Review Article

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Characterization Techniques used in Nanomaterials - A Review

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ABSTRACT

Nanotechnology is the design of science, characterization and production of nano scale, which is about 1-100 nm. Nano science can be used across other field like Chemistry, Electronics Engineering, Physics, Biology, and Material Science. In the current scenario nano materials are used significantly quite different from their bulk counterparts used traditionally. Nano Science R&D includes manipulation under control of nano structure and their integration into larger material component. This paper will be a brief idea of various techniques which are used to characterize the nanomaterials.

Keywords: AFM; Nonmaterial; Raman spectroscopy; Scanning Electron Microscopy; Scanning probe microscopy; TEM; X-RD.

1. INTRODUCTION

Over the past few decades nano size and nano dimension materials exhibits much attractionand improve versatile chemical and biological properties and functionality due to their nano size and high surface to volume ratio. Nanotechnology is an emerging interdisciplinary area that has wide range implication to all other fields in science and technology such as Chemistry, Material science, Polymers, Bio medicines, energy, physics and aerospace etc.

Nano materials are present in 0D, 1D, 2D, 3D morphology .One dimension nano tube and nano wire is used in hybrid molecular and semiconductor devices (Huang, 2001). Metal oxide and sulphide is used in quantum dots (Hale, 2005). Nano size plays an important role in the study of properties like (optical, electrical, mechanical, electronics) and application (Asthana *et al.* 2006). Nano coating is useful for the thermal resist material and cutting tools and ceramic materials are harder than steel and better heat and thermal resistance. In 1991 S.lijima discovered carbon nano tube (CNT) and special nano materials. They have good mechanical strength, high flexibility and better electrical conductivity than copper (Avadhani, 2009).

2. NANO MATERIALS CHARACTERIZATION BY MICROSCOPY TECHNIQUE

To gain some information of the nano particles located on the surface some techniques are used. Transmission electron microscope (TEM) and scanning electron microscope (SEM) give information on the particles size, shape, topology and their distribution. Electron diffraction confirms the structure, size and the phase (liquid and solid).STM confirms the size and the internal structure of the particles. Adsorption of gases informed surface to volume ratio on particles. The techniques using SEM, TEM and electron diffraction provide information on the particles in the bulk. X-RD technique can be determined the particles size and the crystal structure. Electron Microscopy is a power full and modern technique and allows investigation of the morphology and properties of solid surface body with high resolution, which employs beams of accelerated electrons and also different versions of probe microscopes. Electron microscopy is divided into the following types:

2.1 Scanning Electron Microscope (SEM)

The scanning electron microscope (SEM) is electron microscope. It uses electrons rather than light to form an image of sample surface by scanning with highly energetic beam of electron scattered or emitted from the sample and then be detected. The incident beam is raftered across the sample surface to produce an image. High spatial resolution makes it powerful to characterize the material nanometer to micrometer (Goldstein, 2003).

Basic principal

Accelerated electrons in a scanning electron microscope (SEM) carry significant amounts of kinetic energy and this energy is dissipated as a variety of signals produced by electron-sample interactions when the incident electrons are decelerated in the solid sample. These signals include secondary electrons (that produce SEM images), backscattered electrons (BSE), diffracted backscattered electrons (that are used to determine crystal structures and orientations of minerals), photons (characteristic X-rays that are used for elemental analysis and continuum X-rays), visible light, and heat. Secondary electrons and backscattered electrons are commonly used for imaging samples secondary electrons are most valuable for showing morphology and topography on samples and backscattered electrons are most valuable for illustrating contrasts in composition in multiphase samples (Reimer, 1998). X-ray generations is produced by inelastic collisions of the incident electrons with electrons in discrete shells of atoms in the sample. As the excited electrons return to lower energy states, they yield X-rays that are of a fixed wavelength. Thus, characteristic X-rays are produced for each element in a mineral that is "excited" by the electron beam. SEM analysis is considered to be "non-destructive"; that is, X-rays generated by electron interactions do not lead to volume loss of the sample, so it is possible to analyze the same materials repeatedly (Egerton, 2005). The SEM images the surface structure of bulk samples, from the biological, medical, materials sciences, and earth sciences up to magnifications of ~ 100,000 xs. The images have a greater depth of field and resolution than optical micrographs making it ideal for rough specimens such as fracture surfaces and particulate materials. Some SEM images are given in fig no.1&2 (Joo *et al.* 2003; Fu *et al.* 2001; Li *et al.* 2002; Wang *et al.* 2005).

