NANOMATERIALS AND NANOCHEMISTRY

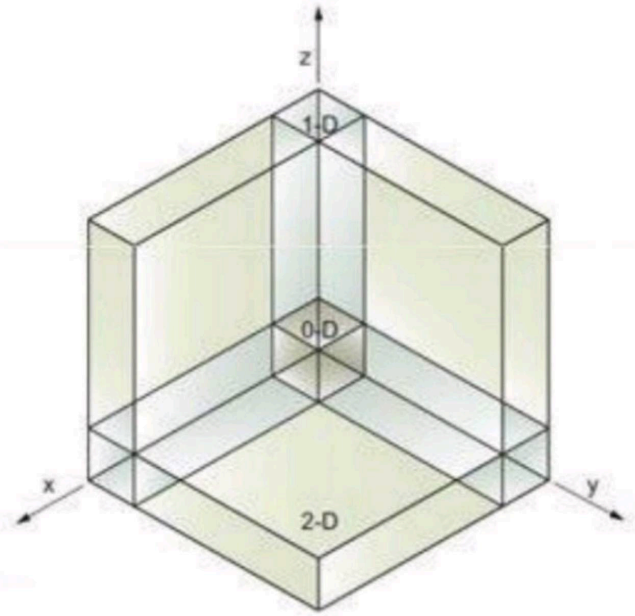
It deals with the chemical application of nano materials along with their synthesis and characterization. Nano materials are mostly in the range of 10^{-9} m.

Size of nano materials is between 1 to 100 nm. Nano materials have one of its dimensions (length, breadth or diameter) in the nano range (i.e. < 100 nm)

Classification of nanomaterials:

- **0-D (Three dimensions in nano scale)**
  - Nanoparticles
  - Precipitates
  - Colloids
  - Quantum dots (small particles of semiconductor materials)
- **1-D [Two dimensions in nano scale (one dimension is not in nano scale)]**
  - Nano wires
  - Nano tubes
- **2-D [One dimension in nano scale (other two dimensions are not in nano scale)]**
  - Thin film
  - Surface coating
  - Computer chips
- **3-D (All three dimensions are not in nano scale)**
  Bulk materials, Crystals etc.

Scanned with CamScanner

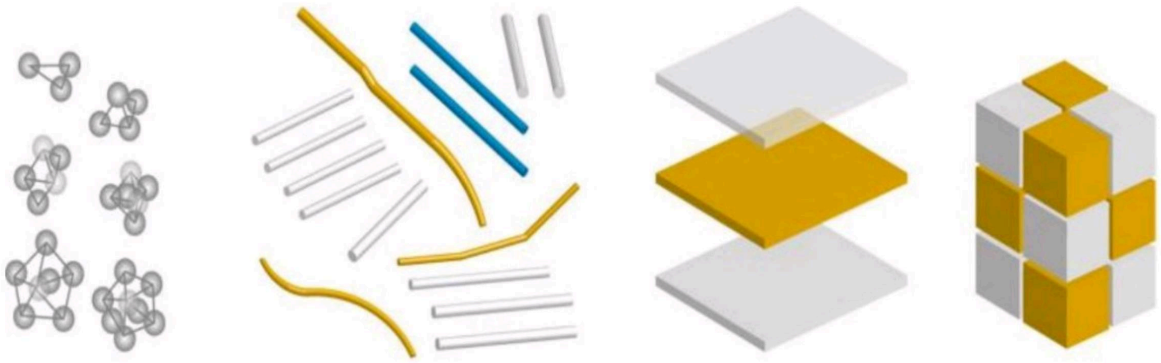


0-D: All dimensions at the nanoscale

1-D: Two dimensions at the nanoscale, one dimension at the macroscale

2-D: One dimension at the nanoscale, two dimensions at the macroscale

3-D: No dimensions at the nanoscale, all dimensions at the macroscale



Clusters 0D | Nanotubes, fibers and rods 1D | Films and coats 2D | Polycrystals 3D

Scanned with CamScanner

Examples of nanomaterials with their size:

A. Visible through naked eye:

- Head of a pin – 10^6 nm
- Page of a book – 10^5 nm
- Human hair – 75,000 nm

B. Using microscope:

- RBC – 7000 nm across
- Bacteria – 1000 to 10,000 nm
- Paint pigment – 100 to 5,000 nm

C. Using electronic microscope:

- Cooking smoke – 10 to 700 nm
- Quantum dot – 1 to 5 nm
- DNA molecule – 2 nm
- Atoms – 0.1 to 0.2 nm
- Carbon nanotube - length -100 nm, Width – 3nm

Effect of size on material properties :

Property changes at nano scale with respect to physical-chemical,optical ,electrical and magnetic behavior.

