CYE12 **Unit- 4, Nanomaterials and Electrochemical Sensors**

31-01-2023

Nano materials

Introduction:

Nanomaterials are corner stones of nanoscience and nanotechnology. Nanostructure science and technology is a broad and interdisciplinary area of research and development activity that has been growing explosively worldwide in the past few years. It has the potential for revolutionizing the ways in which materials and products are created and the range and nature of functionalities that can be accessed. It is already having a significant commercial impact, which will assuredly increase in the future.

Nanoscience: The study of phenomena and materials at the atomic, molecular and macromolecular scales, where properties differ significantly from those at the larger scale

Nanotechnology: Design, characterization, production and application of structures, devices and systems by controlling morphology (size, shape and distribution) at the nano-scale.

Q What are nanomaterials?

Nanoscale materials are defined as a set of substances where at least one dimension is less than approximately 100 nanometers. A nanometer is one millionth of a millimeter - approximately 100,000 times smaller than the diameter of a human hair. Nanomaterials are of interest because at this scale unique optical, magnetic, electrical, and other properties emerge. These emergent properties have the potential for great impacts in electronics, medicine, and other fields.

Q How nanomaterials are synthesized?

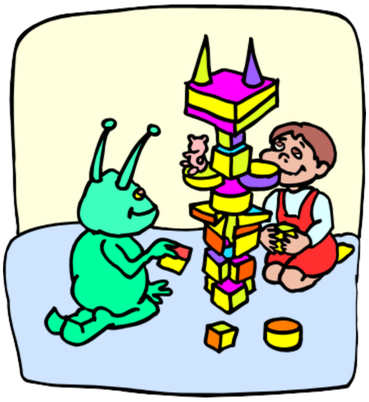
Nanomaterials are made by two generalized processes

(i) **Top down:** Start with the big chunk and cut away material to make what you want. It begins with bulk materials that are subsequently reduced into nanomaterials.

Ex: Inert gas condensation, Ion beam technique, Laser ablation, etc

(i) **Bottom -up:** Building what you want by assembling it from small prefabricated units molecules react under chemical or physical circumstances to form nanomaterials. such as atoms and molecules. It *begins* with atoms and molecules/. These atoms or

