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Biomaterials

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قسم الفيزياء الطبية
المواد الاحيائية
المرحلة الرابعة

BIOMATERIALS

المحاضرة الرابعة

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CHARACTERIZATION OF MATERIALS — II

1- Physical and Chemical Characterization

1.1. MICROSTRUCTURAL CHARACTERIZATION

The physical, chemical and often mechanical properties of materials are interrelated to its internal microstructural features. The microstructure of the material involves specifying the crystallography, morphology and chemical composition of the material, Crystallographic analysis includes identifying the different phases which are present in the structure of the material and the nature of the atomic packing within the phases. Most phases are crystalline phases with highly ordered and regularly repeated arrangement of atoms. But some phases are amorphous or glassy, which do not posses any long-range ordered arrangement of atoms. The morphological analysis corresponds to the characterization of the size, shape and spatial distribution of the phases or particles, as stated above, the compositional analysis involves identification of the chemical constituents of the material and its relative abundance. In all the cases of microstructural characterization, a carefully prepared specimen sample is interacted with some form of probe and the scattered or excited signal from the sample is collected for analysis. The visible light, X-rays and energetic electrons are the most commonly used probes for the characterization of materials. All the probes can interact with the sample through elastic or inelastic processes.

1.2. FT-IR SPECTROSCOPY

The spectroscopy is a fast, relatively inexpensive and widely used analytical technique for the characterization of biomaterials. It is a form of vibrational spectroscopy based on the interaction of IR radiation and natural vibrations of the chemical bonds among atoms that compose the material. In IR spectroscopy, the sample is irradiated with IR radiation and the changes in the absorption of this radiation by the sample are measured. The sample absorbs radiation in the IR region only whenever there is a coincidence (resonance) among the frequencies of the IR radiation with the molecular vibration and the natural vibration causes a change in the dipole moment during vibration. Molecular vibrations are two types: stretching (that changes the bond length) and bending (that changes the bond angle). These changes in vibrational motion give rise to absorption bands in the vibrational spectrum. For the IR region, the position of absorption bands in the spectra are presented not as wavelength (λ) but as wave number (ν), using the reciprocal centimetre as its unit (cm-1), because it is directly proportional to energy (E) and frequency (ν) of radiation. The IR region is subdivided into three spectra vl regions, i.e. the near IR (NIR - from 4000 to approximately 14,000 cm-1), mid IR (MIR - from 400 to 4000 cm-1) and far IR (FIR - from approximately 25-400 cm-1). The MIR is the most common and widely employed region for the characterization of materials as it depicts the primary molecular vibrations. The NIR and FIR are not frequently employed because only skeletal and secondary vibrations (overtones) occur in these

regions producing spectra that are difficult to analysis.

1.3. DLS TECHNIQUES

The nanoparticles also scatter (part of the radiation in all directions) visible light and occur everywhere as a natural phenomenon, e.g. the light scattering by atmospheric particles is the reason for the blue color of the sky and brilliant colors seen at sunrise

and sunset. It is basically due to the discrete variation in the refractive index within the medium of travel such as solid particles in a liquid. The scattered light may be analyzed either in terms of its intensity or in terms of its fluctuations. The former is called static light scattering (SLS), also as multiangle laser scattering, Rayleigh or classical scattering technique. where-in a laser is used to illuminate the particles suspended in a liquid and the time-averaged intensity of the scattered light by the particles is measured. A complex function of maxima and minima with respect to angle is observed if the size of the particles is similar to the wavelength of the laser used and by modelling the scattering profile with optical model such as Mie theory, size distribution is obtained. However, if the particles are small compared to the wavelength of the illuminating light, typically less than wavelength/10 around 60 nm for a He-Ne laser), then as per Rayleigh approximation, the scattering will be essentially isotropic, i.e. equal in all directions and also of low intensity, i.e. smaller particles generate low-intensity signals at wide angles, whereas larger particles generate high-intensity signals at small scattering angles. Additionally, the small (nano) particles in suspension undergo Brownian motion (random thermal motion), which causes rapid fluctuations in the intensity of light scattered due to interference, as the distance between the particles is varying. The fluctuation contains the information about the particles' size as the frequency of fluctuation relates to the size of the particles as schematically shown in Figure 1.
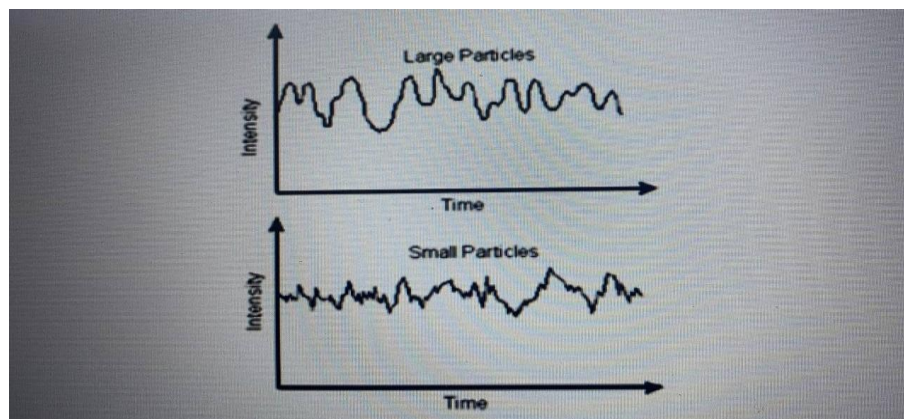
1.4. CONTACT ANGLE MEASUREMENTS