1) Au nps change their colour by changing their size. 5 nm- red, 60nm -pink, 90 nm-violet.
2) A drop of water (5 nm) boils at 95.9^0c compared to normal water.
3) Adhesive property increases by decreasing the size as surface area increases.
4) Anti bacterial property increases as size decreases.
5) Optical properties of nps are dependent on size. [nps – nanoparticles]

Scanned with CamScanner

All these changes in nps compared to the bulk materials are due to a large s/v ratio which is given by,

$S/V = 4\pi r^2 / 4/3\pi r^3 = 3/r$

Materials with high s/v value possess very small diameter, porous and react with a much faster rate. Extra chemical reactivity is due to this high S/ V ratio.(s = surface area, v = volume)

Synthesis of nano materials :

There are two common approaches for the synthesis of nanoparticles. They are: 1) Top- down and 2) Bottom –up approach.

Top-down Approach: It is a solid-state process involving size reduction from bulk materials. It mostly follows physical processes like crushing, grinding, milling, etc.

Limitations :

- A slow process & not suitable for large scale applications
- leads to various defects and imperfections on the surface
- particles of uniform size and morphology are not formed

Some well known processes are electro-explosion, scattering, laser absorption.

Bottom-up Approach: It is purely a build-up of material in which atom-by atom, molecule-molecule or cluster-cluster combination is made. The examples of the processes (use this approach) are: sol-gel, chemical reduction, combustion, chemical vapor deposition, microwave synthesis, Green route synthesis, etc.

Advantages:

- Generates particles of uniform size, shape, & morphology.
- particles of excellent quality and quantity
- an environmental friendly process.

Scanned with CamScanner

Green synthesis of Nano materials:

This method involves the preparation of nanoparticles by using plant extract, yeast, fungi, etc. This is called biological synthesis of nanoparticles which is a cost effective & eco-friendly method.

Synthesis of nanoparticles by using plant extract has attracted many researchers as it is a clean, non toxic, biocompatible & eco-friendly method. In this process nanoparticles are formed at a faster rate with controlled toxicity.

During the process the plant extract is mixed properly with the solution of metal salt either at room temperature or slightly higher temperature. Nanoparticles are formed within few minutes.

Nanoparticles of Au, Ag, Cu, Zn, Pd, etc. are formed by using plant extracts like Neem, Tulsi, Papaya, Aloevera, Turmeric, Arka, etc.

The properties & time of production of nps depends on the following conditions:

- Concentrations plant extract
- Concentrations of salt solutions
- pH of the medium
- Temperature
- Contact time

Advantages of using plant extract:

- Produces much less toxic waste
- Plants are easily available & does not require complex process
- Extract can be used directly for the synthesis of nanoparticles
- act as both reducing and capping agent
- a safe process

Scanned with CamScanner

- nanoparticles obtained, have excellent medicinal properties.

Preparation of NPS :

The essential materials required for the synthesis are;

1. Precursor salt, 2. Reducing agent, 3. Stabilizing agents

1) Precursor salt : $AgNO_3$, $AuCl_3$, $ZnSO_4$, $CuSO_4$ etc.
2) Reducing Agent: These are mostly phyto-chemicals (like, flavonoids, polyenes, carotenoids, terpenes, & alkaloids) , plant extracts, polyphenols. Other chemicals like citric acid, H_2O_2, Hydrazine, etc., can also be used as reducing agents.
3) Stabilizing agents: Also known as capping agents these are mostly polymers like PVA, PVP, surfactants. These stop the agglomeration and growth of nano particles.
   The reducing agent provides electrons where as the capping agent makes the mixing process complete and faster.

Synthesis and characterization of gold nps :

Gold nps are synthesized by following a green route process using various plant extracts .

IMP: It is an environment friendly, low-cost and effective process. The phyto chemicals (Alkaloids, flavonoids) present in plant extract can act both as capping and reducing agent.

