

Lecture 10

Characterization Methods

This lecture summarizes some of the methods used for imaging and characterization of nanomaterials, meaning materials with at least one dimension at the nanoscale level (1–100 nm). These include nanostructured surfaces, nanoparticles, nanoporous materials, etc. The aim of this lecture is to answer the question: How are nanomaterials imaged and characterized?

There are many methods available to image nanostructured materials (e.g. a nanostructured surface) and to characterize their physical and chemical properties. Here, only a short review and description of these methods is provided.

In general, two fundamental types of characterization methods exist: imaging by microscopy and analysis by spectroscopy. The methods employed have been developed specifically to meet the characterization needs of nanomaterials.

Microscopy

An optical microscope uses visible light (i.e. electromagnetic radiation) and a system of lenses to magnify images of small samples. For this reason, it is also called a light microscope. Optical microscopes are the oldest and simplest of the microscopes. The resolution limit of an optical microscope is governed by the wavelength of visible light (As a general rule of thumb, the resolution is about half the wavelength used in the measurement). Visible light is the part of the electromagnetic spectrum with wavelengths between 400 and 700 nm and the resolving power of an optical microscope is around 0.2 μm or 200 nm: thus, for two objects to be distinguishable, they need to be separated by at least 200 nm. Single objects smaller than this limit are not distinguishable: they are seen as ‘fuzzy objects’. This is known as the ‘diffraction limit’ of visible light.

In order to overcome the limitations set by the diffraction limit of visible light, other microscopes have been designed which use other beams: rather than light, they use **electron beams** to illuminate the sample. **Electron microscopes** have much greater resolving power than light microscopes that use electromagnetic radiation and can obtain much higher magnifications of up to two million times, while the best light microscopes are limited to magnifications of 2000 times. Both electron and light microscopes have resolution limitations, imposed by the wavelength of the radiation used. The greater resolution and magnification of the electron microscope is because the wavelength of an electron (its de Broglie wavelength) is much smaller than that of a photon of visible light.

There are various types of electron microscopes, such as the **scanning electron microscope** (SEM) and or the **transmission electron microscope** (TEM). Conceptually, these microscopes are similar to an optical microscope in the sense that they use radiation to visualise a sample: photons in the case of an optical microscope, and electrons (i.e. particles) in the case of electron microscopes.

In 1981, a totally new concept of imaging was introduced by Binning and his co-workers from IBM. They used a small metal tip placed at a minute distance from a conducting surface: when the two are placed very close together, but not actually touching, a bias between the two can allow electrons to tunnel through the vacuum between them. This creates a tunnelling current, which can be measured and which is a function of the electron density on the surface. Electron density is the probability of finding an electron in a particular place: there is high electron density around the atoms and bonds in molecules.

This type of microscope is called the **Scanning Tunnelling Microscope** (STM). Variations in current as the probe passes over the surface are translated into an image. The STM can create detailed 3D images of a sample with atomic resolution. This means that the resolution is actually so high that it is possible to see and distinguish the individual atoms ($0.2 \text{ nm} = 2 * 10^{-10} \text{ m}$) on the surface. The invention of the STM earned Binning and his co-worker Heinrich Rohrer (at IBM Zürich) the **Nobel Prize in Physics in 1986**.

1. **Scanning tunnelling microscope (STM)**

The STM is a fundamental tool in nanoscience and nanotechnologies. It is used in both industrial and fundamental research to obtain atomic-scale images of metal and semiconducting surfaces (**Figure 29**). It provides a three-dimensional profile of the surface roughness, allowing the observation of surface defects and the determination of the size and conformation of molecules and aggregates.

Another astonishing property of the STM is that it can be used to manipulate (move!) individual atoms, trigger chemical reactions, as well as performing electronic spectroscopy.

➤ **Operational principle of the STM**

STM is a **Scanning Probe Microscopy** (SPM) technique. SPM provides images of surfaces by scanning the surface line by line with a probe. Scanning works very similarly to the way the blind read Braille, line by line, by moving a finger over buds on the paper. In an STM, the probe is a very thin needle called the 'tip' that is so small that its point is just a few atoms across. The tip is made of a conducting material (e.g. metal, typically tungsten). The precise movement of the tip is controlled by a piezomotor.

