MODULE-4

NANOMATERIALS & CHARACTERIZATION TECHNIQUES

15ME82

• <u>SYLLABUS</u>

- Introduction: Importance of Nano-technology, Emergence of Nanotechnology, Bottomup and Top-down approaches, challenges in Nanotechnology
- Nano-materials Synthesis and Processing: Methods for creating Nanostructures; Processes for producing ultrafine powders- Mechanical grinding; Wet Chemical Synthesis of Nano-materials- sol-gel process; Gas Phase synthesis of Nano-materials- Furnace, Flame assisted ultrasonic spray pyrolysis; Gas Condensation Processing (GPC), Chemical Vapour Condensation (CVC).
- **Optical Microscopy** principles, Imaging Modes, Applications, Limitations.
- Scanning Electron Microscopy (SEM) principles, Imaging Modes, Applications,
- Limitations.
- Transmission Electron Microscopy (TEM) principles, Imaging Modes, Applications,
- Limitations.
- X- Ray Diffraction (XRD) principles, Imaging Modes, Applications, Limitations.
- Scanning Probe Microscopy (SPM) principles, Imaging Modes, Applications, Limitations.
- Atomic Force Microscopy (AFM) basic principles, instrumentation, operational modes,
- Applications, Limitations.
- Electron Probe Micro Analyzer (EPMA) Introduction, Sample preparation, Working
- procedure, Applications, Limitations.

Nanotechnology

- *Nanotechnology* can be a complicated topic with new advances being made on an almost daily basis. Many people need a resource for learning about and keeping up with changes in the field.
- The engineering of functional systems at a molecular scale.
- The manipulation of the structure of a matter at the molecular level.
- Nano means 10⁻⁹ and unit of a nanomaterial is in nanoscale i.e, nanometer(nm).

IMPORTANCE OF NANO-TECHNOLOGY

- The implications of nanotechnology are wide-ranging and could include medicine, military applications, computing and astronomy.
- Nanotechnology is being used already in sunscreens, self cleaning windows, stain repellent fabrics etc.,

- The emergence of nanotechnology has led to the design, synthesis, and manipulation of particles in order to create a new opportunity for the utilization of smaller and more regular structures for various applications.
- In recent years, nanosized metal oxide particles have gotten much attention in various fields of application due to its unique optical, electrical, magnetic, catalytic and biomedical properties as well as their high surface to volume ratio and specific affinity for the adsorption of inorganic pollutants and degradation of organic pollutants in aqueous systems

EMERGENCE OF NANOTECHNOLOGY

- The history of nanotechnology traces the development of concepts and experimental work falling under the broad category of nanotechnology.
- Although it is a relatively recent development in scientific research, the development of its central concepts happened over a longer period of time.
- Although nanoparticles are associated with modern science, they were used by artisans as far back as the ninth century in Mesopotamia for creating a glittering effect on the surface of pots.

For example pottery of the middle ages often retains a distinct gold or copper coloured metallic glitter, this is caused by a metallic film that was applied to the transparent surfaces of a glazing , which contains silver and copper nanoparticles dispersed in the glassy matrix of the ceramic glaze.

TWO BASIC APPROACHES

- There are two types of approaches for synthesis of nano material and fabrication of nano structures.
- Top-down approach
- Bottom-up approach

Top-down approach

•Top-down approaches refers to slicing or successive cutting of a bulk material to get nano sized particles.

•They are simpler and rely on either the removal or division of bulk material to produce the desired structure with the appropriate properties.

Bottom-up approach

- Bottom-up approach refers to methods where devices create themselves by selfassembly. Chemical synthesis is a good example.
- In bottom-up approach, atoms, molecules and even nanoparticles themselves can be used as the building blocks for the creation of complex nanostructures.
- Bottom-up approach is cheaper than top-down approach, but getting control over the methods is difficult.

Challenges in Nanotechnology

- The most immediate challenge in nanotechnology is that we need to learn more about materials and their properties at the nanoscale.
- Because elements at the nanoscale behave differently than they do in their bulk form, there is also a concern that some nanoparticles could be toxic.
- Since they are so small, they could easily cross the blood-brain barrier, a membrane that protects the brain from chemicals in the bloodstream.

