Spin dynamics in electrochemically charged CdSe quantum dots

N. P. Stern, M. Poggio, M. H. Bartl, E. L. Hu, G. D. Stucky, and D. D. Awschalom

Center for Spintronics and Quantum Computation,
University of California, Santa Barbara, CA 93106

(Dated: October 28, 2021)

We use time-resolved Faraday rotation to measure coherent spin dynamics in colloidal CdSe quantum dots charged in an electrochemical cell at room temperature. Filling of the 1S\(_e\), electron level is demonstrated by the bleaching of the 1S\(_e\)-1S\(_{3/2}\) absorption peak. One of the two Landé g-factors observed in uncharged quantum dots disappears upon filling of the 1S\(_e\), electron state. The transverse spin coherence time, which is over 1 ns and is limited by inhomogeneous dephasing, also appears to increase with charging voltage. The amplitude of the spin precession signal peaks near the half-filling potential. Its evolution at charging potentials without any observable bleaching of the 1S\(_e\)-1S\(_{3/2}\) transition suggests that the spin dynamics are influenced by low-energy surface states.

PACS numbers: 78.67.Hc, 78.47.+p, 71.35.Pq, 73.22.-f

In recent years, chemically synthesized semiconductor quantum dots (QDs) have been used in a wide variety of applications from QD-lasers\textsuperscript{7,8} and light emitting devices\textsuperscript{9,10} to fluorescent labels\textsuperscript{11,12,13}. The size-tunable spectrum of energy levels and the ease of colloidal nanocrystal synthesis make these nanocrystals versatile systems for the study of confined charges; the ability to optically excite carriers has spurred work on coherent spin dynamics in colloidal QDs revealing multiple Landé g-factors and spin coherence times reaching several nanoseconds at room temperature\textsuperscript{14,15}. Advances in electrochemical charging of such nanocrystals have given researchers exquisite control over the electronic state of the QD and assembly of the cell are conducted inside of an argon atmosphere glove box. Before removal from the glove box, the cell is sealed with epoxy and enclosed within a vacuum-tight vessel to prevent oxidation; external feedthroughs connect the contacts within the vessel to a potentiostat which maintains a voltage \(V_{\text{cell}}\) between the reference and working electrodes. Negative \(V_{\text{cell}}\) injects electrons into the 1S\(_e\) state of the QDs, evidenced by bleaching of the 1S\(_e\)-1S\(_{3/2}\) interband absorption peak measured using a white light source and a spectrometer. After measurement at the desired \(V_{\text{cell}}\), a positive bias of \(V_{\text{cell}} = 0.5\) V is applied in order to discharge the quantum-confined states and any long-lived localized trap states which may also have been filled. Repeated charging can cause the bleaching process to slow or eventually cease as oxygen or other impurities induce irreversible chemical reactions in the film and electrolyte. Careful fabrication of the cross-linked QD film and assembly of the air-tight electrochemical cell are critical for a sample with long-lived reproducible charging behavior.

Typical optical absorbance spectra \(\alpha(E)\) are shown in Fig. 1b, showing the 1S\(_e\)-1S\(_{3/2}\) absorption peak bleaching with negative \(V_{\text{cell}}\). The bleaching spectrum is calculated as \(\alpha - \alpha_0/\alpha_0\), where \(\alpha\) is the film’s absorption at a given \(V_{\text{cell}}\) and \(\alpha_0\) is the absorption for \(V_{\text{cell}} = 0\) V, and is shown in Fig. 1c for representative values of \(V_{\text{cell}}\). The average number of electrons occupying the 1S\(_e\) state in the QD ensemble can be controlled between 0 and 2 with the appropriate \(V_{\text{cell}}\) so that the degree of bleaching has a direct relation to the occupation of the 1S\(_e\) state. \(V_{\text{half}}\) corresponds to an average electron occupation of 1 in the 1S\(_e\) state of each quantum dot and \(\alpha - \alpha_0/\alpha_0 = 0.5\). \(V_{\text{half}}\) varies from \(-0.85\) to \(-1.0\) V between QDs with nominally similar sizes due to variations in cell assembly and film quality. Bleaching of the 1S\(_e\)-1S\(_{3/2}\) transition occurs over a range of \(+0.1\) V around \(V_{\text{half}}\).

