

Day 5

NANOTECHNOLOGY

- science, engg., and applicn of materials & devices at nanometer scale - (1 to 100 nanometers)
($1\text{nm} = 10^{-9}\text{m}$)
- manipulating atoms & molecules - create new materials with unique physical, chem., and biological props.

KEY POINTS : Scale : Atomic / molecular level.

Goal : Design / control structures for specific func'

Properties: May have higher strength, lighter wt.,

WHY NANOSCALE

better conductivity, novel optical behavior

compared to bulk materials.

$1\text{nm} (\text{Nanometer}) = 10^{-9}\text{ m}$ (1 thousand millionth) of m.

Interest: At nanoscale, materials have physical and chemical properties that differ significantly from their larger-scale counterparts.

Example: • water molecule : 0.1 nm

• gold particle : 10 nm

• Virus

: 100 nm to 1 mm

Hair : 100 nm

RBC : $5-10\text{ nm}$

full stop (dot) : 1 mm

Watermelon : 10 cm

Benzene : 0.5 nm

Carbon nanotube : 5 nm (diameter)

Nanomaterial - Nano Powder

- Fine powdered material → nanometer scale ($< 100\text{ nm}$)
- Key properties: High surface area to vol^m ratio:
Responsible for special properties not found in bulk material
- Advantages / special properties:
 - Enhanced reactivity
 - Improved mechanical strength
 - Unique optical, magnetic & Electrical behavior
 - Better sintering for ceramics & metals

What is nanomaterial

↳ at small scale → materials have fundamentally different properties than at the bulk due to increased surface area to volume ratio.

- Increased interaction & reactivity
- Nanoscale effects (less material needed)
- Diff properties at nanoscale

Characteristics [Most of them are novel, why?]

novel materials: new forms of existing materials with characteristics that differ significantly from familiar naturally occurring forms

Nanomaterials can have, one, two or three dimensions in the nanoscale:

- Classification of Nanomaterials by Dimensions
- 0 Dimensional → nanospheres, clusters → fullerenes, gold nanoparticles etc.
 - 1 Dimensional → nanotubes, wires, rod → carbon/gold nanotubes etc.
 - 2 Dimensional → Thin films, plates → carbon coated nanoplate, etc.
graphene sheet
layered
 - 3 Dimensional → Bulk NMs. → Liposomes, Polycrystalline etc.
polycrystals

0-D Nanomaterials : nanoscale range (1-100 nm).

e.g. - gold nanoparticles : properties - no dimension exceeds nanoscale
(Au NPs)

- Quantum dots (CdSe, PbS) : nanoscale size rods

- Fullerenes (C_60)

1-D Nanomaterials : 2 dimension in nanoscale, 3rd dimⁿ much larger

e.g. - Carbon nanotube properties: High aspect ratio, nano-wires, nano-tubes.
(CNT)

- Zinc Oxide nanowire ($ZnO W$)

- Silver nanorods

2-D Nanomaterials → 1 dimension in nanoscale, two dimensions much larger

e.g. - Graphene properties - sheet like, large S: A, unique.
- Molybdenum disulphide (MoS_2) nanosheets
- Hexagonal boron nitride ($h-BN$) sheets

3-D Nanomaterials - Extend in all 3 dimensions, but properties: Bulk materials composed of nanoscale building blocks, with nanocrystalline structure of nanocomposites

e.g. → Nanocrystalline metals

- Nano composites (polymer matrix with nanosilica)

- Nanoporous materials (PPG)

TYPES OF NANOMATERIALS

- Most current nanomaterials could be organized in 4 types
- Carbon Based Materials
 - Metal Based Materials
 - Dendrimers
 - composites

Types of Nanomaterials

- Earlier known natural Carbon allotropes : Diamond, Graphite

→ Carbon based nanomaterials : Composed of carbon atoms

→ Classification: Based on geometrical structure

• Carbon nanostructures: particles can be

- e.g. • Graphite
• Amorphous Carbon
• Diamond
• Fullerene
• Carbon Nano tubes
• Graphene

- Tube shaped
- Horn-shaped
- Spherical
- Ellipsoidal

Applications :

