

Characterizations of Nanomaterials

- The great advances made in nanosciences and nanotechnology would not have occurred without the ability to characterize the nanoscale structural, chemical, and physical properties of materials.
- *Spectroscopy such as UV-vis, photoluminescence, Raman scattering spectroscopies, etc. can be used for the **characterization of various nanoparticles**.*
- However, the **direct observation** of nanostructure allows meaningful relationships between **processing and properties to be made**. Size, morphology, and physicochemical properties of the nanoparticles are closely interrelated.
- Techniques such as **electron microscopy and scanning probe microscopy are employed to visualize materials at shorter distances**, down to 1 nm, and many of the advances made in nanosciences and nanotechnology *would not have occurred* without the ability to characterize the nanoscale structural, chemical, and physical properties of materials.
- Several other techniques are used for studying the particles in the bulk. For example, *X-ray diffraction can be used for determining the particle sizes and internal structures*.
- Extended X-ray absorption fine structure (EXAFS) technique makes it possible to measure the particle sizes.

Various Characterization Techniques

❑ Electron Microscopy

- Transmission Electron Microscopy (TEM)
- Scanning Electron Microscopy (SEM)

❑ Probe Microscopy

- Scanning Tunneling Microscopy (STM)
- Atomic Force Microscopy (AFM)

❑ Diffraction Techniques

- X-ray Diffraction
- Neutron Diffraction

❑ Spectroscopy

- Ultraviolet–Visible Spectrometry (200–800 nm)
- Photoluminescence Spectroscopy
- Raman Spectroscopy

❑ Miscellaneous Techniques

- Dynamic Light Scattering (DLS)
- EXAFS
- X-ray Fluorescence

A summary of investigative methods for the characterization of nanoparticles is listed in Table 3.1.

TABLE 3.1 Common Investigation Techniques for the Characterization of Nanoparticles

Techniques	Characterization Parameters
Dynamic light scattering (DLS)/particle size analyzer	Size and size distribution of nanoparticles suspended in a liquid phase
Zeta potential analyzer	Surface charge of nanoparticles in aqueous solutions or suspensions
Scanning electron microscopy (SEM)	Shape and surface structure
Transmission electron microscopy (TEM)	Size, shape, and morphology (including internal structure), especially useful for biological specimen
Atomic force microscopy (AFM)	Shape and surface morphology of nanoparticles with high lateral and vertical resolutions
Scanning tunneling microscopy (STM)	Surface images with atomic-scale lateral resolution; modification of material at atomic/molecular/nanometer scale with high precision
Laser scanning confocal microscopy (LSCM)	Noninvasive technique provides information about migration of nanoparticles into bio-barrier; 3D morphology of nanoparticles
Brunauer–Emmett–Teller (BET) technique	Surface area analysis, porosity, and adsorption capability
X-ray diffraction (XRD) technique	Crystal structure, phase, and average particle size
X-ray photoelectron spectroscopy (XPS, ESCA)	Chemical composition (both elemental and chemical states) information on nanoparticle’s surface
Fourier transform infrared spectroscopy (FTIR)	Assisted analytical tool for chemical composition
Differential scanning calorimetry (DSC)	Thermal analysis and phase transition studies
High-performance liquid chromatography (HPLC)	Detection, separation, and quantification of nanoparticles/nanomaterials with different particle size

Scanning probe microscopy (SPM)

- ❖ **Key points:** *Scanning tunneling microscopy (STM) uses the tunneling current from a sharp conductive tip to image and characterize a conductive surface; atomic force microscopy (AFM) uses intermolecular forces to image the surface.*
- The STM was developed at IBM by Gerd Binnig and Heinrich Rohrer in 1981, earning them the Nobel Prize in Physics just five years later. (Sharing that Nobel Prize was Ernst Ruska for his part in developing the electron microscope.) Binnig developed the more general atomic force microscopy (AFM) in 1986, working with Calvin Quate and Christoph Gerber.
- *Scanning probe microscopy (SPM) is a collection of techniques that can be used to image and manipulate objects as small as atoms on surfaces.*
- **Scanning tunneling microscopy (STM) and atomic force microscopy (AFM) were first discovered and are now most widely used examples of scanning probe microscopies (SPMs).**
- *This family of techniques allows **the three-dimensional imaging of the surface of materials** by using a sharply pointed **probe** brought into close proximity (or in contact) with the specimen. As the probe is moved across the surface **an image is constructed by monitoring the spatial variation in the value of a physical parameter such as potential difference, electric current, magnetic field, or mechanical force.***

- In **STM**, an atomically sharp conductive (a platinum–rhodium or tungsten) tip is scanned at about 0.3–10 nm above the surface of the sample (Figure 8.54a). **Electrons** in the conductive tip, which is held either **at a constant potential** or **at a constant height** above the sample, can **tunnel through** the gap with a probability that *is related exponentially to the distance* from the surface. *As a result, the electron tunneling current reflects the distance between the sample and the tip.*
- *If the probe is given a positive voltage, a very small current of electrons will flow from the surface to the probe. The probes may be formed with tip diameters of only a few Å, and the tunneling current is extremely sensitive to the distance between the probe and the surface.* Therefore, by moving the probe along the surface and measuring the current, an STM map of the conducting surface can be generated.

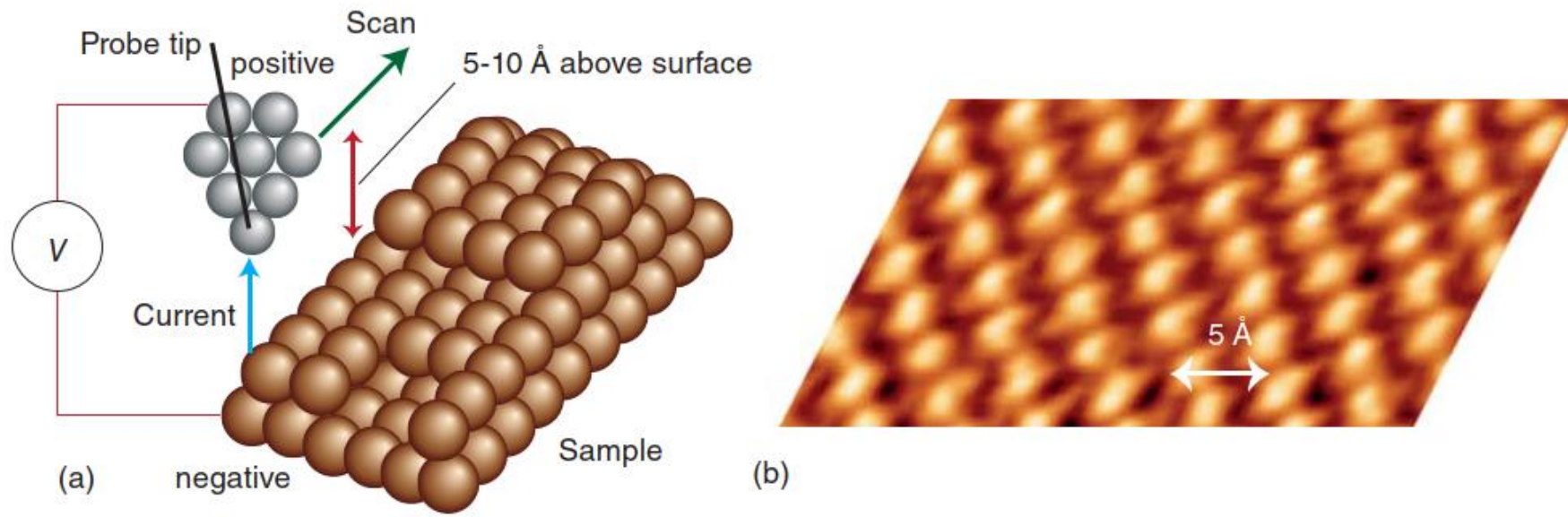


Figure 8.54

- (a) Schematic of the operation of a scanning tunneling microscope (STM);
- (b) STM image of a graphite surface.

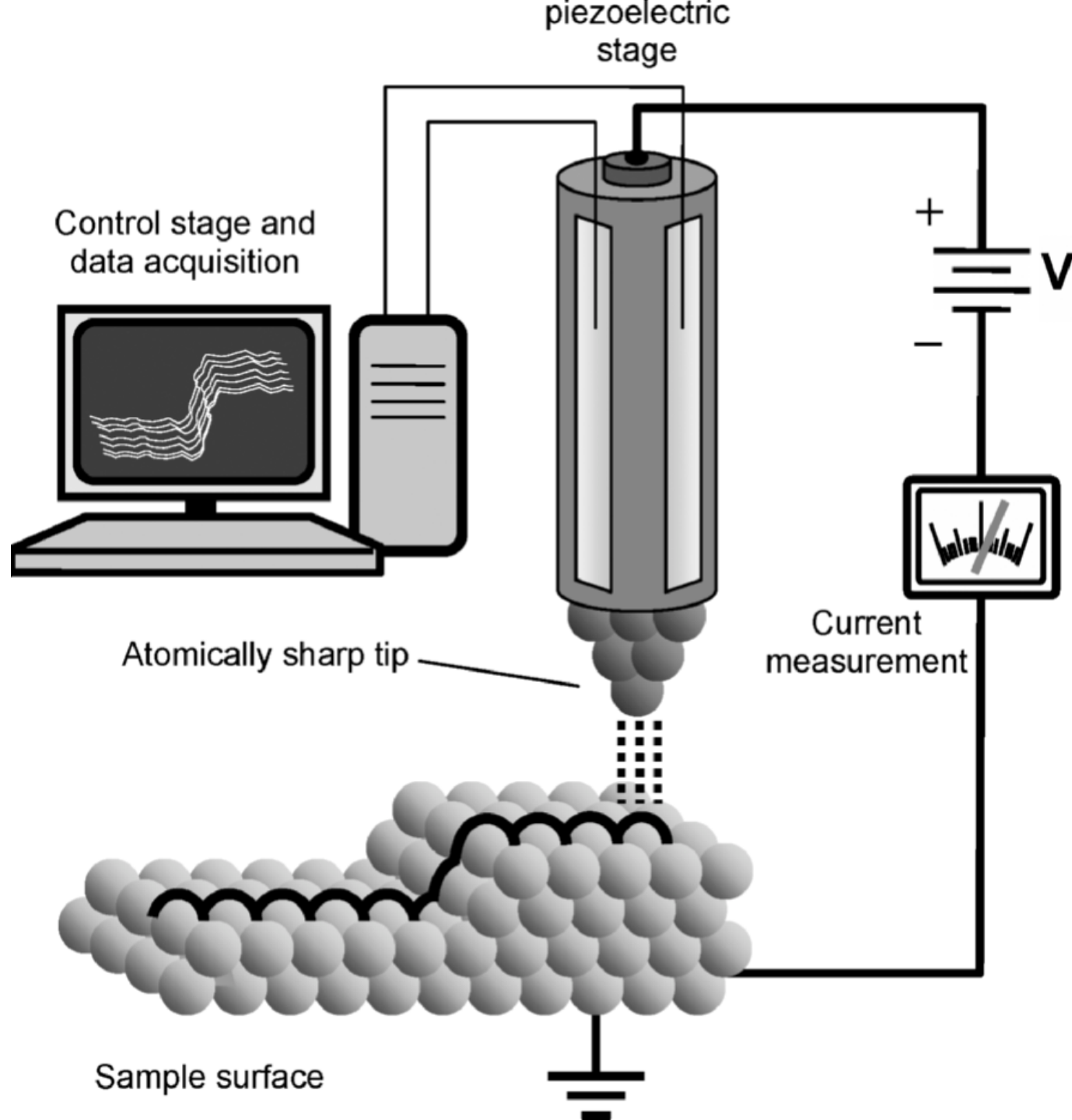


Fig. 5.43 Example of an STM setup.

➤ A scanning tunneling microscope utilizes **a wire with a very fine point**. This fine point is positively charged and acts as a probe when it is lowered to a distance of *about* 1 nm above the surface under study. Electrons at individual surface atoms are attracted to the positive charge of the probe wire and jump (tunnel) up to it, thereby generating a weak electric current. The probe wire is scanned back and forth across the surface in a raster pattern, in either a **constant-height mode**, or a **constant-current mode**, in the arrangements sketched in Fig. 3.18. *In the constant-probe-height mode the tip is constantly changing its distance from the surface, and this is reflected in variations of the recorded tunneling current as the probe scans.* The feedback loop establishes the initial probe height and is then turned off during the scan. *In the constant current mode, a feedback loop maintains a constant probe height above the sample surface profile, and the up/down probe variations are recorded.* This mode of operation assumes a constant tunneling barrier across the surface. The scanning probe provides a mapping of the distribution of the atoms on the surface.

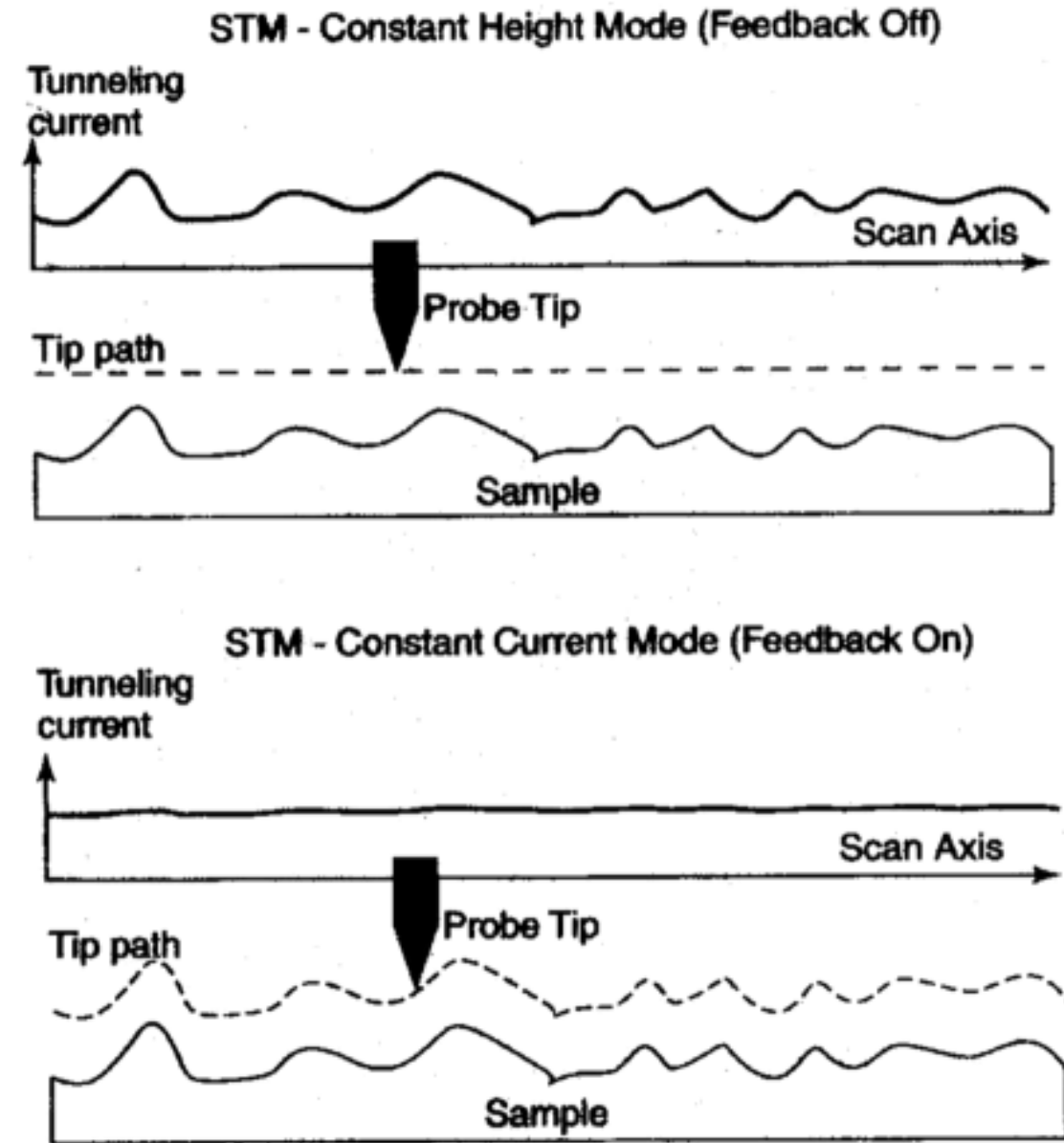


Fig. 3.18 Constant height (top) and constant current (bottom) imaging mode of a scanning tunneling microscope.

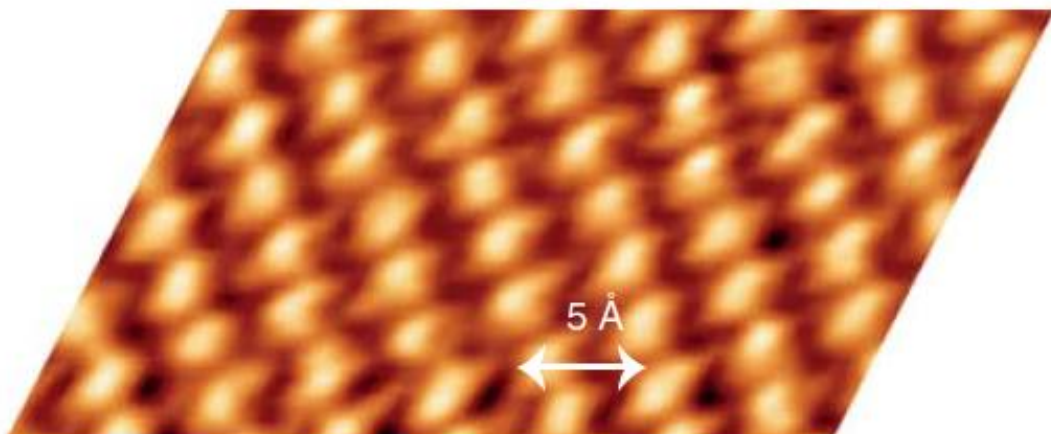
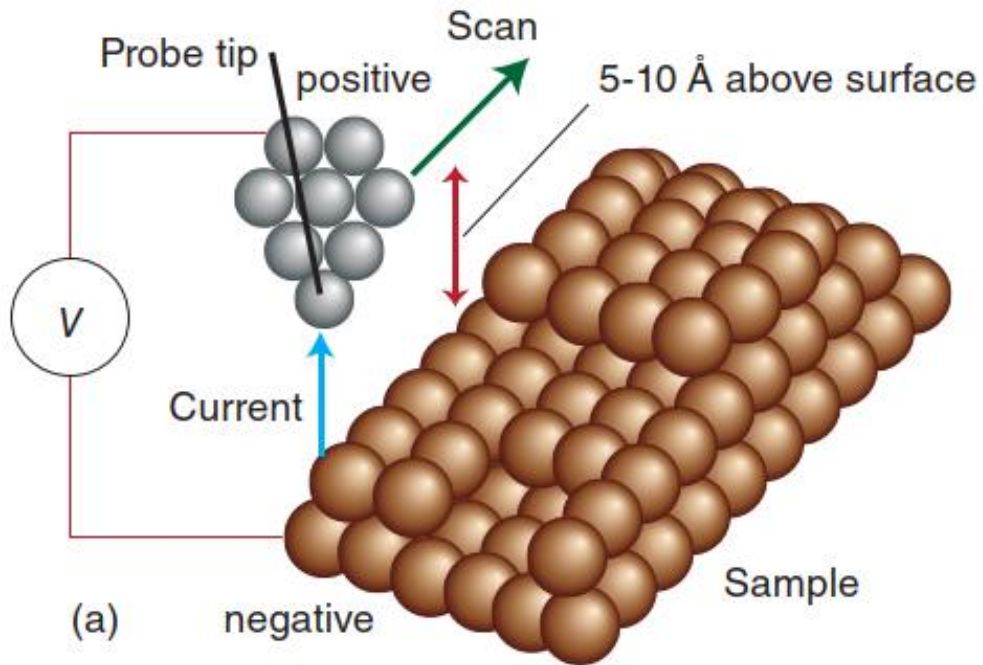


Figure 8.54 (a) Schematic of the operation of a scanning tunneling microscope (STM); (b) STM image of a graphite surface.

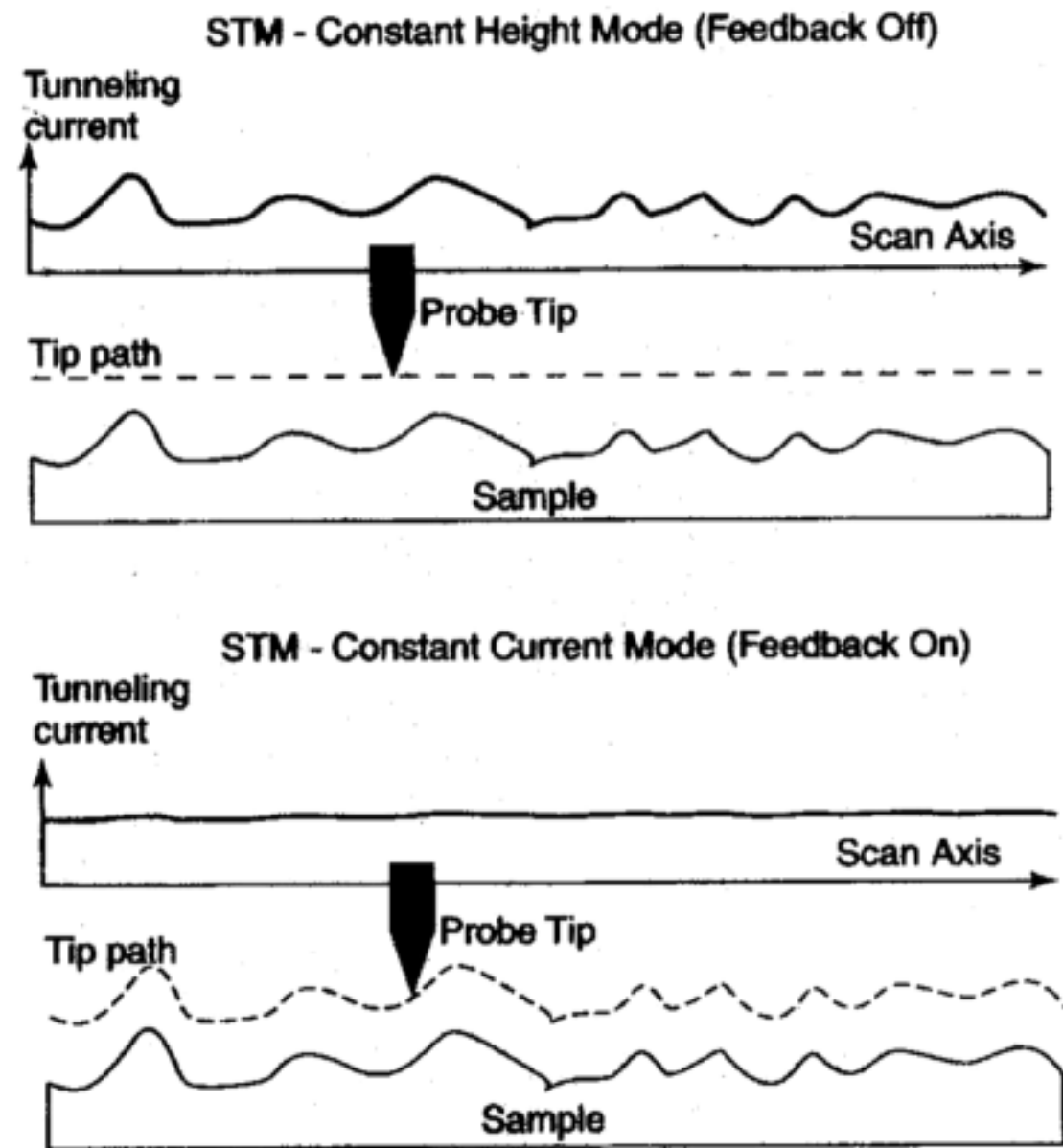


Fig. 3.18 Constant height (top) and constant current (bottom) imaging mode of a scanning tunneling microscope.

