Direct determination of the absolute electron density of nanostructured and disordered materials at sub-10-nm resolution

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We report the development of a novel experimental approach to the direct determination of the absolute electron density of nanostructured and disordered materials. By calibrating the incident coherent x-ray flux and the diffraction pattern intensity and using the oversampling method, we have directly determined the absolute electron density of a porous silica particle at ~9-nm resolution. This general approach can be used for the quantitative characterization of nanocrystals and noncrystalline materials at nanometer or better resolution.

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There is an important need in nano science and materials science to develop quantitative methods for determining the absolute electron density (or electrostatic potential) of nanostructured materials at nanometer or better resolution in three dimensions.[1] To achieve this goal, x rays are an ideal candidate due to the fact that x-ray wavelengths are on the order of the size of atoms, and that the penetration length of x rays is much longer than that of electrons. X rays are, however, much more difficult to focus than electrons. The smallest focal spot currently achievable is ~30 nm for soft x rays[2] and ~100 nm for hard x rays.[3] To dramatically improve the resolution, diffraction-based methodology such as x-ray crystallography has to be employed, which can routinely visualize an arrangement of atoms in three dimensions. But the three-dimensional structures obtained by x-ray crystallography are globally averaged from a large number of unit cells inside a crystal. To overcome these limitations, a diffraction-based imaging method has recently been developed to determine the nonaveraged local structures of nanocrystals and noncrystalline materials by using the oversampling method and coherent x rays.[4–11] However, the imaging method has thus far been used to determine the relative electron density of the local structures. Here we report an experimental approach to the quantitative determination of absolute electron density of nanostructured and disordered materials at sub-10 nm resolution.

The experiment was carried out on a synchrotron undulator beamline at SPring-8 with an x-ray wavelength of 2.3 Å.[12] A Si (1,1,1) double crystal was used to produce good temporal coherence ($E/\Delta E \sim 7500$) and a 150-μm slit, placed at a distance of 27 m upstream of the experimental instrument, to achieve good spatial coherence (divergence angle $\sim 5.5\times10^{-6}$ rad). The first element inside the instrument was a 20-μm pinhole to create a small and clean beam which was placed in front of the sample at a distance of 38 mm. The sample was a disordered porous silica particle with a ~15-nm pore size.[13] Between the pinhole and the sample was mounted an L-shaped guard slit to eliminate the scattering from the edge of the pinhole. An x-ray photodiode mounted downstream of the sample was used to align the pinhole and measure the incident flux. At a distance of 743 mm downstream of the sample was a detector, which is a deep depletion and direct illumination CCD with a pixel size of 22.5×22.5 μm^2. To reduce the dark noise, the CCD was operated at liquid nitrogen temperatures. To eliminate the scattering from the air molecules, the experiment was carried out in vacuum with a pressure of 10^{-4} Pa. Additional details of the experimental setup can be found elsewhere.[14]

Figure 1 shows a coherent diffraction pattern recorded from a single porous particle with a size of ~2 μm. To make the detailed features visible, only the central part (512×512 pixels) of the diffraction pattern is shown whereas the whole diffraction pattern has 1600×1600 pixels with a resolution of 9.3 nm at the edge. Due to the low dynamic range of the CCD, a small patch of the lower resolution diffraction pattern (60×60 pixels) was blocked to facilitate the record-

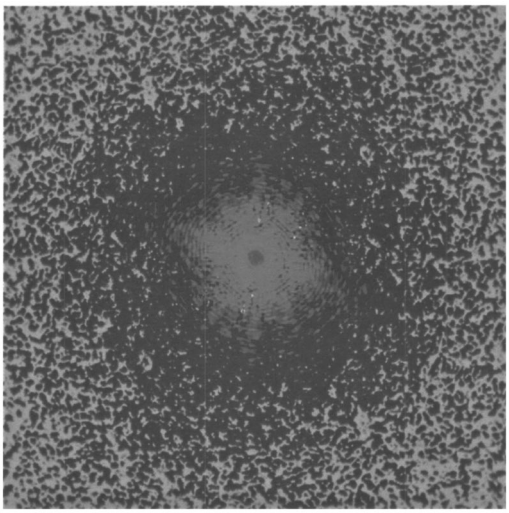

FIG. 1. (Color online) The central part (512×512 pixels) of an x-ray diffraction pattern recorded from a porous silica particle with ~2 μm in size. The whole diffraction pattern has 1600×1600 pixels with a resolution of ~9 nm at the edge.