- ↳ micro & nano electronics
- ↳ gas storage,
- ↳ addition of conductive plastic
- ↳ composites, displays, antifouling
- ↳ textiles, batteries with paint
- ↳ improved durability
- ↳ gas biosensors & others

* Fullerene

→ Allotropic form of Carbon
(molecular form, carbon molecules)

→ Family: Atomic C_n clusters ($n > 20$) on spherical surface

→ Carbon atoms at vertices of pentagons & hexagons ; sp^2 hybrid, covalent bonds

→ C₆₀: Most common, 60 atom, 20 hexagon + 12 pentagon

diameter $\approx 0.7 \text{ nm}$

→ Discovery Nobel Prize (1996) : R.F. Curl Jr., H.W. Kroto,
R.E. Smalley.

Carbon Nanotubes (CNTs)

- C-allotropes with exceptional technical properties
- cylindrical, nm-scale diameter, made by rolled graphene sheets
- vary in length, diameter, chirality, and layers
- Types: SWCNTs (single walled)
MWCNTs (multiple-walled)
- Discovered 1991 by Sumio Iijima (no nobel prize)
- SWCNTs: Dia 1-3 nm, length few μm
- MWCNTs: Dia 5-40 nm, length ~10 μm
- properties: High rigidity, strength, elasticity, thermal & electrical conductivity

CNTs (Chirality & Types)

- SWCNTs based on chirality:
 - a. Arm chair - Electrical conductivity > copper
 - b. Zigzag - Semiconductive
 - c. Chiral - Semiconductive
- MW CNTs: Multiple layers, variable chirality, excellent mechanical & electrical properties.

Graphene

- 2D allotrope of C, single atom-thick layer
- sp^2 hybrid., σ & π bonds in hexagonal lattice,
- C-C-distance: 0.142 nm
- Structural element of graphite, CNTs, fullerenes.

Properties: • extremely high rigidity
high thermal stability

Applications • Electronics • Energy Storage • Composites • sensors
• Water filter • Biomedical

Nanomaterial's Characteristics

- 1-D N.M. → layers, multilayers, thin films, platelets and surface coatings. They have been developed and used for decades, particular in the electronics industry.
- 2-D N.M. → nanowires, nanofibres made from a variety of elements other than Carbon, nanotubes and, as part of this group, Carbon nanotubes.
- 3-D N.M. → nanoparticles and include precipitates, colloids and quantum dots.
(tiny particles of semiconductor material) and nanocrystalline materials

When Did Nano-Tech start?

- ↳ Nanotech & Nanosci. aren't entirely new
- ↳ nanoscale polymers are made from decades
- ↳ Nano tech used in Computer Chips for 20+ years
- ↳ Recent advances in atom/molecule manipulators have accelerated nano technology

Nanotech Approaches

- Bottom-up:
- Build structures atom by atom / molecule - by - molecule
 - Used to synthesize nanomaterials

- Top-down:
- Shapes larger materials into nanoscale forms using cutting, milling, etching

- Used mainly for patterning existing materials.

CNT SYNTHESIS : Bottom Up, or, Top-down?

- Both possible, but mostly done by bottom-up methods:
 - Arc discharge, laser ablation, chem vapour deposition (CVD)
 - Build CNTs atom by atom /molecule-by-molecule
- Top-down used for structuring, not for synthesis of CNTs.
- CNT synthesis \Rightarrow Bottom-up method

Top-down v/s Bottom-up approaches

• Top-down

- ↳ start with large structures, break down to nanoscale
- ↳ Hierarchical, central command (lithography)

• Bottom-up

- ↳ Build up from small units (atom/molecule)
- ↳ collective, decentralized assembly

Magnetism

- ↳ key property in nanotech. materials
- ↳ Used in various applications, often manipulated at the nanoscale.

Application of Nanotech

- ↳ Medicine: Diagnostic, drug delivery, tissue engg., cryonics
- ↳ Info/communication: Memory storage, novel semiconductors & optoelectronics, quantum computers
- ↳ Heavy industry: Aerospace, catalysis, construction, space vehicle
- ↳ consumer goods: Foods, optics, textiles, cosmetics, sports
- ↳ Environment: Soil remediation, sensing, air/water purification

Environmental applications

- ↳ carbon capture
- ↳ sensors
- ↳ Remediation
- ↳ wastewater treatment

- ↳ Energy
- ↳ Point-of-use water purification

After this

Major forces acting in nature

gravity, electricity, and magnetism.

