



NANOMA TERIALS

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• Introduction, Terminology & History Optical Properties and its Characterization Interaction of light with matter Surface plasma resonance, Characterization methods: Electron microscopy, SEM, TEM. Top-down, Bottom-up fabrication (Colloidal route, sol-gel method, chemical reduction method, electrochemical method) • Applications of nanomaterials.

According to U.S. National Science Foundation

The study that deals with materials and systems having following key operators

- Dimensions: 1- 100 nm

- Process: Methodology that shows fundamental control over physical and chemical properties of molecular scale structure.

- Building block property: They can be combined to form larger structures.

Too long Prepared and used in 19th century Decorative coloured glass windows of old churches and palaces. (Fe, Ni, Co, Ag, Au, etc) Michael Faraday (1857): Prepared colloidal solution of Au NPs Photographic plates covered by Ag NPs >In 19th century people were unknown about size of NPs.

Year	Scientist name &	Invention		
	Information			
1959	Richard Feyman (Nobel)	-There is plenty of room at the bottom		
		-NPs have tremendous applications & diff.		
		properties.		
1981	Binning & Rohrer	Scanning Tunneling Microscope (STM)		
	(Nobel 1986)	Atomic size images		
1990	Don Eigler & Erhard Shucizer	Atomic manipulation is possible		
		(Milestone advancement of science)		
1985	Curl, Kroto & Smalley	Fullerene NP (C ₆₀)		
	(Nobel 1996)			
1991	Iijima	Carbon nanotubes		
2004	Gem & Nevoselve	Graphene (Allotope of 'C')		
	(Nobel 2010)			
All properties of NPs are differing than its bulk materials. (Mechanical, thermal, optical,				
magnetic, etc.)				
Very Smaller size and larger surface area changes properties				
e.g. Graphene good conductor of electricity, thin , strong, transparent, elastic than Cu				

Optical Properties of Nanomaterials

Interaction of light with matter

Various changes in properties of matter when exposed to EMR.

1. Optical properties of Semiconducting NPs

Conductor: VB & CB overlaps. Insulator: VB & CB separated by large distance. Semi-conductor: VB & CB separated by finite distance.

Exciton: When e- passes from VB to CB, a hole is left behind and e- hole pair formed in the particle called exciton.

i.e. bound state of an e- & hole

- this binding is due to electrostatic attraction

- Exciton has lower energy than unbound e-.

Two types of Exciton a) Frankel Exciton: Distance between e- & hole is comparable to lattice constant.

(Lattice constant: A parameter measures length or angle of the unit cell of a crystal lattice, which defines size & shape of it.)

b) Mott-Wannier Exciton:

Distance between e- & hole is larger than lattice constant. This free exciton can move in crystal. Energy of such exciton is slightly less than energy gap (E_g) betⁿ VB & CB.

E_g is energy necessary to create free hole and free e-

The Hamiltonian for Mott-Wannier exciton is given as, (Hamiltonian: Sum of K.E & P.E. of particles)

Where,

 $m_e \& m_h = Effective mass of e- \& hole$ $P_e \& P_h = Momentum (p=mv) of e- \& hole respt.$ E = dielectric const. of semiconductor material. $|r_e-r_h| = Dist. between e- \& hole$

Then, Bohr's radius of exciton is,

- $r_B = Bohr$'s radius of exciton
- $h = Planck's \ const \ (= energy \ of \ quantum \ of \ EMR / freq).$ $(6.626 * 10^{-34} \ m^2 \ Kg/s)$
- e = Charge
- E Dielectric const. of medium
 (Ability of sub. to store electrical energy) or
 (Permitivity of sub. / Permitivity of free space)

Permitivity: Measure of resistance when electrical field forms in medium Wave Function: A function satisfies wave equation & describes properties of wave.(describes position & state of an e-) Wave Equation: Differential eqn expressing the properties of motion in waves Using eqn[1] & considering certain wave functions & potentials, exciton energy (ΔE) or effective band gap (E_g) of particle having radius (R) can be given by eqn.

