# **MODULE-5**

# **Instrumental methods of analysis and Nanomaterials**

# **Instrumental Method of Analysis**

## **Colorimetry**

**Theory:-** Chemical analysis through measurement of absorption of light of a particular wavelength is known as Colourimetry.

#### Beer - Lambert's Law:

When a monochromatic (light having only one colour) radiation of intensity 'I' is passed through a solution of a sample under investigation taken in a cell of thickness 't' a portion of radiation is absorbed ( $I_a$ ), a portion is reflected ( $I_r$ ) and the remainder is transmitted ( $I_t$ ) then,  $I = I_a + I_r + I_t$ 

In the case of transparent medium the intensity due to reflection is negligible, Therefore,  $\mathbf{I} = \mathbf{I_a} + \mathbf{I_t}$ 

### Lambert's Law:

It states that "when monochromatic light passes through a transparent medium, the rate of decrease in intensity with the thickness of the medium is proportional to the intensity of the light mathematically it can be expressed as

$$\frac{-dI}{dt} = KI$$

Here 'K' is proportionality constant

Writing the above eqn

$$-dI$$
 = K. dt

Integrating this eqn & substituting  $I = I_0$  when t=0

$$\frac{\ln I_0}{I_t} = Kt \qquad \qquad \mathbf{I_t} = \mathbf{I_0} \ \mathbf{e^{-kt}}$$

This eqn shows the exponential decrease in intensity of transmitted light with the increase in thickness of the medium

#### Beer's law:

This law is stated as 'The intensity of the transmitted light decreases exponentially as the concentration of the medium increases arithmetically, mathematically this may be expressed as

It = 
$$I_0 e^{-kc}$$

Where C – Molar Concentration (mol/dm3) of the sample solution combining eqn for beer's law & Lambert's law eqn for **Beer Lambert's** law can be written as

$$\mathbf{I_t} = \mathbf{I_0} e^{-kct}$$
$$\mathbf{I_t} = \mathbf{I_0} / \mathbf{10}^{\text{ ect}}$$

Where  $\varepsilon$  called molar absorption coefficient is is a constant for a given substance at a given wavelength,

It is expressed in dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>. The above eqn can be written as

$$\underset{I_t}{\text{Log}}\,\underline{I_0} \!= \epsilon c$$

If  $\underline{I_0}$  is called transmittance then  $\underline{Log I_0}$  is called absorbance (A),

E- Molar absorption co-efficient is constant for a given substance at a given wavelength,

C- concentration of the medium and path length or thickness (t) of the medium and is referred as Beer – lambert's law

$$A = \epsilon ct = Log \underline{I}_0 = Log \underline{1} = -log T$$

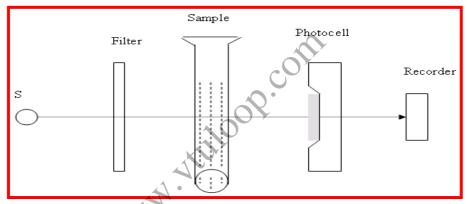
$$\underline{I}_t \qquad T$$

Path length of the cell is kept constant, and then absorbance 'A' is proportional to the concentration.

#### **Instrumentation**

The essential parts of colorimeter are

- 1. Light Source-Mercury lamp.
- 2. Filter- To filter undesired radiations, it allows radiations of a definite wave length range to pass through it and reach the sample
- 3. Kuwatte- To take sample
- 4. Photocell- To receive the transmitted light.
- 5. Recorder to record the absorbance in nm.



# **Application:** Colorimetric determination of copper

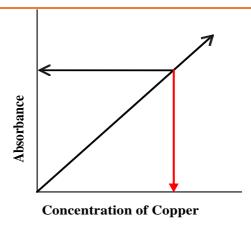
When cupric ions are treated with ammonia, it gives deep blue coloured cupra ammonium compound. The absorbance is measured at 620 nm( $\lambda_{max}$ ). Since the complex shows the absorbance maximum at this straight line will be obtained. From this unknown solution concentration can be obtain by measuring the absorbance of unknown solution.

$$Cu^{2+} + 4(NH_3)$$
  $\longrightarrow$   $[Cu(NH_3)_4]^{2+}$   
Deep blue colour

#### **Procedure:-**

Take known amount of standard solution 2, 4, 6, 8 and 10 cm<sup>3</sup> in deferent 25 cm<sup>3</sup> standard flasks, add 2.5 ml of ammonia into each of these flask and make up to the mark with distilled water. Stopper the flask and mix the solutions well. After measure the absorbance of all solutions against blank at 620 nm using a photo electric colorimeter. Note down the optical density of all solutions and tabulate the readings. Draw a calibration curve by plotting absorbance against concentration of copper or volume of copper of solution taken. Using fine calibration curve find out the unknown volume of copper sulphate solution

given and calculate the amount of copper present in it (Blank solution -2.5 ml ammonia and water in standard flask)



# **Potentiometry**

#### **Theory**

Determination of concentration of ionic solution by measuring the emf (electromotive force) is reffered to as potentiometry.

