Effect of Surfactant and Solvent on Spin–Lattice Relaxation Dynamics of Magnetic Nanocrystals

Sourav Maiti, Hsiang-Yun Chen, Tai-Yen Chen,[†] Chih-Hao Hsia,[‡] and Dong Hee Son*

Department of Chemistry, Texas A&M University, College Station, Texas 77842, United States

Supporting Information

ABSTRACT: The effect of varying the surfactant and solvent medium on the dynamics of spin–lattice relaxation in photoexcited Fe_3O_4 nanocrystals has been investigated by measuring the time-dependent magnetization employing pump–probe transient Faraday rotation technique. The variation of the surfactants having surface-binding functional groups modified not only the static magnetization but also the dynamics of the recovery of the magnetization occurring via spin–lattice relaxation in the photoexcited Fe_3O_4 nanocrystals. The variation of the polarity and size of the solvent molecules can also influence the spin–lattice relaxation dynamics. However, the effect is limited to the nanocrystals having sufficiently permeable surfactant layer,



where the small solvent molecules (e.g., water) can access the surface and dynamically modify the ligand field on the surface.

INTRODUCTION

The effect of surface-passivating surfactant and the surrounding medium on the relaxation rate of the excited state is an important topic in the research of various nanocrystalline materials and their applications. For instance, the relaxation of the photoexcited excitons or electrons in semiconducting or metallic nanocrystals, important in determining their photovoltaic and photocatalytic efficiency, is sensitive to the chemical environment at the nanocrystal surface.¹⁻³ For this reason, the effect of varying the surface-passivating molecules and the surrounding medium in the decay of the excited electronic states and phonons of the nanocrystals has been studied extensively.4-8 In the case of semiconductor nanocrystals, significant effort was made in understanding the role of surfactant molecules in the charge transfer processes that affect the relaxation dynamics of the charge carriers.⁹⁻¹² The effect of the molecules in the solvent medium close to the nanocrystals that do not specifically bind to the nanocrystal surface on the dynamics of exciton relaxation through charge transfer or (and) energy transfer was also investigated.^{13,14} It was also recognized that the surfactant molecules can provide an extra vibrational bath for the nonradiative relaxation of the charge carriers in addition to the phonons of the nanocrystal lattice.⁴ In metallic nanocrystals, the effect of varying the surrounding medium was mostly focused on phonon cooling that follows the rapid electron relaxation.7

Although the role of surface-passivating surfactant on the surface and surrounding medium in the electronic and phonon relaxation of the nanocrystals is relatively well studied, much less is known about their effect on the relaxation of the spin degrees of freedom. In magnetic nanocrystals of ferromagnetic metals and metal oxides, earlier studies investigated the effect of varying the surfactant molecules on the static magnetic properties. For instance, the role of surfactant molecules on restoring the disordered surface spin and on the strength of surface spin-orbit coupling and surface anisotropy were investigated.¹⁵⁻¹⁷ Recently, our group studied the dynamic magnetism of the optically excited Fe_{3-r}Co_rO₄ nanocrystals, where the rate of the recovery of magnetization following the optically induced demagnetization was measured as a function of particle size and chemical composition.¹⁸ The rate of magnetization recovery occurring via spin-lattice relaxation became faster with decreasing particle size. This observation was explained by the average spin-orbit coupling having contribution from both the interior and the surface of the nanocrystals, where the surface experiences the stronger spinorbit coupling than the interior part. Considering the surfactant's influence on the surface spin order and surface spin-orbit coupling, it is conceivable that varying the surfactant also influences the dynamics of spin-lattice relaxation in magnetic nanocrystals. Furthermore, if the solvent molecules can access the surface of the nanocrystals, they may also participate in the spin-lattice relaxation playing a similar role as the surface-bound surfactant molecules.

In this study, we examined whether varying the surfactant and solvent medium can influence the spin–lattice relaxation of the magnetic nanocrystals via time-resolved measurement of the magnetization in photoexcited Fe_3O_4 nanocrystals. Pump– probe Faraday rotation technique was used to measure the

Special Issue: Paul F. Barbara Memorial Issue

Received:July 24, 2012Revised:September 8, 2012Published:September 24, 2012



Figure 1. (a) TEM image of 7.5 nm Fe₃O₄ nanocrystals. UV–vis absorption spectra of Fe₃O₄ nanocrystals (b) before and after TMAH-exchange dispersed in cyclohexane and water, respectively (diameter = 7.5 nm), and (c) with different surfactants in 1-octadecene after further surfactant exchange from TMAH-passivated nanocrystals (diameter = 5.3 nm).

dynamics of the magnetization recovery following the pumpinduced partial demagnetization. The results indicate that spin–lattice relaxation rate in Fe₃O₄ nanocrystals is affected by the surface-binding functional groups of both the surfactant molecules and surrounding solvent molecules. The influence of the solvent molecules on the spin–lattice relaxation is, however, more apparent in the nanocrystals with thin surface passivation that allows the solvent molecules an easier access to the surface of the nanocrystals. The observation made in this study shows that the variation of the chemical environment on and near the surface of the magnetic nanocrystals can modify not only the static magnetic properties but also the dynamic magnetism.

