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Spectroscopic Characterization of the Surface of Iron Oxide Nanocrystals

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The surface of highly monodisperse magnetic iron oxide (γ-Fe_2O_3) nanocrystals was thoroughly investigated by FTIR, NMR, and mass spectroscopy. The nanocrystals were prepared by a thermal decomposition method now widely used for the preparation of magnetic metal and metal oxide nanocrystals. This method takes advantage of oleic acid as a means to passivate the surface and render the particles stable with respect to aggregation or grain growth and keeps them highly dispersed in a variety of organic media. The nature of this surface in terms of ligand structure and the role of oleic acid during the synthesis remained somewhat undetermined until this report. We provide spectroscopic evidence of an oleic acid ligand structural change during γ-Fe_2O_3 nanocrystal synthesis.

Introduction

Magnetic nanocrystals have attracted much interest recently because of their unique size-dependent properties, which are not observed in the molecular or bulk phases.[1−6] The size dependent properties and biocompatibility of these magnetic nanocrystals have potential for many biological applications such as magnetic resonance imaging (MRI),[7] DNA detection,[8] and drug delivery.[9] Iron oxide nanocrystals are of particular interest for applications such as MRI and cell separation because of their unique magnetic properties and biocompatibility. Because of the emerging applications of nanocrystals, it is of importance to gain a full understanding of the structure, both in terms of the inorganic core and organic capping shell, to develop an accurate and universal description of the system.

Nanocrystals are isolated three-dimensional nanometer scale units of materials, typically with symmetrical spherical or geometrical morphology and optimally a well-formed crystalline core. The concepts of surface capping and solution stabilization have been developed to allow suspensions of nanoparticles to exist as solutions in a variety of aqueous[10] and nonaqueous (organic solvent) media. The recent history of organometallic precursor-based synthesis has evolved because it proved very successful in the preparation of nanoparticles stabilized with a capping group. This type of procedure is best illustrated by the cadmium selenide system first conceived by Brus, Steigerwald, and co-workers and later developed by Murray et al.[1] and Trindade et al.[11] The nanoparticles resulting from these procedures are stable in nonpolar solvents (such as hexane) and have nonpolar capping groups. These methods are distinct from sol−gel chemistry and other more traditional methods of producing colloids as discerned by the nature of the product. The capping groups (also called ligands because they bind to the surface of the nanocrystal) are typically long-chain alkyl surfactants with heteroatom or polar headgroups that react with and bind to the nanocrystal surface via covalent, electrostatic, or coordination bonds (or some combination of all three), generally to the metal atoms. The lability of the surface ligand (ease with which it can be exchanged) depends on the strength of the binding interaction.

The nanoparticles remain highly stabilized in solution because they have a surface that is mutually unreactive and repulsive toward other particles. This can be considered as steric stabilization.[12] During the solvent evaporation process, self-assembly of the nanocrystals can readily occur into ordered regions and ultimately self-assembled superlattices. During preparation of nanoparticle dispersions, use of organic ligands is critical in order to obtain stable, well-dispersed

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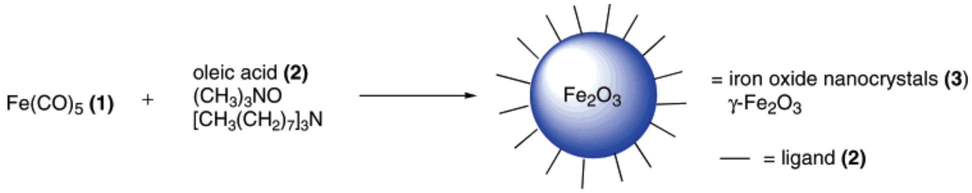
Scheme 1. Preparation of γ-Fe_2O_3 Nanocrystals



solutions. Long-chain fatty acids are widely used in metal oxide nanocrystal syntheses because they can form a dense protective monolayer by adsorbing to the nanocrystal surface through bonding of the carboxylic acid group to the metal oxide surface.[13] Oleic acid $[CH_3(CH_2)_7CH{=}CH(CH_2)_7$-COOH], which possesses a double bond at the 9,10 position, is a widely used ligand for passivation of iron oxide nanocrystal surfaces because it produces nanocrystals that are highly uniform and monodisperse. Other ligands such as long-chain fatty acids, alkylamines, and diols are also commonly used ligands for iron oxides.

