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Nanoparticles advanced characterization techniques: A view point

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ABSTRACT:

Nanoparticle implies any particle with at least one dimension of less than 100 nm. Growing emphasis on research in the field of nanoscience and its applications in different arena cannot be overlooked. Over the past few decades, nanoparticles are being widely used in different fields such as medicine, information technology, agriculture, material science, space research etc. In order to accurately determine particle size, size distribution, and individual/agglomerate morphologies of nanoparticles, an understanding of various characterization methods and advancements thereof is imperative. Characterization techniques most commonly employed in the study of nanoparticles include dynamic light scattering to measure the hydrodynamic radius of the nanoparticles, transmission electron microscopy for direct imaging of atomic structures in solids and surfaces, scanning electron microscopy for information about the samples' surface topography, composition etc. and atomic force microscopy for characterizing nanoparticles in different mediums with an advantage of 3D visualization. These techniques have been successfully used in the characterization of curcumin nanoparticles, starch nanoparticles, nano-pesticides etc.

KEY WORDS: Nanoparticles, Nanoscience, nanotechnology, curcumin nanoparticles

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INTRODUCTION:

The need to sort, name, categorize, catalog, & detail the things, parts, & components of our world has accompanied humanity since the dawn of civilization. Characterization is fundamental to science. This is the means by which we communicate our scientific achievements [1]. Measurement is accomplished with tools: the instruments, machines, equipments, & computer hardware & software. There are many types of characterization methods & most predate the

advent of nanoscience & nanotechnology. Some methods have actually evolved alongside nanoscience & helped launch the *Nano Age* itself. The development of novel, integrated methods designed specifically to probe the nanoworld is an ongoing & evolutionary process [2]. Characterization refers to study of materials features such as its composition, structure, and various properties like physical, electrical, magnetic, etc. Nanoparticle is a microscopic particle whose size is measured in nanometers (nm). It is defined as a particle with at least one dimension <100nm [3].

CATEGORIZATION OF NANOPARTICLE:

Nanoparticles can be broadly categorized as organic & inorganic nanoparticles. Nanoparticles are very unique in their nature owing to wonderful inherent capacities such as: small size, high surface area, eases to suspend in liquids, deep access to cells and organelles and variable optical & magnetic properties. The most obvious difference between nanoparticles and their bulk counterparts is in terms of size [4]. The ability to design nano-size structures and components has resulted in materials with novel and significantly improved physical, chemical, and biological properties. Conventional diffraction methods often fail to yield accurate measurements of their various aspects. These methods assume an infinitely periodic system, which does not work with nanosizes [5]. Quality, affordability, and reproducibility are essential if the nanotechnology is to become a large-scale commercial reality. One of the most critical steps to achieve these objectives is the development of characterization methods which can accurately determine fine particle size, size distribution, and particle/agglomerate morphologies [6]. Choice of a method or methods in characterization of nanoparticles depends on the need to balance the restriction of the type of sample, the information required, time constraints and the cost of the analysis. A straight forward technique may simply detect the presence of nanoparticles, others may give the quantity, the size distribution or the surface area of the nanoparticles [7]. These measurement techniques differ from characterization techniques for assessing the chemical content of a nanoparticle sample, the reactions on the surface of the nanoparticles or for the interactions with other chemical species present. Different techniques suit different types of samples, for example, some techniques require the sample to be as an aerosol and others will use a suspension or liquid sample. There may be a sample protocol to be followed for collection of the sample for analysis by a certain technique [8]. There are techniques for in situ measurements of samples and others that require treatment of the sample before analysis. Sometimes samples may not be able to withstand the required treatment and decompose or react [9]. The amount of sample required can also vary and restrict choice of technique.

ENCROACHMENT IN CHARACTERIZATION TECHNIQUES:

Dynamic light scattering:

Dynamic light scattering, sometimes referred to as photon correlation spectroscopy (PCS) or quasi-elastic light scattering (QELS) is a non-invasive, well-established technique for measuring the size of molecules and particles typically in the submicron region, and with the latest technology lower than 1 nanometre. Particles, emulsions and molecules in suspension undergo Brownian motion. This is the motion induced by the bombardment of Solvent molecules that themselves are moving due to their thermal energy. If the particles or molecules are

