

Nanotechnology

PhD Course By Dr. Mohammed F. Al-Mudhaffer





Nanotechnology Materials

• Preparation methods of Nanostructure materials

Characterization of Nano-materials

Electronic Application of Nano-material



Fundamentals of Nanotechnology



What is Make Nano Work?



1- The surface to volume ratio (S/V)



Simply the surface area of an object divided by its volume

More atoms/molecules of the material become exposed to the surroundings and a larger number of the so-called "dangling bonds" become available at the surface, thus making the particle more active chemically.



sides = 3 surface = $3^2 \times 6 = 54$ volume = $3^3 = 27$

surface/volume = 2



sides = 2 surface = $2^2 \times 6 = 24$ volume = $2^3 = 3$





sides = 1 surface = $1^2 \times 6 = 6$ volume = $1^3 = 1$



2- Quantum Confinement

A smaller (or bigger) particle size results in a stronger (or weaker) confinement which gives rise to enhancement (or decrease) of the band gap and modifies the band structure of the material

Arises from the size reduction of material leading to the electronic wave functions being more tightly confined and resulting in changes associated with electronic and optical properties of the nanomaterial.

quantum wire



quantum well

quantum dot



• Automobile:

- ultralight nanocomposite materials for sport cars and
- high-performance bikes and dirt-resistant paints
- better fuel anti-fog windshields/mirrors with hydrophobic Nano coatings,
- cells for hybrid/electric vehicles.

• Aerospace:

- Carbon fiber composites for modern aircraft
- helicopters that help decrease weight and enhance fuel efficiency.
- Also the carbon fiber composites help decrease the RADAR profile of combat aircrafts.
- Shape-shifting aerofoils and winglets in future aircrafts/space shuttles for extreme maneuverability

• Construction:

- "Self-repairing" concrete made from application of nanocomposites
- Nano biotechnology, easy to clean window glass for skyscrapers having coating of nanorods on the surface which can be cleaned only with water without soap/surfactants.

• Defense:

- Lighter and better nanocomposite helmets and
- Bulletproofing for security/counterterrorism personnel,
- Self-monitoring, analysis and reporting technology (SMART) uniforms for tactical and special forces are a major research area in the defense sector.
- SMART weapons and even SMART ammunition may soon be seen in the inventory of the modern militaries of the world.

• Electronics:

- Nanoscale MOSFETs, carbon nanotube (CNT) FETs,
- graphene FETs, CNT field emitters,
- quantum cascade laser, single electron transistors (SET) to name a few.

• Health care:

 Nano-enabled drug delivery where particular agents are site selectively being delivered to treat complex diseases like cancer, tumors,

Nanomaterials and Nanostructures

Lecture2





2D - Molybdenum disulfide (MoS₂) and Other Transition Metal Di-chalcogenides

Graphite

Having a layered structure of sp2 bonded sheets held together by weak Van der Waals bonds

The individual sheets are of honeycomb structure with C–C sp2 bond length 0.142 nm

The interlayer separation is about 0.335 nm and the unit cell c axis has length 0.67 nm

Due to the weak bonds holding these layers together, the layers are able to slide over one another upon application of shearing stress and thus graphite is able to provide good lubricating action in certain applications.

Depending on the relative stacking of the layers, graphite can be alpha (hexagonal) or beta (rhombohedral) phase.







Graphene

- Individual freestanding honeycomb layers of graphite
- Chemically/ mechanically exfoliated from the bulk show remarkably different properties than the bulk graphite
- In such a material the carriers are effectively confined in one direction (e.g., z) and are free to move in the other two (x-y).
- This gives rise to quantum confinement in the (say z) direction.
- The carriers in such a material have only 2 degrees of freedom and therefore such materials are known as 2D materials.