EXPERIMENTAL SECTION

Synthesis of Iron Oxide (Fe₃O₄) Nanocrystals and Surfactant Exchange. Spherical Fe₃O₄ nanocrystals (diameter = 5.3-7.5 nm) were prepared following the procedure reported earlier.^{19'} The surface of the nanocrystals was passivated with several different surfactants having different head and tail groups to lender solubility in various polar and nonpolar solvents and imposes varying degree of ligand field on the nanocrystal surface. Initially, Fe₃O₄ nanocrystals were synthesized and then separate surfactant exchange reactions were performed to change the surfactants on the nanocrystal surface. In brief, Fe₃O₄ nanocrystals were synthesized by heating iron(III) acetylacetonate with a mixture of oleic acid, oleylamine and 1,2-dodecandiol using benzyl ether as the solvent under nitrogen atmosphere. A different particle size was achieved by varying the reaction temperature and reaction time. The resulting nanocrystals were precipitated with ethanol and redispersed in hexane multiple times to remove the excess surfactant.

Fe₃O₄ nanocrystals that are dispersed in polar solvents were prepared by the surfactant exchange process. The initially prepared Fe₃O₄ nanocrystals (7.5 nm) were dissolved in hexane (8.5 μ M, 20 mL). The solution (4 mL) was mixed with hexane (10 mL), toluene (10 mL), methanol (10 mL), and water (2 mL) to form a biphasic mixture. A 0.4 mL aliquot of 0.06 M methanolic solution of tetramethylammonium hydroxide (TMAH) was further added to the mixture to initiate the phase transfer. Upon gentle agitation in a separating funnel, the nanocrystals transferred from nonpolar to polar phase as a result of the surfactant exchange. Methanol was evaporated under nitrogen flow from the recovered polar phase and the TMAH-passivated Fe₃O₄ nanocrystals were precipitated Fe₃O₄ nanocrystals were dried with nitrogen before dispersing in the

required polar solvents. To prevent the partial oxidation of the nanocrystal to Fe₂O₃ phase during the process of surfactant exchange and rinsing, the exposure of the nanocrystals to atmospheric oxygen was minimized. TMAH-passivated Fe₃O₄ nanocrystals were used to prepare the nanocrystals passivated with different nonpolar surfactant molecules. For instance, to prepare the nanocrystals passivated with oleic acid functionalized surfactants, an excess amount of oleic acid in hexane was mixed with the TMAH-passivated nanocrystals dispersed in methanol. The exchange of surfactant from TMAH to oleic acid results in the transfer of the nanocrystals from polar phase back to nonpolar phase. After the completion of the phase transfer, the nanocrystals in hexane were precipitated and rinsed with ethanol to remove the excess surfactant. During the surfactant exchange process, potential partial oxidation of the surface was checked by measuring the absorption at near-infrared that correlated with the degree of oxidation. When partial oxidation occurs on the surface, gentle heating of the nanocrystal solution in octadecene at 200 °C under nitrogen atmosphere with small amount of oleic acid restored Fe₃O₄ back to the initial state.

The nanocrystals with long chain alcohol surfactants were also prepared from TMAH-passivated nanocrystals in a similar method. Excess 4-(*n*-octyloxy)phenol (or octadecanol) was added to a methanolic dispersion of TMAH-passivated nanocrystals. The methanol was removed under vacuum and the iron oxide nanocrystals in the solution were reduced at 200 $^{\circ}$ C under nitrogen atmosphere for 1 h. The alcohol-passivated nanocrystals were dissolved in hexane and precipitated with ethanol to remove the excess surfactant. The nanocrystals having different nonpolar surfactants were dispersed in 1-octadecene to measure the transient Faraday rotation and transient absorption.

The size and shape of the nanocrystals were confirmed with transmission electron micrograph (TEM). The TEM of 7.5 nm nanocrytals is shown in Figure 1a. Figure 1b shows the UV–vis absorption spectra of Fe_3O_4 nanocrystals dispersed in cyclohexane before surfactant exchange and TMAH-passivated nanocrystals dispersed in water. The two spectra are very close even in the regions longer than 600 nm that is sensitive to the partial oxidation. In Figure 1c, the UV–vis absorption spectra of the nanocrystals having different surfactants prepared from the TMAH-passivated nanocrystals and dispersed in 1-octadecene are shown. The similarity of the UV–vis spectra longer than 600 nm indicates that the nanocrystals used in this study have the nearly identical degree of oxidation.