The tip of an STM is about 3 nm (3×10^{-9} m) long and should be located very close to the surface to be scanned. In practice, the distance between the end of the tip and the surface must be less than 0.1 nm (10^{-10} m), without the tip actually hitting the surface. To visualize how small and precise this actually is, it corresponds to placing the 300 m tall Eiffel Tower (3×10^2 m) top down with a

distance of 0.01 mm (1×10^{-5} m) over a neighbourhood and scanning across it without actually touching it (**Figure 30**). One of the fundamental elements of the STM is the tip of the probe that scans the surface, which must be sharpened to a very fine tip (**Figure 31**). The fabrication of sharper probes allows for better resolution of surface features. Ultimately, a probe tip sharpened to one atom would provide the best resolution.

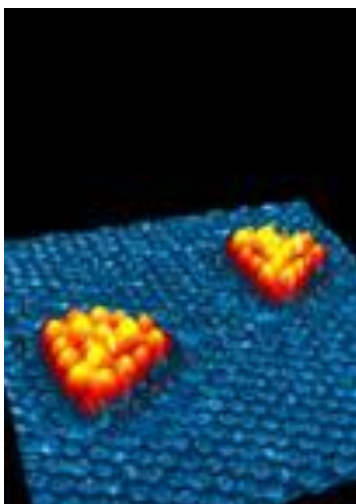


Figure 29: Nanocatalyst used for cleaning sulphur from crude oil: this STM image shows two molybdenum-disulfide nanoclusters consisting each of 15 Mo atoms and 42 S atoms.

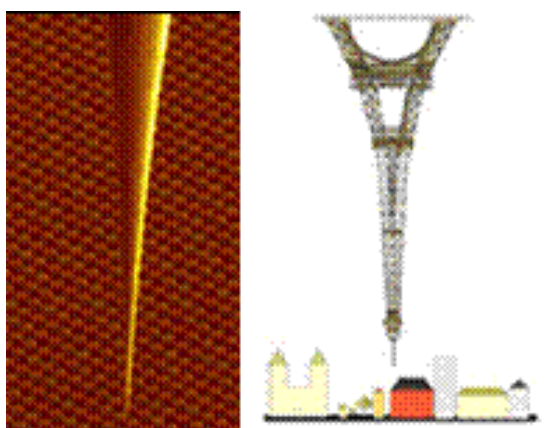


Figure 30: Left: 3 mm tip positioned 0.1 nm above the surface; right: macroscopic analogy: a 300 m high Eiffel Tower located 0.01 mm above the city



Figure 31: SEM image of a tungsten tip for STM imaging

When a conducting tip is brought very near to a metallic or semiconducting surface, at a distance of about 0.1 nm, it can induce the formation of a tunnel current between the tip and the surface: a bias between the two atoms (tip and surface) can allow electrons to tunnel through the vacuum between them and induce the formation of a current. Variations in current as the probe passes over the surface are translated into an image (**Figure 32**).

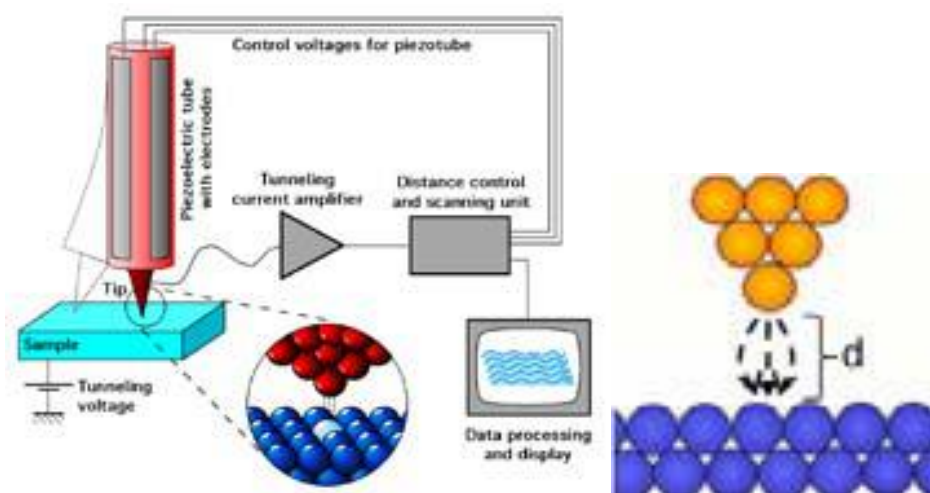


Figure 32: Schematic representation of STM scanning over a surface: (left) overview of an STM; (right) close-up of the tunnelling effect between the tip of the probe and the surface atoms. The intensity of the tunnel current depends on the distance d .

As the conducting tip of an STM scans over a conducting or semiconducting surface, a ‘tunnel current’ is formed, which arises from electrons jumping from the surface to the tip of the STM probe. The probability of this happening depends largely on the distance **d** between the surface and tip, thus the size of the current depends on this distance. Small changes in the distance between the probe tip and the substrate surface translate into large changes in tunnel current: atomic scale resolution by STM is possible in the x, y and z directions due to this phenomenon.