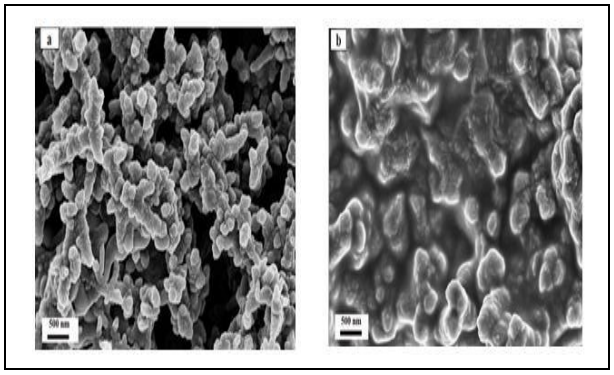

Fig. 1: SEM images of PANI (a) and PANI/nano-TiC (b) modified glassy carbon electrode

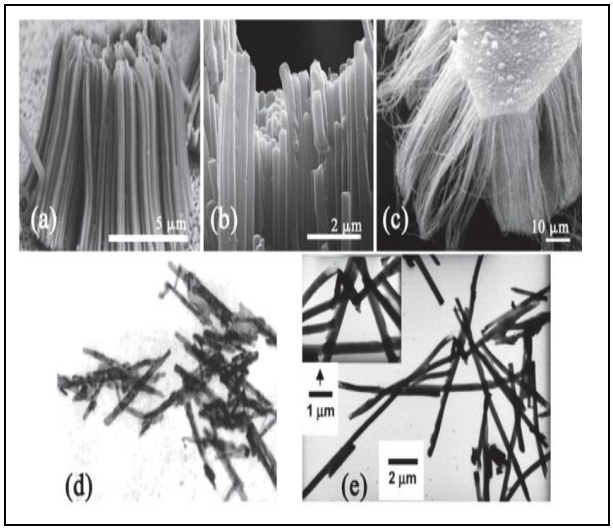

Fig. 2: SEM Images of (a) poly(3-methylthiophene) nanowires, (b) polypyrrole nanowires and (c) polythiophene nanowires on flexible substrate TEM images of (d) polypyrrole/polyaniline copolymer nanowires and (e) polypyrrole-carbon nanotube composite nanowires

2.2 Energy Dispersive X-ray (EDX)

EDX is a technique which is identify the composition and the phase of the sample. These causes indicate the SEM near powerful tool to the study the crystal growth morphology and assist to micrometer to nanometer.

Basic Principle

This technique is used to conjugate with the SEM. The beam energy range between 10-20 kev. The cause X-ray is emitted and its emission depends on the material under the examination. The X-rays are generated in the region 2 to 3 micron in depth. Due to low X-ray intensity image take much time to acquire. Electron beam across the material and each sample image is obtained.EDX images are shown in fig. 3.

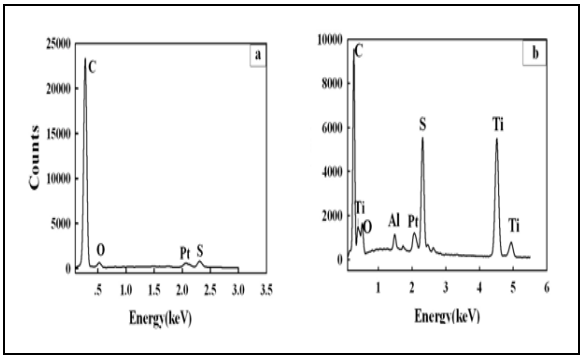

Fig. 3: EDX Pattern of PANI (a) and PANI/nano-TiC (b) modified electrode (Zhencui, 2015)

2.3 Transmission Electron Microscopy (TEM)

In this technique a beam of electrons is transmitted through an ultra-thin specimen, interact with the specimen as it passes through by this interaction an image is formed. Electrons that travel through the sample are detected. Electrons have a shorter wavelength than photons and can therefore provide a higher resolution than conventional light microscopes. TEM can provide two separate kinds of information about a specimen – a magnified image and a diffraction pattern. Some TEM images are shown in fig. 2 & 4.

