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Surface Sensing of Quantum Dots by Electron Spins

Fabrizio Moro,†‡ Lyudmila Turyanska,†‡ James Wilman,† Huw E. L. Williams,§ Alistair J. Fielding,‖ and Amalia Patane†~

†School of Physics and Astronomy, The University of Nottingham, Nottingham NG7 2RD, United Kingdom
‡School of Chemistry, University of Lincoln, Lincoln LN6 7DL, United Kingdom
§Centre for Biomolecular Sciences, School of Chemistry, The University of Nottingham, Nottingham NG7 2RD, United Kingdom
‖The Photon Science Institute and School of Chemistry, University of Manchester, Manchester M13 9PL, United Kingdom

ABSTRACT: The nanoscale design of quantum dots (QDs) requires advanced analytical techniques. However, those that are commonly used do not have sufficient sensitivity or spatial resolution. Here, we use magnetic resonance techniques combined with paramagnetic Mn impurities in PbS QDs for sensitive probing of the QD surface and environment. In particular, we reveal inequivalent proton spin relaxations of the capping ligands and solvent molecules, strengths and anisotropies of the Mn nuclear spin interactions, and Mn nuclei distances with ~1 Å sensitivity. These findings demonstrate the potential of magnetically doped QDs as sensitive magnetic nanoprobes and the use of electron spins for surface sensing.

KEYWORDS: Colloidal quantum dots, magnetic doping, nuclear magnetic resonance (NMR), electron spin resonance (ESR), electron spin echo envelope modulation (ESEEM), electron–nuclear double resonance (ENDOR)

Nano scale design of colloidal quantum dots (QDs) by the controlled incorporation of paramagnetic impurities or modification of the surface by capping ligands requires analytical techniques with sufficient sensitivity to resolve single atoms and to probe surface properties. Both the position of the impurities in the host crystal lattice and their interaction with the surrounding environment (e.g., capping ligands, solvent, etc.) are central to the design and exploitation of the nanocrystals in several applications spanning optoelectronics and medical imaging. For example, multimodal imaging could be enabled by doping QDs with paramagnetic centers.

Among several spectroscopic techniques, nuclear magnetic resonance (NMR) and electron spin resonance (ESR) stand out as they can resolve the structure and functionalities of systems that lack long-range order (e.g., proteins and biological membranes), which are otherwise inaccessible with more conventional techniques, such as X-ray diffraction (XRD). To date, NMR has been employed to probe the structure and surfaces of colloidal metal nanoparticles and quantum dots (QDs). In particular, solid-state NMR has enabled studies of the incorporation of low concentration of impurities. However, sample preparation involves the precipitation of the nanoparticles, which can affect the nanocrystal surface. In contrast, solution proton-NMR (1H NMR) is a nondestructive technique and could be equally informative. Indeed, spectral broadening and proton spin relaxations studies have been used to investigate the interfacial electronic structure in colloidal QDs as well as surface charge transfer processes.

ESR is less commonly used than NMR because it relies on the presence of unpaired electrons. This requirement can be fulfilled by doping the nanocrystals with paramagnetic centers. The detection of electron spin impurities by pulsed-ESR methods combined with theoretical modeling enables the determination of structural and dynamical properties with nanosecond resolution. Pulsed-ESR has now become a standard approach for the characterization of proteins using site-directed mutagenesis and spin labeling. Colloidal nanocrystals doped with magnetic impurities or radiation defects as well as a method for the detection of NV-centers in diamond for biomarkers, spin qubits, and nanoscale sensors.

Here, we demonstrate that the combined use of 1H NMR and pulsed-ESR in colloidal QDs containing paramagnetic impurities enables sensitive probing of the QDs surface and environment. We probe the location of Mn2+ and spin qubits in colloidal PbS QDs and show that the interaction of single impurities with near protons provides a tool for discrimination between inequivalent proton spin relaxations of surrounding molecules, i.e., capping ligands and solvent molecules. In addition, we determine the strength and anisotropies of the...
interactions between surface Mn electron spins and near nuclear spins, as well as the Mn nuclei distances with ~1 Å sensitivity. The proximity of the Mn ions to the surface of the QDs provides us with a nanostructure whose magnetic properties are strongly sensitive to its environment. On the one hand, these results provide insight on the sources of decoherence for electron spins in QDs relevant for their application as qubits. On the other hand, they are relevant for future exploitation of magnetically doped QDs as sensitive magnetic nanoprobes in medical imaging.