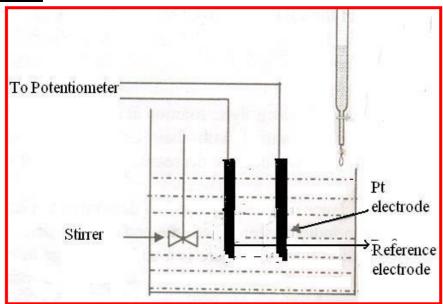
Potentiometric methods include two types of measurement a) direct measurement of an electrode potential from which the concentration of an active ion may be found.
b) changes in the emf of an electrolytic cell brought about by an addition of a titrant.

The potential of an electrode is given by Nernst eqn,

$$E = E^{0} + \frac{0.0591}{n} log [M^{n+}]$$

 $E^0 \Longrightarrow Standard$  electrode potential, Electro potential depends on the concentration of the ion. ( $E^0$  – It is the electrode potential of a metal in contact with its ions in 1 molar)

#### **Instrumentation:-**



The Potentiometer consists of a reference electrode, an indicator electrode and potential measuring device. The indicator electrode response rapidly to the changes in the

concentration of analysis i.e the solution understudy. This is made up of platinum, indium, gold and other noble gases. The potential of the indicator electrode is measured using an electrode known as reference electrode. It is made up of mercury, mercury oxide or silver-silver chloride. A known volume of analyte is taken and its potential is determined. The titrant is added in increment of 1ml and the emf is measured each time at equivalence point, the emf tends to increase rapidly.

At this point readings are more taken frequently at the intervals of 0.1cm3 to find the equivalence point plot a graph of  $\Delta E/\Delta V$  Vs volume of the titrant added.

# **Applications**

# a) Acid-base titration

It is known that the neutralization of acid and bases is always accompanied by the changes in the concentration of H<sup>+</sup> and OH<sup>-</sup> ions, Hydrogen electrode is measured in these titration A known volume of an acid (HCl) to be titrated is kept in a beaker having an a automatic stirrer and is titrated against base NaOH. An electrode potential depends on hydrogen ion concentration is analyte emf of the cell (H<sub>2</sub> electrode) is given by

# $E = E^0 - 0.0591 \log [H^+]$

E<sup>0</sup> Standard electrode potential

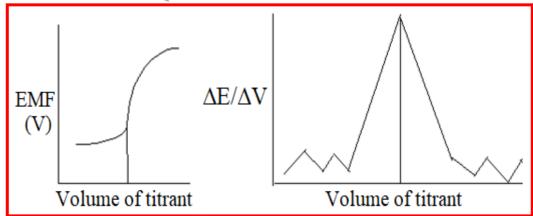
We know  $pH = -log [H^+]$ 

$$E = E^0 + 0.0591 \text{ pH}$$

When the titration proceeds H<sup>+</sup> ion concentration goes on decreasing this results pH goes on increasing, the changes in electrode potential (or) emf of the cell is proportional to the change in pH during titration.

Therefore emf of the cell increases, initially the emf changes slowly and then rapidly as the neutralization point approach. After equivalence point, further addition of NaoH produces the little change in H+ concentration and hence there is no significant change in emf

For finding endpoint plot a graph of change in emf again the volume of titrant . A more sensitive and satisfactory method of finding the endpoint to plot a graph of  $\Delta E/\Delta V$  against V.



b) Oxidation Reduction reactions; Estimation of amount FAS in FAS solution FAS vs.  $K_2Cr_2O_7$ 

Redox reaction can be followed by an inert indicator electrode (i.e Pt).

The Electrode potential is proportional to log of the concentration ratio of the oxidation states of reactant

#### Oxidized form + n electrons → Reduced form

Electrode potential at 25 °C is given by

$$E = E^0 + 0.0591 \log_{10} \text{ (Oxidized form)}$$
  
-n (Reduced form)

- These titration involves the transfer of electrodes from the substance being oxidized to the substance being reduced
- In this titration the potential of the two systems are important i.e the one oxidized and one reduced, the change of potential end point is maximum generally the oxidizing agent is placed in burette.