$\Delta E = E_{g}^{\text{eff.}} = h^{2}\pi^{2}/2R^{2} \left[1/m_{e}^{+} + 1/m_{h}^{-} \right] - \left(1.8 \ e^{2}/4 \ \pi \ \epsilon_{0}^{-} \ \epsilon \ R \right) + P.E. ----[3]$

 ϵ = dielectric const. of medium.

From eqn [3]; as particle size (R) decreases, first term becomes dominates & <u>A E increases</u>.

i.e. energy gap in semiconductor is a characteristics of the material

hence, here as energy gap increases in semiconductor material with decreasing particle size, is given by,

Eg. In case of GaAs semiconductor

Particle Size	2	5	10	20
(nm)				
Energy gap	2.78	1.61	1.46	1.42
(ΔE)				

Characterization of semiconductor nanoparticle

Optical properties of metallic NPs

When light is incident on metallic NP solution,

it may be absorbed, transmitted or scattered.

According to *Mie theory* phenomenon can be explained as,

When an EMR is incident on **spherical particle** of uniform size which distributed uniformly in medium, then a part of light may be absorbed, a part may be transmitted & scattered.

It is observed that, when light is incident on solution of NP, decrease of intensity takeplace, due to extinction of light. Therefore, amount of light extinguished is given by, $[Q_{ext} = C_{ext}/\pi R^2]$

Where, $Q_{ext} = extinction \ coefficient$ (how strongly sub. absorbs light) $C_{ext} = Cross \ section \ of \ particle \ (Probability \ that \ two \ particle \ colloid \ \& react \ in \ certain \ way.)$

i.e. No. of particles scattered per unit time / No. of particles passing.

If I_0 is intensity of radiation of wavelength λ , passing thro' medium having dielectric constant ϵ_m and thickness 'X', Then intensity of transmitted light is $I = I_0 * e^{-\mu X} - -----[1]$ $\mu = Extinction coefficient = (N/V). C_{ext}$ $C_{ext} = Cross section of particle$ N = No. of particle in mediumV = Volume of colloidal particle

According to Mie theory, $C_{ext} = C_{obs} + C_{scatt.}$

In Mie Theory,

 $C_{\text{ext}} = \left[24 \, \pi^2 R^2 \, \epsilon_{\text{m}}^{3/2} / \lambda \right] * \left[\epsilon_2 / \left(\epsilon_1 + 2 \epsilon_{\text{m}} \right)^2 + \epsilon_2^2 \right] - --- \left[2 \right]$

 $\epsilon_1 \& \epsilon_2 = \text{Real \& imaginary parts of complex dielectric functions}$ $i.e \ \epsilon = \epsilon_1 + i\epsilon_2$ of the constituent material of NP. **Real**: Polarization & anomalous dispersion of particle **Imaginary**: Dissipation of energy into medium by which energy becomes not available

> ϵ_{m} = dielectric const. of surrounding medium(real number) (for air $\epsilon_{m} = 1$ & blood $\epsilon_{m} = 1.4$) These dielectric const. for particle obtained from literature.

From eqn [2] indicates that maximum
extinction is possible when,
$$\epsilon_1 + 2\epsilon_m = 0$$
 i.e $\epsilon_1 = -2\epsilon_m$
(This depends only on material, not size of
material)
Therefore wavelength of strong SPR peak
doesn't change with particle size
doesn't change with particle size
[2] becomes invalid & wavelength of SPR
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Surface Plasma resonance

Plasmon: Quantum of plasma oscillation or quasi-particle (weakly interacting particles of free space)

Plasma: Form of matter where many e- wander freely among the nuclei of atom **or** electrically neutral medium of unbound positive & negative particles.

Plasma oscillation or Langmuir waves: Rapid oscillation of *e- density* (measure of probability) in conducting media such as plasmas or metal

Resonance: Freq. of incident photon matches with natural frequency of surface e-.

AuNPs are very strong absorbers of visible light because of high resonance condition is achieved.

SPR: When light incident on the surface of particle, ecloud of NPs oscillate due to electric field of light. This condition of resonance known as SPR.

When NPs is much smaller than wavelength of light, oscillations induced in conduction band e- by interaction with EMR.

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Light resonance with the surface Plasmon oscillation causes the free electrons in the metal to oscillate.

