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Scanning Transmission Electron Microscopy for Nanostructure Characterization

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1. Introduction

The scanning transmission electron microscope (STEM) is an invaluable tool for the characterization of nanostructures, providing a range of different imaging modes with the ability to provide information on elemental composition and electronic structure at the ultimate sensitivity, that of a single atom. The STEM works on the same principle as the normal scanning electron microscope (SEM), by forming a focused beam of electrons that is scanned over the sample while some desired signal is collected to form an image [1]. The difference with SEM is that thin specimens are used so that transmission modes of imaging are also available. Although the need to thin bulk materials down to electron transparency can be a major task, it is often unnecessary for nanostructured materials, with sample preparation requiring nothing more than simply sprinkling or distributing the nanostructures onto a commercially available thin holey carbon support film. No long and involved grinding, polishing, or ion milling is required, making the STEM a rapid means for nanostructure characterization.

As in the SEM, secondary or backscattered electrons can be used for imaging in STEM; but higher signal levels and better spatial resolution are available by detecting transmitted electrons. A bright field (BF) detector includes the transmitted beam and so the holes appear bright, whereas a dark field detector excludes the transmitted beam and holes appear dark. Each detector provides a different and complementary view of the specimen. It is one of the key advantages of the STEM to have multiple detectors operating simultaneously to collect the maximum possible information from each scan. Although transmitted electron detectors are usefully fitted to conventional SEM instruments working at relatively low voltages, there are major advantages in increasing the accelerating voltage. Increased specimen penetration means that thicker specimens can be tolerated; but more importantly, the decreasing electron wavelength leads to higher spatial resolution and the ability to see the actual atomic configurations within the nanostructure.

Thus the STEM can take many forms: a simple add-on detector to a standard low-voltage SEM; a dedicated, easy-to-use, intermediate voltage STEM with
rapid throughput; or an instrument more comparable to a high-resolution transmission electron microscope (TEM), which is able to provide the ultimate spatial resolution and analytical sensitivity. All have important and complementary roles in nanostructure characterization. Rapid feedback is critical to synthesis, and commercially available SEMs with subnanometer resolution at 30 kV have the ability to image tens of samples within a few hours. Similar throughput is also available with dedicated STEMs giving at best around 0.2-nm resolution at 200-kV accelerating voltage. Such instruments can be used to guide the synthesis on a day-to-day basis and represent an invaluable first step in characterization. An example of the imaging of a gold nanocatalyst supported in mesoporous silica is shown in Fig. 6.1.

These microscopes are ideal for determining size distributions of nanoparticles at the level of 1 nm and above, but they lack sensitivity at the atomic level. For understanding the functionality of nanostructures, it is highly desirable to examine individual nanostructures with atomic level sensitivity. This requires a more sophisticated instrument at the forefront of what is technologically achievable in electron optics, electronics, and environmental stability. STEMs of this type are generally based on high-resolution TEM columns, operating at 200–300 kV. Ideally, we would like to see every atom in its 3D location, a dream that Feynman first laid forth in his famous lecture “There’s Plenty of Room at the Bottom,” where he not only forecast the nanotechnology era but also explicitly called for 100-fold improvement in the resolution of the electron microscope [3]. If we could see the atoms clearly, then surely we would be able to see how the nanostructure functioned.

Today we are well on the way along this path. We are able to see individual atoms of high atomic number (Z), either on surfaces or inside bulk materials [4,5]. We can even identify single atoms spectroscopically and analyze their local

![Figure 6.1](image.png)
electronic environment by electron energy loss spectroscopy (EELS) [6]. The advances in STEM capability in the past few years have been quite dramatic, comparable to progress in the previous two decades, through the successful realization of another innovation that Feynman called for in his lecture, the correction of lens aberrations. Feynman explicitly called for the incorporation of nonround lens elements to improve the resolution beyond the limit imposed by the unavoidable spherical aberration of the traditional round microscope objective lens. These revolutions in nanoscience and in electron microscopy are going on at the same time, and indeed one is fuelling the other. The ability of aberration-corrected microscopes to image nanostructures more clearly than ever is significantly increasing the demand for these instruments.

It is often said that a picture is worth a thousand words, but in the area of nanoscience a picture can sometimes be a revelation, showing up structures or phenomena that were totally unexpected. Such is the importance of feedback to synthesis, but at the same time a picture can just be a starting point into a quantitative insight into atomistic processes. Catalysis provides a perfect example where images can furnish information on the size and shape of nanoparticles, and how they change with processing conditions. From such knowledge, it becomes possible to perform theoretical modeling of the atomistic processes themselves, calculations of the binding energy of molecules onto the clusters observed, calculation of migration energies and diffusion pathways. It is also possible to calculate actual reaction pathways, processes that can never be observed directly in any microscope. Of course, it is always possible to calculate such things without any image, but then all possible configurations of a nanostructure need to be calculated, which is a vast number of trial structures. Without an image for guidance, it is certain that large numbers of irrelevant structures will be calculated, and there is the possibility that the right structure might be missed.

Poised between synthesis and atomistic processes, the STEM fills an exciting and central area of nanotechnology. In this chapter we will cover the basics of the technique, including probe formation, image resolution and contrast in different modes, and analytical techniques. More details on imaging theory have been given elsewhere [7–11]. Here, we will illustrate the discussion with a number of examples in different areas of nanotechnology, including nanocatalysis, nanocrystals, nanotubes, nanostructured magnetic materials, and nanoscale phase separation in complex oxides, pointing out how this level of characterization can provide new insights into the functionality at the nanoscale [12,13]. Other applications in material science have recently been reviewed by Varela et al. [14]. In addition, we present a new possibility that is opened up by the new aberration-corrected STEMs. Correcting the lens aberrations allows the objective aperture to be opened up, thereby obtaining higher resolution. At the same time, as in an optical instrument like a camera, the depth of field is reduced. Present-day aberration-corrected STEMs have a depth of field of only a few nanometers, and so it becomes possible to effectively depth slice through a sample and to reconstruct the set of images into a 3D representation of the structure. The technique is
comparable to confocal optical microscopy, but provides a resolution that is on the nanoscale.

2. Imaging in the Scanning Transmission Electron Microscope

Figure 6.2 shows the main components comprising the aberration-corrected STEM. Electrons are accelerated from a source and focused into a point on the specimen by a set of condenser lenses and an objective lens. An objective aperture limits the maximum angle of illumination included in the incident probe, which is scanned across the sample by a set of scan coils. The output of a variety of possible detectors can then be used to form an image. In fact, multiple detectors can be used simultaneously to give different views of the sample, providing different but complementary information. The usual detectors include a BF detector that intercepts the transmitted beam and an annular dark field (ADF) detector that surrounds the transmitted beam to collect scattered electrons. The inner angle of this detector can be changed with postspecimen lenses from just outside the incident beam cone, which gives maximum efficiency for collecting scattered electrons, to several times this angle, that enhances the atomic number (Z) dependence of the image contrast. This latter configuration is often referred to as a Z-contrast or high-angle ADF (HAADF) image. Also, normally, part of the STEM is an EELS system, comprising spectrometer and parallel detection system using a charge-coupled device (CCD). Coupling lenses may be required to provide sufficient collection efficiency into the spectrometer.

Other detectors are also possible; an energy-dispersive x-ray detector is common; also secondary electrons, cathodoluminescence, or electron beam-induced

Figure 6.2. Schematic showing the main components of a high-resolution dedicated STEM [adapted from ref.14].
current can all be used to form an image. However, these signals tend to be lower, possibly very much lower, in intensity and therefore may be insufficient to form a clear, high-resolution image of a nanostructure in a reasonable exposure time. Typically, one would image a nanostructure using the high-intensity transmitted electron detectors, then stop the beam on the nanostructure for detection of x-rays or EELS data. Alternatively, one may be able to scan with a larger, higher current beam to obtain sufficient signal-to-noise ratio in some weaker signal of interest, sacrificing spatial resolution. Low-loss features in the energy loss spectrum or low-energy core loss edges are particularly useful in this regard.

In the past few years, the achievable resolution in STEM has more than doubled, and the first direct image of a crystal showing sub-Ångstrom resolution has been achieved with a 300-kV STEM (see Fig. 6.3) [15]. The reason for this impressive progress is that it has become possible to correct the major geometrical aberrations of the probe-forming lenses [16–18]. The traditional round magnetic lens has unavoidable aberrations that have limited the useful aperture that could be used, thus limiting resolution.

