

## **A brief review of X-ray Photoelectron and Raman spectroscopic techniques : basic principle and instrumentation**

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### **Abstract**

The objective of this paper is to give an overview of a group of non-destructive optical spectroscopic techniques like X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy which are used required by materials science technologist for characterization of nanomaterials. The structural parameters of nanostructures are studied by Raman spectroscopy. XPS is employed to study the elemental or chemical composition of nanomaterials. In this review, working principle, instrumentation, and importance of above-mentioned techniques are discussed briefly so that analysis of nanomaterial properties can be done in a productive way.

**Keywords:** X-ray photoelectron spectroscopy (XPS), Raman spectroscopy.

### **1. Introduction**

During the past few years, research on nanomaterials or low dimensional systems has been the subject of intensive interest due to its novel optical, electrical, mechanical, catalytic properties because of high surface to volume ratio and quantum confinement effects making it different from bulk material properties. Nanomaterials are

found to be useful for the production of new optoelectronic devices, defence field, information technology and bioimaging applications. Tools such as X-ray photo spectroscopy, absorption spectroscopy, photoluminescence spectroscopy, Raman spectroscopy are increasingly used by researchers to study different materials properties and to investigate materials quality. Applications of these techniques in different sectors like chemistry, drugs, agro-food, life sciences and environmental inspection are being constantly described. The advancement of above-mentioned spectroscopic techniques has been hastened by the development of light sources.

XPS, a chemical surface analysis analytical technique based on the photoemission process was developed by Kai Siegbahn in the mid-1960s who was rewarded with Nobel Prize in 1981 for his contribution towards the evolvement of high resolution electron spectroscopy. Photoemission process refers to electron emission process from a specimen after the absorption of photon. The first experimental evidence of this phenomenon was given by Heinrich Hertz who detected electrons emitted from a secondary arc due to the irradiation of ultraviolet light in 1887. The theoretical explanation of this process was given by Einstein in 1905.

The history or development of fundamental concepts involved in understanding photoemission process is reported in literature in a more detailed way. XPS involves exposing the sample with monoenergetic soft x-rays and analyzing the electron energy collected by the detector. Electrons come out from the top 3–5 nm of material surface have kinetic energies in the range of 10–1,000 eV. The obtained XPS spectrum is a plot of the number of detected electrons per unit time versus their binding energy. Peaks in XPS spectrum corresponds to unique element binding energies which can be used to identify elements present in the surface. It is different from energy dispersive X-ray spectroscopy (EDS) in the sense that EDS gives information about chemical composition of top 1mm of material and sensitive to lighter elements. It is valuable tool for studying tribological systems, identify different chemical states of element present on surface, for both qualitative and quantitative measurement and investigating the film functionality. Deep depth measurement can be made by ion sputter etching method. This technique measures the binding energies of detected element with an uncertainty of about 0.5 eV.

Raman spectroscopy also known as vibrational spectroscopy is another useful tool for the study of nanomaterials structure. It uses the principle of inelastic scattering of light called Raman effect discovered by an Indian physicist Chandrashekhara Venkata Raman. This technique gives information about molecular vibrations, symmetry, electronic environment, molecule bonding and useful for the quantitative and qualitative measurement of the

individual compounds. Above mentioned both characterization techniques is beneficial for analysis of certain material properties but not a single technique is having the potential to fully characterize all material properties.

This paper describes the basic principle of X-ray Photoelectron spectroscopy and Raman spectroscopy techniques with explanation of their instrumentation, advantages, limitations and applications in different fields so that study of material properties can be done in a satisfactory way.

