How the technique works

While light microscopes use visible light (400-700 nm), electron microscopes use beams of electrons, which have wavelengths about 10,000 times shorter.\(^1\) The shorter wavelengths allow for the images to be better resolved, down to about 0.1 nm. An electron beam is produced by heating a tungsten filament and is focused using magnetic fields.\(^2\) A high vacuum is needed to prevent collisions between the high-energy electrons and air molecules, which would absorb energy from the electrons.

To obtain a TEM image, a thin sample of about 200 nm is subjected with a high energy electron beam, which is directed using electromagnetic lenses. The electrons are elastically or inelastically scattered as they penetrate the sample. Either the transmitted electrons or the scattered electrons can be imaged, known as dark-field and light-field imaging, respectively (See Bright/Light field versus dark field and EDS). Although atomic resolution is theoretically possible, it is difficult to achieve due to defects in the lenses.

Imaging depends on contrast, which can arise from three processes: mass-thickness contrast, diffraction contrast, and phase contrast.\(^3\)

1. Mass-density contrast: Scattering increased with the atomic number and thickness of the sample. For example, contrast in amorphous materials arises from mass-density contrast. This is often the case for biological materials.

2. Diffraction contrast: Electrons are deflected according to Bragg’s law and depends on the crystal structure. Often this is used to examine crystal lattice defects.

3. Phase contrast: Several beams are admitted on the sample, and the interaction of the deflected beams with the transmitted beams give high-resolution images useful for determining crystal structure.
STEM (Scanning transmission electron microscopy)

STEM is similar to TEM. While in TEM parallel electron beams are focused perpendicular to the sample plane, in STEM the beam is focused at a large angle and is converged into a focal point. The transmitted signal is collected as a function of the beam location as it is rastered across the sample.

There are multiple detectors for STEM imaging:

1. BF (bright-field) detector: small angles (<0-10 mrad). These images are similar to the bright-field images obtained using TEM.
2. ADF (annular dark-field) detector: larger angles (10-50 mrad)
3. HAADF (high-angle annular dark-field) detector: Angles > 50 mrad

None of the elastically scattered electrons reach the detector, so it only images from inelastically scattered electrons. This is also known as Z-contrast imaging because there is a direct correlation between the local contrast and local mass-thickness, which depends on the atomic number Z. HAADF imaging allows for enhanced contrast, especially at lower atomic numbers, compared to TEM.

How to interpret the data

Characteristics of solids such as structure, morphology, and crystallite size can be studied using electron microscopes, often to characterize defects and elemental distribution. STEM is particularly useful for examining particle size, crystal morphology, magnetic domains, and surface defects. TEM is useful for imaging the bulk structure, allowing better observations of crystal defects.

Contrast in the image is produced by the scattering of electrons due to their interaction with atoms in the sample. Scattering depends on thickness of the sample as well as the material itself, where heavier atoms deflect more electrons. Bright and dark areas refer to the density of electrons hitting the detector. Therefore, brighter areas correspond to where more electrons are transmitted, while darker areas correspond to where electrons are scattered. The darker the area, the heavier the atom at that location.

Possible issues that may arise are particle agglomeration and impurities.

1. Particle Size

The size of particles can be manually determined from a TEM or STEM image by measuring the distance across the particle. To obtain an accurate particle size, the average of many particles should be used. As the particle size decreases to only several nanometers, there may be difficulties in having poor contrast between the particle and the background.

-HAADF may allow for better contrast in materials with lower Z compared to conventional TEM imaging. For an example, see Figure 1 below. Figure a shows the HAADF image of Pt nanoparticles while figure b shows the bright-field image of the same sample.
2. Morphology

Determining crystal morphology with TEM or STEM may be more difficult because a 2D image is produced, while morphology is a 3D property. To accurately determine the crystal morphology, the sample should be imaged along several different crystal planes. Some morphologies that might be identified are lamellar (nanosheet, plate or belt-like), nanoneedle, nanorod or nanowire. The figure 2 below [5] highlights the difficulty in determining a 3D structure with TEM. A cubic morphology may show a square 2D image if the beam is directed directly at one of the faces, but could also show a rectangular image if the cube is tilted.

Crystal habit - the external shape of a crystal. This may be easier to distinguish simply by examining the TEM or STEM image. For example, in Figure 3 below the crystal habit is cubic [6]. Other crystal habits may be hexagonal, rhombohedral, etc.

3. Crystal defects

Crystal defects may be observed in TEM or STEM images because they change the contrast in the image compared to what would be expected in a repeating crystal structure. See figure 4 below for example.

4. Other examples:

A. The phase boundary between between fcc silicon (Si) and hexagonal palladium silicide (Pd$_2$Si) can be seen in figure 5 below.

B. Crystal identity can be determine from the different d-spacings. In figure 6, SnO$_2$ could be distinguished from Pt.

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**Good literature examples**

One study used TEM and STEM to show the transformation of Pt-MnO heterodimers into seven different Pt-MnX$_y$ heterodimer derivatives. Figure 7a shows the TEM and STEM-EDS images of the starting Pt-MnO material, and figure 7b shows that of Pt-MnS. It is clear that the particles maintain their morphology after the anion exchange of S for O. The anion can be distinguished by the darker contrast compared to the MnO or MnX. In the STEM-EDS image, red represent Pt, blue represents Mn, and yellow represent S. In figure 7b, the HAADF image is also shown, which has better contrast than the TEM image. Because this is a dark-field image, the Pt now appears brighter than MnS.

**Figure 7.** a) The TEM and STEM-EDS images of Pt-MnO. b) The TEM, STEM-EDS, HAADF and SAED images of Pt-MnS.

TEM was also used to show that these particles maintained their domain size throughout the exchange process. In figure 8, the transformation of Pt-MnO to PtMnS and finally Pt-Cu$_2$S is shown for domain sizes of Pt-MnO of a) 8 nm, b) 13 nm, and c) 23 nm. Because the scale is the same for images, it is easy to see that the domain sizes increase for a, b, and c. Moreover, it can be seen that after the ion exchange processes, the domain size is maintained.

What the TEM and STEM showed is described in figure 9 below.
References


9. 5.3.2 Phase Boundaries, https://www.tf.uni-kiel.de/matwis/amat/iss/kap_5/backbone/r5_3_2.html (accessed Apr 29, 2019).