Transient Faraday Rotation and Transient Absorption Measurements. To measure the spin–lattice relaxation rate, pump–probe transient Faraday rotation was employed to

The Journal of Physical Chemistry B

record the time-dependent magnetization, M(t), following the optically induced partial demagnetization. The details of the measurements are described elsewhere.^{18,20} Briefly, a 780 nm pump pulse (50 fs pulse width) from an amplified titaniumsapphire laser excited the intervalence charge transfer transition in the iron oxide nanocrystals, which rapidly induces the demagnetization. The recovery of the magnetization via spinlattice relaxation was monitored with 635 nm probe pulse derived from white light continuum generated in a sapphire crystal. The time-dependent magnetization of the nanocrystal sample was measured in Faraday geometry with a pair of permanent magnets applying 0.35 T of a magnetic field at the sample location. The polarization direction of the incident probe beam was defined by a Glan polarizer placed in front of sample. The probe beam passing through the sample was split into two orthogonal polarization components using a Wollaston prism set at 45° angles with respect to the polarization direction of the probe beam. A pair of balanced photodiodes measured the difference in intensities between the two orthogonal components of the polarized light, which is proportional to Faraday rotation angle $\theta(t)$. The fractional change in Faraday rotation between with and without pump, $\Delta \theta(t)/\theta_0$, represents the fractional changes in magnetization $\Delta M(t)/M_0$, where θ_0 and M_0 are the Faraday rotation and magnetization without pump, respectively. To remove the nonmagnetic contribution to $\Delta \theta(t)/\theta_0$ signal, the difference between the two sets of data taken with parallel and antiparallel magnetic field to the probe beam direction was used to measure $\Delta \theta(t)/\theta_0$. The values of θ_0 for the samples of given nanocrystal concentrations were determined from the slope of the Faraday rotation vs nanocrystal concentration measured using a separate setup as described in the earlier report.²¹ The relative values of θ_0 of different Fe₃O₄ nanocrystal samples with respect to the oleic acid-passivated nanocrystal dispersed in cyclohexane are summarized in Table 1. To avoid the potential complication

Table 1. Comparison of the Relative Static Faraday Rotation (θ_r) of Fe₃O₄ Nanocrystals with Different Surfactants (Diameter = 5.3 nm) with Respect to the Oleic Acid-Passivated Nanocrystals^{*a*}

surfactant	$ heta_{ m r}$
oleic acid	1.0
4-(octyloxy)benzoic acid	1.0
4-(<i>n</i> -octyloxy)phenol	0.69
octadecanol	0.69
^{<i>a</i>} The uncertainty of $\theta_{\rm r}$ is <5%.	

from the lattice heating by the pump, all the measurements were made at low excitation intensity ranges that does not affect the dynamics of $\Delta\theta(t)/\theta_0$.²²

Transient absorption of the nanocrystal samples were measured simultaneously at the same pump (780 nm) and probe (635 nm) wavelengths for the transient Faraday rotation. The comparison of the transient absorptions with and without the external magnetic field indicated that transient absorption is completely insensitive to the external magnetic field applied in this study. For all the comparisons, the same pump fluence and sample concentrations were used to create the same level of excitation in the nanocrystals. The concentration of the nanocrystal samples was kept at ~10 μ M for 5.3 nm nanocrystals and ~3 μ M for 7.5 nm nanocrystals to avoid interparticle dipolar interaction that can change the dynamics.²³

For both transient Faraday rotation and transient absorption measurements, the sample solutions of nanocrystals were constantly circulated through a flat jet nozzle to avoid any spurious thermal effect from the repeated excitation of the same sample area.