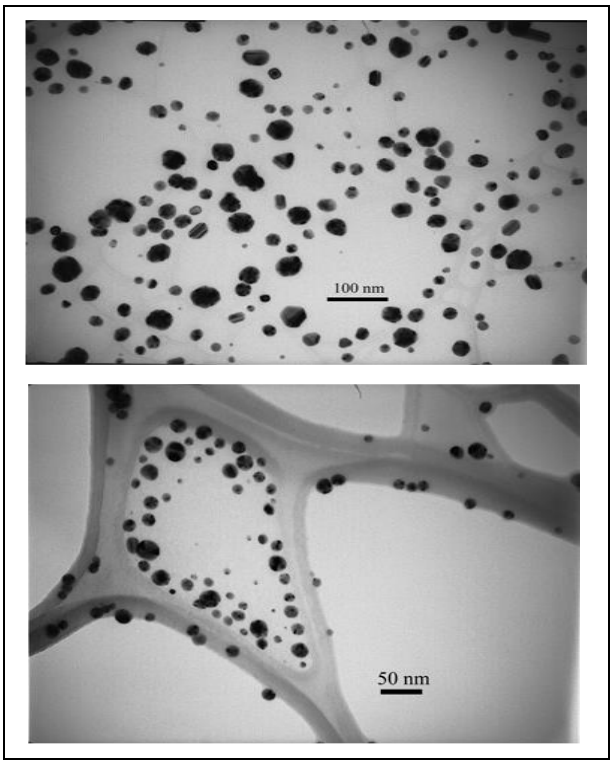

Fig. 4: TEM micrographs for silver nanoparticles under the reaction of AgNO3=0.0267 g in 20ml ethylene glycol, PVP=0.5317 g in 20 ml ethylene glycol at 180 °C by VFM radiation (Hongjin *et al.* 2006)

Basic Principle

The electrons are focused into a very thin beam which are transmitted through the specimen and finally projected on a fluorescent screen giving a "shadow image" of the specimen. The image contrast depends on the density of the material. The TEM has a better resolution then the light microscopy due to the much lower wavelength of electrons (Egerton, 2005). TEM forms a major analysis method in a range of scientific fields, in both physical and biological sciences. TEMs find application in cancer research, virology, materials science as well as pollution, nanotechnology, and semiconductor research (Rose, 2008; Oura *et al.* 2003). The contrast in a TEM image is not like the contrast in a light microscope image. A crystalline material interacts with the electron beam mostly by diffraction rather than absorption, although the intensity of the transmitted beam is still affected by the volume and density of the material through which it passes. A high-contrast image can therefore be formed by blocking electrons deflected away from the optical axis of the microscope by placing the aperture to allow only unscattered electrons through. This produces a variation in the electron intensity that reveals inform about the crystal structure.

2.4 Atomic Force Microscope (AFM)

This is very high resolution type of scanning microscope, resolution in order to the fraction of nanometer. It can be operated by two types of mode dynamic mode and static mode. The AFM operates like a record player except that it has flexible cantilevers, sharp tips and a force feedback system. It is ideally quantitatively measuring nano scale surface roughness and for visualizing surface nano-texture on many type of material surface including polymer and nanocomposites (Robert et *al.* 2007). AFM images are shown in figs. 5 (A) & 5(B).

Basic Principal

In atomic force microscope a probe consisting of a Sharpe tip located near the end of cantilever beam is raster scanned across the surface of the specimen using piezoelectric scanners. Change in the tip specimen interaction is often monitored using an optical lever detection system, in which laser is reflected off of the cantilever and onto a position sensitive photodiode. During the scan operating parameter is at constant level and images are generated through a feedback loop between the optional detection system and the piezoelectric scanners. There are two modes of operation:

(1) Contact Mode where the sample-tip distance is so small that the important force is the core-core repulsive one.

(2) Non-contact mode where the force is the Vander Walls one. It can achieve a resolution of ~1nm. The AFM can scan both hard and soft samples in ambient air or in a fluid environment**.** For an application atomic force microscope can be use to explore the nano structures, properties, surface and interface of fiber or fabrics.

3. X-RAY DIFFRACTION (XRD)

This technique is a very useful characterization tool to study the physical properties of material, thin film, chemical composition and crystallographic structure. The XRD has the potential to provide information on anatomic scale especially for crystalline species.This technique measures various structural properties of the crystalline phase such as defect structure, strain, grain size and phase composition. It determines not only

thickness of the film but also the arrangement in amorphous material such as polymeric material. X-RD graphs shown in figs. 7 & 8.