- ❑ In the '**constant-current mode**' of operation, the tip moves up and down according to the form of the surface, and the topography of the surface, including any adsorbates, can be mapped on an atomic scale.
- The vertical motion of the tip is achieved by fixing it to a **piezoelectric cylinder, which contracts or expands according to the potential difference it experiences.**
- ❑ In the '**constant-z mode**', the vertical position of the tip is held constant, and *the current is monitored*. Because the tunneling probability is very sensitive to the size of the gap, the microscope can detect tiny, atom-scale variations in the height of the surface.
- **If the tip is scanned over the surface at a constant height, then the current represents the change in the topography of the surface.**
- The movement of the tip at a constant height with great precision is accomplished by using piezoelectric ceramics for the displacement of the tip.
- Figure 8.54b shows the results of an STM study of a graphite substrate.

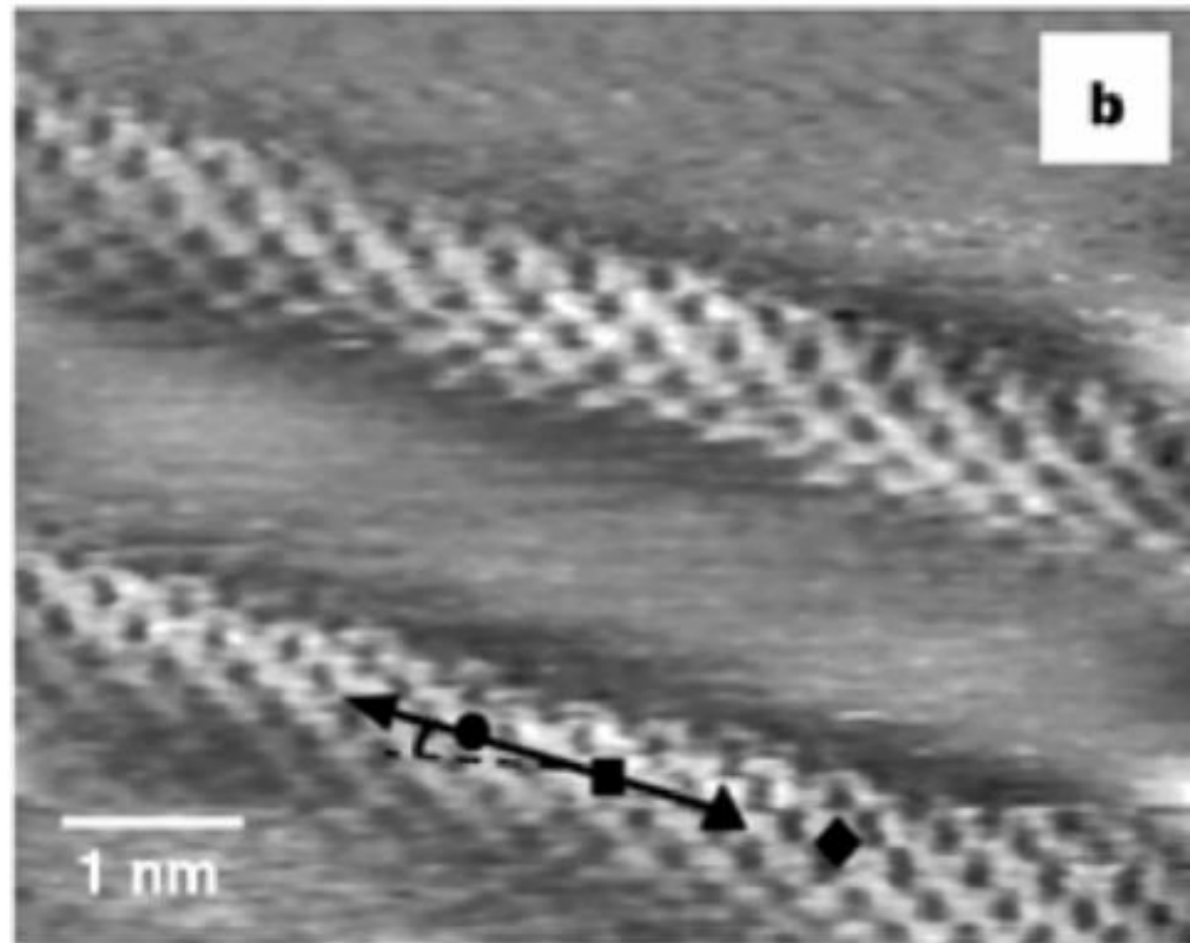
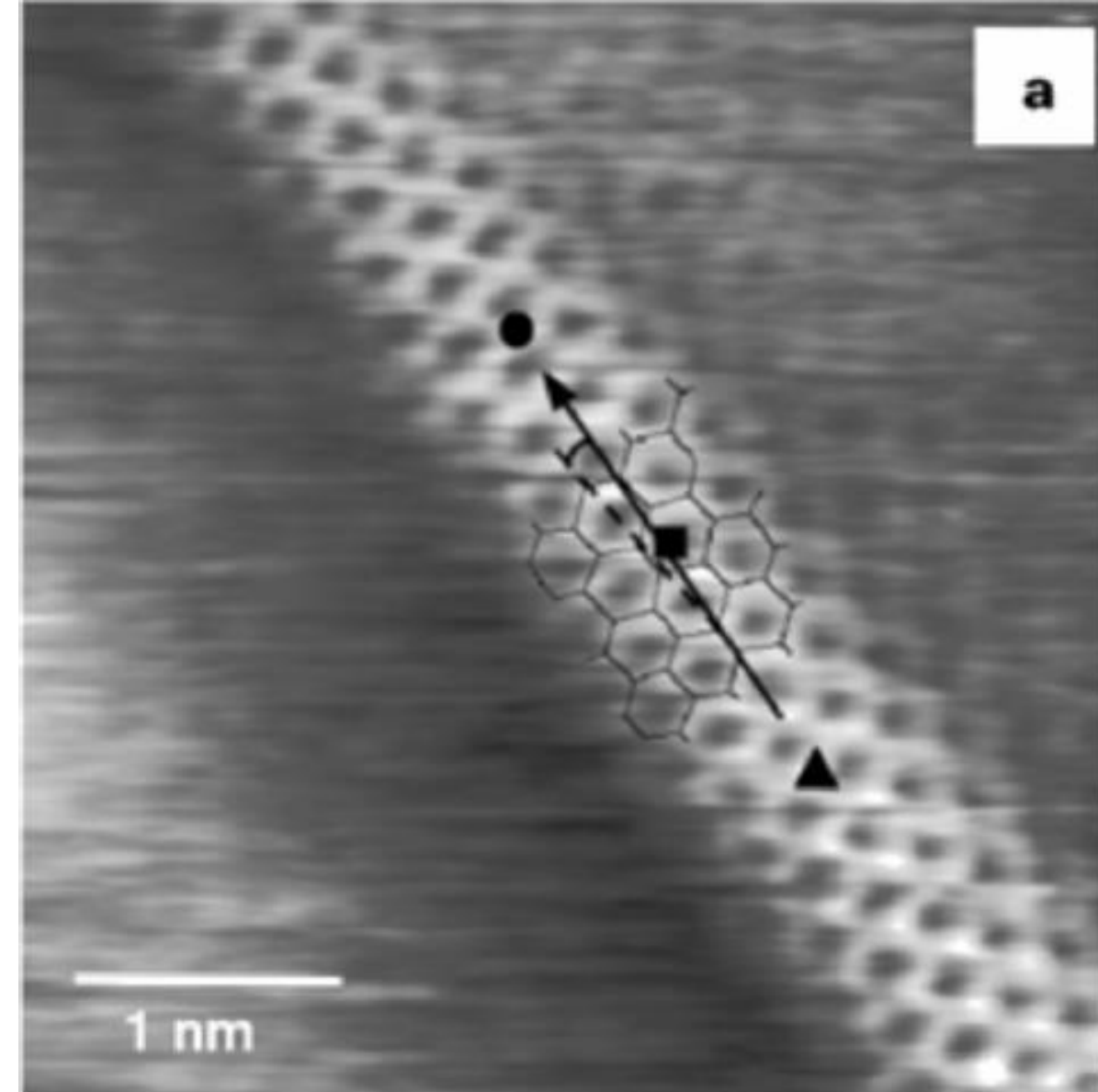


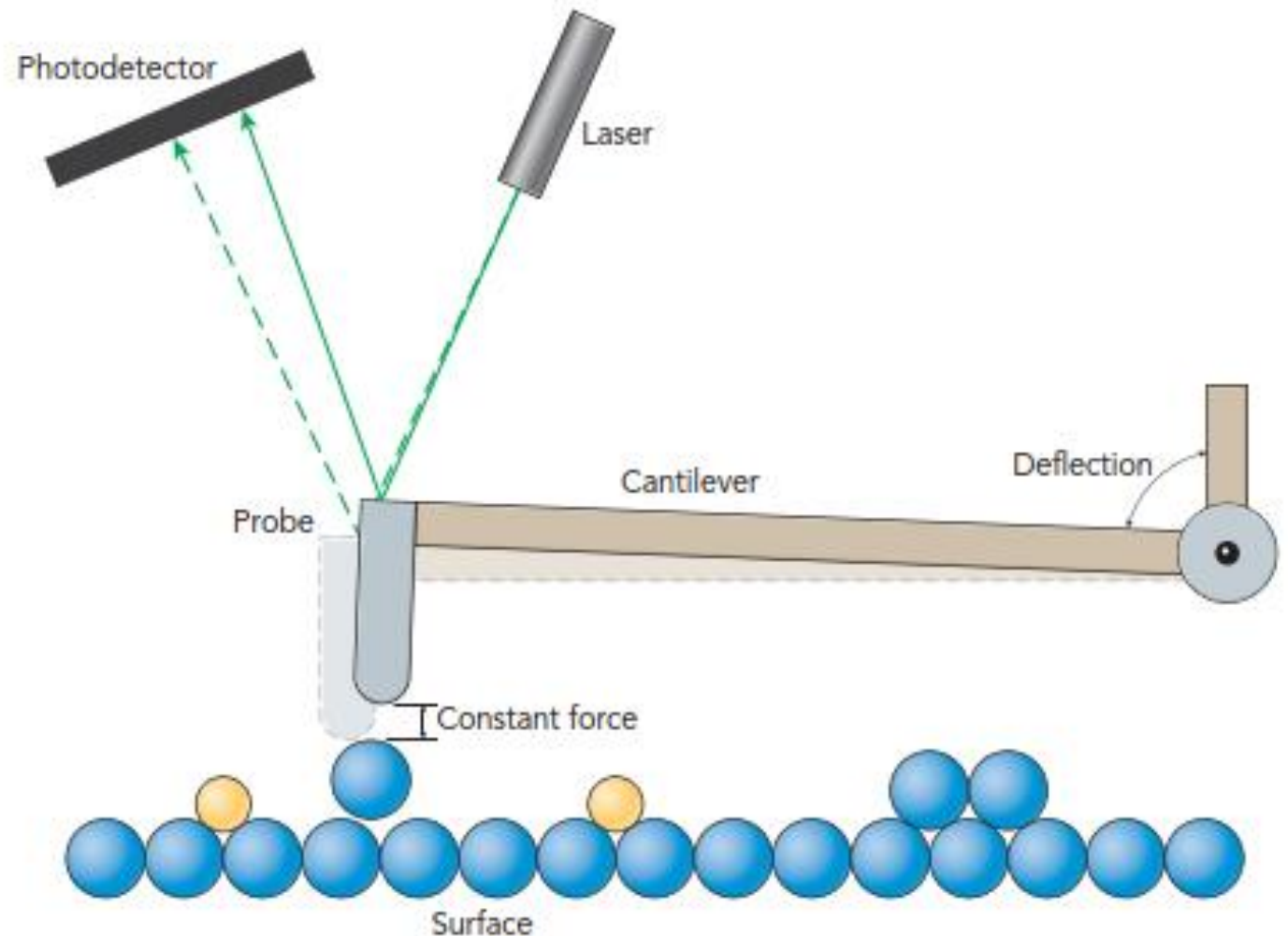
Fig. 5.44 STM images of (a) a SWCNT exposed at the surface of a rope and (b) isolated SWCNTs on a Au(111) substrate. The tube axes in both images are indicated with solid, black arrows, and the zigzag direction are highlighted by dashed lines. A portion of a two-dimensional graphene layer is overlaid in to highlight the atomic structure. (Reprinted with permission from the Nature publications.)

- ❑ In **atomic force microscopy (AFM)**, the *atoms at the tip of the probe interact with the surface atoms of the sample through intermolecular forces* (such as van der Waals interactions).
- In AFM, a *sharpened tip attached to a cantilever* is scanned across the surface. **The force exerted by the surface and any molecules attached to it pushes or pulls on the tip and deflects the cantilever** (Fig. 19A.7). *The cantilever holding the probe bends up and down in response to the forces and the extent of deflection is monitored with a reflected laser beam.*
- Because **no** current needs to pass between the sample and the probe, the technique can be applied to **non-conducting** surfaces and to the study of solid–liquid interfaces.
- **Two modes of operation of AFM** are common: '*contact mode*', and '**non-contact mode**'.
- ✓ In '*contact mode*', or '*constant-force mode*', the force between the tip and surface is held constant and the tip makes contact with the surface. This mode of operation can damage fragile samples on the surface.
- ✓ In '**non-contact**', or '**tapping**' mode, the tip bounces up and down *with a specified frequency* and *never quite touches the surface*. **The amplitude of the oscillation of the tip changes when it passes over a species adsorbed on the surface.**

Figure 19A.7 In atomic force microscopy, a laser beam is used to monitor the tiny changes in position of a probe as it is attracted to or repelled by atoms on a surface.

Atomic force microscopy.

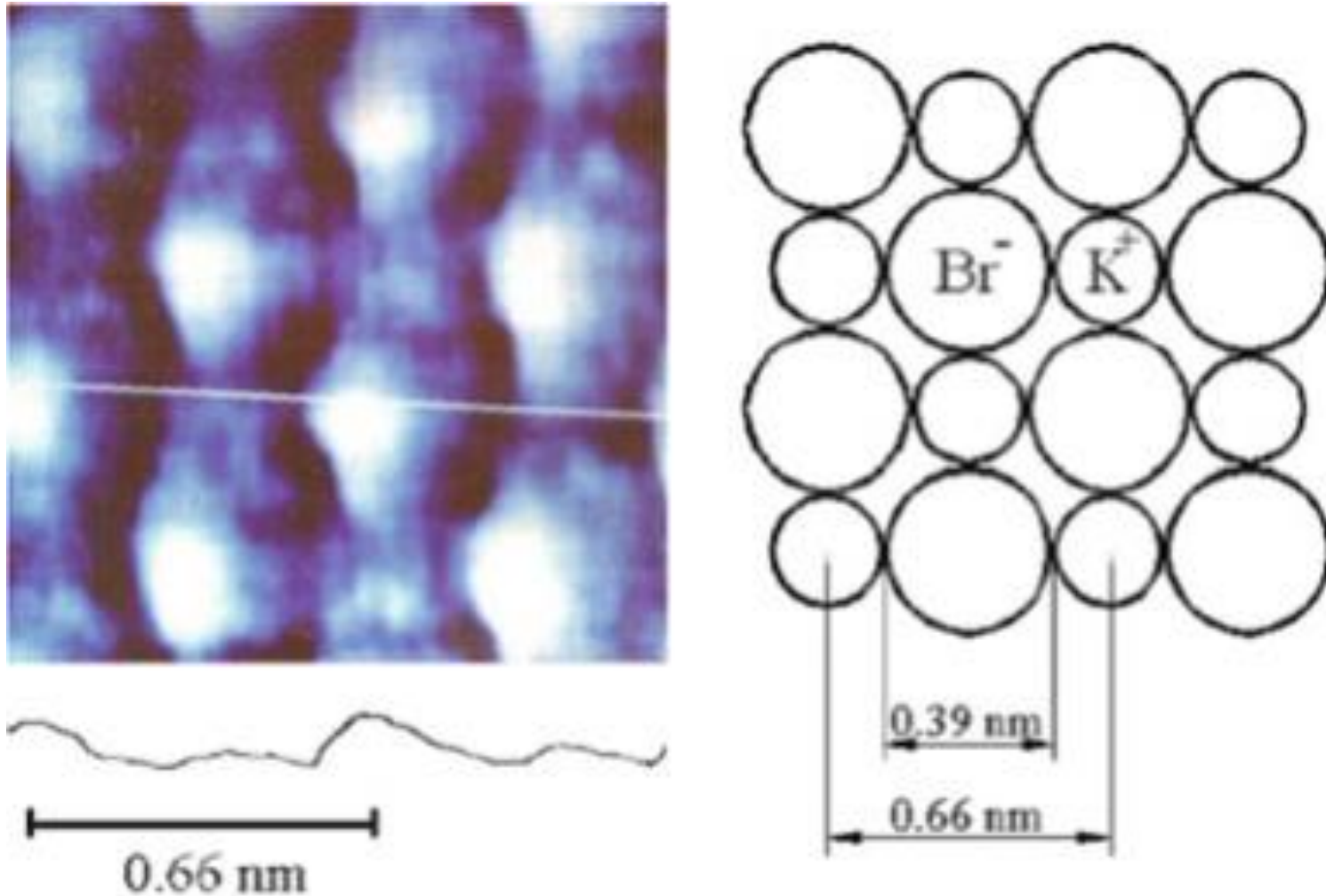
In this design, the probe is maintained at a constant distance from a surface by a feedback circuit that maintains a constant intermolecular attractive force for AFM. The surface structure is mapped by measuring the deflection of the probe arm (the cantilever) as the surface is moved beneath it.



Variations on AFM include:

- **frictional force microscopy**, which measures variations in the lateral forces on the tip that are based on chemical variations on the surface
- **magnetic force microscopy**, which uses a magnetic tip to image magnetic structure
- **electrostatic force microscopy**, which uses the tip to sense electric fields
- **scanning capacitance microscopy**, in which the tip is used as an electrode in a capacitor
- **molecular recognition AFM** is also now being carried out, in which the tip is functionalized with specific ligands and the interaction between the tip and surface is measured. Such microscopes can provide resolution of the chemical properties on the surface.

Fig. 2.2 Atomically resolved image of KBr(001) *in contact AFM mode*.
The small and large protrusions are attributed to K^+ and Br^- ions, respectively.



- ❑ In a **further variation of the STM technique**, the tip may be used to *nudge single atoms* around on the surface, making possible the **fabrication of complex nanometer-sized materials and devices**.
- AFM can also act as a **patterning tool**.
- Atomic resolution together with atomic positioning of the tip leads to the controlled manipulation on the atomic level and the **prospects of creating atomic-scale devices**.
- Interest in AFM and STM is also motivated by **numerous potential applications to industry, such as the capability of AFM and STM to write and then read back specific arrangements of individual atoms, perhaps pointing the way to a new generation of high-density data storage devices**.

❑ **Scanning probe microscopes are operated after the following common principles:**

- A very fine, nanosized probe tip interacts with a specimen surface and is scanned line by line over this surface.
- Commonly, the relative movement between tip and specimen surface is effectuated by piezo-drives. The data registered by the tip in dependence of the lateral and normal movements are stored in a computer and displayed in a color code on a monitor. With the scanning probe microscopy techniques presently available, a wide field of applications in nanotechnology emerges.

❑ **Comparison between STM and AFM:**

- The scanning tunneling microscope measures the electrical current of electrons that tunnel across a small gap between sample and probe.
- The atomic force microscope measures the force arising from intermolecular interactions between the probe tip and sample surface.
- Both methods are used to map—or even to alter—the structure of a surface with single-atom precision.
- The AFM and STM techniques provide that local information, measuring point by point the distribution of atoms across the surface. For example, the distance between circuit elements in a typical microcircuit can be measured by an AFM directly.

AFM versus STM: It is interesting to compare AFM and its precursor, scanning tunnelling microscopy. In some cases, the resolution of STM is better than AFM because of the exponential dependence of the tunnelling current on distance. Only conducting samples can be studied by STM, while AFM can be applied to both conducting and non-conducting samples. AFM is more versatile than STM. In AFM, the voltage and tip-to-substrate spacing can be controlled independently, while in STM these two parameters are connected.

AFM versus SEM: Compared with the scanning electron microscope, AFM provides extraordinary topographic contrast, direct height measurements and unobscured views of surface features (no coating is necessary). Both these techniques measure surface topography. However, both types of microscopes can also measure other surface physical properties. SEM is preferred for measuring chemical composition and AFM for measuring mechanical properties of surfaces.

AFM versus TEM: Compared with the transmission electron microscope, three-dimensional AFM images are obtained without expensive sample preparation and yield far more complete information than the two-dimensional profiles available from cross-sectioned samples.

AFM versus optical microscope: Compared with the optical interferometric microscope (optical profiles), AFM provides unambiguous measurement of step heights, independent of reflectivity differences between materials.

Electron microscopy (or Electron nanoscopy ??)

- The basic approach of illuminating a small area of a sample and collecting light with a microscope has been used for many years to image small specimens.
- However, **the resolution of a microscope**, the *minimum distance between two objects that leads to two distinct images, is on the order of the wavelength of the light being used.* Therefore, *conventional microscopes* employing visible light have resolutions of the order of micrometers and *are blind to features on a scale of nanometers.*
- When the *distance between two particles in the sample approaches the wavelength of the light being observed*, beams of light from the two particles to the observer will *interfere with each other*. At a limit of about 200 nm, the interference fringes become too strong for the particles themselves to be distinguished.
- One technique often used to image nanometer-sized objects is **electron microscopy**, in which *a beam of electrons with a well-defined de Broglie wavelength replaces the light source found in traditional microscopes.* Instead of glass or quartz lenses, *magnetic fields are used to focus the beam.*

- Working in the years immediately after Davisson and Germer verified the wave character of electrons, Max Knoll and Ernst Ruska invented the electron microscope, a device that works on the same principle as the optical microscope but that manipulates the paths of electron beams to image the sample. At easily attainable speeds, the de Broglie wavelength of electrons drops to less than an angstrom, and the resolution limit of the electron microscope is instead determined by our ability to control the electric fields used for focusing the electron beams. By 1950, the resolution of the electron microscope was 2 nm, far beyond the capabilities of the optical microscope.
- In **transmission electron microscopy (TEM)**, the electron beam passes through the specimen and the image is collected on a screen.
- In **scanning electron microscopy (SEM)**, electrons scattered back from a small area of the sample are detected and an image of the surface is then obtained by scanning the electron beam across the sample.
- As in traditional light microscopy, the wavelength of the incident beam and the ability to focus it governs the resolution. It is **now possible to achieve atomic resolution** with TEM instruments, and SEM instruments can achieve resolution on the order of a few nanometers.

❑ Electron microscopy:

- ❖ Key point: *Transmission and scanning electron microscopes use electrons to image the sample in a similar fashion to optical microscopes but at a much higher resolution.*
- An imaging electron microscope operates like a conventional optical microscope, but instead of imaging photons, as in the visible microscope, electron microscopes *use electrons*.
- In these instruments, electron beams are **accelerated** through 1–200 kV, and electric and magnetic fields are used to focus the electrons.WHY...???