Ex: Hydrothermal, Sol-gel method, Co-precipitation and Combustion synthesis

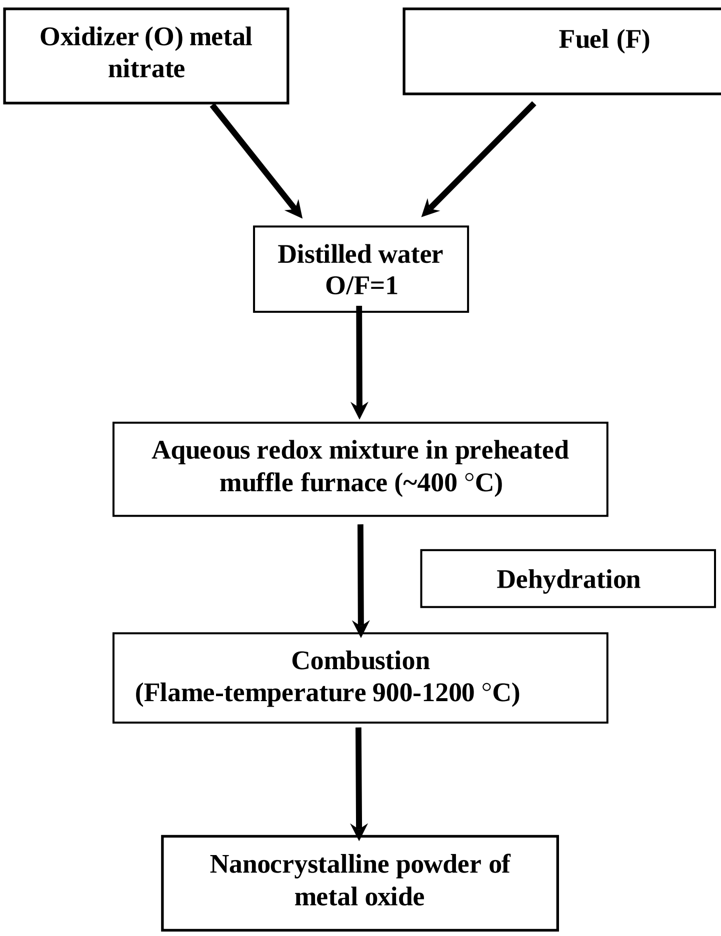


Bottom -up

Top down

Q. What is solution combustion synthesis? Explain synthesis of nano ZnO particles using solution combustion method.

Solution combustion process is a self-propagating high temperature synthesis in which exothermic reaction takes place accompanied by the evolution of gases



Flow – Chart for synthesis of nano particles by solution combustion method

Solution combustion method is a wet-chemical method, which has been proved to be an excellent technique for preparing nanocrystalline materials due to its short processing time, low processing temperature. This technique is based on exothermic redox reactions that undergo self-sustaining combustion. Mixtures of oxidizer (usually metal nitrates) and a fuel (organic compound containing carbon and hydrogen; e.g. urea, citric acid or glycine as fuel) undergo spontaneous combustion under heating and the chemical energy from the exothermic reaction heats the precursor mixture to high temperatures. Such a high temperature leads to formation and crystallization of nano materials.).

Advantages of solution combustion method:

Among wet chemical routes, the low temperature ***solution combustion process*** is an attractive one and finds several advantages like-

- The synthesis temperature (300 ^{0}C) employed is lower than those currently used in conventional route.
- Simple and energetically attractive process.
- Ability to dope desired amounts of impurity ions with better homogeneity.
- The powders are voluminous, foamy, sinteractive and in nanoscale having large surface area.
- Short reaction time (few seconds to 5 minutes)
- Chemical homogeneity

Example: Synthesis of ZnO nano particles by solution combustion method: **Refer lab manual, page -24**

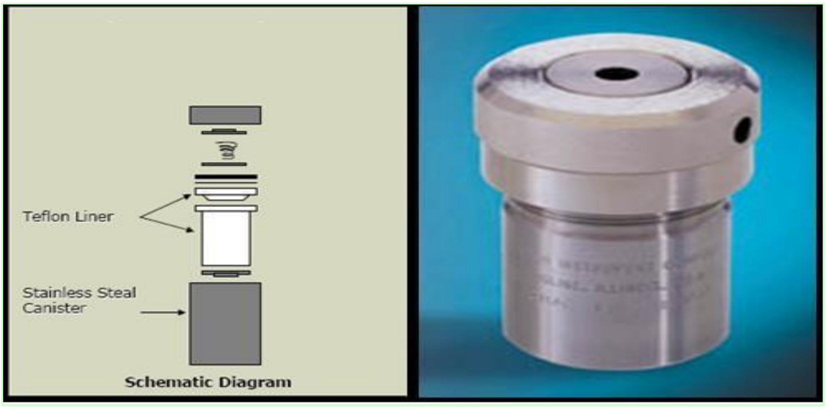
Q. Explain synthesis of nano particles using hydrothermal method

It is a solution based method to prepare wide range of nanomaterials having diverse shapes and size. It is a method to produce different chemical compounds and materials using closed-system in aqueous solutions at temperatures above 100°C and pressures above 1 atm.

Principle: It is based on the principal of dissolution and recrystallizing substances from high temperature aqueous solutions at high vapour pressure. The crystal growth is performed in an apparatus consisting of a steel pressure vessel called autoclave, in which a nutrient (precursors) is supplied along with water. A gradient of temperature is maintained at the opposite ends of the growth chamber so that the hotter end dissolves the nutrient and the cooler end causes end causes seeds to take additional growth.

Procedure: In typical hydrothermal synthesis, stoichiometric amount of precursors and ~20-25 ml of double distilled water is taken in a Teflon liner. In few cases to maintain the basic pH alkali like NaOH or KOH are also added. Then the mixture are stirred well using magnetic stirrer to ensure complete homogenous mixing, until all the contents are evenly distributed. Later, the Teflon liner is kept inside the autoclave and sealed firmly. The complete autoclave assembly is then kept in a Hot air oven at a desired temperature (generally < 150 ^{o}C) and reaction is carried for desired time (Depending on material time varies between 2 and 24 h). Then, after the reaction, the product is washed with water and ethanol to remove impurities and the products are dried at 60 ^{o}C for 3 h in a dust proof hot air oven to get nanocrystalline materials.