Although it has long been known that multipole lenses could in principle be used to correct these aberrations, successful implementations of aberration-correcting systems have only appeared in the past few years. The reason for this is the need to tune all the low-order aberrations simultaneously for the best focused spot. Optimization of the first-order aberrations astigmatism and focus

![Figure 6.3](image.png)

**Figure 6.3.** Z-contrast image of silicon taken along the (112) zone axis, resolving columns of atoms just 0.78 Å apart [adapted from ref. 15]. Image recorded with the ORNL 300 kV VG Microscopes HB603U STEM equipped with Nion aberration corrector. Image has been filtered to remove noise and scan distortion.
can be done by hand, but it is impossible to focus by hand in the much higher
dimensional space needed to correct all nine first- and third-order aberrations.
Computer autotuning procedures are essential, where the computer takes over the
measurement of the aberrations, adjusts the multipole lenses, and iterates to the
optimum settings. Commercial systems are now available from Nion and CEOS
based on a quadrupole, octupole, or hexapole system, respectively [19,20]. It is
also possible to insert a postspecimen aberration corrector, to cure the spectrom-
eter aberrations and provide efficient collection of EELS data with the highest
possible resolution.

2.1. Probe Formation

The STEM probe is a demagnified image of the source, as seen clearly from the
ray diagram in Fig. 6.2. For high resolution a small probe is required, and source
brightness then becomes an important limiting characteristic. The commonly
used sources are a heated tungsten filament, a LaB₆ pointed filament, a Schottky
or thermal-assisted field emission source, and a cold field emission source.
Brightness depends both on the current density per unit area and on the angular
range filled by the beam. It is defined as

$$B = \frac{I}{\pi A \theta^2}$$  \hspace{1cm} (6.1)

where \(I\) is the beam current, \(A\) is the area of the beam, \(\theta\) is the illumination semi-
angle. The four sources are compared in Table 6.1, in the order of increasing
brightness, monochromaticity, and vacuum requirements.

It may be noted that brightness scales with beam energy, hence values for 200-
or 300-kV operation are 2× or 3× higher than that shown in Table 6.1. Brightness
is conserved in an optical system that is free of aberrations. Given the source sizes
in Table 6.1, it is clear that high demagnifications are needed to achieve probes of
atomic dimensions. If the source of radius \(r_s\) is demagnified by a factor \(M\) to form
the probe, giving a geometric probe radius of \(r_s/M\) in the absence of aberrations,
the angular divergence will be increased by a factor \(M\). To avoid broadening the
probe due to lens aberrations, the angular aperture therefore has to be restricted
at some point in the optical column. In practice, this means that only a small frac-
tion of the emitted beam current will end up in the probe, and the choice of probe

<table>
<thead>
<tr>
<th>Source size</th>
<th>Energy spread FWHM (eV)</th>
<th>Brightness ((\text{Asr}^{-1}\text{ cm}^{-2})) at 100 kV</th>
<th>Total emission current (µA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tungsten filament</td>
<td>30 µm</td>
<td>5 \times 10^5</td>
<td>100</td>
</tr>
<tr>
<td>LaB₆</td>
<td>10 µm</td>
<td>1 \times 10^6</td>
<td>50</td>
</tr>
<tr>
<td>Thermal field emission</td>
<td>100 nm</td>
<td>0.6 \times 10^6</td>
<td>100</td>
</tr>
<tr>
<td>Cold field emission</td>
<td>5 nm</td>
<td>0.3 \times 10^6</td>
<td>5</td>
</tr>
</tbody>
</table>
size becomes a trade-off between resolution and signal-to-noise ratio. The ultimate resolution can be achieved only with zero beam current.

Lens aberrations fall into two main classes: (1) geometric aberrations due to errors in the optical path lengths and (2) chromatic aberration due to a spread in energy of the beam. Geometric aberrations mean that rays traveling at an angle to the optic axis are focused at a different point to rays traveling almost parallel to the optic axis, which define the Gaussian focus point. Spherical aberration is the most well-known geometric aberration because it was the dominant aberration before correction became possible. A schematic depiction of spherical and chromatic aberration is presented in Fig. 6.4.

The aberration is the error in optical path length between the actual wave front and the perfect sphere, which is conventionally expressed as a power series in angle \( \theta \). If, for simplicity, we ignore all nonrotationally symmetric aberrations, the aberration function becomes

\[
\chi(\theta) = \frac{1}{2} \Delta f \theta^2 + \frac{1}{4} C_S \theta^4 + C_5 \theta^6 + \frac{1}{8} C_7 \theta^8 + \ldots + \chi(\theta),
\]

where \( \Delta f \) is the defocus, \( C_S \) is the coefficient of third-order spherical aberration, the dominant geometric aberration in an uncorrected microscope, and \( C_5 \) and \( C_7 \) are the coefficients of fifth- and seventh-order spherical aberrations, respectively. For round magnetic lenses, these are all positive coefficients and have dimensions of length. The aberration in radians is just \( \gamma = 2 \pi \chi / \lambda \), where \( \lambda \) is the electron wavelength. Before aberration correction, it was normal to partially compensate for the \( C_S \) term by a small amount of negative defocus, weakening the lens slightly to give less aberration at high angles. In Fig. 6.4b, the effect is seen by

![Figure 6.4. Schematic showing the action of a perfect lens (a), the effect of geometrical aberrations that bring rays at different angles to a different focus (b), the chromatic aberration which blurs any single ray path (c), and the definition of the aberration length (d), the path length from the Gaussian sphere to the true wavefront.](image)
imagining the specimen raised to a point where the rays cross closest to the axis forming a disk of least confusion. However, compensation can only be achieved over a restricted range of angles because spherical aberration and defocus have a different angular dependence.

Geometric aberrations bring the rays at different angles to different focus points along the optic axis, meaning that they are displaced laterally in the Gaussian focus plane. The amount of sideways displacement \( \delta \) is related to the gradient of the aberration function [21]

\[
\delta(\theta) = \Delta f \, \theta + C_3 \, \theta^3 + C_5 \, \theta^5 + C_7 \, \theta^7 + \ldots + ,
\]

which is the reason why the \( C_3 \) term is referred to as third-order spherical aberration. An approximate idea of the magnitude of these different terms can be seen by plotting their separate contributions, as shown in Fig. 6.5.

This illustrates well how the optimum probe represents a balance between diffraction broadening at the aperture, which is less for a large aperture, and the geometrical aberrations, which are reduced for a small aperture. The diffraction pattern of the circular aperture is an Airy disk with first minimum at a radius \( 0.61 \, \lambda / \theta \), so we have taken \( 0.3 \, \lambda / \theta \) as a measure of the average sideways displacement due to diffraction. For an uncorrected system, the conditions around point A represent the optimum probe size; if third-order spherical aberration is corrected,

![Figure 6.5](image-url)

**Figure 6.5.** Sideways image spread introduced by the third-, fifth-, and seventh-order geometric aberrations, by chromatic aberration and by diffraction by the aperture of semiangle \( \theta \).
then the probe will be limited by the fifth-order term and the optimum probe will be achieved around point B, approximately a factor of two smaller. This is the reason for the factor of two gain in resolution with a third-order aberration-corrected STEM [8,12,13,16,22]. More advanced correctors are currently being constructed that will correct fifth-order aberrations, when the limiting geometric aberration will become seventh order, and another factor of two reduction in probe size is anticipated [22]. Also shown on the plot is the effect of chromatic aberration, which introduces a focal spread given by

\[
\Delta = C_v \sqrt{\left(\frac{\Delta V}{V}\right)^2 + \left(\frac{2\Delta I}{I}\right)^2},
\]  

where \( \Delta V \) is the standard deviation of the energy spread of the beam, assumed Gaussian, \( V \) is the accelerating voltage, and \( \Delta I \) is the standard deviation of fluctuations in objective lens current \( I \). In this case the sideways spread is a little misleading, because we will see that at the limit of resolution the STEM image is insensitive to chromatic aberration effects. They do not limit the maximum resolution; instead, they reduce the contrast at lower spatial frequencies.