The chemistry of nanocrystal surface ligands has been of interest for over 20 years; however, it has been difficult to study because the commonly used ligands (oleic acid, TOPO) are difficult to remove and replace. Although oleic acid is frequently used as a capping group for iron oxide nanocrystals, few studies have examined and characterized the oleic acid/nanocrystal interface. Other ligands that are similar to oleic acid (such as stearic acid, octadecanol, or methyl oleate) are not reportedly used as ligands in the preparation of iron oxide nanocrystals, which suggests that they do not produce nanocrystals of comparable quality to oleic acid. In this study, we sought to characterize this interface in an attempt to shed light on why fatty acids give rise to such uniform, monodisperse iron oxide nanocrystals.

Experimental Section

Fe_2O_3 Nanocrystal Synthesis. Monodisperse iron oxide nanocrystals (γ-Fe_2O_3) were prepared following a standard literature procedure pioneered by Hyeon et al.[14] Trioctylamine (14 mL, 32 mmol) and oleic acid (2 mL, 6.3 mmol) were combined under a N_2 atmosphere and heated at 180 for 1 h. The temperature was lowered to 100 °C, and $Fe(CO)_5$ (0.4 mL, 3.0 mmol) was added to the solution and heated at 350 °C for 1 h. During this process, the color of the solution changed from orange to black. After 1 h the temperature was lowered to 70 °C, and $(CH_3)_3NO$ (0.68 g, 9.12 mmol) was added to the solution and heated at 130 °C for 2 h, followed by refluxing at 350 °C for 1 h. The solution was cooled to room temperature, dissolved in hexanes, and centrifuged to precipitate the largest particles. The supernatant was washed with ethanol and centrifuged. The precipitated particles were redispersed in hexanes. The diameter of the nanocrystals was 11 nm with 5% (rms) polydispersity and was characterized by TEM, with structure confirmed by X-ray diffraction (Scintag X2), ^1H and ^{13}C NMR, FTIR, and XPS. Images of the particles were taken on a JEOL cx100 transmission electron microscope (TEM) in bright field (BF) mode at 100 kV. Samples were prepared by drying solvent dispersions of the nanoparticles onto Formvar amorphous carbon backed 400 mesh grids and then drying under vacuum at RT. FTIR experiments were performed on a Nicolet 8700 fitted with a DRIFT Smart collector. NMR experiments were preformed on a Bruker 400 MHz spectrometer at RT. The locking solvent was $CDCl_3$. GC−MS was conducted with a Varian Saturn 2100. The XPS experiment was performed on PHI 5500 model spectrometer equipped with an Al Kα monochromator X-ray source running at 15 kV, a hemispherical electron energy analyzer, and a multichannel detector. The test chamber pressure was maintained below 2×10^{-9} Torr during spectral acquisition. A low-energy electron flood gun was used to neutralize the possible surface charge. The XPS binding energy (BE) was internally referenced to the aliphatic C(1s) peak (BE, 284.6 eV).

Results and Discussion

Highly crystalline and monodisperse nanocrystals of magnetic iron oxide (γ-Fe_2O_3) were synthesized according to the procedure outlined in Scheme 1. Scheme 1 also illustrates that the nanocrystals produced possess a ligand shell around the inorganic iron oxide core. This ligand shell is one monolayer of organic molecules, calculated from TEM, spectroscopy, and previous literature.[14] The starting material for the preparation of the ligand shell is oleic acid. The ligand existing in the product shell is denoted **2**.

