

Use of Surfactant Micelles to Control the Structural Phase of Nanosize Iron Clusters

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We have synthesized iron nanoclusters using two chemical types of inverse micelle systems to control the growth process. Surprisingly, we have found that the phase of the resulting nanosize iron depends strongly on the chemical nature of the surfactant used during the growth of the clusters. For example, use of nonionic surfactant micelles for this room-temperature synthesis produces the normally-high-temperature γ -phase with a fcc structure as determined by selected area electron diffraction (SAD) and high-resolution lattice fringe images. Use of a cationic quaternary ammonium surfactant micelle system, on the other hand, produces the normal bcc α -iron phase as determined by SAD. This strong dependence of the structure of nanosize clusters on surfactant type may reflect different binding-site preferences for the chemically different surfactants during the growth stage of the cluster synthesis. This is analogous to the well-known role of surfactants as habit modifiers during macroscopic crystalline growth processes in solution, but is the first example of such control of structural phase during nanocluster synthesis.

Introduction

The properties of nanometer-sized magnetic particles of iron have been studied both experimentally and theoretically for more than sixty years.^{1–4} Interest in these materials has remained high because of their use in numerous practical applications in catalysis, magnetic recording, magnetic fluids, and permanent magnets. In addition, there are fundamental research questions concerning the development of long-range magnetic order and associated hysteric properties such as coercivity and remanence as the cluster size increases from a few atoms with all atoms at the surface to a large cluster with predominantly interior atoms. Cluster synthesis and experimental handling and processing play crucial roles in understanding the magnetic properties, particularly in separating the intrinsic properties from the effects of a surface layer^{5–8} (such as a thin oxide shell) or particle–particle interactions due to agglomeration.⁸ Also, the synthetic method used may influence the final structural phase of the clusters, which will have a major influence on the magnetic properties of the clusters. Here, we report studies on the phase of nanosize iron clusters prepared using inverse micelles as reaction vessels which yields monodisperse particles and, we believe, mitigates both surface layer and agglomeration effects. We show, using transmission electron microscopy, that not only are nanoparticles of iron synthesized at room temperature highly crystalline, but also that both the normal bcc α -Fe as well as the high-temperature fcc γ -Fe phase may be produced by altering the surfactant micelle used in the synthesis.

Experiment

Size-selected nanosize Fe clusters were grown by a process which is described in detail elsewhere.^{9–12} Controlled nucleation and growth of metal clusters occur in the interior of surfactant aggregates called inverse micelles. In our process an ionic salt (e.g., $\text{Fe}(\text{BF}_4)_2$ or anhydrous FeCl_3) is dissolved in the hydrophilic interior of the micelles, while the surrounding continuous

hydrophobic oil limits nucleation and growth to the micelle interior volume. We emphasize that the anhydrous salt is dissolved to form a transparent ionic solution but with a complete absence of water; in a sense, the salt is “hydrated” by the micelles. The absence of water allows extremely novel and aggressive chemistry to be used in the reduction and growth process, and prevents any formation of oxide or boride phases as is typically found in synthesis using microemulsions containing water or water itself.^{9,10} Encapsulation of the ionic salt solely in the micelle interior ensures spatial homogeneity during the nucleation process, while the growth kinetics are determined by the rate of reduction of the metal salt and the diffusion of the micelles themselves (not the Fe atoms)! In this sense our synthetic method for size-selected clusters is fundamentally different from other cluster growth processes which occur in a continuous medium (e.g., gas- or liquid-phase growth) which result in a power-law (i.e., log-normal) cluster size distribution.

Three conditions can be used to control the final cluster size: the micelle size, intermicellar interactions (e.g., proximity to phase boundaries which determine micelle diffusion rates), and reaction chemistry. Since the micelle size is determined by the chemical structure of the surfactant, and the chemical structure of the surfactant strongly affects its binding to the growing iron cluster, variation of the surfactant has the possibility of affecting the phase of the iron as well as changing the final cluster size. As we shall show, this phase variation actually occurs in the growth of iron clusters.