For example: Preparation of $BiFeO_4$ by hydrothermal - Equimolar mixtures of bismuth nitrate ($Bi(NO_3)_3.5H_2O$) and iron nitrate ($Fe(NO_3)_3.9H_2O$) are dissolved in distilled water. Add 8 M sodium hydroxide (NaOH) and stir for 30 min and poured into an autoclave. The hydrothermal treatment is conducted at 180 ^{o}C for 12 h. The produced powder is collected at the bottom of the autoclave after cooling to room temperature. The product is washed several times by repeated cycles of centrifugation in distilled water and ethanol. The obtained powder is heated at 80 ^{o}C for 1 hr.



Q - Mention the various techniques used in characterization of nano powder sample

The various characterization techniques used are – (i) Powder X-ray diffraction (ii) Scanning electron microscopy (SEM) (iii) Transmission electron microscopy (TEM)

Q - What are the applications of nonmaterials

Nanomaterials possess unique optical, electronic and magnetic properties that make them unique and widely applicable in various fields.

Application (field)	Examples
Medicine	Diagnostics, Drug delivery, Tissue engineering, Cryonics
Information and communication	Memory storage, Novel semiconductor devices, Electronic devices, Displays, Quantum computers
Heavy Industry	Aerospace, Catalysis, Catalysis, Construction Vehicle manufacturers
Consumer goods	Foods, Household, Optics, Textiles, Cosmetics, Sports
Environment	Water treatment: The removal of colour, heavy metal, fluoride, etc Nanomaterials have better photo catalytic activity than their bulk counterparts due to very high surface area. Nano photo catalysts like ZnO, TiO_2 and CuO are used to degrade organic dyes and other impurities from waste industrial waste water.

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Types of Instrumental Methods of Analysis:

i. **Electrical methods (Electro analytical)**: Electrical method of analysis involves the measurement of current, voltage or resistance in relation to the concentration of a certain species in solution. For example potentiometry involves the measurement of the potential of an electrode in equilibrium with an ion to be determined.

ii. Optical methods (Spectro analytical): Optical methods are based on, how the sample acts towards the electromagnetic radiation. For example in colorimetry the intensity of the color of the solution is a measure of the concentration of the substance. The intensities are determined visually or with the help of a colorimeter.

Potentiometry:

Q- What is potentiometry? Explain its principle/theory of potentiometer.

The procedure of using measurement of e.m.f to determine the concentration of ionic species in solution is referred to as potentiometry.

The relation between electrode potential and metal ion concentration is given by the Nernst equation.

$$E = E^o + \frac{0.0591}{n} \log M^{n+}$$

It can be seen from the equation that the potential of an electrode E depends upon the concentration of the ion M^{n+} to which it is reversible.

The principle involved in potentiometric titration is the measure of e.m.f. between two electrodes, an indicator electrode, the potential of which is a function of the concentration of the ion to be determined and a reference electrode standard calomel electrode (SCE) of constant potential. In these titrations the measurements of emf are made while the titration is in progress. The equivalence point of the reaction is revealed by a sudden change in potential in the plot value against the volume of titrant.

Instrumentation:

A potential consists of a reference electrode, an indicator electrode and a device for measuring the potential. The indicator electrode responds rapidly to the changes in the potential due to the concentration changes of the analyte.

A known volume of the analyte is taken in a beaker and its potential is determined by connecting the assembly to a potentiometer. The titrant is added in increments of 0.5 ml and the potential is measured each time. Close to the equivalence point, there is a sharp increase in the potential ... At this point, small readings are taken beyond the end point. The end point is determined by plotting change in potential against the volume of titrant.