The synthesis of γ-Fe_2O_3 nanocrystals involves heating at temperatures as high as 350 °C.[14] The heating of fatty acids can cause isomerization and loss of unsaturation.[15−18] Indeed, it was recently claimed that oleic acid “polymerizes” when tethered to a calcite surface and heated.[19] Wu et al. also recently reported on their surfactant characterization for Co nanoparticles synthesized with oleic acid capping groups.[20] Thus, there is a concern that the oleic acid might suffer a structural change during synthesis. In this study, we employed TEM, ^1H and ^{13}C NMR spectroscopy as well as FTIR, high-resolution mass spectroscopy (HRMS), elemental analysis,[21] and X-ray photoelectron spectroscopy (XPS) to monitor

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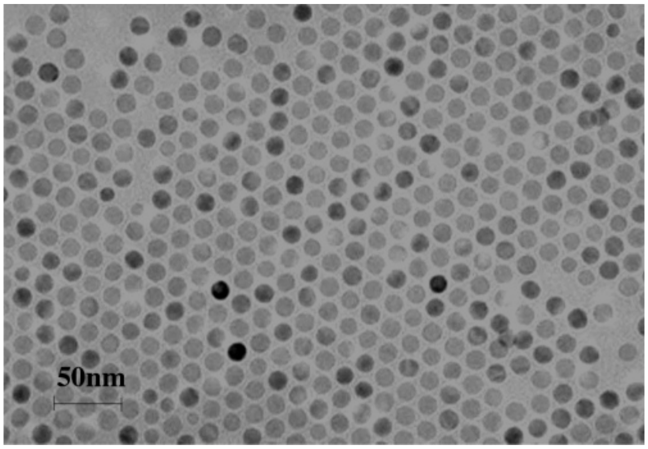

Figure 1. TEM image of 13 nm Fe_2O_3 nanocrystals prepared as described herein.

the chemical structure of the surfactant changes of the ligand during nanocrystal synthesis. This report suggests that the loss of unsaturation of oleic acid on an iron oxide nanocrystal surface occurs during nanocrystal synthesis.

TEM. Transmission electron micrographs of γ-Fe_2O_3 nanocrystals (Figure 1), synthesized with oleic acid as a surfactant, showed well-formed, monodisperse, spherical nanocrystals that assemble when deposited onto a TEM grid. They are surrounded by an organic surfactant layer, which separates them from each other and prevents aggregation. The interparticle separation is approximately commensurate with two interdigitated layers of surfactant molecules of comparable length to oleic acid (23.0 Å).

NMR. NMR of nanocrystal surfactants has been used in the past to understand interactions at the nanocrystal−ligand interface and to characterize the topography of the surface of *diamagnetic* nanocrystals.[22−27] However, study of ligands on paramagnetic materials by ^1H NMR has been difficult due to large broadening effects caused by the paramagnetic materials, and we were interested to find relatively sharp NMR resonances. To the best of our knowledge, we report here for the first time the ^1H NMR spectrum of a ligand bound to a *paramagnetic* nanocrystal and also a change in chemical structure of a ligand, putatively oleic acid, during nanocrystal synthesis.

Figure 2 compares the ^1H NMR spectra of free oleic acid (A), the ligand on the Fe_2O_3 nanocrystals (B), and surfactant removed from nanocrystal surface (C). Iron, being paramagnetic. is known to broaden the resonances in ^1H NMR spectra.[28] Thus, the sharp resonances were unexpected in the ^1H NMR of surfactant bound to γ-Fe_2O_3 nanocrystals, as shown in Figure 2, spectrum B.

The ^1H NMR of Fe_2O_3 (Figure 2B) is different than that of pure oleic acid (Figure 2A). In particular, in Figure 2B there is a lack of vinyl and allyl proton resonances, which appear at 5.5 and 2.0 ppm in the spectrum of pure oleic acid. The absence of the allyl and vinyl peaks suggests the reduction of the oleic acid double bond during nanocrystal synthesis. The ligand was removed from the nanocrystal surface by washing the nanocrystal hexane dispersion with an equal volume of EtOH several times. The surfactant was subsequently characterized by ^1H NMR and FTIR, which also proved that the removed ligand was no longer oleic acid.