Nano-materials Synthesis and Processing

- Methods for creating Nanostructures
- Top-down approach
- Bottom-up approach

Top-down approach

- Milling process:-
- This mechanical production approach uses milling to crush microparticles.
- This approach is applied in producing metallic and ceramic nanomaterials.



Bottom-up approach

- This approach is also known as chemical approach.
- This is based on the physicochemical principles of molecular or atomic self- organization.
- This Approach Produces selected, more complex structures from atoms or molecules, better controlling sizes, shapes and size ranges.

Nanomaterials synthesis approach



1. Top down approach: Breaking of bulk material

2.Bottom approach: Build up of material Atom \rightarrow molecule \rightarrow cluster

Preparation

Nanomaterials preparation

Physical Methods Ball milling Laser ablation Gas condensation processing (GPC) Chemical Methods Sol-gel synthesis Solution phase (stabilizing Ligands) Precipitation method Chemical vapour condensation Catalytic chemical vapour deposition Template assisted CVD Electrochemical method

Preparation

Any Preparation technique should provide:

- 1. Identical size of all particles (mono sized or uniform size distribution).
- 2. Identical shape or morphology.
- 3 Identical chemical composition and crystal structure.
- 4 Individually dispersed or mono dispersed i.e., no agglomeration.

SYNTHESIS OF NANOPARTICLES

MECHANICAL GRINDING



Preparation – Physical method

High-Energy ball milling (Top down

approach)

- Interest in the mineral, ceramic processing, powder metallurgy and industry.
 - Involves milling process include particle size reduction
 - Restricted to relatively hard, brittle materials which fracture and/or deform during the milling operation.
 - Different purposes including; tumbler mills, attrition
 - mills, shaker mills, vibratory mills, planetary mills,
 - et Hardened steel or tungsten carbide (WC) coated balls \rightarrow the basic
 - process of mechanical attrition (rubbing away) .



 $\begin{array}{l} \mbox{Violent or agitation,} \\ \ \sim 50 \ \mbox{\mu m} \rightarrow \ \ \mbox{nm} \\ \ \mbox{Schematic representation} \\ \ \mbox{of} \end{array}$

the principle of mechanical milling.

Preparation – physical method

- <u>Limitation of Ball milling:</u> (Even though high production rates)
 - 1. Severe plastic deformation associated with mechanical attrition due to generation of high temperature in the interphase, 100 to 200° C.
 - 2. Difficulty in broken down to the required particle size.
 - 3. Contamination by the milling tools (Fe) and atmosphere (trace elements of O2, N2, in rare gases) can be a problem. (inert condition necessary)

SOL-GEL PROCESS

- \succ chemical process.
- metal alkoxide-sol.
- ➤ converts sol into gel.

STEPS IN SOL-GEL PROCESS ;

- Hydrolysis.
- Condensation.
- Drying.



Advantages of Sol-Gel Technique:

- Can produce thin bond-coating to provide excellent adhesion between the metallic substrate and the top coat.
- Can provide a simple, economic and effective method to produce high quality coatings.
- Can easily shape materials into complex geometries in a gel state.
- Can produce thick coating to provide corrosion protection performance.
- Can produce high purity products because the organo-metallic precursor of the desired ceramic oxides can be mixed, dissolved in a specified solvent and hydrolyzed into a sol, and subsequently a gel, the composition can be highly controllable.
- Can have low temperature sintering capability, usually 200-600°C.

FURNANCE METHOD

 \succ It is gas phase synthesis of nanoparticles .



- Advantages of gas phase synthesis
 - Excellent control of size and shape
 - Highly pure materials can be obtained
 - Easy control of reaction mechanism

GAS CONDENSATION PROCESS



<u>Chemical vapour condensation process</u>



Preparation

(C) Chemical Vapour Condensation (CVC) (Bottom-up

 Involves approach): pyrolysis treatment) of (hea organic (startint precvægoors of metæd slexcærbeeitals)disilazane (CH₃)₃/Skie NH-

Si- $(CH_3)_3$ to produce SiC_xN_yO_z. •Evaporate source in the GPC is replaced by a hot wall reactor in the CVC process (Fig.5).

