Synthesis & Characterization of Silica Coated Iron oxide Nanoparticles by Sol-Gel Technique

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DT: 7th May   Meera Basa

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Certificate

This is to satisfy that the thesis entitled **"SYNTHESIS & CHARACTERIZATION OF SILICA COATED IRONOXIDE NANOPARTICLES BY SOL GEL TECHNIQUE"** being submitted by **Miss Meera Basa** (Roll No. – 407CY102) for the partial fulfillment of the requirements for the award of M.Sc. degree in Chemistry at the National Institute of Technology, Rourkela, is an authentic work carried out by her under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University or Institute for the award of a degree or diploma.

Date:
Place: **Dr. Garudadhwaj Hota**

ABSTRACT

α-Fe$_2$O$_3$ nanoparticles and Silica Coated Fe$_2$O$_3$ Particles were synthesized by hydrothermal method and acid - base hydrolysis of TEOS respectively. The Core Shell Particles has been characterized by SEM, XRD, and Particle size analysis. From particle size analysis, it was seen that, the distribution maxima of Fe$_2$O$_3$ and Fe$_2$O$_3$@SiO$_2$ coated nanoparticle were of 120 & 350 nm, 150nm & 550 nm respectively. From XRD analysis, it was confirmed that silica sample nanoparticles is amorphous in nature.The SEM/EDX analysis data represents the presence of Fe$_2$O$_3$@SiO$_2$ and show only the compositions of Si ,O & Fe$_2$O$_3$ peaks. As Fe$_2$O$_3$ nanoparticles show applications in many fields including high density magnetic storage devices, ferrofluids, magnetic refrigeration systems, and catalysis. Aggregation of nanoparticles can be prevented by coating the particles with other materials. The core/shell structure enhances the thermal and chemical stability of the nanoparticles, improves solubility, makes them less cytotoxic and allows conjugation of other molecules to these particles.

CONTENTS

CHAPTER -1

1. INTRODUCTION

1.1 Introduction to Nanotechnology:

The term nanotechnology is employed to describe the creation and exploitation of materials with structural features in between those of atoms and bulk materials, with at least one dimension in the nanometer range (1 nm $=10^{-9}$ m). Properties of materials of nanometric dimensions are significantly different from those of atoms as well as those of bulk materials. It will offer better built, longer lasting, cleaner, safer, and smarter products for the home, for communications, for medicine, for transportation, for agriculture, and for industry in general. A key understanding of nanotechnology is that it offers not just better products, but a vastly improved manufacturing *process*. It covers fields from biology to material science, physics to chemistry, and can include development in a variety of specialties. Nanofilm's areas of expertise are in self-reactive thin films, nanocomposites and surfactants. Nanofilm's self-reactive thin films are ultrathin and invisible on a surface. They chemically react with a substrate to bond with it, rather than being "painted" onto it. They impart new functionalities to the surface. Nanocomposites are another Nanofilm R&D area. Nanocomposites are the blend of nanomaterials into a matrix of another substance. This imparts characteristics of the nanomaterial to a larger body of matter. In parallel with Nanofilm's decades of work in creating self-reactive thin films, we've developed a depth of knowledge in surfactants to care for those surfaces.

1.2. Nanostructured materials:

Nanostructured materials have attracted considerable attention in recent years because they exhibit useful and unusual properties compared to conventional polycrystalline materials. In particular, iron- and iron-oxide based nanomaterials have potential applications in reading and writing technologies on magnetic media, in catalysis, color imaging, magneto-optical devices, ferrofluids, and particularly as super paramagnets Infact , their super paramagnetic clusters provide magnetic refrigerants with large magnetocaloric effects that can be used at a higher temperature and/or with a smaller

applied magnetic field than that of classic paramagnetic refrigerants. Moreover they exhibit coercivity and saturation magnetization (Ms), values which strongly depend on the size and magnetic anisotropy of the particles. These materials are often prepared as nanocomposites to avoid the tendency of nanoparticles to aggregate .The sol-gel-derived amorphous silica matrix is an excellent host for supporting different types of guest nanoparticles like α-Fe2O3 or Fe. The porous nature of the amorphous silica matrix provides nucleation sites for α-Fe2O3 or Fe guest particles and minimizes the aggregation phenomena imposing an upper limit to the size of the particles.

1.3. Nanocomposites:

Nanocomposite materials formed by metallic or oxide particles dispersed in polymer, ceramic or vitreous matrices have important application in areas such as catalysis and electronics. An interesting class of nanocomposite materials is formed by nanometer sized magnetic particles dispersed in insulating matrix. These nanocrystalline particles have a high surface/volume ratio, leading to magnetic properties different from those of bulk materials. Such properties are also highly dependent on the particle size distribution as well as on the aggregation of particles when compared to different production methods. Sol-gel process has proved to be an efficient method to prepare ultra-fine particles dispersed in different matrices and, particularly, to produce thin film. Through this method, a good control of the sample morphology, texture, structure, and chemical composition can be attained by carefully monitoring the preparation parameters. The use of an inorganic matrix allows narrow dispersion of particle size, and homogeneous distribution.