The ^1H NMR of the material stripped from the nanoparticle surface (**2**, Figure 2C) also shows an absence of the allylic and vinylic resonances present in the oleic acid ^1H NMR. When elaidic acid, the trans isomer of oleic acid, is used as a surfactant in the synthesis of γ-Fe_2O_3, the allylic and vinylic resonances are also absent in the ^1H NMR of the surfactant-capped nanocrystals, indicating that the configuration about the double bond is not important in this transformation.

IR. The DRIFT IR spectrum of the synthesized γ-Fe_2O_3 (**3**) is shown in Figure 4, spectrum A. A weak vinyl C−H stretch located at 3003 cm^{-1} indicates that some oleic acid is still present on the nanocrystal surface. Two very weak carbonyl stretches are present at 1738 and 1710 cm^{-1}, which confirm the existence of a mixture of ligand components. The weak carbonyl stretch at 1710 cm^{-1} is assigned to the free oleic acid carbonyl. The presence of the very weak vinyl and carbonyl peaks at 3003 and 1710 cm^{-1} suggest the presence of trace amounts of free oleic acid. While this conflicts with the NMR observations, the lack of evidence of oleic acid in the NMR spectra could be due to the lower sensitivity of NMR as an analytical method. The broad peaks in spectrum A at 1527 and 1430 cm^{-1} can be assigned to a carboxylate (COO^-) stretch. Overall, the broad appearance of the peaks in this spectrum further suggests the presence of a mixture of compounds on the nanocrystal surface. Spectrum B in Figure 4 represents the DRIFT IR of the surfactant stripped from the nanocrystal surface. Similar to spectrum A, the peaks are broadened and suggest a mixture of compounds. There is no evidence of a vinyl C−H stretch, similar to the IR of γ-Fe_2O_3 nanocrystals; however, there is a significant carbonyl stretch centered at 1710 cm^{-1} that is slightly broadened and may suggest a mixture of ligands on the surface. The very broad feature from 3500 to 2500 cm^{-1} in spectrum C is assigned to a very broad O−H stretch; it is quite typical of carboxylic acids that dimerize due to strong hydrogen bonding.

XPS. Further characterization of the ligand-coated γ-Fe_2O_3 nanocrystals was performed with XPS, as shown in Figure 5. The C1s spectrum contains two peaks with binding energies of 284.8 and 287.9 eV. The peak at 284.8 eV is assigned to the carbons in the aliphatic chain, and the

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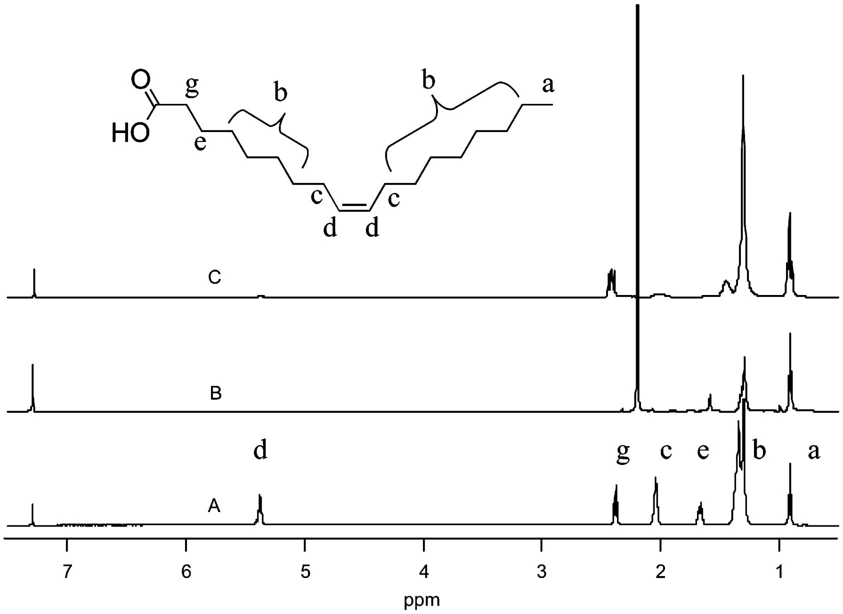

Figure 2. ^{1}H NMR of oleic acid (A), surfactant bound to Fe_2O_3 nanocrystals (B), and surfactant removed from Fe_2O_3 surface (C).