### Eg: Iron (II) with K2Cr2 O7

$$Fe^{2+} \longrightarrow Fe^{3+} + 1e$$

$$K_2Cr_2O_7 + 14H + 6e \longrightarrow 2 Cr^{3+} + 7 H_2O$$

$$E = E_{\frac{Fe^{3+}}{Fe^{2+}}}^{\circ} + \frac{0.0591}{1} \log \left(\frac{Fe^{3+}}{Fe^{2+}}\right)$$

$$E = E_{\frac{Cr^{6+}}{Cr^{3+}}}^{\circ} + \frac{0.0591}{3} \log \left(\frac{Cr^{6+}}{Cr^{3+}}\right)$$

#### **Conductometry**:

Conductometry is an electrochemical method of analysis based on measuring the resistance of an electrolytic solution.

**<u>Definition of conductance:</u>** Reciprocal of resistance is called conductance i.e. C=1/R It is expressed in ohm<sup>-1</sup> or Mho.

**Theory:** Ohm's law states that the current (I) in amperes flowing in a conductometer is directly proportional to the applied emf. E (vol) and inversely proportional to the resistance, R (ohm) of the conductor.

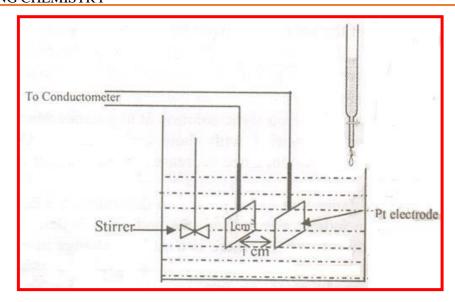
$$I = E$$

The reciprocal of resistance is called the conductance.

The theory involved in conductometric titration is that conductance of an electrolytic solution depends upon the nature, number, and mobility of the ions in solution. Larger the concentration of fast mobile ions higher will be the conductance and Vice versa.

#### Instrumentation:

Conductometer consists of two platinum electrodes and a conductance measuring device. The two electrodes have unit area of cross section and are placed unit distance apart. The assembly responds rapidly to the changes in the concentration of the analyte.



### **Applications:**

1. Strong acid Vs strong base: (HCL V/S NaOH)

$$HCl(H^+ + Cl^-) + NaOH(Na^+ + OH^-) \longrightarrow NaCl(Na^+ + Cl^-) + HQ$$

In the case of strong acid and strong base, the conductance 1<sup>st</sup> falls, due to the replacement of highly mobile H<sup>+</sup> ion by less mobile Na<sup>+</sup> ions. After the equivalence point, the conductance rapidly rises with further addition of strong base and is due to increase in the concentration of the OH<sup>-</sup> ions.

# 2. Mixture of strong acid and a weak acid Vs strong base (HCl & CH3COOH V/S NaOH)

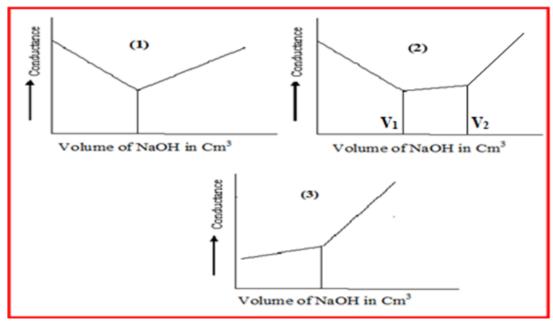
$$HC1(H^{+} + C1^{-}) + CH_{3}COOH(CH_{3}COO^{+} + H^{+}) + NaOH(Na^{+} + OH^{-})$$
 NaC1 + CH<sub>3</sub>COONa + H<sub>2</sub>O

In aqueous solution of a mixture of acids, one can expect preferentially the neutralization of a strong acid with a strong base like NaOH and the completely ionized H<sup>+</sup> ions of the strong acid reacts with OH<sup>-</sup> ions of the strong base giving unionized water. When every H<sup>+</sup> ions of the strong acid is neutralized; the first end point is obtained.

The weak acid does not get neutralized initially because of the well-known commonion effect. In the presence of excess of  $H^+$  ions, the ionization of the weak acid is suppressed and hence, the weak acid does not provide  $H^+$  ions for neutralization during the first phase of titration.

A weak acid like CH<sub>3</sub>COOH, ionizes gradually after the first end point and the available H<sup>+</sup> ions are neutralized, giving the second end point.

### 3. Weak acid Vs strong base (CH<sub>3</sub>COOH V/S NaOH)



#### Advantages:

- 1. Mixtures of acids can be titrated
- 2. Accurate in dilute solutions
- 3. Very weak acids which can't be titrated potentiometrically but it can be titrated conductometrically

# Advantages of Instrumental method of Analysis over Chemical analysis:

- 1. Chemical methods are time consuming procedures. It requires large time for analysis but instrumental methods are much faster.
- 2. Chemical methods require large amount of the analyte (sample) but instrumental method requires very small amount of sample like ppm level.
- 3. They are wide applications in industries.
- 4. The analytical process can be automated.

