Characterization of Core/Shell Nanoparticles by X-Ray Absorption Spectroscopy

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ABSTRACT

Nanoparticles with iron cores and oxide shells were prepared by a reverse micellar method in which a number of synthetic variables were investigated. X-ray absorption near edge structure (XANES) was used to determine that the fraction of oxide present was between 35 and 50% in most cases; this was consistent with TEM images. Extended x-ray absorption fine structure (EXAFS) was then used to determine the structure of the iron cores. Depending on the surfactant used in the synthesis, up to 50% of the cores were nanocrystalline bcc iron, with the remainder adopting an amorphous configuration based on a close-packed structure.

Keywords: XAS, EXAFS, XANES, nanoparticles, core/shell

1 INTRODUCTION

One current focus of nanoparticle research is the synthesis of spherically symmetric particles with one phase encompassing another: *core/shell* morphology. Sometimes the core is the functional phase with the shell providing protection or passivation. Nanoparticles made purely of iron metal, for example, oxidize almost immediately in air. By adding an oxide shell, it is possible to create air-stable particles. In other cases, the shell may be present to functionalize the particles. Magnetic nanoparticles have been proposed as a method for targeted drug delivery; the shell material would then be chosen to allow attachment of the desired pharmaceutical.

Various methods have been proposed for synthesizing particles of this type, but it is often difficult to ascertain whether the synthesis was successful. Many conventional methods of characterization, such as x-ray diffraction (XRD), become more difficult when the crystallite size is very small.

2 X-RAY ABSORPTION SPECTROSCOPY

In x-ray absorption spectroscopy (XAS), quasi-monochromatic x-rays are projected at the sample of interest and the absorption measured as a function of x-ray energy. When the x-ray energy exceeds the amount required to promote a core electron of one of the elements in the sample to an available state, the absorption jumps sharply (see Fig. 1). This energy is dependent on the element absorbing the x-ray; the sharp jump is referred to as an *edge*. The spectrum above the edge is conventionally divided into the x-ray absorption near edge structure (XANES) and the extended x-ray absorption fine structure (EXAFS), with the division often being arbitrarily assigned at 30 eV above the edge. Although the underlying physics for the features seen in the two regions is the same, in practice the interpretation is different. The relatively low-lying energy states of XANES frequently include bound states and thus XANES probes the valence, bonding, and symmetry of the local environment for the absorbing atom. EXAFS, on the other hand, arises primarily from the scattering of the photoelectron off of surrounding atoms out to a distance of nearly a nanometer (beyond that distance the process is not coherent enough to lead to measurable structure). Factors that contribute to EXAFS include the identity, coordination number, location, and disorder of the scattering atoms.

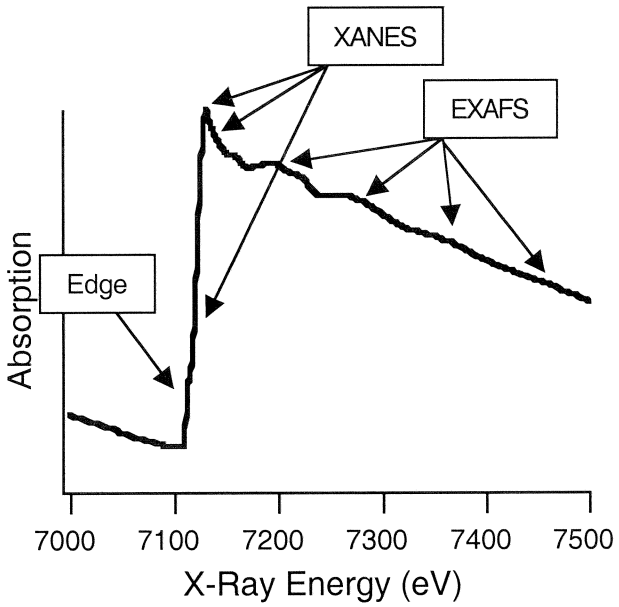

Figure 1: X-ray absorption spectrum of a sample with an iron core and an oxide shell.

Although EXAFS is dependent on nearly all features of interest in the local structure, the problem of extracting the information present in the spectrum is generally underdetermined. One common method is to calculate the spectrum of an arrangement of atoms thought to be similar to that of the sample (an *empirical standard*). Small variations in the structure are then made to try to fit the

standard to the data. If the resulting fit is poor, the model is not representative of the atomic arrangement within the sample. If the fit is good, however, the possibility remains that a completely different model might do as well or better. For example, the spectrum of a material with a small number of atoms in highly-ordered positions about the absorbing atom may look quite similar to the spectrum of a material with a larger number of more disordered atoms about the absorbing atom. Thus, although EXAFS can yield information that is difficult to obtain from other techniques, the results must always be interpreted with caution.