Coherent spin dynamics are measured by time-resolved Faraday rotation (FR) in the Voigt geometry.\textsuperscript{15} A mode-locked 76-MHz Ti:Sapphire laser pumps an optical parametric oscillator, producing 200-fs pulses tunable between energies of 1.97 and 2.21 eV which are split into...
a circularly polarized 1-mW pump and linearly polarized 30-µW probe beam. We also use a regeneratively amplified Ti:Sapphire laser to pump two optical parametric amplifiers (OPA) allowing independent tuning of pump and probe energies. The dual OPA system improves signal-to-noise, but the qualitative features of the FR were unchanged between laser systems. The pump helicity is varied at 40 kHz by a photo-elastic modulator, while the probe beam is chopped at 1 kHz for lock-in detection. Both beams are focused to an overlapping 100-µm diameter spot on the QD film which is positioned between the poles of two permanent magnets. The pump pulse excites spin-polarized electron-hole pairs at time \( t = 0 \), which we assume relax to the lowest energy exciton state within a picosecond.\(^{1,16,17}\) The pump-excited spins precess about the applied magnetic field \( B \) at the Larmor frequency \( \nu_L = \mu gB/\hbar \), where \( g \) is the Landé g-factor, \( \mu_B \) is the Bohr magneton, and \( \hbar \) is Planck’s constant. By the Faraday effect, the probe beam polarization axis rotates by an angle \( \theta_p \) proportional to the spin polarization along the beam path; this angle is measured as a function of the time delay \( t \) between pump and probe pulses. For consistency, all reported FR measurements are at room temperature with \( B = 0.28 \) T from a single film with \( V_{\text{cell}} = -0.95 \) V. Variations in charging behavior between different samples due to nanocrystal size variation and sample quality make direct quantitative comparison between any two samples difficult, although the qualitative results from all samples measured agree with those reported here.

Figure 2 shows typical time-resolved FR time scans (Figs. 2a-d) and the corresponding Fourier transforms (Figs. 2e-h) for representative charging voltages with the pump and probe energies tuned to the 1S\(_e\)-1S\(_{3/2}\) exciton resonance in this sample at 2.03 eV. The data for \( V_{\text{cell}} = 0.0 \) V are characterized by an oscillating component superimposed on a decaying background. The Fourier transform for this voltage (Fig. 2e), reveals two distinct frequencies (\( \nu_1, \nu_2 \)) contributing to the oscillation, consistent with previous FR studies of CdSe QDs.\(^{10,17}\) On charging, the FR amplitude increases while the relative weight of the higher frequency component (\( \nu_2 \)) decreases until disappearing completely around \( V_{\text{cell}} \).\(^*\) The amplitude of the lower frequency component (\( \nu_1 \)) decreases beyond \( V_{\text{cell}} \). Monitoring the absorbance of the probe beam, \( \alpha_{\text{probe}} \), ensures that the QDs within the laser focus spot are charging with the application of \( V_{\text{cell}} \) as the absorbance peak bleaches (Fig. 3a).

In order to more carefully examine these parameters, the FR time-domain data are fit to two decaying cosinusoidal components, given by Eq. (1):

\[
\theta_F = \theta_0 + \theta_1 \exp(-t/T_{2,1}^*) \cos(2\pi \nu_1 t + \phi_1) + \theta_2 \exp(-t/T_{2,2}^*) \cos(2\pi \nu_2 t + \phi_2) + \theta_{\text{exp}} \exp(-t/\Delta t) \tag{1}
\]

where \( \theta_0 \) is an offset, \( \theta_1(\theta_2) \) the amplitude of the first (second) frequency component, \( T_{2,1}^*(T_{2,2}^*) \) the transverse spin coherence time, \( \nu_1(\nu_2) \) the Larmor frequency, and \( \phi_1(\phi_2) \) the phase, \( \theta_{\text{exp}} \) and \( t \) the amplitude and decay time respectively of the non-oscillating exponential background. At voltages \( V_{\text{cell}} < -0.9 \) V, the second frequency component (\( \nu_2 \)) is not present and only one of the cosinusoidal terms is kept in the fit function.

The non-oscillating component with a decay time of \( t = 0.9 \pm 0.1 \) ns disappears when the film is charged
beyond $V_{\text{half}}$. (Fig. 3b) The origin of this component is unclear, as earlier studies of confined nanostructures have attributed similar non-oscillating signals as to the decay of hole spins pinned along the growth axis\cite{17} to the leakage of longitudinal spin relaxation signal\cite{18} or the decay of non-oscillating exciton populations\cite{19}.

The quenching of $\theta_{\exp}$ with charging is consistent with the latter two explanations.

The lower frequency FR amplitude $\nu_1$ decays with a Gaussian envelope, indicating that the relaxation of coherent spins in the QD ensemble is dominated by inhomogeneous dephasing. The effect of the inhomogeneous QD size can be modeled as a Gaussian distribution of $g$-factors with width $\Delta_g$. Averaging the FR contributions over the ensemble introduces an additional Gaussian envelope to the oscillatory terms of Eq. 1 with a width $\Delta_i = h/\mu_B B \Delta_g$. Fits to the FR yield both the Gaussian decay width and the transverse spin lifetimes (Fig. 3c).