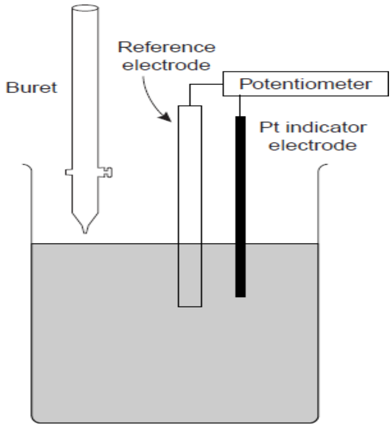

Fig.- Potentiometer

Q Explain determination of Iron using potentiometer

Refer manual – Page 7

Colorimetry:

Q- What is colorimetry? Explain its principle/theory

The procedure of using measurement of optical density of the coloured solution to determine the concentration of ionic species in solution is referred to as colorimetry.

Chemical analysis through measurements of absorption of light radiation in the visible region of the spectrum with respect to a known concentration of the substance is called calorimetry. Colorimeter is an instrument used for measuring absorption in the visible region. The wave length of Ultraviolet radiation, visible region lies between 8000-4000 À and UV region lies between 4000 – 2000 À. Colorimetry concerned with the visible region of the spectrum.

Colorimetry is used for determination of concentration of compounds in a solution which are themselves colored or which give a color when mixed with a suitable reagent. The intensity of the color of the solution is a measure of the concentration of the substance. The intensities are determined visually or with the help of a colorimeter.

Theory:

Light from suitable source is passed through a filter to produce monochromatic light. The monochromatic light is passed through the solution to be tested when part of the light is absorbed by the solution. The extent of absorption depends on the concentration of the solution and on the path length of the light through the solution. These generalizations are stated in the form of Beer-Lamberts law.

Beer's Law: the intensity transmitted light decreases exponentially as the concentration of the medium increases arthemetically $I_t = I_0 e^{-kc}$.. (1)

Lambert's- Law: the intensity transmitted light decreases exponentially as the thickness absorbing medium increases arthemetically

$$I_t = I_0 e^{-kt} \text{..........................} (2)$$

From equation (1) and (2)

$$I_t = I_0 e^{-kct}$$

$$\log (I_0/I_t) = € ct \text{ (Beer-Lambert law)}$$

$$A = € ct$$

A = absorbance

c = concentration of the solution

T = path length

€ = molar absorption which is a constant at given wavelength.

If the path length kept constant then A is proportional to c. The absorbance of the solution is measured at an optimum wavelength.

Instrumentation:

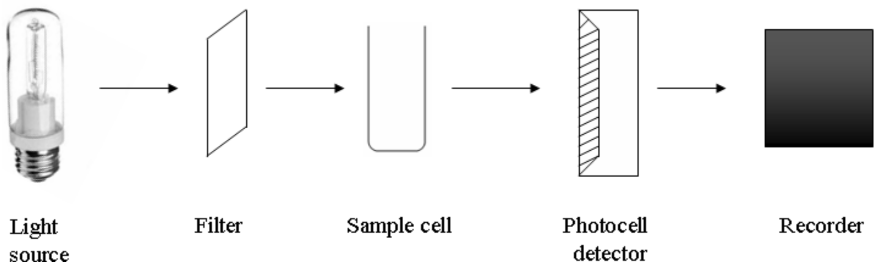

Fig.- Colorimeter

Photoelectric colorimeter consists of following parts

1. Tungsten lamps as light source
2. A filter which provides the desired wavelength range where in the solution gives the maximum absorbance.
3. A sample cell.

4. A photocell detector.

Light from tungsten lamp, after passing through the filter is allowed to fall on the solution taken in the filter is allowed to fall on the solution taken in the sample cell. First , a blank solution is taken in the sample cell and placed in the path of light beam. It absorbance is adjusted to zero (or transmittance placed in the path of the light beam and the quantity of light absorbed is measured as its absorbance (or transmittance).

Q Explain determination of Copper calorimetrically

Refer manual – Page number 3

Glass electrode- its application in the determination of pHof beverages.

Glass electrode is an example for Ion selective electrode, which selectively responds to specific ion in a mixture and the potential developed at the electrode is a function of the concentration of that ion in the solution. Ion selective electrodes make use of a kind of membrane which is sensitive to a particular chemical species. Therefore, these electrodes are also known as membrane electrodes. The electrode generally consists of a thin membrane which is capable of exchanging the specific ion with the solution it is in contact.