•Precursor residence time is the key parameter to control the size of nanoparticle here (gas flow rate, pressure,

heating temperature can be controlled).



• Other procedure similar to GPC. Production capabilities are much larger than in the GPC

Microscope

- Microscope is a tool which can help you see tiny objects and living organisms. It makes them look bigger.
- This ability of the microscope is called its magnifying power or magnification.





Microscope

 The microscope also has the capacity to distinguish small gaps between two separate points which humans cannot distinguish. It is called its resolving power or resolution.





2 objects visualized with poor resolving power

Same 2 objects visualized with good resolving power

OPTICAL MICROSCOPY

- Optical microscopy is a technique employed to closely view a sample through the magnification of a lens with visible light
- An optical microscope, also sometimes known as a light microscope, uses one or a series of lenses to magnify images of small samples with visible light.
- The lenses are placed between the sample and the viewer's eye to magnify the image so that it can be examined in greater detail.
- Simple microscope, Compound microscope, Digital microscope, Stereo microscope, Comparison microscope, Inverted microscope

Operation, applications and limitations

- In order to use an optical microscope effectively, it is important to ensure that the microscope is set up correctly.
- The objective lens should be brought close to the study sample to allow the light inside the tube of the microscope.
- This creates an enlarged, inverted image of the sample, which can be viewed through the eyepiece of the microscope.

Continued....

- Optical microscopy is commonly used in many research areas including microbiology, microelectronics, nanophysics, biotechnology and pharmaceutical research.
- There are some instances when optical microscopy is not well suited to the task at hand due to limitations of the technique.
- For example, at very high magnifications airy disks may be visible, which are fuzzy discs surrounded by diffraction rings, which appear in place of point objects.
- When the limitations of optical microscopy are significant, alternative types of microscopy may be more useful.

Magnified virtual image



SCANNING ELECTRON MICROSCOPE(SEM)



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Principle

- A scanning electron microscope (SEM) scans a focused electron beam over a surface to create an image.
- The electrons in the beam interact with the sample, producing various signals that can be used to obtain information about the surface topography and composition.



A scanning electron microscope scans a beam of electrons *over* a specimen to produce a magnified image of an object. That's completely different from a TEM, where the beam of electrons goes right through the specimen.

- 1. Electrons are fired into the machine.
- 2. The main part of the machine (where the object is scanned) is contained within a sealed vacuum chamber because precise electron beams can't travel effectively through air.
- 3. A positively charged electrode (anode) attracts the electrons and accelerates them into an energetic beam.
- 4. An electromagnetic coil brings the electron beam to a very precise focus, much like a lens.
- 5. Another coil, lower down, steers the electron beam from side to side.
- 6. The beam systematically scans across the object being viewed.
- 7. Electrons from the beam hit the surface of the object and bounce off it.
- 8. A detector registers these scattered electrons and turns them into a picture.
- 9. A hugely magnified image of the object is displayed on a TV screen.



ADVANTAGES AND LIMITATIONS

SEM Advantages

- Advantages of a Scanning Electron Microscope include its wide-array of applications, the detailed three-dimensional and topographical imaging and the versatile information garnered from different detectors.
- SEMs are also easy to operate with the proper training and advances in computer technology and associated software make operation user-friendly.

SEM Limitations

- The disadvantages of a Scanning Electron Microscope start with the size and cost.
- SEMs are expensive, large and must be housed in an area free of any possible electric, magnetic or vibration interference.
- Maintenance involves keeping a steady voltage, currents to electromagnetic coils and circulation of cool water.
- Special training is required to operate an SEM as well as prepare samples.
- The preparation of samples can result in artifacts. The negative impact can be minimized with knowledgeable experience researchers being able to identify artifacts from actual data as well as preparation skill. There is no absolute way to eliminate or identify all potential artifacts.
- In addition, SEMs are limited to solid, inorganic samples small enough to fit inside the vacuum chamber that can handle moderate vacuum pressure.
- Finally, SEMs carry a small risk of radiation exposure associated with the electrons that scatter from beneath the sample surface.
Transmission Electron Miroscopy(TEM)



PRINCIPLE AND WORKING

- Transmission electron microscopy (TEM) is a microscopy technique in which a beam of electrons is transmitted through an ultra- thin specimen.
- Interacting with the specimen as it passes through it. It works on the principle of nature of electrons as they exhibit less wavelength when bombarded at high velocity.