Synthesis: 1**) Preparation of Plant Extract :** It is a bio reduction process in which leaves of Papaya and Tulsi are used. The leaves are cut into small pieces.10 gm of such leaves are taken in a beaker & boiled with 200ml of distilled water for 30 minutes. Then it is cooled and filtered through 0.45mm membrane filter.

2) Precursor salt: The precursor salt is prepared by taking 20 mg of $AuCl_3$ in 5 ml of distilled water.

Scanned with CamScanner

3) Preparation of NPs: For the preparation of gold nps, 20 ml of plant extract is taken in a beaker and placed in a hot magnetic stirrer at 40^0c. Then 1 ml of gold salt solution is added to it drop wise. The solution turns pink indicating formation of gold nps.

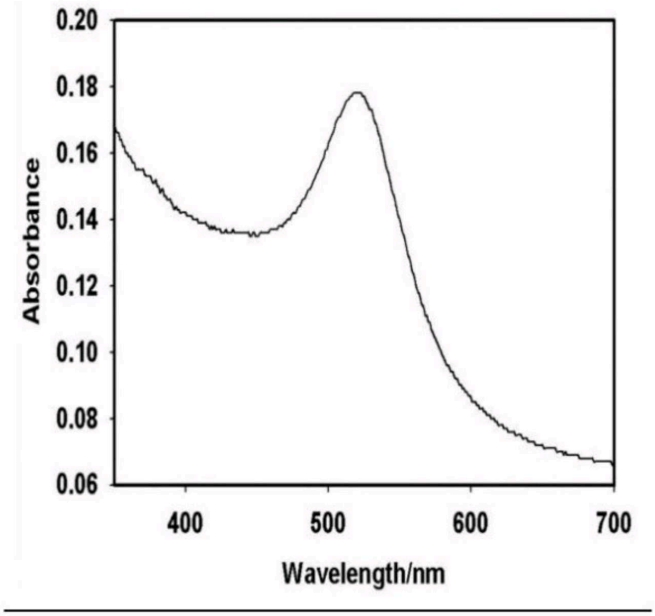
Reaction:

$$Au^{3+} + 3e^- \rightarrow Au^0$$

Characterization :

i. **UV-Visible Analysis**: The absorption spectrum shows formation of Au as it shows a Surface Plasmon resonance (SPR) band at 550nm. Plasmons are sub particles arising out of quantization of plasma oscillations. **SPR results from the resonant oscillation of free electrons at the interface between positive and negative permittivity mutually stimulated by light. It is otherwise a manifestation of a coherent oscillation of conduction band electrons.** This is represented below with the UV - visible spectrum diagram. **SPR band occurs at 550nm which indicates the formation coloured gold nps.**

Scanned with CamScanner



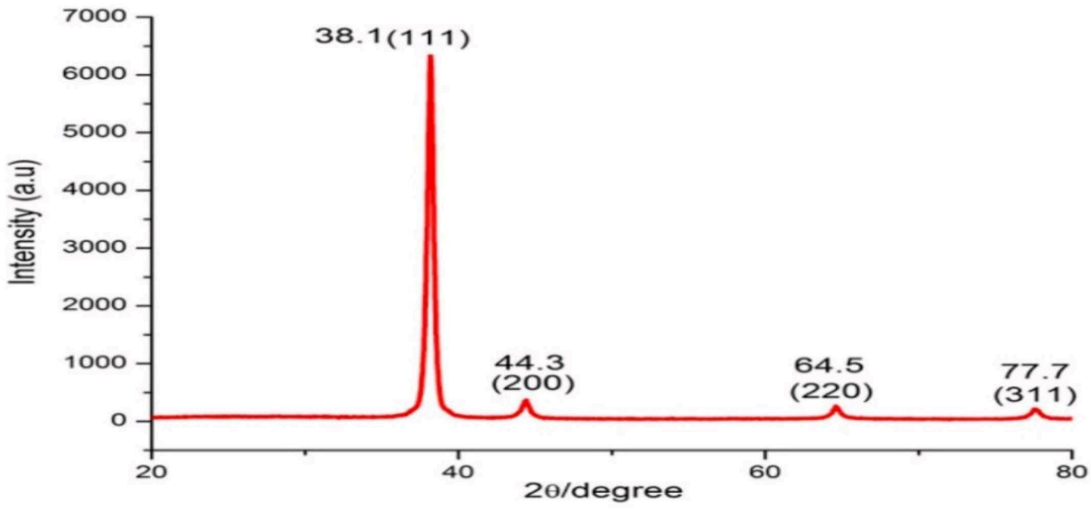
ii. X-ray diffraction study (XRD Study):