- ❑ The **resolution (d)** can be expressed as **$d = 0.61\lambda/n.\sin\theta$** , where n is the refractive index of the medium and θ is the semi-angular aperture of the lens. The quantity ($n.\sin\theta$) is the **numerical aperture (NA) of the lens**. The maximum angular aperture of an objective is around 144° . The sine of half of this angle is 0.95 (~ 1.0). The NA (usually taken ~ 1.0) is engraved on each objective and condenser lens system and is a measure of the electron-gathering ability of the objective and the electron-providing ability of the condenser.
- ❑ *The theoretical limit of the resolving power of an instrument is determined by the wavelengths of the electron beam used and the numerical aperture of the system. The **resolving power R of an instrument** is defined as **$R = \lambda/2 NA$** .*
- Abbe's diffraction formula for lateral (i.e., XY) resolution is: **$d = \lambda/2 NA$** , where λ is the wavelength of light used to image a specimen.
- ✓ If using a green light of 514 nm and an oil immersion objective with an NA of 1.45, then the (theoretical) limit of resolution will be 177 nm.
- Abbe's diffraction formula for axial (i.e., Z) resolution is: **$d = 2 \lambda/NA^2$** .
- ✓ Again, if we assume a wavelength of 514 nm to observe a specimen with an objective of NA value of 1.45, then the axial resolution will be 489 nm. ***As a consequence, nanoscale features are not observable with optical microscopes.***

- **To maximize the resolving power, λ must be **decreased** and the **refractive index** of the medium, n , or the semi-angular **aperture** of the lens, θ , must be **increased**.**
- Thus, to obtain the resolution of separations as small as 0.2 nm, we need a wavelength of about 0.005 nm. (From Bragg's law, the minimum separation, d_{\min} , which can be resolved by any microscope, is given by: $d_{\min} = \lambda/2\sin\theta$.)
- **Electrons behave both as particles and as waves.** The wavelength associated with an electron is given by the de Broglie relation: $\lambda = h/mv$, where v is the velocity of an electron with its wavelength (λ), where h is Planck's constant.
- An electron of charge e and mass m when passes through a potential difference of V volts, acquires kinetic energy of $mv^2/2 = eV$, giving $v = (2eV/m)^{1/2}$ and $\lambda = \frac{h}{\sqrt{2meV}}$.
- However, at high potential, when electron velocity approaches the speed of light (c), relativistic corrections to mass are applied. Electrons' wavelength may be about 0.005 nm, which allows the resolution of separations as small as 0.2 nm.
- ❖ Electron microscopes have a much better resolution than their optical counterparts because of the interaction of an electron's matter wave with the sample.

- The *electrons in the microscope obtain their kinetic energy by an applied electric potential in the order of kilo or even megavolts.*
- Depending on the kinetic energy, **a typical range of wavelengths can be between 1–0.005 Å**, which is much smaller than that of visible light (400-700 nm) used in optical microscopes, resulting in far better resolution.
- As a consequence, *nanoscale features*, not observable with optical microscopes, can be *observed*.
- The high magnification and resolution of all TEM is a result of the effective electron wavelengths (λ) and the resolution (d).
- In case of TEM, $n = 1$ (vacuum), $\sin\theta = 10^{-2}$, and λ is of the *order of* 0.005 nm, and thus, the resolution $d = 0.3$ nm.
- The higher the operating voltage of a TEM instrument, **the greater the lateral spatial resolution** (e.g., at 400 kV, the resolution is <0.2 nm) ***and has an additional advantage of greater electron penetration, allowing to work with thicker samples.***

- In **transmission electron microscopy (TEM)**, a beam of *focused high-energy electrons* is transmitted through the ***thin sample*** being examined and is imaged on a phosphorescent screen.
- TEM reveals information about its ***particle size distribution, morphology, crystallography, and elemental composition.***
- It is capable of providing ***atomic-resolution lattice images***, as well as giving *chemical information* at a spatial resolution of 1 nm or better.

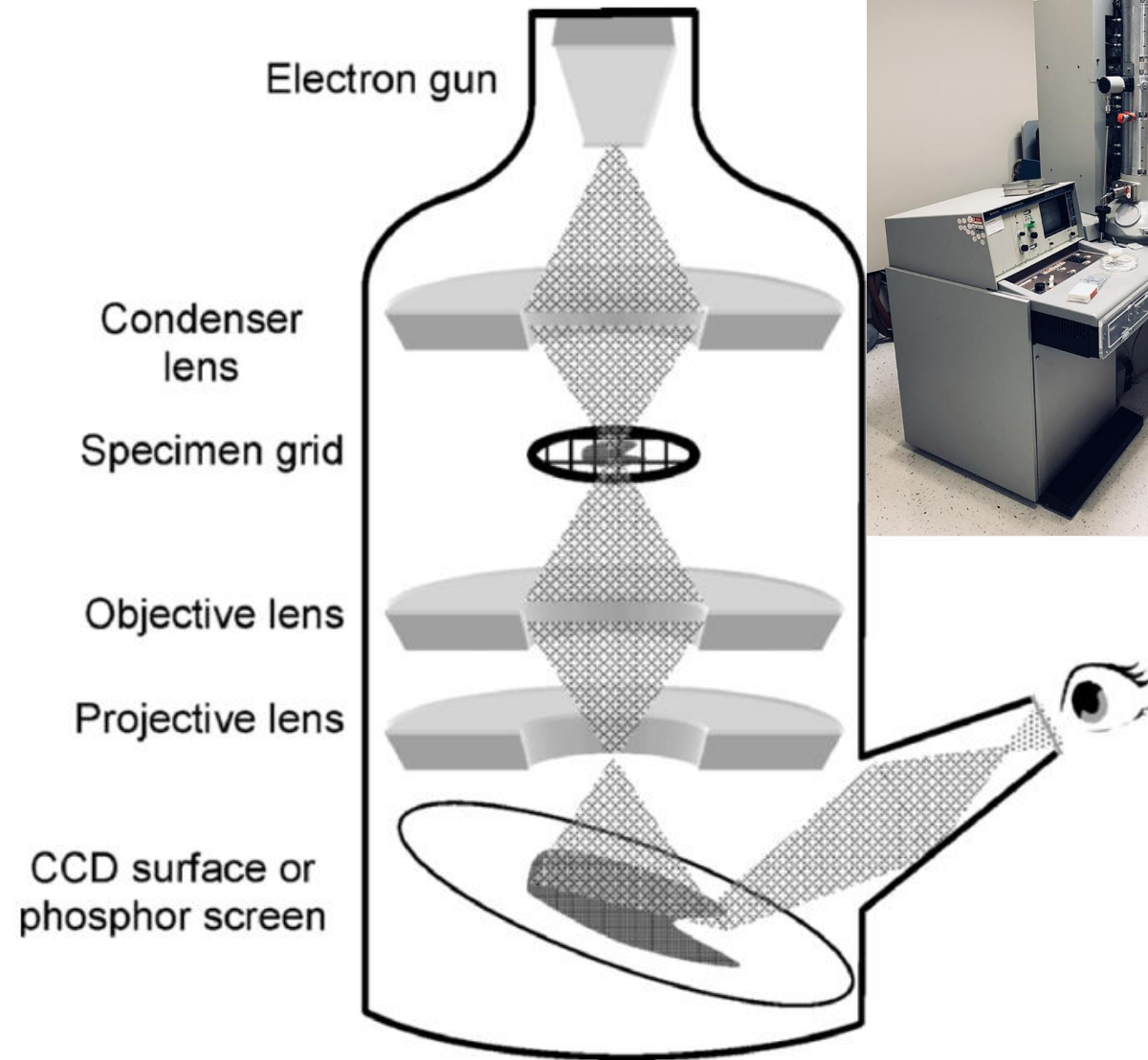


Fig. 5.35 Schematic diagram of a TEM set-up.

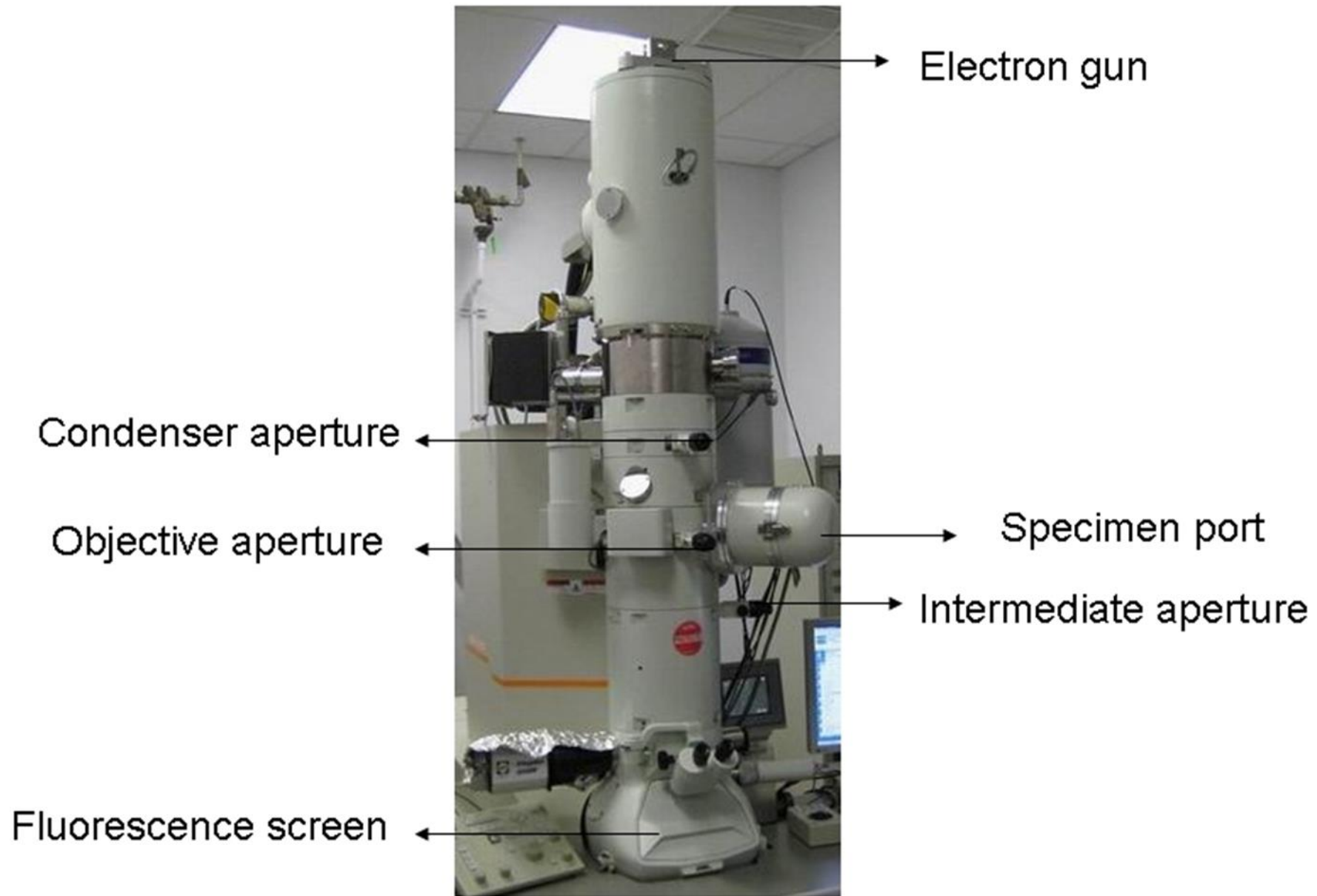


Figure 8.2.9 Position of the basic components in a TEM.

➤ In **scanning electron microscopy (SEM)** the electron beam is scanned over the object and the reflected (scattered) beam is then imaged by the detector. When the *primary electrons* hit the sample, they give part of their energy to electrons in the sample, resulting in the emission of *secondary electrons*. These *secondary electrons* have lower energies (around 20 eV). These secondary electrons are collected by a detector, converted to a voltage, amplified, and built into the image. Their intensity is displayed versus the position of the primary beam on the sample.

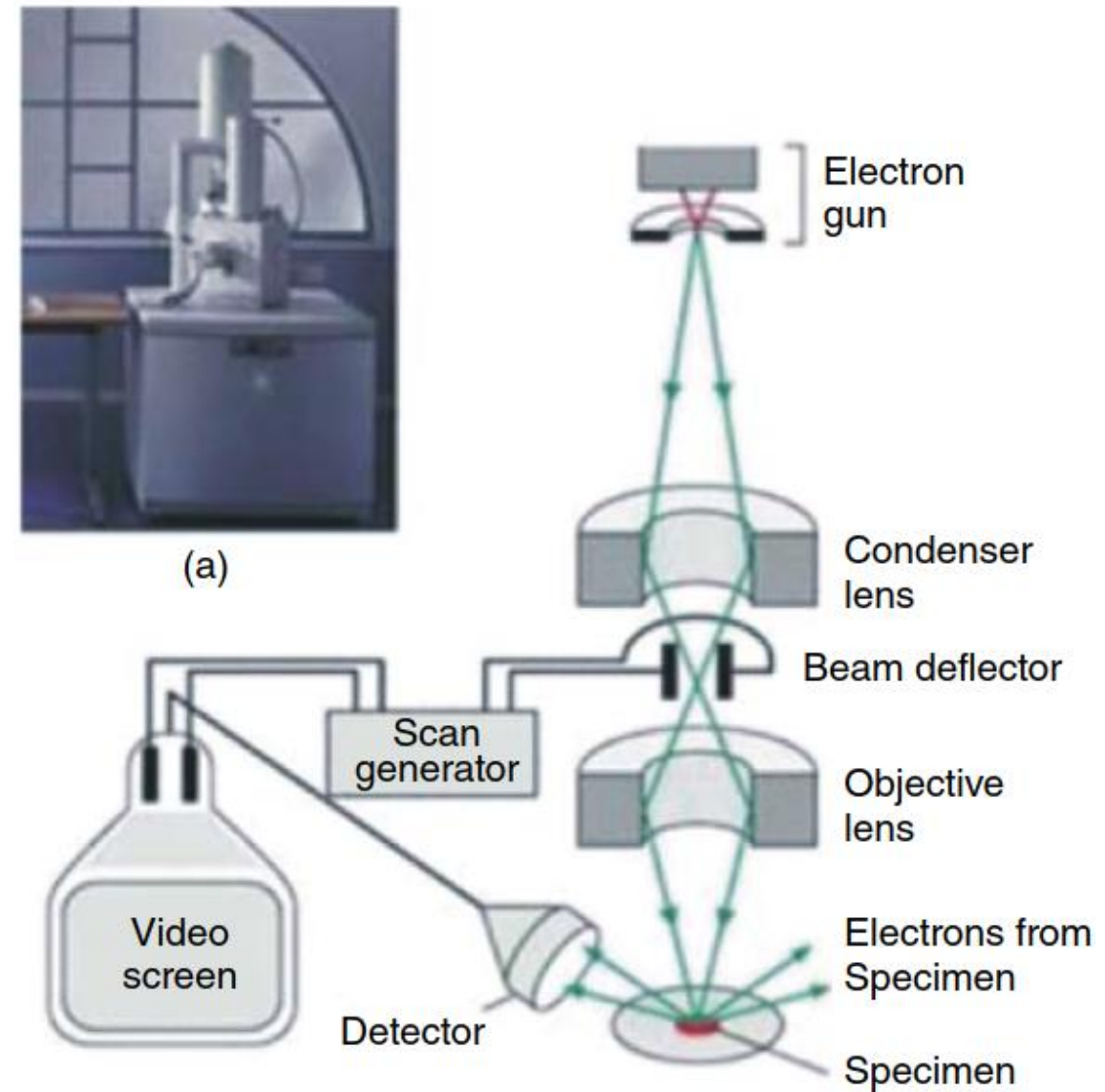


Fig. 5.30 Schematic diagram of an SEM set-up.

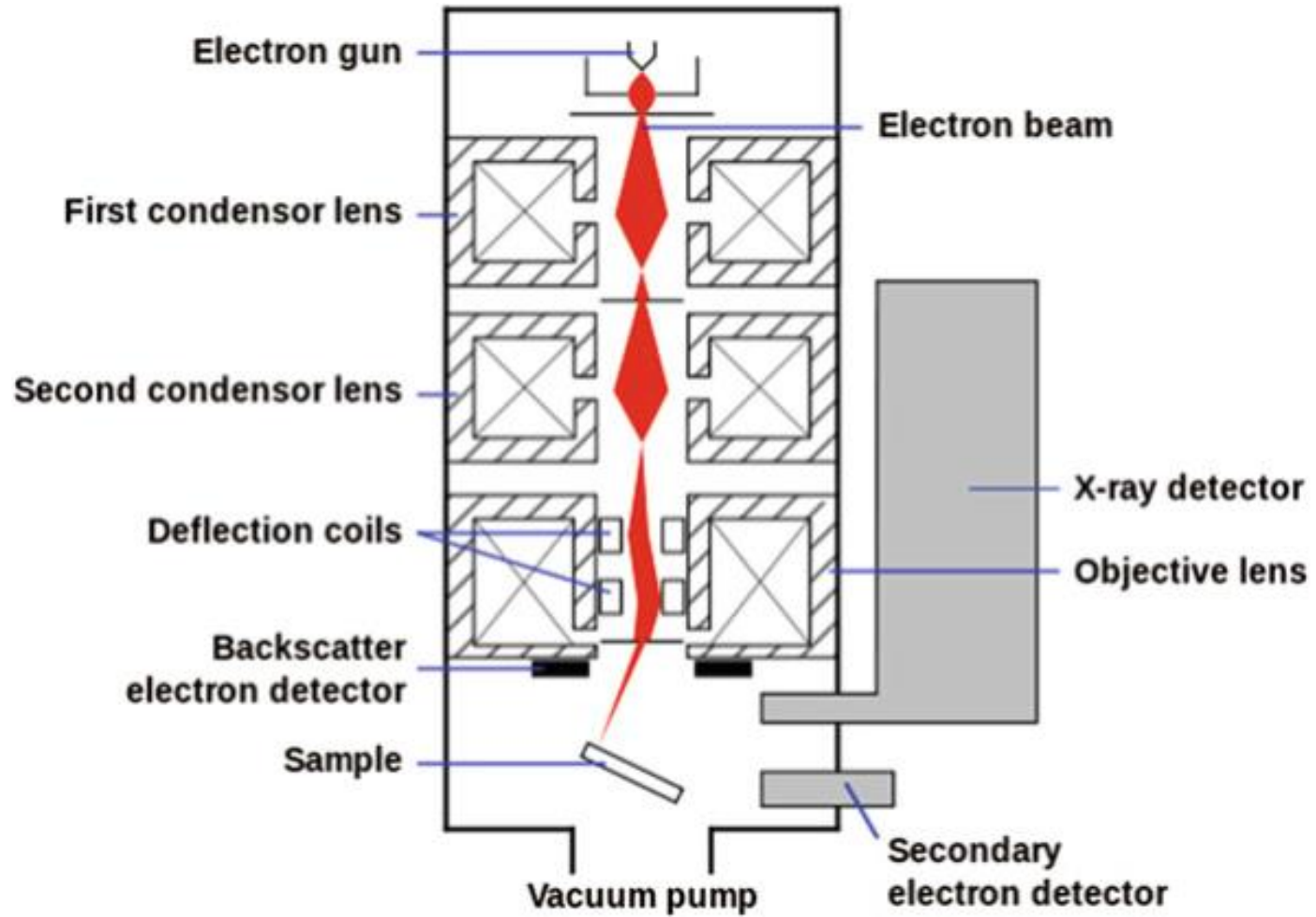


Fig. 9 Schematic diagram of the **SEM** apparatus (Source Wikipedia)

❑ Transmission Electron Microscopy

- A sample shaped as a ***thin film*** is transilluminated by a beam of accelerated electrons with an energy of **50–300 keV** in a vacuum of ca. 10^{-6} mmHg.
- Electrons that were deflected at small angles by atoms in a sample and passed through the sample get into a system of magnetic lenses to form a bright-field image of the sample's internal structure on a screen and a film.
- A resolution of 0.1 nm was achieved, corresponding to a magnification factor of 10^6 . The resolution depends on the nature of the sample and the method of its preparation.
- Usually, films of 0.01- μm thickness are studied; *the contrast range can be extended* using carbon replicas.
- Modern ultramicrotomes allow obtaining sections 10–100-nm thick.
- Metals are studied as thin foils.
- Transmission microscopes make it possible to obtain ***diffraction patterns***, which provide ***information on the crystalline structure*** of a sample.

❑ Scanning Electron Microscopy

- This technique is largely used for *studying the surface of particles*.
- An electron beam is constricted by magnetic lenses to give a thin (1–10 mm) probe, which *travels point by point over a sample progressively*, thus scanning the latter. The interaction of electrons with the surface generates several types of emission:
 - secondary and reflected electrons;
 - transmitted electrons;
 - X-ray slowing-down radiation; and
 - optic radiation.
- Any of the radiation types listed above can be registered and converted into electrical signals. The signals are amplified and fed to a cathode-ray tube. A similar situation occurs in TV kinescopes. Images are formed on the screen and photographed. The major advantage of this technique is the great body of information it provides; *its significant drawback concerns long scanning times*. High resolution is possible only for low scanning rates. *The method is usually employed for particles measuring more than 5 nm*. A restriction on the sample thickness limits the method of application. For electrons with energies of 100 keV, the sample thickness should be about 50 nm. To prevent the destruction of samples, special procedures are used for sample preparation.

- Moreover, the possible effect of electron emission on the samples should be taken into account—for instance, the electron-beam-induced aggregation of the particles.
- One method used for the preparation of samples consists in employing ultramicrotomes (their use is problematic for the cases of nonuniform deposition, particularly in islets).
- Chemical methods are also applied, especially matrix dissolution. The general view of a histogram obtained in microscopic studies often depends on the way the sample was prepared.
- In the 1980s, a great breakthrough was observed in electron microscopy. Microscopes equipped for the computer analysis of the ***elemental composition*** were developed on the basis of energy-loss spectrometers. The energy-loss spectrometry was used in combination with TEM and SEM. A rearrangement of the magnetic-prism system allowed one to regulate the image contrast, which depends on the incidence angle, atomic number, and the reflection factor. Modern devices make it possible to obtain selective images of elements from boron to uranium with a resolution of 0.5 nm and sensitivity up to 10–20 ng, which amounts to (for example) 150 atoms of calcium. High-resolution electron microscopy provides insight into such objects.

- An important stage in the development of electron microscopy was associated with elaborating computerized techniques for processing images, which allowed histograms over shapes, orientations, and sizes to be obtained.
- Now, it is also possible to separate details of the structure, statistically process information, estimate local microconcentrations, and determine lattice parameters. Built-in processors make it possible to exercise versatile control over microscopes.
- The ultimate resolution of SEM depends on how sharply the incident beam is focused on the sample, how it is moved over the sample, and how much the beam spreads out into the sample before it is reflected but features with dimensions of 1 μm or less are typically resolved.

- However, *electron microscopy must be carried out in a vacuum*, and single-atom resolution is achieved only for electrons accelerated to over 100 kV.
- *Electron microscopies occur at low pressures* so that the electrons are not scattered by gas molecules inside the chamber.
- The obvious way *to reduce the number of impacts* is to reduce the pressure to an ultra low value.
- A simple calculation shows that when the pressure is reduced to 0.1 mPa (as in a simple vacuum system) the collision flux falls to about $10^{18} \text{ m}^{-2} \text{ s}^{-1}$, corresponding to one hit on a surface atom in each 0.1 s.
- In *ultrahigh vacuum* (UHV) techniques, pressures as low as 0.1 μPa (when $Z_w \approx 10^{15} \text{ m}^{-2} \text{ s}^{-1}$) are reached and as *low as 1 nPa* (when $Z_w \approx 10^{13} \text{ m}^{-2} \text{ s}^{-1}$) are reached with special care. These collision fluxes correspond to *each surface atom being hit once every 10^5 – 10^6 s, or about once a day.*

- *The primary advantage of SEM over TEM is that it can form images of electron-opaque samples without the need for difficult specimen preparations: SEM is therefore the electron microscopy method of choice* for the straightforward characterization of materials.
- ✓ However, ***SEM samples need to be conductive***; otherwise, electrons collect on the sample and interact with the electron beam, resulting in blurring. ***Nonconductive samples must be coated with a thin layer of conducting material***, usually gold or graphitic carbon.
- ❑ In both microscopes, the electron probes **cause the production of X-rays** with energies ***characteristic of the elemental composition of the material***. As such, **energy-dispersive spectroscopy (EDS)** of ***these characteristic X-rays is used to quantify the chemical make-up of materials*** using electron microscopes.
- ✓ EDS, EDX, EDXS or XEDS, sometimes called energy dispersive X-ray analysis (EDXA) or energy dispersive X-ray microanalysis (EDXMA), is an analytical technique used for the elemental analysis or chemical characterization of a sample.