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A **transmission electron microscope** fires a beam of electrons *through* a specimen to produce a magnified image of an object.

- 1. A high-voltage electricity supply powers the cathode.
- 2. The cathode is a heated filament, a bit like the electron gun in an old-fashioned cathode-ray tube (CRT) TV. It generates a beam of electrons that works in an analogous way to the beam of light in an optical microscope.
- 3. An electromagnetic coil (the first lens) concentrates the electrons into a more powerful beam.
- 4. Another electromagnetic coil (the second lens) focuses the beam onto a certain part of the specimen.
- 5. The specimen sits on a copper grid in the middle of the main microscope tube. The beam passes through the specimen and "picks up" an image of it.
- 6. The projector lens (the third lens) magnifies the image.
- 7. The image becomes visible when the electron beam hits a fluorescent screen at the base of the machine. This is analogous to the phosphor screen at the front of an old-fashioned TV.
- 8. The image can be viewed directly (through a viewing portal), through binoculars at the side, or on a TV monitor attached to an image intensifier.



Working of TEM



- Tungsten filament: generates a beam of electrons that is then focused on the specimen by the condenser
- Magnetic lenses: are used to focus the beam
- The column containing the lenses and specimen must be under high vacuum to obtain a clear image because electrons are deflected by collisions with air molecules.
- Magnetic lenses : Form the Enlarged, visible image of the specimen on a fluorescent screen.
- Photographic film: The screen can also be moved aside and the image captured on photographic film as a permanent record.

Advantages And Limitations

Advantages of TEM

- A Transmission Electron Microscope is an impressive instrument with a number of advantages such as:
- TEMs offer the most powerful magnification, potentially over one million times or more.
- TEMs have a wide-range of applications and can be utilized in a variety of different scientific, educational and industrial fields.
- TEMs provide information on element and compound structure
- Images are high-quality and detailed.
- TEMs are able to yield information of surface features, shape, size and structure.
- They are easy to operate with proper training.

Disadvantages of TEM

- TEMs are large and very expensive.
- Laborious sample preparation.
- Potential artifacts from sample preparation.
- Operation and analysis requires special training.
- Samples are limited to those that are electron transparent, able to tolerate the vacuum chamber and small enough to fit in the chamber.
- TEMs require special housing and maintenance
- Images are black and white.

TEM Applications

- A Transmission Electron Microscope is ideal for a number of different fields such as life sciences, nanotechnology, medical, biological and material research, forensic analysis, gemology and metallurgy as well as industry and education.
- TEMs provide topographical, morphological, compositional and crystalline information.
- The images allow researchers to view samples on a molecular level, making it possible to analyze structure and texture.
- This information is useful in the study of crystals and metals, but also has industrial applications.

TEM Applications

- TEMs can be used in seconductor analysis and production and the manufacturing of computer and silicon chips.
- Technology companies use TEMs to identify flaws, fractures and damages to micro-sized objects; this data can help fix problems and/or help to make a more durable, efficient product.
- Colleges and universities can utilize TEMs for research and studies.
- Although electron microscopes require specialized training, students can assist professors and learn TEM techniques.
- Students will have the opportunity to observe a nano-sized world in incredible depth and detail. 45

X-ray powder diffraction (XRD)

- X-ray powder diffraction (XRD) is a rapid analytical technique primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions.
- The analyzed material is finely ground, homogenized, and average bulk composition is determined.

What is X-ray diffraction?

- Crystalline substances (e.g. minerals) consist of parallel rows of atoms separated by a 'unique' distance.
- Diffraction occurs when radiation enters a crystalline substance and is scattered
- Direction and intensity of diffraction depends on orientation of crystal lattice with radiation



Basic Components of XRD Machine



• Monochromatic X-ray source .

•Sample-finely powdered or polished surface-may be rotated against the center – (goniometer).

•Data collector- such as film, strip chart or magnetic medium/storage



1.0 What is X-ray Diffraction ?



www.micro.magnet.fsu.edu/primer/java/interference/index.html

Why XRD?