Although these considerations give a good feel for the magnitude of the various aberrations, calculation of the probe intensity profile and optimization of the conditions require a wave-optical formulation of the problem. As seen from Eq. (6.2) the geometrical aberrations are not independent terms to be added in quadrature, but one aberration can be balanced against another to produce an optimum result. As already noted, in the case of a \( C_S \) limited system, the optimum conditions were established a long time ago [23,24]. The optimum aperture is chosen to allow one wavelength of third-order spherical aberration at its perimeter, and is therefore given by

\[
\alpha_{\text{opt}} = \left(\frac{4\lambda}{C_s}\right)^{1/4},
\]  

Optimum defocus is chosen to provide an exactly compensating contribution at the aperture rim and is given by

\[
\Delta f_{\text{opt}} = -\sqrt{C_s\lambda},
\]  

and the two contributions give a maximum aberration of \(-\lambda/2\) at an angle of \(\alpha_{\text{opt}}/\sqrt{2}\). The probe profile is then quite similar to an Airy disk distribution and the resolution due to aberrations alone \(d_a\) is normally taken as the Rayleigh criterion for a circular aperture, the radius of the first zero, 0.61 \( \lambda / \alpha_{\text{opt}} \), giving

\[
d_a = 0.43\lambda^{3/4}C_s^{1/4}
\]  

This is also approximately the full-width-half-maximum (FWHM) of the probe intensity profile, which we shall use as the definition of probe size. Similar
considerations apply to aberration-corrected probe-forming systems. The optimum resolution for a C₅ limited system is [25]

\[ d_a = 0.43 \lambda^{5/6} C_5^{1/6} \]  

(6.8)

and for a C₇ limited system

\[ d_a = 0.43 \lambda^{7/8} C_7^{1/8} \]  

(6.9)

although by this time nonround aberrations are likely to be limiting the resolution quite significantly [25,26].

These limiting values for resolution do not include any contribution due to the geometrical source size. Clearly, for the highest possible resolution, the size of the geometrical image of the source, \( d_s \), should be arranged to be significantly less than the size of the spot determined by aberrations, \( d_a \); otherwise, the image will be blurred and the resolution degraded. Sources are usually considered to be incoherent emitters, with each point on the source emitting independently. Then the overall probe size \( d \) is approximately given by adding the two contributions in quadrature,

\[ d = \sqrt{d_s^2 + d_a^2}. \]  

(6.10)

For \( d_s << d_a \), we achieve the electron-optical resolution limit. Under these conditions the probe will therefore be highly coherent, that is, each point on the objective aperture and each point in the probe profile will have strong and constant phase relationships with each other. At the opposite extreme, if \( d_s \) is comparable or larger than \( d_a \), we have an essentially unaberrated image of the source, an incoherent probe. Lattice imaging, both BF and Z-contrast, relies on interference to form the image; the incoherent portion of the probe reduces the visibility of the interference fringes or may eliminate them altogether. The lattice image is generated by the coherent part of the probe \( d_a \) and blurred by the incoherent part \( d_s \). The effect can be modeled by convoluting a simulated image with a Gaussian of FWHM \( d_s \). To see a spacing \( d \) with high contrast, the source contribution \( d_s \) must be small compared with \( d \).

Calculation of the actual probe profile must be done wave-optically, by integrating the contributions of partial waves within the objective aperture, including their phase aberration term \( \exp (i \gamma) \). For convenience, we separate the electron wave vector into one longitudinal and two transverse components, i.e., \( \mathbf{k} = (K, k_z) \), where we have defined \( | \mathbf{k} | = 1 / \lambda \), and similarly the object space \( \mathbf{r} = (R, z) \), where \( \mathbf{R} \) is a vector representing the transverse coordinates and \( z \) is the coordinate along the optic axis. Gaussian focus is at \( z = 0 \). The phase error from the Gaussian sphere to a transverse point \((\mathbf{R},0)\) is then \( \exp (2\pi i \mathbf{K} \cdot \mathbf{R}) \), so the probe amplitude at point \( \mathbf{R} \) in object space is obtained by integrating the aberrated partial waves over the objective aperture,

\[ P(\mathbf{R}) = \int e^{2\pi i \mathbf{k} \cdot \mathbf{R}} e^{i\gamma(k)} d\mathbf{K}, \]  

(6.11)
which is simply the Fourier transform of the aberrated wave over the objective aperture. The probe intensity profile is then

\[
P^2(R) = \left| \left| e^{i2\pi k \cdot R} e^{i\gamma(k)} \right| \right|^2,
\]

Figure 6.6 shows probe intensity profiles as a function of defocus for a 300-kV STEM with and without the correction of third-order spherical aberration. Note that the defocus is inserted into the aberration function to give the probe profile in the plane, \( z = \Delta f \). The profiles are shown on the same axes and for the same total current in the probe. It is immediately clear that aberration correction not only gives a smaller probe, but also much higher peak intensity. This is very important for the imaging of individual atoms or nanostructures, because it results in a higher signal-to-noise ratio.

Figure 6.7 compares an image of Pt\(_3\) trimers on a \( \gamma \)-Al\(_2\)O\(_3\) substrate taken before [27] and after [28] aberration correction. The improved image quality is striking, both in terms of resolution and signal-to-noise ratio. It is significant that the three Pt atoms do not form an equilateral triangle. This is visible in the uncorrected image, but the corrected image allows a more precise measure of the atomic configuration. The explanation for the distorted shape comes through density functional total energy calculations. Placing bare Pt\(_3\) trimers on a \( \gamma \)-Al\(_2\)O\(_3\) \( \langle 110 \rangle \) surface and relaxing the structure to equilibrium results in an almost equilateral triangle with bond lengths of 2.59, 2.65, and 2.73 Å, close to the interatomic spacing in metallic Pt. The longer bonds can only be explained by adding an OH group to the top of the trimer, when two of the bonds lengthen to 3.1 and 3.6 Å, in excellent agreement with observation. The addition of the OH group also changes the electron density on the Pt, from slightly electron-rich to electron-poor, which explains the observed chemical nature of the Pt [28].

\[
P^2(R) = \left| \left| e^{i2\pi k \cdot R} e^{i\gamma(k)} \right| \right|^2,
\]
2.2. Image Contrast

The BF and ADF detectors in STEM can be arranged to give very different and complementary images. Figure 6.8 shows a through-focal series of images of gold nanoparticles. At each focus value images were recorded simultaneously with the two detectors, although only a few representative values of defocus are shown from each series. Linescan A shows how the dark field image is sensitive to individual gold atoms; isolated gold atoms can be seen away from the nanocrystal out on the carbon film. These atoms provide an absolute intensity calibration; peaks of the same height that are seen at the edge of the nanocrystal can therefore be identified as single gold atoms. As the gold atoms move into the nanocrystal, the intensity increases according to the number of atoms in the column [29,30]. Notice that the image does not reverse contrast at any defocus value. These are the characteristics of an incoherent image, as familiar from normal photography, and the optimum focus is therefore that which reveals the nanocrystal with the best contrast. In an incoherent image the intensity is a simple convolution of a (positive) function representing the scattering cross section of the object, \( O(R) \), and a resolution function, \( P^2(R) \) i.e.,

\[
I(R) = O(R) \otimes P^2(R), \tag{6.13}
\]

The BF image, on the other hand, gives an image equivalent to that obtained with an aberration-corrected TEM, a coherent phase contrast image. The gold nanocrystal is seen with high contrast and minimal Fresnel fringes blurring the

Figure 6.7. Images of Pt₃ trimers on γ-Al₂O₃ (110) surfaces obtained (a) before [27], and (b) after aberration correction, showing the improved resolution and contrast. Measured spacings from (b) are shown on the right, and closely match with first-principles simulations (c) if the Pt₃ is capped with an OH group [adapted from ref. 28].
FIGURE 6.8. Selected images of gold nanoparticles supported on a thin carbon film taken from a through-focal series of (a) ADF Z-contrast images and (b) simultaneously collected BF phase contrast images, showing their very different characteristics. Defocus is shown in the lower right corner of each frame. Linescan A across the Z-contrast image shows single gold atoms (c). Linescan B can be quantified to give the number of gold atoms per column (d), based on image simulations (e), and allow the approximate 3D shape of the nanocrystal to be estimated (f) [adapted from ref. 30].
edge of the particle (which is often referred to as image delocalization). However, the image changes form with defocus, reversing contrast from 0 to 5 nm, and does not detect the individual gold atoms. The reason that individual gold atoms cannot be located from the BF image alone is because of the speckle pattern contrast from the thin carbon film used to support the sample. The signal of a single gold atom cannot be distinguished from the speckle of the support, whereas in a Z-contrast image the single gold atom \((Z = 79)\) scatters about as many electrons as the whole thickness of the carbon support \((Z = 6)\). The advantage of the phase contrast image is that it is more sensitive to light atoms. Figure 6.9 compares the images of multiwall carbon nanotubes in Z-contrast and phase contrast modes. The multiwall structure can just be seen in the Z-contrast image, but shows stronger contrast in the phase contrast image.

