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Raman Spectroscopy in Nanotechnology Applications

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ABSTRACT

Raman spectroscopy has proven to be a powerful and versatile characterization tool used for determining chemical composition of material systems such as nanoscale semiconductor devices or biological systems. Raman spectroscopy is based on the concept of the Raman effect. Raman spectroscopy generally does not require sample preparation for obtaining the response from varied biological samples. Raman spectroscopy is non-destructive. There is no need to dissolve solids, press pellets, compress the sample against optical elements or otherwise alter the physical or chemical structure of the sample. The fundamental of nanotechnology lies in the fact that properties of materials change dramatically when their size is reduced to the nanometer range. , nanotechnology has motivated the upsurge in research activities on the discovery and invention of sophisticated nano characterization techniques to allow a better control of morphology, size and dimensions of materials in nano range. The important characterization techniques used for nanotechnology research. The field of nanotechnology is set to grow ever rapidly as new applications and avenues of research are explored over the coming decade. Crucially, characterization and visualization methods in a medical setting must develop in tandem, to access the applicability of such nanotechnology. Raman spectroscopy represents a method proven in the field of disease diagnostics and biomedical imaging and thus by extension holds the capability to progress the field of nanomedicine.

Keywords: Raman Spectroscopy; Raman Microscopy, Nanomaterials & Nanotechnology

Introduction:

In 1928, Sir C.V. Raman documented the phenomenon of inelastic light scattering. Radiation, scattered by molecules, contains photons with the same frequency as that of the incident radiation, but may also contain a very small number of photons with a changed or shifted frequency. The spectroscopic process of measuring these shifted photons was later named after Sir Raman, with the shifting of frequency referred to as the Raman effect and frequently shifted light as Raman radiation. By the end of the 1930s, Raman spectroscopy had become the principle method of non-destructive chemical analysis.

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based on the inelastic scattering of incident photons by atoms and molecules in a sample. The incident photons enter a virtual energy state when they interact with sample. The eventual return of photons to ground state results in the inelastic scattering. The wavelength of scattered photons can be determined by calculating the induced dipole moments in molecules due to vibrational displacements. If the final ground state has more
energy than initial state, then emitted photon will be shifted to lower frequency. This scattering is called as Stokes scattering. If the final state is more energetic than initial, the emitted photon will be shifted to higher frequency, resulting in anti-Stokes scattering. Depending on the amount of scattered photons, Raman spectrum shows various peaks which undergo changes with changes in the characteristics of a sample. These characteristic peaks can be used to identify the structural components or chemical composition of the sample.

One major advantage of Raman spectroscopy in the case of biological molecules is that water gives very weak, uncomplicated Raman signal. Another advantage of Raman spectroscopy in the case of biological molecules is the ability of Raman spectroscopy to analyze *in-vivo* samples. Raman spectroscopy generally does not require sample preparation for obtaining the response from varied biological samples. .This aspect gives this technique an edge over other methods such as Infra-Red (IR) spectroscopy which requires elaborate signal preparation for excitation and complex instrumentation for signal processing after the excitation. Raman spectroscopy is fast emerging as an important characterization tool for biological systems.

Raman spectroscopy is a branch of vibration spectroscopy which is capable of probing the chemical composition of materials. Recent advances in Raman microscopy have added significantly to the range of applications which now extend from medical diagnostics to exploring interfaces between biological organisms and nanomaterials.

Why Raman Spectroscopy?

Raman spectroscopy has major advantages over other analytical techniques. The most important advantages are the ease of sample preparation and the rich information content. Raman is a light scattering technique, so all that is required for the collection of a spectrum is to place the sample into the excitation beam and collect the scattered light. There are few concerns with sample thickness (as in transmission analyses) and little contribution from the ambient atmosphere, so there is no need for high-vacuum or desiccated sample holders.

Raman spectroscopy is non-destructive. There is no need to dissolve solids, press pellets, compress the sample against optical elements or otherwise alter the physical or chemical structure of the sample. Thus, Raman has been used extensively for analysis of such physical properties as crystallinity, phase transitions and polymorphs. The lack of sample preparation also minimizes cleanup and the possibility of cross-contamination.