illuminated with a laser, the intensity of the scattered light fluctuates at a rate that is dependent upon the size of the particles as smaller particles are "kicked" further by the solvent molecules and move more rapidly [10]. Analysis of these intensity fluctuations yields the velocity of the Brownian motion and hence the particle size (radius *r*) using the Stokes-Einstein relationship. The advantages are mmeasurements are fast, from seconds to minutes; the technique is absolute, from first principles; calibration with a known size distribution is not necessary to get answers; very small quantities of sample can be measured; any suitable suspending liquid can be used provided it is non-absorbing, relatively clear and not too viscous; the technique is applicable from about 0.001 to several microns; instrumentation is commercially available for both research and QC measurements with automation including data analysis; although the interpretation of particle size is least ambiguous with a narrow distribution, an effective diameter and polydispersity index are measurable even with broad distributions [11]. The disadvantages are it does not produce a high-resolution histogram of the size distribution; like other non-imaging techniques an equivalent sphere diameter is usually, although not always, assumed; shape information is not easily obtained; when proper measurements are made, the parameters which are most often obtained are the inverse z-average moments of the size distribution, not the usually reported parameters of a size distribution; dust can make measurement and interpretation difficult [12].

Scanning Electron Microscopy (SEM):

SEM 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 & create a magnified image while the SEM creates the magnified images by using electrons instead of light waves. When the beam of electrons strikes the surface of the specimen & interacts with the atoms of the sample, signals in the form of secondary electrons, back scattered electrons & characteristic X-rays are generated that contain information about the sample's surface topography, composition etc [13]. The SEM can produce very high resolution image 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 & vertically so that it scans in a raster fashion over a rectangular area of the sample surface [14]. Electronic devices are used to detect & amplify the signals & 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 & that the electrons have a path to ground for conventional imaging [15]. 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.

Environmental Scanning Electron Microscopy (ESEM):

While using the environmental scanning electron microscope (ESEM), it is not necessary to make nonconductive samples conductive. Materials samples do not need to be desiccated and coated with gold–palladium, for example, and thus their original characteristics may be preserved for further testing or manipulation. In ESEM, samples can be looked at in a low pressure gas environment as opposed to a vacuum [16]. The gaseous secondary electron detector (GSED) possesses as much as a 600-Volt positive bias on it to attract secondary electrons compared to the Everhart-Thornley secondary electron detector (ET SED) on a normal SEM, which ordinarily has only as much as a 300-Volt positive bias and also the former is relatively far from the sample [17]. Thus the GSED is set up to collect secondary electrons very efficiently.

Transmission Electron Microscopy (TEM):

TEM is a microscopy technique whereby a beam of electrons is transmitted through an ultra-thin specimen & interacts as passes through the sample. An image is formed from the electrons transmitted through the specimen, magnified & focused by an objective lens & appears on an imaging screen. The contrast in a TEM image is not like the contrast in a light microscope image. In TEM, the crystalline sample interacts with the electron beam mostly by diffraction rather than by absorption. The intensity of the diffraction depends on the orientation of the planes in a crystal relative to the electron beam; at certain angles the electron beam is diffracted strongly from the axis of the incoming beam, while at other angles the beam is largely transmitted. Modern TEMs are equipped with specimen holders that allow to tilt the specimen to a range of angles in order to obtain specific diffraction conditions. Therefore, a high contrast image can be formed by blocking electrons deflected away from the optical axis of the microscope by placing the aperture to allow only unscattered electrons through [18]. This produces a variation in the electron intensity that reveals information on the crystal structure. This technique particularly sensitive to extended crystal lattice defects is known as ‘bright field’ or ‘light field’. It is also possible to produce an image from electrons deflected by a particular crystal plane which is known as a dark field image. The specimens must be prepared as a thin foil so that the electron beam can penetrate. Materials that have dimensions small enough to be electron transparent, such as powders or nanotubes, can quickly be produced by the deposition of a dilute sample containing the specimen onto support grids. TEM enables direct 2-D imaging of particle size, shape & surface characteristics. Changes in nanoparticle structure as a result of interactions with gas, liquid & solid-phase substrates can also be monitored.

High Resolution Transmission Electron Microscopy (HRTEM):

HRTEM is an imaging mode of TEM that allows the imaging of the crystallographic structure of a sample at an atomic scale. As opposed to conventional microscopy, HRTEM does not use absorption by the sample for image formation, but the contrast arises from the interference in the image plane of the electron wave with itself [19]. As a result of the interaction with the sample, the electron wave passes through the imaging

system of the microscope where it undergoes further phase change & interferes as the image wave in the imaging plane. It is important to realize that the recorded image is not a direct representation of the samples crystallographic structure. It can be used to study local microstructures like lattice fringe, glide plane or screw axes & the surface atomic arrangement of crystalline nanoparticles.