The reason for the very different forms of the BF and ADF images is quite simple to understand. It is related to the different angular sizes of the detectors. In Section 2.1, we have seen that for high-resolution imaging the incident probe is a coherent spherical wave (slightly aberrated) that converges onto the specimen. It generates some scattered waves which propagate out of the specimen and onto the detectors. Most of these scattered waves remain coherent with the unscattered beam, and will interfere with it. The important length scale here is set by the atomic spacings \(d\), which are around 1–3 Å in all materials and lead to diffraction at angles \(n\lambda/d\) where \(n\) is an integer. Typical first-order diffraction angles are around 10–20 mrad. Detectors that are small on this scale are sensitive to the details of the interference pattern, and phase contrast results. On the other hand, detectors that are large with respect to typical diffraction angles will not be sensitive to any fine details of the interference pattern, but only to the overall intensity integrated over a large number of diffraction peaks. A large detector, therefore, gives an image whose contrast is based on intensities, which is the definition of an incoherent image. This is illustrated schematically in Fig. 6.10, which shows the diffraction pattern in the detector plane for a simple cubic crystal.

The central disk is just the transmitted probe falling on the detector, and all the other disks are caused by diffraction. The BF detector is small in angular extent compared to the diffraction angles, while the ADF detector is large. Note that if

![Figure 6.9](image)

**Figure 6.9.** Images of multiwall carbon nanotubes in (a) ADF Z-contrast and (b) BF phase contrast modes.
you were to look at an actual diffraction pattern, then it would not show spots or disks at high angles because of the influence of thermal vibrations. Each successive electron can see the atoms in a slightly different position because of their thermal motion, and the details of the pattern are different at high angles. The actual pattern from many scattering events looks diffuse, and the scattering is referred to as thermal diffuse scattering. Thermal effects actually assist in breaking the coherence of the ADF image.

For the same reason, the overall form of the ADF image is relatively insensitive to the thickness. Dynamical diffraction shifts the amplitude between different diffracted beams, which causes changes in the details of the diffraction pattern. The phase contrast image changes form and can reverse contrast as the thickness increases. However, the Z-contrast image does not show any dramatic changes in form, as seen from Fig. 6.8. The reason again is that changes in the interference pattern are on a local scale with respect to the ADF detector and are integrated by it. Only the changes in the total intensity falling on the detector affect the image. The thickness dependence of the Z-contrast image is therefore much simpler than that of a BF image. The signal increases initially as the number of atoms increases, but then reaches a point where much of the probe has been scattered onto the detector and the signal saturates. This leads to characteristic curves that have approximately the same shape for all materials, scaled by the overall $Z^2$ factor of the scattering cross section. The simulated thickness dependence for gold is shown in Fig. 6.8e for various values of defocus, and all curves show this characteristic thickness behavior.

These simulations can be compared with the experimental data to estimate the number of atoms in each column of the nanocrystal. The intensity scale is calibrated by the intensity of the single gold atom in linescan A. Short columns at the...
edge of the nanocrystal are in the linear range of the thickness dependence, and the precision in column length is just a single atom. In the thicker region of the nanocrystal, where saturation sets in, the precision is lower. The defocus scale is set by the image where the single atoms show the best contrast, linescan A. Optimum defocus for these conditions is 2 nm. The maximum contrast in the center of the nanocrystal is obtained at a defocus of 1 nm (linescan B), showing that the entrance face of the nanocrystal is flat to about 1 nm. Hence the approximate 3D shape of the nanocrystal can be determined, as shown in Fig. 6.8f.

Figure 6.10 also illustrates another important difference between BF and ADF imaging, the achievable resolution. Image contrast requires interference, and the example of a crystal specimen shows clearly that for this crystal spacing the BF detector sees no interference because all the diffracted disks fall outside the detector. The atoms are too close to be resolved. The ADF detector, however, does see interference effects, and will show an image. In practice, the situation may be more complicated because the BF detector can see contrast formed as a result of multiple scattering. Sum and difference frequencies can appear giving spurious image features, and image simulations are important to interpret the complicated contrast effects that result.

It seems obvious that in an incoherent image, the smaller the probe the better the resolution, or the sharper the atoms. This is true at present-day resolutions of around 0.6–1 Å, because the probe is still large compared to the region of the atom that scatters to high angles, which is just a few tenths of an angstrom. The images of Pt atoms seen in Fig. 6.7 are therefore the images of the probe rather than the images of the atoms. The same applies to crystals. As the probe is sharpened, it picks out the individual columns of atoms with more contrast; more of the probe strikes the target column and less is spread over neighboring columns. This can also be seen from the diffraction perspective in Fig. 6.10. Making the probe smaller requires enlarging the probe-forming aperture, and the diffraction disks will overlap to a larger extent. As the probe scans a crystal, the overlap region experiences alternating constructive and destructive interference. The intensity changes from white to black to white as the probe scans from one column to the next. Since it is the overlap region that gives the contrast, larger overlaps mean larger contrast. Quantitatively, this is usually expressed in terms of a transfer function in reciprocal space,

\[ I(\mathbf{K}) = O(\mathbf{K}) \cdot T(\mathbf{K}), \quad (6.14) \]

where \( O(\mathbf{K}) \) is the spatial frequency spectrum of the object and \( T(\mathbf{K}) \) is an optical transfer function (OTF) or modulation transfer function of the imaging system. Equation 6.14 is the Fourier transform of Eq. 6.13. Therefore, for a thin object, the OTF is the Fourier transform of the probe intensity. If the probe is much sharper than any details in the object, its Fourier transform is very broad in reciprocal space, so all spatial frequencies in the object are transferred to the image and a true representation of the nanostructure is seen. However, even the aberration-corrected probe is still significantly larger than the screened nuclear potential that scatters the beam to the ADF detector. High spatial frequencies in the object are therefore seen with reduced contrast in the image. This is how the probe controls the transfer of spatial frequencies to the image.
Figure 6.11a shows transfer functions for the ORNL VG Microscopes HB603U 300-kV STEM, before and after aberration corrections up to third-order, and the expected transfer function for a fifth-order corrected 200-kV Nion UltraSTEM. All have a generally triangular transfer function, with slowly decreasing transfer at higher spatial frequencies as the diffraction disks overlap progressively less. There is about a factor two improvement in resolution for each order of aberration correction, in agreement with the rough estimates from Fig. 6.5. Note that the information transfer cutoff for the third-order corrected microscope is near 0.5 Å, whereas the fifth-order corrected microscope still shows good contrast in this regime despite an accelerating voltage of only 200 kV.

Also shown is the transfer function for the third-order corrected 300-kV STEM with an unrealistically high energy spread of 1 eV, showing how the information limit and therefore resolution in the STEM is robust to chromatic aberration effects [31]. The explanation is that near the limit of resolution the diffraction disks are overlapping only at the edge of each disk. The beams responsible for the image contrast are passing almost symmetrically on either side of the optic axis. The relative phase of beams at equal angles to the optic axis is insensitive to a change in focus, and so there is an achromatic line along the center of each overlap region. Only away from this line is the interference sensitive to defocus, and hence as the disks overlap more, the image contrast becomes more sensitive to chromatic instabilities. Thus it is the mid-range spatial frequencies that suffer reduced contrast. This is an important advantage compared with the BF phase contrast image, in which chromatic instabilities have always been and remain an important limiting factor for achieving the highest resolution.

Equation 6.14 applies only if the specimen is sufficiently thin that the probe profile inside the specimen is the same as the incident probe profile; in other words, there has been no significant dynamical scattering or beam broadening. Figure 6.11b compares the Fourier transform of a simulated image of Si (112) just 1-nm thick with the Fourier transform of the incident probe. The probe indeed acts as the envelope of the frequencies seen in the image. The simulation was performed using Bloch wave calculations [32,33], and the probe for this comparison has been convoluted with a Gaussian source of size $d_s = 0.31$ Å, reducing the high-frequency transfer significantly. As the specimen becomes thicker, the incident probe is no longer the effective transfer function because dynamical scattering and beam broadening take place. The general effect is to add a uniform background to the image, reducing the magnitude of the contrast over the whole frequency range. The best defocus is no longer the electron optical optimum defocus, but one that pushes the focus into the specimen so that more of the specimen thickness is close to optimum focus. However, the image retains its incoherent characteristics and the optimum focus can still be chosen by eye to be the focus that gives the sharpest image.