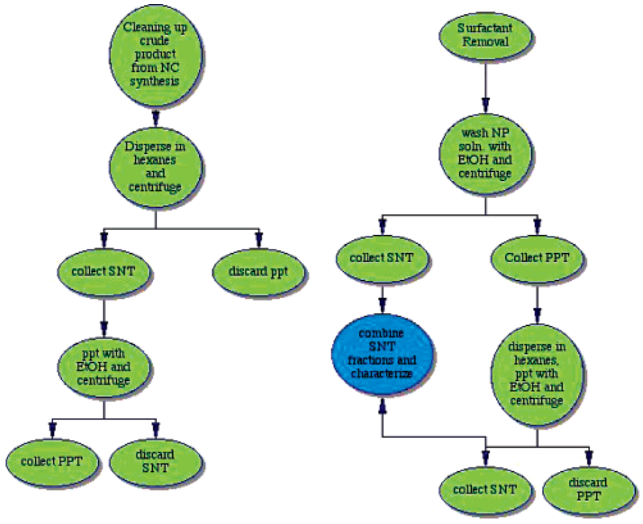

Figure 3. Flowcharts illustrating details of nanocrystal isolation, surfactant removal, component separation, and characterization.

shoulder peak at 287.9 eV is assigned to the carboxylate carbon, which are both in agreement with previous literature reports.[20,29−31] Neither of the peaks in the spectrum can be assigned to a carboxylic carbon, which demonstrates that there is no free oleic acid present on the iron oxide nanocrystal surface. The O1s core level spectrum has peaks with binding energies of 529.6 and 531.1 eV. The peak at 529.6 eV corresponds to the γ-Fe_2O_3 nanocrystals, while the peak at 531.1 eV is assigned to the carboxylate on the nanocrystal surface. From this we can conclude that the two oxygen atoms must be symmetric since there is no C═O peak present in the spectrum. The Fe(3p) spectrum has one peak with a maximum at 55.7 eV, and the Fe(2p) spectrum has peaks at 709.9 eV (Fe $2p_{3/2}$) and 723.5 eV (Fe $2p_{1/2}$). This is in agreement with previous XPS analysis of γ-Fe_2O_3 nanocrystals.[32]

Effect of Heating on Oleic Acid and Related Structures. It has been previously reported that long-chain fatty acids undergo loss of unsaturation when subjected to high temperatures.[15−18] We have observed that if oleic or elaidic acid is heated slowly to 350 °C, a similar loss of unsaturation is observed by ^{1}H NMR and FTIR. Aliquots of the acid were taken as heating progressed and analyzed by ^{1}H NMR and FTIR. We observed a loss of unsaturation to begin at approximately 290 °C, as evidenced in both the ^{1}H NMR and FTIR spectra.[33] Previous literature reports have found that the structure of oleic acid changes upon heating in excess of 300 °C; and long-chain monoolefinic C_{18} fatty acids are believed to dimerize and polymerize when heated above 300 °C.[19,34−36]

The significance of the carboxylic acid headgroup in facilitating uniform nucleation and growth of γ-Fe_2O_3 nanocrystals is clarified by substituting methyl oleate $[CH_3(CH_2)_7CH{=}CH(CH_2)_7COO(CH_3)]$ instead of oleic acid and maintaining all other conditions. The products observed by TEM from this reaction exhibit poor yield and high polydispersity. Since the aforementioned results confirm a loss of unsaturation in oleic and elaidic acid during nanocrystal synthesis, an attempt was made to synthesize γ-Fe_2O_3 nanocrystals with stearic acid $[CH_3(CH_2)\ 16COOH]$, the saturated analogue of oleic acid, and also with 1-octadecanol $[CH_3(CH_2)_{16}COH]$. In both cases the nanocrystals produced were of irregular shape and low monodispersity, which