Graphene

The primitive vectors are given by

 $\vec{u}_1 = a\left(\frac{\sqrt{3}}{2}, \frac{1}{2}\right)$ $\vec{u}_2 = a\left(\frac{\sqrt{3}}{2}, -\frac{1}{2}\right)$

The valence and conduction bands of graphene touch each other at the **six K** points of the Brillouin zone making it **a zero bandgap material** and giving it **exceptional electrical** and thermal conduction properties

The dispersion (E_k) relation at those points of the B_z are linear in nature

$$E(k) = \pm \hbar v_F \sqrt{k_x^2 + k_y^2}$$



Intrinsic graphene has a very high amount of carrier density given by:

$$n_i = \frac{\pi}{6} \left(\frac{\kappa_B T}{\hbar v_F} \right)^2$$

which corresponds to a <u>value of $=10^{10}$ cm² at room temperature.</u>

Such huge availability of carriers makes graphene an excellent conductor. Freestanding sheets of graphene show doping-independent high carrier mobility of over <u>200 cm² V⁻¹S⁻¹</u> (carriers in graphene are considered to be massless Dirac Fermions).

Further, it is optically transparent and highly flexible but stronger than steel.



Fig. 20 Graphene is a 2D building material for carbon materials of all other dimensionalities. It can be wrapped up into 0D buckyballs, rolled into 1D nanotubes or stacked into 3D graphite. Reprinted with permission from Geim and Novoselov [4], © Nature Publishing Group 2007

Graphene Nanoribbon

If graphene sheets are cut into thin strips

The confinement in the vertical z direction, a lateral confinement in x or y is also introduced



Fig. 21 Zigzag, Armchair, and Chiral Graphene Nanoribbon (GNR)

The degree of this confinement depends upon the width of the thus fabricated nanoribbon and also the nature of the cut of the edges

Depending on the cut on the sides of the ribbon, they are categorized as zigzag, armchair and chiral (mixture of armchair and zigzag edges) nanoribbons (Fig. 21).

- Zigzag GNR is always metallic
- Armchair GNR may be metallic or semiconducting

 $C_h = n\vec{a}_1 + m\vec{a}_2$

where a1 and a2 are the basic vectors of the graphene unit cell, and n, m are positive integrate



Fig. 23 a Schematic plot of the chiral vector (C_h) in a graphene 2D lattice. b The relationship between integers (n, m) and the metallic or semiconducting nature of nanotubes. c The structure of "armchair", "zigzag", and "chiral" nanotubes. Reprinted with permission from Zhang et al. [5]. © Royal Society of Chemistry 2011

Fullerene



Fullerenes is known as the buckyballs

The chemical formula for fullerene is C_{60} (60 represents the number of C atoms)

The first carbon-based nanomaterials discovered in 1985

Fullerene-like materials with smaller number of atoms 20, 24, 26 etc. are also possible.

In a fullerene, the electrons are confined in all three directions and hence it represents a 0D material.



One-dimensional (1D) nanomaterials





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Two-dimensional (2D) nanomaterials.



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Three-dimensional (3D) nanomaterials



2-D Materials/ Brief History& Motivation





High number of 2-D materials are known today (ca 140).



Transition Metal Dichalcogenides (TMD)

TMD is a class of layered materials having general formula

A 1000-fold increase in photoluminescence intensity.

MoS₂ monolayers are flexible (suitable for flexible electronics)

In field-effect transistors, (massive on/off ratios of 10⁸, making them attractive for high-efficiency switching)

Molybdenum Disulfide (MoS₂)

Molybdenum **atoms (blue) sandwiched** between two layers of **sulfur atoms (yellow**)



Molybdenum Disulfide (MoS₂)



Band structure diagram of (left) bulk and (right) monolayer MoS₂ showing the crossover **from indirect to direct bandgap** accompanied by a widening of the bandgap.

The bulk MoS₂ is an **indirect bandgap semiconductor** with an **intrinsic bandgap of 1.2** eV.

The monolayers (S– Mo– S sheets) display direct bandgap of 1.8 eV.

Molybdenum Disulfide (MoS₂)

Applications of Monolayer MoS₂

Field-effect transistors (The large direct bandgap and relatively high carrier mobility)

Solar cells

Monolayer MoS₂ has visible optical absorption that **is an order of magnitude greater than silicon**, making it a promising solar cell material

Photodetectors

(The large direct bandgap)

Other 2D-TMD



Band structures of some 2D TMD materials

Nanomaterials Preparation

Lecture3

Synthesis and characterization of Nanomaterials

1. Methods to Synthesis of Nanomaterials

Top-down: size reduction from bulk materials.

