3. Techniques for viewing objects at the nanoscale

With increasing research in nanosciences, scientists and engineers have designed excellent techniques for viewing objects at the nanoscale. Some of the most important techniques are identified below.

X-ray diffraction (XRD)

XRD is a technique to determine the atomic structure of the crystal. XRD is a vital tool in material sciences as it helps us to know the crystal structure and the molecular arrangement of atoms in the crystal. The following information can be obtained from XRD:

a) Particle size
b) Structure of the crystal
c) Lattice parameters
d) Amorphous or crystalline nature of the sample

In 1915, Sir William Henry Bragg and William Lawrence Bragg carried out ground-breaking research to show that x-rays can be used to determine the atomic structure of crystals. Named after these two pioneering scientists, Bragg's law is written as: $n\lambda = 2d\sin\Theta$, where d is the distance between the atomic layers in a crystal, λ is the wavelength of X-rays, n is an integer and Θ is the angle of incidence. When the X-ray beams are scattered by the sample, interference takes place that leads to patterns of high and low intensity. This technique is useful only for crystalline materials because for amorphous materials like glass, only broad diffraction patterns are observed. **Figure 5** shows a typical X-ray diffractogram.

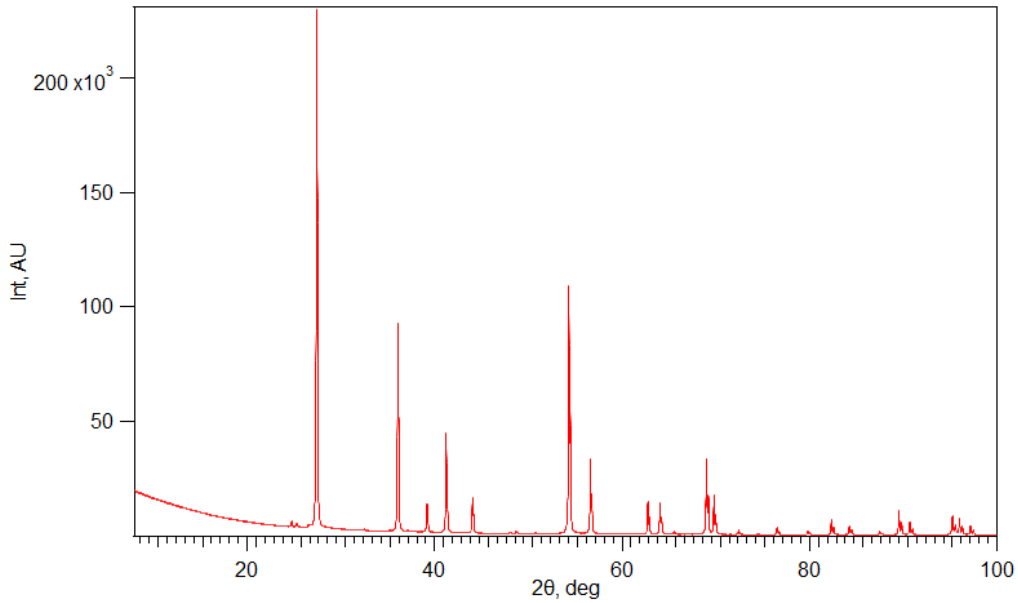


Figure 5: A typical X-ray diffractogram of TiO2
Credit: RaidoEnn. Creative Commons Attribution-Share Alike 4.0 International license.