The surface properties of biomaterial have profound effect on the biomaterial-tissue interactions with subsequent consequences on the host responses. Hence, it is very essential to understand the unique properties of the surfaces and the methods to characterize them in striving towards more 'biocompatible materials' which either elicits a specific cellular response or evokes a minimal inflammatory response. For example, the surface composition is different from its bulk composition due to energy minimization, which drives some of the elements of the bulk material to its surface. Similarly, the absence of periodic arrangement of the outermost atomic layers of the surface causes relaxation of the atoms from their regular periodic position leading to rearrangement of atoms with different lattice spacing with same periodicity or reconstruction to new periodic arrangement of atoms at the surface. The surfaces are also always covered with few contaminated layers as hydrocarbons, adsorbed layers of oxygen and carbon, etc. due to the exposure to the atmosphere. So, many techniques are needed for a complete description of the surface. However, the surface energy of the biomaterial has been found to be strongly correlated with the biological interactions such as cell adhesion. The surface energy can be quantitatively characterized from the contact angle of a liquid drop (Θ) with the biomaterial surface and geometrically Θ is defined as the angle formed by the liquid at the phase boundary of liquid, gas and solid interacting phases. Experimentally, Θ is measured by drawing a tangent at the contact where the liquid and solid phases intersect.

2- Surface Characterization

2.1. X-RAY PHOTOELECTRON SPECTROSCOPY

X-ray photoelectron spectroscopy (XPS), which is also called electron spectroscopy for chemical analysis, is the most widely used analytical technique to monitor the surface chemistry of solid materials due to its simplicity, flexibility, and sound theoretical basis. The typical XPS instrument includes an ultra-high vacuum system, X-ray source, electron energy analyzer, and data acquisition system. In XPS, the sample surface is irradiated by monochromatic X-ray and the emitted photoelectrons are detected. Figure 2 describes the general mechanism of photoelectron creation and the energy of the photoelectron is given by:

$$E_B = h\nu - KE$$

where EB is the binding energy of the electron in the atom, $h\nu$ is the energy of the X-ray source (a known value in the experiment), and KE is the kinetic energy of the emitted electron that is measured. E_B is usually expressed in electron volts (eV) and l eV - 1.6×10^{-19} J. Since there are different electrons and binding energies in an atom, each element produces a set of unique peaks in the photoelectron spectrum and the peak intensity is a direct measure of the elemental concentration. As XPS is extremely surface sensitive, surface contamination can lead to stray results. XPS can provide qualitative and quantitative information on all elements except hydrogen and helium and furthermore, the shape of each peak and the exact binding energy can be slightly altered

by the chemical state of the emitting atom. Hence, XPS can provide chemical bonding information as well.
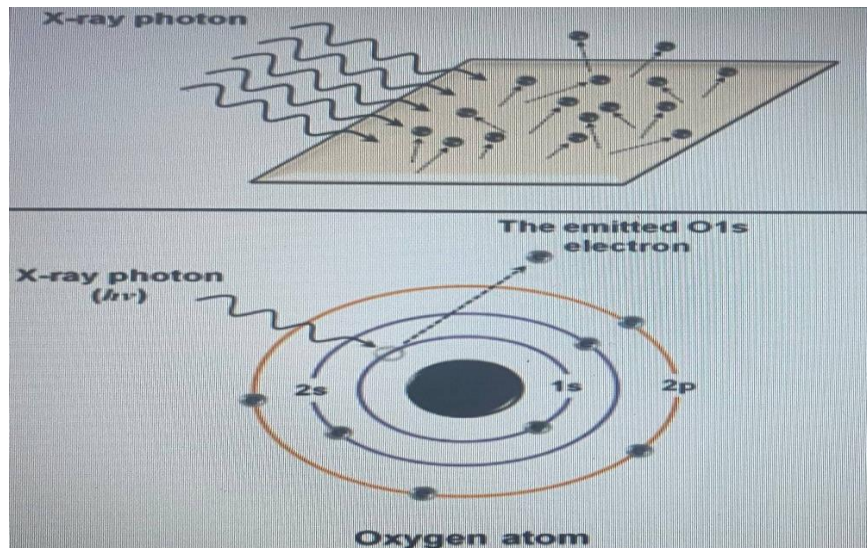

