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## Comparison of extended x-ray absorption fine structure and Scherrer analysis of x-ray diffraction as methods for determining mean sizes of polydisperse nanoparticles

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Curve fitting of extended x-ray absorption fine structure (EXAFS) spectra, transmission electron microscopy (TEM) imaging, and Scherrer analysis of x-ray diffraction (XRD) are compared as methods for determining the mean crystallite size in polydisperse samples of platinum nanoparticles. By applying the techniques to mixtures of pure samples, it is found that EXAFS correctly determines the relative mean sizes of these polydisperse samples, while XRD tends to be weighted more toward the largest crystallites in the sample. Results for TEM are not clear cut, due to polycrystallinity and aggregation, but are consistent with the other results. © 2005 American Institute of Physics. [DOI: 10.1063/1.2137872]

Many nanocrystalline<sup>1</sup> materials exhibit moderately broad crystallite size distributions.<sup>2</sup> If narrow size distributions are desired, subsequent filtering steps or a refinement of the synthesis protocol may be called for. These later efforts are only worthwhile if the distribution contains a substantial fraction of particles of the desired size. It is thus important to be able to estimate the mean size of nanocrystals early in the development of a new material or synthesis technique. Among the most commonly employed techniques for determining mean crystallite size are Scherrer analysis of x-ray diffraction (XRD) data and imaging from transmission electron microscopy (TEM). In this work, we compare the merits of these two techniques to the use of extended x-ray absorption fine structure (EXAFS) spectroscopy.

For this study, we synthesized platinum nanoparticles using a polyol technique.  $H_2PtCl_6 \cdot H_2O$  was added to ethylene glycol, taken to reflux for 1 h, and then allowed to cool to room temperature. Table I gives the concentration of the platinum salt used for each sample and the conditions under which the  $H_2PtCl_6 \cdot H_2O$  was added to the ethylene glycol. Based on experiments in which copper was synthesized by this method,<sup>3</sup> it was expected that particle size should increase with increasing concentration of the platinum salt. Both XRD and EXAFS confirmed that the product was purephase platinum metal. TEM images showed that the results were polydisperse and often appeared to by aggregates; darkfield imagery of some of the larger particles revealed them to be polycrystalline as well (Fig. 1 and EPAPS Ref. 4). XRD data were collected using a Phillips x-ray diffractometer<sup>5</sup> employing Cu  $K\alpha$  radiation from a sealed tube source (50 kV, 30 mA, 0.05° step, 1.0 s/step).<sup>6</sup> Scherrer analysis was then performed according to the method in Ref. 7, using a platinum foil as a standard and the JADE software package<sup>8</sup> to determine peak positions and peak widths at half-height. Results are shown in Fig. 2.

In order to measure the particle size and distribution via TEM, each of the six samples was ultrasonically dispersed in acetone. A carbon-coated TEM grid was dipped into the sample solution and allowed to dry, depositing the nanoparticles onto the carbon films, which were then evaluated with a Philips CM12 TEM operating at 120 kV. TEM images captured with a charge coupled device camera were used to study particle size, morphology, and distribution of the samples. For each of the samples studied, a range of crystallite morphologies were found, with most crystallites occurring in aggregates. Conclusive crystallite size results from TEM images were difficult to obtain because of the presence of aggregates and a higher degree of polydispersion than originally expected.

To estimate the mean size using EXAFS, we employed the method described in Ref. 9. That method assumes spheri-

TABLE I. Synthesis conditions for platinum nanoparticle samples.

| Sample | Temperature at injection | $[H_2PtCl_6 \cdot H_2O]$ |
|--------|--------------------------|--------------------------|
| 1      | Room                     | 0.03                     |
| 2      | Reflux                   | 0.015                    |
| 3      | Room                     | 0.009                    |
| 4      | Room                     | 0.003                    |
| 5      | Reflux                   | 0.003                    |
| 6      | Room                     | 0.0003                   |
|        |                          |                          |

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FIG. 1. TEM image of platinum nanoparticle exhibiting polycrystallinity.

cal particles, yielding coordination numbers which are suppressed relative to a bulk crystal by a factor of

$$1 - \frac{3}{4}\frac{r}{R} + \frac{1}{16}\left(\frac{r}{R}\right)^3,\tag{1}$$

where R is the radius of the particle and r is the distance to the coordinate shell in question. Other methods of estimating nanocrystal size using EXAFS, for example, those given in Refs. 10-12, are based on a similar principle although in some cases are better suited to nonspherical morphologies.