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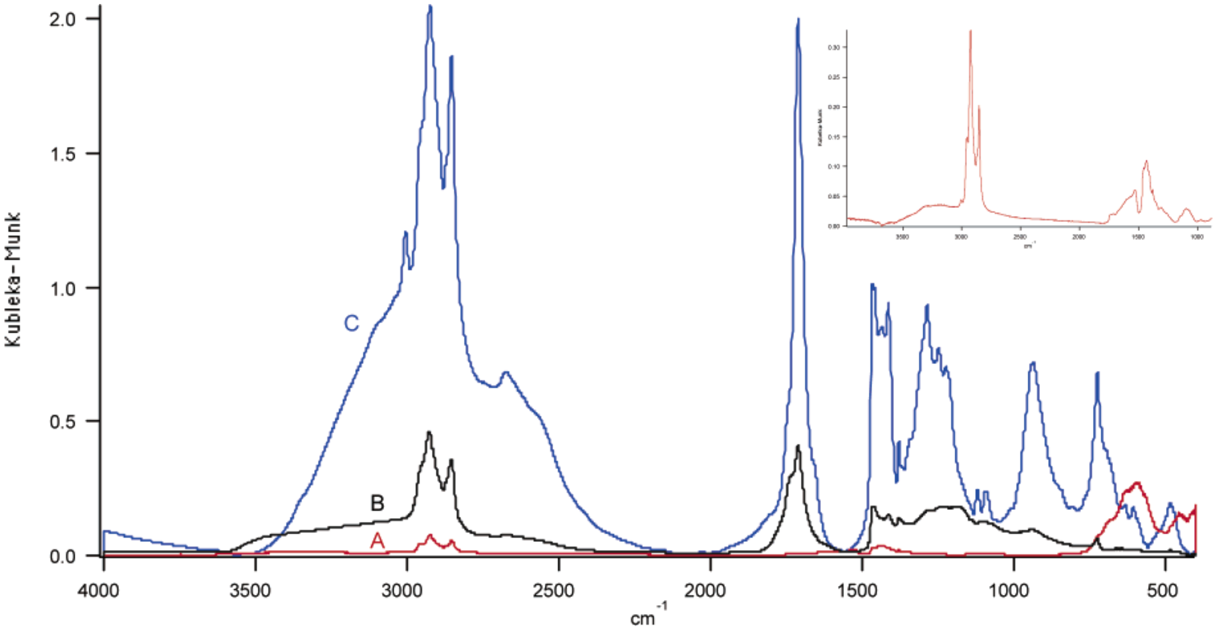

Figure 4. DRIFT IR of Fe_2O_3 nanocrystals (A), stripped surfactant (B), and oleic acid (C). Inset shows enlarged image of spectrum A.