XRD pattern shows the production of Au nps by the reduction of Au^{3+} to Au . It identifies the crystallographic nature of nps. The peak (111) at $2\boldsymbol{\theta} = 38^{o}$ shows nps with fcc structure. The crystallite size (d) is calculated using Debye-Scherres' equation,

$d = 0.94\lambda / \beta\cos\theta \approx 15nm = K\lambda / \beta\cos\theta, K \approx 1, \theta$ = Bragg's angle or diffraction angle, λ = Wavelength($\lambda = 1.54$ Å), β= Full width at half maximum (FWHM) of highly intense peak.(Value of $\beta = 0.001$ to 0.02)

The XRD pattern is shown below.

Scanned with CamScanner



Applications: In drug delivery system, As a catalyst, Sensing agent, anti-fungal agent, In bio-image processing, cosmetic and solar cells, In water treatment, detection of serious diseases.

Synthesis, characterization and application of Ag nps :

It is a bio reduction process.

Synthesis:

1) Preparation of plant extract: 20 gm of finely cut Neem leaves are boiled with 100 ml of double distilled water for 30 minutes. It is then filtered using a 0.45mm membrane filter to get the extract.

2) Preparation of $AgNO_3$ solution: Suitable amount of $AgNO_3$ salt is added to double distilled water to prepare 10 ml of the solution after boiling.

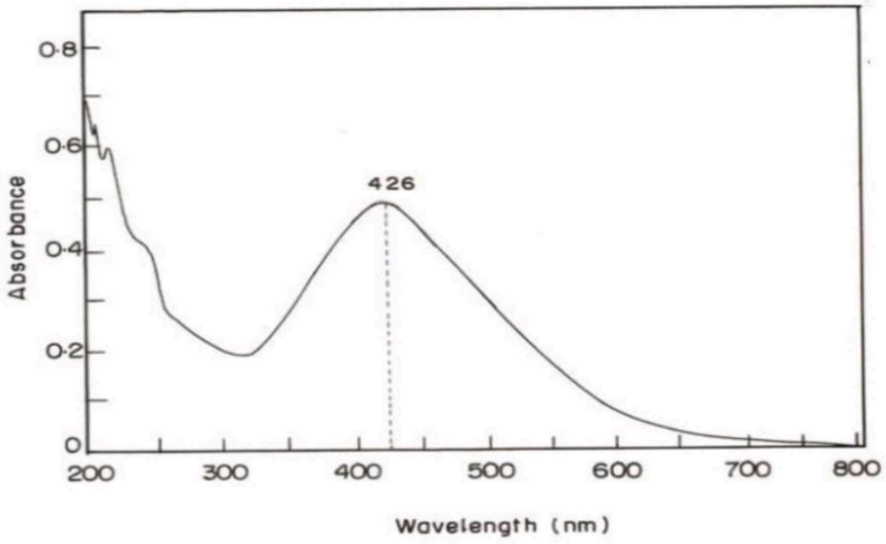
3) Synthesis of Ag np : 5 ml of extract is taken inside a 50 ml beaker and placed in a magnetic stirrer. Then 1 ml of above salt solution is added to it drop wise using a micropipette. The colour suddenly changes to yellowish brown indicating formation of silver nps.

$Ag^+ + e^- \rightarrow Ag^0$

Characterization : The sample is characterized using UV-visible spectroscopy and x-ray diffraction study.

