

Automated system for x-ray absorption spectroscopy of nanoparticle nucleation and growth

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X-ray absorption spectroscopy (XAS) is a useful tool for studying nanoparticle synthesis and growth. Described here is a system for automating synthesis and data collection, allowing time-resolved XAS measurements at a synchrotron to be accurately combined with measurements made under identical conditions elsewhere, and promising the ability to use XAS with experiments in combinatorial chemistry. The primary components of this system are a commercial parallel processor and a custom flow cell. The system has been used to collect data on the synthesis of iron oxides from iron(II) acetylacetonate. © 2005 American Institute of Physics.

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X-ray absorption spectroscopy (XAS) has long been an important tool for materials characterization. Because of its ability to probe short range order on the subnanometer scale, it has particular importance for nanoscale and amorphous materials. In recent years, the use of XAS to examine the kinetics and mechanism of reactions *in situ* has become increasingly common.¹ The time scales available for these investigations vary widely: several minutes for conventional extended x-ray absorption fine structure (EXAFS) spectroscopy; a few minutes for x-ray absorption near edge spectroscopy (XANES); less than 1 min for quick scan EXAFS (QEXAFS); less than 1 s for energy dispersive EXAFS; and subnanosecond for certain laser spectroscopies.²

Nanoparticle nucleation and growth often occurs on time scales of minutes to hours, and thus we will focus on a system appropriate for the first three techniques here. As useful and productive as XAS is, it suffers from the drawback that for best results data should be collected at a synchrotron light source. Because of space, time, safety, and transport limitations, protocols for reactions performed at a synchrotron often differ from those used in the laboratory of the home institution, creating difficulties when comparison and coordination to other characterization techniques is attempted. In addition, the number of reactions which can be studied in the few days available to the typical synchrotron user is limited.

Fortunately, there is a long history of automating chemical synthesis and characterization,³ including the synthesis of nanoparticles from solutions.⁴ Characterization techniques that have been adapted for use in a “combinatorial” mode include mass spectrometry,⁵ infrared thermography,⁶ and

x-ray diffraction.⁷ Automated systems are often self-contained, thus reducing the risk of spills and other hazards, and are of a size compatible with most synchrotron “hutches” (end stations). In this note, we describe a complete system capable of automating the collection of time-resolved XAS spectra of nanoparticle nucleation and growth in solution at a synchrotron, along with the results of a test run.

The components of the system are shown in Fig. 1. This experiment was performed at beamline X23B of the National Synchrotron Light Source, but there are no outstanding issues which prevent its use at other beamlines. The parallel processor is an Argonaut Surveyor controlled by a computer outside the hutch. The Surveyor processor also communicated with the beamline computer, so that XAS scans could be collected in synchrony with parallel processor events. The flow cell required custom design, and is described in more detail below. The Lytle detector is a standard detector for recording fluorescence-mode XAS spectra. For this experiment, the reactions took place in heated reaction vessels within the parallel processor; the processor then periodically injected an aliquot of one of these reactions into the flow cell for measurement.

The requirements for an XAS solution flow cell are fairly stringent. In fluorescence mode, there should be a thin window free of high-Z elements, with a clear line of sight over a 90° angle. Bubbles of air or evolved gas can be a problem, primarily if they are so large as to reach from front to back of the sample cell. For time-resolved experiments, if the entire contents of the cell do not flush when a new aliquot is injected, then spectra will be a combination of those due to old and new aliquots. It is thus crucial that solution does not linger in the cell when a new injection is made. Likewise, if a precipitate forms, it must be entirely cleared from the cell with each injection. For examples of previously published cell designs, see Refs. 8–10.

The design of the flow cell is shown in Fig. 2. To reduce the effect of bubbles, the cell is 9.5 mm deep. (In fluorescence mode XAS bubbles have little effect as long as there