## **2. Optical spectroscopic techniques :**

### **Basic principle and instrumentation**

#### **2.1 X-ray photoelectron spectroscopy (XPS)**

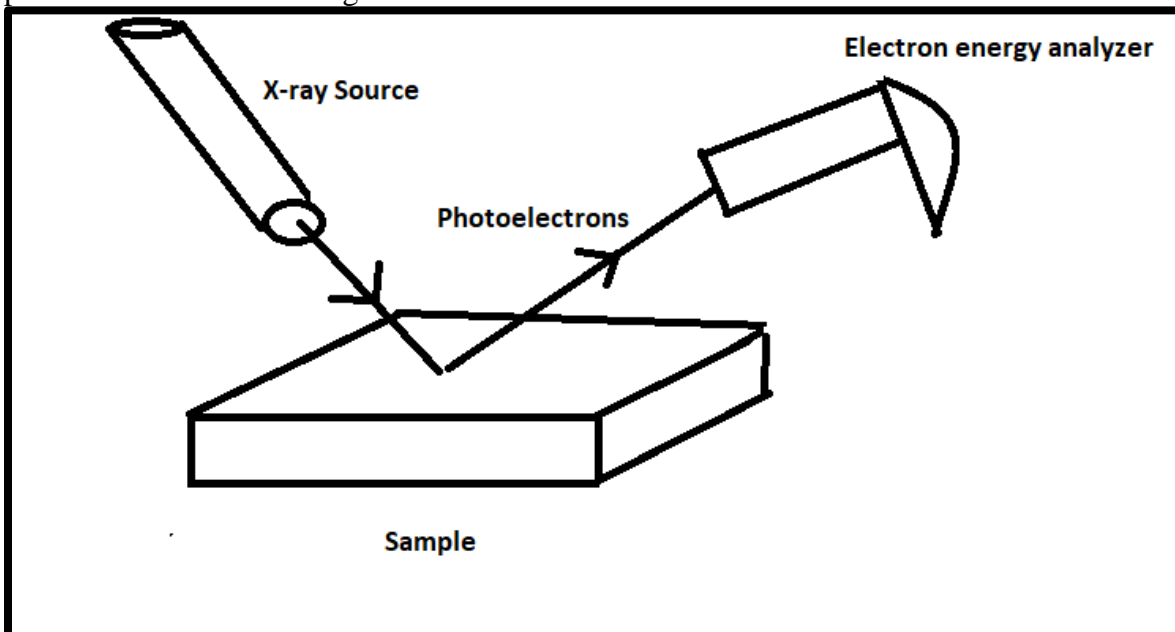
X-ray photoelectron spectroscopy (XPS) also known as electron spectroscopy for chemical analysis (ESCA) is a non-destructive powerful tool for measuring quantitatively the chemical composition of elements that present within the top material surface. XPS spectra is obtained by allowing a beam monochromatic X-rays of low energy to fall on sample placed in an ultrahigh vacuum and simultaneously noting the number of electrons along with kinetic energy that come out from the top material surface as shown in Fig. 1. The binding energy of the emitted electrons can be determined by knowing the energy of incident X-rays via the equation

$$K_e = hv - BE - \phi$$

.....(1)

Where B.E. is the electron binding energy which is to be measure,  $h\nu$  is the known energy of the incident X-ray photons,  $K_e$  is the electron kinetic energy measured by the instrument and  $\phi$  is the work function of the spectrometer. The kinetic energy of emitted core electron is depends on its binding energy which is a function of the element from which it is emitted. In this process, emission of Auger electron also occur in addition to the emission of the photoelectrons when X-ray hit the sample resulting in the ejection of core electrons and the corresponding created vacancy in the inner shell of atom is filled by electrons present in the outer shell. Primary data used for analysis of XPS is computing the number of photoelectrons and Auger electrons

detected as a function of their energy. The energy is determined as a function of their velocity by using electron energy analyzer resulting in a spectrum showing material surface composition. Peak appear in XPS spectrum corresponds to electron binding energy indicating characteristic of particular element present in the sample under investigation. Study of element chemical state and relative amount can be determined by noting XPS peak position, shape and area under peak in the spectrum. The ability of this technique to give quantitative analysis of sample surface composition and provide information of element chemical state information present in the topmost layer of material makes it an extraordinary and effective tool for acquiring the knowledge about any material surface chemistry.



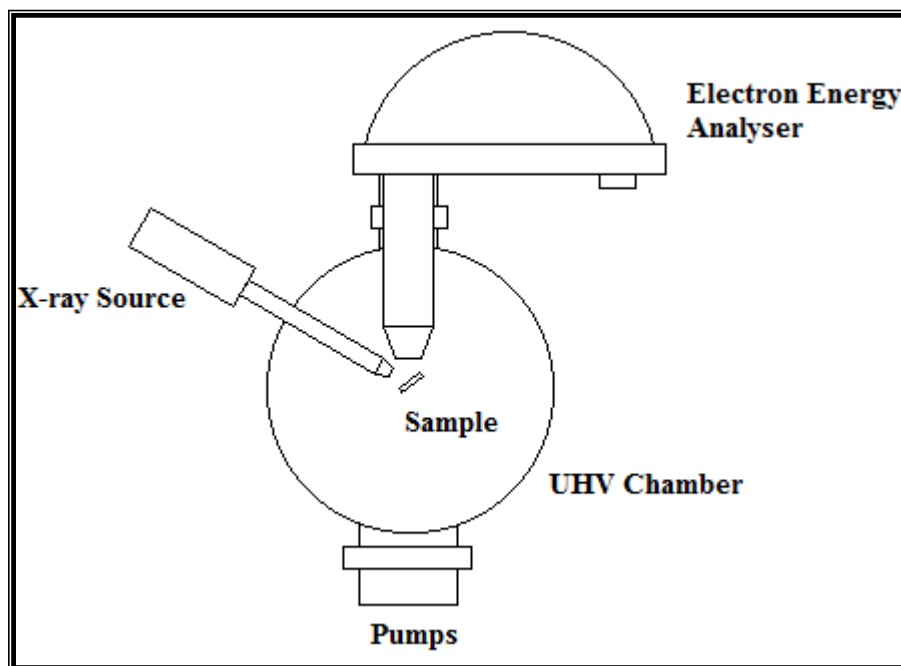
**Figure 1. Principle of X-ray photoelectron spectroscopy**