Samples were prepared and uniformity verified by the method described in Ref. 13. Five additional samples were assembled by mixing more than one of the as-prepared materials and referred to as, e.g., "2-3" for a mixture of Samples 2 and 3. Two mixtures of Samples 1 and 2 were prepared: One with more of Sample 1 ("1-2") and one with more of Sample 2 ("2–1"). A platinum foil was also included as a bulk standard. Pt L III edge x-ray absorption spectra were collected at Beamline X-11A of the National Synchrotron Light Source at the Brookhaven National Laboratory. Background subtraction (up to 0.0925 nm in the Fourier transform) was performed using the method described in Ref. 13. In Fig. 3, which shows the Fourier transforms of selected samples, the decrease in amplitude modeled by Eq. (1) is clearly evident. The  $\chi(k)$  data for all samples is available in Ref. 4.





FIG. 3. (Color online) Fourier transform of  $k^2$ -weighted EXAFS data for selected samples and a reference foil.

Because differences between the EXAFS spectra of bulk materials and nanoparticles can stem from relaxation effects, such as changes in lattice constants and Debye-Waller factors, as well as the termination effect modeled by Eq. (1), multiparameter analyses were performed. EXAFS data with values of the photoelectron wave number k from  $30-180 \text{ nm}^{-1}$  were weighted by factors of k,  $k^2$ , and  $k^3$  and Fourier transformed. These Fourier transforms over a range of 0.15–0.75 nm (Ref. 14) were then compared to a theoretical standard generated by FEFF6L (Ref. 15) using the ATH-ENA, ARTEMIS, and IFEFFIT software packages,<sup>16</sup> and procedures such as those found in Ref. 13. In addition to crystallite radius R, EXAFS third cumulants for the nearest-neighbors  $C_3$  and the lattice parameter a were allowed to vary freely for each sample (see Table II). The fitted spectra are available in EPAPS Ref. 4. Parameters not expected to differ between nanoparticulate samples were fit for the sample set as a whole: EXAFS amplitude reduction factor  $S_o^2$  (1.16+0.05), photoelectron energy origin  $E_o(8.1+0.1 \text{ eV})$ ,<sup>17</sup> broadening  $E_i(2.3+0.2 \text{ eV})$ , and mean-square radial displacements.<sup>18</sup>

Synthesis, XRD, EXAFS, and TEM were initially performed and analyzed by researchers who knew neither the results of the other measurements nor the expected relative sizes of the nanocrystals. Although this was no longer the case by the late stages of the analyses, the XRD and EXAFS results given below are substantially similar to the results found during the "blind" stage of this study. Because of aggregation and polycrystallinity, however, the procedure and final values for TEM were strongly influenced by the range of particle sizes found by the other techniques.

The measured particle sizes are summarized in Fig. 4. The error bars for XRD and EXAFS are not a measure of

TABLE II. Parameters found via EXAFS analysis. Uncertainties in the last digit shown are given in parentheses.

| Sample  | <i>a</i> (nm) | $C_3 ({\rm pm}^3)$ | <i>R</i> (nm) |
|---------|---------------|--------------------|---------------|
| Foil    | 0.3933(4)     | 63(22)             |               |
| 1       | 0.3922(3)     | 46(28)             | 1.80(54)      |
| 1-2 mix | 0.3920(4)     | 53(33)             | 1.38(30)      |
| 2-1 mix | 0.3917(4)     | 30(32)             | 1.18(20)      |
| 2       | 0.3917(2)     | 58(15)             | 1.03(23)      |
| 2-3 mix | 0.3922(3)     | 54(22)             | 1.46(29)      |
| 3       | 0.3923(3)     | 44(23)             | 2.35(73)      |
| 1-4 mix | 0.3923(2)     | 51(16)             | 1.50(24)      |
| 4       | 0.3920(3)     | 53(23)             | 1.46(27)      |
| 1–5 mix | 0.3919(5)     | 43(43)             | 1.39(36)      |
| 5       | 0.3916(5)     | 55(36)             | 1.13(21)      |
| 5       | 0.3916(5)     | 55(36)             | 1.13(21)      |