❑ The different aspects of crystallite information that can be investigated using **SEM** are listed below:

- **Topography:** The *surface features* of an object or ‘how it looks’; detectable features are limited to a few nanometers.
- **Morphology:** The shape, size, and arrangement of the particles making up the object that are lying on the surface of the sample or have been exposed by grinding or chemical etching; detectable features limited to a few nanometers.
- **Composition:** The elements and compounds the sample is composed of and their relative ratios, in areas ~1 micrometer in diameter and depth.
- **Crystallographic information:** The arrangement of atoms in the specimen and their degree of order; only useful on single-crystal particles >20 micrometers.

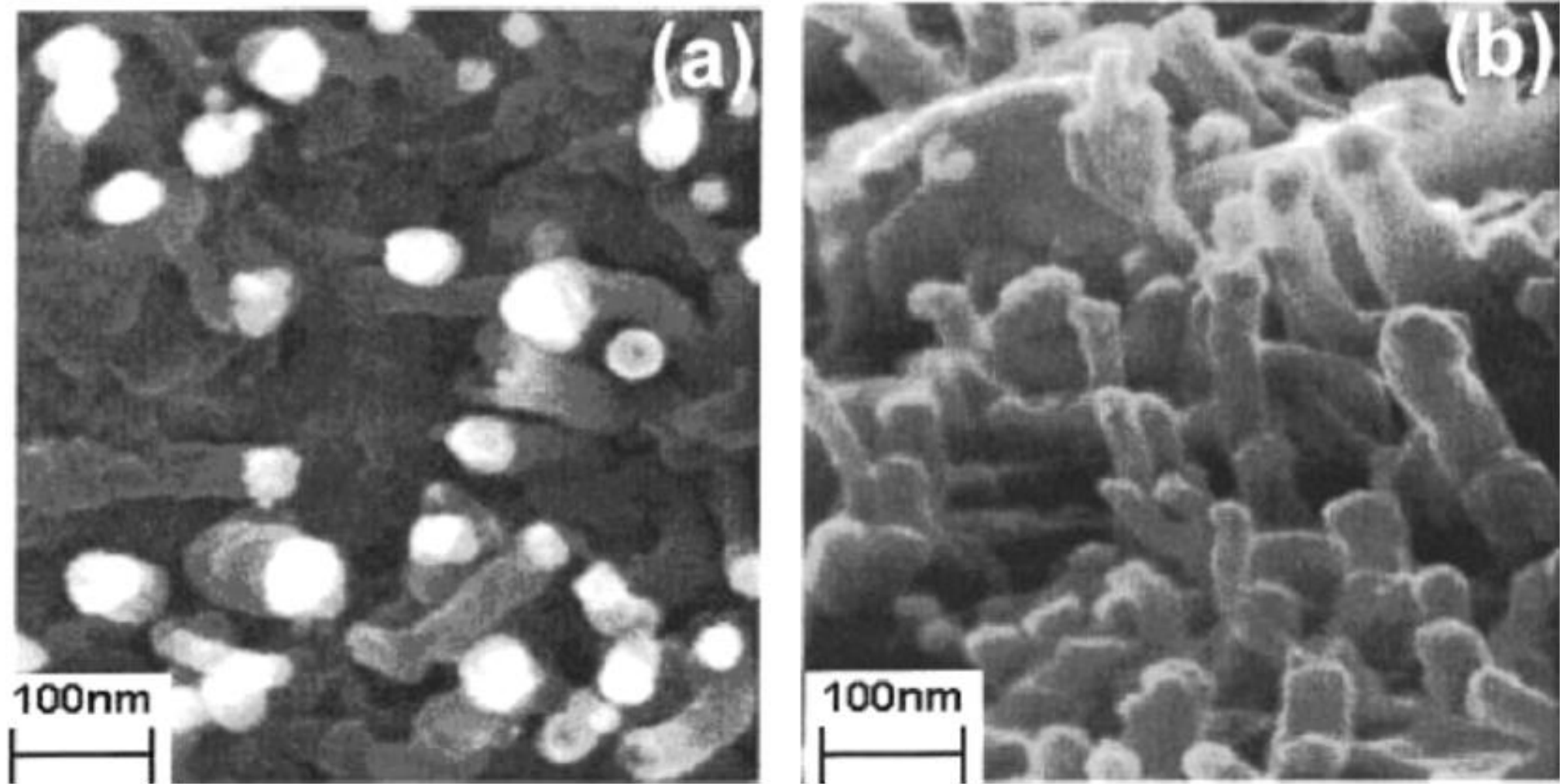


Fig. 5.33 High-resolution SEM images of carbon nanotubes grown on a 5 nm Ni catalyst layer thickness; (a) top view and (b) side view.

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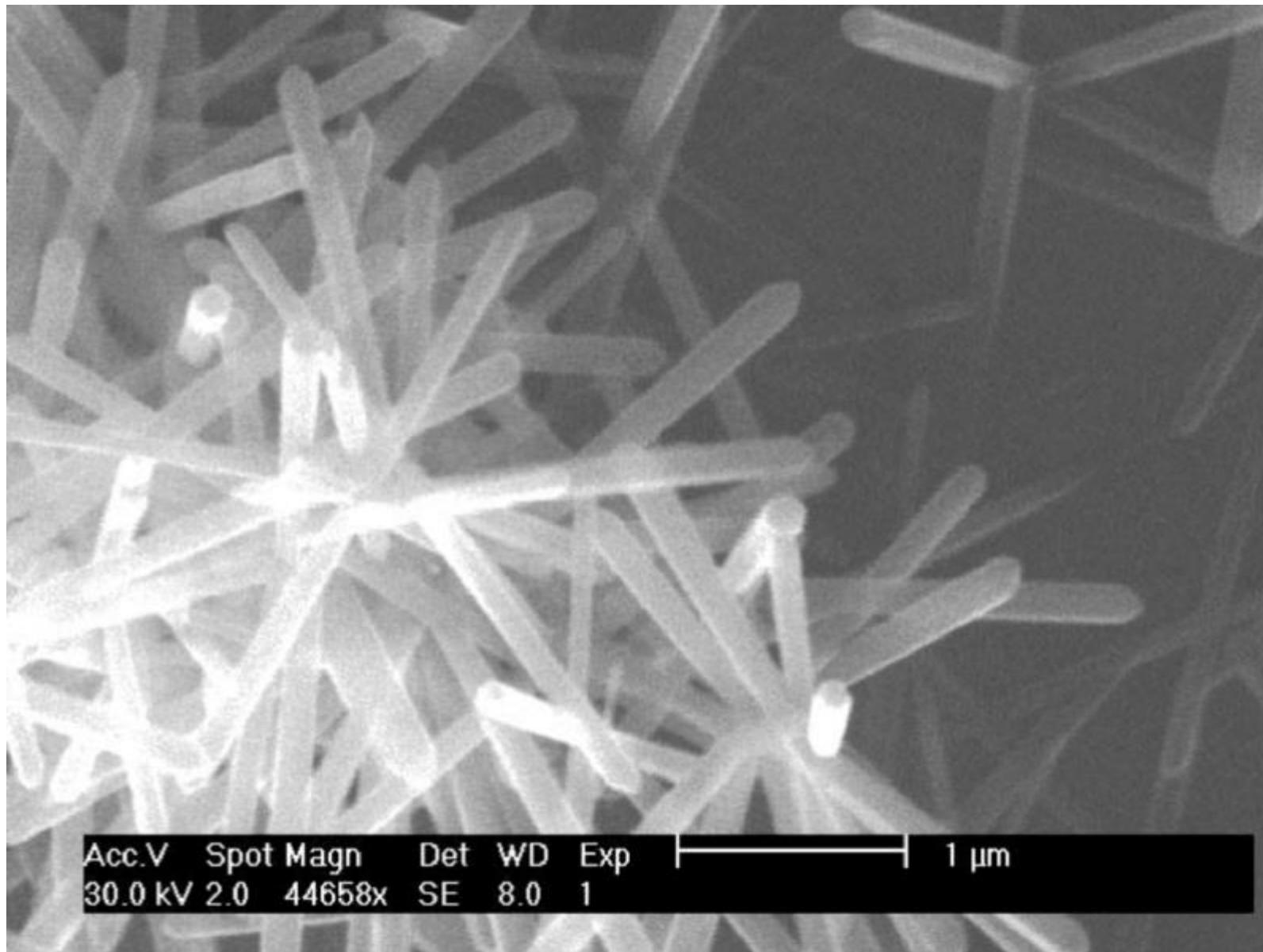


Fig. 5.31 SEM image of ZnO nanorods fabricated via liquid phase deposition.

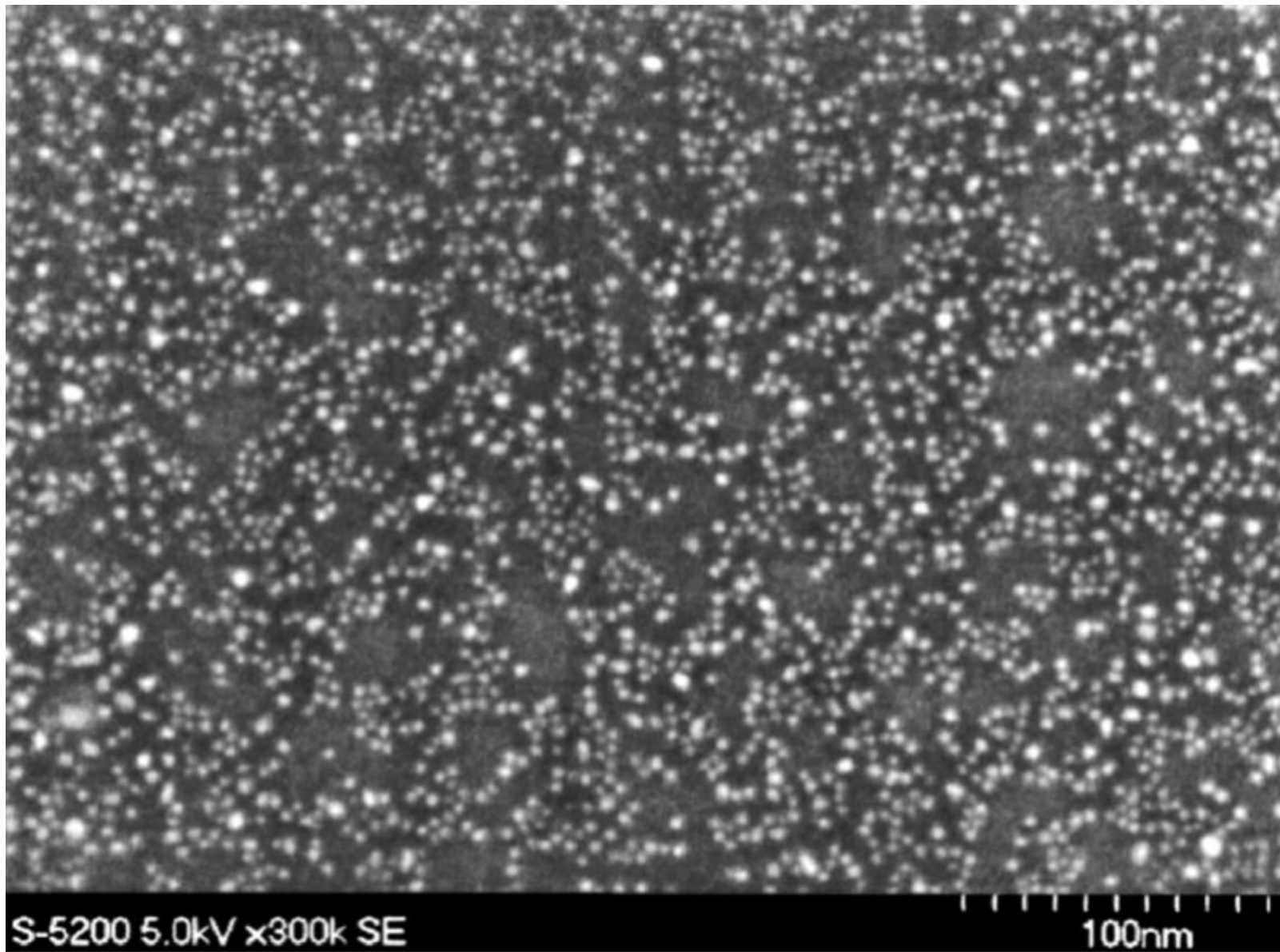


Fig. 5.32 High-resolution SEM image of a monolayer FePt nanoparticle film.
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❑ **TEMs** are patterned after transmission light microscopes and will yield the following information.

- **Morphology:** The size, shape and arrangement of the particles which make up the specimen as well as their relationship to each other on the scale of atomic diameters.
 - **Crystallographic information:** The arrangement of atoms in the specimen and their degree of order, detection of atomic-scale defects in areas a few nanometers in diameter.
 - **Compositional information:** The elements and compounds the sample is composed of and their relative ratios, in areas a few nanometers in diameter.
- ✓ The high magnification or resolution of TEM is a result of the small effective electron wavelengths, λ , which is given by the de Broglie relationship:

$$\lambda = \frac{h}{\sqrt{2meV}}$$

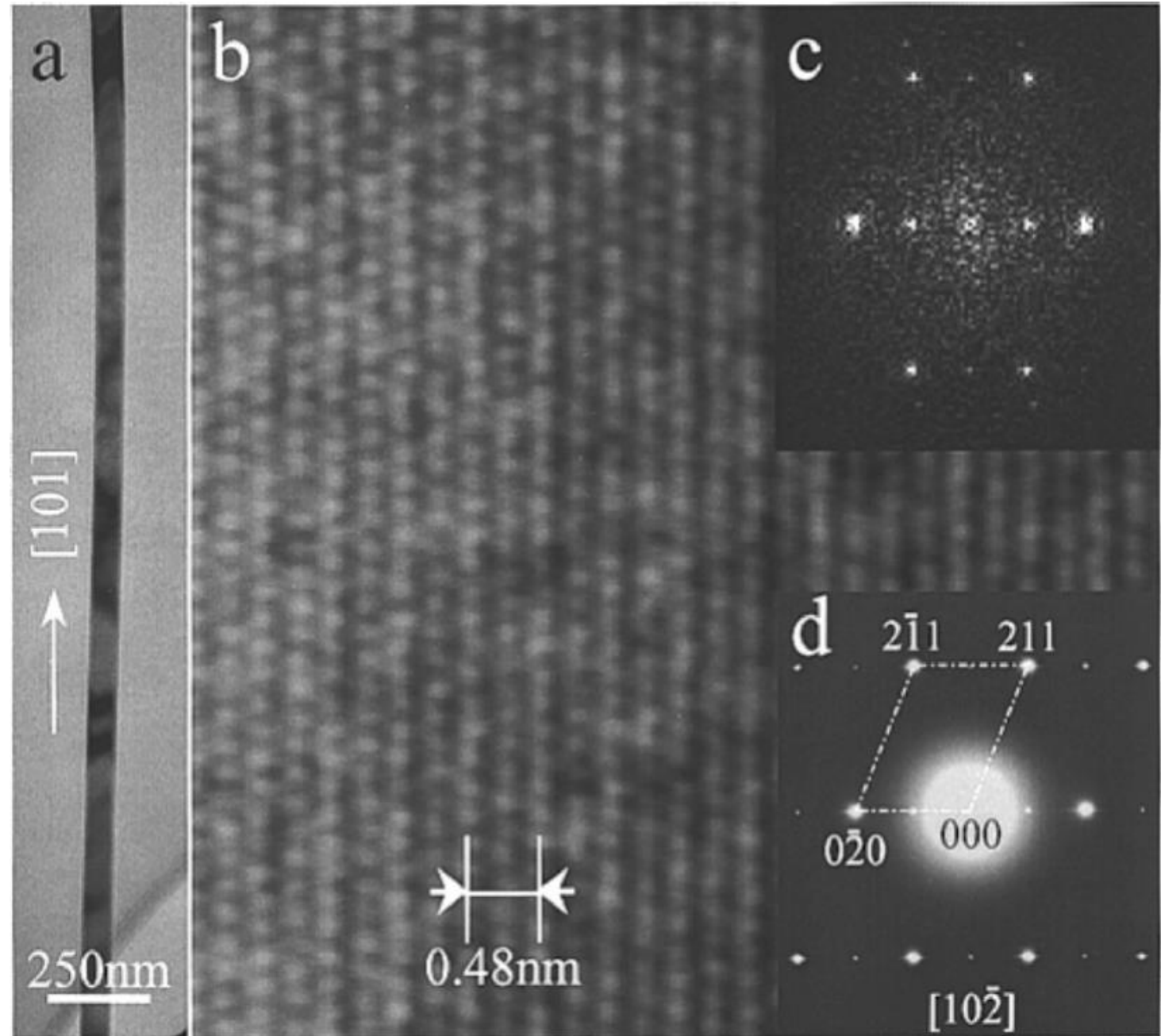
where m and e are the electron mass and charge, h is Planck's constant, and V is the **potential difference** through which electrons are accelerated. For example, electrons of 100 keV energy have wavelengths of 0.37 nm and are capable of effectively transmitting through $\sim 0.6 \mu\text{m}$ of silicon.

❑ The higher the operating voltage of a TEM instrument, the greater its lateral spatial resolution.

- High-voltage TEM instruments (for example, 400 kV) have point-to-point resolutions better than 0.2 nm.
- High-voltage TEM instruments have the additional advantage of greater electron penetration, because high-energy electrons interact less strongly with matter than lower energy electrons.
- ✓ So, it is possible to work with thicker samples on a high-voltage TEM.
- Unfortunately, *the depth resolution of TEM is poor*. Electron scattering information in a TEM image originates from a three-dimensional sample but is projected on a two-dimensional detector.

Fig. 5.36 (a) TEM image of a rutile structured SnO_2 nanowire.
 (b) **High-resolution TEM image** of the nanowire.
 (c) Corresponding FFT of the image, and
 (d) **selected area electron diffraction** (SAED) pattern from the nanowire.

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High resolution transmission electron microscope (HRTEM) is able to resolve the **hexagonal arrangement of atoms in the graphene** (Fig. 8.4) while the atomic force microscope can reveal the contrast between the regions of different thicknesses.

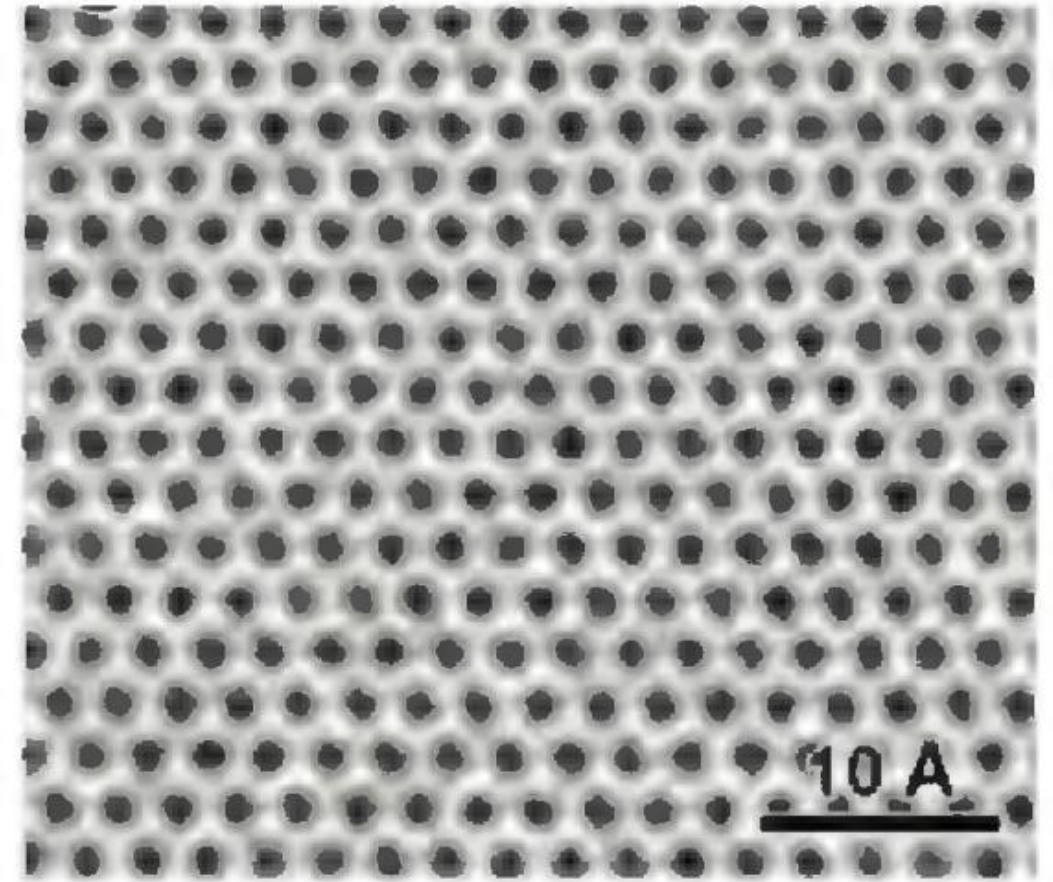


Fig. 8.4. A high-resolution transmission electron micrograph of graphene; *atoms are the white dots*.

DIFFRACTION TECHNIQUES

- These techniques include diffraction of *X-rays and neutrons* and are *less general* when compared with electron microscopy.
- At the same time, the analysis of diffraction reflexes induced by atomic structures of the separate particles can be used for studying very small particles.
- The reflex angle width $\Delta\theta$ decreases with an increase in the particle size ($\Delta\theta \sim 1/R$, i.e., the **Scherrer effect**).
- The **smaller sizes** correspond to smaller numbers of lattice planes that give rise to interference of the **diffraction spot**, while in **larger clusters diffraction rings** are usually observed.

❑ X-ray Diffraction

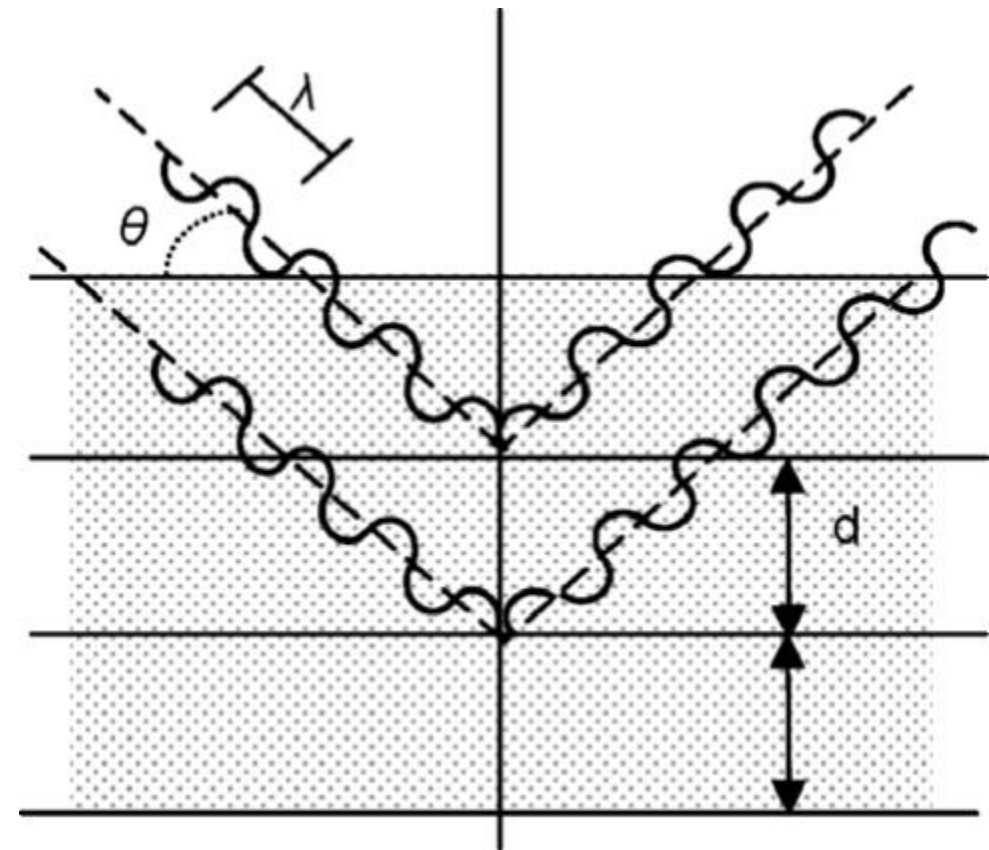
- When interacting with crystals, metal particles, and molecules, X-ray are scattered.
- An initial beam of rays with a wavelength $\lambda \sim 0.5 - 5\text{\AA}$ gives **rise to secondary rays with the same wavelength**, the **directions and intensities of which are related to the structure of scattering samples**.
- The **intensity of a diffracted ray also depends on the sizes and shapes of the particles**.
- **Polycrystalline particles give rise to secondary ray cones, each cone corresponding to a certain family of crystal planes**. For small and abundant crystals, **the cone is continuous, which results in a nonuniformly darkened ring**.