RESULTS AND DISCUSSION

Effect of Varying Surfactants on Spin-Lattice **Relaxation.** To examine whether varying the surface-binding functional group of the surfactant influences the dynamics of spin-lattice relaxation, we prepared Fe₃O₄ nanocrystals (5.3 nm in diameter) passivated with carboxylic acids and alcohols after phase transfer from the TMAH-passivated nanocrystals, as described in the Experimental Section. We chose these functional groups because the earlier study indicated that they exhibit different surface spin-orbit coupling resulting in the difference in the coercivity in MnFe₂O₄ nanocrystals.¹⁷ For the surfactants with carboxyl group, oleic acid (CH₃(CH₂)₇CH=CH(CH₂)₇CO₂H) and 4-(octyloxy)benzoic acid (CH₃(CH₂)₇OC₆H₄CO₂H) were used. Octadecanol $(CH_3(CH_2)_{17}OH)$ and 4 - (n - octyloxy) phenol $(CH_3(CH_2)_7OC_6H_4OH)$ were used as the surfactants having hydroxyl group. All of these surfactants produced highly dispersible nanocrystals in nonpolar solvents, which are consistent with relatively large free energy of adsorption $(-\Delta G = 14-18 \text{ kJ/mol})$ of linear aliphatic acids and alcohols from *n*-heptane and *n*-decane to the iron oxide surface.²⁴ This allowed us to examine the effect of varying the surfactant for the sufficiently well isolated nanocrystals in dilute dispersion without the complication arising from the aggregates of the nanocrystals.²⁵ The interparticle magnetic dipolar interaction in the aggregate or assembly is known to change static magnetic properties.^{23,26} Thiols, which are also known to passivate the Fe₃O₄ surface, were not used in this study because of their higher tendency to form the aggregated nanocrystals. The optical absorption spectra of 1-octadecene solutions of Fe₃O₄ nanocrystals passivated with the four surfactants are almost identical throughout the visible and near-infrared spectral region except in 4-(n-octyloxy)phenol-passivated nanocrystals (Figure 1c). The origin of a small additional absorption in the visible region in 4-(n-octyloxy)phenol-passivated nanocrystals is not clear; however, it may arise from the charge transfer absorption between phenolic group and Fe³⁺ ion.²⁷ The absorption spectra of Fe₃O₄ nanocrystals are sensitive to the partial surface oxidation to Fe_2O_3 phase in the >600 nm region, where the absorption from the intervalence charge transfer between Fe²⁺ and Fe³⁺ absorption becomes weaker with oxidation of Fe^{2+} to $Fe^{3+}e^{28}$ The similarity of the absorption spectra in this region in all the nanocrystal samples indicates that the degree of oxidation is maintained closely in all the samples during the surfactant exchange process.

Figure 2a compares transient Faraday rotation data $(\Delta\theta/\theta_0)$ of Fe₃O₄ nanocrystals passivated with four different surfactants and dispersed in 1-octadecene at the same concentration. We also compared the corresponding transient absorption data (ΔOD) to examine the effect of varying the surfactants on the electronic relaxation in Figure 2b. The recovery of $\Delta\theta/\theta_0$ represents the recovery of the magnetization following the photoinduced demagnetization by the pump pulse. The slower component of the recovery, occurring on a hundreds of picoseconds time scale, was assigned to the recovery of magnetization by spin–lattice relaxation in our earlier studies.^{18,29} Therefore, we will compare the slower recovery



Figure 2. (a) Transient Faraday rotation and (b) transient absorption data of Fe_3O_4 nanocrystals passivated with four different surfactants and dispersed in 1-octadecene. Solid and dashed lines are samples passivated with carboxylic acid and alcohols, respectively.

components of $\Delta \theta / \theta_0$ to examine the effect of surface passivation on the dynamics of spin-lattice relaxation. In Figure 2a, the nanocrystals passivated with alcohols exhibit the slower recovery of $\Delta \theta / \theta_0$ than those passivated with carboxylic acids. On the other hand, the difference in the tail group for a given surface-binding functional group has little influence on the dynamics. Variation of the surfactants also affects θ_0 that represents the relative static magnetization of the nanocrystals. Alcohol-passivated nanocrystals exhibit ~30% smaller θ_0 than those passivated with carboxylic acids as shown in Table 1. Varying the tail group for a given surface-binding functional group does not affect θ_0 . The surfactant molecule, although nonmagnetic by itself, influences the total magnetization of the magnetic nanocrystals by partially reestablishing the order of the surface spins that would disorder in the absence of the surfactants.¹⁵ Therefore, the dependence of θ_0 on the surfacebinding functional groups can be ascribed to the difference in the surfactant's capability to order the surface spins. The larger value of θ_0 for the carboxylic acid-passivated nanocrystals is also consistent with the carboxylic acid's particularly strong ability to restore the order in the surface spins due to its coordination character close to the lattice oxide.¹⁵