Assembly of XPS instrument consists a source of monochromatic X-ray beam, unit for analyzing electron energy, an ultra-high-vacuum system, an arrangement for preventing sample from charging. X-ray source is made up of a cathode (filament), which emits thermal electrons through heating (usual emission current of about 30mA), and an anode to which the electrons are accelerated by applying a high voltage of typically 9kV to 12kV. The construction of the X-ray source allows to choose magnesium and aluminium as the material of the anode, each of one give a characteristic emission spectrum. Core electron of atom will come out from sample surface when it is hit by X-ray of high energy resulting in building some charge on the surface due to which kinetic energies of core electrons reduces and leads to shifting of XPS peaks towards higher binding energy. Peaks are shifted back to original position by calibrating instrument against internal standard reference such as carbon or a known species in that particular sample.

Sample charging creates problem for insulating materials as it can deform the photoelectron spectrum but not for conducting materials. To solve this problem, most modern instruments are provided with low-energy electron gun source which can be set to the right value of current to bring the XPS peaks back to the original position. Each element present in the sample has

distinct binding energy which is very sensitive to element chemical atmosphere.

The alteration of binding energy due to the different chemical environment results in changing the XPS peak position between the range from 0.1eV to 10eV. Different designs of electron analyser are used for measuring the photoelectron energy emitted from the sample. The most favoured design of electron energy analyser is a concentric hemispherical analyser (CHA) on which electric field is applied so that electrons can be distributed as per their kinetic energy. Output of XPS experiment which is electron kinetic energy spectrum obtained by noting the photoelectron current at the detector as a function of the voltage applied to the hemispherical plates. The kinetic energy is calculated by using voltage parameter. This experiment requires the availability of high vacuum chamber attain through turbo molecular pump in connection with rotary vane pump so that the sample does not get oxidised. Such a system is illustrated schematically in Fig. 2. A spectrum containing great signal amplification is achieved through electron multipliers. Peaks appearing in the spectrum are the characteristic of particular element binding energy which help in figure out kinds of elements present on the material surface being tested.



**Figure 2. Schematic representation of the components necessary for performing X-ray photoelectron spectroscopy (XPS)**

## 2.2 Raman spectroscopy

In this technique, incident monochromatic light, generally from a laser source suffer inelastic scattering on interaction with sample under analysis. Inelastic scattering means that there is a change in frequency of emitted light being shifted up or down in comparison with original monochromatic frequency, which is called the Raman effect. by This shift or change gives details about vibrational, rotational and other low frequency modes present in molecules. This effect is depend on molecular deformations caused by electric field  $E$  of light and determined by molecular polarizability ( $\alpha$ ). The laser beam can be viewed as an oscillating electromagnetic wave having electric field vector  $E$ . When light of frequency  $\nu_0$  is incident on the sample it generates electric dipole moment  $P = \alpha E$  which deforms

molecules. Due to this molecules start vibrating and behave as oscillating dipole of characteristic frequency  $\nu_m$ . Frequencies of emitted light from oscillating dipoles are of three types as shown in Fig. 3 when:

1. Frequency of emitted light is same as incident light  $\nu_0$  from a molecule having no Raman-active modes. In this case, the excited molecule comes back to the same basic vibrational state. This type of interaction is called an elastic Rayleigh scattering.
2. Frequency of scattered photon is  $\nu_0 - \nu_m$  which is less than frequency of incident light  $\nu_0$  from a molecule having Raman -active modes of frequency  $\nu_m$ . Molecule is in the basic vibrational state at the time of its interaction with photon. This