is subject to the term§at: http://scit9.3916(3)org/termsc61(24).ns. Downl9.92(10)o IP: 70.82.110.48 FIG. 2. (Color online) X-ray diffractograms for all samples.



FIG. 4. Crystallite size found by each technique. TEM shows full range of crystallites found; error bars on XRD and EXAFS measurements show uncertainty rather than dispersion.

dispersion. For XRD, the error bars are the standard deviation of the sizes found by applying Scherrer analysis to different diffraction peaks, while for EXAFS they are indicative of the sensitivity of the fit to particle size. In both cases, the error bars are a measure of uncertainty in the *absolute* mean as determined by each method. Changing the details of the fitting method in EXAFS or the assumed peak profile in XRD, for example, leads to all of the determined sizes increasing or decreasing in a correlated way. Thus, the *relative* sizes of the samples are determined to a greater accuracy than is implied by the error bars. In order to estimate the uncertainty in the relative sizes determined from EXAFS, fits to an empirical standard using crystallite size as the only fitting variable were also performed (this method is described further in Ref. 19). These one-parameter fits do not allow for relaxation of the nanoparticles, and thus may suffer from systematic bias. Any relaxation effects, however, are likely to be given by slowly varying monotonic functions of size; thus, the uncertainties found by the one-parameter fits are a reasonable estimate of the uncertainty in relative sizes for the multiparameter fits.

As with other EXAFS studies of particles with broad size distributions,<sup>19–21</sup> it is striking how much larger the XRD-determined size is than the EXAFS size. This is partly attributable to the different weighting implied by the two methods; the difference between the two measurements is thus a marker for polydispersion. We have previously shown that for a moderately polydisperse sample XRD becomes dominated by the size distribution of the largest particles, while EXAFS is still sensitive to the lower end of the distribution.<sup>9</sup> It can be seen from Fig. 4 that EXAFS correctly yields relative sizes for the mixed samples between those of the corresponding as-synthesized samples, while XRD yields a result more similar to that of the unmixed sample with the larger mean. This is consistent with behavior that would be expected for samples with a large degree of polydispersion.<sup>9</sup>

Because the particles were polycrystalline, the TEM images were quite difficult to interpret. An attempt was made to measure crystallite sizes within each sample, with the resulting ranges shown as grey bars in Fig. 4.<sup>22</sup> As can be seen, these ranges generally fall between the XRD and the EXAFS results. It is not surprising that the ranges do not generally extend to sizes as small as indicated by EXAFS, as no attempt was made to use TEM to count crystallites smaller than 1.5 nm radius due to the difficulty in identifying small crystallites in much larger, irregular particles. There may also have been occasional large crystallites in the samples that did not appear in any of the TEM images. Since XRD is particularly sensitive to these large crystallites, it is reasonable that the XRD results would be at or above the top end of the range found via TEM, as here. Both of these complications underscore the difficulty of determining crystallite size distributions via TEM for samples of this type.

Based on the results of this study, we suggest that caution is warranted in applying Scherrer analysis to estimate the relative mean sizes of distributions of nanocrystals when the distribution may be broad. TEM is, of course, the most accurate method when sufficient data are collected, and aggregation, polycrystallinity, and contamination are not suspected, but in cases such as the one examined here can be problematic and very time consuming. EXAFS, although as yet little used in this capacity, shows promise for being a robust method for determining relative sizes of samples.<sup>23</sup>

<sup>1</sup>The term *nanocrystal* is used here for either a monocrystalline nanoparticle or a nanocrystalline inclusion within a matrix.