In principle, different surfactants can have different surface spin-orbit coupling or (and) vibronic coupling. Due to the relatively large surface to volume ratio of the nanocrystals of <10 nm, the differences in the surface can be seen in the experimentally measured overall spin-lattice relaxation rate.²⁹ Generally, as the strength of ligand field exerted on the magnetic ion becomes weaker, the effective spin-orbit coupling will become stronger and increase the spin-lattice relaxation rate.³⁰ Stronger vibronic coupling can increase the spin-lattice relaxation rate as well. According to the study on the Langmuir

adsorption isotherm of aliphatic alcohols and carboxylic acids to Fe₂O₃ surface from hydrocarbon solvent, carboxylic acids bind a bit more strongly than alcohols.²⁴ If one interprets the stronger binding as the stronger ligand field exerted to the metal ions on the surface, the slower recovery of $\Delta\theta/\theta_0$ in alcohol-passivated nanocrystals may seem in contradiction to the expectation based on the above argument. However, different surface coordination geometry (e.g., mixed bidentate 31,32 and monodentate binding of $-\mathrm{CO}_2^-$ vs monodentate binding of -OH) and possible differences in the surface grafting density and the vibronic coupling make the prediction of the effect of surfactants on spin-lattice relaxation difficult. Furthermore, whether the difference in the surface spin disorder can influence the spin-lattice relaxation rate is another issue that adds the complexity to the problem. Nevertheless, the data shown in Figure 2a clearly show that the surface-binding functional group can modify not only the static magnetization but also the rate of its relaxation in magnetic nanocrystals. Disentangling all the contributing factors determining the dynamics of spin-lattice relaxation in Fe₃O₄ nanocrystals passivated with different surfactants is beyond the scope of this study and will require further investigation.

The transient absorption (ΔOD) data shown in Figure 2b indicate that varying the surfactants also influences the dynamics of electronic relaxation. The transitions excited by the pump pulse and monitored by the probe pulse correspond to the intervalence charge transfer between Fe²⁺ and Fe³⁺ ions.³³ In such a case, the electronic relaxation occurring near the nanocrystal surface can be viewed as the photoinduced charge transfer process coupled to the nuclear motions of not only the lattice but also the surfactant molecules. Among the factors determining the rate of charge transfer, the vibrational organization energy associated with Fe-surfactant bonding is the most likely one that will vary with the nature of the surfacebinding functional group. It is interesting to note that ΔOD data show a grouping based on the surface-binding functional group similarly to $\Delta \theta / \theta_0$ data. Oleic acid and 4-(octyloxy)benzoic acid-passivated nanocrystals exhibit very similar decay dynamics of $\Delta \theta / \theta_0$. In the two alcohol-passivated nanocrystals, although both exhibit slower decay than the carboxylic acidpassivated nanocrystals, the difference in the dynamics is larger. This is possibly due to the additional spectroscopic process probed in octyloxypheol-passivated nanocrystals as evidenced in the extra absorption in the visible region of the absorption spectrum shown in Figure 1c. Because both spin-lattice relaxation and electronic relaxation of Fe₃O₄ nanocrystals are affected by the nature of the bonding (e.g., strength and coordination geometry) between metal ions and the functional group, the similar grouping of the dynamics in both $\Delta \theta / \theta_0$ and ΔOD may not be surprising.

Effect of Varying Solvent on Spin–Lattice Relaxation. To investigate the effect of varying the surrounding solvent medium on the dynamics of spin–lattice relaxation, we prepared two groups of Fe_3O_4 nanocrystal samples (7.5 nm in diameter). One group of the samples (group A) is the organic-soluble nanocrystals initially synthesized using oleic acid and oleylamine as the surfactants as described in the Experimental Section. Infrared spectroscopy confirmed the presence of carboxylate on the surface, but the presence of oleylamine was unclear.³⁴ Group A represents the nanocrystals passivated with surfactants with a long carbon chain forming a relatively thick layer and soluble in organic solvents. Chloro-



Figure 3. (a), (b) Transient Faraday rotation data of group A and B nanocrystals, respectively. (c), (d) Transient absorption data of group A and B nanocrystals, respectively.

form, iodopropane, cyclohexane, and 1-octadecene were chosen as the solvents, because they encompass the varying degrees of polarities and sizes with potentially different surface accessibility and surface-solvent interaction. For the second group (group B), tetramethylammonium hydroxide (TMAH) was used as the surfactant to disperse the nanocrystals in the mixtures of water and propanol in varying proportions. Group B represents the nanocrystals passivated with a thin surfactant layer allowing the surface more accessible to the solvent molecules. Short-chain carboxylic acids could not be used to prepare the nanocrystals with thin surfactant layer due to either nanocrystal chemical instability (e.g., dissolution by benzoic acid) or a higher tendency to aggregate. The UV-vis absorption spectra of the group A and B samples are nearly identical, as shown in Figure 1b, despite the large differences in the structure of the surfactant and solvent environment. The purpose of the comparison in these two groups of nanocrystals is to examine whether the solvent molecules can influence the spin-lattice relaxation, and how the structure of the surfactants affects the contribution of the solvent molecules to spin-lattice relaxation.