Size-selected iron metallic clusters with diameters between 1.4 and 15 nm were produced using our synthetic approach. UV–visible spectroscopy using a photodiode array combined with liquid chromatography was used to demonstrate 100% reduction of the $\text{Fe}(\text{II})$ to the final $\text{Fe}(\text{0})$ cluster form, and complete details of this characterization process will appear in a subsequent paper.¹¹ All reactions took place in anaerobic conditions in a Vacuum Atmospheres drybox with continuous oxygen and moisture removal and appropriate sensors. Typical oxygen levels were 0.1 to 1 ppm and moisture levels were 0.5 to 3 ppm in the drybox. All solvents and surfactants used were

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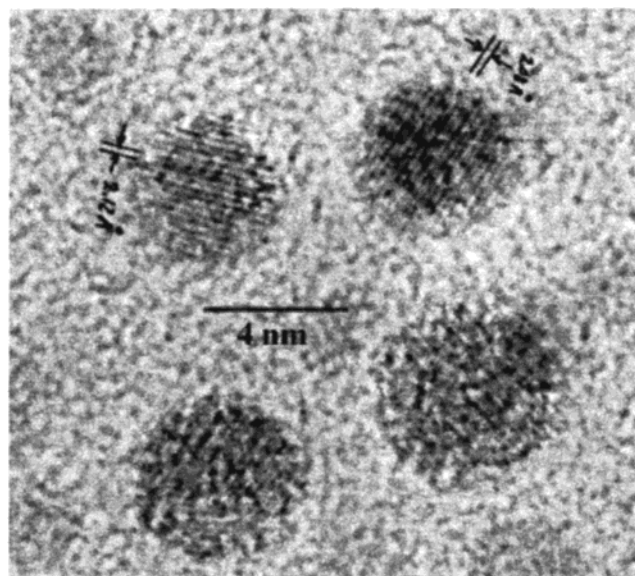


Figure 1. High-resolution transmission electron micrograph (HRTEM) of γ -Fe clusters with a typical size of 4.3 nm grown using a nonionic surfactant by the inverse micelle synthetic method.

TABLE 1: Predicted and Observed d Spacings from Figures 2 and 4

index	$d(\gamma\text{-Fe}), \text{bcc}$	$d(\alpha\text{-Fe}), \text{fcc}$	$d(\text{Figure 2})$	$d(\text{Figure 4})^a$
110	2.027	none	2.00	none
111	none	2.08	none	2.08
200	1.4332	1.80	1.41	1.78
211	1.1702	none	1.165	none
220	1.0134	1.27	1.01	1.26
310	.9064	none	.896	none
311	none	1.083	none	1.089
222	.8275	1.037		1.049
400	none	.90		.92

^a Includes data from wider angle (shorter sample-to-detector distances) than Figure 4.

HPLC grade and were completely dust free. The latter is critical to prevent inhomogeneous nucleation.

Results

Figure 1 shows a high-resolution transmission electron micrograph (HRTEM) of Fe clusters with a typical size of 4 nm produced by the inverse micelle synthetic method. To grow these clusters we employed a nonionic surfactant solution which consisted of 10 wt % C_{12}E_4 in octane. $\text{Fe}(\text{BF}_4)_2$ was dissolved at a concentration of 0.01 M in this solution and then reduced while stirring rapidly by using an excess of LiBH_4 in tetrahydrofuran (0.04 M final concentration). The nonionic surfactant was obtained from Nikko, Japan, and the other chemicals were from Aldrich. The HRTEM holey carbon grid was prepared by direct deposition of the clusters from the final octane solution. During this process, molecular oxygen in the air could conceivably oxidize the clusters, but in reality, no iron oxides were observed by selected area diffraction (SAD) from the TEM grid. Presumably the oil (octane) or surfactant at the cluster surface protects the clusters from oxidation while they are being transferred to the high vacuum of the electron microscope. From several measurements as shown in Figure 1 of fringe spacings we found $d(111) = 2.01 \pm 0.02 \text{ \AA}$, and Table 1 shows that SAD yields $d(111) = 2.00 \text{ \AA}$ which corresponds best to the spacing of $d(111) = 2.027 \text{ \AA}$ found for the γ -phase by XRD on synthetic bulk samples. By contrast, $d(110)$ is 2.08 \AA for bcc α -Fe bulk phase by XRD.