- XRD involves monitoring the diffraction of X-rays after they interact with the sample.
- It is a crystallographic technique used for identifying and quantifying various crystalline phases present in solid materials and powders.
- ***In XRD*** the ***crystal structure*** can be determined as well as the ***size of grains and nanoparticles***.
- XRD is one of the most utilized techniques for determining the structure of inorganic and organic materials.
- It is also widely used for studying nanostructured thin films and nanoparticles.
- However, the materials must have ordered structure, and it cannot be used directly to study amorphous materials.
- Another inherent limitation of XRD is that mixtures of phases that have low symmetry are difficult to differentiate between because of the larger number of diffraction peaks. Furthermore, organic materials such as polymers are never completely crystalline, therefore XRD is primarily used to determine their crystallinity.

- When X-rays are directed at a regular crystalline sample, a proportion of them are diffracted to produce a pattern. From such a pattern the crystal phases can be identified by comparison to those of internationally recognized databases (such as International Center of Diffraction Data - ICDD) that contain reference patterns.
- In crystallography, the solid to be characterized by XRD has a space lattice with an ordered three-dimensional distribution (cubic, rhombic, etc.) of atoms. These atoms form a series of parallel planes separated by a distance d , which varies according to the nature of the material. For any crystal, planes have their own specific d -spacing.
- When a monochromatic X-ray beam with wavelength λ is irradiated onto a crystalline material with spacing d , at an angle θ , diffraction occurs only when the distance traveled by the rays reflected from successive planes differs by an integer number n of wavelengths to produce constructive interference (Fig. 5.21).

Bragg condition: $n\lambda = 2d \sin\theta$.

Fig. 5.21 Condition for constructive interference.



- Such constructive interference patterns only occur when incident angles fulfill the Bragg condition such that: **$n\lambda = 2d \sin\theta$** .
- By varying the angle θ , the Bragg Law condition is satisfied for different d -spacings in polycrystalline materials.
- Plotting the angular positions versus intensities produces a *diffraction pattern*, which is characteristic of the sample.
- When a mixture of different phases is present, the resultant diffractogram is a superposition of the individual patterns.
- In a typical XRD pattern, the diffracted intensities are plotted versus the detector angle 2θ . Each peak is then assigned a label indicating the spacing of a crystal plane.

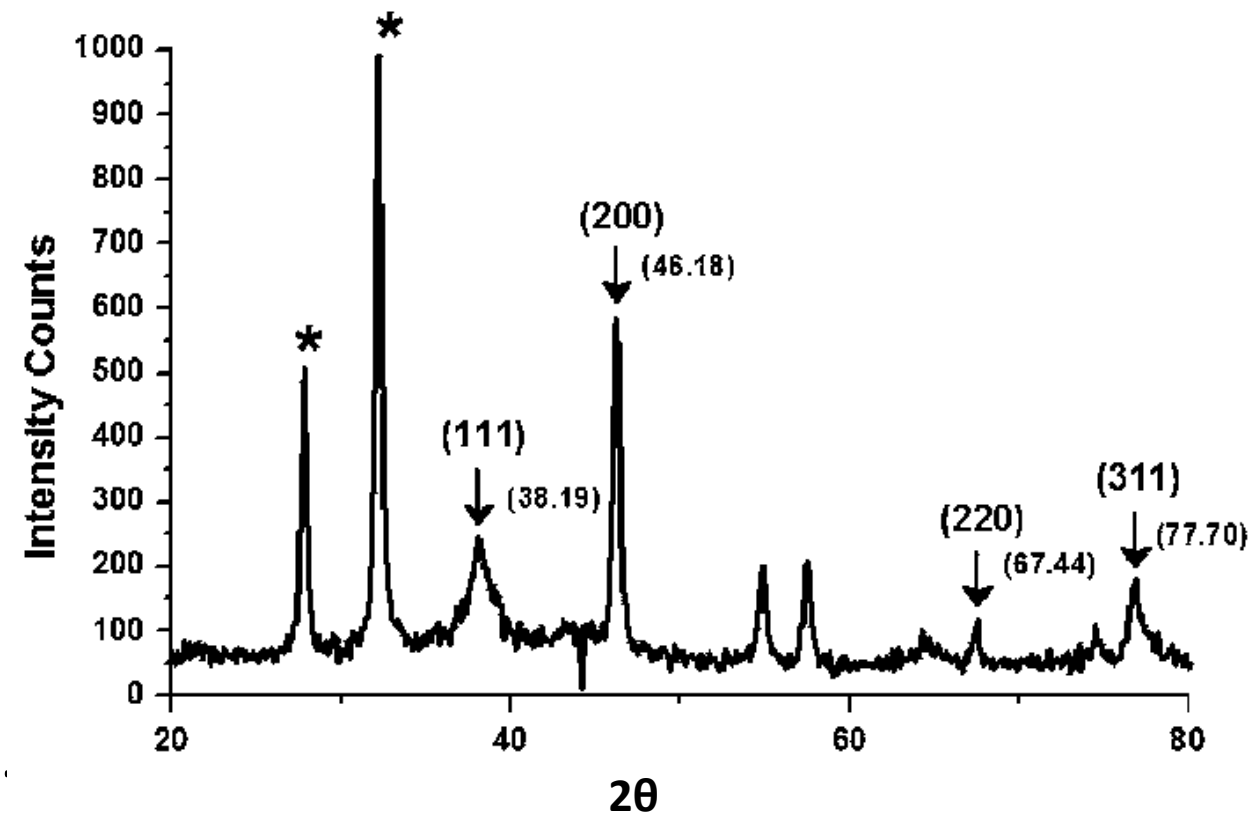


Figure.... XRD pattern of silver nanoparticles.

- A crystal represents a natural diffraction grating with strict periodicity. The *crystals for studies should have sizes of ca. 0.1 mm and perfect structures*. To elucidate a structure of average complexity, which contains 50–100 atoms in a unit cell, intensities of hundreds and even thousands of diffraction reflections are measured. This procedure is accomplished by means of microdensitometers and diffractometers controlled by computers. Earlier, these operations took months, but today they can be carried out in a single day.
- When studying ***amorphous materials and incompletely ordered particles in polycrystals***, X-ray diffraction allows one to ***determine the phase composition, size, and orientation of grains (texture)***.
- The method of *low-angle scattering, which allows studying spatial heterogeneities with sizes of 5–10 Å, is widely applied to date. It is used for studying porous, finely dispersed materials and alloys*.
- The determination of atomic structure, which involves size and shape estimation and assignment to a symmetry group, represents a complex analysis and cumbersome mathematical processing of intensities of all diffraction reflections. X-ray diffraction of materials embraces methods based on X-ray diffraction techniques for studying equilibrium and nonequilibrium states of materials, phase compositions, phase diagrams, residual stresses, etc.

- Bragg's law states the condition for *sharp diffraction peaks* arising from crystals which are perfectly ordered. *Actual diffraction peaks have a finite width* resulting from imperfections, either the irradiation source or the sample.
- ***A useful phenomenon is that as crystallite dimensions enter the nanoscale the peaks broaden with decreasing crystal size.***
- It is known that the ***widths of the diffraction peaks*** allow the determination of ***crystallite size***.
- Practically, the size of crystallites can be determined using variants of the **(Debye-)Scherrer**

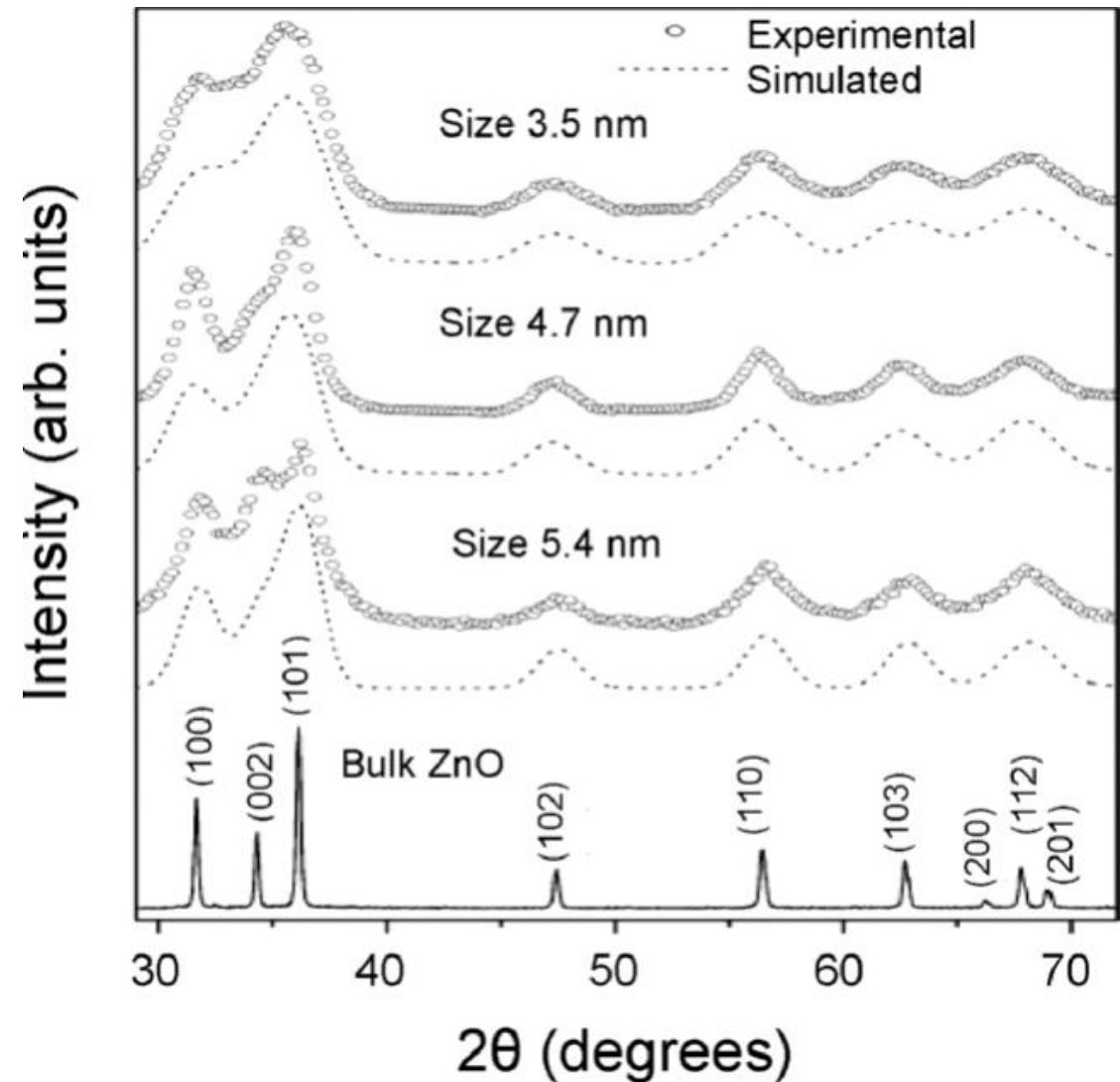
equation:

$$t = \frac{K\lambda}{B \cos\theta}$$

- ✓ ***t*** is the thickness of the crystal. *It is the mean size of the ordered (crystalline) domains, which may be smaller or equal to the grain size, which may be smaller or equal to the particle size (diameter).*
- ✓ *K* is a dimensionless shape factor, with a value close to unity (typically 0.89, if a Gaussian function is used to describe the broadened peak but varies with the actual shape of the crystallite.
- ✓ λ is the X-ray wavelength used for diffraction. (Copper K- α , which is the x-ray energy frequently used on lab-scale x-ray instruments, has a wavelength of 1.5406 Å).
- ✓ ***B*** is the ***full width at half maximum*** (FWHM) of the broadened peak in **radians** (after subtracting the instrumental line broadening, if any). This quantity is also sometimes denoted as $\Delta(2\theta)$.
- ✓ θ is the Bragg angle.
- ✓ This relation is used in the ***determination of size of crystals in the form of powder***.
- ✓ The Scherrer equation is derived from Bragg's law and may be used to determine crystallite sizes if the crystals are smaller than 1000 Å (or 100 nm).

□ In Fig. 5.22, XRD patterns for ZnO nanocrystals synthesized from zinc acetate and sodium hydroxide are shown. As seen in the figure, **peaks are broadened with respect to those of the bulk material**, and the **broadening increases** as the crystallite **size decreases**. The crystal structure of the bulk (wurtzite) has been preserved in the nanocrystals, despite being significantly broadened.

Fig. 5.22 Experimental XRD patterns of ZnO nanocrystals (circles) and the corresponding *simulated patterns (dotted line)* for different particle sizes. (Reprinted with permission from the Royal Society of Chemistry publications.)



- Performing **XRD** on powders made of nanocrystals can **provide information about their structure and size**. For instance, the powder diffraction patterns of InAs and InP nanocrystals of different sizes, are shown in Fig. 5.23.
- **Peak broadening occurs as the dimensions of the nanocrystals decrease.**
- **From the width of the reflections the crystalline domain size may be calculated.**
- The peak positions for the nanocrystals shown agree with those of the bulk, demonstrating that the crystal structure hasn't changed as the particle sizes decrease, despite the substantial changes in the domain size.
- A small shift in peak positions can also be seen in Fig. 5.23 patterns when crystallite size decreases which is due to lattice relaxation.

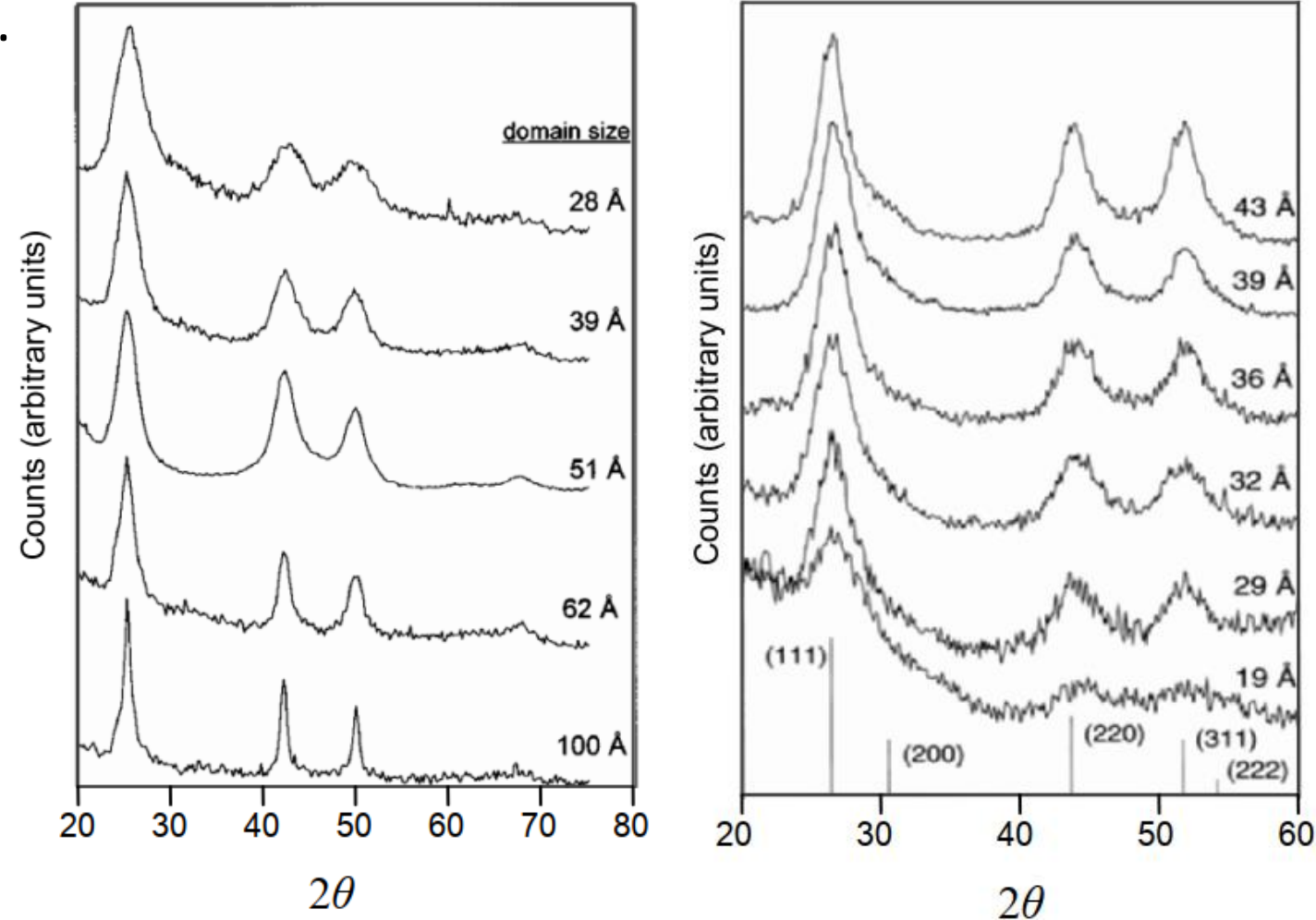


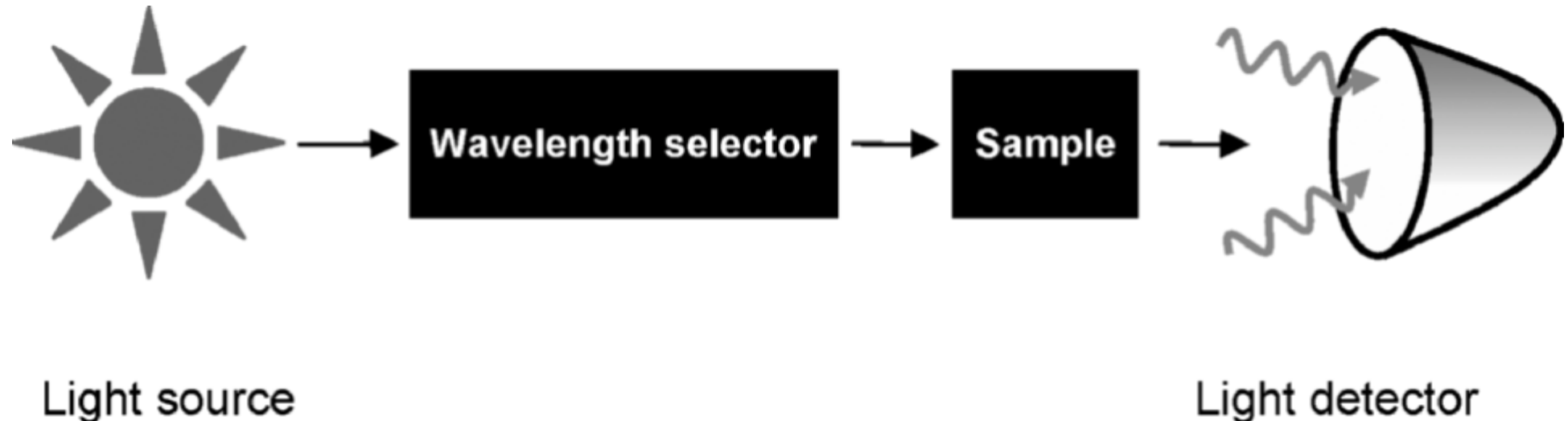
Fig. 5.23 Left: Powder XRD spectra of a series of InAs (left) and InP (right) nanocrystal sizes. The stick spectrum at the bottom gives the bulk reflection position with relative intensities. Reprinted with permission from the ACS publications.

Neutron Diffraction

- A neutron is a particle; the properties of which make it suitable to be used in the analysis of various materials. Nuclear reactors produce thermal neutrons with a maximum energy of 0.06 eV, which corresponds to the de Broglie wave with $\lambda \sim 1\text{\AA}$ commensurable interatomic distances.
- This forms the basis of the method of structural neutron diffraction.
- The commensurability of energies of thermal neutrons with those of thermal oscillations of atoms and groups of molecules is used for the analysis in neutron spectroscopy, while the presence of a magnetic moment lays the basis for magnetic neutron diffraction.

SPECTROSCOPY

- *Electromagnetic spectroscopy concerns the interaction of electromagnetic waves and matters, whether they are in the form of atoms, molecules, or larger assemblies.*
- These interactions involve the electromagnetic radiation absorption (e.g., UV-visible, IR, NMR spectroscopy), emission (e.g., photoluminescence spectroscopy), and/or scattering (e.g., Raman spectroscopy) by the matter.
- In the electromagnetic *spectroscopy, the intensity of the absorbed/emitted/scattered electromagnetic waves is plotted against wavelength or frequency.*
- From this spectrum, *materials can be identified and quantified.*
- A block diagram for a basic spectrometer is shown in Fig. 5.