Parts a and b of Figure 3 show the transient Faraday rotation data $(\Delta\theta/\theta_0)$ of group A and B samples in various different solventss respectively. Parts c and d of Figure 3 are the corresponding transient absorption data. In Figure 3a, group A samples having thick passivation exhibit essentially the same dynamics in $\Delta\theta/\theta_0$ data. The slow-recovery component has the time constant of ~250 ps for all three samples indicating that the solvent does not affect the spin–lattice relaxation rate in group A samples. In a separate experiment, we made an additional comparison using iodopropane as the solvent. It has the highest dielectric constant ($\varepsilon = 7$) among the solvents used for group A samples and contains a heavier atom that can potentially have the stronger influence on the ligand field and spin–orbit coupling on the surface. In this comparison, due to the relatively low solubility of the oleic acid-passivated

nanocrystals in iodopropane, the comparison was made between octadecene and mixture of octadecene and iodopropane (15 and 26 vol % of iodopropane). The recovery of $\Delta \theta / \theta_0$ signal in different solvent mixtures exhibited no noticeable difference (see Supporting Information), also indicating the absence of the influence from the solvent on the spin-lattice relaxation in group A samples. ΔOD data shown in Figure 3c are only weakly dependent on the solvent. The average decay time of the Δ OD signal varies slightly in the range 61–53 ps. On the other hand, group B samples passivated with TMAH exhibit quite different behavior from group A samples in both $\Delta\theta/\theta_0$ and Δ OD data. In Figure 3b, the recovery of $\Delta\theta/\theta_0$ becomes significantly faster as the water content increases in the solvent. In 100% water, $\Delta \theta / \theta_0$ recovered nearly completely by 200 ps. The average decay time of the Δ OD signal also became shorter by 40% (61-39 ps) as the water content increased from 4 to 50%.

We ascribe the observed difference in the effect of the solvent on the spin-lattice relaxation in group A and B samples mainly to the difference in the accessibility and affinity of the solvent molecules to the surface of the nanocrystals. For the solvent molecules to influence the spin-lattice relaxation, they should be sufficiently close to the magnetic ions on the surface to affect the surface spin-orbit coupling or (and) vibronic coupling. Because the oleyl group forms relatively well-passivating and thick surface layer, the penetration of the solvent molecules through the surfactant layer to the nanocrystal surface could be restricted for all the solvent molecules. In that case, varying the solvent in group A samples will not change the surface coordination environment, therefore having little influence on the spin-lattice relaxation rate.

In group B samples, on the other hand, OH⁻ ions coordinate to the metal ions and tetramethylammonium cations form the outer layer.³⁵ Due to the relatively thin passivation layer formed by TMAH, solvent molecules may access the surface of the

The Journal of Physical Chemistry B

nanocrystals more readily in contrast to group A samples. The stronger dependence of the decay of ΔOD signal in group B compared to group A samples also corroborates the easier access of solvent molecules to TMAH-passivated surface. On the clean Fe_3O_4 surface exposed to the water vapor, dissociative chemisorption of water molecules into OH⁻ and H⁺ occurs favorably during the initial phase of water adsorption followed by physisorption of water molecules at the higher coverage.³⁶ Because the surface of TMAH-passivated Fe₃O₄ nanocrystals is already sufficiently coordinated with OH-, water molecules will likely physisorb on the surface. The enthalpy of desorption of physisorbed water molecules on the epitaxial Fe₃O₄ surface is $\Delta H_{des} = \sim 50 \text{ kJ/mol}$, which is larger than the enthalpy of vaporization of water ($\Delta H_{vap} = 44.0 \text{ kJ/mol}$).^{37,38} Although ΔG of physisorption of a water molecule from the liquid water in the solvent to Fe₃O₄ surface is not available, the larger $\Delta H_{\rm des}$ than $\Delta H_{\rm vap}$ suggests that physisorption of water molecules can be favorable despite the strong hydrogen bonding present in bulk water. Because propanol and water have the same surfacebinding functional group and similar ΔH_{vap} (ΔH_{vap} for propanol = 47.5 kJ/mol), it is reasonable to expect that propanol will adsorb similarly to water.³⁸ However, the overall capability to modify the surface coordination environment will vary depending on ΔG of adsorption and the accessibility of the solvent to the surface, which will be manifested as the difference in the solvent's effect on the spin-lattice relaxation rate. Therefore, one may view the solvent-dependent dynamics of spin-lattice relaxation observed in group B samples from the perspective of the surface adsorption of different solvent molecules.