- Electric current & magnet can exert force on each other

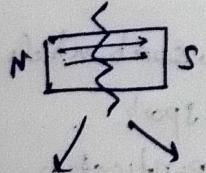
1. Magnetic Levitation: Maglev Train

- Electromagnetic Suspension (EMS)
- Electrodynamic suspension (EDS)
- Magnetic repulsion
- N-N or S-S repulsion
- No contact → No friction → high speed → smooth train

- All magnet have north & south pole
- Like poles repel. Unlike poles attract
- Compas. needle → small bar magnet → freely rotate
 - points N. → north seeking
- Core of earth → giant magnet.

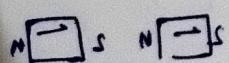
- Northern lights (aurora borealis) & southern lights (aurora australis)
 - are result from the interaction b/w the solar wind and earth's magnetic field (makes the air glow)

Magnetic Materials → Materials in which the domains will line up in order to form mag. field.



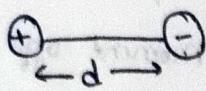
e.g. iron, Cobalt, & nickel

(No monopole in magnet)



Magnetism → attr'n or repul' by magnetic materials

Magnetic dipole - Any two opp. poles separated by a finite distance.



Origin of Magnetic Moment

- 1) orbital Motion - Orbital magnetic moment
- 2) spin Motion - spin magnetic moment

Magnetic Moment: $M_{eff} = M_{s,0} = 2\sqrt{s(s+1)} = \sqrt{n(n+1)} \cdot BM$

$n \rightarrow$ no. of odd e^-

If there is a possibility from the orbital angular momentum

$$\bullet M = \sqrt{L(L+1)} + m_s(s+1)$$

• if $L > 0$, it's possible.

• of orbital contrib. like $3d^7$ of our body.

• Complexes of Cobalt(II)

→ An atom is said to be magnetic if it carries a permanent dipole moment.

→ Every substance is formed from an assembly of atoms which can be either non-magnetic or magnetic.

Magnetic materials classification

1. Diamagnetic Materials -

2. Paramagnetic Materials -

3. Ferrimagnetic Materials -

4. Antiferromagnetic Materials

5. Ferromagnetic Materials.

DIAMAGNETISM

- Non magnetic atoms (no permanent dipole moment)
- ORIGIN:
 - ↳ Random orbital orientations → net moment = 0
 - ↳ Electron motion around nucleus → magnetic moment.
 - ↳ External field → induced magnetic moment opp to applied field
- PROPERTIES:
 - ↳ Weak magnetization; repel mag. field. lines
 - ↳ Exist in magnetic - atom substances but masked by strong magnetic
 - ↳ Relative permeability < 1
 - ↳ Magnetic susceptibility independent of field strength
- SUSCEPTIBILITY:
 - ↳ Small & -ve → Temp. independent (organic, light elements)
 - ↳ Intermediate & --ve → $< 20\text{K}$ varies (alkali earth, Bismuth)
 - ↳ Large & +ve → Below T_c (superconductor)

PARAMAGNETISM

- Magnetic atoms with permanent dipole moments.
- ORIGIN:
 - ↳ Electron → orbital + spin magnetic moments
 - ↳ No field → moments random (thermal motion) → no magnetization
 - ↳ Field applied → dipoles align → induced +ve dipole moment.
- PROPERTIES:
 - ↳ small & +ve susceptibility; independent of field
 - ↳ Random spin alignment w/o field
- SUSCEPTIBILITY:
 - ↳ small & +ve → Temp. independent [Alkali metals, transition metals, rare earth]
 - ↳ Large & +ve →
 - $\chi = \frac{C}{T}$ (Curie law)
 - $\chi = \frac{C}{(T-\Theta)}$ (Curie-Weiss Law)

FERROMAGNETISM

- Strong magnetisation even w/o field (exchange coupling)
- Field \rightarrow strongly attracts magnetic ions
- Characteristic T_c (curie temp) \rightarrow below T_c spontaneous magnetization exist.
- Spin alignment : parallel
- Exhibits hysteresis ; consist of domains
- Susceptibility : Very large & +ve $\rightarrow \chi = \frac{c}{(T-\Theta)}$
 - $T > T_c \rightarrow$ paramagnetic
 - $T < T_c \rightarrow$ ferromagnetic
- Examples: Fe, Co, Ni, Cd.