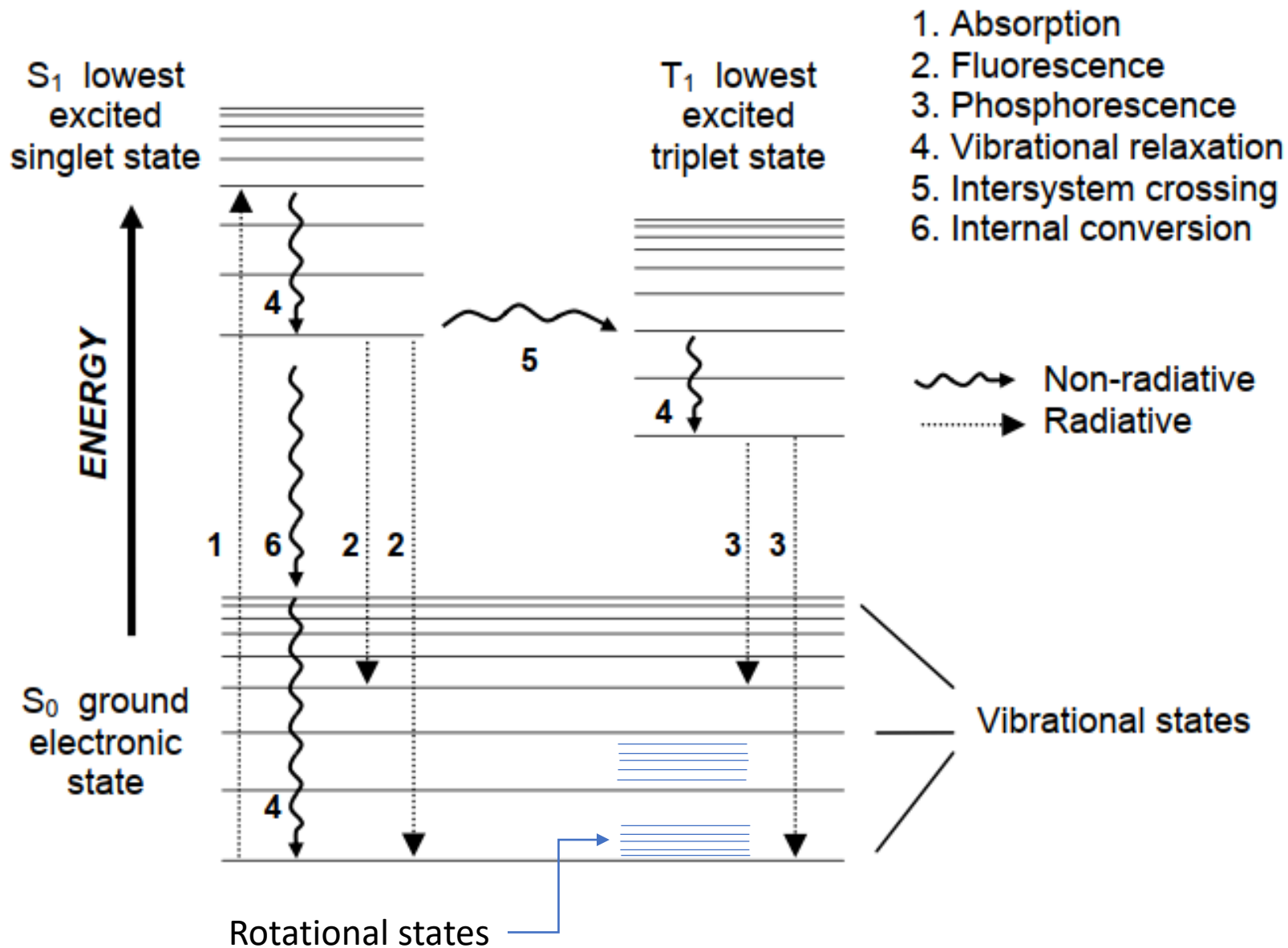
- The measured ***spectrum strongly depends on the ambient environment and the presence of other molecules nearby***. Therefore, electromagnetic spectroscopy techniques can be directly ***employed for sensing applications***, with ***the intensity of electromagnetic waves absorbed or emitted, or the shift in absorption/emission wavelengths as the output parameters***.
- Electromagnetic spectroscopy also provides a contactless way to probe materials.
- The ***information that can be obtained from a material strongly depends on the interaction wavelengths*** of electromagnetic wave.
- The relationships between frequency f , wavelength λ , and energy of the particle E , are given by: $E = hf = hc/\lambda$ where h is Planck's constant (6.626×10^{-34} J·s), and c is the speed of light. In free space, c has the value of 2.998×10^8 m/s, whereas, in other media, its value is adjusted to c/n , where n is the *refractive index* of the medium.
- From Table 5.1 it is observed that different wavelengths of incident waves are responsible for the observation of various phenomena. For example, microwaves stimulate rotations of molecules; infrared waves stimulate vibrations of higher energy orbitals; visible and ultraviolet waves promote electrons to higher energy orbitals, and X-rays and short wavelengths break chemical bonds and ionize molecules and can even damage living tissue.

Table 5.1 Types of interactions between electromagnetic waves of different frequencies with matter.

Region	Frequency (Hz)	Wavelength	Effect and Information	Energy, E (kJ/mol)
Radio waves	$< 3 \times 10^8$	Larger than 1 m	Nuclear and electron spin transitions	$E < 0.001$
Microwaves	$3 \times 10^8 - 3 \times 10^{11}$	$1 - 10^{-3}$ m	Rotation	$0.001 < E < 0.12$
Infrared	$3 \times 10^{11} - 0.37 \times 10^{15}$	10^{-3} m – 800 nm	Vibration	$0.12 < E < 150$
Visible	$0.37 \times 10^{15} - 0.75 \times 10^{15}$	800 nm – 400 nm	Outer shell electron transitions	$150 < E < 310$
Ultraviolet	$0.75 \times 10^{15} - 3 \times 10^{16}$	800 nm – 10^{-8} m	Electronic excitation	$310 < E < 12000$
X- rays	$3 \times 10^{15} - 3 \times 10^{19}$	10^{-8} m – 10^{-11} m	Bond breaking and ionization	$12000 < E < 1.2 \times 10^7$
γ - rays	$3 \times 10^{19} - 3 \times 10^{20}$	10^{-11} m – 10^{-12} m	Nuclear	$1.2 \times 10^7 < E < 1.2 \times 10^8$
Cosmic rays	$> 3 \times 10^{20}$	$< 10^{-12}$ m		$1.2 \times 10^8 < E$

- When the near ultraviolet, visible, and near/mid infrared regions of the electromagnetic spectrum are utilized, the electromagnetic spectroscopy techniques are referred to as ***spectrophotometry***.
- In these techniques, the wavelengths of the incident electromagnetic waves are generally scanned across a range to produce an absorption or emission spectrum. Analogous phenomena occur in the X-ray, microwave, radio, and other regions of the electromagnetic spectrum.
- In spectrophotometry, several processes occur after the material absorbs energy; these are changes in the electronic energy, vibrational and rotational relaxations, intersystem crossings, as well as internal conversions as shown in Fig. 5.2. Owing to the quantum nature of molecules, their energy distribution at any given moment can be defined as the sum of the contributing energy terms:
- $E_{\text{total}} = E_{\text{electronic}} + E_{\text{vibrational}} + E_{\text{rotational}} + E_{\text{translational}}$.

Fig. 5.2 Possible physical processes following absorption of a photon.



- The electronic energy components correspond to all electrons energy transitions throughout the molecule and may be either localized, within specific bonds, or delocalized over structures such as aromatic rings.
- ***Electronic transitions can occur when a molecule absorbs visible and ultraviolet electromagnetic radiations.***
- Vibrational energy is an energy of less magnitude arising from the absorption in the infrared region, where the constituent atoms vibrate about the mean center of their chemical bonds.
- Absorption of radiation in the microwave region gives rise to the rotational energy component, which is associated with tumbling motion of a molecule, and the translational energy is related to molecules being displaced as a function of the thermal motions of matter.
- Having discussed some background of electromagnetic spectroscopy, the main techniques that are used in this field, namely ultraviolet-visible spectroscopy, photoluminescence spectroscopy, and infrared spectroscopy, will be presented.

❑ Ultraviolet–Visible (200–800 nm) Spectroscopy (or UV-Visible or UV-Vis Spectroscopy)

- The energies associated with **UV-visible ranges are sufficient to excite molecular electrons to higher energy orbitals.**
- Photons in the visible range have wavelengths between 800-400 nm, which corresponds to energies between 36 and 72 kcal/mol. The near UV range includes wavelengths down to 200 nm and has energies as high as 143 kcal/mol. UV radiation of lower wavelengths is difficult to handle for safety reasons and is rarely used in routine UV-vis spectroscopy.
- Ultraviolet-visible (UV-vis) spectroscopy is widely utilized to *quantitatively characterize organic and inorganic nanosized molecules.*
- A sample is irradiated with electromagnetic waves in the ultraviolet and visible ranges and the absorbed light is analyzed through the resulting spectrum.

- The *energy per unit area* of the beam is the ***irradiance***, P , and is related to the fraction of the light that passes through a sample, the transmittance, T , by:

$$T = P_{\text{out}}/P_0 \quad (5.3)$$

where P_0 is the impinging light on a sample and P_{out} is the light that emerges from the sample.

- The ***absorbance***, A , is generally defined as:

$$A = \log(P_0/P_{\text{out}}) = -\log T. \quad (5.4)$$

- The absorbance is directly proportional to the ***concentration***, c (in mol/l), of the light absorbing species and can be obtained from the Beer-Lambert law:

$$A = \epsilon bc, \quad (5.5)$$

where b (in cm) is the *path length* and ϵ is the *molar absorptivity* or *molar extinction coefficient* (l/mol.cm).

- Molar absorptivity is characteristic of a substance and indicates the amount of light absorbed at a particular wavelength.
- The Beer-Lambert law applies to monochromatic (single frequency) radiation and is valid for dilute solutions of most substances; however, it fails at high concentrations as solute molecules influence one another as a result of their proximity.

- ***Many nanomaterials absorb UV and visible light.***
- Solid samples can be studied using UV diffuse reflectance attachment, and band gaps can be determined in this way.
- In solution, UV and visible absorption spectra are very useful.
- For example, ligand-stabilized gold and silver nanoparticles exhibit particular colors due to visible-light absorption known as plasmon bands.
- ✓ These absorptions are very characteristic; for example, 5 nm gold with thiol ligand shows absorption at about 520 nm, and this can shift slightly due to larger nanoparticle size (shift to longer wavelength), or smaller (shift to shorter wavelength), the solvent employed, and ligand attached to the gold.
- ✓ For silver, the visible absorption is usually nearer 420 nm.
- The advantage of UV-vis spectra is that characteristic groups can be recognized in molecules or nanomaterials of widely varying complexities.

- UV-vis spectroscopy offers a relatively straight forward and effective way for quantitatively characterizing both organic and inorganic nanomaterials. Furthermore, as it operates on the principle of absorption of photons that promotes the molecule to an excited state, it is an ideal technique for determining the electronic properties of nanomaterials.
- ***It can be employed to identify the constituents of a substance, determine their concentrations, and to identify functional groups in molecules.***
- Consequently, UV-vis spectroscopy not only is used for characterization, but also for sensing applications.
- The samples can be either organic or inorganic, and may exist in gaseous, liquid or solid form.
- Different sized materials can be characterized, ranging from transition metal ions and small molecular weight organic molecules, whose diameters can be several Ångstroms, to polymers, supramolecular assemblies, nanoparticles and bulk materials.
- ***Size and shape dependent properties can also be observed in a UV-visible spectrum, particularly in the nano and atomic scales. These include peak broadening and shifts in the absorption wavelength.***
- Many electronic properties, such as the ***band gap of a material***, can also be determined by this technique.

Figure 7. UV-Vis absorption spectra of nanosized silver particles. (Inset) Different colours arising from different sizes.

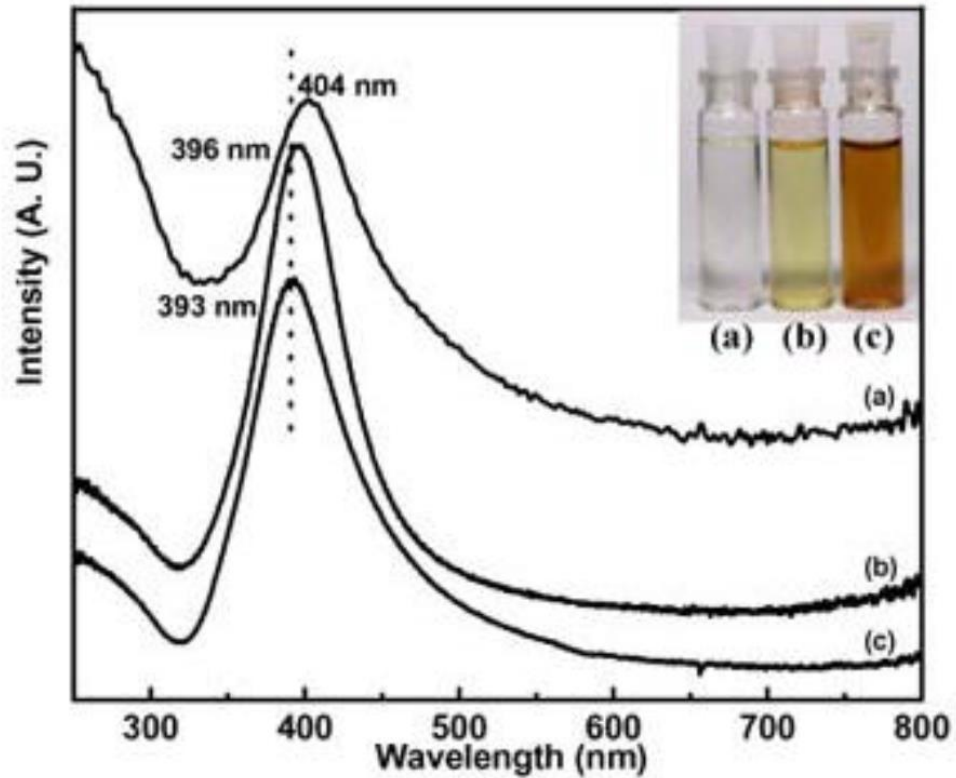
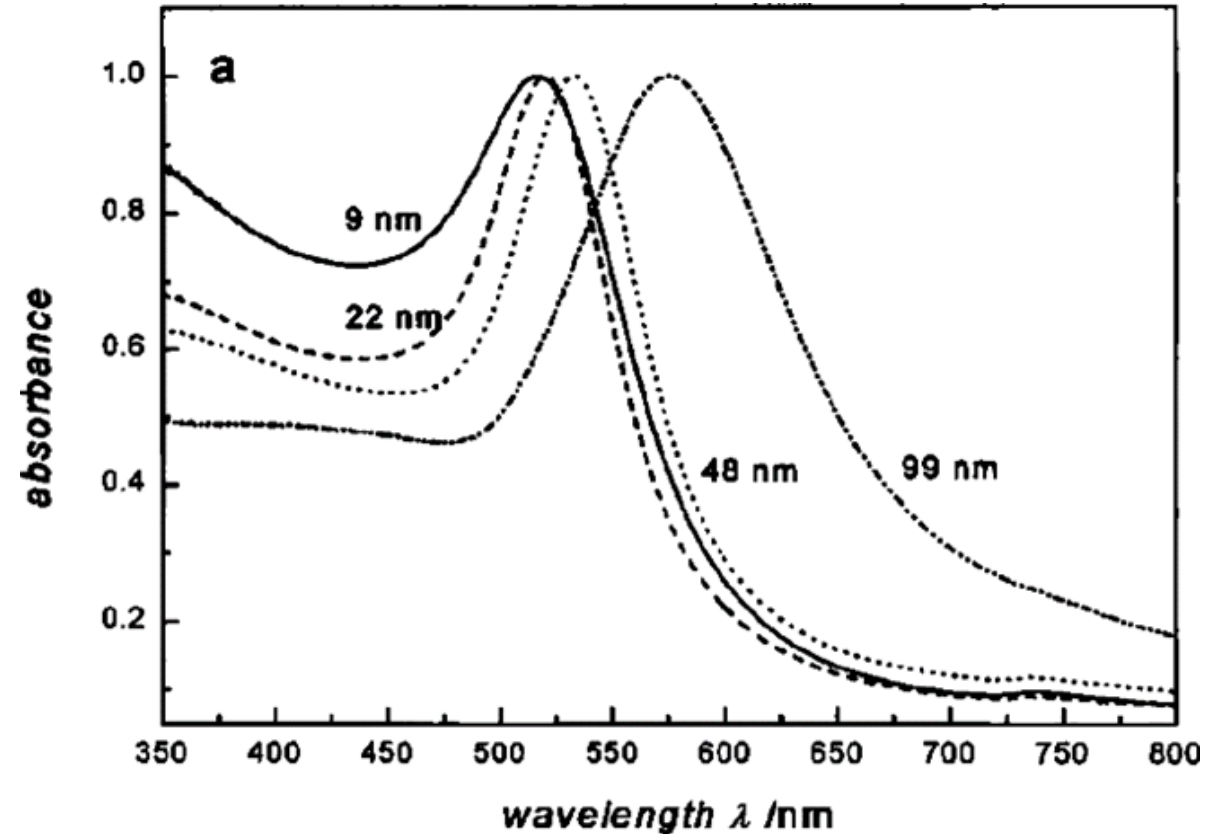


Fig. 5.4. Experimental UV-Vis extinction spectra of gold nanoparticles of ***diameters 9, 22, 48 and 99 nm.*** (reprinted with permission from American Chemical Society).



- In *the spectrum of nanoparticles, the absorption peak's width strongly depends on the chemical composition and the particle size*. As a result, their spectrum is different from their bulk counterparts. For instance, *for semiconductor nanocrystals, the absorption spectrum is broadened owing to quantum confinement effects, and as their size reduces, there is no longer a distinct peak, rather there is a band*. Furthermore, *semiconductor nanoparticles' absorption peaks shift towards smaller wavelengths (higher energies) as their crystal size decreases*.
- As an example, the UV-vis absorption spectra of different sized ZnO nanocrystals are shown in Fig. 5.5. In this figure, there is no absorption peak; rather the absorption spectra of the ZnO nanocrystals resemble hyperbolic tangents. In this case, the band gap energy is the energy corresponds to the excitation wavelength at the variation point of each spectrum (indicated by the arrows).
- *Due to quantum confinement effects, it is seen that the band gap is size-dependent, and it increases as the particle dimensions decrease*.

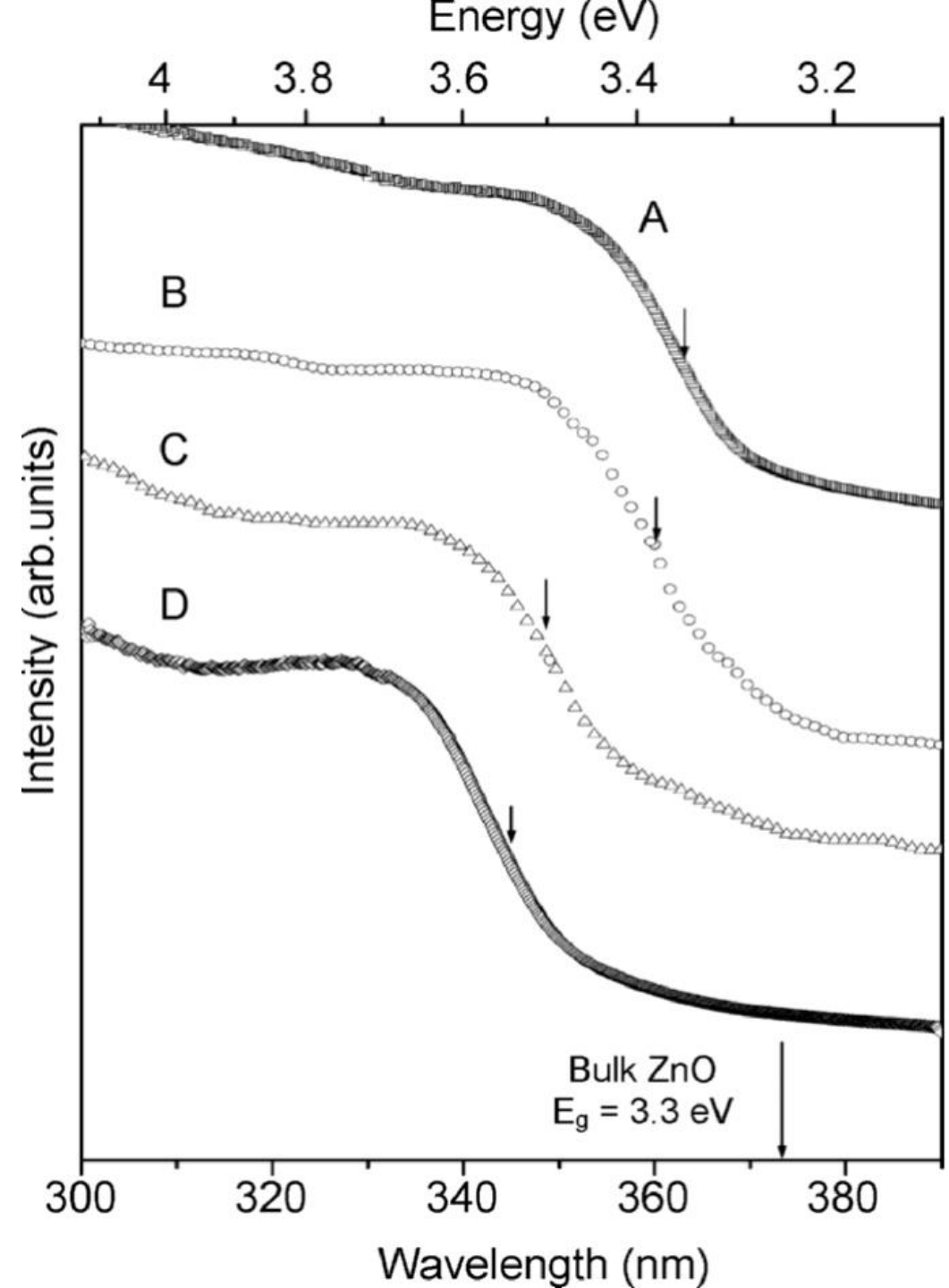
➤ *semiconductor nanoparticles' absorption peaks shift towards **smaller wavelengths** (**higher energies**) as their **crystal size decreases**.*

Fig. 5.5 UV-vis absorption spectra of various sizes of ZnO nanocrystals.

The band gap of the **bulk ZnO** is **3.32 eV** and is marked by an arrow.

The **absorption edges of the nanocrystals are marked by arrows and correspond to 3.42 eV (A), 3.44 eV (B), 3.55 eV (C) and 3.59 eV (D).**

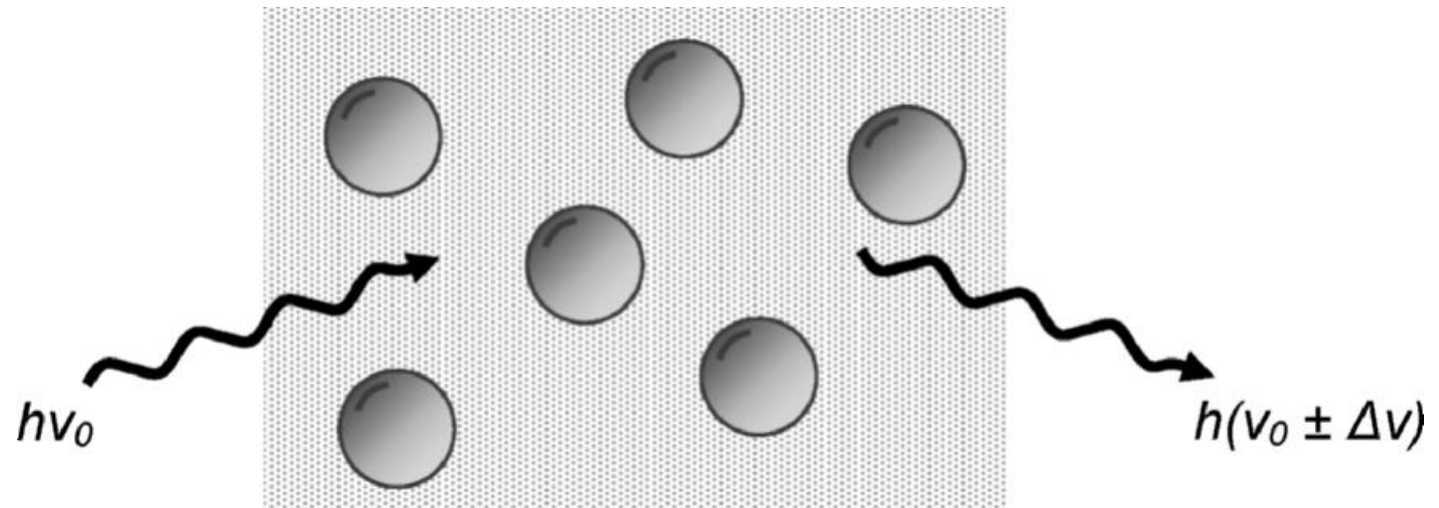
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Raman Spectroscopy

- *Raman spectroscopy is based on monitoring the intensity and wavelength of light that is scattered inelastically from molecules or crystals.*
- It is suitable for characterizing organic and inorganic samples.
- In a Raman experiment, a sample is irradiated with light of known polarization and wavelength (generally in the visible or infrared ranges). Inelastic (or Raman) scattering occurs and the scattered light is wavelength-shifted with respect to the incident light (Fig. 5.27).
- The spectrum of the scattered light is then analyzed to determine the changes in its wavelength.