The general class of nanocomposite organic/inorganic materials is a fast growing area of research. Significant effort is focused on the ability to obtain control of the nanoscale structures via innovative synthetic approaches. The properties of nano-composite materials depend not only on the properties of their individual parents but also on their morphology and interfacial characteristics.

The inorganic components can be three-dimensional framework systems such as zeolites, two-dimensional layered materials such as clays, metal oxides, metal phosphates, and

2

chalcogenides. Experimental work has generally shown that virtually all types and classes of nanocomposite materials lead to new and improved properties when compared to their macrocomposite counterparts. Therefore, nanocomposites promise new applications in many fields such as mechanically reinforced lightweight components, non-linear optics, battery cathodes and Ionics, nano-wires, sensors and other systems.

The general class of organic/inorganic nanocomposites may also be of relevance to issues of bio-ceramics and biomineralization in which *in-situ* growth and polymerization of biopolymer and inorganic matrix is occurring. Finally, lamellar nanocomposites represent an extreme case of a composite in which interface interactions between the two phases are maximized. Since the remarkable properties of conventional composites are mainly due to interface interactions, the materials dealt with here could provide good model systems in which such interactions can be studied in detail using conventional bulk sample (as opposed to surface) techniques. Inorganic layered materials exist in great variety. They possess well defined, ordered intra lamellar space potentially accessible by foreign species. This ability enables them to act as matrices or hosts for polymers, yielding interesting hybrid nano-composite materials.

1.4. Nanoparticles:

Nanoparticles and metal clusters represent an important state of condensed matter. Such systems display many peculiarities and physical and chemical properties that were never observed earlier. Nanoparticles may be considered as intermediate formations, which are limited by individual atoms on the one hand, and the solid phase on the other. Such particles exhibit the size dependence and a wide spectrum of properties. Thus, nanoparticles can be defined as entities measuring from 1 to 100 nm and built of atoms of one or several elements. Presumably, they represent closely packed particles of random shapes with a sort of structural organization. One of the directions of nanoscience deals with various properties of individual nanoparticles. Another direction is devoted to studying the arrangement of atoms within a structure formed by nanoparticles. Moreover, the relative stability of individual parts in this nanostructure can be determined by variations in kinetic and thermodynamic factors.

Nanoparticles are larger than individual atoms and molecules but are smaller than bulk solid. Hence they obey neither absolute quantum chemistry nor laws of classical physics and have properties that differ markedly from those expected. There are two major phenomenons that are responsible for these differences. First is the high dispersity of nanocrystalline systems. As the size of a crystal is reduced, the number of atoms at the surface of the crystal compared to the number of atoms in the crystal itself, increases. Properties, which are usually determined by the molecular structure of the bulk lattice, now become increasingly dominated by the defect structure of the surface. The second phenomenon occurs noticeably only in metals and semiconductors. It is called size quantization and arises because the size of a nanoparticle is comparable to the de Broglie wavelength of its charge carriers (i.e. electrons and holes). Due to the spatial confinement of the charge carriers, the edge of the valance and conduction bands split into discrete, quantized, electronic levels. These electronic levels are similar to those in atoms and molecules.

1.5. Different types of nanoparticles:

1. **Fullerenes: Bucky balls and Carbon tubes**

Both members of the fullerene structural class, bucky balls and carbon tubes are carbon based, lattice-like, potentially porous molecules. Bucky balls are spherical in shape while carbon tubes are cylindrical. The diameter of a carbon tube can be several nm but the length can be much greater, up to several mm, depending on its intended use. Carbon tubes have many applications in materials science due to their strength and unique electrical properties. However, they have also found use in the field of biomedicine as carriers for vaccines, drugs and other molecules. A single wall carbon tube is a one-atom-thick sheet of graphite, resembling chicken wire, rolled seamlessly into a tube. There are also multi-walled and other types of tubes depending on the shape, diameter, density (hollow versus solid) and other properties.

2. Liposomes

Liposomes are lipid-based nanoparticles used extensively in the pharmaceutical and cosmetic industries because of their capacity for breaking down inside cells, once their delivery function has been met. Liposomes were the first engineered nanoparticles used for drug delivery but problems such as their propensity to fuse together in aqueous environments and release their payload, have lead to replacement, or stabilization using newer alternative nanoparticles.

3.Nanoshells

Also referred to as core-shells, nanoshells are spherical cores of a particular compound surrounded by a shell or outer coating of another, which is a few nanometers thick. One application in biomedicine is to create nanoshells that absorb at biologically useful wavelengths, depending on the shell thickness. One common formula for the construction of nanoshells is to use silica for the core and another sticky compound to adhere gold particles to the outside surface, creating the shell. Nanoshells such as these have been used to kill cancer cells in mice. Once injected into a tumor, radiation is applied and the nanoshells heat up enough to kill the tumor cells.