The final resolution is determined not by the aperture cutoff, which is 0.45 Å for the 22-mrad aperture used, but by the signal-to-noise ratio of the data. In the Fourier transform of the experimental data, the (173) reflection at 0.71 Å had a signal-to-noise ratio of about 2.5, giving a 99% confidence that it is real. However, the (555)
FIGURE 6.11. (a) Transfer functions for incoherent imaging in the ORNL 300 kV STEM before and after correction of third-order aberrations showing the greatly extended information transfer. Parameters are $C_s = 1.0$ mm, $C_c = 1.6$ mm, $\alpha_{opt} = 9.5$ mrad, $\Delta f = -45$ nm for the uncorrected case and $C_s = -37$ µm. $C_5 = 100$ mm, $\alpha_{opt} = 22$ mrad, $\Delta f = 2$ nm after correction, energy spread 0.3 eV in both cases. The dotted line shows the effect of increasing the energy spread to 1 eV, giving reduced midrange transfer but no reduction in resolution limit. Also shown is the transfer expected for a 200-kV STEM with full fifth-order aberration correction ($C_s = 23$ µm, $C_5 = -2$ mm, $C_7 = 100$ mm, $C_c = 1.5$ mm, energy spread 0.3 eV). (b) Comparison of the Fourier transform of a simulated image of Si (112) with the Fourier transform of the probe showing how the latter is acting as the transfer function for the image ($C_s = -37$ µm, $C_5 = 100$ mm, $C_7 = 1.6$ mm, energy spread = 0.3 eV, $\alpha_{opt} = 22$ mrad, $\Delta f = 2$ nm, thickness = 1 nm, source size = 0.31 Å, detector angles 90-200 mrad).
reflection at 0.63 Å had a signal-to-noise ratio of only 1.4, giving a confidence level of only 84%. It can be seen that the Fourier transform method is a valuable means for accurate determination of information limit. However, a word of warning is needed. Great care must be taken to ensure that the recorded data is a true representation of the intensity. No black level should be used to enhance contrast, because any clipping of the signal will introduce spurious high frequencies. Similarly, spurious spots can be introduced from instabilities in the scans or selection of a section of image whose dimensions are not exact numbers of lattice spacings. Information transfer, although important, does not define resolution, which should always be determined from a real space image as shown in Fig. 6.3 [15, M. A. O’Keefe, L. F. Allard, and D. A. Blom, J. Electron Microsc. 54 (2005) 169].

It may seem surprising at first sight that the STEM BF image is equivalent to that obtained in an aberration-corrected TEM, but this is solidly based on time-reversal symmetry and is known as the reciprocity principle. To make the equivalence clear, Fig. 6.12 compares the essential optics for BF imaging in the fixed beam TEM and the STEM. The ray diagrams are shown for one image pixel, and it is seen that for equivalent apertures the only difference is the direction of electron propagation. Elastic scattering is the basis of phase contrast imaging, and depends only on scattering angle and not on propagation direction. Therefore, the two optical arrangements will give identical results; the TEM condenser aperture is equivalent to the STEM BF collector aperture and the objective aperture remains the same. Note, however, that the terminology can be confusing: in a TEM/STEM microscope, the STEM objective (probe-forming) aperture is usually the same.

**FIGURE 6.12.** Ray diagrams for TEM and STEM to illustrate the reciprocal nature of the bright field images. The BF image in aberration-corrected STEM gives an image optically equivalent to that obtained with aberration-corrected TEM.
aperture used as the condenser aperture in TEM mode. The difference between the two arrangements is that in the TEM all pixels in the image are obtained in parallel, whereas in the STEM they are obtained one at a time by scanning the probe.

The BF image amplitude is now given by a convolution of the exit face wave function $\psi_e(R)$ with the complex impulse response function of the lens $P(R)$ given by Eq. 6.11. The image intensity becomes the square of the convolution,

$$I(R) = |\psi_e(R) \otimes P(R)|^2$$  

(6.15)

This is much more complicated than the corresponding expression for an incoherent image (Eq. 6.13), which is a convolution of intensities. In phase contrast imaging it is the amplitudes that are transferred through the lens system, and the intensity is taken later. As noted earlier, interference in the detector plane is important for coherent imaging, and we cannot approximate the image to any simple incoherent form as we can for the ADF image. This means that coherent image contrast can be varied from black to white through a change in one of the terms of the aberration function, for example, the defocus. It also means that information on the phases is lost on taking the image intensity, and unique structure inversion becomes difficult.

Therefore, resolution of a BF phase contrast image cannot be defined on the basis of image intensities but on the amplitude transmission characteristics of the objective lens. It is conventionally defined in terms of a weak phase object. The specimen is considered to be vanishingly thin, so it acts as a weak phase grating, refracting the incident beam but not changing its amplitude. It is simplest to consider the TEM geometry, when the exit-face wave function is given by

$$\psi_e(R) = \exp \{ -i \sigma \phi(R) \} = 1 - i \sigma \phi(R),$$  

(6.16)

where $\sigma = 2 \pi m e A / h^2$ is the interaction constant and $\phi(R) = \int \phi(r) dz$ is the projected potential. Phase changes in the exit wave therefore map the projected potential of the specimen. These phase changes can be represented vectorially by the generation of a scattered wave $\psi_s(R) = -i \sigma \phi(R)$, which is oriented at $\pi/2$ to the incident wave as shown in Fig. 6.13a. The principle of phase contrast imaging is to rotate the phase of the scattered beams by an additional $\pi/2$. This converts the phase changes in the exit-face wave function to amplitude changes in the image, to give an image amplitude

$$\psi_i(R) = 1 - \sigma \phi(R).$$  

(6.17)

In light optics this can be done with a phase plate, but in electron optics we must use the lens aberration function itself. We therefore try to optimize the aberration function $\gamma$ to be as close to $\pi/2$ as possible over as large a range of angles as possible. Expressing the aberration phase change as $e^{i\gamma} = \cos(\gamma) + i \sin(\gamma)$, it is clear that it is the sin term that we need to maximize, and $\sin(\gamma)$ is defined as the phase contrast transfer function. Figure 6.13 compares phase contrast transfer functions for a 300-kV STEM before and after aberration correction. Since it is the lens aberrations that are used to give the image contrast, both begin at zero contrast for low spatial frequencies where the aberration function is zero.
With increasing angle to the axis (increasing spatial frequency), the aberration function increases quickly for the uncorrected case, oscillating rapidly for spacings below 2 Å. This rapid oscillation means different frequencies are seen with different contrast, but also sets stringent conditions on the maximum beam divergence that can be used (the incident beam divergence or condenser aperture size
in TEM, the collector aperture size in STEM). The angular aperture must be kept small on the scale of the oscillations or the aperture will average over the oscillating transfer function and the image contrast will be reduced. The effect can be simulated with an exponential damping function

\[
D_a = \exp \left[ -\pi^2 \alpha^2 K^2 (\Delta f + \frac{\lambda^2 K^2 C_S}{2} + \frac{\lambda^4 K^4 C_5}{2})^2 \right]
\]  

(6.18)

which multiplies the transfer function. It is shown in Fig. 6.13b for an aperture semiangle \(\alpha\) of 0.25 mrad (modeled as a Gaussian with standard deviation 0.25 mrad [34]). After aberration correction the oscillations are pushed to higher spatial frequencies, resulting in an increased pass band before contrast reversals set in. Another consequence of the reduced aberrations is that the damping factor is also much reduced, which has important implications for the STEM. It allows the STEM collector aperture to be increased by a factor 10 to 2.5 mrad, as shown in Fig. 6.13c. The collection efficiency increases by two orders of magnitude, and BF STEM becomes a viable means for obtaining phase contrast images with the advantage that ADF images are available simultaneously and EELS can be performed with the same probe used for imaging.