3 EXPERIMENTAL

3.1 Synthesis

For this experiment, core/shell particles were synthesized by the *reverse micellar* method [1]. When a small quantity of water is mixed with a hydrocarbon and a surfactant (a material with a hydrophobic and a hydrophilic end), micelles filled with water are formed. The size of the micelles is determined by the ratio of surfactant to water. In effect, this creates nanoreactors for reactions that take place in aqueous solution.

In our experiment, iron cores were formed by reduction of an iron salt using sodium borohydride. Water was then added to enlarge the micelles; the addition of a metal chloride along with more sodium borohydride resulted in a protective shell. Subsequent exposure to air caused partial oxidation, giving the desired core/shell structure. Synthetic variables that were investigated included the counterion in the initial iron salt, the surfactant, and the metal used in the second step.

3.2 Data Collection

X-ray absorption spectra were collected at beamline X11A of the National Synchrotron Light Source at Brookhaven National Laboratories. Synchrotron radiation is the preferred source for XAS because of its high intensity and broad spectrum. A schematic of the apparatus is shown in Fig. 2 (this is the usual *transmission* geometry).

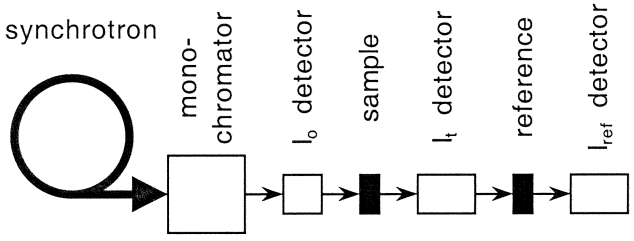

Figure 2: Schematic of transmission XAS experiment.

By comparing the intensity of the x-rays at the detectors, the absorption of the sample and the reference were simultaneously measured.

3.3 Supporting Probes

Initial yields of the procedure were often less than two milligrams, limiting the applicability of many characterization techniques (e.g. conventional XRD). Magnetic properties, as measured by a superconducting quantum interference device (SQUID), strongly suggested the presence of metallic iron. Transmission electron microscopy (TEM) was performed on some samples, confirming a core/shell morphology (Fig. 3, top). In some cases, the core/shell nanoparticles are found to have been cemented into larger grains about sixty nanometers across (Fig. 3, bottom). In both cases, the cores were found to be less than ten nanometers in diameter.

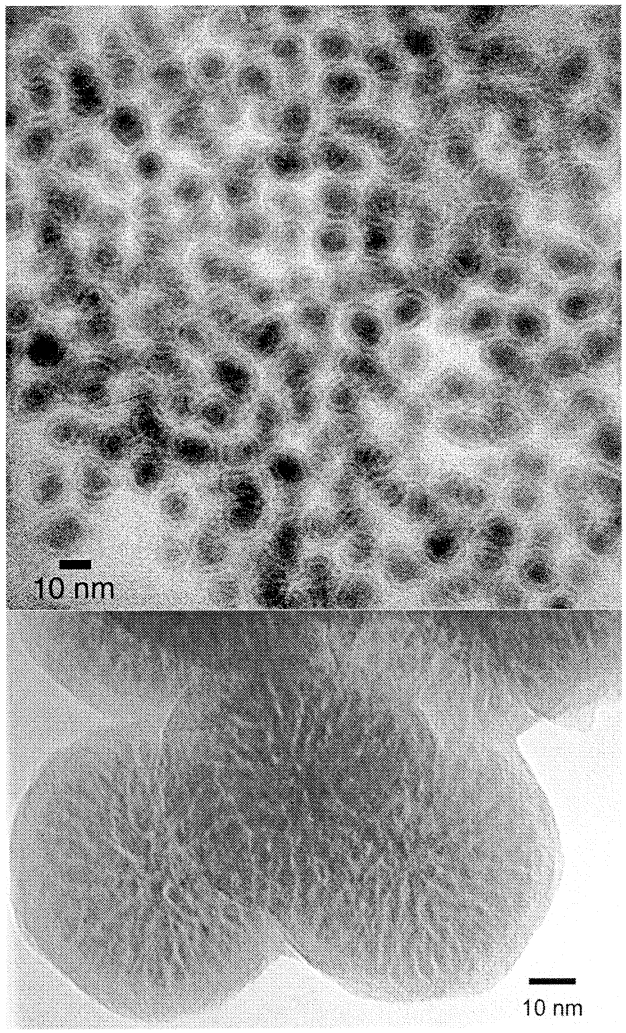

Figure 3. TEM images. Top: Discrete core/shell structures. Bottom: More complex morphology exhibiting core/shell structures similar to those in top image cemented into roughly spherical aggregates.

