NANO 703/703L
Lab: TEM Analysis of Nanoparticles
Due: Following Lab Session

BACKGROUND

TEM is an excellent tool for measuring the structural properties of individual nanoparticles (NPs) and NP ensembles. Features such as NP size and shape are accurately determined at high magnification under bright-field conditions. However, size and packing information is also available in selected-area diffraction mode, using long camera lengths. Usually, a high-density of material is needed to generate sufficient diffracted intensity for measurement. Also, the interpretation of the diffraction pattern may be dependent on the configuration of the particles in direct space. Alternatively, one can compute the fast-Fourier transform (FFT) of the image, which reveals comparable reciprocal-space information about the particle distribution.

The most accurate representation of the size of a single particle is made at high magnification using a well-focused objective lens. Often, the lens is slightly underfocused to improve the image contrast. At high magnification, sample drift during the exposure causes noticeable distortion in the image. Other effects, such as deviations in the beam tilt, can lead to astigmatism in the image, but these can usually be corrected using the objective stigmators. Most TEMs allow storage of multiple objective stigmator settings. Whenever a user is unsure about the optimal settings, it is always best to switch to an alternative memory location before altering the present settings. If the astigmatism deteriorates during the adjustment, just restore the original settings at any time.

In NP systems with sufficient size and shape uniformity, ordered arrays of NPs are formed by so-called "bottom-up" self-assembly methods. It is useful to determine the collective arrangement in these periodic NP ensembles, such as the 2-D or 3-D symmetry of the packing sequence, and the interparticle distance. For example, 2-D collections of spherical particles can form a close-packed triangular lattice.

The diffraction from a 2-D ensemble of identical, close-packed spheres, with only short-range order, is not identical to that from a random, 2D ensemble of spheres (which may overlap). Neither diffraction pattern is identical to that of a periodic, ordered array of spheres [Fig.]. The interpretation of the diffraction pattern, or an FFT of the image, requires identifying features in the image that correspond to the particular frequency information. The FFTs of images from random NPs show intensity maxima that are not precisely equal to the inverse of the particle size. In the case of ordered NPs, the largest lattice spacing is slightly less than the constituent particle size.

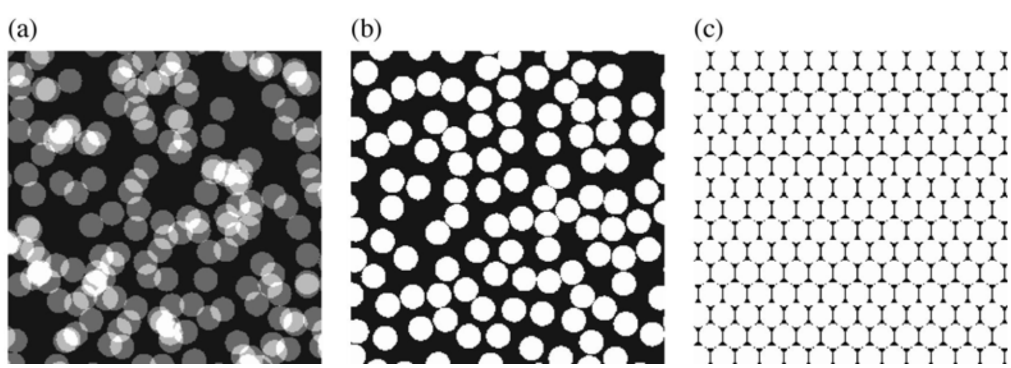

Fig.: Calculated arrangements of circles in 2-D: (a) random; (b) random, close-packed; (c) ordered.

EXPERIMENT

We will prepare and examine colloidal NPs on grids for TEM analysis. We will acquire images and diffraction patterns of the particles, observe the shapes of the individual NPs, and measure the NP sizes.

Prepare a TEM sample from a colloidal suspension:

1) Place a carbon-coated copper TEM grid on a glass surface. The coated side of the grid, which appears dark, smooth, and reflective, should face up.

2) Place one or two drops of the colloidal solution on the grid. Allow the solvent to evaporate. (Water is relatively slow to dry. You may need to slide the grid out of the solution to the edge of the glass.)

Acquire the following data:

Low Concentration (LC) Region

A high-magnification (≥200 Kx) image. Try to isolate several individual NPs. It may be necessary to adjust the objective stigmators. Use the real-time FFT as a guide.

High Concentration (HC) Region

a) A medium-magnification (50-80 Kx) image.

b) A short-camera-length (30 cm) diffraction pattern.

c) A long-camera-length (200 cm) diffraction pattern. Look for features close to the direct beam.

ANALYSIS

1) Determine various sizes related to the NP configuration using three different methods:

a) In direct space, from high-magnification bright-field images of an LC region:

i) Record the lateral dimension of several (at least 12) particles using the measurements tools.

ii) Evaluate the average and the standard deviation of the particle-size measurements ($\bar{D}_1 \pm \delta_{D_1}$).

b) In reciprocal space, from an FFT of a medium-magnification image of an HC region:

i) Compute an FFT on an intermediate magnification image showing randomly oriented nanoparticles.

ii) Measure the diameter $2/d$ of the intensity maximum in the FFT corresponding to the NP size.

iii) Compute the corresponding size $D_2 = 2d/\sqrt{3}$ (assuming close-packing) in direct space.

c) In reciprocal space, from the long-camera length diffraction pattern of the HC region, measure the diameter of the low-angle $2/d$ intensity maximum (if observed) corresponding to the NP size. Compute the corresponding length $D_3 = 2d/\sqrt{3}$ in direct space.

2) From the short camera-length diffraction pattern of an HC region, determine the lattice spacings d_i $(i = 1,2,3)$ corresponding to the first three rings.

REPORT

1) Report size measurements D_1, D_2, and D_3 including relevant calculations.

2) Report the lattice spacings measured from the short-camera length diffraction pattern.

3) Provide representative images and diffraction patterns.