ligand effects, and two of these reports[5,6] claim that the observed magnetism is due to *ferromagnetic* ordering. In this communication, we provide conclusive evidence that magnetism in CdSe QDs can be induced via manipulation of the surface chemistry. We demonstrate that the paramagnetic behavior of the CdSe QDs can be enhanced by variation of the end-group functionality of the passivating layer and that there is no evidence for ferromagnetism.

Magnetic susceptibility measurements were made using a SQUID magnetometer and provided evidence of changes in the magnetic properties of the CdSe QDs relative to those of bulk CdSe. Figure 1 displays $\chi(T)$ for 15 Å radius CdSe QD samples passivated with hexadecylamine (HDA) or trioctylphosphine oxide (TOPO) along with the expected value for bulk CdSe.[7] The QD samples obey a modified Curie law with $\chi_0 > 0$ and Curie constants (C) that are strongly dependent on the surface termination: $C = 32 \times 10^{-6}$ and $\pm 1.2 \times 10^{-6}$ emu K g^{-1} for TOPO and HDA surface ligand passivation, respectively. These values consider only the total sample mass and do not separate the contributions due to the surface ligands. This aspect, along with a complete size-dependence study, will be addressed in detail in a future manuscript.[8] Atomic emission indicated non-Cd transition-metal impurities of <1 ppb, suggesting that chemical bonding induces local paramagnetic moments on the particle surface. Neither $\chi(T)$ nor $M(H)$ measurements [see Supporting Information (SI), Figure S3] showed any indication of ferromagnetic ordering in these samples, so experiments were performed to ensure that we could attribute the observed paramagnetism to a surface effect. We performed both X-ray magnetic circular dichroism (XMCD) and X-ray absorption spectroscopy
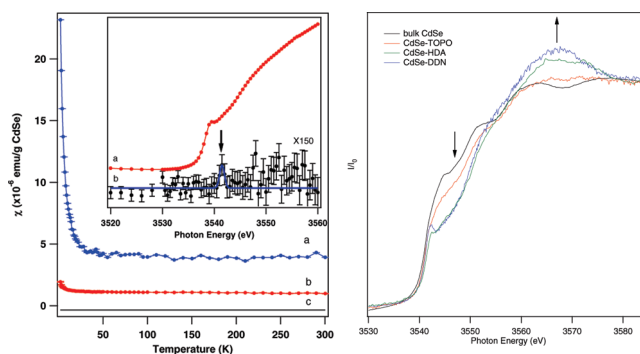

Figure 1. (left) Magnetic susceptibility for $R = 15$ Å CdSe QDs passivated with (a) TOPO and (b) HDA and for (c) bulk CdSe. Inset: Cd L_3-edge (a) XAS and (b) XMCD measurements for a 13 Å CdSe−TOPO QD. The blue line in the inset is a guide for the eye. (right) Cd L_3-edge XAS spectra of bulk CdSe and $R = 15$ Å CdSe QDs passivated with TOPO, HDA, and DDN.

(XAS) to directly probe the Cd electronic structure of the particles. Since we propose that the magnetic properties are induced by a chemical bonding effect, XMCD experiments at the Cd L_3-edge (probing 4d states, where chemistry is most likely to occur[9]) should yield detailed, element-specific information about the spin polarization in these materials. As plotted in the Figure 1 inset, CdSe−TOPO QDs ($R = 13$ Å) exhibited an XMCD signal at 3542 eV, an energy where vacant Cd 4d levels are expected to arise.[10] The signal was on the order of $\sim 5 \times 10^{-4}$, which is consistent with a moment of ~ 0.01 μ_B per Cd. Although this value for the magnetic moment is consistent with both ref 4 and our $M(H)$ measurements,[8] it must be noted that the signal is only $\sim 2\sigma$ above the noise, so additional experiments would be required for a more conclusive measurement.

In regard to the temperature-independent part of the magnetic susceptibility, the appearance of positive χ values is intriguing because bulk CdSe has $\chi = -0.334 \times 10^{-6}$ emu g^{-1}.[7] If one considers the diamagnetic contribution from the TOPO and HDA ligands ($\chi = -0.73 \times 10^{-6}$ and -1.4×10^{-6} emu g^{-1}, respectively), then the overall magnetic susceptibility for the QD materials should be slightly more negative than that of bulk CdSe. Thus, ignoring interaction effects, one would expect the χ value of bulk CdSe to be an upper limit on the magnetic susceptibility, in contrast to the experimental observations. This behavior can be explained by considering the main components of the magnetic susceptibility (χ), which can be described as $\chi = \chi_c + \chi_L + \chi_s + \chi_{vv}$, where χ_c is the core−electron diamagnetic contribution, χ_L is the Langevin contribution, χ_s is the surface-ligand diamagnetic contribution, and χ_{vv} is the Van-Vleck contribution. While χ_c, χ_L, and χ_s are negative contributors to the magnetic susceptibility, χ_{vv} has a positive value and represents the paramagnetic contribution to the magnetic susceptibility. According to ref 7, both χ_L and χ_{vv} should vary with particle size, as χ_L depends on the bond length, which is a size-