4 ANALYSIS

4.1 XANES

Consideration of the synthetic mechanism, the results of probes such as selected area diffraction, and the results or preliminary EXAFS fits suggested we consider three possible iron phases: crystalline bcc iron (α-Fe), an amorphous iron oxide phase, and an amorphous phase based on close-packed iron. To confirm this and fix the fraction of oxide present, we first considered the XANES spectra. XANES is relatively insensitive to particle size, crystallinity, or structure beyond the first coordination shell; the XANES of all iron (II) oxides, for example, are fairly similar. Accordingly, we chose the following three known materials to use as empirical standards:

- An iron-nickel composite. The iron in this material was in a somewhat disordered bcc lattice segregated from the nickel [2].
- An iron-nickel alloy. In this material, the iron resides in an fcc (close-packed) lattice along with the nickel. This provided a good model for the immediate environment of the iron atoms in the amorphous close-packed phase; the substitution of nickel atoms for some iron atoms has very little effect on the XANES.
- A mixture of iron oxides.

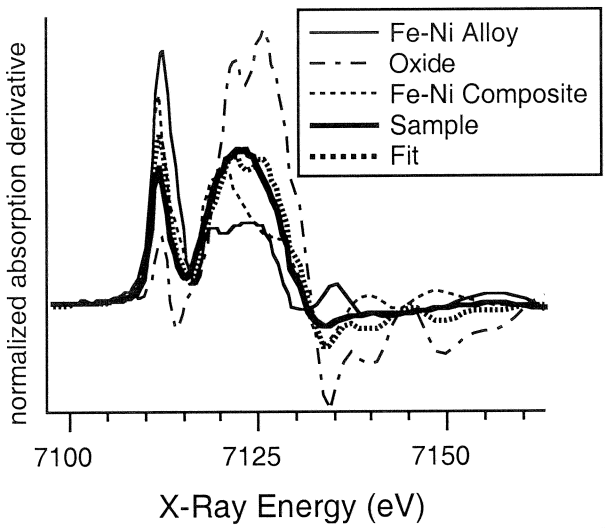

Figure 4. Normalized derivative of XANES for empirical standards and sample. "Fit" is a linear combination of the empirical standards with the fraction of the composite constrained by EXAFS and the fraction of the oxide optimized by a least-squares algorithm.

To correct for differences in sample thickness, the spectra of the samples and the standards was normalized by the edge step. The first derivative of each was then plotted (Fig. 4). Initially, a fit was performed in which a linear combination of the oxide and alloy was sought. The composite and alloy, although different crystal structures, exhibit similar bonding and thus have similar XANES. Subsequently, EXAFS was used to determine the fraction of bcc iron present; this fixed the fraction of iron-nickel composite in a subsequent refinement. The final fit for the spectrum shown in Fig. 1 is given in Fig. 4.

4.2 EXAFS

Using well-established procedures [3], a smooth background was subtracted from the spectra of the samples. The resulting data were then converted to a function of photoelectron momentum k. These k-space plots are generally oscillatory, with the frequency of oscillation depending on the distance between the atom absorbing the x-ray and its neighbors, as well as other factors. The amplitude of the oscillations usually decreases with increasing k, partly due to thermal vibration and other sources of disorder. For this reason, the data have been multiplied by k^2 ("k-weight 2"). The k-weight 2 spectrum corresponding to Fig. 1 is shown in Fig. 5.

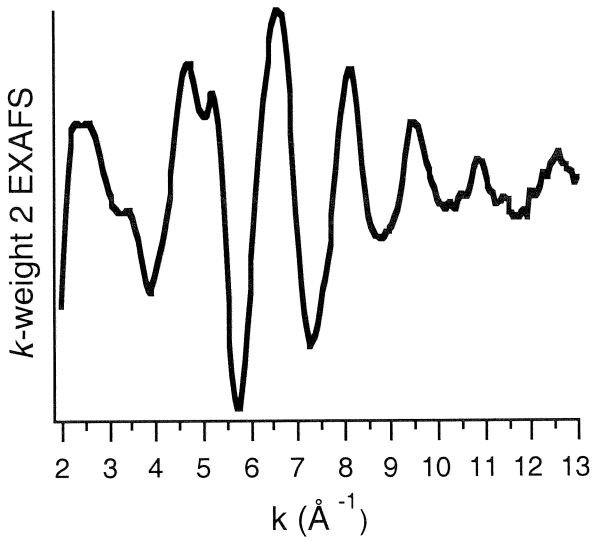

Figure 5. k-weight 2 EXAFS spectrum corresponding to Fig. 1.