Scanned with CamScanner

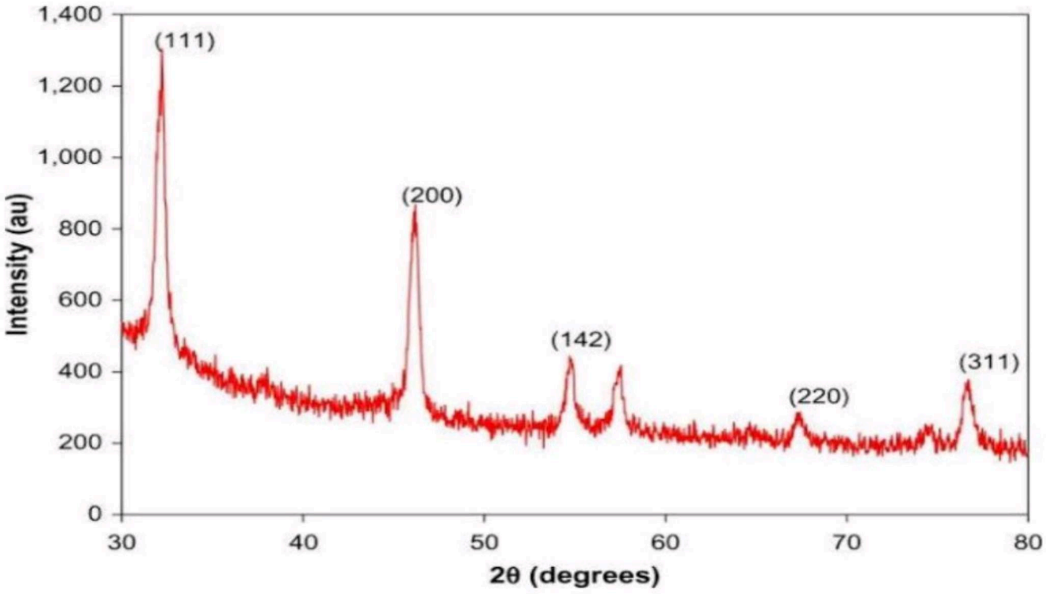
UV-Visible study : The absorption maxima occurs at nearly 420nm, indicates the formation of $AgNO_3$ nano particles. It indicates the existence of coloured Ag nano particles.



XRD STUDY: It provides information about the crystalline nature and size of nps. The peak at $2\theta = 38^0$ corresponds to (111) plane of nps and reveals fcc structure of silver nps. The size of nps can be calculated by Debye-Scherer equation,

$d = 0.94\lambda / \beta\cos\theta \approx 13nm$ ($\beta = 0.001 - 0.02$), ($\lambda = 1.54$ Å , θ = Bragg's Angle or diffraction angle)

Scanned with CamScanner



Appilication : Food packaging, cosmetic industry, bio-sensors, catalysis, coating materials, textile industry.

Synthesis, characteristics and application of Cu_2O nps.

It is a semi conducting material. Cu_2O nps are prepared following a green route process by using leave extract of Arka plant.

Synthesis These nanoparticles can be obtained by using $CuSO_4.5H_2O$ crystals as precursor salt, Arka leaves extract as capping agent and hydrazine hydrate as reducing agent in an aqueous medium.

1) Preparation of Precursor salt solution : 1M solution is prepared by dissolving suitable amounts of $CuSO_4.5H_2O$ crystals in double-distilled water.

2) Preparation of Plant Extract : 10 gm of Arka leaves are taken in a beaker/ conical flask with 100 ml of double distilled water and boiled for 1 hour on a hot plate. After cooling, it is filtered by using a 0.45mm membrane filter to get the extract

3) Synthesis of NPs : The plant extract & the precursor salt solution are mixed in a proper ratio and stirred in a magnetic stirrer for 30 minutes at 70^0C. Under stirring conditions, hydrazine solution is added drop wise till the colour changes to

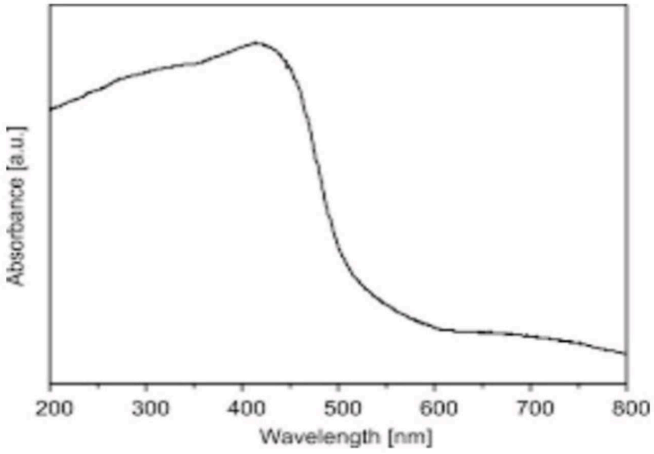
Scanned with CamScanner

reddish brown suspension from blue. This indicates the formation of Cu_2O nano particles.