Chromatic aberration effects due to a spread in beam energy or objective lens current lead to a focus spread, given by Eq. 6.4, and will again decrease the transfer. In phase contrast imaging, the effect is also described by an exponential damping factor [35]

\[
D_E = \exp \left[ -0.5 \pi^2 \frac{\lambda^2}{2} K^4 \Delta^2 \right]
\]  

(6.19)

and applies irrespective of whether the geometric aberrations are corrected or not. It is shown in Fig. 6.13b for an energy spread \(\Delta\) of 0.6 eV as appropriate for a thermal field emission gun, and in Fig. 6.13c for a spread of 0.3 eV appropriate for a cold field emission gun.

3. Spectroscopic Imaging

One of the key advantages of the STEM is the availability of the EELS signal, which can be obtained simultaneously with an atomic-resolution ADF image [36–40]. It is therefore straightforward to place the probe on an atomic column seen in the image and obtain a spectroscopic analysis. EELS reveals elemental features through characteristic core loss edges corresponding to inner shell excitations into the first available unoccupied states. The fine structure on such edges therefore provides information on the density of states seen in the vicinity of the excited species. EELS is similar to x-ray absorption spectroscopy, except that it can provide atomic-scale spatial resolution. The brightness of the STEM probe substantially exceeds that of third-generation synchrotron sources, making the STEM a powerful means for analyzing electronic structure and identifying impurity species or dopants within nanostructures. Spectroscopic imaging can also be achieved in the TEM through use of an energy filter; images are obtained in parallel and the energy is scanned. In the STEM the spectrum is obtained in parallel.
and the image is scanned. The key difference between the two arrangements is that in the TEM the energy loss electrons need to be brought to a focus on the image plane, and different energies will need a different focus. For an atomic-resolution image, the spread of energies allowed to contribute to the image needs to be a fraction of an eV to avoid chromatic damping, as discussed earlier. Therefore, given the small cross section for inner shell excitations, very little signal would be detected, and so far no atomic resolution spectroscopic images have been obtained in TEM mode. In the STEM arrangement, the focusing is done before the specimen; although there may be coupling lenses into the spectrometer, the focus precision required is only that needed to maintain the energy resolution on the CCD chip, which is orders of magnitude less than needed to maintain atomic resolution in the TEM image.

With the successful correction of aberrations in the STEM, the probe is now smaller and brighter, bringing major gains for EELS analysis as well as imaging. The smaller probe brings not only better spatial resolution but also more current on an individual column, resulting in a better signal-to-noise ratio and a higher sensitivity analysis. The highest sensitivity so far achieved has been the spectroscopic identification of an individual atom in a single atomic column of a thin crystal [6]. The sample was specially made by molecular beam epitaxy to contain various known concentration of La dopants in specific layers in a CaTiO₃ matrix. The lowest concentration layer was La₀.₀₀₂Ca₀.₉₉₈TiO₃, grown just one-unit-cell thick. A cross-section sample revealed bright spots as shown in Fig. 6.14. The expected frequency in the thin regions of the sample was consistent with the concentration and sample thickness, confirming that individual columns contained mostly individual atoms. Placing the probe over any one of the bright columns,

![Figure 6.14](image-url)
the EELS spectrum showed two distinct peaks corresponding to the La M$_{4,5}$ lines at 832 and 849 eV. This demonstrates the first spectroscopic identification of a single atom in its bulk environment. In addition, placing the probe at the neighboring TiO or O column positions that are located 2.8 and 1.9 Å away, respectively, the majority of the La M$_{4,5}$ signal disappeared, leaving a residual of about 10% and 20%, respectively. These distances are large compared to the probe size, and the residual intensity is due to dynamical diffraction and beam broadening that occur between the probe entering the crystal and reaching the depth of the atom.

It is now possible to perform full quantum-mechanical simulations for EELS core loss images, using accurate atomic wave functions and a full treatment of dynamical diffraction [6,41]. Simulated linescans are shown in Fig. 6.14 running from the Ca column through the adjacent O column for the La atom located at different depths. With the La atom close to the probe entrance surface, maximum signal occurs near the Ca column reducing monotonically toward the O column. With the La atom located deeper in the crystal, more of the probe intensity is scattered off the column before it reaches the atom, resulting in less signal when the probe is over the Ca column and correspondingly more signal when the beam is over the O column. The ratio of the two, therefore, indicates roughly the depth of the atom within the crystal and matches the experimental data for the La at around 100 Å in depth.

Figure 6.14 predicts that the peak La M$_{4,5}$ signal should appear just off the Ca column. This reflects the slightly less localized nature of the inelastic interaction with respect to the elastic image. The spatial resolution of a core loss EELS image is therefore expected to be quite as high as that of the corresponding ADF image. With the probe centrally located over the Ca column, there is maximum scattering into the ADF detector and minimum collected by the spectrometer. As the probe moves off the column the ADF scattering reduces faster than the EELS image, and the result is an increase in EELS signal.

There have been a large number of simplified treatments of EELS localization in the past, with conflicting conclusions. These calculations now provide a definitive answer. Figure 6.15 shows plots of the FWHM across EELS images of single atoms, thus removing any contribution of channeling effects and leaving only the probe itself and any ionization delocalization effect [42]. Results are shown for two aberration-free probes with 10 mrad and 20 mrad objective semiangles, resulting in FWHM intensities of 1.0 and 0.5 Å, respectively. The calculations reveal that the extent of the ionization delocalization can be of the order of 1 Å for the lighter elements.

Another potential pitfall using core loss excitations arises because they have a much lower cross section than the elastic (or quasielastic) scattering used to form the ADF image. To achieve a usable signal, beam exposure per pixel is often increased from microseconds for an ADF image to seconds for a core loss such as the O K edge near 532 eV. Consequently, there is a much-increased likelihood of beam damage occurring. A time sequence of spectra is useful to test for beam-induced damage artifacts. If the first and last spectrum look identical, then beam damage is not likely to be a problem. Various techniques can be used to reduce
exposure, such as rastering the beam in a 1 Å by 1 Å image or scanning a 2D image but collecting the EELS data only along the slow scan direction, but all reduce the spatial resolution of the data collected. Another useful reference, if possible, is to compare the spectra obtained by scanning a large area with minimal exposure per pixel. With nanostructures, one spectrum from one nanostructure can be compared to the sum of ten spectra from ten identical nanostructures each taken with one tenth the exposure. Such methods are necessary to ensure that data are representative of the specimen in its original state. For details on the quantification of the data and interpretation of the spectral features, see for example the book by Egerton [43].

4. 3D Imaging

In recent years, major progress has been made in obtaining 3D information from nanostructured materials through the use of tilt series tomography. A series of views in different projections can be reconstructed into a single 3D data set, which can then be viewed in any desired orientation. Spatial resolution has been demonstrated at the nanometer level [44]. The ADF image is very suitable for this procedure because it shows much reduced diffraction contrast effects compared with a BF image. This is important since the back-projection reconstruction procedure relies on the images being good representations of the projected mass thickness, so the incoherent characteristics of the ADF image are required. An additional constraint with present reconstruction algorithms is that they assume a perfect projection, that is, they assume the incident beam to be parallel. This
works in practice as long as the depth of focus is long compared to the sample thickness. However, as the desired spatial resolution increases, this requirement can no longer be met; a small probe is necessarily convergent and the projection becomes sensitive to the focus, with different parts of the sample in focus at different settings.

Aberration correction provides the increased spatial resolution by allowing the objective lens aperture to be increased. Just as in a camera, this results in a reduced depth of field. In fact, the depth of field $d_z$ decreases as the square of the aperture angle, whereas the lateral resolution, which has been the main motivation for aberration correction, increases only linearly with aperture angle. Depth resolution on the 300-kV STEM today is on the nanometer scale, and we can optically slice through a sample simply by changing the objective lens focus. With aberration correction, we find a natural changeover from the conditions appropriate for a tilt-series reconstruction to those for optical sectioning. A through-focal series now becomes a through-depth series, which can be recombined into a 3D data set [45] in a similar manner as used for confocal optical microscopy. However, the electron technique retains single-atom sensitivity in each image if the specimen is sufficiently thin, as shown by the recent location of individual Hf atoms in a subnanometer-wide region of SiO$_2$ in a high-K device structure [46].