Since $\Delta_i$ is about 0.7 ns for all $V_{\text{cell}}$, the dephasing is due to structural properties such as orientation and size variation that are not affected by changes in electronic occupation. Assuming all inhomogeneities are size related, this dephasing rate corresponds to a $g$-factor width $\Delta_g = 0.06$ and a size distribution of about 15%. The size distribution of the synthesized QDs is estimated to be closer to 5%, suggesting contributions to the inhomogeneous broadening by shape anisotropy and random nanocrystal orientation which are not accounted for in this simple size-averaging procedure. The spin coherence time of the $\nu_1$ component, $T_{2,1}^*$, increases dramatically with charging, though quantitative fit results for coherence times above 2 ns are not reliable because of the vanishing of the FR signal due to dephasing. This result is consistent with the large increase in spin lifetimes reported in $n$-doped self-assembled InAs-GaAs QDs compared to undoped QDs\cite{18}. Further experiments in systems with less inhomogeneity or on single quantum dots will help avoid the limitations of inhomogeneous broadening and isolate the effects of charging upon the spin lifetime.

The amplitudes of the two FR components behave quite differently from each other (Fig. 4a). The lower frequency amplitude $\theta_1$ increases significantly, reaching a maximum near $V_{\text{half}}$ before decreasing toward zero in doubly-charged QDs. $\theta_2$ vanishes sharply at $V_{\text{half}}$ due to the presence of charges in the 1S state.

Comparison between Figs. 3a and 4a show that $\nu_1$ increases at $V_{\text{cell}}$ well below the 1S charging near $V_{\text{half}}$. The amplitude increase between 0 V and $V_{\text{half}}$ may be due to the filling of low-energy surface states on the nanocrystals which have been shown to provide fast non-radiative pathways for carrier relaxation. Surface defect states in uncharged QDs, in addition to influencing energy levels\cite{20} and photoluminescence dynamics\cite{21}, account for the relaxation of up to half of optically injected carriers within a few ps (Fig. 4c)\cite{22}. For $V_{\text{cell}}$ between 0 V and $V_{\text{half}}$, these empty surface states in the QD band gap can be filled by electrochemically injected charges, blocking the relaxation pathway and increasing the number of QDs in the ensemble with long-lived coherent electron populations (Fig. 4d). This interpretation is supported by the disappearance in charged QDs of the spikes in the FR near $t = 0$ which may denote decay processes on the order of a few ps (Fig. 2a-d). The FR amplitude reduction for charging beyond $V_{\text{half}}$ is due to Pauli blocking of absorbing 1S$_e$-1S$_g$ transitions, as evidenced by the commensurate bleaching (Fig. 1c) and reduction in probe beam absorption (Fig. 3a) in this regime.

The two constant precession frequencies (Fig. 4b) correspond to Landé $g$-factors of $g_1 = 1.15$ and $g_2 = 1.63$, in agreement with what would be expected for a 6-nm diameter QD\cite{23}. The origin of the two $g$-factors in CdSe QDs has been attributed to multiple sources in the literature\cite{24}. Theoretical calculations from effective mass models suggest that the lower frequency $g_1$ is electron spin precession\cite{25,26} Ref. 10 follows this assignment and subsequently attributes $g_2$ to exciton precession in a subset of quasispherical QDs where the spin-splitting due to shape and wurtzite crystal anisotropies cancel. Another interpretation of the time-resolved FR data in Ref. 11 proposed by Chen and Whaley\cite{27} attributes the two observed $g$-factors to the two anisotropic components of the $g$-tensor $g_\perp$ and $g_\parallel$ predicted by tight-binding calculations. As noted in Ref. 28 however, this calculation does not account for the random orientation of the nanocrystal axes relative to the spin injection axis. Previous experimental work shows that anisotropic $g$-factors should lead to a single averaged frequency in the FR data\cite{29}. Further, the markedly different qualitative behavior of the two precession frequencies with charging in the current experiment supports the interpretation by Ref. 10 of distinct states giving rise to the components. These details favor the conclusion that $g_2$ is an excitonic $g$-factor, but neither the original FR measurements nor the charging experiments give any details as to which fine-structure exciton state may be involved in the precession.
The quenching of the $g_2$ component can be explained within this exciton precession model by noting that in an idealized QD, selection rules dictate that circularly polarized pump pulses can only interact with a subset of singly-charged QDs in the ensemble. When the single $1S_e$ electron is spin up (down), only $\sigma^+(\sigma^-)$ polarized pump pulses can be absorbed. Since the $1S_e$ electrons of the resulting charged exciton must be in a singlet state, the delayed probe pulse cannot interact with the pumped QDs (Fig. 4e). Thus, the FR signal from a charged QD ensemble is likely due to QDs which had no initial charge and were optically excited, or singly-charged QDs which have not absorbed the pump pulse because the $1S_e$ charge has the opposite spin for the pump helicity. For a $V_{\text{cell}}$ where QDs are at least singly-charged, the probe pulse will not measure any QDs with optically generated excitons, but rather only those with a single electrically injected $1S_e$ electron (Fig. 4f). Hence, for $V_{\text{cell}}$ corresponding to a charged ensemble, only electron spin precession is observed whereas exciton precession is quenched.