Characterization:

The Cu_2O NPs are characterized by UV-Visible and XRD study.

i. UV- Visible Spectral analysis: A broad 'SPR' band at 470 nm in the absorption spectrum suggests formation of NPs which is due to colored particles.



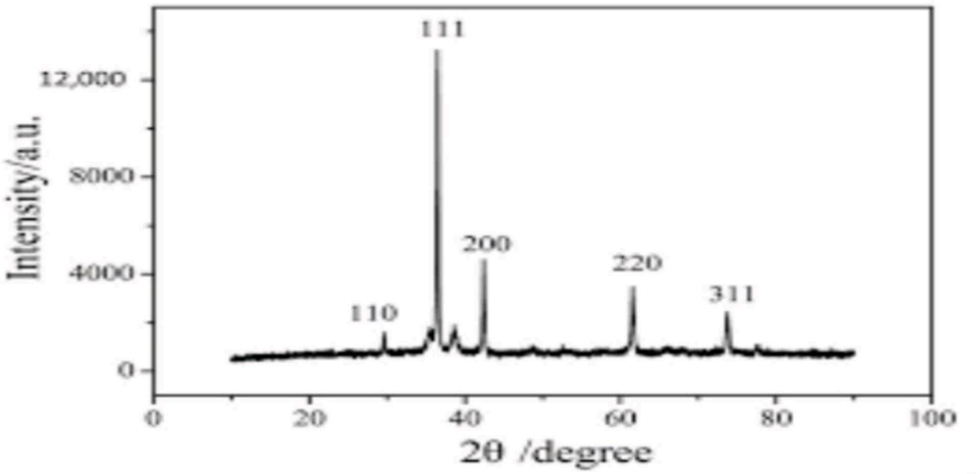
ii.XRD Study:

Characteristic XRD peaks obtained at 36.8^0 and 42.3^0 correspond to (111) and (200) plane suggesting fcc crystalline nature of NPs. The crystallite size can be obtained using Debye-Scherer Equation as given below.

$d = 0.94\lambda/\beta \cos \theta \approx 17$ nm, where λ= Wavelength ($\lambda = 1.54$ Å),

β = FWHM(Full Width at Half Maximum), θ = Diffraction angle.

Scanned with CamScanner



Reactions:

The bio-surfactant ' Saponin' acts as the capping agent.

$NH_2\text{-}NH_2 + H_2O \leftrightarrow NH_2NH_3^+ + OH^-$

$CuSO_4.5H_2O + OH^- \rightarrow Cu(OH)_2 + SO_4^{2-} + H_2O$

$Cu(OH)_2 + NH_2NH_3^+ \rightarrow Cu_2O(NPs) + N_2 + H_3O^+ + 2H_2$

Applications: **Superconductivity/ Photo catalysis / Anti bacterial agent/ water treatment/ solar cells/ magnetic storage device.**

Synthesis and characterization of ZnO NPs.

It is a bio reduction process using an extract of Hibiscus leaves.

Synthesis

1) Plant Extract : 20 gm of dry Hibiscus leaves is boiled in a beaker containing double distilled water for 30 minutes. Then it is filtered through a 0.45mm membrane filter to get the extract.

Scanned with CamScanner

2) Preparation of Pre cursor salt solution: Salt solution is prepared by adding $Zn(NO_3)_2$ crystals to suitable amount of double distilled water to form a 0.5M solution.

3)**Preparation of NPs**: 20 ml of the extract is taken in a 100 ml beaker and placed on a magnetic stirrer. To this 2 ml of $Zn(NO_3)_2$ and 1 ml of NaOH is added drop wise with the temperature maintained at 90^0C for 10 minutes. **White precipitate of ZnO is formed & collected for characterization.**

Chemical Reaction :