#### **Disadvantages:**

- 1. The instruments are expensive
- 2. An initial or continuous calibration is required using a sample of material of known composition
- 3. The concentration range is limited
- 4. Specialized training is needed for the operation of certain sophisticated instruments

#### Flame photometry

#### **Principle**

Sodium, potassium, calcium and lithium and other common elements impart characteristic colors with the bunsen flame. the intensity of the colored flame varies with the amount of element introduced, this forms the basis of flame photometry

When a solution containing a compound of the metal to be investigated is aspirated into a flame, the following processes occur.

- i) Solvent evaporates leaving behind a solid residue.
- ii) Vaporization of the solid coupled with dissociation into its constituent atoms, which are initially in the ground state.

iii) Some gaseous atoms get excited by the thermal energy of the flame to higher energy levels.

The excited atoms, which are unstable quickly, emit photons and return to lower energy state i.e. ground state. Flame photometry involves the measurement of emitted radiation.

The relationship between the ground state and excited state populations is given by the Boltzmann equation:

 $N_1/N_0 = (g/g) e^{\Delta E/kT}$ 

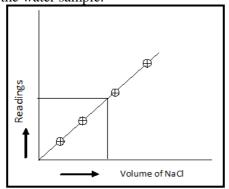
N = Number of atoms in the excited state; <math>N = Number of atoms in the ground state, <math>g/g = ratio

of statistical weights for ground and excited states;  $\Delta E$  = Energy of excitation = hv, k is the Boltzmann constant; T = Absolute Temperature

From the above equation, it is evident that the ratio  $N_1/N_0$  is dependent upon both the excitation energy E and the temperature T. An increase in temperature and a decrease in  $\Delta E$  will both result in a higher value for the ratio  $N_1/N_0$ .

#### **Procedure:**

- 1. Transfer 2, 4, 6, 8, 10 ml of standard NaCl solution (which is prepared by weighing accurately 1.271 g NaCl into a 1 liter standard volumetric flask and dissolving the crystals and diluting the solution up to the mark with distilled water and mixing. The solution gives 1 ppm Na/ml) into 50 ml standard volumetric flasks and dilute up to the mark with distilled water.
- 2. Place the distilled water in the suction capillary of the instrument and set the instrument to read zero.
- 3. Place each of the standard solutions in the suction capillary and set the instrument to read the flame emission intensity 2, 4, 6, 8 and 10 respectively (rinse with distilled water between each reading) using sodium filter (598 nm).
- 4. Dilute the given test solution up to the mark with distilled water, mix well and place the solution in the suction capillary and record the reading.
- 5. Draw a calibration curve by plotting the emission intensity (Y-axis) and volume of NaCl solution (X-axis).
- 6. From the calibration curve, find out the volume of the given test solution and from which calculate the amount of Na in the water sample.



# **Atomic Absorption Spectroscopy**

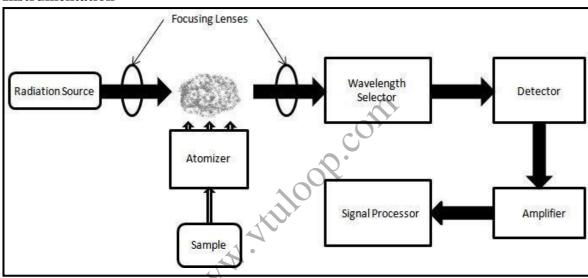
**Atomic absorption spectroscopy** (**AAS**) is a spectroanalytical procedure for the quantitative determination of chemical elements using the absorption of optical radiation (light) by free atoms in the gaseous state.

#### **Principle:**

The technique makes use of absorption spectroscopy to assess the concentration of an analyte in a sample. It requires standards with known analyte content to establish the relation between the measured absorbance and the analyte concentration and relies therefore on the **Beer-Lambert Law.** 

In short, the electrons of the atoms in the atomizer can be promoted to higher orbitals (excited state) for a short period of time (nanoseconds) by absorbing a defined quantity of energy (radiation of a given wavelength). This amount of energy, i.e., wavelength, is specific to a particular electron transition in a particular element. In general, each wavelength corresponds to only one element, and the width of an absorption line is only of the order of a few picometers (pm), which gives the technique its elemental selectivity. The <u>radiation flux</u> without a sample and with a sample in the atomizer is measured using a detector, and the ratio between the two values (the absorbance) is converted to analyte concentration or mass using the Beer-Lambert Law.