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ing of the higher resolution diffraction pattern. The missing data at the center were filled in by the magnitude of Fourier transform calculated from an x-ray microscopy image.[15] We believe this problem will be solved in the future by using two-dimensional area detectors with both higher quantum efficiency and higher dynamic range.[16]

The intensity of the diffraction pattern is related to the Fourier transform of the electron density, $F(\vec{\mathbf{k}})$, by

$$I(\vec{\mathbf{k}}) = \frac{I_0 L r_e^2}{r^2} |F(\vec{\mathbf{k}})|^2, \tag{1}$$

where $I(\vec{\mathbf{k}})$ is the intensity of the diffraction pattern, I_0 the incident x-ray flux, L the polarization factor, r_e the classical electron radius, and r the distance from the sample to the CCD. To obtain the absolute value of $|F(\vec{\mathbf{k}})|$, both the absolute values of $I(\vec{\mathbf{k}})$ and I_0 have to be measured. We determined the absolute value of $I(\mathbf{k})$ based on

$$M = \frac{Q h_1 h_2}{N_c}, \tag{2}$$

where M is the CCD counts per x-ray photon, Q the efficiency of converting x-ray photons to electron-hole pairs, h_1 the average number of electron-hole pairs created by a single photon, h_2 the ratio of the electrons (or holes) reaching the electrodes and N_c the average number of electrons needed to produce one count. Q is determined to be 77% for x rays with a wavelength of 2.3 Å. h_1 is given by E/e where E is the x-ray photon energy and e the average energy for an electron-hole creation ($\sim$3.7 eV). N_c/h_2 was measured by the CCD manufacturer (Roper Scientific) to be 4.33 electrons/count. The CCD counts per x-ray photon was determined to be $M=256.7$. To obtain I_0, the x-ray photodiode (100-μm-thick Si) was used to measure the incident x-ray flux before and after the recording of the diffraction patterns. By averaging the two measurements and taking into account the exposure time, the incident x-ray flux for the diffraction pattern of Fig. 1 was determined to be 6.4×10^9 photons/μm^2.

To determine the absolute electron density, one needs to know the phases of the Fourier transform which were obtained by using the oversampling method.[17] When a diffraction pattern is sampled at a fine enough frequency, the phase information exists inside the diffraction pattern and can be directly retrieved by using an iterative algorithm. The algorithm iterates back and forth between real and reciprocal space with a random phase set as an initial input. An R factor is used to monitor the reliability of the reconstruction process,

$$R_{i,j} = \frac{\Sigma_{\vec{\mathbf{r}}} |\rho_i(\vec{\mathbf{r}}) - \rho_j(\vec{\mathbf{r}})|}{\Sigma_{\vec{\mathbf{r}}} |\rho_i(\vec{\mathbf{r}}) + \rho_j(\vec{\mathbf{r}})|}, \tag{3}$$

where $\rho_i(\mathbf{r})$ and $\rho_j(\mathbf{r})$ represent the ith and jth reconstructed electron density with different random phase sets as the initial input. We have carried out a total of five reconstructions for Fig. 1 and the R factors were calculated to be $R_{12}=3.7\%$, $R_{13}=3.72\%$, $R_{14}=3.8\%$, and $R_{15}=3.64\%$.[18] The consistent and small R factors demonstrated the robustness of the phase retrieval. We also compared the five sets of the reconstructed electron density. They are almost identical except for some small differences at high spatial resolution which, according to the computer simulation results,[17] are due to the noise in the diffraction pattern.

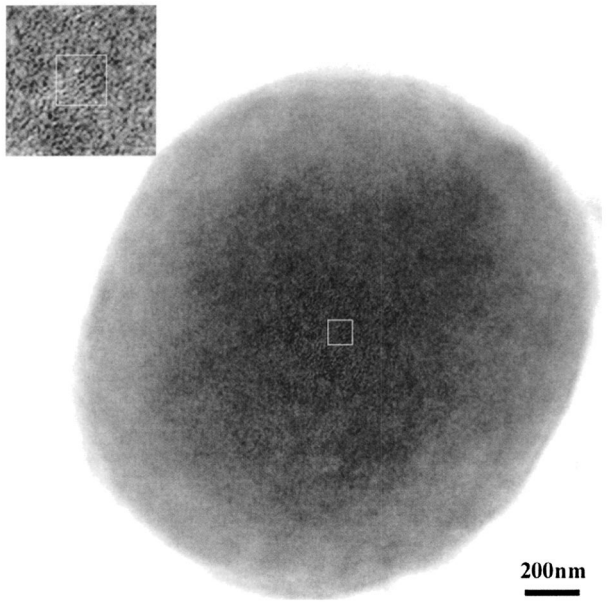

FIG. 2. The absolute electron density reconstructed from Fig. 1 in which the absolute electron density inside the little square (100×100 nm^2) at the center is shown in Fig. 3. The worm-like structures in the inset are due to the disordered and porous nature of the particle.