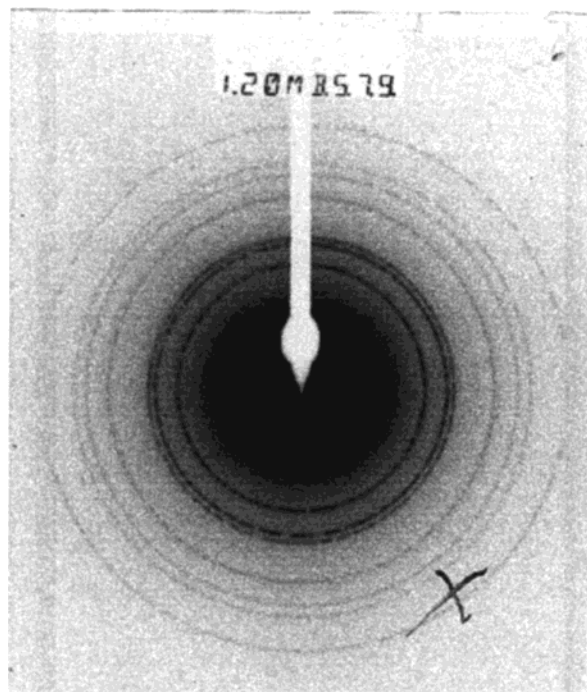


Figure 2. Diffraction pattern of the sample of Figure 1 shows the structure to be fcc, not bcc as expected for the normal equilibrium α -Fe phase found at room temperature.

To our surprise, SAD observations of this sample prepared using the nonionic surfactant C_{12}E_4 revealed the diffraction pattern shown in Figure 2. The spacing in this pattern shows the structure to be fcc, not bcc, as expected for the normal equilibrium α -Fe phase found at room temperature! Table 1 shows the observed and expected d spacings and the index corresponding to them derived from measurements of the ring diameters and using the known sample-to-detector distance and electron energy. It is clear that the Fe sample of Figures 1 and 2 is γ -Fe with lattice spacing closely matching that of bulk synthetic fcc γ -Fe. There was no evidence, as claimed by Martino et al.¹² in the case of a similar inverse micellar synthesis process for the formation of FeB, a product that requires the presence of water to form and is known to form in inverse microemulsion systems (i.e., systems containing water added deliberately to solubilize the salt). No B could be detected in the clusters by analytic TEM analysis.

Figure 3 shows a high-resolution transmission electron micrograph of α -Fe clusters with a typical size of 4.2 nm also produced by the inverse micelle synthetic method but using a cationic surfactant. Specifically, we employed a cationic surfactant solution which consisted of 10 wt % dodecyltrimethylammonium bromide (DTAB, Fluka) in octane containing 10 wt % hexanol as a cosurfactant. The identical metal salt, salt concentration, and reducing agent were used in this case, only the surfactant was altered. In Figure 4 we show SAD from this sample, which reveals the normal bcc bulk phase diffraction pattern and lattice parameters shown in Table 1.

In some earlier work,¹² use of a chemically similar cationic surfactant, DDAB (didodecyltrimethylammonium bromide) in toluene was claimed to yield α -Fe as determined by SAD, but the particles were only about 2 nm in diameter, much too small to yield SAD patterns because of line broadening effects. No HRTEM was shown in this earlier work, but after workup of the sample by methanol precipitation, an FeB phase was claimed to be observed by Mossbauer analysis. Because of the near impossibility of removing water and oxygen from methanol,