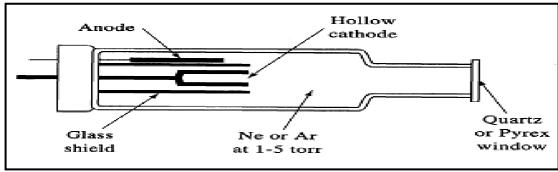
#### Instrumentation



# **Light sources**

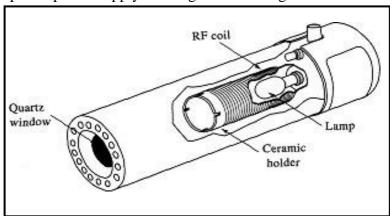
#### a). Hollow Cathode Lamps

Hollow cathode lamps (HCL) are the most common radiation source in LS AAS. Inside the sealed lamp, filled with argon or neon gas at low pressure, is a cylindrical metal cathode containing the element of interest and an anode. A high voltage is applied across the anode and cathode, resulting in an ionization of the fill gas. The gas ions are accelerated towards the cathode and, upon impact on the cathode, sputter cathode material that is excited in the glow discharge to emit the radiation of the sputtered material, i.e., the element of interest. Most lamps will handle a handful of elements, i.e. 5-8. A typical machine will have two lamps, one will take care of five elements and the other will handle four elements for a total of nine elements analyzed.



#### b). Electrodeless Discharge Lamp

<u>Electrodeless discharge lamps</u> (EDL) contain a small quantity of the analyte as a metal or a salt in a quartz bulb together with an inert gas, typically argon gas, at low pressure. The bulb is inserted into a coil that is generating an electromagnetic radio frequency field, resulting in a low-pressure inductively coupled discharge in the lamp. The emission from an EDL is higher than that from an HCL, and the line width is generally narrower, but EDLs need a separate power supply and might need a longer time to stabilize.



### **Atomizers**

The atomizers most commonly used nowadays are (spectroscopic) flames and electrothermal (graphite tube) atomizers. Other atomizers, such as glow-discharge atomization, hydride atomization, or cold-vapor atomization might be used for special purposes.

#### Flame atomizers

The oldest and most commonly used atomizers in AAS are flames, principally the airacetylene flame with a temperature of about 2300 °C and the nitrous oxide system (N<sub>2</sub>O)-acetylene flame with a temperature of about 2700 °C. The latter flame, in addition, offers a more reducing environment, being ideally suited for analytes with high affinity to oxygen. Liquid or dissolved samples are typically used with flame atomizers. The sample solution is aspirated by a pneumatic **analytical nebulizer**, transformed into an **aerosol**, which is introduced into a spray chamber, where it is mixed with the flame gases and conditioned in a way that only the finest aerosol droplets ( $< 10 \, \mu m$ ) enter the flame. This conditioning process is responsible that only about 5% of the aspirated sample solution reaches the flame, but it also guarantees a relatively high freedom from interference.

#### **ELECTROTHERMAL ATOMIZER**

A cylindirical graphite tube
Inert gas medium (Argon gas)
Longer anlaysis time than flame
Superior sensitivity, high accuracy

#### Monochromator

Also it is called wavelengh selector
Select the specific wavelenght
Polychromatic light →monochromatic light
Simple one is enough for AAS

#### **DETECTOR**

A detector can be a mechanical, chemical, or electrical device that measures the change of a variable in its environment. In Atomic Absorption Spectroscopy, the amount of radiation that passes through a sample is measured and quantitatively described by transmittance.

	APPLICATIONS OF AAS
	Water analysis (e.g. Ca, Mg, Fe, Si, Al, Ba content)
	Food analysis
	Analysis of animal feedstuffs (e.g. Mn, Fe, Cu, Cr, Se,Zn)
	Analysis of soils
П	Clinical analysis (blood samples: whole blood, plasma, serum: Ca. Mg. Li. Na. K. Fe)

# **NANOTECHNOLOGY**

**Introduction**: Nanotechnology originates from the Greek word meaning " $\underline{dwarf}$ ". A nanometer is one billionth ( $10^{-9}$ ) of a meter, which is tiny, only the length of ten hydrogen atoms, or about one hundred thousandth of the width of a hair, Although scientists have manipulated matter at the nanoscale for centuries, calling it physics or chemistry, it was not until a new generation of microscopes was invented in the nineteen eighties in IBM, Switzerland that the world of atoms and molecules could be visualized and managed.