The software package FEFF8 [4] was then used to calculate a theoretical standard for each posited phase *ab initio*. Since the frequency of the oscillations in k-space is related to the distance between the absorbing atom and its neighbors, the k-weight 2 spectrum of the samples and the theoretical standards were subjected to identical Fourier transforms. It is important to emphasize that the Fourier transform of EXAFS data, while related to the radial distribution about the absorbing element, is also influenced by other factors such as a chemical shift due to the potential

of the neighboring atoms. Peaks in the EXAFS Fourier transform generally appear up to 0.05 nm lower than the actual distance from the absorbing atom to the neighbors responsible for the peak. In addition, multiple-scattering events in which the photoelectron interacts with more than one neighbor can also contribute peaks that have no direct counterpart in the true radial distribution function. Finally, the details of the Fourier transform used can itself influence the appearance of the spectrum. All of these factors, however, modify both the data and the theoretical standard in the same way, and thus do not affect a comparison between them. This is, in fact, the primary reason for using theoretical standards.

For each sample in this study, the fraction of the oxide standard included was fixed by the result of the XANES fit. The fraction of metal which was crystalline bcc (versus amorphous close-packed); as well as modifications to the theoretical standards based on thermal disorder, nearest-neighbor distance, and other factors; were allowed to vary in least-squares fits. Using results from information theory, each Fourier transform fit corresponded to 13 independent points, compared to 8 parameters that were allowed to vary. The Fourier transforms of the data and fit are shown in Figure 6. As can be seen in the figure, the fit above 3 Å in the Fourier transform is almost entirely due to bcc iron, confirming the presence of that component. The broad peak below 3 Å is quite well fit by the combination of the three phases. There is a mismatch between fit and data evident around 3 Å; this is probably due to some order beyond the first coordination shell in the oxide (modeled here as completely amorphous).

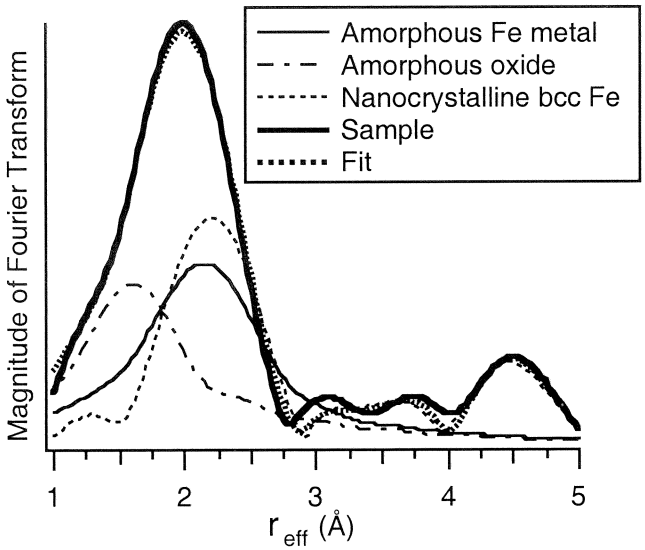

Figure 6. Magnitude of Fourier transform of spectrum shown in Fig. 5, result of fitting theoretical standards, and contribution of theoretical standard to the fit.

5 RESULTS

In all cases of successful core/shell synthesis, from 35-50% of the iron atoms were in the oxidized shell, with the remainder being metallic. This result is broadly consistent with the relative sizes of the shell and core on the TEM images.

Of the synthetic variables investigated, only the choice of surfactant had a substantial effect on the core/shell particles produced. When a nonionic surfactant was used, no crystalline iron was present; the core was entirely amorphous metal based on a close-packed structure. When a cationic surfactant was used, up to 50% of the core was crystalline. These results were consistent with the magnetic properties of the materials.

6 CONCLUSIONS

XAS is a powerful tool for characterization of multi-phase nanoparticles, although it is most effective when used in combination with other probes. Unlike many techniques, it is element specific. Even when the sample contains only one metallic element, as in this study, this property is an advantage because it allows the choice of empirical XANES standards that contain elements not present in the nanoparticles.

Since EXAFS is sensitive to the atomic environment out to nearly a nanometer, it fills a gap between techniques sensitive to the immediate environment of an atom (*e.g.* Mossbauer) and diffraction-based techniques, which are most effective in materials exhibiting long-range order. In the core/shell particles investigated here, this property was particularly useful for confirming the presence of nanocrystalline bcc iron.

ACKNOWLEDGEMENTS

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