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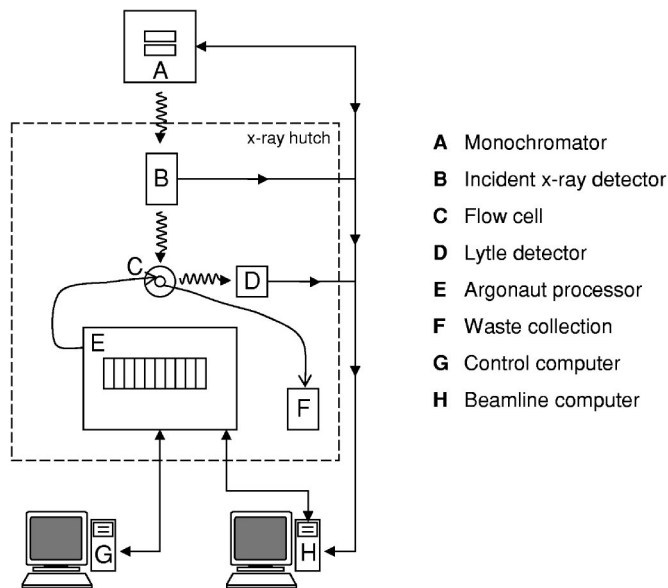


FIG. 1. Components of system.

are at least several absorption lengths of solution at all points in the cell.) To minimize the amount of the previous aliquot left behind with each injection, the input and output taps are displaced both vertically and horizontally, thus creating a swirling motion. The cell is demountable for ease of cleaning, and to allow the Kapton window to be replaced periodically. To avoid the use of adhesives which might dissolve or affect the chemistry, a Viton¹¹ O ring is used along with the mechanical pressure exerted by the screws to form a seal. Since we were interested in collecting data on iron-based nanoparticles, it was important to avoid the use of iron or other high-Z elements in the flow cell construction. Thus, the cell was constructed of Teflon, with nylon screws.

We have tested a variety of data collection modes, including XANES scans, EXAFS scans, and a rotation mode in which EXAFS scans were alternately collected from five reaction vessels, each of which were running under different conditions. All modes performed as planned. In one test, we reacted 300 mg of iron(II) acetylacetonate with 10 ml of ethoxyethanol and 10 ml of ethylene glycol at 150 °C. Similar reactions have been shown to produce iron oxide nanoparticles on a scale of tens of minutes.¹² As the nanoparticles began to form, some of them coated the Kapton¹³ window. To avoid contaminating the measurement of subsequent aliquots with this precipitate, we programmed the processor to flush the cell with acidified methanol between each aliquot.

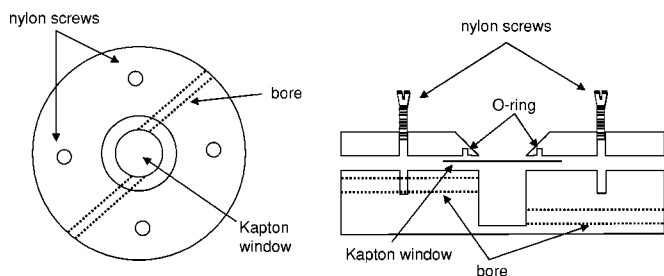


FIG. 2. Design of flow cell. The solution enters and leaves the cell through the bores, which are offset in two dimensions.

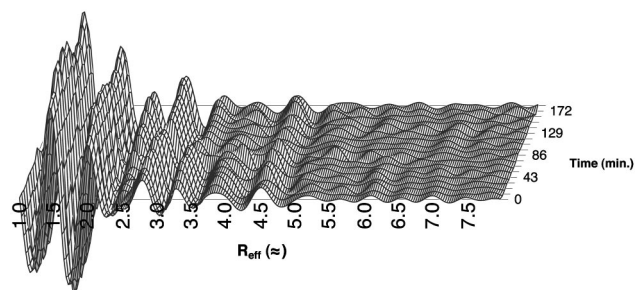


FIG. 3. Time-dependent Fourier transform of EXAFS data.

XAS scans taken during each flush confirmed the efficacy of this procedure.

The EXAFS results are shown in Fig. 3. In this case, parameters were chosen so that each scan took about 4 min. Because of the need to flush the cell between scans, approximately 10 min elapsed between the start of one scan and the start of the next. Normalization, background subtraction, and Fourier transforms were performed¹⁴ according to standard procedures.¹⁵ Changes over time are evident, particularly in the peak between 3.0 and 3.5 Å. These changes are suggestive of a change in crystal structure at that time, most likely from one oxide phase to another.¹⁶ The initial particle growth can also be observed in the increase in amplitude of all peaks over the first half hour. As expected for growth¹⁷ (rather than just continuing nucleation), the relative increase in peaks at high R (e.g., 4.0 Å) is greater than for those corresponding to nearest neighbors (<2.5 Å). The rapidity with which some changes take place confirms that the flow cell is being properly flushed between scans, as otherwise the spectra