dependent value,[11] and χ_{vv} depends on the matrix elements between cation bonding orbitals and anion (or ligand) antibonding orbitals, which, we propose, change with surface termination. This implies experimentally that both the lattice contraction and the increasing degree of charge-transfer bonding between the Cd atoms and the surface ligands could result in a positive χ value, although charge transfer is expected to play a more dominant role (see SI). This charge-transfer effect can manifest itself in the form of π back-bonding, whose degree depends on the ligand π-acceptor strength. Following the π-acceptor scale,[12] we expect TOPO > HDA as a π acceptor and similar trends in the strength of charge transfer. We note that although TOPO is a phosphine oxide, trioctylphosphine impurities in the TOPO passivate some of the CdSe QD surface.[13] In addition, we would expect that although oxygen is typically thought of as a donor atom, the P=O bond of TOPO contains empty π^* orbitals and should therefore be a good π acceptor. Therefore, the correlation between the positive χ_{vv} values and the increase in the ligand π acidity indicates that paramagnetism arises from the molecular-level interactions occurring between Cd atoms and the surface ligands.

One oddity in this observation is that the alkylamines possess no low-lying orbitals and do not provide an obvious means of withdrawing electron density from the 4d orbitals of Cd. It is suggested, therefore, that the paramagnetic properties of the CdSe−HDA QDs are induced by a chemical impurity in the bulk HDA solvent. Time of flight−secondary-ion mass spectrometry (TOF−SIMS) measurements verified that organic impurities were present in the bulk HDA and therefore were present on the surface of the CdSe−HDA QDs. In addition to the anticipated signature for HDA, the TOF−SIMS spectra provide evidence for molecules containing the cyano (−CN) group within the HDA solvent and the CdSe−HDA QD samples. The presence of the cyano functionality is extremely significant because, in contrast to the amine group of HDA, −CN is capable of accepting Cd 4d electron density via back-donation into the π^* orbitals of the CN triple bond. Indeed, when the ligand dodecanitrile (DDN) was intentionally ligand-exchanged onto the CdSe QD surface, a modest increase in the Curie constant ($C = 3.8 \times 10^{-6}$ emu K g^{-1}) was observed via magnetic susceptibility (Figure S2 in the SI). This result implies that we can "switch" the magnetic behavior "on and off" on one particle simply by changing the ligand molecule on the same particle. Therefore, as the TOPO ligand can also participate in π back-bonding, back-donation between Cd and −XL (where X is the end-group functionality and L is the ligand) is proposed as the mechanism for enhancement of the vacant 4d density of states (DOS) and the origin of paramagnetic properties in CdSe QDs.

Although the $\chi(T)$ and XMCD data provide strong evidence of a surface-termination-driven dependence of the magnetic susceptibility, the contribution that dangling bonds may play in the magnetic properties of the CdSe QDs must be addressed. As shown in the dilute magnetic semiconductor literature[14] and in radiation damage studies of normally nonmagnetic systems,[15] defects can play a role in determining the magnetic properties of these systems. As our QDs were of the highest quality (Figure S1 in the SI), however, we do not believe that any defect-induced magnetism was present. We have previously shown that Cd L$_3$-edge XAS is an excellent tool for probing the s and sp-hybridized DOS.[16] Since the XAS experiments enable investigation of sp-hybridized states,

the measurements can indirectly probe the relative amount of empty p-like states in the CdSe QDs that are related to dangling bonds, as predicted by theory.[10] The right panel of Figure 1 plots Cd L$_3$-edge XAS spectra for 15 Å radius CdSe QDs passivated with different surface ligands alongside the bulk CdSe spectrum. In the 3540−3550 eV energy region, a large reduction (15%) in the XAS intensity (decrease in empty states) was seen as the ligand was changed from TOPO to HDA, which is consistent with the relative increase in passivation by HDA.[9c] Even so, the associated reduction in the number of dangling bonds could not account for the nearly *order of magnitude* increase in the Curie constant as suggested by Neeleshwar et al.[4] In addition, the dangling-bond concentrations derived in ref 4 do not make physical sense: a concentration of 2000 ppm for 14 Å radius CdSe QDs gravely underestimates the number of dangling bonds, on the basis of the wealth of literature on this subject.[9] When the dangling-bond contributions are ruled out, the contrasting behavior of the CdSe−HDA, CdSe−TOPO, and CdSe−DDN systems indicates that the paramagnetic properties of the CdSe QDs depend on their interactions with the organic ligand molecules.

Supporting Information Available: Synthesis, ligand exchange, and characterization (TEM, UV−vis); experimental details; magnetization measurements; and the charge-transfer model. This material is available free of charge via the Internet at http://pubs.acs.org.

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