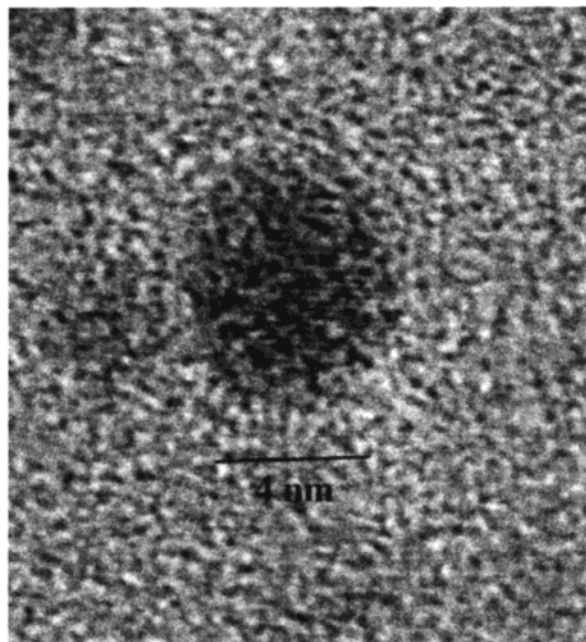


Figure 3. High-resolution transmission electron micrograph of α -Fe clusters with a typical size of 4.2 nm produced by the inverse micelle synthetic method using a cationic surfactant.

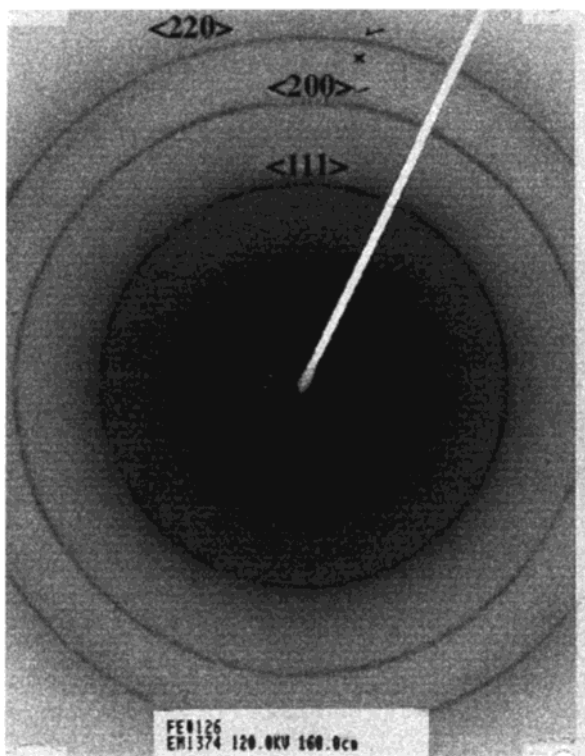


Figure 4. Selected area diffraction from the sample of Figure 3, showing the normal bcc bulk-phase diffraction pattern.

the authors claim that FeB was present in the original oxygen and water-free system is moot.

Though we cannot definitively rule out the possibility of a very thin oxide layer from the data of Figures 1–4, deliberate exposure of the samples to even small amounts of oxygen results in spectroscopic changes in the samples as well as changes in the liquid chromatographic elution behavior, a technique very sensitive to the surface properties of nanoclusters. Further details of this oxidation behavior will be given in a future paper in which we will also discuss the differences in the superpara-

magnetic behavior of both nanosize iron phases. At the present time, we strongly believe that due to the complete absence of oxygen and water during the synthesis, these samples do not even have even a thin oxide layer on their surface.

Discussion

Surfactants have been used to modify the growth rate and crystal habit of a variety of materials. An early publication by A. S. Michaels and A. R. Colville¹³ studied growth of adipic acid crystals in the presence and absence of small concentrations of cationic and anionic surfactants. Individual growth rates of the (001), (010), and (110) faces were studied. The anionic surfactant caused greater reduction in the growth rate of the (010) and (110) faces than the (001) face, while the cationic surfactants had the opposite effect. They found the influence of the surfactants was much greater on small crystals than on larger ones and, on the basis of this observation, they inferred that growth at dislocations is the dominant mechanism for large crystallites.

Later work by B. R. Smith and A. E. Alexander¹⁴ on the effect of surfactant additives on the process of crystallization of calcium sulfate found very similar effects. They showed that surface-active agents could act like mobile impurities and thus affect the step velocity and rate of crystal growth in certain preferred directions, which affected the final habit of the crystal.