Fig. 5.27 Representation of Raman scattering from particles.

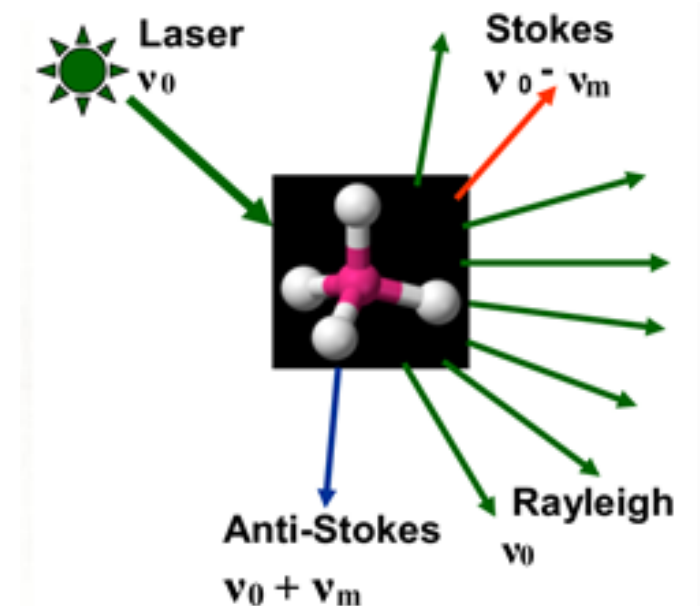


- Raman spectroscopy is a powerful analytical tool for qualitatively and quantitatively investigating the composition of materials.
- In a Raman spectrum, the wavenumbers of the Raman shifts are plotted against their respective intensities, which originate from the interaction photons with molecular vibrations (phonons in a crystal).
- When irradiation from a laser source interacts with phonons in the sample, there can be an exchange of energy between them.
- The phonons may either gain or lose energy.
- The phonon modes are intrinsic properties related to chemical bonding.
- Therefore, the information contained within a Raman spectrum may provide a “fingerprint” by which molecules can be identified.
- This not only serves for ***characterization purposes, but also in sensing applications***. When molecules bind together, new bonds may appear, the number of existing types of bonds may increase/decrease, functional groups may change.
- In sensing applications, monitoring the peak intensities and positions can provide quantitative information on the number of analyte molecules that have taken part in the interaction, such as in affinity-based sensing.

- If the ***Raman scattered photon has a lower energy*** than the incident light, its frequency is shifted down and is referred to as a ***Stokes scattering***.
- On the other hand, if the ***scattered photon has higher energy*** than the incident light, the frequency is shifted up and it is referred to as an ***anti-Stokes scattering***.
- The energy of the scattered photon, E , is related to the energy of the incident photon, $E_0 = h\nu_0$, by: $E = h\nu_0 \pm \Delta E_v$,
- Stokes: $\nu = \nu_0 - \Delta\nu$,
- anti-Stokes: $\nu = \nu_0 + \Delta\nu$.

where ΔE_v is the change in energy and $\Delta\nu$ is the change in frequency.

- Although there is a change in wavelength, no energy is lost during the interaction. This is because the electron cloud in a bond becomes deformed during interaction with the impinging light. The amount of deformation is the polarizability, and this determines the shift Raman of intensity and frequency.



- *Raman scattering comprises a very small fraction of the scattered light, only one Raman scattered photon from 10^6 to 10^8 excitation photons.*
- Therefore, the main limitation of Raman scattering is discerning the ***weak inelastically scattered light from the intense Rayleigh scattered light***.
- Furthermore, ***depending on the incident light energy, photoluminescence may occur which can obscure the Raman spectrum***.
- The *Raman scattering intensity is inversely proportional to the fourth power of the scattered wavelength*. So, decreasing the wavelength of the light source should result in an increase in the Raman signal. However, decreasing the wavelength increases the likelihood of observing photoluminescence.
- ***Stokes shifts are susceptible to photoluminescence interference***, but not anti-Stokes.
- If the sample is highly fluorescent then a different excitation, one that will not cause electronic excitation, can be employed to circumvent this problem.
- Unlike IR spectroscopy, where *water contamination can block out entire regions of the spectrum*, a Raman spectrum is less susceptible to the presence of water.

- The ***Raman signal is inherently weak, which prevents achieving low detection limits with normal Raman*** spectroscopy.
- The Raman signal can be enhanced if molecules are adsorbed on roughened metal surfaces, typically gold or silver. This is called **Surface Enhanced Raman Spectroscopy (SERS)** and ***exploits changes in analyte polarizability perpendicular to the surface, which enhances scattering by factors of more than a million-fold.***
- The metal surface must have a plasmon in the frequency region close to that of the excitation laser.
- Surface roughness or curvature is required for the scattering of light by surface plasmons, however, it is not the defining factor, as an intrinsic surface enhancement effect plays a fundamental role.
- ***SERS is an ideal technique in nanotechnology enabled sensing, particularly for monitoring very small traces of an analyte.***
- In order for SERS to occur, the particles or features must be small when compared the wavelength of the incident light.
- SERS-active systems should possess structures typically in the 5–100 nm range.

- The following examples illustrate the applicability of Raman spectroscopy for sensing as well as in compound identification.
- Fig. 5.28 shows an example of SERS in chemical sensing, where the Langmuir-Blodgett (LB) technique was used to assemble monolayers of aligned, thiol capped silver nanowires that are ~50 nm in diameter and 2–3 μm in length. The fluorescent molecule Rhodamine 6G (R6G), which produces a distinct Raman spectrum when excited by light of wavelength 532 nm, was adsorbed onto the films. The inset of the figure shows that there is a linear relationship between the R6G concentration and the intensity of the Raman peak at 1650 cm^{-1} . This ***system was capable of detecting 0.7 pg of the analyte.***

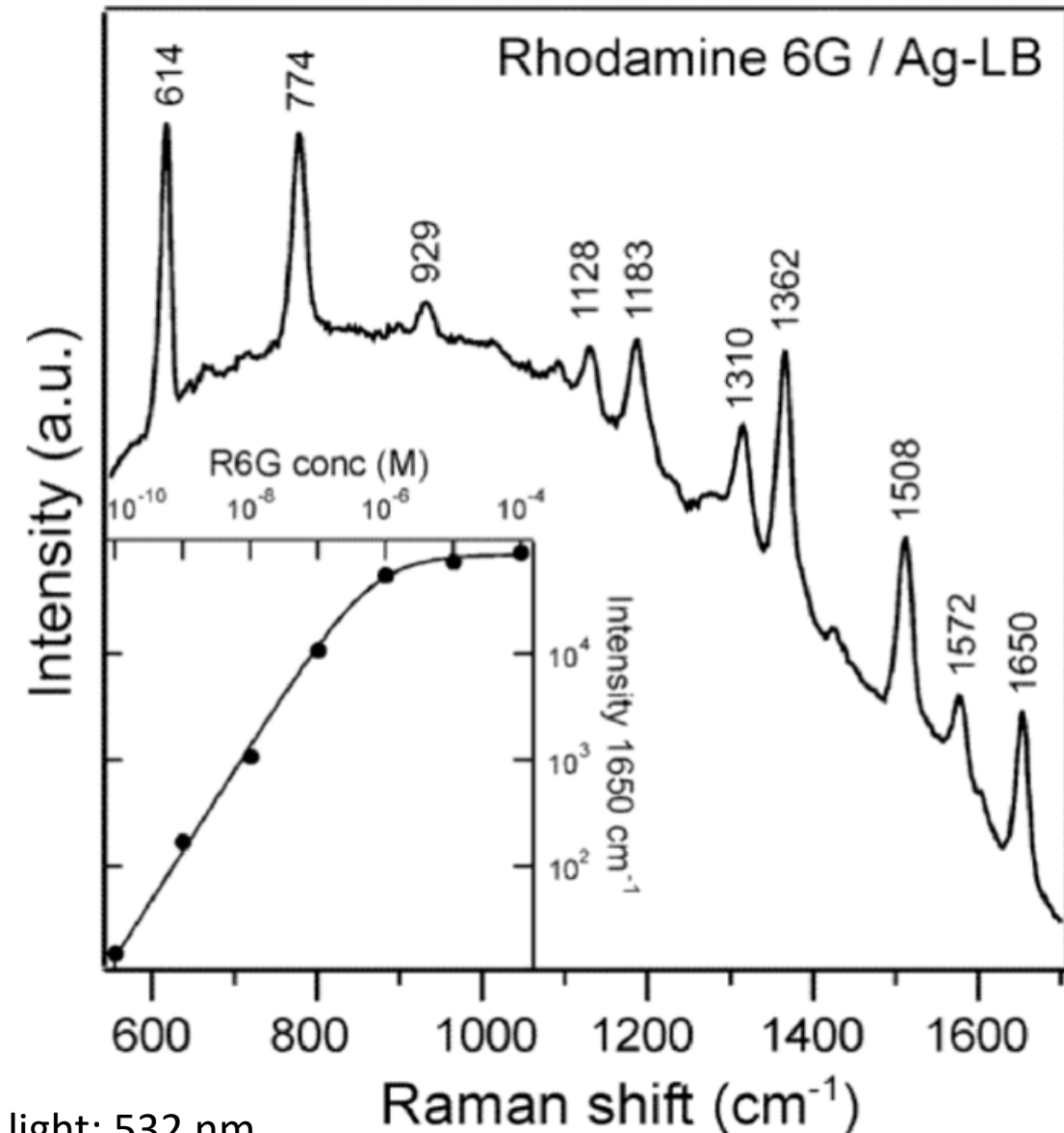


Fig. 5.28 SERS spectrum of R6G on the thiol-capped Ag-LB film (incident light: 532 nm, 25 mW) after 10 min incubation in a 10^{-9} M R6G solution. The inset shows the linear relationship between the Raman intensity at 1650 cm^{-1} and the R6G concentration. (Reprinted with permission from the American Chemical Society publications.)

MISCELLANEOUS TECHNIQUES

❑ Light Scattering Techniques

- These techniques involve analyzing the light that is scattered from materials.
- The **types of light scattering** include: **elastic**, where *the wavelength of the scattered light remains unchanged from the incident light*, and **inelastic**, where *the scattered light's wavelength is different from that of the incident light*.
- *Depending on the frequency of light and the type of scattering, these techniques can provide information regarding the size, chemical composition and structure of nanomaterials.*
- Changes in these material properties can be monitored with such techniques, and in some cases, the ***technique itself may be used for signal transduction in sensing applications.***
- **Rayleigh scattering**, which occurs when the particles are much smaller than the wavelength of the impinging light, is an example of elastic scattering.
- Conversely, **Raman scattering is inelastic**, where the scattering of a photon creates or annihilates a phonon, and the scattered light has a different wavelength than the incident light.
- Two of the ***most relevant light scattering characterization techniques for nanotechnology*** are **Dynamic Light Scattering** and **Raman Spectroscopy**.

Dynamic Light Scattering (DLS)

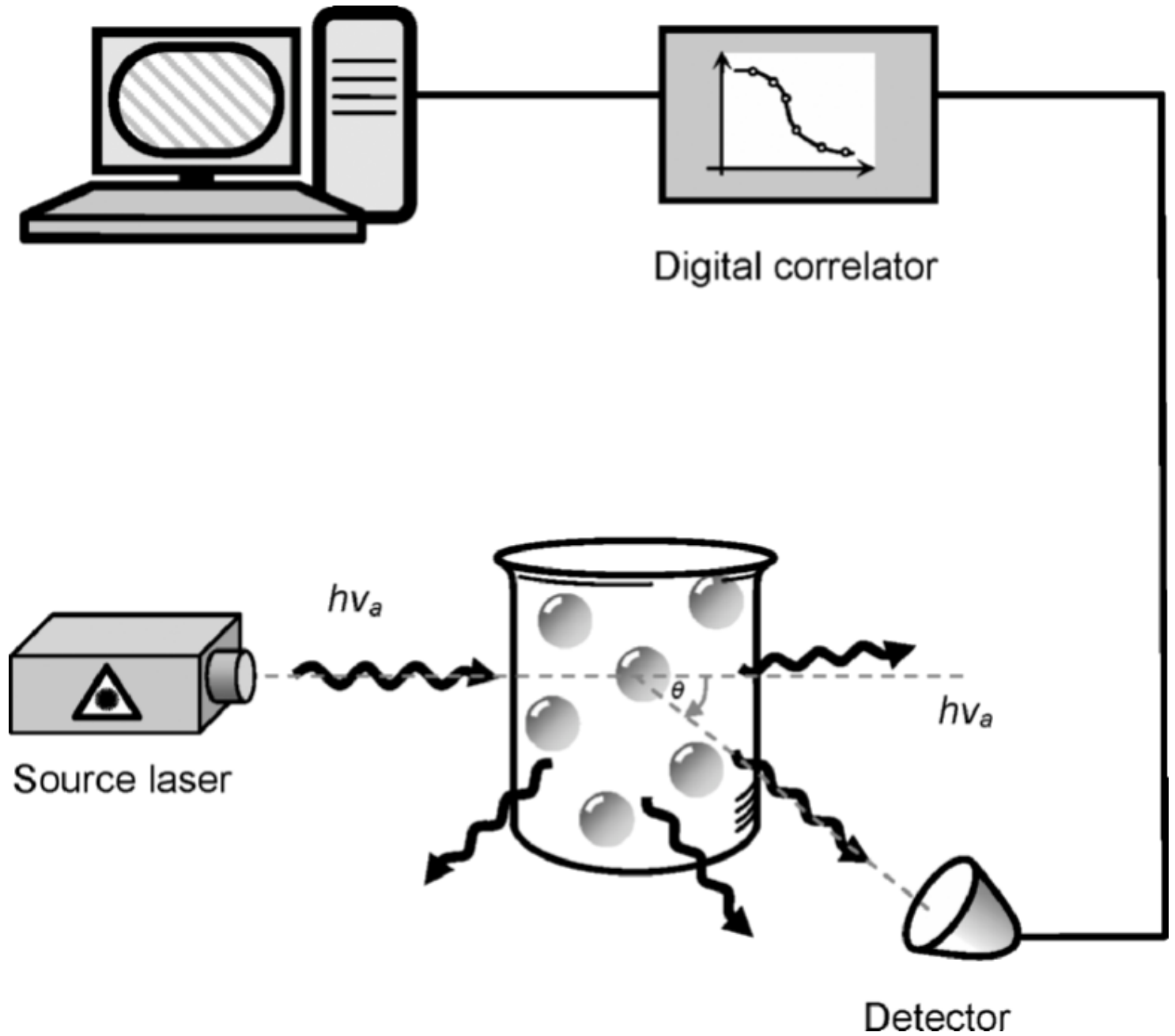
- Dynamic Light Scattering (DLS), also known as *Quasi-Elastic Light Scattering (QELS)*, *Photon Correlation Spectroscopy (PCS)*, and *Light Beating Spectroscopy*, is a technique that relies upon ***temporal fluctuations in the light scattered from an ensemble of the particles*** to determine their motion.
- Usually, ***the motion in any colloid or aerosol is a random Brownian diffusion that is quantified by a size-dependent diffusion coefficient, D.***
- The DLS method measures the ***decay of the temporal fluctuations in the scattered light, which is related to their diffusion which, in turn, is related to their size.***

$$r = \frac{kT}{6\pi\eta D}$$
 (Stokes-Einstein Eqn.) where r is the radius of a spherical particle, η is the viscosity coefficient, k is Boltzmann's constant ($1.3806505 \times 10^{-23}$ J/K) and T is the absolute temperature.

- Since the size is determined from diffusion, the viscosity of the suspending medium must be known. The ***size is an effective mobility size*** related to ***both size and shape.***
- Size ranges from nearly molecular dimensions—a few nanometers to many microns can be determined.

- As with any light scattering measurement, ***larger particles scatter more than smaller, and hence they dominate the measurement in any polydisperse system.***
- DLS has two main applications: the study of ***system dynamics*** in real time; and the absolute determination of ***nanoparticle sizes***, with perhaps the latter being more important in nanotechnology.
- In fact, it is well suited for ***examining the monodispersity of synthesized nanoparticles***, and for ***determining small changes in particles' mean diameter after the adsorption of molecules/layers***, such as when forming a coating.
- DLS is commonly employed for studying colloidal systems as it is a relatively fast and straightforward technique in which a light beam is directed onto a sample that scatters the light elastically.
- This light is scattered over a period of time and then analyzed statistically.
- A typical setup is shown in Fig. 5.24.

Fig. 5.24 An illustration of a DLS experiment.



- A beam of monochromatic light passes through a solution containing the particles, which are generally colloids or micelles and scattering occurs.
- The intensity of the scattered light is uniform in all directions with the amount of Rayleigh scattering depending on the size of the particles and the wavelength of the incident light.
- Whilst in solution, the particles move about in small random patterns (Brownian motion).
- *At constant temperature, larger particles move more slowly than the smaller ones, and hence the distance between the particles is constantly varying.*
- Therefore time-dependent fluctuations in the scattering intensity can be observed by counting the number of photons returning to the detector after scattering.
- These time dependent fluctuations can then be related to particle speed by autocorrelation of the average of the product of the photon count with a delayed version as a function of the delay time.
- The autocorrelation function is analyzed by numerically fitting the data with calculations based on assumed particle size distributions.
- Analysis of the time dependent fluctuation gives the diffusion coefficient of the particles, D .
- The radius of a spherical particle, r , can be obtained from the Stokes-Einstein relation:

$$r = \frac{kT}{6\pi\eta D} \quad \text{where } k \text{ is Boltzmann's constant } (1.3806505 \times 10^{-23} \text{ J/K}), \text{ } T \text{ is the Kelvin temperature and } \eta \text{ is the viscosity coefficient.}$$

- Fig. 5.25 shows an example where DLS has been employed to determine the size of helical rosette nanotubes, built from multiple stacks of the rosette shaped compound shown.
- The average size of the nanotubes (32.5 nm) derived from the dynamic DLS was used to reveal that the nanotubes are composed on average of a stack of approximately 140 rosette molecules.
- However, this example highlights one of the **key assumptions in DLS calculations**, which is that **the molecules must be spherical**. Therefore, the actual length is most likely larger.

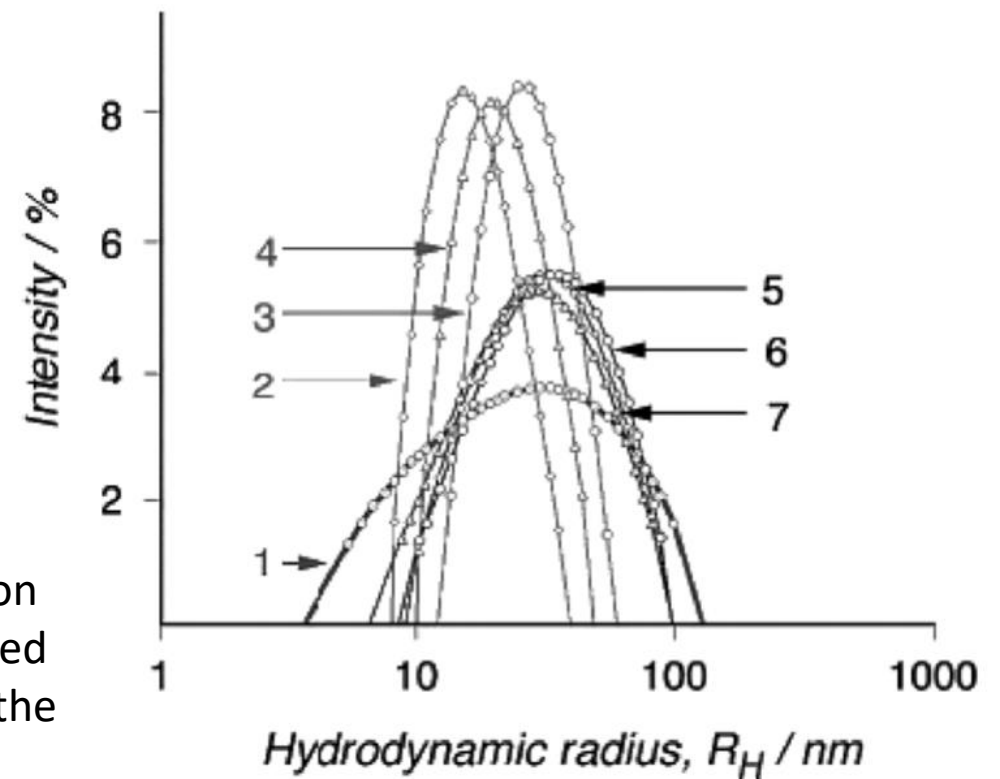
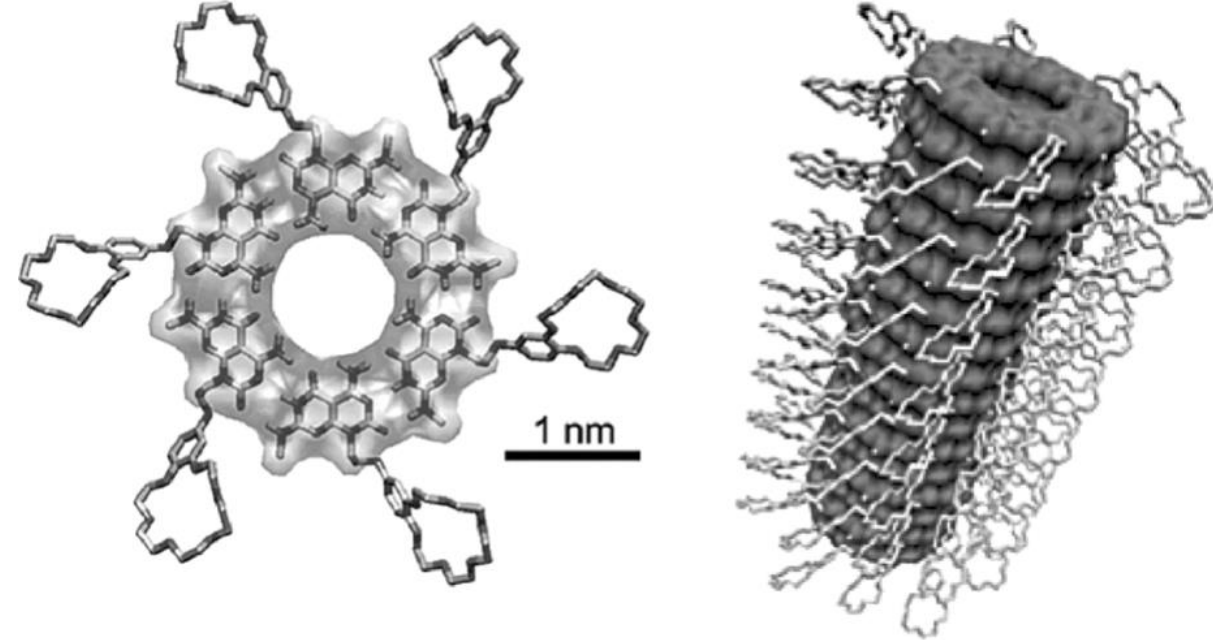


Fig. 5.25 Top: The hierarchical self-assembled six-membered ring supermacrocycle (rosette) on the left and the resulting nanotube stack on the right. Bottom: DLS regularization diagrams of the nanotube, measured in solution at different concentrations. Reprinted with permission from the American Chemical Society publications.

➤ In another example shown in Fig. 5.26, the advantage of DLS over other particle size determination techniques is highlighted. Here, ***time-dependent DLS*** was performed on a ***crystallizing solution*** to study ***the growth of CaCO_3 crystallites***. After 20 minutes the particle size distribution shows particles with dimensions well in excess of the micron range. With time, peak broadening becomes prevalent, as this represents the increasing polydispersity of the particle sizes during their nucleation and growth processes.