Scanning Transmission Electron Microscopy (STEM):

This technique works as a mapping device unlike TEM where a stationary, parallel electron beam is used to form images. In STEM, a fine electron probe is scanned over a sample. Since it is a serial recording, the image generation takes longer time as compared to that in TEM. It combines the ideas of looking at the surface of the sample and into the sample with an electron beam. STEM is an invaluable tool for the characterization of nanostructures, providing a range of different imaging modes with the ability to provide information on elemental composition and electronic structure at the ultimate sensitivity. The STEM works on the same principle as the normal SEM, by forming a focused beam of electrons that is scanned over the sample while some desired signal is collected to form an image [19]. The difference with SEM is that thin specimens are used so that transmission modes of imaging are also available. A new possibility is opened up by the new aberration corrected STEMs. Correcting the lens aberrations allows the objective aperture to be opened up, thereby obtaining higher resolution. At the same time, as in an optical instrument like a camera, the depth of field is reduced. Present-day aberration corrected STEMs have a depth of field of only a few nanometers, and so it becomes possible to effectively depth slice through a sample and to reconstruct the set of images into a 3D representation of the structure [20]. The technique is comparable to confocal optical microscopy, but provides a resolution on nanoscale.

Atomic Force Microscopy (AFM):

AFM is ideal for both qualitatively & quantitatively measuring the nanometer scale surface roughness & for visualizing the surface nano-texture on many types of material surfaces including polymer nano-composites & nano-coated materials. Advantages of the AFM for such applications are derived from the fact that the AFM is non-destructive technique & it has a very high 3d spatial resolution [21]. In AFM, a probe consisting of a sharp tip (nominal tip radius is in the order of10 nm) located near the end of a cantilever[15] beam is raster scanned across the surface of a specimen using piezoelectric scanners [22]. Changes in the tip specimen interaction are often monitored using an optical lever detection system, in which a laser is reflected off the cantilever & onto a position-sensitive photodiode. During scanning, A particular operating parameter is maintained at a constant level & images are generated through a feedback loop between the optical detection system & the piezoelectric scanners [23]. There are 3 scan modes for AFM those descriptions are shown below:

Scanning Tunneling Microscopy (STM)

STM is an instrument for producing surface images with atomic scale lateral resolution, in which a fine probe tip is scanned over the surface of a conducting specimen, with the help of a piezoelectric crystal at a distance of 0.5-1 nm, & the resulting tunneling current or the position of the tip required to maintain a constant tunneling current is monitored. It is based on the concept of quantum tunneling

[24]. When a conducting tip is brought very near to a metallic or semi-conducting surface, a bias between the two can allow electrons to tunnel through the vacuum between them. Variations in tunneling current as the probe passes over the surface are translated into an image [25]. They normally generate image by holding the current between the tip of the electrode & the specimen at some constant value by using a piezoelectric crystal to adjust the distance between the tip & the specimen surface, while the tip is piezoelectrically scanned in a raster pattern over the region of specimen surface being imaged by holding the force, rather than the electric current, between tip & specimen at a set-point value [26].

X-Ray Diffraction (XRD)

X-rays are electromagnetic radiation similar to light, but with a much shorter wavelength (Few Angstrom). They are produced when electrically charged particles of sufficient energy are decelerated [27]. In an X-ray tube, the high voltage maintained across the electrodes draws electrons toward a metal target (the anode). X-rays are produced at the point of impact & radiate in all directions.

Other Important Techniques:

There are few techniques also those are used for specific study of nanoparticles. These include: nanoparticle tracking analysis, tilted laser Microscopy, turbidimetry , field Flow Fractionation, hydrophobic interaction chromatography, electrophoresis, isopycnic centrifugation, zeta potential measurements [28-29].

CONCLUSION:

Nanotechnology is the essence of molecular synthesis, manipulation, and manufacturing. Nanoparticle-based technologies cover different fields, ranging from environmental remediation, energy generation and most recent applications in bioscience. Nanoparticles, are, key components in the development of new advanced technologies. Nanoparticle characterization is necessary to establish understanding and control of nanoparticle synthesis and applications. Nanotechnology has a lot of potential as a futuristic approach but would be largely governed by simultaneous progress in the newer, faster, simpler & more efficient characterization techniques for nanoparticles. Integration of different techniques for better understanding of particle characters is needed. AFM with modern probes for attachment with fluorescent particles to study rate kinetics/degradation kinetics can be an effective step in future. Integration of surface morphology based techniques with 3D imaging techniques can make the measurement easier & faster.

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