Generally interaction of light & particle can be characterized in terms of its extinction (light removed from incident light)

Light is extinguished either by absorption or scattering. Beam of light excites the loosely bound surface e- to form SPR.

SPR can generate heat by absorption of light or acts as dipole shaking at the freq. of light & becomes source of light.(Scattering of light)

Applications

Scattering of light: To detect cancer position for treatment by optical microscope.

Absorption: Heat generated is used to treat hyperthermia.

Extinction of particle depends on optical properties
of material & medium in which it is distributed.
As per eqⁿ [2]in Mie Theory & above discussion, we can say that
For larger NP, the wavelength of SPR peak is size dependant.
Now,
$$Q_{ext}$$
 (Extinction coefficient) = $C_{ext}/\pi R^2$
By putting value of C_{ext} , we have
 $Q_{ext} = [24 \pi^2 R^3 \epsilon_m^{3/2} / \lambda \pi R^2] * [\epsilon_2 / (\epsilon_1 + 2\epsilon_m)^2 + \epsilon_2^2]$
 $= [24 \pi R \epsilon_m^{3/2} / \lambda] * [\epsilon_2 / (\epsilon_1 + 2\epsilon_m)^2 + \epsilon_2^2]$
i.e Q_{ext} depends upon R & dielectric const. medium.

Relative amount of extinction & absorption depends on the particle size. **In Small NPs: Extinction due to absorption In large NPs:** Extinction due to absorption & scattering. **Relative proportion of scattered & absorbed light varies as a function of particle size.**

Freq. of SPR oscillation is given by,

$$W_p = \sqrt{4\pi} N_e^2 / m^*$$

N = No. of e-in plasmae = Charge on e $m^* = effective mass of e-$ It is observed that wavelength for resonance of pure Au NP remains in visible region.

- We also know that this wavelength decides wavelength of scattered or absorbed light which is dependent on particle size of material.

Again we know that wavelength of scattered light decides color of solution
Hence gold solution shows different color depending upon size.

Characterization Methods

To know about size, structure, types of atoms, arrangement of atoms, etc. of NPs

Sr. No.	Techniques	Use
1	XRD, e- diffraction, neutron	Particle Size & type of crystal
	diffraction	structure.
2	UV, IR, FTIR, ESR, AAS, NMR, etc.	Information about electronic
		structure, chemical state
		analysis & other properties.
3	Optical Microscope, SEM,	Morphology, <mark>Size</mark> , Structure,
	<i>ТЕМ, STМ,</i>	image of atomic level, etc.
	Atomic force Microscope	
	(<i>AFM</i>), etc.	

Electron Microscopy

(Similar to Optical Microscopy: EMR of proper wavelength, glass lenses used to focus radiations.)

In electron spectroscopy e- beam & electrostatic or magnetic lenses used.

Wavelength of e- is given by de-Broglie eqn.
 λ = h/mv
 Wavelength of e- is very small (0.001-0.02)
 Due to smaller wavelength e- microscope can be used to image tiny particles.

Interaction of e- with solid is complicated due to i) charge on e- ii) Interaction of e- with ions in solids.

Due to interaction of ewith sample, a **tear shaped volume of interaction** is formed.

Principle

When e- interacted with surface of solid material, many phenomenon takes place such as scattering of e-, production of 2° e-, Production of X-ray etc.

e- beam should focused on sample without getting scattered or deflected by air, therefore emicroscopy requires

vaccum.

Specimen-Beam Interaction

Construction & Working

Electron Source: Tungsten(highest M.P. & Lowest V.P.) filament or Lanthanum hexaboride cathode. e- beam energy = 1000-50000 ev

> These beam is focused by two successive condenser lenses in very fine spot (5 nm). Then beam of e- is then pass thro' pairs of scanning coils which deflects beam linearly thro' objective lens over sample surface. Deflection is done magnetically thro' m.f. generated by electric current flowing thro' coils.

I° e- strikes surface inelastically & scattered from atoms of sample Due to this scattering 1° beam spreads & fills the tear-drop shaped volume into surface. > Now, due to interaction in the tear-drop, emission of 2° e- takeplace. These 2° e- are detected to produce an image. \succ X-ray are also produced & can detected by dispersive X-ray spectroscopy (composition analysis of sample).