**Definition**: Nanotechnology can be defined as the manipulation of atoms and molecules (one billionth) scale (1-100 nm) to produce devices, structures or systems having at least one novel or superior property. Materials having at least one dimension in the nanoscale are called nanomaterials. **Conceptualization of nanotechnology was done by Richard Feynman in 1959.** The impact of nanotechnology is quite significant. When the bulk materials are reduced to nanometer size, the properties exhibited by these nonmaterial's are of tremendous use. For example,

- 1. Opaque materials become transparent (copper),
- 2. Insoluble substances become soluble (gold),
- 3. Stable materials become combustible (aluminium).

In fact, at normal scales, gold is chemically inert but at nanoscales, gold nanoparticles can serve as potent chemical catalysts. The study of these nanomaterials is known as **nanoscience**.

**Properties of nanomaterials**: Physical and chemical properties of nonmaterial's are significantly different from those of single atoms/molecules and bulk material of the same chemical composition.

#### Difference in properties is related to,

- 1. The spatial arrangement of molecules/structure,
- 2. Electronic structure,
- 3. Energetic,
- 4. Chemical reactivity
- 5. Phase change or catalytic activity.

Properties remain same at first (size being reduced from macro to micro), and slowly small changes begin to take place as the particle size is reduced further from micro to the nanoscale range (generally observed below, 100 nm).

# Size dependent properties

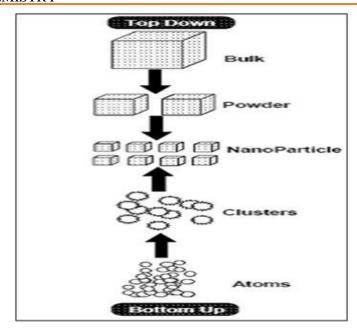
1). <u>Surface area:</u> If a macroscopic object is divided into smaller parts, the ratio of surface atoms to interior atoms becomes a significant number of total fractions of atoms. The inverse relation between the particle size and surface area is responsible for the remarkable changes in the physical properties of nonmaterial's.

Properties like catalytic activity, gas adsorption; chemical reaction depends on surface area. Ex: Gold is catalytically inactive in bulk but nano gold is highly catalytically active.

- 2). <u>Electrical properties:</u> Electronic bands in bulk material are continuous due to the overlap of billions of atoms, but in nano-size material very few molecules are present so electrical band separates. Hence some metals which are good conductors in bulk become semiconductor and insulator at the nano level.
- 3). <u>Optical Properties:</u> Nanomaterials exhibit different colors from bulk materials. The discrete electronic state of nanomaterial allows absorption and emission of light of specified.
- 4). Thermal properties: The large increase in surface energy and the change in interatomic spacing as a function of nanoparticle size mentioned above have a marked effect on material properties. For instance, the melting point of gold particles, which is really a bulk thermodynamic characteristic, has been observed to decrease rapidly for particle sizes less than 10 nm. Smaller particles have higher melting points.
- 5). <u>Catalytic properties</u>: Nanomaterial-based catalysts are usually heterogeneous catalysts broken up into metal nanoparticles in order to speed up the catalytic process. Metal nanoparticles have a higher surface area so there is increased catalytic activity because more catalytic reactions can occur at the same time. Nanoparticle catalysts can also be easily separated and recycled with more retention of catalytic activity than their bulk counterparts.

# **General methods of Synthesis:**

There are two approaches for the synthesis of nanomaterials and the fabrication of nanostructures. Top down approach refers to slicing or successive cutting off a bulk material to get nano-sized particle. Bottom-up approach refers to the build-up of a material from the bottom: atom by atom, molecule by molecule or cluster by cluster. Both approaches play very important role in modern industry and most likely in nanotechnology as well. There are advantages and disadvantages to both approaches.



#### Sol-gel process:

The sol-gel method of synthesizing nanomaterial is very popular amongst chemists and is widely employed to prepare oxide materials.

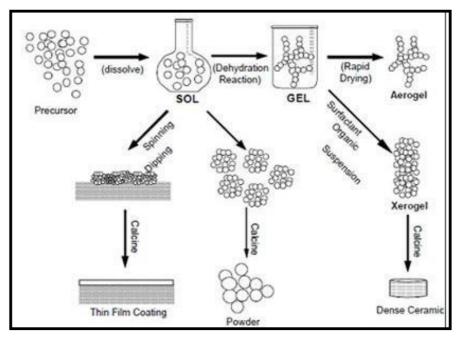
The sol-gel process can be characterized by a series of distinct steps.

**Step 1:** Formation of different stable solutions of the alkoxide or solvated metal precursor (**the sol**).

**Step 2: Gelation** resulting from the formation of an oxide- or alcohol- bridged network (the gel) by a polycondensation or polyesterification reaction that results in a dramatic increase in the viscosity of the solution.

 $MOR + H_2O \rightarrow MOH + ROH$ (hydrolysis)

 $MOH+ROM \rightarrow M-O-M+ROH$  (condn.)