FIGURE 2 (Top) A surface irradiated by X-ray photons resulting in emission of photoelectrons and (bottom) the X-ray photon transfers its energy to a core-level electron imparting enough energy for the electron to leave the atom.

2.2. SECONDARY ION MASS SPECTROMETRY (SIMS)

Secondary ion mass spectrometry (SIMS) is a sensitive technique to determine the elemental and molecular contents. Besides popular applications in semiconductors, new SIMS advances such as the time-of-fight technique enable the analysis of organic biomaterials. The surface sensitivity of low-bombardment-energy SIMS is quite high as the sampling depth is only about 1-2 nm compared to that of about 5-10 nm for XPS. Furthermore, it can detect all elements including hydrogen and helium as well as atomic ions and molecular ions at low concentrations. A basic SIMS instrument consists of three main components: the primary ion source, ion filtering system which selects ions with a defined energy, and mass spectrometer in vacuum. No special sample preparation is required for SIMS, but similar to XPS and AES, the sample surface should be relatively free of adventitious contaminants from storage or transport. In SIMS, the sample surface is bombarded by ions or neutrals (normally between 1 and 40 k eV). The momentum transfer

initiatesa collisional cascade, in which some atomic and molecular species are emitted as secondary ions. Ion mixing, knock-on, and sample roughening limit the depth resolution which depends on several instrumental factors such as primary ion energy, primary ion mass, and incident angle. Typical secondary ions originate approximately from the top two or three layers of the solid and have kinetic energy on the order from several to hundreds of electron volt. After leaving the solid surface, the positive or negative secondary ions are filtered by energy and mass-to-charge (m/z) ratio and detected by an electron multiplier or image detector composed of micro-channel plates. The secondary ion fragments often impart characteristic information about molecular information and sometimes chemical information. A pictorial presentation of the sputtering process in SIMS is illustrated in Figure 3.
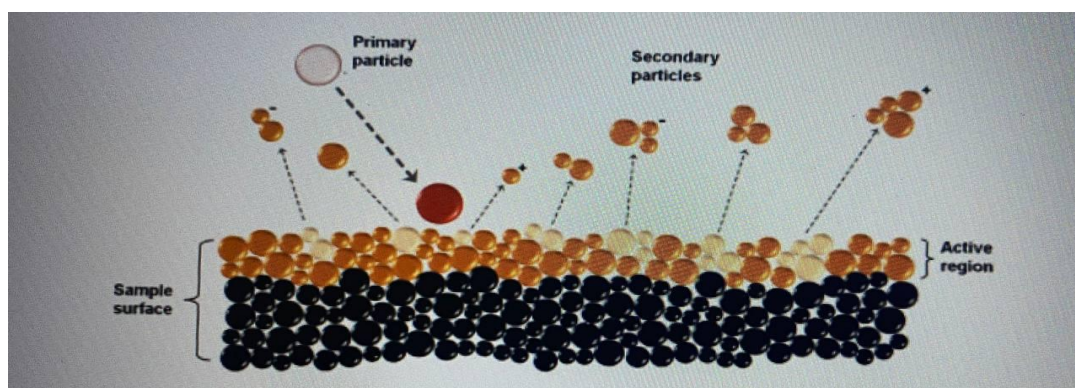

FIGURE 3 Schematic illustration of the secondary ion emission process initiated by the impact of a primary particle. Extensive fragmentation occurs near the collision site producing mainly atomic particles. Away from the point of impact collision, the process becomes less energetic resulting in the emission of larger molecular fragments.

2.3. RAMAN SPECTROSCOPY

When a light quantum to impacts a surface, an elastic scattering process termed Rayleigh scattering ensues, this process has the highest probability but there are also inelastic processes in which the vibrational energy is altered by hrs. The inelastic process is called Raman scattering and an energy of $h\nu_0 \pm h\nu_s$