➤ How are images created?

One way of using the STM to image the surface of the substrate is to keep the tunnel current constant, typically nanoamps (nA) (10^{-9} A) by applying a constant tunnel current, the tip of the probe is kept at a specific distance above the surface. When the tip scans a surface, it will rise when it scans over an atom and drop when scanning between two atoms in the surface, as shown in **Figure 33**, where the STM tip moves from left to right.

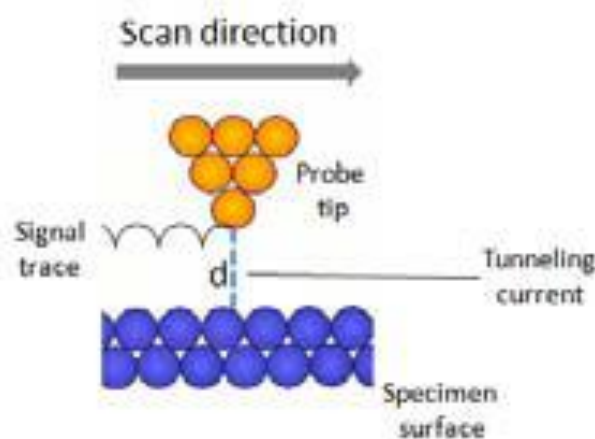


Figure 33: Schematic representation of the signal trace as a tip of an STM probe scans a surface

The movement of the tip can be transformed into a **coloured height map** of the surface. This map corresponds to an atlasmap, where each colour indicates a specific height, as in **Figure 34**.

Using the STM, surfaces can be scanned by moving the tip in steps of 0.1 nm (10⁻¹⁰ m), thus providing a very accurate representation of the surface. For the technique to work, it is necessary that, as the tip scans the surface, a tunnel flow is induced. **Thus, the surface must be conductive to some extent** (the substrate must be a conductor or semiconductor).

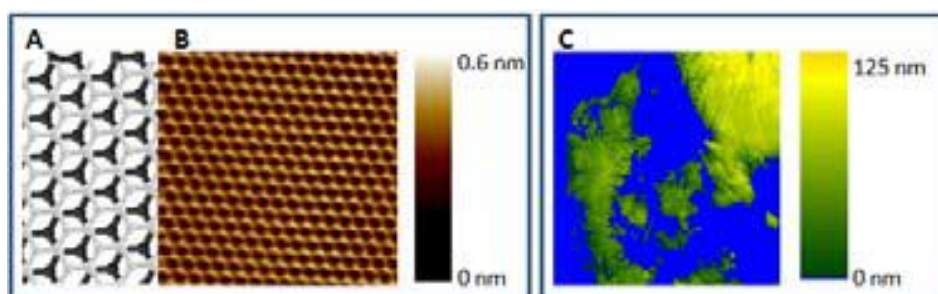


Figure 34: (A) model of two layers of graphite; (B) STM image of a graphite sheet (height scale on the right, note how the image fits the model); (C) relief map of Denmark (height scale on the right)

If it is necessary to scan a surface which in itself is **not electrically conductive**, it can be coated with a very thin layer of a conductive material such as gold. This does, however, imply that the STM is less suitable for some studies (e.g. to study biological molecules such as DNA (which is not conductive)). For these types of samples, other SPM techniques are more suitable, such as the **Atomic Force Microscope** (AFM). An AFM does not measure the tunnel current, but the forces between the tip and the surface and, therefore, does not require the surface to be conductive. The AFM was developed in 1985, also by Binnig and co-workers at IBM Zürich. It was developed specifically to image materials that are insulating.

2. Atomic force microscope

The **Atomic Force Microscope** (AFM) was developed specifically to overcome the intrinsic limitations of the STM, which is not suitable for imaging surfaces coated with biological entities such as DNA or proteins. The AFM operates in air and not under a vacuum. Some versions of the instrument also allow operation in liquid, which is very advantageous when imaging biological samples that often need buffers to remain biologically active.