**Step 3: Aging of the gel (Syneresis)**, during which the polycondensation reactions continue until the gel transforms into a solid mass, accompanied by contraction of the gel network and expulsion of solvent from gel pores. The aging process of gels can exceed 7 days and is critical to the prevention of cracks in gels that have been cast.

**Step 4: Drying of the gel**, when water and other volatile liquids are removed from the gel network. This process is complicated due to fundamental changes in the structure of the gel. The drying process has itself been broken into four distinct steps: (i) the constant rate period, (ii) the critical point, (iii) the falling rate period, (iv) the second falling rate period.

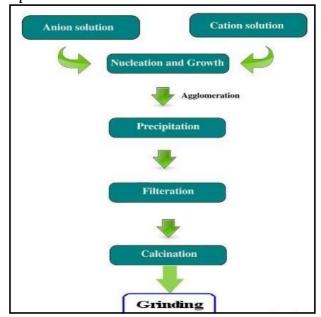
If isolated by thermal evaporation, the resulting monolith is termed a *xerogel*. If the solvent (such as water) is extracted under supercritical or near supercritical conditions, the product is an *aerogel*.

**Step 5: Dehydration**, during which surface- bound M-OH groups are removed, thereby stabilizing the gel against rehydration. This is normally achieved by calcining the monolith at temperatures up to  $800^{\circ}$ C.

**Step 6: Densification and decomposition** of the gels at high temperatures (T>800<sup>o</sup>C). The pores of the gel network are collapsed, and remaining organic species are volatilized. The typical steps that are involved in sol-gel processing are shown in the schematic diagram below.

# **Precipitation method**

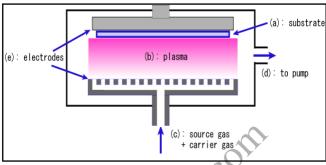
- In this technique, an inorganic metal such as acetate, chloride, nitrate is dissolved in aqueous medium.
- Metal cations exist in the form of metal hydrate species such as  $[Al(H_2O)_6]^{3+}$  and  $[Fe(H_2O)_6]^{3+}$ .
- When a precipitating agent such as NaOH or NH<sub>4</sub>OH is added, these species get
  hydrolysed with the increase in pH, condensation of hydrolysed species takes place.
  These concentration of the solution is is termed as supersaturation. At this concentration
  only, formation of nucleation initiates. The particles get precipitated into metal
  hydroxide.
- The above precipitate is filtered, washed with water and calcined at higher temperature to remove the counter anions of the metal salt used such as acetate or nitrate then finally grinding to get a fine powder.



### **Chemical Vapour Condensation (CVC) method**

Chemical vapor deposition (CVD) is a chemical process used to produce high quality, high-performance, solid materials. The process is often used in the semiconductor industry to produce thin films. In typical CVD, the wafer (substrate) is exposed to one or more volatile precursors, which react and/or decompose on the substrate surface to produce the desired deposit. Frequently, volatile by-products are also produced, which are removed by gas flow through the reaction chamber.

Microfabrication processes widely use CVD to deposit materials in various forms, including: monocrystalline, polycrystalline, amorphous, and epitaxial. These materials include: silicon, carbon fiber, carbon nanofibers, fluorocarbons, filaments, carbon nanotubes, SiO2, silicon-germanium, tungsten, silicon carbide, silicon nitride, silicon oxynitride, titanium nitride, and various high-k dielectrics. CVD is also used to produce synthetic diamonds.



# **Carbon Nanotubes**

- 1. In 1991, during the optimization of the fullerene-synthesis by arc discharges, small tubes were found (by Sumio Iijima, characterized by transmission electron microscopy TEM).
- 2. Nanotubes are members of the fullerene structural family (a name derived from their long, hollow structure with the walls formed by one-atom-thick sheets of carbon, called graphene).
- 3. These sheets are rolled at specific and discrete ("chiral") angles, and the combination of the rolling angle and radius decides the nanotube properties.
- 4. Individual nanotubes naturally align themselves into "ropes" held together by van der Waals forces, more specifically, pistacking.
- 5. Nanotubes are categorized as singlewalled nanotubes (SWNTs) and multiwalled nanotubes (MWNTs) and Doublewall Nanotubes (DWNT).
- The chemical bonding of nanotubes is composed entirely of  $sp^2$  bonds, similar to those of graphite. These bonds, which are stronger than the  $sp^3$  bonds found in alkanes and diamond, provide nanotubes with their unique strength.