In summary, we have studied the effects of electrochemical charging on the spin dynamics of optically injected carriers in colloidal CdSe quantum dots. The charging of the nanocrystals suppresses the higher of two spin precession frequencies, which is most likely of excitonic nature. Further, the amplitude of the spin precession increases up to near the half-filling potential and decreases in completely charged dots, likely due to surface defects and Pauli blocking. Inhomogeneous dephasing limits interpretation of spin coherence times, though there is evidence for an increase in transverse electron spin lifetime.

We thank J. Berezovsky for illuminating discussions. This work was supported by DARPA and the NSF. N. P. S. acknowledges the Fannie and John Hertz Foundation.

References:

1. V. I. Klimov, et al., Science 290, 314 (2000).
2. H.-J. Eisler, et al., Appl. Phys. Lett. 80, 4614 (2002).
3. M. Kazes, D. Y. Lewis, Y. Ebenstein, T. Mokari, and U. Banin, Adv. Mater. 14, 317 (2002).
4. J. N. Cha, M. H. Bartl, M. S. Wong, A. Popitsch, T. J. Deming, G. D. Stucky, Nano Lett. 3, 907 (2003).
5. M. C. Schlamp, X. G. Peng, and A. P. Alivissats, J. Appl. Phys. 82, 5837 (1997).
6. H. Mattoussi, et al., J. Appl. Phys. 83, 7965 (1998).
7. M. Bruchez, M. Moronne, P. Gin, S. Weiss, and A. P. Alivissats, Science 281, 2013 (1998).
8. W. C. Chan and S. Nie, Science 281, 2016 (1998).
9. J. A. Gupta, D. D. Awschalom, X. Peng, and A. P. Alivissats, Phys. Rev. B 59, R10 421 (1999).
10. J. A. Gupta, D. D. Awschalom, A. L. Efros, and A. V. Rodina, Phys. Rev. B 66, 125307 (2002).
11. C. Wang, M. Shim, and P. Guyot-Sionnest, Science 291, 2390 (2001).
12. P. Guyot-Sionnest and C. Wang, J. Phys. Chem. B 107, 7355 (2003).
13. C. Wang, B. L. Wehrenberg, C. Y. Woo, and P. Guyot-Sionnest, J. Phys. Chem. B 108, 9027 (2004).
14. L. Qu, Z. A. Peng, and X. Peng, Nano Lett. 1, 333 (2001).
15. S. A. Crooker, D. D. Awschalom, J. J. Baumberg, F. Flack, and N. Samarth, Phys. Rev. B 56, 7574 (1997).
16. U. Woggon, et al., Phys. Rev. B 54, 17681 (1999).
17. J. Berezovsky, M. Ouyang, F. Meier, and D. D. Awschalom, Phys. Rev. B 71, 081309(R) (2005).
18. A. I. Tartakovskii, et al., Appl. Phys. Lett. 85, 2226 (2004).
19. S. Cortez, et al., Phys. Rev. Lett 89, 207401 (2002).
20. A. Franschetti and A. Zunger, Phys. Rev. B 62, R16287 (2000).
21. V. I. Klimov, D. W. McBranch, C. A. Leatherdale, and M. G. Bawendi, Phys. Rev. B 60, 13740 (1999).
22. J. Schrier and K. Birgitta Whaley, Phys. Rev. B 67, 235301 (2003).
23. A. V. Rodina, Al. L Efros, A. Yu. Alekseev, Phys. Rev. B 67, 155312 (2003).
24. P. Chen and K. B. Whaley, Phys. Rev. B 70, 045311 (2004).
25. G. Salis, D. D. Awschalom, Y. Ohno, and H. Ohno, Phys. Rev. B 64, 195304 (2001)