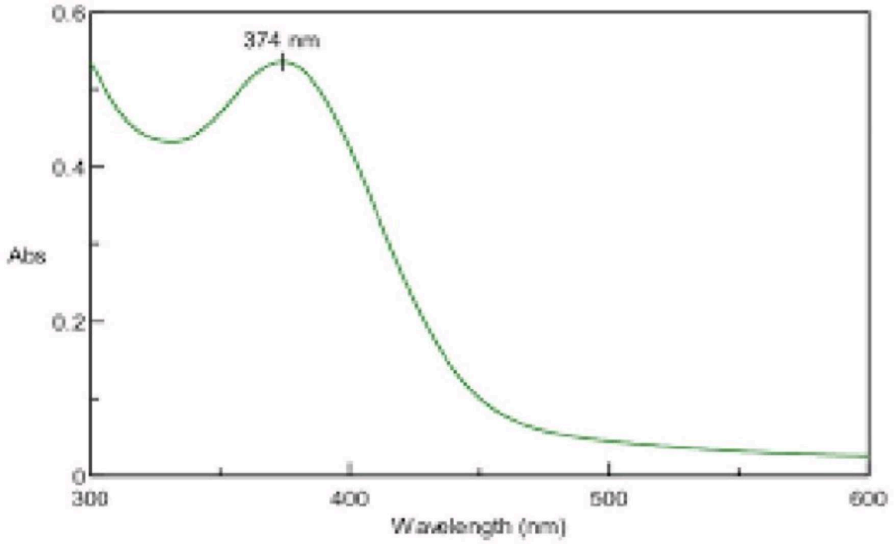
$Zn(NO_3)_2 + 2NaOH \rightarrow Zn(OH)_2 + 2NaNO_3$

$Zn(OH)_2$ + Plant extract + Heat $\rightarrow$ ZnO (NPs) + H_2O

Characterisation:

i. UV-VISIBLE Spectral analysis:

A sharp 'SPR' band at 374 nm shows the formation of ZnO NPs. Only phenols and Flavonoids present in plant extract help in the reduction of Zn^{2+} and encapsulation of NPs.

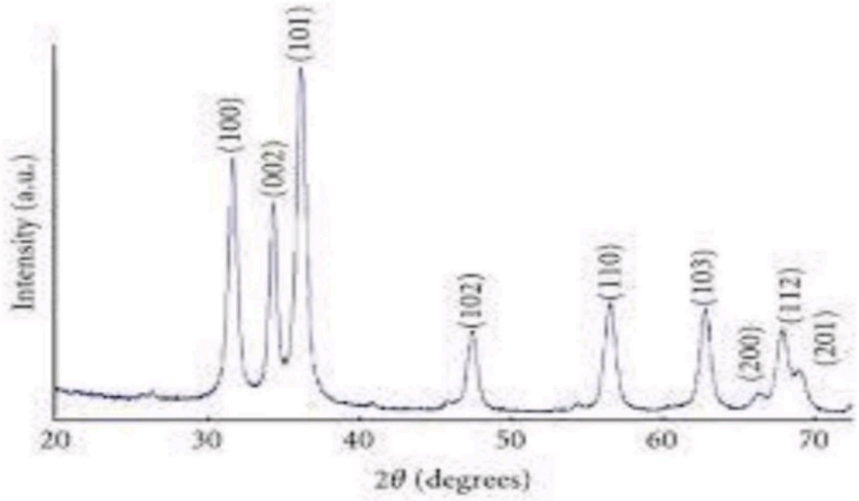


Scanned with CamScanner

ii.XRD Study:

XRD pattern shows the 2ɵ values at 31.77^0, 34.4^0 and 36.2^0 corresponding to (100), (002) and (101) planes of ZnO NPs. The crystallite size has been obtained using the Debye-Scherer Equation,

$d = 0.94\lambda/\beta \cos\theta \approx 20$ nm, [$\lambda = 1.54$ Å , β = FWHM(Full Width at Half Maximum)] ɵ = Diffraction angle.



Applications: As a sensor material/ In cosmetics/ coating agent/ ceramic industry/ UV-filtering agent/ Anti- corrosion Agent

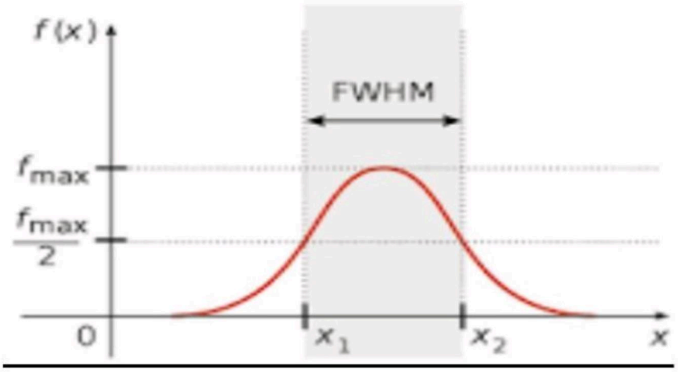
Scanned with CamScanner

Important Terms

Plasmons: These are quasi particles arising out of quantization of plasma oscillations.