Colloidal Mn-doped PbS nanocrystals were synthesized in aqueous solution with Mn content from 0.01% to 0.1% and stabilized with a mixture of 1-thioglycerol (TGL) and 2,3-dimercapto-1-propanol (DTG). Triethylamine (TEA) was used to control the pH of the QD solution. The Mn^{2+} ions are incorporated into the Pb-sublattice sites of the PbS rock-salt cubic crystal. High-resolution transmission electron microscopy (HRTEM) studies (Figure 1a) show that the nanocrystals retain high crystallinity and have an average diameter of 4.5 ± 1.2 nm. Our previous studies have demonstrated room temperature photoluminescence emission tunable by the Mn content in the range 950–1200 nm.

The NMR data were collected at 600 MHz on a Bruker Avance III spectrometer at 298 K on QDs dispersed in H$_2$O:D$_2$O (1:9 v/v). Solvent suppression was achieved using excitation sculpting, where required. Spin–lattice relaxation time ($T_1$) experiments were conducted with an inversion recovery sequence: $rf(\pi) - \text{delay} (T) - rf(\pi/2) - \text{delay} (\pi/2) - \text{free induction decay}$, where $rf$ stands for radiofrequency pulse duration and $\pi/2 = 11.5 \mu s$. Data were acquired as a pseudo 2D spectrum, and the relaxation delay was set at $>5 T_1$ to facilitate complete recovery between transients. Data were phased and baseline corrected prior to integration using TOPSPIN 3 software.

Pulsed-ESR studies were conducted on a PbS:Mn solid state sample with Mn concentrations of 0.03–0.05% (~1 Mn^{2+} ion per QD), which provide a good compromise between long spin relaxation times ($T_1^* \sim 1 \mu s$ and $T_2 \sim 200 \mu s$ at $T = 5 K$) and a large signal/noise ratio in the pulsed-ESR experiments. Electron spin echo envelope modulation (ESEEM) and electron–nuclear double resonance (ENDOR) experiments were conducted on protonated and deuterated (D-PbS:Mn) solid state samples and performed at Q-band ($\nu_{\text{microwave}} = 33.85$ GHz) at the fourth hyperfine peak ($B = 1.211$ T) of an echo field sweep spectrum (see Figure S1 in the Supporting Information), which corresponds to the $m_I = -1/2$ nuclear line of the $m_s = +1/2$ ↔ $-1/2$ transition. ESEEM data were collected using a standard Hahn echo pulse sequence: $\pi/2$–delay ($\tau$) – $\pi$–delay ($\tau$) – echo signal, with $\pi = 48$ ns and $\tau = 200$ ns. ENDOR data were collected using standard Davies: $mw(\pi) - \text{delay} (T) - rf(\pi) - \text{delay} (T) - mw(\pi/2) - \text{delay} (\tau) - mw(\pi) - \text{delay} (\tau) - \text{echo signal}$, where $mw$ stands for microwave pulse duration, $rf(\pi) = 30 \mu s$ and $T = 100$ ns; and Mims: $mw(\pi/2) - \text{delay} (\tau) - mw(\pi/2) - \text{delay} (T) - rf(\pi) - \text{delay} (T) - mw(\pi/2) - \text{delay} (\tau) - \text{echo signal}$ pulse sequences, where $T = 100$ ns. The experimental spectra were simulated using Easyspin software.

Figure 1 shows a typical HRTEM image of Mn-doped PbS QDs and a schematic of a PbS QD with a Mn atom near its surface, a TGL ligand, which binds to the QDs via the SH group, and a TEA molecule. $^1$H NMR spectra were acquired to probe the QD surface and environment and were compared to those of free TGL and TEA molecules.

The $^1$H NMR spectrum of PbS QDs (Figure 2a) reveals two intense peaks centered at $\delta = 1.24$ and 3.12 ppm, which we assign to the CH$_3$ and CH$_2$ groups of the TEA molecule, respectively (see also SI2 in the Supporting Information). The TEA peaks are shifted downfield compared to those of free TGL and TEA molecules. The different color tone is used to distinguish between odd and even CH groups.