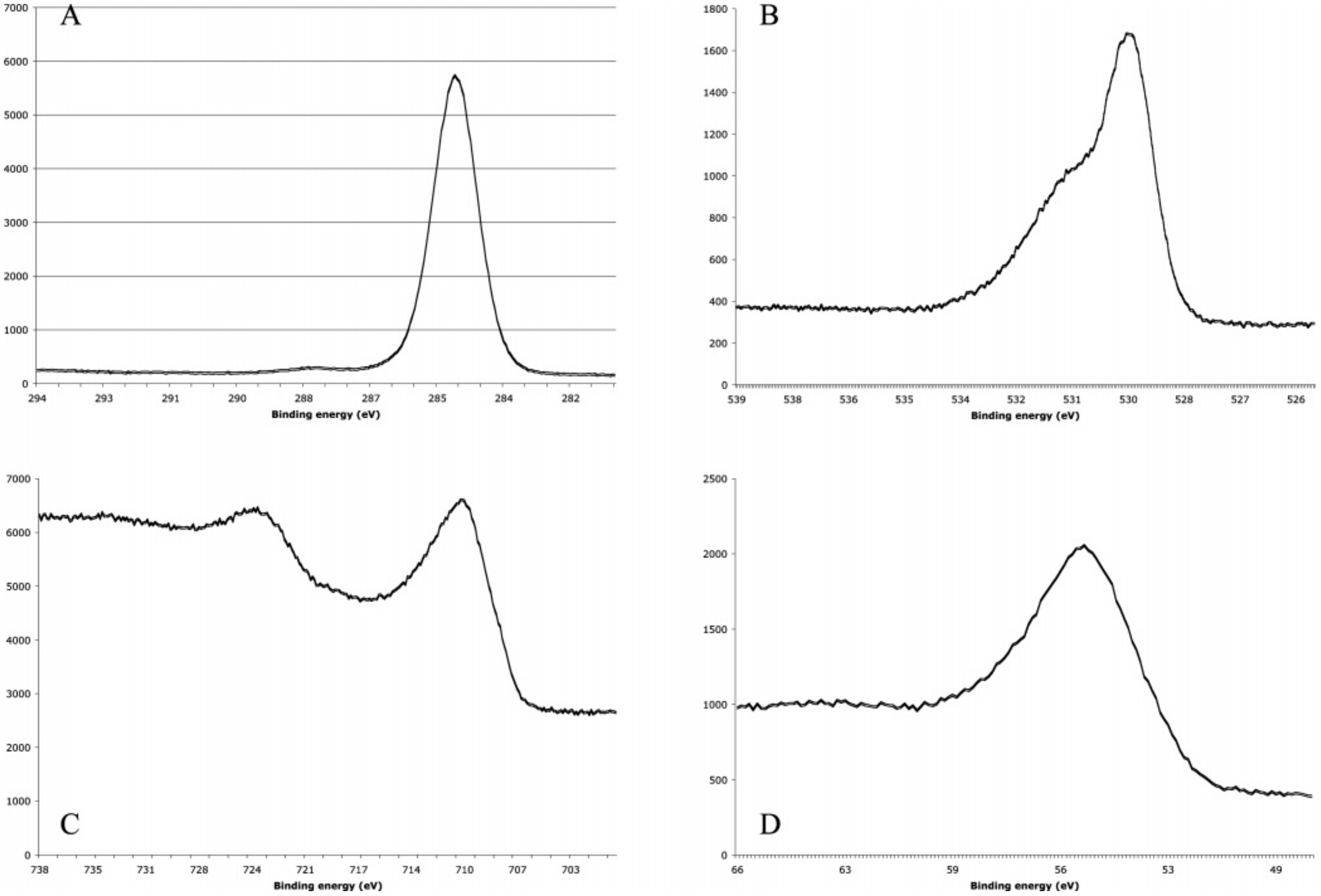

Figure 5. XPS characterization of ligand capped Fe_2O_3 nanocrystals: (A) C1s, (B) O1s, (C) Fe2p, and (D) Fe3p.

suggests that unsaturated bond must exert some kind of influence over the quality of nanocrystals produced, either due to the change in chemistry, structure, or solubility of the ligand. TEM images of γ-Fe_2O_3 nanocrystals synthesized with 1-octadecanol and stearic acid may be found in the Supporting Information. In a previous report,[37] shorter chain alkyl carboxylic acids were employed in the synthesis of iron oxide nanocrystals, and proved to be adequate. We conclude that the presence of the double bond is unlikely to have a strong effect on the chemistry preceding nucleation, although the carboxylic acid headgroup might. We observe that the presence of oleic acid is critical in the synthesis of stable, monodisperse iron oxide nanocrystals. The structure of the

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oleic acid is irreversibly changed during nanocrystal synthesis, and this is expected given previous studies of its thermal history. However, we note that the chemical transformation of this ligand is inextricably linked to the high quality of the nanocrystals produced.