Bottom-up: material synthesis from atomic level.



Top-down routes

This route is based with the bulk material and makes it smaller (i.e breaking up larger particles)

Bottom – up approach

It refers to the build-up of a material from the bottom: atom-by-atom, molecule-by-molecule or cluster-by-cluster.



Ball Milling

- One of the low-cost process
- The main mechanism involved here is the mechanical grinding.
- The axis may be horizontal or at small angle to the horizontal
- We can generate fine powder from bulk system (topdown approach).
- Though this technique is very simple and cost-effective, it has several limitations.
- The main disadvantage of it is that we cannot generate non-agglomerated nanoparticle with homogeneous size distribution, or cannot control shape of the nanoparticles



Physical Vapor Deposition



 Physical vapor deposition (PVD) is a typical technique for thin film formation procedure, where a target is used to transfer the source material to grow on the surface of a substrate.
- Laser ablation is a modified evaporation technique that relies on the heating process by laser [6]. Generally, pulsed beam laser is used for the procedure. Depending on the type of material to be deposited, the wavelength of the laser is modified. Low energy conversion is the main drawback of the process (Fig. 4).
- Molecular beam epitaxy (MBE) is a modified evaporation technique for single crystal growth [8]. The operation principle is the same as evaporation but here <u>ultrahigh vacuum condition is used</u>. Molecular beams are generated by heating the <u>solid materials placed in the source cells</u>, which is referred to as Knudsen cells.

Fig. 3 SEM image of ZnO thin film by thermal evaporation (reprinted with permission from Yao et al. [5]). © AIP 2002



Though **MBE is very expensive**, it is popular because

1.Ultrahigh vacuum guarantees for negligible contamination.

2. Any in situ characterization tools like X-ray photoelectric spectroscopy (XPS), auger electron spectroscopy (AES), reflection high-energy electron diffraction (RHEED), etc., can be attached to monitor and further characterization without altering the ambient condition.

- **3**. Use of single crystal substrate
- 4. Individual evaporation rate control of different sources.
- 5. Slow growth rate
- 6. Low growth temperature
- 7. Formation of hyper abrupt surface
- 8. Precise control helps to grow 2D layers.

Sputtering

• The basic sputtering unit consists of a target or cathode, anode (substrate), and a sputtering medium where the target is bombarded by energetic particles.



Chemical Vapor Deposition

• In CVD, the reaction occurs in gas phase giving a nonvolatile solid, which can be deposited on a suitable substrate to make it a thin film. The CVD includes wide varieties of reactions like pyrolysis, reduction, oxidation, disproportionations, reversible transfer, etc., depending on the activation of the CVD process, it is divided into several methods like:

<u>Thermal activation</u>

In thermally activated CVD, high temperature (>900 °C) is required. But in the case of organometallic components, this operates at relatively low temperature, called metal-organic CVD (MOCVD).

Plasma activation

Basically, it is low-temperature CVD, lies in the range of 300–500 °C. It is typically called as PECVD (**plasma-enhanced CVD**), where the plasma are excited by RF (100 kHz–40 MHz) or by microwave.

• Photon activation

Photon-activated CVD involves the direct activation of reactant in the presence of **shortwave ultraviolet radiation**.

Techniques of obtaining CNTs



Techniques of obtaining CNTs

CVD method



Chemical Bath Deposition

- Preparation of <u>low-cost large</u> area thin film from aqueous solutions (in general)
- It does not require high voltage equipment, works at room temperature, and hence it is inexpensive
- The major problem of the CBD method is the inefficiency of the process which converts the precursor materials into useful deposits.
- Film formation may take place from two distinct mechanisms.
- **The first** one is a growth mechanism involving the reaction of • atom-by-atom process, also called "ion-by-ion."
- The second deposition mechanism is associated to the • agglomeration of colloids formed in the solution that may be considered a **cluster-by-cluster** growth process.



probe

Characterization of Nanomaterials

Lecture4

Characterization Instruments



Scanning Electron Microscope

Transmission Electron Microscope (TEM)

Atomic Force Microscopy

UV-Visible Spectroscopy

Optical Characterization by Ellipsometry

Nuclear Magnetic Resonance

X-ray Diffraction

Characterization by X-ray Diffraction

The wavelength of X-ray (characteristic X-ray is used) is comparable to that of interplanar spacing of crystalline material, so diffraction effects can be observed. This diffraction phenomenon is generally used to determine:

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(1) Fine structure of materials.(2) Chemical analysis.