Figure 2 shows the reconstructed absolute electron density at a resolution of 9.3 nm which is a projection of the nanostructured particle. The inset shows an amplified area (300×300 nm^2) at the center of Fig. 2 in which the worm-like structures are due to the disordered and porous nature of

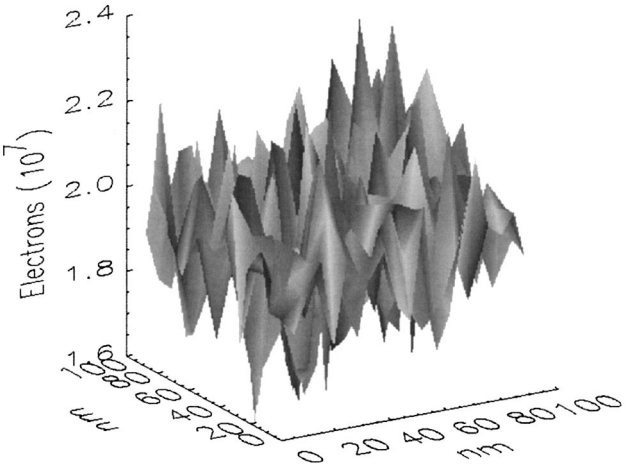

FIG. 3. The variation of the absolute electron density within the area of 100×100 nm^2 which is due to the porous structures with a pore size of $\sim$15 nm.

the particle. A white square in Fig. 2 corresponds to a 100 $\times$100-nm^2 area in which the electron density is shown in Fig. 3. The z axis of Fig. 3 represents the number of electrons in a volume of 4.65 nm$\times$4.65 nm$\times$2 μm, where the pixel dimension in the x and y axes is half of the resolution and the thickness of the particle within the area was estimated to be 2 μm. The averaged electron density within the 100$\times$100-nm^2 area was determined to be 0.45 electrons/Å^3 which is in quite good agreement with 0.4 electrons/Å^3 calculated from the known pore volume of 1.15 cm^3/g. The slight difference is believed due to the error in estimating the particle thickness. By measuring the full width of half maximum of the peaks, the pore size was roughly estimated to be $\sim$15 nm.

By calibrating the incident coherent x-ray flux and the diffraction pattern intensity, we have determined the absolute value of the magnitude of the Fourier transform of a porous silica particle. By using the oversampling method, the absolute electron density was directly reconstructed from the calibrated magnitude of the Fourier transform. A real-space resolution of $\sim$9 nm has been achieved. In combination with the three-dimensional reconstruction algorithm,[7] this experimental approach can be used for a quantitative structure determination of nonaveraged local structures at nanometer or better resolution in three dimensions, which is not accessible to x-ray crystallography. With the prospects of future higher flux and more coherent x-ray sources,[19,20] we expect this approach will find important applications in both nano and materials science.

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[13] The sample, silica materials with a 15-nm pore size obtained from Aldrich Chemicals (product No. 23,684-5, Silica-gel, Davisil), was ground gently while wet for about 5 min using a mortar and pestle. A portion of 100 mg of ground sample was mixed with 45 mL of water in a conical bottomed centrifuge tube. The tube was shaken by hand to disperse the particles and then centrifuged at 3000 rpm for 9 min using a Beckman GS-15 centrifuge and an angle-head rotor. After centrifugation, the top 40 mL of supernate were removed and then freeze dried to minimize aggregate formation. The silica particles were then dispersed in alcohol and picked up on silicon nitride membranes. The silicon nitride membranes were examined under a light microscope and well isolated porous silica particles with a size of $\sim$2 μm were chosen for the study.

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[18] In the reconstructions, the oversampling ratio (σ), a parameter to characterize the oversampling degree, was set to be 12.8 [a detailed discussion of σ can be found elsewhere (Refs. 14 and 17)]. A finite support which is used to separate the electron density and the no-density region was chosen to be 2.09 $\times$2.06 μm^2.

[19] http://ssrl.slac.stanford.edu/lcls.

[20] http://erl.chess.cornell.edu.