Figure 6.16 shows selected frames of a through-depth image series taken from a Pt$_2$Ru$_4$ cluster-derived catalyst on a $\gamma$-alumina support. At $-8$ nm defocus, the lower right-hand corner of the alumina comes into focus and shows a lattice image. Individual Pt atoms are visible as bright spots. As the defocus increases, the focused region moves toward the upper left of the field of view. Profiles across the image frames show the probe FWHM of 0.07 nm. At $-16$ nm defocus, a rather brighter nanocrystal raft is seen. Intensity profiles across this suggest that it is two or three monolayers in thickness. Figure 6.17 shows a Z-contrast and simultaneously recorded BF phase contrast image of Pt$_2$Au$_4$ nanoparticles supported on TiO$_2$. The cluster is seen best in the Z-contrast image, whereas the support is seen more clearly in the phase contrast image. The 3D rendering is shown in Fig. 6.18.

5. Recent Applications to Nanostructure Characterization

5.1. Nanotubes

The Z-contrast image is particularly suited to imaging catalyst particles with high Z that are often used to grow nanotubes. Figure 6.19a shows Co–Ni catalyst particles in a network of single-wall nanotubes grown by laser ablation. The smallest particles observed were of 2-nm diameter, showing that in this case the diameter of the nanotubes was not dictated by the particle diameter.

Figure 6.19b shows a 2-nm diameter catalyst particle with a composition profile obtained by EELS. The Co/Ni ratio is constant across the nanoparticle,
indicating a uniform alloy composition. The intensity of the EELS signal is highest in the center of the nanoparticle, indicating a 3D particle shape.

This is another example where density functional calculations proved highly illuminating. Microscopy could never image the nucleation processes occurring within the laser ablation plume, but theory can investigate candidate processes to
Figure 6.17. Z-contrast (left) and bright field (right) images of Pt$_2$Au$_4$ nanoparticles supported on TiO$_2$, part of a 3D data set used to reconstruct the morphology of the support and location of the nanoparticles, as seen in Fig. 6.18.

Figure 6.18. A 3D rendering of the data set shown in Fig. 6.17 showing the TiO$_2$ support morphology and the metal nanoclusters as elongated ellipsoids. This reflects the lower depth resolution of the STEM image compared with its lateral resolution (a few nanometers in depth compared with a subangstrom lateral resolution). [adapted from A. Y. Borisevich, A. R. Lupini, and S. J. Pennycook, Proc. Natl. Acad. Sci. U. S. A. 103 (2006) 3044].
determine which are energetically favorable. The tube grows out from the cooling metal-carbon droplet, as the temperature falls below the eutectic point. Theory was used to calculate the energy of various trial structures, including graphite flakes, fullerene caps, and spheres, either on a metal surface or free standing. The key driving force is the very high energy of the carbon dangling bond. Without metal the fullerene has the lowest energy, but in the presence of metal it becomes favorable to bury dangling bonds in the metal and the cap or closed nanotube becomes energetically preferred. The calculations revealed that
it is favorable to insert pentagon units into the graphitic flake from the very early stages of growth, because it allows the flake to bend and bury the high-energy dangling bonds at its perimeter. The nucleation pathway will incorporate pentagons from the earliest stages of growth to allow the graphite flake to spontaneously bulge out into a cap shape. Then growth can proceed easily around the perimeter of the cap, and a capped nanotube is extruded [47].

Figure 6.19d shows the imaging of iodine atoms intercalated into single-wall nanotubes. Although taken before aberration correction, the individual iodine atoms could be detected within the tube walls (shown outlined in white in the figure). The shape appeared consistent with a spiral pattern, as indicated schematically, and again density functional calculations explained the spiral form. Iodine atoms like to form 1D chains, and the spiral allows the interatomic spacing of the iodine to match the carbon lattice. The potential energy minimum is very shallow, explaining why the arrangements are not perfect [48]. Electron microscopy of nanotubes is a very active field, see for example the book by Wang and Hui [49].

5.2. Nanocatalysis

Gold is not a good catalyst in bulk or in the form of large particles, but when prepared as nanoparticles on an oxide support, it becomes one of the most active catalysts for the oxidation of CO to CO$_2$. The cause of this activity has been a mystery for many years, with several explanations proposed. Early work suggested that there is a correlation between particle size and activity [50,51] although it is difficult to see the smallest nanoparticles by conventional TEM, hindering the identification of likely sites and mechanisms. We have used aberration-corrected STEM to image the clusters of an Au catalyst prepared by deposition/precipitation onto nanocrystalline anatase [52]. The catalyst showed 50% conversion at 235 K, which is comparable to the highest reported in the literature at this temperature. As seen in Fig. 6.20, most of the nanoparticles are 1–2 nm in diameter, and quantifying the thicknesses by comparing to image simulations revealed that they are just 1- or 2-layers thick. More recent work on model systems has shown that the thickness may be more important than the lateral extent, with bilayer structures having the highest activity [53]. Furthermore, the contrast seen in the image is in fact that of the TiO$_2$ substrate showing right through the Au nanoparticles. Since we certainly have the resolution to resolve an Au crystal, and none were seen on this sample, it seems likely that the nanoparticles may be in a liquid state. This is consistent with the known dependence of Au melting point on particle diameter, which extrapolates to room temperature at the size range of 1–2 nm [54,55].

XANES studies show that the Au particles are not reoxidized by exposure to air at room temperature, or even at 573 K, and so are unlikely to reoxidize under reaction conditions or during transfer into the STEM [56]. Therefore, we believe that the images shown in Fig. 6.20 are representative of the active state of the Au nanocatalysts. Based on these images, it was then possible to perform first-principles calculations to investigate the adhesion energies of Au$_N$ clusters on defect-free TiO$_2$ surfaces and also on the same surfaces with an O vacancy. Single
Au atoms adsorb preferentially at O vacancy sites with a binding energy about 0.9 eV larger on the O vacancy than on the stoichiometric (001) surface. The binding energy of AuN clusters at an O vacancy site is approximately constant with the number N of Au atoms, suggesting that only the Au atom on the O vacancy site forms a strong bond with the substrate. Further evidence for this conclusion is provided by the observation of the relaxed cluster structure, which shows one Au atom displaced into the O vacancy site. We conclude that O vacancies act as “anchors” to suppress coalescence, consistent with earlier calculations [57]. Such anchors facilitate the high areal density of small clusters.

Further calculations were carried out for the binding energies of CO and O₂ molecules. Although a single Au atom binds CO and O₂ only weakly, small Au clusters, such as Au₇ and Au₁₀, can adsorb both CO and O₂, unlike gold steps or surfaces. Thus it seems that the ability to bind both of the reactants is the key to the high activity of this unusual catalyst. For more examples of the electron microscopy of catalysts, see the book by Gai and Boyes [58].

5.3. La-Stabilization of Supports

γ-Al₂O₃ is used extensively as a catalytic support material because of its high porosity and large surface area, but at temperatures in the range of 1,000–1,200°C it transforms rapidly into the thermodynamically stable α-Al₂O₃ phase (corundum), drastically reducing the surface area and suppressing the catalytic activity.
of the system. The phase transformation can be shifted to higher temperatures by
doping with elements such as La, but previously it was not possible to establish
if dopants enter the bulk, adsorb on surfaces as single atoms or clusters, or form
surface compounds.

A Z-contrast image of a flake of La-doped \( \gamma \)-Al\(_2\)O\(_3\) in the [100] orientation is
shown in Fig. 6.21. The square arrangement of Al–O columns is clearly resolved.
Single La atoms are visible in the form of brighter spots on the background of
thicker but considerably lighter \( \gamma \)-Al\(_2\)O\(_3\) support. Most of the La atoms are located
directly over Al–O columns (site A), but a small fraction also occupies a position
shifted from the Al–O column (site B). The images reveal clearly that there is no
correlation in the distribution of dopant atoms, and a through-focal series shows
they are located on the surfaces of the flake. Density functional theory calculations
have demonstrated that La atoms are very strongly bound to the \( \gamma \)-Al\(_2\)O\(_3\) surfaces
(binding energy 7–8 eV), considerably stronger than to the \( \alpha \)-alumina surface
(binding energy 4.3 eV). Thus it became apparent that the stabilization is achieved
by single La atoms adsorbed on the \( \gamma \)-Al\(_2\)O\(_3\) surface, which improve its stability
with respect to phase transition and make sintering highly unfavorable [5].

5.4. Semiconductor Nanocrystals

Due to the quantum confinement of electrons and holes, semiconductor nanocrystals
offer the potential for sensitive tuning of optical emission or absorption wavelength via control of particle size, along with the possibility of 100% quantum
yields through use of a suitable passivating surface layer. Often referred to as
quantum dots, these nanostructured materials are finding major applications in
photovoltaics, photocatalysts, electronics, and biomedical imaging. At present
there is little detailed understanding of structure–property relationships at the
level of individual nanostructures. Z-contrast STEM can provide detailed

![Figure 6.21](image)
information on nanocrystal size, sublattice polarity, surface facets, defect content, and 3D shape [59,60].