•Measure the average spacing's between layers of rows and atoms.

•Determine the orientation of a Single Crystal or grain.

•Find the crystal Structure of an unknown material.

•Measure the size, shape and internal stress of small crystalline regions.

PRINCIPLE

X-ray diffraction is based on constructive interference of monochromatic x-rays and a crystalline sample.

These x-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation ,collimated to concentrate and directed towards the sample.

The interaction of incident rays with the sample produces constructive interference when condition satisfy Bragg's Law.



PRODUCTION OF X-RAYS:

X-rays are generated when high velocity electrons impinge on a metal target.

Approximately 1% of the total energy of the electron beam is converted into x-radiation.

The remainder being dissipated as heat. Many types of x-ray tubes are available which are used for producing x-rays.



• Positive voltage in the form of anode having a target **a**

- Battery (b) to emit thermoionic electrons
- Cathode(c) –filament of tungsten metal
- •The electrons are accelerated towards the target **a**

•On striking the target the electrons transfer their energy to its metallic surface which gives off x-ray radiation



In order to get a narrow beam of x-rays, the x-rays generated by the target material are allowed to pass through a collimator which consists of two sets of closely packed metal plates separated by a small gap. The collimator absorbs all the x-rays except the narrow beam that passes between the gap.

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Working and parts



Brag-Brentano geometry



Bragg's law

- The general relationship between the wavelength of the incident X-rays, angle of incidence and spacing between the crystal lattice planes of atoms is known as Bragg's Law, expressed as:
- $n \lambda = 2d \sin \theta$
- where n (an integer) is the "order" of reflection,
- λ is the wavelength of the incident X-rays,
- d is the interplanar spacing of the crystal and
- θ is the angle of incidence.



Applications of XRD

- The electron density and accordingly, the position of the atoms in complex structures, such as penicillin may be determined from a comprehensive mathematical study of the x-ray diffraction pattern.
- The elucidation of structure of penicillin by XRD paved the way for the later synthesis of penicillin.
- The powder XRD pattern may be thought of as finger print of the single crystal structure, and it may be used conduct qualitative and quantitative analysis.
- XRD can also be used to determine whether the compound is solvated or not.

Scanning Probe Microscopy

- Scanning probe microscopy covers several related technologies for imaging and measuring surfaces on a fine scale, down to the level of molecules and groups of atoms.
- At the other end of the scale, a scan may cover a distance of over 100 micrometers in the x and y directions and 4 micrometers in the z direction. This is an enormous range.
- It can truly be said that the development of this technology is a major achievement, for it is having profound effects on many areas of science and engineering.

Scanning Probe Microscopy

- SPM technologies share the concept of scanning an extremely sharp tip (3-50 nm radius of curvature) across the object surface. The tip is mounted on a flexible cantilever, allowing the tip to follow the surface profile (see Figure).
- When the tip moves in proximity to the investigated object, forces of interaction between the tip and the surface influence the movement of the cantilever.

Scanning Probe Microscopy



Advantages and limitations

Advantages of Scanning Probe Microscopy Technology

- Scanning Probe Microscopy provides researchers with a larger variety of specimen observation environments using the same microscope and specimen reducing the time required to prepare and study specimens.
- Specialized probes, improvements and modifications to scanning probe instruments continues to provide faster, more efficient and revealing specimen images with minor effort and modification.

Disadvantages of Scanning Probe Microscopy Technology:

• Unfortunately, one of the downsides of scanning probe microscopes is that images are produced in black and white or grayscale which can in some circumstances exaggerate a specimens actual shape or size.

• Computers are used to compensate for these exaggerations and produce real time color images that provide researchers with real time information including interactions within cellular structures, harmonic responses and magnetic energy.

Atomic Force Microscopy

- The atomic force microscope (AFM) was developed to overcome a basic drawback with STM – it can only image conducting or semiconducting surfaces.
- The AFM has the advantage of imaging almost any type of surface, including polymers, ceramics, composites, glass, and biological samples.