#### **Preparation:**

Nanocyl uses the "Catalytic Carbon Vapor Deposition" method for producing Carbon Nanotube Technologies. This proven industrial process is well known for its reliability and scalability. It involves growing nanotubes on substrates, thus enabling uniform, large-scale production of the highest-quality carbon nanotubes worldwide.

# **Properties:**

- 1. Carbon nanotubes are the strongest and stiffest materials yet discovered in terms of tensile strength (~100 GPa) and elastic modulus respectively (due to covalent sp² bonds).
- 2. Standard single-walled carbon nanotubes can withstand a pressure up to 25 GPa without deformation.
- 3. Maximum electrical conductance of a single-walled carbon nanotube is  $2G_0$ ,
- 4. All nanotubes are expected to be very good thermal conductors along the tube, exhibiting a property known as "ballistic conduction".

**Applications:** Conductive plastics, Structural composite materials, Flat-panel displays, Gas storage Antifouling paint, Micro- and nano-electronics, Radar-absorbing coating, Technical textiles, Ultra-capacitors, Atomic Force Microscope (AFM) tips, Batteries with improved lifetime, Biosensors for harmful gases, Extra strong fibers.

#### <u>Fullerenes</u>

Fullerene a new allotrope of carbon, in which the atoms are arranged in closed shells, having the structure of a truncated icosahedron (a polyhedron). (Nobel Prize, 1996 for Kroto, Curl and Smalley). Named as Buckminsterfullerene (after Buckminster Fuller who designed geodesic domes in the 1960's).

- 1. First time produced isolable quantities of C60 by causing an arc between two graphite rods to burn in a helium atmosphere (extracting the carbon condensate so formed using an organic solvent).
- 2. Other carbon clusters such as C70, C76, C78 and C84 are also studied, with new and unexpected properties, which lead to a new branch of chemistry developed, with consequences in such diverse areas as astrochemistry, superconductivity and materials chemistry/physics.
- 3. Fullerenes consist of 20 hexagonal and 12 pentagonal rings as the basis of an icosahedral symmetry closed cage structure, with each carbon atom is bonded to three others and is sp2 hybridised.
- 4. C60 molecule has two bond lengths the 6:6 ring bonds can be considered "double bonds" and are shorter than the 6:5 bonds. C60 is not "super aromatic" as it tends to avoid double bonds in the pentagonal rings, resulting in poor electron delocalisation and hence C60 behaves like an electron deficient alkene, and reacts readily with electron rich species.
- 5. The most striking property of the C<sub>60</sub> molecule is its high symmetry. There are 120 symmetry operations (*most symmetric molecule*), like rotations around an axis or reflections in a plane, which map the molecule onto itself.

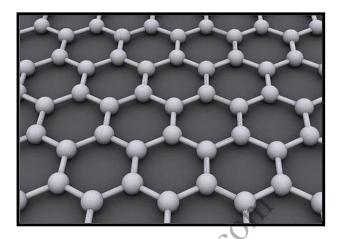
#### **Applications**

Fullerenes have been extensively used for several biomedical applications including the design of high-performance MRI contrast agents, X-ray imaging contrast agents, photodynamic therapy and drug and gene delivery.

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#### Graphenes

Graphene is a semi-metal with small overlap between the valence and the conduction bands (zero bandgap material). It is an allotrope (form) of carbon consisting of a single layer of carbon atoms arranged in a hexagonal lattice. It is the basic structural element of many other allotropes of carbon, such as graphite, diamond, charcoal, carbon nanotubes and fullerenes.



Graphene is a crystalline allotrope of carbon with 2-dimensional properties. Its carbon atoms are densely packed in a regular atomic-scale chicken wire (hexagonal) pattern.

Each atom has four bonds: one  $\sigma$  bond with each of its three neighbors and one  $\pi$ -bond that is oriented out of plane. The atoms are about 1.42 Å apart.

Graphene's hexagonal lattice can be regarded as two interleaving triangular lattices. This perspective was successfully used to calculate the band structure for a single graphite layer using a tight-binding approximation. Graphene's stability is due to its tightly packed carbon atoms and a sp<sup>2</sup> orbital hybridization – a combination of orbitals s,  $p_x$  and  $p_y$  that constitute the  $\sigma$ -bond. The final  $p_z$  electron makes up the  $\pi$ -bond. The  $\pi$ -bonds hybridize together to form the  $\pi$ -band and  $\pi$ \*-bands. These bands are responsible for most of graphene's notable electronic properties, via the half-filled band that permits free-moving electrons.

#### **Applications**

- Graphene is a transparent and flexible conductor that holds promise for various material/device applications, including solar cells, light-emitting diodes (LED), touch panels and smart windows or phones.
- Graphene has also been used in other fundamental electronic devices, such as capacitors and Field Effect Transistors (FETs).