Figure 6.22 shows an image of a Quantum Dot Corp. CdSe/CdS/ZnS core/shell nanorod viewed along the \([010]\) direction. The sublattice polarity is directly observable in the raw data though it can be enhanced by application of a band-pass Fourier filter.

Knowing the beam direction to be \([010]\) and the polarity of the hexagonal wurtzite structure, all the facets of the nanocrystal can be indexed. Furthermore, from the intensity trace the thickness of the nanocrystal can be seen. The entire 3D shape of the nanocrystal can therefore be determined from a single image. As shown in the schematic below the figure, in this particular configuration the nanocrystal is sitting on the carbon support film on a facet junction and rotated out of view before a second scan could be obtained. Images of these structures

![Figure 6.22. Z-contrast image of a CdSe/CdS/ZnS core/shell nanocrystal viewed along the [010] direction as shown in the ball and stick model below. The left-hand image shows raw data, the right-hand image has been band-pass filtered. A line trace across the raw image (left) taken across the long axis of the nanocrystal reveals the thickness profile of the core. The sublattice polarity is also directly visible, but is more clearly seen from a line trace across the filtered image (right). This nanocrystal is oriented as shown in the ball and stick model, the beam direction being vertical, and the scan direction for the thickness profile being shown by the grey arrow [adapted from ref. 60].](image-url)
show the 3D shape of the core and shell, and show the anisotropy of growth. They confirm predictions in the literature that the Se-rich face is the primary growth face for the CdSe core [61].

5.5. Magnetic Nanoparticles

When embedded in a nonmagnetic matrix, magnetic nanoparticles, possibly with a core/shell structure, are of significant scientific and technological interest. As in the case of the optical quantum dots, magnetic nanoparticles show size-tunable magnetic properties of interest for electronic devices and magnetic recording. In addition, engineering the interparticle spacing of nanoparticle arrays allows the interparticle magnetic coupling to be tuned. The Z-contrast STEM again offers the possibility to determine the size, 3D shape, and composition of these metal nanoparticles, even after embedding into a light matrix material such as Al₂O₃. For this application, however, the ability of the STEM to provide simultaneous EELS is a particular advantage. Figure 6.23 shows an example of such an analysis on a Ni nanoparticle embedded in an Al₂O₃ film [62]. The data are collected with a 100-kV STEM in which the resolution is lower, but the multiple-twinned structure of the Ni nanoparticle is clearly seen. The resolution is sufficient to place the probe down the edge of the nanoparticle and analyze those atoms in contact with Al₂O₃.

The EELS data, both from the center of the particle and from the edge, show an L₂₃ ratio characteristic of Ni metal. Taking account of the noise level in the spectra, it was determined that less than 5% of the surface atoms were oxidized. Therefore, these nanoparticles would not be expected to exhibit any magnetic dead layer and, indeed, the magnetic size determined from hysteresis is the same as that seen in the images.

![Z-contrast image of a Ni nanoparticle embedded in an Al₂O₃ film, with EELS spectra taken from the center and edge showing fine structure characteristics of Ni metal](image)

**Figure 6.23.** Z-contrast image of a Ni nanoparticle embedded in an Al₂O₃ film, with EELS spectra taken from the center and edge showing fine structure characteristics of Ni metal [adapted from ref. 62].
5.6. ZnO Nanorods

ZnO nanorods are of major interest as optical components due to their ability to grow as 1D wires, their visible light emission, and their high exciton-binding energy. Figure 6.24 shows a vertically aligned nanorod array containing multiple quantum wells on the tips of each nanorod [63,64]. The sample was grown by a catalyst-free method, using metal-organic vapor phase epitaxy. The interesting aspect of the growth procedure is that a uniform layer of ZnO is deposited initially at low temperature, but when the temperature is raised a spontaneous transition to a nanorod morphology occurs, driven presumably by the high surface energy anisotropy of ZnO. The quantum wells consisted of ten periods of $\text{Zn}_{0.8}\text{Mg}_{0.2}\text{O}/\text{ZnO}$ and exhibited a blue shift dependent on well width, the signature of quantum confinement. The STEM Z-contrast image showed the wells as slightly darker bands. The interfaces are believed to be structurally sharp, but not perfectly flat, accounting for the blurred nature of the image. Atomic-resolution images showed a surprising superlattice structure possibly resulting from ordered oxygen vacancies.

One of the advantages of a scanning microscope is that any signal can be monitored as a function of probe position and used to form an image. In optical materials, a particularly useful signal is the cathodoluminescence generated by the electron beam. Using an optical detection system, the light generated as the beam scans can be collected simultaneously with the ADF image to form a map showing the optical emission. Figure 6.25 shows some examples of ZnO nanorods where it is seen that only certain rods give optical emission. Although the reason for this behavior was not ascertained, the image shows how very different information is available in the cathodoluminescence image. The problem tends to be a low emission probability so that high beam currents are required for good-quality images; but in principle, this technique can be used to correlate optical emission

![Figure 6.24](image-url)
characteristics, such as emission strength and peak wavelength, with the size, shape, defect, or impurity content of individual nanostructures.

5.7. Nanoscale Phase Separation in Complex Oxides

An area of intense interest in recent years has been that of nanoscale phase separation in complex oxides, often referred to as charge-ordering [65]. Recently, we have been successful in observing stripes in Bi$_{0.38}$Ca$_{0.62}$MnO$_3$ with a periodicity of ~12 Å in the [100] direction. This material is ordered at room temperature, and the stripes are detected by EELS using the Mn L$_{2,3}$ ratio, as shown in Fig. 6.26. The ratio of the L$_3$ to L$_2$ peaks is sensitive to the Mn 3D occupation. Mn$^{3+}$ stripes are seen confined to a single Mn plane. No oxygen nonstoichiometry is detected, representing perhaps the first definitive observation of stripes of different valence in the bulk. This result highlights the very different nature of the structural image, which shows the random array of Bi dopants as bright spots, and the electronic effect, which is a quasiperiodic array of 1D stripes. Note that the EELS measure-
ment does not measure actual charge, just orbital occupation. Theoretical calculations indicate that the charges on the different Mn sites are in fact almost equal, the increased electron density that might be expected on the Mn\textsuperscript{3+} site being compensated by an outward structural relaxation of the neighboring oxygen atoms to maintain approximate charge uniformity. Spatially resolved EELS, unlike diffraction techniques, is unique in its ability to measure orbital occupation independent of any structural relaxations.

6. Future Directions

Future generations of aberration correctors promise the ability to correct all aberrations up to and including fifth order, and will bring lateral resolution to the sub-0.5 Å level with nanometer-scale depth resolution. The smaller probe will further improve sensitivity, allowing lighter atoms to be imaged in Z-contrast mode and improved detection limits for EELS. The higher current density available in these probes will enable data to be taken much faster. It will be possible to make movies of dynamical processes. With the depth resolution of the Z-contrast image, it will be possible to directly image atoms diffusing inside a host material or on its surface. We can expect to be able to section through nanostructured materials and reconstruct their 3D morphology, with a precision at the single-atom level. We will have the sensitivity to image single dopant atoms inside nanocrystals or along dislocation lines inside a bulk material and to probe their effect on the host electronic structure by EELS.
Along with such exciting new imaging techniques comes renewed interest in \textit{in situ} capabilities. If it were possible to maintain the resolution while also heating or cooling the sample, it would greatly facilitate studies of atomic diffusion, nanostructure nucleation, and growth processes and phase transformations. If a gas environment could also be maintained, it would be possible to image a catalyst nanocluster in operation or a nanotube growing out of a metal nanoparticle. We are just at the beginning of this revolution in nanostructure imaging. With such improved sensitivity we can look forward to more insights into the origin of the unique properties of the nanoscale, aided by first-principles electronic structure and total energy calculations. We still have a way to go to realize Feynman’s dream to just look at the atoms, but we are progressing toward that goal at a pace more rapid than ever before. The aberration-corrected STEM is allowing us to probe the atomic-level details of the nanoworld with sensitivity and versatility that is unprecedented in history.


\textbf{References}


34. J. Frank, Optik, 38 (1973) 519.