Figure 2. (a) $^1$H NMR spectra for solutions of undoped PbS QDs (top panel), free TEA (middle panel), and free TGL molecules (bottom panel). Insets are skeletal formulas for TGL and TEA. (b) HSQC spectra of TGL and PbS QDs. The peaks assigned to the CH groups of TEA and TGL molecules for the PbS QDs are indicated. The different color tone is used to distinguish between odd and even CH groups.
0.1%, the characteristic resonance peaks of TEA (Figure 3a) broaden and shift upfield with greater chemical shifts observed for protons on CH$_2$-groups (Δδ = −0.08 ppm). More significant changes are observed for the resonant peaks of TGL (Figure 3b). All $^1$H NMR peaks broaden and shift downfield starting from a Mn concentration as low as 0.01%. The most pronounced changes are observed for the 2'-CH$_2$ (δ = 2.54 ppm) and 2''-CH$_2$ groups (δ = 2.65 ppm), where their peaks broaden and their signal becomes undetectable at Mn = 0.1%. These results suggest that the spin relaxation rates of the protons of the capping ligands and solvent molecules increase due to the magnetic dipolar interactions with the Mn ions. It is worth noting that, for the same Mn concentration, we observe a larger degree of spectral broadening for both the TGL and TEA $^1$H NMR peaks in a control sample of MnAc$_2$ mixed with free TEA and TGL molecules (see SI3 in the Supporting Information).

From the analysis of $^1$H NMR spin–lattice relaxation experiments, we estimate the proton spin–lattice relaxation rate constant, 1/$T_1$, for each CH group of TGL (Figure 4a) and TEA (Figure 4b) molecules. We observe a general increase of 1/$T_1$ with increasing Mn content. The relaxation rate in TGL molecules increases by up to one hundred times and is different for each CH group: $1/T_1$(2CH$_2$) > $1/T_1$(3CH) > $1/T_1$(4CH$_2$). In addition, for each CH group, $1/T_1$ increases linearly with increasing Mn content. Instead, the relaxation rate for proton spins of CH$_2$ and CH$_3$ groups in TEA increases by up to ten times following the Mn incorporation. The systematic decrease of 1/$T_1$ along the C chain of TGL molecules confirms the binding of the TGL to the QD surface at the −SH site (Figure 4a), while the slower proton $T_1$ relaxation for TEA indicates efficient passivation of the QDs with capping ligands, which screen the interactions of the Mn spins with the TEA molecules (Figure 4b).

The proton spin relaxation rate depends on the strength of the magnetic field generated by the paramagnetic impurities, $B_0$, and the distance, $d$, between the paramagnetic impurities and the proton spin. The calculated values of $B_0$ and $d$, as derived from classical magnetic dipolar interactions, and measured values of 1/$T_1$ for different CH-groups of TGL and TEA are shown in Figure 4c and d, respectively (see also SI4 in the Supporting Information). For each Mn concentration, the TGL 2CH$_2$-group is always closer to the Mn ions than 3CH and 4CH$_2$, respectively (Figure 4c). With increasing Mn content, the average Mn−$^1$H distance decreases, while $B_0$ increases for all the inequivalent protons. The calculated distance of Mn from the 2CH$_2$ group is $d$ = 4 Å for Mn = 0.1% and $d$ = 6.5 Å for the lowest concentration Mn = 0.01%. Since the S−2CH$_2$ distance in the TGL molecules is $d$ = 1.5 Å, we deduce that the Mn ions are 2.5−5 Å below the QD surface.

For TEA groups (Figure 4d), we find that, for each Mn concentration, the Mn−$^1$H distance is always larger or comparable to the distance between Mn spins and TGL 4CH$_2$ groups. For the lowest concentrations (i.e., Mn = 0.01%) the Mn spin sensitivity to distant TEA protons extends up to $d$ = 8 Å.

Although $^1$H NMR is very sensitive to $^1$H-relaxation induced by surrounding electron spins, it only provides an indirect probe of the location and concentration of Mn ions in the QDs. More generally, the NMR sensitivity is limited by the weak nuclear magnetic moments and fast relaxation times for nuclear species with an electric quadrupole moment making, for instance, $^{55}$Mn- and $^{207}$Pb-NMR transitions undetectable. Pulsed-ESR methods offer the advantage of relying on the
We ascribe the absolute values for the interaction of Mn ions with surface contributions to the hyperfine interaction in spherical coordinates, respectively) and an axial nuclear quadrupole term in the mid-high frequency range.