Sample Preparation

- ✓ Appropriate size to fit specimen chamber
- ✓ Sample should be dry
- Hard dry materials eg. Wood, feather, dried insects can be examined with little further treatment.
- ✓ For living cells, tissues & soft bodied organisms require chemical fixation to preserve & stabilize their strcture.
- \checkmark Dry specimen is mounted on specimen tube using adhesive.

Amplification:

e- amplifiers of various types used to amplify signals

Detectors:

Back scattered e-s & 2° e-s can be detected by specialized detectors. Resulting image will be distribution map of intensity of signal emitted from scanned scanned area of specimen. In older microscopes image was captured. In modern machines image is saved to computer data storage.

Affecting factors

Spatial resolution of SEM depends on size of e- spot (depends upon magnetic e- optical system, which produces scanning beam of e-)

Resolution also depends upon interaction volume or extent of material interacts with e- beam.

Resolution of SEM is not high to produce atomic image.

Applications: Morphology & distribution of NPs

Precautions:

Placed whole system in vaccum (To avoid oxidation & contamination & to prohibit collisions between e- & air)

Advantages

- ✓ First method to obtain image of tiny particles.
 ✓ Biological samples can be analyzed with little treatment.
- ✓ Non-destructive method.

Disadvantages

- ✓ Non conducting material requires coating of thin metal film (Au/pt) [< 10nm]& it becomes conducting
- (Insulating material get charged due to incident e-s & images may become faulty & blurred.)

Transmission Electron Microscopy (TEM)

Principle: Transmitted e- hit fluorescent screen gives shadow image. Sample should be very thin Sample is powdered & made thin film Energy of e- should very high (greater than 50000 ev) Single particle of very small dimension can be analyzed.

Diff. between SEM & TEM

Sr.	SEM	TEM
No.		
1	e- beam scans over surface of	e- beam passes thro'thin film
	sample	
2	Sample can be of any thickness &	Thin sample supported on grid
	mounted on stub	
3	Specimen stage is at bottom	Specimen stage is at halfway
		down
4	Image is of surface of sample	Image is two dimensional
		projection of sample
5	Image shown on TV monitor	Image shown on fluorescent
		screen

Top-Down, Bottom-up Fabrication

Top-Down: Larger Smaller High mfg. capability, low spatial resolution

Bottom up: Molecule or atom come together in proper way to form required nanostructure. High spatial resolution, limited mfg. capability But, now combination of both is most famous & effective

Methods of Synthesis of NPs

A) Colloidal Route: $(10^{-9} to 10^{-6} m)$ To synthesize metal NPs Reduction of metal salt by proper reducing agent

eg. $HAucl_4 + Na_3C_6H_5O_7 \longrightarrow Au^+ + C_6H_5O_7^- + HCl + 3NaCl$ [Chloroauric [Trisod. Citrate] Acid]

 ✓ Au Nps are stabilized by repulsive coulomb interaction (due to formation of double layer at particle)
 ✓ Also stabilized by thiol or other capping molecule
 ✓ AuNPs exhibit intense red, magneta, blue-violet colour depending upon size.

Semiconductor NPs by Colloidal route

e.g. ZnS NPs •ZnCl, or $Zn(NO_3)$, or $ZnSO_4$ dissolved in aq. or non-aq. Solvents •Added Na,S or H,S gas passed •ZnS particles formed i.e. $ZnCl_2 + Na_2S = ZnS + 2NaCl$ $ZnCl_2 + 2NaOH \longrightarrow Zn(OH)_2 + 2NaCl$ $Zn(OH)2 \rightarrow ZnO + H_2O$ Colloids formed in the solution have a tendency to coagulate due 45 to attractive forces existing between them.

Chemical Capping

Capping used in synthesis of NPs.

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- Some chemicals are used in colloidal synthesis to inhibit NP overgrowth & aggregation & to control structural characteristics.
- Thro' colloidal route NPs also obtained by drying off the liquid.
- Spin coating or dipping coating also used to obtain thin film of capped particles.
- Coating should be stable & non interactive with the particle except at surface.