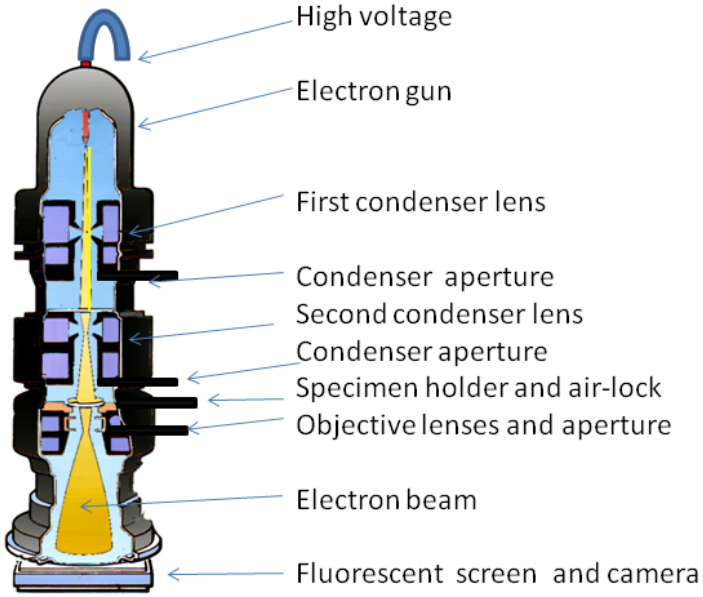
The ratio of the intensities in the diffractogram provides information such as crystallite size and preferred orientation of crystals.

Transmission electron microscope (TEM)

In order to see objects at the nanoscale, optical microscopes cannot be used because they are unable to image objects that are smaller than the wavelength of visible light. To solve this problem, in 1933 Max Knoll and Ernst Ruska developed the first TEM that had a resolution greater than light. The TEM produces a very powerful stream of electrons from the electron gun. The electromagnetic forces are able to manipulate the direction of the electron beam and the beam is focussed on the material to be viewed under the microscope. In the optical section of the TEM, three lenses are present: condenser, objective and projector lenses. Condenser lenses contribute to the primary beam formation, the beam that is transmitted through the sample is converged by the objective lens and the projector lenses expand the beam on the phosphorescent screen. The particles are seen on a phosphorescent screen in this microscope.

Sample preparation is extremely crucial in TEM. The sample grids are usually composed of copper as the grid material. On top of this grid, a lacey carbon or holey carbon layer is generally mounted. The samples are usually drop-casted on these layers to be viewed under the microscope.

Aberration correction electron microscopes are becoming increasingly widely used. It is possible to see even single atoms (which are as small as 0.1 nm) with these microscopes due to their capability to correct aberrations on account of lens deformation. Excellent contrast and particle size determination can be achieved with this new generation of aberration corrected microscopes. **Figure 6** is a diagram of a TEM.



Transmission Electron Microscope

Figure 2

https://commons.wikimedia.org/wiki/File:Electron_Microscope.png

Scanning electron microscope (SEM)

The SEM is a versatile tool for viewing materials at the nanoscale. Manfred Von Ardenne discovered the SEM in 1937. The SEM uses a strong and powerful beam of electrons to scan the surface of a specimen. A specific variety of electromagnetic coil is used to scan the sample surface in a raster pattern. The electrons that are knocked off from the surface of the materials are analysed to generate the morphology of the specimens. Usually specimens bigger than 100 nm are used for SEM analysis. The following information is available from the SEM: a) more information about the topology, morphology and composition data for the materials in question; b) simple sample preparation; c) a more detailed surface picture; d) information about any possible contaminants on the sample.

Sample-electron interactions are the basis of how the SEM works. When the electrons strike the sample surface, backscattered electrons and secondary electrons are ejected, which are detected by the detectors present in the SEM equipment. Sample preparation for SEM analysis is straightforward. For powder or inorganic samples, the samples are simply mounted on a conductive tape followed by platinum sputtering to ensure proper conductivity of the specimens to be analysed. For biological samples, the process is more drawn out. As electron microscopy analysis requires high vacuum conditions, the samples are dehydrated before analysis. Chemical fixative reagents such as formaldehyde are added to the biological samples first. These are then dehydrated and mounted on a conductive tape followed by platinum sputter coating. The main components of the SEM are:

1) Electron gun (or source): Includes mainly tungsten filament, lanthanum hexaboride crystal and field emission gun.
2) Condenser lenses: These lenses focuses the electron beam as it travels from its source to the specimen through the column.
3) Sample chamber: This is the area where the sample is mounted. This area can be rotated and moved in the x, y and z direction.
4) Detectors: Different detectors are present to distinguish and detect different kinds of scattered electron beams, such as secondary electrons, backscattered electrons and x-rays.