The ESEEM spectrum of deuterated Mn-doped PbS QDs (Mn = 0.03%) in Figure 5a reveals a resonant peak centered at the Q-band Larmor frequency of deuterium \( \nu_{\text{Larmor}}(\text{D}) = 7.9 \text{ MHz} \) close to \( 2\nu_{\text{Larmor}}(\text{H}) \) and \( \nu_{\text{Larmor}}(\text{H})/2 \), respectively. The obtained \( \Delta \nu \) is similar to that reported for Mn complexes \(^{55}\text{Mn}\) and ascribed to second-order hyperfine interaction contributions \(^{39,40}\) (see SI8 in the Supporting Information).

Overall, both \(^1\text{H}\) NMR and pulsed-ESR methods enable the observation of electron–nuclear spin interactions at the surface of the QDs and provide us with complementary information on the position and environment of a single paramagnetic center in a nanocrystal. A single Mn\(^{2+}\) impurity in colloidal PbS QDs experiences a rhombic environment as a result of its proximity to the disordered QD surface. We have estimated the hyperfine dipolar interactions between the Mn ions and the nuclei of the capping ligands and solvent molecules and their relative distances.

Our findings demonstrate that Mn\(^{2+}\) spins located near the QD surface \((d < 5 \text{ Å})\) act as sensors of proton spins located at the QD surface with \( \sim 1 \text{ Å} \) sensitivity. Therefore, a minimum amount of Mn ions (as low as a single ion per QD) is sufficient to induce a fast relaxation of the proton spins of the capping ligands as well as of the solvent molecules: a 60-fold and 10-fold enhancement for the protons of the capping ligands and solvent molecules, respectively. These features are relevant for the exploitation of Mn-doped colloidal QDs as imaging labels for molecules, respectively. These features are relevant for the exploitation of Mn-doped colloidal QDs as imaging labels for molecules, respectively. These features are relevant for the exploitation of Mn-doped colloidal QDs as imaging labels for molecules, respectively.
More generally, magnetic doping of QDs may pave the way for the use of electron spins as surface sensors in combined pulsed-NMR and ESR studies. Understanding and control of the QD’s surface morphology is of great importance for the optimization of the optical and magnetic properties of QDs relevant for the development in optoelectronics and medical imaging, and quantum information processing (QIP).27,28

Finally, we envisage that pulsed-ESR could also be sensitive to inequivalent protons53 and different Mn sites, which in our experiments are masked by the line width broadening due to simultaneous excitation of electron–nuclear transitions along different orientations. This sensitivity will provide more information about the distribution of Mn sites and the distances between a Mn$^{2+}$ ion and the surrounding inequivalent protons. For instance, these could be achieved by pulsed-ESR experiments either on ordered arrays of QDs or a single QD. Some progress in these directions has recently been achieved by pulsed-ESR experiments on individual atoms on a surface. Alternatively, more sophisticated pulsed-ESR methods, which greatly increase the resolution of ENDOR spectra, and hence enable us to distinguish between inequivalent nuclear spins, could be implemented.44

■ ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nanolett.6b02727.

Echo field swept spectrum, detailed explanation of the $^1$H NMR spectra for TEA and TGL molecules, $^1$H NMR spectrum of a control sample, $1/T_2$ relaxation rate formula, description of ESEEM and ENDOR simulations, tables of simulation parameters, dipolar coupling formula and description of CW-ESR simulations (PDF)

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: Fabrizio.Moro@nottingham.ac.uk.

Notes
The authors declare no competing financial interest.

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■ REFERENCES

(33) We note that the composition of the solvents, i.e., the ratio of H$_2$O to D$_2$O, has no effect on the chemical shift and line broadening observed in the QD samples.
(35) We note that the contribution of \(^1\)H is not observed in the ESEEM because the modulation depth of nuclear modulations scales with the factor \(I (I + 1)\) in absence of nuclear quadrupole coupling. Given that \(I = 1/2\) for \(^1\)H, the \(^1\)H modulation depth is \(8/3\) times smaller than \(^2\)H.

(36) The combination peak \(\omega_{x} - \omega_{y}\) appears as a narrow feature because orientation-dependent hyperfine interactions are partially refocussed, therefore revealing the orientation dependent contribution to the ESEEM spectral broadening and line shape.