Most recently, Naryanan and Sunbhaiyan¹⁵ showed that the use of cationic surfactants similar to those used in the present study affected the growth and crystal habit of zinc phosphate during electrochemical deposition. The adsorbed surfactants used were found to reduce the rate of grain growth resulting in finer-grained coatings with improved corrosion resistance.

At the present time there have been very few experimental reports of nonequilibrium crystal structures in nanosize particles—a recent example being nanocrystalline Co particles having the cubic symmetry of the β phase of manganese.¹⁶ In this latter work, a complex mixture of surfactants was also present during the synthesis and these surfactants were shown to bind quite strongly to the Co particle surface. Since very little is known concerning the exact mechanism of growth of particles in inverse micelle solutions, it is difficult to know whether the same mechanism which alters the crystal habit of macroscopic crystals is functioning to alter the final structure of our Fe nanocrystals. To learn about this mechanism would require monitoring the nanocrystal surface structure and surfactant binding position during the growth of the nanocrystals from atomic iron. This is an extremely challenging technical problem for growth in solution. Experimentally, we have not observed any deviations from the bulk structure of Ni and Co nanoclusters grown by the methods and surfactant systems described in this paper.

To gain an insight into the role of the surfactant chemical structure on the final structure of nanocrystalline iron, consider the growth process of nanocrystals in a microheterogeneous system such as the present inverse micelle solutions. The critical aspect of this process that differs from, for example, chemical reduction of iron ions in a continuous, polar organic solvent is that, in our process, the ionic iron ions are completely confined to the interior of the micelles, since there is absolutely zero solubility of the ions in the continuous, nonpolar oil phase. In fact, the iron ions may be coordinated to the surfactants in a complicated charge complex-like manner which is reflected in the different colors and corresponding absorbance spectra observed in the precursor solutions before chemical reduction. Various charge-transfer bands in the absorbance spectra shift in position and energy depending on whether Fe(II) ions are

interacting with the polyether chemical groups of the nonionic surfactant C₁₂E₄ (which has four polyether chemical groups and results in the unexpected γ -Fe nanocrystals), or with the single -NBr headgroup of the DDAB cationic surfactant. Also, both of these inverse micelle precursor solutions differ in absorbance characteristics from Fe(II) in water. In both cases, addition of the strong anhydrous reducing agent, LiBH₄, results in the yellow precursor solutions turning nearly clear instantly, indicative of the formation of fully reduced iron atoms, or small molecular iron clusters which scatter a negligible amount of light. The growth of the initial nuclei into larger clusters occurs by diffusion of the micelles containing these atoms and collisions which allow mass transfer between micelles. These larger clusters scatter more light, and so the clear solutions turn dark brown in less than 10 s. Because of the intimate interaction between surfactant headgroup(s) and the atomic clusters during this growth process, we have observed that the final structure depends on the chemical nature of the surfactant headgroup. Thus, we expect that this phenomenon will not be observed in nanocrystalline growth in continuous systems, either gas or liquid, which lack surface-active agents.

Conclusions

We have demonstrated that the chemical nature of the surfactant used to synthesize nanosize iron in inverse micelles can influence the crystalline phase of the nanoparticles. Specifically, we found that nonionic surfactants in the family C_iE_j produced the normally high-temperature fcc γ -Fe phase, while cationic surfactants of the quaternary ammonium variety produced nanoparticles with the typical bcc α -Fe phase. We speculate that the different binding characteristics of the two types of surfactants influence the growth rates of the small clusters in different crystallographic directions. This phenomenon is very analogous to the known role of surfactants as habit modifiers during the growth of large crystals. By varying both the micelle size used to grow the iron nanoparticles and the chemistry of the surfactant, it is now possible to vary both the size and phase of nanoparticles of iron.

A very interesting prospect expected from our ability to control both size and phase of nanosize iron is the alteration of

physical properties such as the magnetic response of the nanoclusters. Preliminary work by Eugene Venturini of our lab indicates significantly different magnetic susceptibility behaviors of similarly sized γ - and α -iron nanoclusters. We will be reporting on these results in the future.

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