Disadvantages: Chemicals used for capping may be toxic & difficult to handle.

✓ Useful for self-assembly process for fabrication of NPs & three dimensional materials as aerogels

Sol: Type of colloid, in which dispersed solid phase mixed in homogeneous liquid mediun.

Process: Formation of colloidal suspension (sol) & gelation of sol (gel) to form network in liquid phase

Four Steps of synthesis of Silica-gel

1) Hydrolysis reaction: -OR group substituted by —OH group Occur without catalyst

If catalyst used increases rate of reaction Catalyst: *NaOH*, *NH*₃, *HF*, *CH*₃*COOH*, *etc*.

$\equiv Si-OEt + H_2O = = Si-OH + EtOH$

2) Condensation: Complex reaction, many intermediate products formed

$\equiv Si-OH \quad = Si-O-Si \equiv + H_2O$

B) Polymerization: Step growth of particle takesplace
 Growth depends upon P^H, tempt, etc.
 Complex reaction
 Si(OEt)₂ -----> -SiO₂-

Agglomeration: Network particles start to form thro' liquid medium due to which gel is formed.
 All 4 steps are affected by P^H, tempt., time of reaction, catalyst.

Application: Inorganic coating, Reactive oxides, Ceramic materials, Ceramic coating, Glasses, Mfg. of silica gel catalyst, Special types of alumino-silicates gels (e.g. Imgolite: ext. dia. = 2.5 nm, int.dia = 1.5 nm).

Chemical reduction Method Metal salt solution treated with suitable reducing agent. Added appropriate stabilizing agent. Further treatmentDried & get NPs. Eg. AgNPs $Ag NO_3 Sol^n + Hydrazine hydrate + Sod. Doacyl sulfate & Sod. Citrate (stabilizing agent)$ Pale yellow or Pale red colour (due to formⁿ of AgNPs)

Purified by centrifugation

AgNPs washed with deionized water under N_2 gas to remove excess Ag ions

Dried powder of nanosize silver can be obtained by freeze drying

Particle size 15 to 48 nm

Electrochemical method

Process of using electric current to coat on electrically conductive object with thin layer of metal.
 As a result of electrical current, electrolysis of electrolytic solution occurs & deposition of metal in the form NP takesplace on cathode, so called as electrodepositon.

As result of reduction reaction metal ions in a solution deposits on negatively charged cathode metal atoms.

e.g. Ag, Cu, Au Nps can be synthesized.

▶ e.g. preparation of AgNP

Advantages:

- Cheap & fast Method.
- > Thickness of layer depends on current density & time of current flow.
- The deposit can be detached by suitable method
 - Recent Mostly used process by many researchers.

Applications of NMs

Electronics: NPs of ZnSe, ZnS, CdS improves resolution of TV screen. So used in HD TV & computer monitors. Energy (Fuel cells): NM as catalyst to produce hydrogen ions from fuel. High Storage capacity batteries: Aerogel & Ni-MH Industry: Tougher & harder cutting tools. e.g. WC, TaC, TiC NPs, etc. Automobile with greater efficiency: engine cylinders (liner) with zirconia & alumina NPs which

retain heat & increases efficiency.

Health Care:

-Heart valves from ZrO ceramics, SiC (low wt., extreme hardness, high strength, corrosion resistance, etc.) -NM used in cancer therapy, drug release, etc. Food- Agriculture: Food packaging, food processing catalyst, food quality analysis sensor, etc. Textile: NM used to produce medical textile, technical textile, antistain textile, self-cleaning textile, etc. **Environment**: **Pollution** scavengers, pollution monitoring sensors, etc.

Cosmetics:Various creams & gels e.g. ZnO, TiO₂

Domestic Appliances: NMs used in various domestic appliances such as air purifiers, air conditioners, water purifiers, refrigerators, window material, etc.

High sensitive sensors: NM of ZrO is used in CO sensor. NM also used in smoke detectors, ice detectors on aircraft wings, automobile engine performance sensors.

NM used in aerospace components, longer lasting satellites, self-cleaning glasses, etc.

Future Applications: Quantum computers, microelectro-mechanical systems, optoelctronic devices, environmental devices, nano-electronic & magnetic devices, etc.