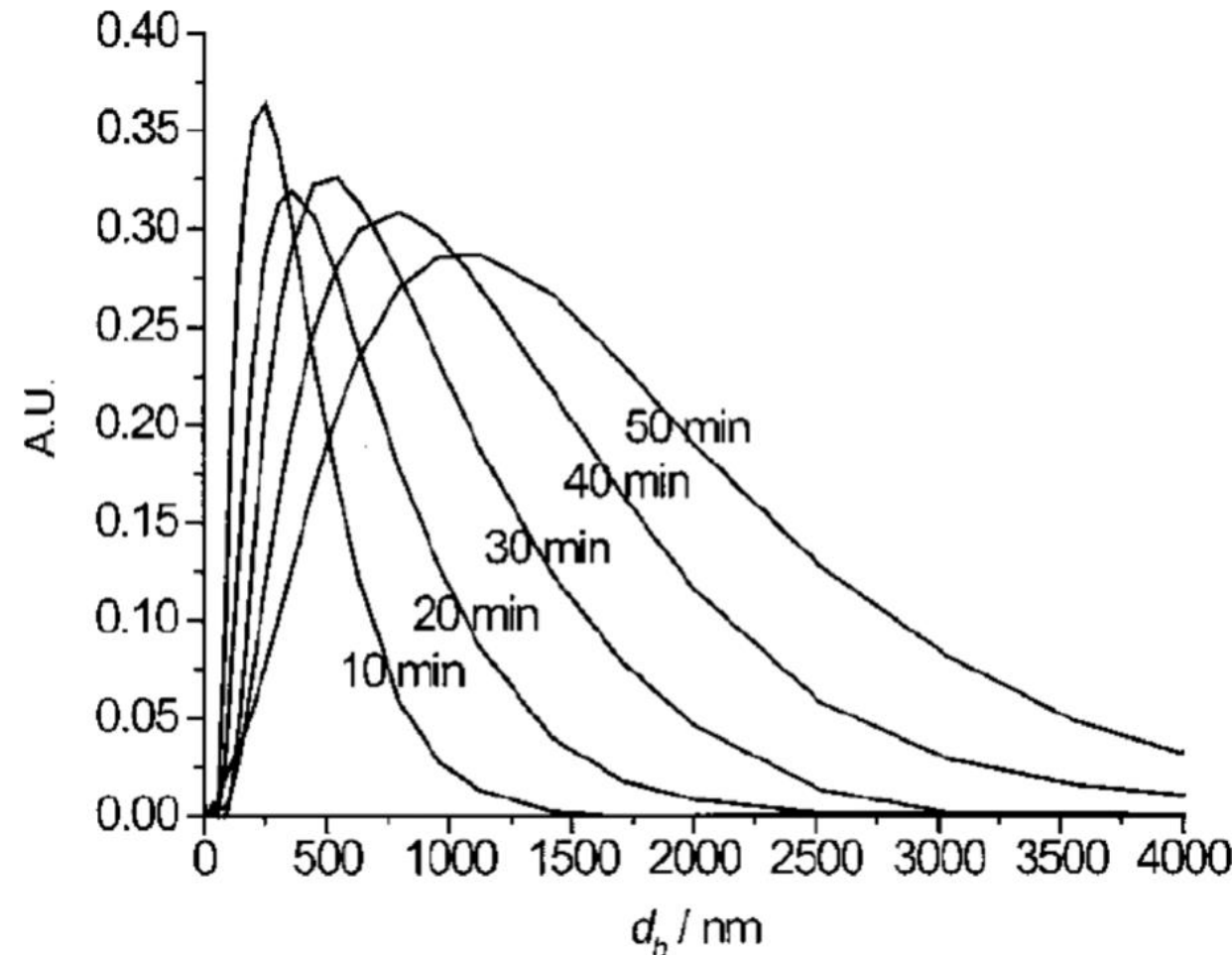


Fig. 5.26 Time dependence particle size distributions of CaCO_3 crystals from dynamic light scattering measurement.

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- DLS has ***several advantages*** over other techniques for particle size determination; while scanning electron microscopy techniques are very accurate a DLS measurement uses non-ionizing lower energy light sources and is carried out at room pressure.
- Also time-dependent DLS is ideal for studying the growth of nanocrystals in solution, unlike other techniques that require the samples be dried.
- DLS is utilized to measure particle sizes in the range from a few nanometers to a few microns.
- ❑ DLS does have ***some limitations***. It is only suitable for particles that exhibit Rayleigh scattering. For particles whose size is *larger than about a tenth of the illuminating wavelength*, the *intensity is angle dependent* and the scattering is explained by Mie theory.
- ❑ Other *limitations include*: the requirement (in most cases) for ***dilute suspensions*** in order to minimize multiple scattering; the difficulty in differentiating between tiny fluctuations and noise; and it is impossible to discriminate between light scattered from a single primary particle agglomerate.
- DLS requires a coherent light source.
- ✓ Most common laboratory lasers such as HeNe, argon ion, Nd:YAG, etc. have enough longitudinal and transverse coherence to be useful for DLS.

- The scattering volume should be small to ensure good transverse coherence on the detector.
- The second thing needed for DLS experimentation is a detector capable of detecting single photons such as a photomultiplier tube or avalanche photodiode.
- The detector output is typically amplified, discriminated, and shaped for the third thing needed, a digital correlator.
- These are available commercially and typically provide analysis routines to make use of the method straightforward.

MISCELLANEOUS TECHNIQUES

- ❑ **EXAFS (Extended X-ray absorption fine structure (EXAFS))**, along with *X-ray absorption near edge structure (XANES)*, is a subset of X-ray absorption spectroscopy (XAS). Like other absorption spectroscopies, XAS techniques follow Beer's law.
- The X-ray absorption coefficient of a material as a function of energy is obtained using X-rays of a narrow energy resolution are directed at a sample and the incident and transmitted x-ray intensity is recorded as the incident x-ray energy is incremented.
- When the incident x-ray energy matches the binding energy of an electron of an atom within the sample, the number of x-rays absorbed by the sample increases dramatically, causing a drop in the transmitted x-ray intensity. *This results in an absorption edge.*
- *Every element has a set of unique absorption edges corresponding to different binding energies of its electrons*, giving XAS element selectivity.
- XAS spectra are most often collected at synchrotrons because the high intensity of synchrotron X-ray sources allows the concentration of the absorbing element to reach as low as a few parts per million. Absorption would be undetectable if the source is too weak.
- Because X-rays are highly penetrating, XAS samples can be gases, solids or liquids.

➤ The method is based on the measurements in the vicinity of the absorption edge, e.g., the K shell. In this case, the observed oscillations as a function of the photon energy are the result of interference of both primary waves and secondary ones scattered by neighboring atoms. The analysis of such oscillations allows one to find distances between neighboring atoms and to study deviations of “neighbors” in the particle surface layer as compared with compact metal lattices. The information on such deviations is important for understanding the optic properties of the metal particles. These deviations can affect the particle size, electron density, and optic properties. For example, atomic distances in Ag_2 and Au_2 are 0.210 and 0.253 nm, respectively, whereas in the compact metal this value is 0.325 nm.

MISCELLANEOUS TECHNIQUES

❑ X-ray Fluorescence Spectroscopy

- The method is based on excitation of atoms in a substance under study by the emission of a low-power X-ray tube. This gives rise to secondary fluorescence emission, which falls on the crystal analyzer and, being reflected from the latter, is registered by a proportional detector. The crystal analyzer and the detector are driven by a goniometer. In doing so, each fixed position of the goniometer corresponds to a definite wavelength of secondary emission selected by the analyzer.
- The elemental composition of a sample is characterized by spectral lines with intensities unambiguously related to the quantitative contents of elements in a sample.
- Concentrations are usually computed by comparing with the values obtained for standard samples.
- The X-ray fluorescence technique allows quick and high-precision analysis of practically all elements in the periodic table in solid, liquid, powder, and film samples.

X-Ray Photoelectron Spectroscopy (XPS)

- ❑ ***XPS can quantify the chemical and electronic states of the elements*** within the first few atomic layers of a surface.
- It can be used to ***identify elements, their chemical bonds, and hence the chemical composition and empirical formulae.***
- The XPS is based on the photoelectric effect, in which X-rays cause photoelectrons to be ejected from a surface. In an XPS experiment, the source of the X-rays is generally the $K\alpha$ emission from magnesium ($K\alpha = 1253.56$ eV) or aluminum ($K\alpha = 1486.58$ eV). The X-rays strike the sample surface and interact with the atomic electrons in the sample, primarily via photon absorption (Fig. 5.17).

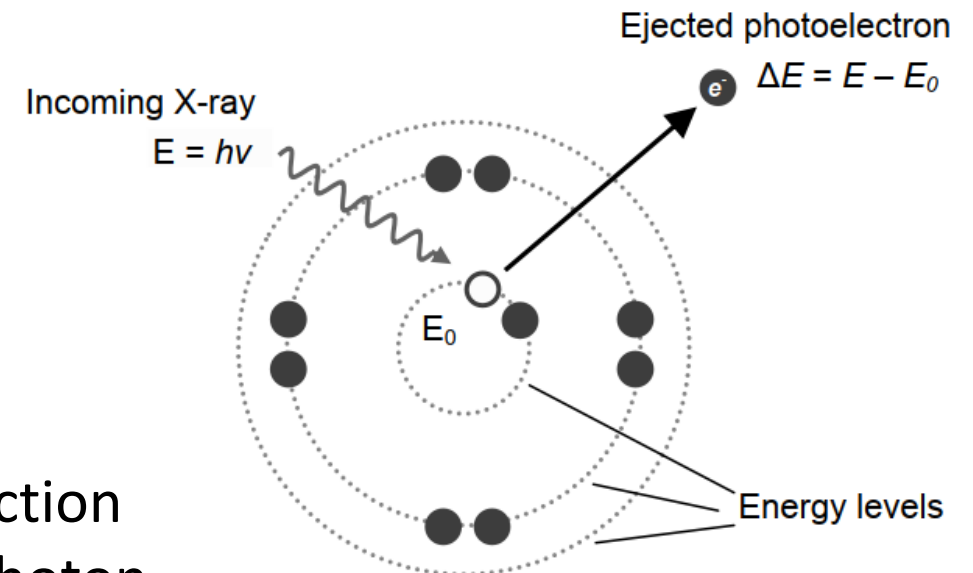


Fig. 5.17 Electronic orbits showing the ejection of a photoelectron after absorption of a photon.

- The method is based on measuring the energies of electrons that escape solids under the action of photons. According to Einstein, the sum of the binding energy of an escaped electron (work function) and its kinetic energy is equal to the energy of the incident photon.
- From the resulting spectra, the binding energies of electrons and their energy levels in a substance under study are determined.
- This method allows study of the electronic distribution in conduction bands and analysis of the substance composition and the chemical bond type.
- Metals are characterized by intense photon reflections and a strong interaction with conduction-band electrons. The quantum yield is small (≈ 1 electron/photon), which complicates application of the method.
- As the incident X-rays can penetrate deep into the atom, they can eject electrons from several energy levels. The incident X-rays have energy of $h\nu$ and can pass on energy to the ejected electron according to the following equation:

$$E_k = h\nu - E_b - \phi_s ,$$

where E_k is the kinetic energy of the ejected electron, E_b is the binding energy of the ejected electron, h is Planck's constant (4.136×10^{-15} eV·s), ν is the frequency of the incident radiation, and ϕ_s is the work function of the material.

➤ If an electron of an inner atomic shell is ejected from the atom, then an electron from the outer shell will fill the empty space it leaves behind. ***Two things may then happen***, either a photon (whose energy is equal to the difference between the two energy levels) will be emitted, or ***the energy is transferred to another outer electron that is then emitted***. ***This emitted outer electron is called an Auger electron, and consequently Auger Electron Spectroscopy (AES) can be used to analyze these emitted electrons***. Both these processes are schematically summarized in Fig. 5.18.

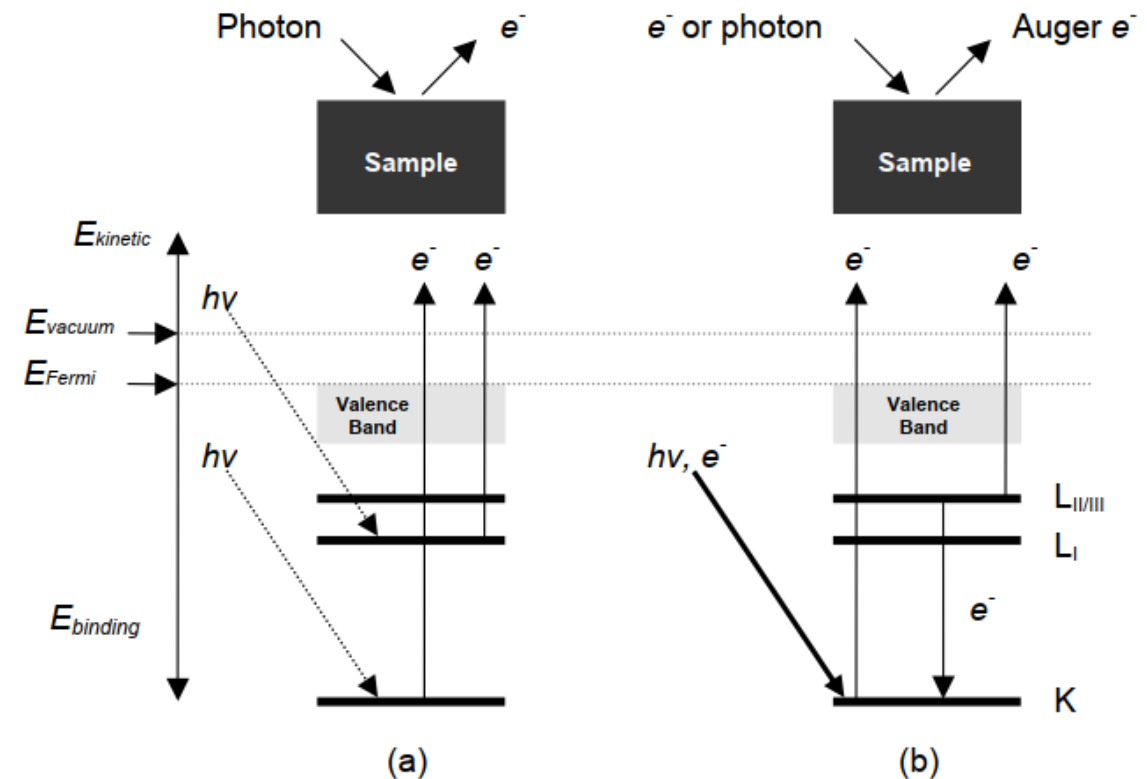


Fig. 5.18 The photoelectric and Auger processes in (a) XPS and (b) AES.

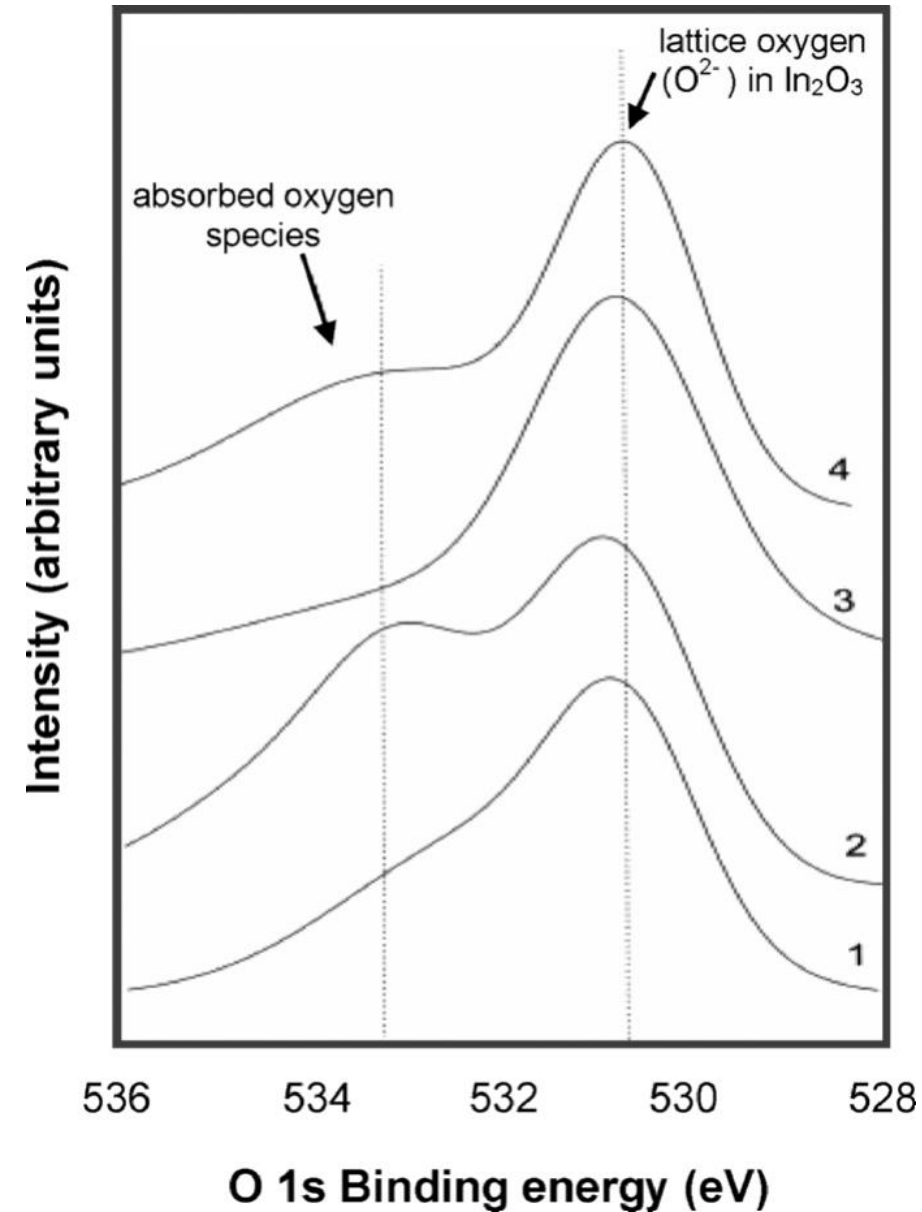
- The focused X-ray beam which impinges on the sample has energy of approximately 1.5 keV while the reflected photoelectrons have smaller energies.
- The reflected photoelectrons only escape from the very top surface of the sample (generally not more than 10 nm).
- The kinetic energy and number of the ejected photoelectrons is plotted as a spectrum of their binding energies. The acquired spectrum is compared with spectra from known databases.
- The peak positions and shapes correspond to the material's electronic configuration, and therefore elements and compounds show their own unique characteristic peaks.
- In sensing applications, XPS is used not only to study the chemical composition of a sensing layer, but also to investigate the interactions between the surface and the target molecules.
- Because XPS is surface sensitive, it is ideal for characterizing sensing layers, as the interaction between the analyte and sensing layer occurs on the surface.
- By performing XPS measurements on the sensing surface, before and after interactions, an understanding of the sensing mechanisms can be obtained. For example, Fig. 5.19 demonstrates how XPS was employed to study the interaction between NO_2 and O_2 gases with nanostructured In_2O_3 thin films. The two peaks in the spectra correspond to the characteristic signatures used for indium metal and indium oxide that are determined from the $\text{In } 3d_{5/2}$ and $\text{O } 1s$ core level emissions, respectively.

➤ By observing the relative increase and decrease in these peaks with respect to each other, XPS was used to confirm the dissociative adsorption of NO_2 and the formation of adsorbed oxygen species on the In_2O_3 surface.

Fig. 5.19 O 1s core level XPS spectra of the In_2O_3 thin films at different conditions:

1. After heating in air for 1 h at 700 °C;
2. Exposure to NO_2 1×10^2 Pa 200 °C for ½ h;
3. Vacuum 1×10^{-4} Pa at 200 °C for ½ h;
4. Exposure to O_2 1×10^4 Pa at 200 °C for ½ h.

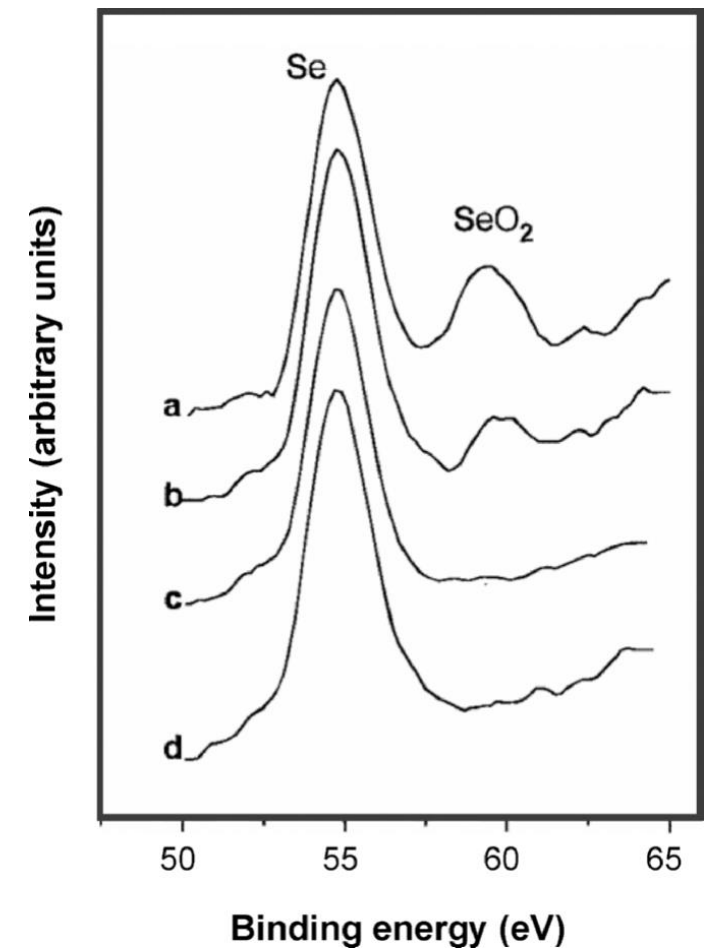
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➤ In another example, the XPS spectra of 40 Å CdSe semiconducting nanocrystals coated with trioctylphosphine oxide (TOPO) are seen in Fig. 5.20. The coating prevents CdSe from oxidization, and in this example XPS was employed to confirm the presence of the coating. As seen in the figure, the Se peaks indicate its presence in the CdSe nanocrystals. An SeO_2 peak confirms the uncoated CdSe sample showing that nanocrystals oxidized in air. However, a smaller SeO_2 peak is present in one of the coated films (sample b), showing that the TOPO coating does not completely cover that CdSe nanocrystals.

Fig. 5.20 X-ray photoelectron spectra highlighting the Se 3d core transitions from ~ 40 Å *bare* and *ZnS overcoated* CdSe dots: (a) bare CdSe, (b) 0.65 monolayers, (c) 1.3 monolayers, and (d) 2.6 monolayers of ZnS. The peak at 59 eV indicates the formation of selenium oxide upon exposure to air when surface selenium atoms are exposed.

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- As XPS involves monitoring emitted photoelectrons, the experiments must be conducted under ultra high vacuum and therefore the sample should not outgas.
- XPS experiments are limited to just a few Ångstroms beneath the surface, despite the incoming X-rays being able to penetrate microns into the surface. This is because the ejected electrons must travel through the sample and yet retain enough energy to reach and excite the detector. *Only electrons that are emitted by atoms near the surface have a chance to leave the sample.*
- Furthermore, exposure to the X-ray beam can damage certain materials, mainly organic molecules and polymers, and they may degrade during the measurement.
- When the XPS instrument is combined with ion beam sputtering, atomic layers can be continuously removed from the surface. After sputtering, the XPS may be performed once again on these layers, and as a result compositional depth profiles can be obtained down to a few micrometers.