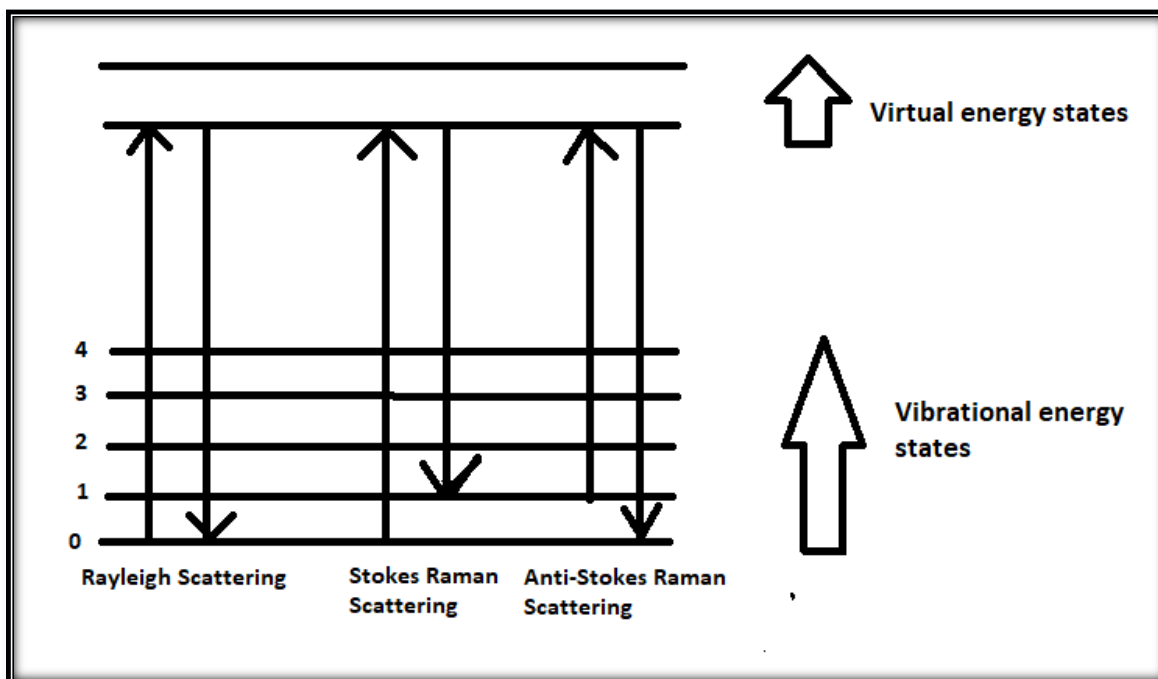
reduced scattered photon frequency is called Stokes.

3. Frequency of scattered photon is  $\nu_0 + \nu_m$  which is more than frequency of incident light  $\nu_0$  from a molecule having Raman -active modes of frequency  $\nu_m$ . Molecule is already in the excited vibrational state at the time of its interaction with photon. This increased scattered photon frequency is called Anti-Stokes.

The Raman shift does not rely upon the frequency of the incident photon but it is regarded as a property of the substance producing Raman effect. For stoke's lines, shift is positive and for anti-stoke's lines shift is negative. Uniform displacement of stokes and anti-stokes lines takes place from the Rayleigh line. This happen because in any case one vibrational quantum of energy is gained or lost. It has been found that intensity of anti-stokes lines is quite less than the stokes line. This arise because before photon irradiation molecules are already in excited vibrational state. Hence, in

Raman spectroscopy, only the more intense stokes line is normally measured.

Infrared absorption spectroscopy is another analogous vibrational technique used to predict molecular structure It is different from Raman spectroscopy in the way the molecular transitions occur. For Raman active transition, polarizability of the molecule must change during the vibration. This means that the electron cloud of the molecule must undergo positional change. On the other hand, for an infrared active transition, molecule dipole moment must change during vibration. Homonuclear diatomic molecules such as  $H_2$ ,  $N_2$ ,  $O_2$ , etc do not manifest infrared spectra because they do not possess a permanent dipole moment but do show Raman spectra as there is a change in molecular polarizability during vibration. Thus, Raman spectroscopy allow us to study the vibrational spectra of compounds that can be study by IR absorption spectroscopy. Raman spectroscopy can be used for investigation of material structure present in any state of matter building it very versatile technique.



**Figure 3. Shows vibrational level of the material**

There are different types of Raman Spectroscopy such as Surface enhanced Raman spectroscopy (SERS), resonance Raman effect (RRE) and Micro Raman spectroscopy (MRS). These techniques are used to intensify the Raman weak signal which aid in observing very low concentrations of elements present in biological and chemical samples with higher accuracy and detecting small sample area by minimizing the spot size of the light source on the sample.