As the water content in the solvent mixture increases in group B samples, $\Delta \theta / \theta_0$ recovers more quickly, as shown in Figure 3b, indicating enhanced spin-lattice relaxation with increasing water content. Potentially more active adsorption/ desorption equilibrium of weakly bound water molecules compared to OH⁻ may have contributed to the enhanced spin-lattice relaxation, because the fluctuation of the ligand field on the magnetic ion causes the spin-lattice relaxation.³ Compared to water, the propanol molecule is larger in size and its self-diffusion coefficient is ~4 times smaller.40 This may impose a higher barrier for propanol molecule's access to the surface of the nanocrystals and lead to the slower fluctuation of the ligand field from the solvent molecules at the surface. In such a case, the slower recovery of $\Delta \theta / \theta_0$ with the lower water content in the solvent may be ascribed to the propanol's poorer capability to access the surface and dynamically disturb the ligand field on the metal ions than water.

CONCLUSIONS

The effect of varying the surface-passivating surfactants and solvent environment on spin–lattice relaxation of the optically excited Fe_3O_4 nanocrystals has been investigated through the transient Faraday rotation measurement. The passivation of the nanocrystal surface with surfactants having different surface-binding functional groups (carboxylate vs hydroxyl group) resulted in different spin–lattice relaxation rates, whereas the variation of tail group had no influence. The dependence of the spin–lattice relaxation on the surfactants is due to the differences in the metal–surfactant coordination strength and structure that affect the surface spin–orbit coupling or (and) vibronic coupling. The effect of varying the solvent environment for a given surface-passivating surfactant depends on the accessibility of the solvent molecules through the surfactant

layer. The nanocrystals with thick and well-passivating layers experienced no effect of varying the solvent molecules of varying size and polarity. For the nanocrystals with thin and more permeable surfactant layer, such as TMAH, spin–lattice relaxation rate changed with the variation of the solvent composition.

ASSOCIATED CONTENT

S Supporting Information

TEM images of iron oxide with different surfactants. Transient Faraday rotation and transient absorption of iron oxide in the presence of iodopropane in 1-octadecene. Absorption spectra of iron oxide. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: dhson@mail.chem.tamu.edu. Phone: 979-458-2990.

Present Addresses

[†]Department of Chemistry and Chemical Biology, Cornell University, Ithaca, NY 14853.

[‡]Department of Chemistry, Princeton University, Princeton, NJ 08544.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by NSF CAREER (DMR-0845645). We thank Microscopy and Imaging Center of TAMU for TEM measurements. D.H.S. dedicates this paper to Paul F. Barbara who has been an inspiring scientist and mentor.

REFERENCES

(1) Kamat, P. V. Acc. Chem. Res., DOI: 10.1021/ar200315d.

(2) Nozik, A. J.; Beard, M. C.; Luther, J. M.; Law, M.; Ellingson, R. J.; Johnson, J. C. *Chem. Rev.* **2010**, *110*, 6873–6890.

(3) Wu, K.; Zhu, H.; Liu, Z.; Rodríguez-Córdoba, W.; Lian, T. J. Am. Chem. Soc. 2012, 134, 10337–10340.

(4) Guyot-Sionnest, P.; Wehrenberg, B.; Yu, D. J. Chem. Phys. 2005, 123, 074709-074707.

(5) Hyun, B.-R.; Bartnik, A. C.; Lee, J.-K.; Imoto, H.; Sun, L.; Choi, J. J.; Chujo, Y.; Hanrath, T.; Ober, C. K.; Wise, F. W. *Nano Lett.* **2009**, *10*, 318–323.

(6) Losego, M. D.; Grady, M. E.; Sottos, N. R.; Cahill, D. G.; Braun, P. V. Nat. Mater. **2012**, *11*, 502–506.

(7) Link, S.; Furube, A.; Mohamed, M. B.; Asahi, T.; Masuhara, H.; El-Sayed, M. A. J. Phys. Chem. B **2002**, 106, 945–955.

(8) Hartland, G. V. Chem. Rev. 2011, 111, 3858-3887.

(9) Knowles, K. E.; Frederick, M. T.; Tice, D. B.; Morris-Cohen, A.

J.; Weiss, E. A. J. Phys. Chem. Lett. 2012, 3, 18-26.

(10) Pandey, A.; Guyot-Sionnest, P. Science 2008, 322, 929–932.

(11) Kambhampati, P. J. Phys. Chem. C 2011, 115, 22089-22109.

(12) Klimov, V. I.; Mikhailovsky, A. A.; McBranch, D. W.; Leatherdale, C. A.; Bawendi, M. G. *Phys. Rev. B* **2000**, *61*, R13349– R13352.

(13) Yang, Y.; Rodríguez-Córdoba, W.; Lian, T. J. Am. Chem. Soc. 2011, 133, 9246-9249.