Principle of Glass elctrode: If solutions of different pH are separated by a thin membrane, the potential develops across the membrane. The magnitude of potential depends on the difference in pH of two solutions. If pH of one of these is held constant, the observed glass electrode potential is a linear function of pH of the second solution.

Construction: Glass electrode is an ion selective reference electrode. It consists of a thin walled glass bulb of special type with high electrical conductivity with low melting point. A portion of the bulb is filled with a solution of constant pH (0.1 M HCl). Ag-AgCl electrode is dipped to provide electrical contact.

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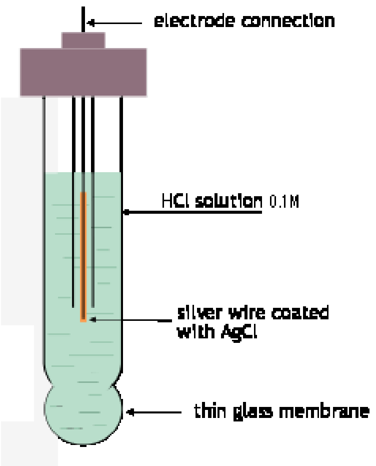

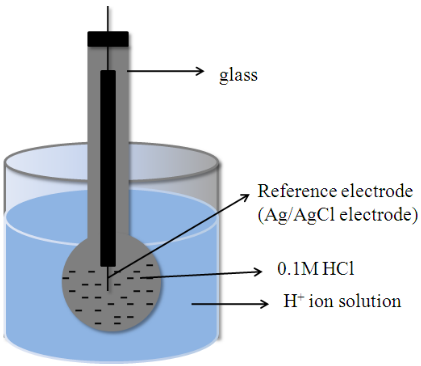

Fig.- Glass electrode

Notation of the electrode potential: Glass electrode can be represented as

Ag/AgCl (s)/0.1 M HCl / glass

Glass electrode Potential $E_G = E_G^0 - 0.0591$ pH

E_G^0 is specific to a particular glass electrode.

Q- Explain determination of pH of an unknown solution using glass electrode.

Glass electrode is used as the internal reference electrode for determining the pH of solution especially colored solution containing oxidizing or reducing agents. Calomel electrode is used as the secondary reference electrode. To determine the pH of the given solution, the glass electrode is placed in the test solution and this half cell is coupled with saturated calomel electrode (Fig). The glass electrode acts as anode calomel electrode behaves as cathode. The *emf* of the cell is determined potentiametrically (pH meter)

$$E_{cell} = E_{cathode} - E_{anode}$$

$$= E_{glass} - E_{SCE}$$

$$= [E_G^0 - 0.0591 \text{ pH}] - E_{SCE} \quad [\text{since } E_G = E_G^0 - 0.0591 \text{ pH}]$$

$$0591\text{pH} = [E_G^0 - E_{cell} - E_{SCE}]$$

$$\text{Or} \qquad \text{pH} = [E_G^0 - E_{cell} - 0.241]/0.0591$$

[Since Electrode potential of saturated calomel is 0.241 V]

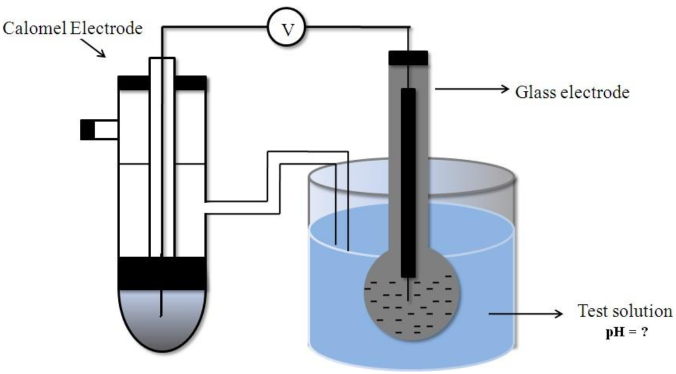

Fig. - Determination of pH of an unknown solution