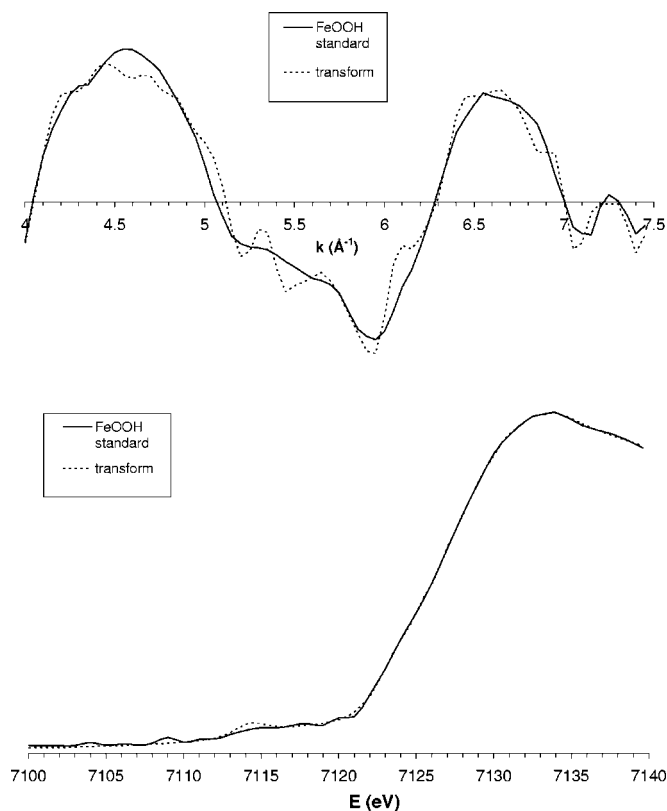


FIG. 4. Spectrum of FeOOH standard and target transform to data series for (top) EXAFS and (bottom) XANES.

would show only gradual transformations due to the averaging of material from multiple aliquots.

Principle component analysis (PCA)¹⁸ was also performed on the run using both the XANES and EXAFS spectra independently. PCA indicated that 79% percent of the variance between EXAFS scans, and 97% of the variance between XANES scans, was attributable to two components.¹⁹ Target transforms to FeO, α -Fe₂O₃, γ -Fe₂O₃, FeOOH, and Fe₃O₄ were attempted. Only FeOOH gave a good fit to the EXAFS (Fig. 4), yielding an *R* factor of 0.03 as compared to 0.12–0.17 for the other oxides. The XANES target transform was less able to discriminate between substances, with all oxides tested except FeO yielding *R* factors below 0.0005 (FeO yielded an *R* factor of 0.005, an order of magnitude higher). Since XANES is primarily sensitive to the electronic structure and immediate environment of the iron atoms, it is not surprising that it was unable to discriminate between oxides with similar iron valence. Taken together, the XANES and EXAFS analyses suggest that FeOOH is one of the oxides present in this reaction. The other major oxide present has not been identified.

We have demonstrated the feasibility of automated, time-resolved XAS at a synchrotron source for reactions with a time-scale of tens of minutes. No significant modifications of this system would be needed for a QEXAFS line, allowing its use with more rapid reactions.²⁰ In addition, the programmability of the processor and the design of the flow cell allow this system to be used in a combinatorial mode, so that rather than a time-series of a single reaction, the products of multiple reactions could be studied in rapid succession.

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¹³Kapton is a registered trademark of DuPont.

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¹⁹It is typical for the variance attributable to a small number of PCA components to be much greater for XANES than for EXAFS. XANES spectra are dominated by the sharp rise attributable to the edge jump, and thus two components are often enough to account for 90% of the variance even when PCA analysis of EXAFS suggests that several components are significant. Since XANES and EXAFS provide somewhat different information (XANES is more weighted toward the electronic structure of the absorbing atoms while EXAFS is more weighted toward the positions, identities, and disorder of the surrounding shells of atoms), it is not possible to directly compare the significance of the XANES and EXAFS values given here. Nevertheless, these results appear consonant, suggesting that the dominant contributor to all the spectra is a mixture of two oxides in varying proportions, with some additional differences which could be due either to the presence of additional phases or to modifications of the spectra reflecting the size or morphology of the growing nanoparticles.

²⁰The long flush times described above were necessitated by precipitate sticking to the windows, which would not be a problem with all reactions. Even if long flushes did prove necessary for a given reaction, better time resolution could be obtained by starting the reaction in different reaction vessels of the Surveyor processor at appropriately offset times.