Several additional advantages are obtained with Raman spectroscopy over other vibrational techniques due to the fact that its operational wavelength range is usually independent of the vibrational modes being studied. Other

vibrational techniques require frequencies that correspond directly to the vibrational modes being studied. Raman allows easy access to vibrational modes associated with frequencies in the far-infrared which can otherwise be very difficult to access. Raman also allows microscopy with spatial resolution as fine as 1 μm and easily executed remote fiber-optics work providing vibrational mode information normally associated with wavelengths ranging from 2 – 100 μm. Achieving results like this using the native frequencies would be a daughnting task, but Raman makes it easy.

Raman Microscopy:

It is advantageous to couple the strength and flexibility of Raman spectroscopy with a microscope that allows analysis of very small samples. The goal of microscopy is to analyze the smallest samples possible and to distinguish the substance of interest from its surroundings. This is known as spatial resolution, and in microscopy, the highest spatial resolution is attained using small pinholes or "apertures" somewhere in the microscope. To reach higher resolution, it is necessary to use smaller apertures. As light passes through these smaller apertures, diffraction becomes the limiting factor.

Shorter excitation wavelengths provide the highest spatial resolution, so dispersive Raman microscopy offers excellent spatial resolution (<1 μm). In addition, by placing a sufficiently small aperture in the focal plane of the microscope, it is possible to perform confocal microscopy, in which light rays from surrounding regions of the sample are blocked by the aperture and only rays from the optical focal point pass to the detector. This is a useful technique for non-destructively probing the depths of the sample without cross-sectioning. Confocal microscopy is done best by dispersive Raman microscopy with short wavelengths because diffraction at longer wavelengths limits how small the confocal aperture can be, thus limiting the z-axis resolution. The technique is quite useful for analyzing polymer laminates, stacked structures and inclusions, as long as fluorescence is not an issue.

Over the past few decades nano size and nano dimensional materials whose structures exhibit significantly novel and improved physical, chemical and biological properties, phenomena, and functionality due to their nanoscaled size, have drawn much interest. Nanotechnology is an emerging interdisciplinary area that is expected to have wide ranging implications in all fields of science and technology such as material science, mechanics, electronics, optics, medicine, plastics, energy, aerospace, etc. Nanophasic and nanostructured materials are also attracting a great deal of attention of the textile and polymer researchers and industrialists because of their potential applications for achieving specific processes and properties, especially for functional and high performance textiles applications

The fundamental of nanotechnology lies in the fact that properties of materials change dramatically when their size is reduced to the nanometer range. But measuring this nano dimension is not a very easy task. Although research is going on to synthesise nanostructured and nanophasic materials, characterizing these nano sized materials is also an emerging field posing lot of challenges to scientists and technonologists. Thus, nanotechnology has motivated the

upsurge in research activities on the discovery and invention of sophisticated nano characterization techniques to allow a better control of morphology, size and dimensions of materials in nano range. The important characterization techniques used for nanotechnology research.

Nanomaterials Characterization by Microscopy:

Optical microscopes are generally used for observing micron level materials with reasonable resolution. Further magnification cannot be achieved through optical microscopes due to aberrations and limit in wavelength of light. Hence, the imaging techniques such as scanning electron microscopy (SEM), transmission electron microscopy (TEM/HRTEM), scanning tunneling microscopy (STM), atomic force microscopy (AFM), etc. have been developed to observe the sub micron size materials. Though the principles of all the techniques are different but one common thing is that they produce a highly magnified image of the surface or the bulk of the sample. Nanomaterials can only be observed through these imaging techniques as human eye as well as optical microscope cannot be used to see dimensions at nano level. Basic principles and applications of all these imaging techniques used in nanotechnology research are described below.

Scanning Electron Microscopy (SEM):

The scanning electron microscope is an electron microscope that images the sample surface by scanning it with a high energy beam of electrons. Conventional light microscopes use a series of glass lenses to bend light waves and create a magnified image while the scanning electron microscope creates the magnified images by using electrons instead of light waves.

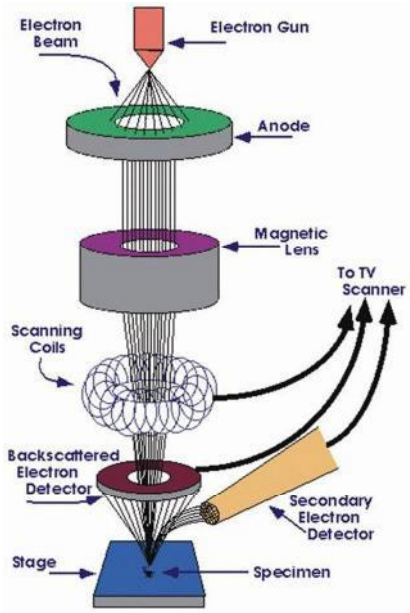
Basic Principle of Scanning Electron Microscopy (SEM):

