Probing the Local Microenvironments in Cr:CdSe Quantum Dots Using High Frequency EPR

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Introduction

The effect of surface passivation and lattice truncation on local environments within a CdSe QD is an active area of research; however, probing the microenvironments within QDs has been met with significant challenges.[1] In our previous work at the National High Magnetic Field Laboratory (NHMFL) we showed that high-frequency EPR (HF-EPR) can be used to probe the local site environment of CdSe when the QDs have been doped with Mn(II) paramagnetic ions. The site dependent perturbation experienced for Mn(II) allowed for the distinction of two unique micro-environments within the QD, namely an unperturbed core and an electronically distorted surface[1,2]. In an attempt to probe the local site environments in Cr:CdSe QDs our most recent effort at the NHMFL (April 9-13, 2012) once again employed HF-EPR. The room temperature spectra of several sized Cr:CdSe QDs (2.0, 2.5, 3.0, 3.5, and 4.0 nm) were obtained at 240 GHz. Temperature dependent measurements were performed on the 3.0 nm sample at 100, 50, 25, 12.5, and 6.25 K. The results of these studies are discussed below.

Experimental

The synthesis of Cr:CdSe QDs was performed under N_2 using a lyothermal method using a pre-doped single source cluster route based on $[M_xCd_{10-x}Se_4(SePh)_{16})]^{4-}$ (Cd_{10} cluster), where M = Cr^{2+}. Briefly, 480 mg of Cd_{10} and 21mg of $CrCl_2$ were dissolved in 20 mL of hexadecylamine and heated to 120 ^{O}C for several hours to induce metal ion exchange within the cluster. The reaction temperature was then raised to 220 ^{O}C to induce QD growth. Isolation of the QDs was achieved by addition of a minimal amount of toluene followed by addition of methanol to induce QD precipitation.

Multi-frequency EPR measurements were performed with microwave detection using a low-noise InSb hot-electron botometer. A quasi-optical 240 GHz spectrometer was used to study the temperature dependence.

Results and Discussion

The spectral studies with the sensitive HF-EPR instrumentation at the NHMFL showed that the Cr^{2+} ion concentration within the CdSe QDs was extremely low. We did see a weak single peak in the room temperature spectra from the 2.5, 3.0, 3.5, and 4.0 nm samples. We had expected to see at least two peaks in our data, one generated from Cr ions at the surface of CdSe and one from the core, where the local environments around the Cr differ. In an attempt to resolve these states and increase the ground state population of Cr we performed temperature dependent measurements at 240 GHz; however, these results (see **Figure 1**) did not allow us to distinguish core and surface states.

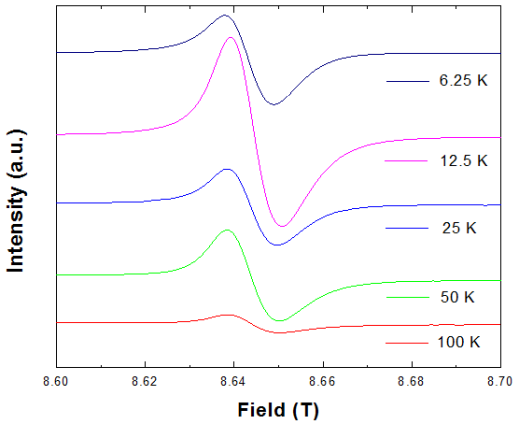

Figure 1. Temperature dependent 240 GHz EPR of 3.0 nm Cr:CdSe QDs.

Conclusions

Although our results were marred by our synthetic limitations, we were able to detect the existence of Cr in the QDs. Synthetic efforts have been underway to increase the Cr ion concentration within the QDs with the hope that an increase in the Cr concentration will lead to the ions being doped stochastically on both the surface and core of CdSe.

Acknowledgements

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References

[1] Zheng, W., *et al.*, J. Phys. Chem. C, **115**, 23305-23314 (2011).
[2] Zheng, W., *et al.*, J. Am. Chem. Soc., **133**, 7482-7489 (2011).