SPR Band : It originates due to the resonant oscillation of the free electrons of the conduction band of the metal induced by a resonant electric field.

FWHM: Full width at Half Maximum. It is an expression for the extent of a function given by the difference between two extreme values of the independent variables at which the dependent variable is equal to half of its maximum values as shown below.



It can be applied to any bell-shaped curve, such as a Gaussian, Lorentian, triangle, rectangle. Take the highest point of the peak and walk along the slopes on both sides until you trespass half that maximum value.

Precursor salt : chemical useful to form another chemical by a chemical reaction.

Scanned with CamScanner

Questions & Answers

1. What is nanochemistry?

   Ans: It is the branch of science which deals with the study of the synthesis, & characterization of nanomaterials (of size 10^{-9} nm).

2. What are nanomaterials?

   Ans: Particles of size 1nm to 100nm are generally called nanomaterials. These have one of its dimensions (length, breadth or diameter)in the nano range (< 100 nm). Examples: nanowires, nanotubes, quantum dots, thin films, etc.

3. Give examples (4) of reducing agents used in the synthesis of nanomaterials.

   Ans: H_2O_2, citric acid, hydrazine, phytochemicals (in plant extracts)

4. Name the precursor salts used to synthesize the following nanoparticles; Cu_2O, Ag, Au,& ZnO

   Ans: Cu_2O – $CuSO_4.5H_2O$

   Ag - $AgNO_3$

   Au – $AuCl_3$ or $HAuCl_4$(Hydrochloro auric acid)

   ZnO – $Zn(NO_3)_2$

5. What is the need for capping agents in the synthesis of nanoparticles?

   Ans: They are used to prevent the overgrowth & agglomeration of nanoparticles.

6. What is the objective of XRD analysis? Explain the XRD analysis of Cu2O & ZnO nanoparticles with a suitable graph.

Scanned with CamScanner

Ans: The objective of the XRD analysis is to determine the crystalline size of the nanoparticles by using the Debye- Scherrer equation. (Refer to the note for the graph)

7. What do you mean by the 'Surface Plasmon Resonance' band? Draw a UV-visible absorption plot to show the SPR band of Au & Ag nanoparticles.

   Ans: 'Surface Plasmon Resonance'band is a prominent feature of a metal nanoparticle. It originates due to the collective resonant oscillations of the free electrons of the conduction band of metals induced by a resonant electric field.

8. What are the 'Top-down' & 'Bottom-up' approaches to the synthesis of nanoparticles? Explain them with suitable examples.

   Ans: Refer to the note for the answer.

9. What are the advantages of synthesizing nanoparticles using plant extract?

   Ans: Refer to the note for the answer.

10. Discuss the method of preparation, characterization & applications of the following nanoparticles; Au, Ag, Cu_2O, & ZnO

    Ans: Refer to the note for the answer.

11. What is the importance of FWHM in NPs study?
    Ans: It helps in determining the size of the nanoparticles. If value of the β is small, then size(d) of the nanoparticles will be more.
12. Which is a better approach for synthesis of NPs and why?
    Ans: Bottom-up approach is better for synthesizing nanoparticles for its various advantages.

    Advantages:

    - generates particles of uniform size, shape, & morphology.
    - particles of excellent quality and quantity
    - an eco- friendly process.

Scanned with CamScanner

13. Why Silver nitrate is used as a precursor salt instead of silver chloride in synthesis of Ag nanoparticles?

Ans) Silver chloride has very little solubility in water. Therefore, when reducing its ions, very few silver nanoparticles are obtained as compared to silver nitrate.

14. What is the objective of UV-Visible spectral analysis for the synthesis of the nanoparticles?

Ans: UV-visible spectral analysis shows the SPR band in the visible range indicating the formation of colored nanoparticles.

Scanned with CamScanner