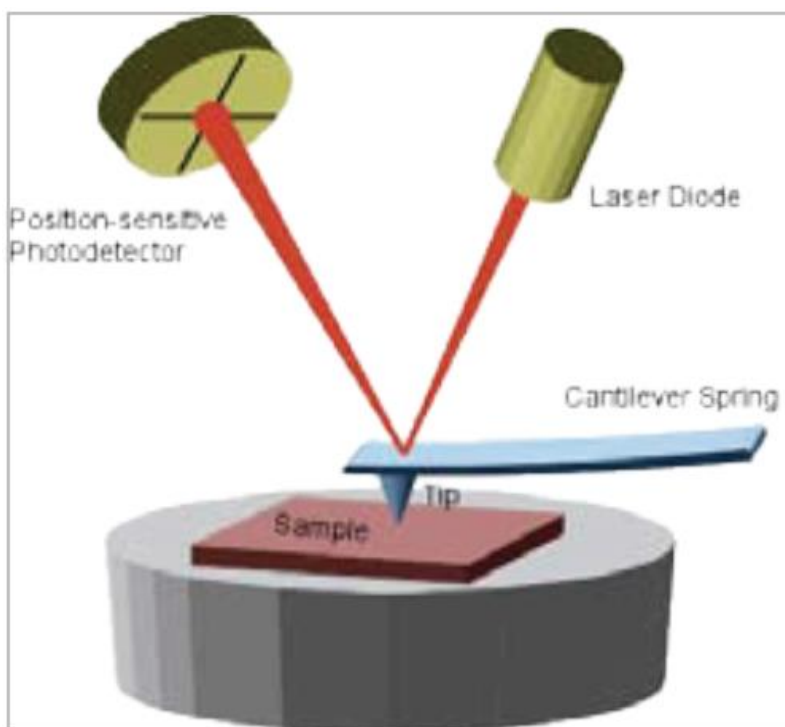


Figure 35: Operation principle of an AFM source

The AFM measures the **interaction force** (attractive or repulsive) between the probe and the surface. The solid probe is located at the end of a very flexible cantilever; an optical system detects the deflection of a laser beam that bounces off the reflective back of the cantilever, thus reporting cantilever fluctuations, which are proportional to the applied force. The probe is continuously moved along the

surface and the cantilever deflection is constantly monitored. A feedback loop continuously changes the height of the probe on the surface in order to keep the applied force constant. The vertical movement of the probe is recorded to create a **topographic map** of the surface under study.

The AFM probe tip is very sharp, with a radius of curvature in the range of tens of nanometres. If the surface under analysis is soft, the probe can penetrate it, with the risk of damaging it and degrading the spatial resolution of the resulting micrograph. To overcome this limitation, instruments working in dynamic modes have been developed. In these systems, the probe is not simply dragged on the surface but oscillated vertically with respect to the surface while it is scanned. These techniques (tapping mode and non-contact mode) significantly reduce the damage that can be caused by the probe and allow the imaging of soft, compressible samples, such as biomolecules and cells. On the other hand, the tip of an AFM can be used to **deliberately ‘scratch’ and remove some molecules from a surface** or to write with an ‘ink’. Both are ‘writing’ methods in the sense that they allow the creation of nanostructures on a surface with any geometry. This technique is called Dip Pen Nanolithography (DPN).

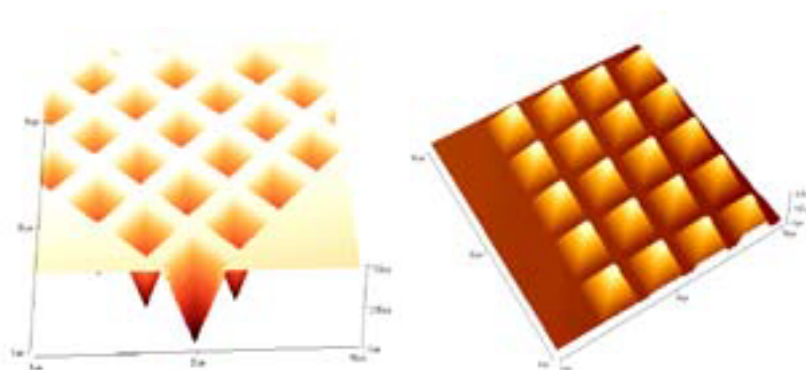


Figure 36: AFM image of an array of pyramidal wells (left) and pyramidal posts (right): the tips of the posts are about 100 nm wide

Spectroscopy methods

Spectroscopy is defined as the branch of science that is concerned with the investigation and measurement of spectra produced when matter interacts with or emits electromagnetic (EM) radiation. Depending on the wavelength of the electromagnetic used and the type of interaction with matter that occurs (absorption, scattering, etc.), different spectra are measured from which much information can be inferred.

Next, the spectroscopy methods that are most relevant in the characterization of nanomaterials (particles and surfaces) are briefly reviewed.