Surfactant Removal and Characterization. The surfactant was removed from the γ-Fe_2O_3 nanocrystals by precipitating the nanocrystals with EtOH several times to isolate the surfactant as illustrated in Figure 3. Separation of the observed mixture into its constituents was attempted by column chromatography; however, the component R_f values appeared to be too similar to achieve isolation. The removed surfactant was further analyzed by electron impact mass spectroscopy (EIMS). The EIMS (spectrum in Supporting Information), similar to the FTIR, suggests the presence of multiple products. Although the molecular ion peak for oleic acid was not detected, the spectrum shows evidence of small quantities of an oleic acid dimer. Peaks at 376.5, 362.5, and 348.5 may correspond to fragments of the oleic acid dimer. These peaks are very weak, however, suggesting that there is only a small amount of dimer in the surfactant mixture. This hypothesis is also supported by the ^{1}H NMR and FTIR data, which show the presence of only trace quantities of unsaturated and carbonyl containing compounds. The spectrum also points toward the presence of stearic acid (MI^+ at 284.4, fragments at 270.4, 256.4). There is also evidence for the formation of a species possessing the composition of oleic acid plus an additional O atom. The formation of an epoxide at the 9,10 position on the oleic acid carbon chain would be consistent with this FW. There is evidence in the literature[30] that oleic acid can absorb oxygen to form an epoxide and destroy the double bond. In the spectrum the molecular ion of the epoxide appears at 298.4. Overall, the spectrum contains many peaks and few distinguishable patterns among them, which ultimately suggests a mixture of several compounds.

The removed surfactant was also analyzed by C, H, and O elemental analyses. The result of the analysis was a surfactant composed of 78.3% carbon, 14.13% hydrogen, and 5.62% oxygen. Oleic acid is 76.54% carbon, 12.13% hydrogen, and 11.33% oxygen. The experimental results do not confirm or identify the removed ligand as a single product. The results were compared to the theoretical ratios of potential products such as stearic acid, octadecanol, or a dimer of oleic acid, and none matched closely. These results also favor the hypothesis that the composition of the surfactant is a mixture.

FeO, Fe_3O_4, MnO, and Mn_3O_4 nanocrystals have also been studied with ^{1}H NMR, however not inasmuch depth as γ-Fe_2O_3. The preparation of all of these nanocrystals used oleic acid as a surfactant, and all have ^{1}H NMR spectra similar to that of the surfactant bound to γ-Fe_2O_3. Albeit preliminary, this result shows that this change in surfactant structure during nanocrystal synthesis is not unique to γ-Fe_2O_3 but is common to several metal oxide species.

Conclusions

We report the first example of a change in surfactant structure during nanocrystal synthesis. We have demonstrated that oleic acid is transformed during synthesis of γ-Fe_2O_3 nanocrystals. The NMR, FTIR, and MS results suggest the presence of a mixture of compounds. The results presented in this report suggest that the decomposition of oleic acid, which occurs at high temperature, promotes the formation of high-quality γ-Fe_2O_3 nanocrystals. This mixture of ligands that forms has the unusual ability to give rise to γ-Fe_2O_3 nanocrystals of higher monodispersity and uniformity than most other ligands. So far this transformation has only been observed on γ-Fe_2O_3 and other metal oxide nanoparticles that use oleic acid as a surfactant; however, it is possible that this phenomenon occurs when oleic acid is added as the surfactant in the synthesis of other types of nanoparticles.

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Supporting Information Available: Transmission electron micrograph of γ-Fe_2O_3 nanocrystals synthesized with stearic acid surfactant and with 1-octadecanol surfactant; EIMS of surfactant removed from surface of γ-Fe_2O_3 nanocrystals; ^{13}C NMR of oleic acid and surfactant stripped from Fe_2O_3 nanocrystals after purification by column chromatography; ^{1}H NMR of oleic acid and oleic acid after heating for 4.5 h; comparison of the integration values obtained from ^{1}H NMR spectra of aliquots taken from heating oleic acid slowly to 350 °C as they change with time and temperature; FTIR of oleic acid and aliquots taken during heating at 325 and 340 °C. This material is available free of charge via the Internet at http://pubs.acs.org.

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