- (3) stress determination.
- (4) particle size calculation.

The condition of interference maxima i.e., 2d sin h ¼ nk ('n' is any integer) is known as Bragg's law

B. Scanning Electron Microscopes (SEM) and Transmission Electron Microscopes (TEM)

Scientific instruments that use a beam of energetic electrons to examine objects on a very fine scale

Visualize very small topographic details of the sample surface



Scanning Electron Microscopes (SEM) and Transmission Electron Microscopes (TEM)

- For both techniques, electrons are used in order to acquire images of samples.
 their main components are the same; An electron source
- A series of electromagnetic and electrostatic lenses to control the shape and trajectory of the electron beam;
- ✤ Electron apertures.
- ✤ All of these components live inside a chamber which is **under high vacuum**.

	SEM	ТЕМ
Type of electrons	Scattered, scanning electrons	Transmitted electrons
Specimen thickness	Any	Typically <150 nm
Type of info	3D image of surface	2D projection image of inner structure
Max. magnification	Up to ~1 – 2 million times	More than 50 million times

The main difference between SEM and TEM is that SEM creates an image by detecting reflected or knocked-off electrons while TEM uses transmitted electrons (electrons which are passing through the sample) to create an image.

TEM offers valuable information on the inner structure of the sample, such as crystal structure, morphology and stress state information,

SEM provides information on the sample's surface and its composition.





Figure 1: Electron microscopy images of silicon. a) SEM image with SED offers information on the morphology of the surface, while b) TEM image reveals structural information about the inner sample.

UV-Visible Spectroscopy



Fig. 14 Schematic of UV-visible spectrophotometer (Source www.wikipedia.org)

Optical Characterization by Ellipsometry



Application of Nanomaterials

Lecture5

Photovoltaic Devices

Principles- Conduction mechanisms of semiconductors

- Intrinsic conductivity: Semiconductors are conductive beyond a certain temperature level as valence electrons are released from their chemical bonds with increasing temperatures and thus reach the conduction band (intrinsic conductivity).
 - Once electrons are able to move freely through the crystal lattice (i.e. electron conduction)= Semi. Will be a conductive material.
- Movement of electron= left holes in the V.B
- Holes thus **contribute equally to conductivity** (hole conduction).
- At Semiconductor both types (e&h) of charge carriers equally exists.



Principles- Conduction mechanisms of semiconductors

- If an external voltage is applied to such a crystal lattice from outside, electrons move to the positive pole while the holes move to the negative pole.
- Extrinsic conduction:
- In addition to the low intrinsic conduction of pure crystal lattices extrinsic conduction is created by intentional incorporation of foreign atoms ("doping").
- Such *impurities* are effective if their number of valence electrons differs from that of the base material.



Principles- Conduction mechanisms of semiconductors

- The valence electron number of the incorporated impurities exceeds that of the lattice atom (e.g. in pentavalent arsenic (As) incorporated into tetravalent silicon (Si) lattice, the excess electron is <u>only weakly bound to the impurity atom</u>.
- It thus separates easily from the impurity atom due to thermal movements within the lattice and increases the conductivity of the crystal lattice as a freely moving electron.
- Such foreign atoms which increase the number of electrons are referred to as **donor atoms**.
- In this case electrons are called majority carriers, whereas the holes constitute the minority carriers.



Principles- Photo effect

- The term "photo effect" refers to the energy transfer from photons (i.e. quantum of electromagnetic radiation) to electrons contained inside material.
- Photon energy is thereby converted *into potential and kinetic energy of electrons*.



• The electron absorbs the entire quantum energy of the photon defined as the product of Planck's quantum and the photon frequency.