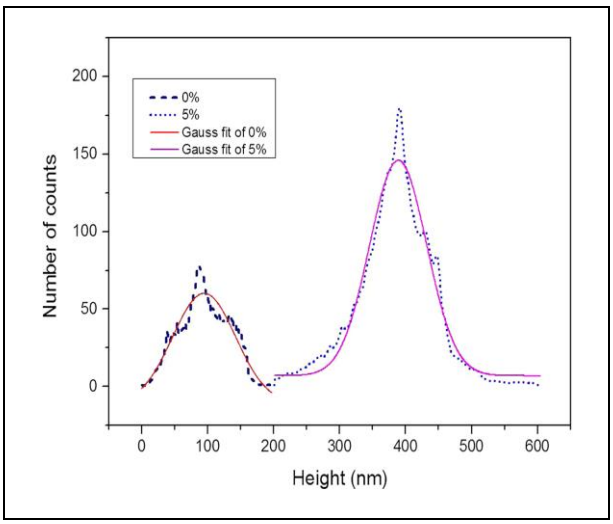

Fig. 5(A): Histograms and simulated normal distribution of the histogram plot corresponding to AFM images

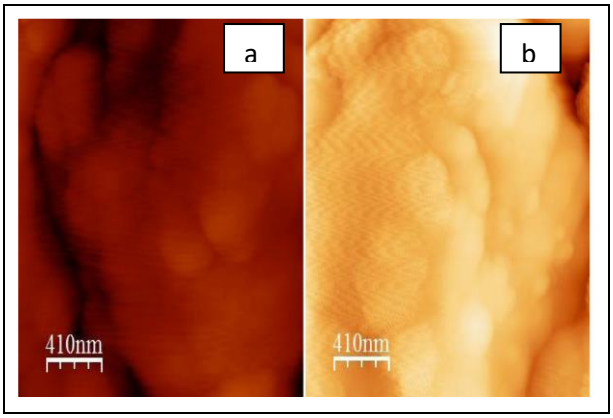

Fig. 5(B): Two AFM topography images of (a) PPy and (b) PPy-MWCNT (5%)

Basic principle

Its basic constituents are the X-ray source and the X-ray detector which lie on the circumference of a circle (focusing circle) with the specimen. The x-ray source is one which generates x-rays by directing an electron beam of high voltage at a metal target anode inside an evacuated x-ray. X-ray striking an electron produces secondary spherical waves emanating from the electron. A regular array of electrons produces a regular array of spherical waves. These waves cancel one another out in most directions through destructive interference and add constructively in a few specific directions, determined by Bragg's law: $2d \sin\theta = n\lambda$. The detector is capable of counting the number of x-ray protons of a particular energy for each angle 2θ which is a proportional reflection of the peak intensity.

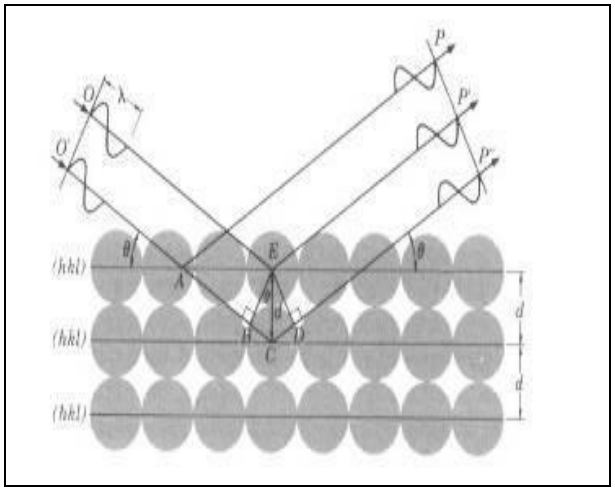

Fig. 6: Diffraction of x-rays by crystal planes

In case of nano materials this technique is useful for the determination for particle size. The particle size is determined by the Scherrer formula:

$$Dv = K Q / \langle \cos M$$

Where Dv – Average Particle Size, Q- Wave length of the radiation <cosM –Full width at half maximum of the reflection peak that has the same maximum intensity in the diffraction pattern.