Reading links:

https://www.nanoscience.com/techniques/scanning-electron-microscopy/components/

http://blog.phenom-world.com/what-is-sem

Ultraviolet and visible spectroscopy (UV-vis)

The electromagnetic spectrum comprises of a range of wavelengths from as short as (gamma and x-rays) to as long as microwave and broadcast waves. **Figure 7** shows the electromagnetic spectrum of waves. It can be seen that for nanomaterials, the

region of the wavelength concerned is the ultraviolet and visible region suitable for spectroscopy. UV-vis technique is a spectroscopy technique which is used to quantify the amount of light that is either passed or absorbed by the sample. Certain nanomaterials like gold and silver have strong optical properties due to which they interact strongly with light. The UV-vis peaks shift on account of nanoparticle aggregation. The shifting of the UV-vis peaks is an indication of whether or not the nanoparticles have agglomerated.

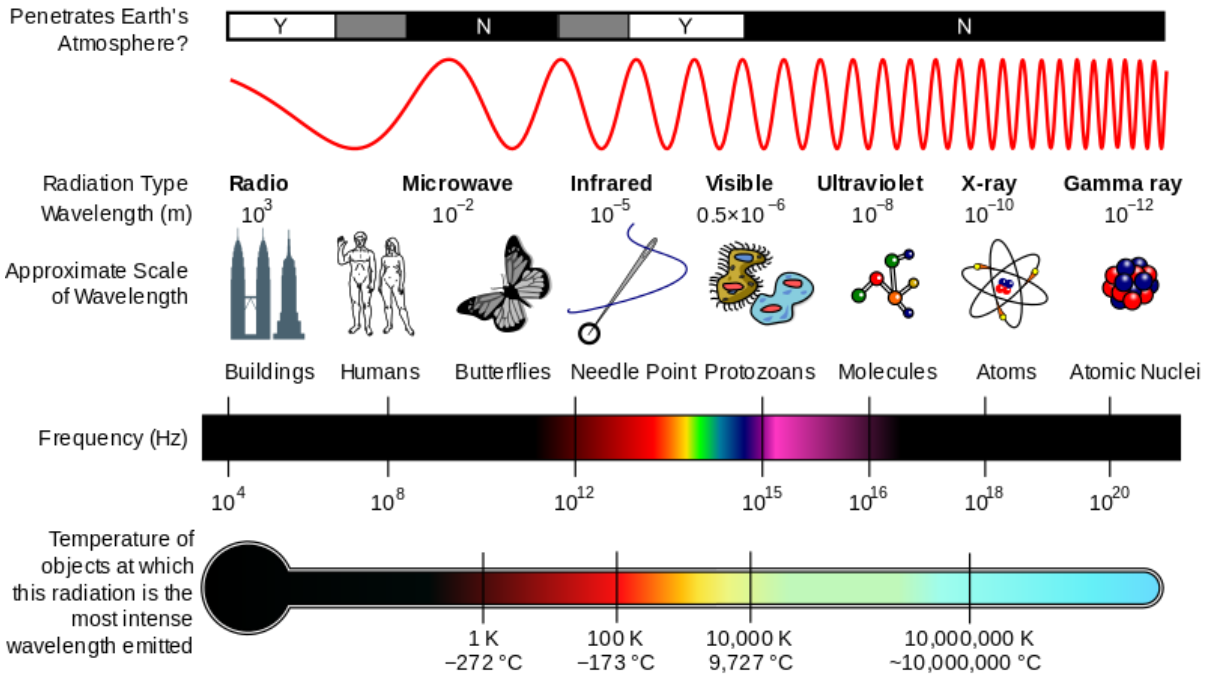


Figure 7
https://commons.wikimedia.org/wiki/File:EM_Spectrum_Properties_edit.svg
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In the case of gold nanoparticles, different sizes have their absorption peaks at different wavelengths.

Further reading:

http://50.87.149.212/sites/default/files/nanoComposix%20Guidelines%20for%20UV-vis%20Analysis.pdf

1) What kind of electron microscopy would you use for a sample that is approximately 500 nm big?

2) What are the limitations of electron microscopy?

3) You have synthesized a sample in your lab and now you want to identify the chemical signature of it. Which technique should you use and what information will you get from this technique?