- <sup>2</sup>C. G. Granqvist and R. A. Burhman, J. Appl. Phys. 47, 2200 (1976).
- <sup>3</sup>L. K. Kurihara, G. M. Chow, and P. E. Schoen, Nanostruct. Mater. 5, 607 (1995).
- <sup>4</sup>See EPAPS Document No. E-APPLAB-87-031548 for supplemental images,  $\chi(k)$  data, and  $\chi(R)$  fits. This document can be reached through a direct link in the online article's HTML reference section or via the EPAPS homepage (http://www.aip.org/pubservs/epaps.html).
- <sup>5</sup>It is probable that data with lower noise levels could have been collected using synchrotron radiation. Our intention here is to compare crystallite size determination techniques commonly found in the literature; for this purpose, Scherrer analysis is generally performed using laboratory x-ray sources.
- <sup>6</sup>Some samples (primarily the mixed samples) were also analyzed using a Scintag XDS 2000 diffractometer to test for instrument variability. Samples analyzed on both instruments produced particle size measurements consistent to within the reported uncertainties.
- <sup>7</sup>A. West, *Solid State Chemistry and Its Applications* (Wiley, West Sussex, 1984).
- <sup>8</sup>JADE 6.1 (Materials Data, Livermore, CA, 2002).
- <sup>9</sup>S. Calvin, C. J. Riedel, E. E. Carpenter, S. A. Morrison, R. M. Stroud, and V. G. Harris, Phys. Scr., T **115**, 744 (2005).
- <sup>10</sup>R. B. Greegor and F. W. Lytle, J. Catal. **63**, 476 (1980).
- <sup>11</sup>A. I. Frenkel, C. W. Hills, and R. G. Nuzzo, J. Phys. Chem. B **105**, 12689 (2001).
- <sup>12</sup>I. Arcon, A. Tuel, A. Kodre, G. Martin, and A. Barbier, J. Synchrotron Radiat. 8, 575 (2001).
- <sup>13</sup>S. Calvin, E. E. Carpenter, B. Ravel, V. G. Harris, and S. A. Morrison, Phys. Rev. B **66**, 224405 (2002).
- <sup>14</sup>699 independent points, 41 free parameters, and 658 degrees of freedom for the 12 samples according to the Nyquist criterion. The EXAFS  $\mathcal{R}$ -factor, a measure of mismatch between data and fit, was 0.03.
- <sup>15</sup>J. J. Rehr, S. I. Zabinsky, and R. C. Albers, Phys. Rev. Lett. **69**, 3397 (1992).
- <sup>16</sup>B. Ravel and M. Newville, J. Synchrotron Radiat. 12, 537 (2005).
- <sup>17</sup>Relative to the first peak of the derivative of the energy spectrum.
- <sup>18</sup>The mean square radial displacements were initially allowed to vary for each sample, but were not found to differ significantly between samples; thus in the final fits all samples were fit to one set of same values:  $(5.0\pm0.1, 6.4+0.2, \text{ and } 7.9\pm0.3) \times 10^{-5} \text{ nm}^2$  were found for the nearest, next-nearest, and more distant neighbors, respectively.
- <sup>19</sup>S. Calvin, M. M. Miller, R. Goswami, S.-F. Cheng, S. P. Mulvaney, L. J. Whitman, and V. G. Harris, J. Appl. Phys. **94**, 778 (2003).
- <sup>20</sup>C. Calais, M. Matsubayashi, C. Geantet, Y. Yoshimura, H. Shimada, A. Nishijima, M. Lacroix, and M. Breysse, J. Catal. **174**, 130 (1998).
- <sup>21</sup>A. I. Frenkel, S. Nemzer, I. Pister, L. Soussan, T. Harris, Y. Sun, and M. H. Rafailovich, J. Chem. Phys. **123**, 184701 (2005).
- <sup>22</sup>Note that, due to the difficulties posed by aggregation and polycrystallinity, observer bias was undoubtedly present for the TEM results.
- <sup>23</sup>The method used here is somewhat time-consuming and requires considerable specialized expertise. In cases in which EXAFS is already being used to determine other characteristics of the sample, however, an analysis of this type requires little additional effort. If an easier, quicker, and less for the sample of the sample of the sample of the sample of the sample.