Principles- Photovoltaic cell and module



I : current flowing through the terminals

IPh: photocurrent

*I*₀: saturation current of the diode e_0 represents the elementary charge (1.6021 10^{-19} C)

•An illuminated solar cell ideally can be considered as a current source provided with a parallel diode.

•The photocurrent IPh is assumed to be proportional to the photon flow incident on the cell.

•<u>The Shockley equation for ideal diodes</u> describes the interdependence of current and voltage (current-voltage characteristic) of a solar cell.

Efficiencies and Losses



CuInSe: Copper indium diselenide InP: Indium phosphide

CdTe: Cadmium telluride

Theoretical efficiencies of various types of simple solar cells under average conditions



What is an OPV?



^[1] Gómez, R. Segura, J, L. Plastic Solar Cells: A Multidisciplinary Field to Construct Chemical Concepts from Current Research, Journal of Chemical Education, 84

Why are OPVs Attractive?

Solution processed device

- Access printing fabrication on flexible substrates.
 - ➤Large area, fast deposition

≻Low cost

However, the <u>materials costs</u> for efficient devices <u>still high</u>







OPVs Device Architectures





Light incident

(a) Bilayer OPV





Light incident

(b) BHJ device structure





(c) NPs device structure

What we are need in OPVs?

(1) Light absorption

- (2) Exciton diffusion
- (3) Exciton dissociation
- (4) Charge carrier transport
- (5) Charge extraction
- (6) Charge carrier recombination



A good device should has a charge transport process higher than recombination losses.

Fabrication steps of Organic Nanoparticle ink.



Nanoparticle ink

Nanoparticle dispersion

Preparing OPV – P3HT: PCBM (NPs)

- Devices prepared by standard procedures
 - Active layer thickness ~100 nm
 - HTL→ PEDOT:PSS (40 nm)
- Active area (5 cm²)
- Device JV properties were measured with AM1.5 lamp at clean room before and after preformed the transient PAIOS measurements.



Gas Sensor

Fundamental of Gas Sensor

(i) Oxygen monitoring for health and combustion engines, boilers, etc.

(ii) Inflammable gases like methane, LPG, CNG, hydrogen) monitoring to prevent hazards.

(iii) For toxic gases (i.e., gases like carbon monoxide, sulfur dioxide, chlorine) and automobile exhaust polluants like SOx, KNOx, etc.).

(iv) **Relative humidity** is an important parameter in weather monitoring and climate control.



Gas sensor **Response and Requirement**



Sensor structure and its measurement



Layered Double hydroxides (LDHs)

Layered Double hydroxides (LDHs)

- LDHs are highly class of layered materials for many applications (e.g. supercapacitors, Lithium Ion batteries, Dye-Sensitized Solar cells).
- LDHs structure is similar magnesium hydroxide brucite structure. The divalent cation is substituted by trivalent cation in the cationic sheets.
 - The general formula is





Wang, Qiang, and Dermot O'Hare. *Chemical reviews* 112.7 (2012): 4124-4155. Shao, Mingfei, et al. *Chemical Communications* 51.88 (2015): 15880-15893. Wang, Jun, et al. *Energy & Fuels* 24.12 (2010): 6463-6467. Guoxiang, Pan, et al. *Applied Clay Science* 102 (2014): 28-32. Sideris, Paul J., et al. Science 321.5885 (2008): 113-117.













SIU Southern Illinois University

Ahmed S. Al-Asadi et al 2017 (Under Preparation)

Summery and Conclusion

- □ 2D materials have a great potential <u>on various applications</u>.
- □ 2D materials can be obtained using <u>simple chemical methods</u>.
- □ High electrochemical performance can be achieved using 2D
 - materials as electrodes.

What is next?





2D materials: Graphene and Beyond Graphene

Well-Known Energy Storage systems

What exactly we are looking for?



Energy Density (Wh/kg)

- ✤ High energy and power density.
- Long life cycle.
 - Fast charging cell.
 - ✤ Safety
 - Low cost





Mechanism of Energy Storage systems



CARBONDALE

TEM images