1. X-ray methods

X-ray methods involve exciting a sample either with X-rays (creating more X-rays) or with electrons (creating X-rays). X-rays can be also generated by bombarding a sample with alpha particles. The energy of emitted X-rays is equal to the difference between the binding energies of the electrons involved in the transition. There are various methods that use X-rays: **X-ray fluorescence (XRF)**, **X-ray diffraction (XRD)**, etc. In the context of nanomaterials, the most important method is **small-angle X-ray scattering (SAXS)** analysis. Like XRD, this method is based on the principle of scattering of X-rays. Diffraction of X-rays is a result of scattering from atoms configured in regular arrays. In conventional XRD, only crystalline materials can be visualized, as it is necessary to have a periodicity in the structure in the long-range, which nanomaterials lack (owing to their size). XRD is used for bulk crystals. With SAXS, particle sizes of the order of 1–100 nm can be analyzed.

The method can be used to image powders in the dry state or suspended in a medium. The method can also be used to measure the nanoparticle size.

2. UV-visible plasmon absorption and emission

Metal nanoparticles, in particular gold and silver, are characterized by a plasmon resonance absorption that gives rise to intensely coloured solutions.

The absorption band is due to electrons confined at the particle surface that collectively oscillate at a specific frequency, commonly referred to as the surface plasmon resonance frequency. As examples, the plasmon band of a 20 nm silver (Ag) particle is centred at 395 nm, resulting in a yellow solution, while a 20 nm gold (Au) particle absorbs at 520 nm resulting in a red solution. The **plasmon absorption effect** occurs for particles up to approximately 50 nm in diameter and scales with particle volume. Absorption can be in the visible and UV area of the spectrum. Particles can be visualised by absorbance in solution at nanomolar and picomolar concentrations.

➤ Plasmon resonance light scattering

In **larger metal nanoparticles** (> 30 nm) another effect, light scattering, is observed. When illuminated with white light, metal nanoparticles in the 50–120 nm diameter size range scatter light of a specific colour at the surface plasmon resonance frequency. This effect is called **plasmon resonance light scattering**. As in the case of plasmon absorbance, light scattering scales with particle volume, but the scattered light can be detected at much lower concentrations than absorbed

light. For example, light scattered by a solution of 80 nm diameter gold particles is detectable down to 5 fM concentration (fM = 10^{-15} M). For this reason, metal nanoparticles are interesting materials for use in techniques that rely on labelling (such as microarray technology).

➤ **Surface-enhanced Raman scattering**

Metal surfaces with nanometre scale roughness have the property of amplifying the Raman scattering signals of absorbed molecules. In simple terms, Raman scattering is the inelastic scattering of photons. Normally, when light is scattered from an atom or molecule, it has the same energy (frequency) and wavelength as the incident light (Rayleigh scattering). This is an elastic scattering. However, a small fraction of the scattered light (approximately 1 in 10 million photons) is scattered by excitation, with the scattered photons having energy (frequency) different to the frequency of the incident photons. Metal surfaces with nanoscale roughness increase the Raman scattering of molecules absorbed on them. This effect is due to chemical and electromagnetic factors, as well as increased surface area. The details of this effect will not be considered here: what is important is that the **surface-enhanced Raman scattering** (SERS) effect can induce a signal enhancement of up to 10^8 times. In one specific case, it has been possible to achieve a Raman enhancement effect of 10^{15} times! This means that the SERS effect makes it possible to push the detection limit of surface detection techniques. The SERS signal depends on the characteristics of the nano-substrate: the size, shape, orientation and composition of the surface nano-roughness. Advancements in SERS technology will allow detection at the attomole (10^{-18} mol) level, and single molecule detection.

Non-radiative and non-electron characterisation methods

There are numerous methods used to characterise nanomaterials which do not rely on the use of EM radiation. They include methods to determine particle size, surface area and porosity; thermodynamic methods (such as thermogravimetric analysis, TGA) to evaluate the temperature dependence of the nanomaterial (melting, etc.); and mass spectroscopy, to determine the chemical composition of the nanomaterial. An important surface method is the **quartz crystal microbalance** (QCM), which can measure mass changes as small as a few nanogrammes per square centimetre. This is sensitive enough to detect **monolayers** of deposited materials. It can be used to measure the amount of metal deposited on a surface after sputtering or evaporation, or to measure the amount of protein absorbed on a surface. Due to this great sensitivity, the QCM is used in the design of biosensors.

Reference:

- Luisa Filipponi and Duncan Sutherland, Nanotechnologies: Principles, Applications, Implications and Hands on Activities, Edited by the European Commission Directorate-General for Research and Innovation Industrial technologies (NMP) programme, 2013, Chapter 6.