(14) Boulesbaa, A.; Huang, Z.; Wu, D.; Lian, T. J. Phys. Chem. C 2009, 114, 962–969.

(15) Salafranca, J.; Gazquez, J.; Pérez, N.; Labarta, A.; Pantelides, S. T.; Pennycook, S. J.; Batlle, X.; Varela, M. *Nano Lett.* **2012**, *12*, 2499–2503.

(16) Guardia, P.; Batlle-Brugal, B.; Roca, A. G.; Iglesias, O.; Morales, M. P.; Serna, C. J.; Labarta, A.; Batlle, X. *J. Magn. Magn. Mater.* **2007**, *316*, e756–e759.

The Journal of Physical Chemistry B

(17) Vestal, C. R.; Zhang, Z. J. J. Am. Chem. Soc. 2003, 125, 9828– 9833.

- (18) Chen, T.-Y.; Hsia, C.-H.; Chen, H.-Y.; Son, D. H. J. Phys. Chem. C 2010, 114, 9713–9719.
- (19) Sun, S.; Zeng, H. J. Am. Chem. Soc. 2002, 124, 8204-8205.
- (20) Hsia, C.-H.; Chen, T.-Y.; Son, D. H. Nano Lett. 2008, 8, 571–576.
- (21) Jia, S.; Hsia, C.-H.; Son, D. H. J. Phys. Chem. C 2011, 115, 92–96.
- (22) Chen, T.-Y.; Hsia, C.-H.; Son, D. H. J. Phys. Chem. C 2008, 112, 10125-10129.
- (23) Vestal, C. R.; Song, Q.; Zhang, Z. J. J. Phys. Chem. B 2004, 108, 18222–18227.
- (24) Bellobono, I. R.; Selli, E.; Righetto, L.; Muffato, F.; Ermondi, C. Mater. Chem. Phys. **1989**, 21, 155-167.
- (25) The absence of aggregation was confirmed from the inspection of TEM images showing various different areas on the grid. Typical TEM images of the nanocrystals are shown in the Supporting Information.
- (26) Chen, J.; Dong, A.; Cai, J.; Ye, X.; Kang, Y.; Kikkawa, J. M.; Murray, C. B. *Nano Lett.* **2010**, *10*, 5103–5108.
- (27) Mayilmurugan, R.; Visvaganesan, K.; Suresh, E.; Palaniandavar, M. Inorg. Chem. 2009, 48, 8771–8783.
- (28) Tang, J.; Myers, M.; Bosnick, K. A.; Brus, L. E. J. Phys. Chem. B 2003, 107, 7501-7506.
- (29) Hsia, C.-H.; Chen, T.-Y.; Son, D. H. J. Am. Chem. Soc. 2009, 131, 9146-9147.
- (30) Stöhr, J.; Siegmann, H. C. In Magnetism: From Fundamentals to Nanoscale Dynamics; Springer: Berlin, Germany, 2006.
- (31) Polito, L.; Colombo, M.; Monti, D.; Melato, S.; Caneva, E.; Prosperi, D. J. Am. Chem. Soc. 2008, 130, 12712–12724.
- (32) Zhang, L.; He, R.; Gu, H.-C. Appl. Surf. Sci. 2006, 253, 2611–2617.
- (33) He, Y. P.; Miao, Y. M.; Li, C. R.; Wang, S. Q.; Cao, L.; Xie, S. S.;
- Yang, G. Z.; Zou, B. S.; Burda, C. Phys. Rev. B 2005, 71, 125411.
 (34) Klokkenburg, M.; Hilhorst, J.; Erné, B. H. Vibr. Spectrosc. 2007, 43, 243–248.
- (35) Cheng, F.-Y.; Su, C.-H.; Yang, Y.-S.; Yeh, C.-S.; Tsai, C.-Y.; Wu,
- C.-L.; Wu, M.-T.; Shieh, D.-B. Biomaterials 2005, 26, 729-738.
- (36) Tombácz, E.; Hajdú, A.; Illés, E.; László, K.; Garberoglio, G.; Jedlovszky, P. *Langmuir* **2009**, *25*, 13007–13014.
- (37) Joseph, Y.; Kuhrs, C.; Ranke, W.; Weiss, W. Surf. Sci. 1999, 433-435, 114-118.
- (38) Section 6. Enthalpy of Vaporization; CRC Handbook of Chemistry and Physics, 92nd ed.; Taylor & Francis Group: Boca Raton, FL, 2012.
- (39) Shrivastava, K. N. Phys. Status Solidi B 1983, 117, 437-458.
- (40) Pratt, K. C.; Wakeham, W. A. J. Chem. Soc., Faraday Trans. 2 1977, 73, 997–1002.