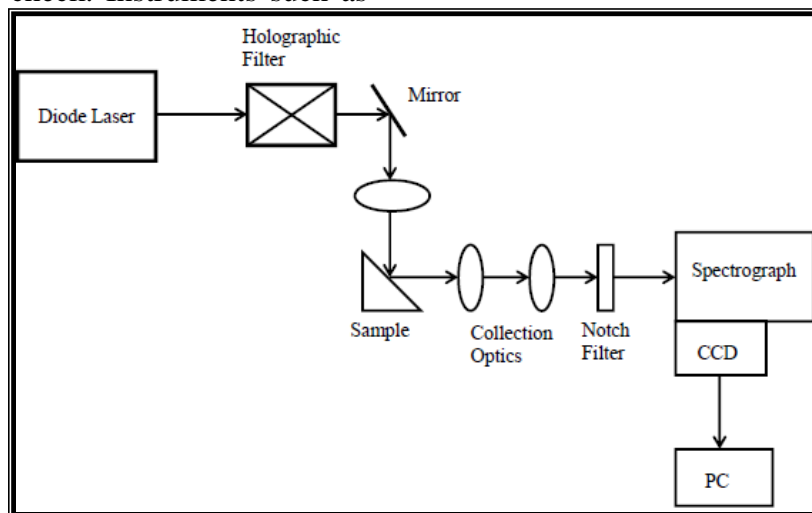
A typical Raman system mainly contain four parts: light source (laser), monochromator, sample holder and detector which can be Photodiode array, Charge-coupled device (CCD) and Photomultiplier tube. In earlier single-point detectors such as photon-counting Photomultiplier Tubes (PMT) was employed for taking Raman spectrum. However, due to the use of very long

time PMT is not accepted because any research or industrial project based on Raman analytical technique was getting slow down. Raman spectroscopy has now become easier and more precise due to developments in the field of optics, light source and computer technology. Researchers employ multi-channel detectors like Photodiode Arrays (PDA) or, more commonly, a Charge-Coupled Devices (CCD) to see the Raman scattered light. Charge coupled Device (CCD) detectors have benefitted the scientist in a huge way by acquiring the data rapidly with more accuracy that were not able to obtain with old photomultiplier tubes. The CCD has an assembly of detectors that can scan a range of wavelengths one by one greatly minimizing the collection time. The use of highly sensitive detectors in addition to the use of optical fibers and microscopes help in increasing the



capacity of analysis. In Raman instrument a sample is put into the cryostat chamber where the low temperature is attained by employing liquid helium and is illuminated with a laser beam. Vacuum is maintained in the cryostat chamber so that laser light bear no scattering from the air particles. Light from the illuminated spot is gathered using lens, sent through interference filter and finally through spectrometer to acquire the Raman spectrum of a sample. Scattered light of wavelengths near to incident laser light caused by elastic Rayleigh scattering are filter out while the remaining scattered light is collected and fed into a detector. By switching the wavelength of laser light, emitted spectra whether contain a true Raman peak or a peak just associated with the wavelength of the used laser light can be check. Instruments such as

notch filters, tunable filters, laser stop apertures, double and triple spectrometric systems are employed to achieve high-quality Raman spectra by minimizing Rayleigh scattering. Layout diagram of Raman spectrometer is used as shown in Fig. 4. The parameters which influence the analysis of Raman spectra are high signal-to-noise ratio, instrument stability and sufficient resolution. The evolution of dispersive Raman spectroscopy and fourier transform Raman spectroscopy employing near infrared or red lasers as excitation light sources help in minimizing the problem of fluorescence that influence Raman signals. Both these methods are different in the sense of type of laser light sources used and the way by which Raman scattering is detected and examined.



**Figure 4. Layout diagram for Raman spectroscopy**

### Conclusions

Optical spectroscopy techniques are emerged as powerful non-destructive analytical tools for extracting chemical

and structural information about nanomaterials by providing unique fingerprint spectra. This paper discusses basic principle and instrumentation of X-



ray Photoelectron spectroscopy and Raman spectroscopy with the various possibilities of their advancement in instrument section. XPS technique involves measuring the energy of emitted electron when sample is irradiated with monoenergetic soft X-rays. It is a useful tool for studying chemical composition of the outermost surface of conducting and non-conducting sample. The high surface sensitivity, precise depth profile measurement, determination of chemical bond and element oxidation state makes it different other techniques. Raman spectroscopy is one of the speedy and non-destructive analytical technique that provide vibrational spectrum thereby help in getting molecular and chemical structure information of any kind of sample. Huge growing fascination in using these techniques for structure determination may be due to getting straight results of analysis which are easy to elucidate without sample preparation, making it as a time saving and cost-effective technique.

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