ANTIFERROMAGNETISM

- Weak magnetism ; similar to paramagnetism
- close atoms \rightarrow antiparallel spin alignment
- Susceptibility \uparrow with temp till Néel temp (T_N), then decreases
- Spin alignment : antiparallel
- Susceptibility : small & +ve
 - $\chi = \frac{c}{(T+\Theta)}$ when $T > T_N$
 - $\chi \propto T$ when $T < T_N$
- Examples: salts of transition metals

FERRIMAGNETISM

- Special case of antiferro ; antiparallel spins of unequal magnitudes
- Possesses a net magnetic moment that disappears above Curie Temp (T_c) \rightarrow net magnetiz. $\neq 0$ (analogous to Néel Temp. T_N)
- Above $T_c \rightarrow$ thermal agitation randomizes spins \rightarrow material becomes paramagnetic.
- Spin alignment : antiparallel, diff magnitudes
- Ferrimagnetic domain can form magnetic bubbles for memory storage.
- Susceptibility (χ) : very large & +ve
- $\chi = \frac{c}{(T \pm \Theta)}$, paramagnetic for $T > T_c$
- e.g. Ferrites

Magnetic Material Types

1. Ferromagnetism - parallel spins ($\uparrow\uparrow\uparrow$), strong magnetization
2. Antiferromagnetism - antiparallel equals spins ($\uparrow\downarrow\uparrow\downarrow$), net $M=0$
3. Ferrimagnetism - antiparallel unequal spins ($\uparrow\downarrow\uparrow\downarrow$), net $M \neq 0$

Application of Magnetic Materials

- Soft Magnetic Materials - Enhance magnetic flux (B), used in cores of electro magnets, motors, transformers.
- Data Storage Materials - For magnetic recording.
- Permanent Magnets - For strong, stable magnetic fields.
- Power - High inductance \times magnetic field product.

Hysteresis Loop

- soft magnets \rightarrow narrow loop, low coercivity \rightarrow electrical application
- Hard magnets \rightarrow wide loop, high coercivity \rightarrow permanent magnets
- Square loop \rightarrow memory storage (computer application).

SOFT MAGNETIC MATERIALS (TABLE: HIGHLIGHTS)

- High permeability (μ), low coercivity, low resistivity.

Examples:

- Ingot iron: $\mu_r(\text{max}) = 5000$, $H_c = 80 \text{ A/m}$, $B_r = 2.14 \text{ T}$
- Silicon iron (3% Si): $\mu_r(\text{max}) = 50000$, $H_c = 60 \text{ A/m}$.
- Permalloy (Fe-79% Ni): $\mu_r(\text{max}) = 1000000$, $H_c = 4 \text{ A/m}$

Magnetic Recording Materials

- key parameters: Particle length, aspect ratio, magnetization, coercivity, surface area
- Example: $\gamma = \text{Fe}_2\text{O}_3 \rightarrow M = 0.44 \text{ Wb}/\text{m}^2$, $H_c = 22-34 \text{ kA/m}$, Curie temp. $T_c \approx 600^\circ\text{C}$

Hard / Permanent Magnet Materials

- High coercivity (H_c), high energy product $(BH)_{\text{max}}$.

Examples:

- Fe-Co steel: $H_c = 0.02 \text{ T}$, $T_c = 887^\circ\text{C}$
- $\text{Nd}_2\text{Fe}_{14}\text{B}$: $(BH)_{\text{max}} = 210-445 \text{ kJ/m}^3$, $T_c = 312^\circ\text{C}$
- SmCo₅: $H_c = 0.91 \text{ T}$, $T_c = 727^\circ\text{C}$