When the beam of electrons strikes the surface of the specimen and interacts with the atoms of the sample, signals in the form of secondary electrons, back scattered electrons and characteristic X-rays are generated that contain information about the sample's surface topography, composition, etc. The SEM can produce very high-resolution images of a sample surface, revealing details about 1-5 nm in size in its primary detection mode i.e. secondary electron imaging. Characteristic X-rays are the second most common imaging mode for an SEM. These characteristic X-rays are used to identify the elemental composition of the sample by a technique known as energy dispersive X-ray (EDX). Back-scattered electrons (BSE) that come from the sample may also be used to form an image. BSE images are often used in analytical SEM along with the spectra made from the characteristic X-rays as clues to the elemental composition of the sample.

In a typical SEM, the beam passes through pairs of scanning coils or pairs of deflector plates in the electron column to the final lens, which deflect the beam horizontally and vertically so that it scans in a raster fashion over a rectangular area of the sample surface. Electronic devices are used to detect and amplify the signals and display them as an image on a cathode ray tube in which the raster scanning is synchronized with that of the microscope. The image displayed is therefore a distribution map of the intensity of the signal being emitted from the scanned area of the

specimen.

SEM requires that the specimens should be conductive for the electron beam to scan the surface and that the electrons have a path to ground for conventional imaging. Non-conductive solid specimens are generally coated with a layer of conductive material by low vacuum sputter coating or high vacuum evaporation. This is done to prevent the accumulation of static electric charge on the specimen during electron irradiation. Non-conducting specimens may also be imaged uncoated using specialized SEM instrumentation such as the "Environmental SEM" (ESEM) or in field emission gun (FEG) SEM operated at low voltage, high vacuum or at low vacuum, high voltage.



Applications:

The SEM shows very detailed three dimensional images at much high magnifications (up to ×300000) as compared to light microscope (up to × 10000). But as the images are created without light waves, they are black and white. The surface structure of polymer nanocomposites, fracture surfaces, nanofibres, nanoparticles and nanocoating can be imaged through SEM with great clarity. As very high resolution images of the dimension 1 – 5 nm can be obtained, SEM is the most suitable process to study the nanofibres and nanocoatings on polymeric/textile substrate.

Electrospun nanofibres are extensively studied in biomedical, environmental and other technical textile applications for their huge surface area. Electrospun nylon 6 nanofibres decorated with surface bound silver nanoparticles used for antibacterial air purifier can be characterized using SEM. In tissue engineering or cell culture applications, the SEM image is the prime characterization technique for scaffold construction, cell development and growth. SEM technique is used to

observe the plied CNT yarns in 3D braided structures.

The SEM technique can also be used to view dispersion of nanoparticles such as carbon nanotubes, nanoclays and hybrid POSS nanofillers in the bulk and on the surface of nanocomposite fibres and coatings on yarns and fabric samples.

Areas which benefit from Raman spectroscopy include:

- Identification of materials constituting nanostructures
- Number of layers for graphene and TMDC layers
- Thickness of heterostructure layers
- Diameter and chirality of carbon nanotubes
- Stress/strain characterization
- Electronic properties of materials (metallic/semiconductive, doping)
- Localization of separated carbon nanotubes or quantum dots

Conclusions:

The field of nanotechnology is set to grow ever rapidly as new applications and avenues of research are explored over the coming decade. Crucially, characterisation and visualisation methods in a medical setting must develop in tandem, to access the applicability of such nanotechnology. Raman spectroscopy represents a method proven in the field of disease diagnostics and biomedical imaging and thus by extension holds the capability to progress the field of nanomedicine.

Spontaneous Raman spectroscopy provides a versatile and truly label free method which has seen success in a number of different medical applications, most notably in disease diagnostics. Key enabling technological developments in this context include endoscopic and other in vivo probes. Relatively Low signal strengths currently limit the technique to small areas and/or long scan times, however, and continuing improvements in signal throughput and detector sensitivities are important. EU Directives limiting the use of animal models will put increasing emphasis on the development of in vitro screening methods and Raman is a potential candidate for high content analysis of, for example, the efficacy and mode of action of novel chemotherapeutical agents of toxicants. The high optical resolutions obtainable make Raman particularly suitable for acellular or subcellular studies of nanobio interactions.

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