M- Integral breadth of the peak located at angle
K- scherrer constant

K in the formula accounts for the shape of the particle and is generally taken to have the value 0.9

It is also determines the residual stress, texture and crystallinity of nano particles. Some X-RD graphs are shown in fig. 7:

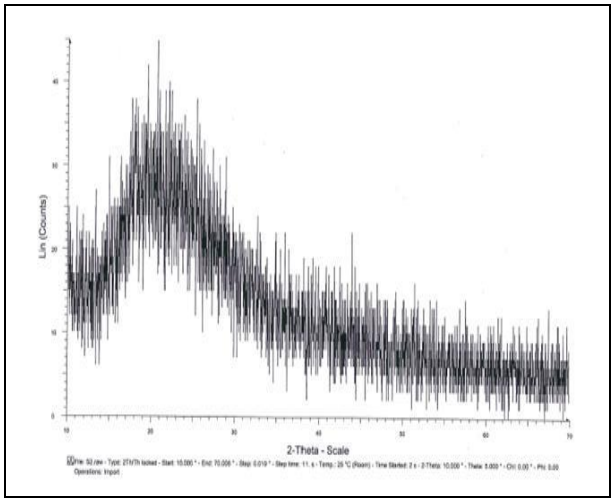

Fig. 7: XRD Pattern of 1gm $MnCl_2.4H_2O$ Manganese Bakelite Composite (Raj and Tiwari, 2013)

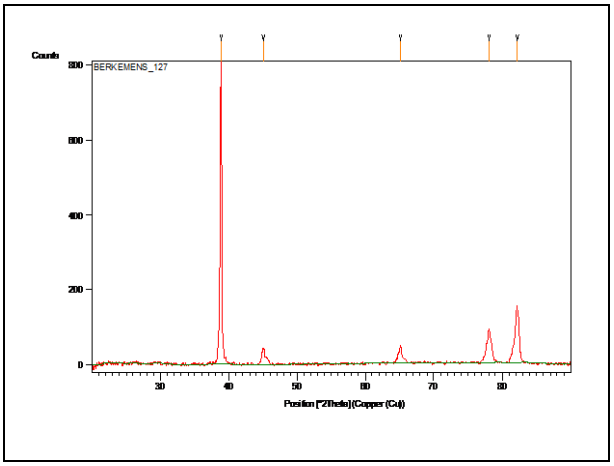

Fig. 8: XRD measurement – Al-Mg (Marimuthu and Berchmans, 2013)

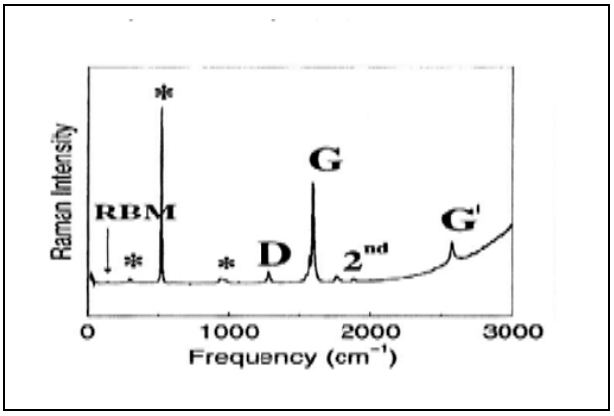

Fig. 9: Raman spectrum from one nano tube taken over a broad frequency rang using E 5785 nm 51.58 ev excitation showing laser the radical breathing mode (RBM), the D band and G band

4. RAMAN SPECTROSCOPY

Its introduction is now extended here to show the underlying theory. When light interacts with matter, the photons may be absorbed or scattered, or may not interact with the material and pass straight through. If the energy of an incident photon corresponds to the energy gap between the ground state of a molecule and an excited state, the photon may be absorbed and the molecule promoted to a higher energy excited state. It is this change that is measured in absorption spectroscopy, such as conventional UV-vis or IR spectroscopy. These methods measure the frequencies of light missing from the transmitted beam of light in order to determine the energies of the transitions of excited in the molecule. However, it is also possible for the photon to interact with the molecule and scatter from it. Spectra are shown in fig. 9.

Basic Principle

Raman Effect occurs when light impinges upon a molecules, interact with the electron cloud of the molecules and incident photon excites one of the electrons into a virtual state. Raman scattering generated when molecule will be excited from the ground state to a virtual energy state and relax into a vibrational excited state. This Raman scattering is called anti raman scattering. The amount of polarizability change will be determine the Raman scattering intensity, where as the Raman shift is equal to the vibration level that include. The molecular polarizability change with respect to the vibration coordinate is required for the molecules to exhibit the Raman Effect.

5. CONCLUSION

Past few years have witnessed various innovations in the field of nano materials growth and applications. In this review two method of nano materials characterized have been presented-Electron microscopy and X-Ray diffraction. By scanning electron microscopy we get useful information about Particle size, morphology and surface topology thickness. X-Ray technique determines composition, grain size, powder or amorphous form of material. These techniques have been proved to be most effective instrument that can be utilized for the characterization of new generation nano materials.

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CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest.

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