Atomic Force Microscopy



Advantages and Limitations

- AFM has several advantages over the scanning electron microscope (SEM). Unlike the electron microscope which provides a two-dimensional projection or a two-dimensional image of a sample, the AFM provides a three-dimensional surface profile.
- Additionally, samples viewed by AFM do not require any special treatments (such as metal/carbon coatings) that would irreversibly change or damage the sample.

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- While an electron microscope needs an expensive vacuum environment roper operation, most atomic force microscopy modes can work perfectly well in ambient air or even a liquid environment. This makes it possible to study biological macromolecules and even living organisms.
- AFM can only image a maximum height on the order of 10-20 micrometers and a maximum scanning area of about 150×150 micrometers.
- Highly dependent on probes.
- Error occurring due to interaction.

Electron Probe Micro Analyzer (EPMA):



EPMA works by bombarding a micro-volume of a sample with a focused electron beam (typical energy = 5-30 keV) and collecting the X-ray photons thereby emitted by the various elemental species.

Electron probe micro-analyzer (EPMA) Instrumentation - How Does It Work?

EPMA consists of four major components, from top to bottom:

- An electron source, commonly a W-filament cathode referred to as a "gun."
- A series of electromagnetic lenses located in the column of the instrument, used to condense and focus the electron beam emanating from the source; this comprises the electron optics and operates in an analogous way to light optics.
- 3. A sample chamber, with movable sample stage (X-Y-Z), that is under a vacuum to prevent gas and vapor molecules from interfering with the electron beam on its way to the sample; a light microscope allows for direct optical observation of the sample.



Schematic cut-away diagram of a typical microprobe. Details

4. A variety of detectors arranged around the sample chamber that are used to collect x-rays and electrons emitted from the sample.

A typical arrangement in a probe lab is a vertical electron-beam column, an array of detectors placed around the sample chamber block, a sample entry vacuum lock, a console to control operating conditions, screens to view control interfaces and sample output, and a computer for control of data acquisition.





EPMA works by bombarding a micro-volume of a sample with a focused electron beam (typical energy = 5-30 keV) and collecting the X-ray photons thereby emitted by the various elemental species. Because the wavelengths of these X-rays are Characteristic of the emitting species, the sample composition can be easily identified by recording WDS spectra (Wavelength Dispersive Spectroscopy). WDS spectrometers operate based on Bragg's law and use various moveable, shaped monocrystals as monochromators.

- ➢ EPMA is a fully qualitative and quantitative method of non- destructive elemental analysis of micron-sized volumes at the surface of materials, with sensitivity at the level of ppm. Routine quantification to 1% reproducibility is obtained over several days. It is the most precise and accurate micro-analysis technique available and all elements from B to U and above can be analyzed.
- EPMA is fully compatible with routine analysis sessions, with easy
 and direct interpretation of the results.
- EPMA instruments are equipped with a complete kit of built-in microscopy tools that allow simultaneous X-ray (WDS and EDS), SEM and BSE imaging, plus sophisticated visible light optics; they provide very flexible sample inspection with image magnification ranging from 40 to 400,000.
Working Principle

- When the probe (electron beam) strikes the specimen, repeated interaction between electrons and atoms of the specimen occurs till they come to rest or emerge out from the specimen surface.
- In the keV energy range, the expected interactions of electrons with atoms are scattering (elastic and inelastic), and bremsstrahlung emission.
- Elastic collision is the phenomenon in whichboth the states of the atom (i.e. initial and final states) remain the same, generally the ground state.
- In this case direction of the movement of electrons is changed.
- Inelastic interactions are the phenomena wherein the atom is promoted to an excited state, i.e., a share of the electron's kinetic energy is given to the electrons of the atom.

Major applications

- Geochemistry, mineralogy, geochronology, physical metallurgy, nuclear metallurgy, materials science including glass, ceramics, superconductors, cements, microelectronics, and biochemistry.
- EPMA provides much better results than standard SEM/EDS systems. Because of the internal properties of WDS, the general sensitivity, analysis of light elements and risks of erroneous interpretation of qualitative spectra are all superior with EPMA.
- Spectral resolution and detector dead time are much better than EDS (Energy Dispersive Spectroscopy).
- The excitation beam regulation system and sophisticated sample stage capabilities guarantee that this technique provides outstanding stability and measurement repeatability.

Thank You...!!!