4.Dendrimers

Dendrimers are highly branched structures gaining wide use in nanomedicine because of the multiple molecular "hooks" on their surfaces that can be used to attach cell-identification tags, fluorescent dyes, enzymes and other molecules. The first dendritic molecules were produced around 1980, but interest in them has blossomed more recently as biotechnological uses are discovered.

Nanomedical applications for dendrimers are many and include nanoscale catalysts and reaction vessels, micelle mimics, imaging agents and chemical sensors, and agents for delivering drugs or genes into cells. There are two basic structural types. One is the globular structure with a central core from which branches radiate. The second type has no central core and consists simply of a series of highly branched polymers.

5.Quantumdots

Also known as nanocrystals, quantum dots are nanosized semiconductors that, depending on their size, can emit light in all colours of the rainbow. These nanostructures confine conduction band electrons, valence band holes, or excitons in all three spacial directions. Examples of quantum dots are semiconductor nanocrystals and core-shell nanocrystals, where there is an interface between different semiconductor materials. They have been applied in biotechnology for cell labelling and imaging, particularly in cancer imaging studies.

6. Superparamagnetic nanoparticles

Super paramagnetic molecules are those that are attracted to a magnetic field but do not retain residual magnetism after the field is removed. Nanoparticles of iron oxide with diameters in the 5-100 nm range, have been used for selective magnetic bioseparations. Typical techniques involve coating the particles with antibodies to cell-specific antigens, for separation from the surrounding matrix.

Used in membrane transport studies, superparamagenetic iron oxide nanoparticles (SPION) are applied for drug delivery and gene transfection. Targeted delivery of drugs, bioactive molecules or DNA vectors is dependent on the application of an external magnetic force that accelerates and directs their progress towards the target tissue. They are also useful as MRI contrast agents.

7.Nanorods

Typically 1 – 100 nm in length, nanorods are most often made from semiconducting materials and used in nanomedicine as imaging and contrast agents. Nanorods can be made by generating small cylinders of silicon, gold or inorganic phosphate, among other materials.

1.6. Core-shell nanoparticles:

Core/shell nanoparticles are nanostructures that have core made of a material coated with another material. They are in the size range of 20nm-200nm. Also, composite structures with these core/shell particles embedded in a matrix material are in use. The necessity to

shift to core/shell nanoparticles is the improvement in the properties. Taking into consideration the size of the nanoparticles, the shell material can be chosen such that the agglomeration of particle can be prevented. This implies that the monodispersity of the particles can be improved. The core/shell structure enhances the thermal and chemical stability of the nanoparticles, improves solubility, makes them less cytotoxic and allows conjugation of other molecules to these particles. The shell can also prevent the oxidation of the core material. "When a core nanoparticle is coated with a polymeric layer or an inorganic layer like silica because the polymeric or inorganic layer would endow the hybrid structure with an additional function/property on top of the function/property of the core hence synergistically emerged functions can be envisioned".Recently; core/shell nanoparticles are finding widespread application. There is a class of Core/shell nanoparticle that has its entire constituent in the nanometer range.

1.7. Various techniques used for Synthesis of nanoparticles:

Nowadays, the attention of many scientists is focused on the development of new methods for synthesis and stabilization of nanoparticles. Moreover, special attention is paid to monodispersed and stable particles formation. Different metals, metal oxides, sulfides, polymers, core-shell and composite nanoparticles can be prepared using a number of synthetic techniques, which are broadly classified into two categories, namely, physical methods and chemical methods.

A. Chemical techniques:

- Chemical vapor deposition
- vapor-phase synthesis:
- Hydrothermal synthesis
- Sol-gel technique
- Sonochemical technique
- Microemulsion technique
- Wet-chemical Process

- **Chemical vapor deposition:**

is a chemical process used to produce high-purity, high-performance solid materials. The process is often used in the semiconductor industry to produce thin films. In a typical CVD process, 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.

- **vapor-phase synthesis:**

In vapor-phase synthesis of nanoparticles, the formation of nanoparticles takes place in gas phase. In this synthesis technique the condensation of atoms and molecules is carried out. The vapor phase synthesis is not new and many multinational companies have been using flame reactors for decades for producing large quantities of nanoparticles. The flame reactors were used for forming various nanoparticles such as carbon black and titanium dioxide.

- **Hydrothermal synthesis:**

Hydrothermal synthesis can be defined as a method of synthesis of single crystals which depends on the solubility of minerals in hot water under high pressure. The crystal growth is performed in an apparatus consisting of a steel pressure vessel called autoclave, in which a nutrient 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 seeds to take additional growth. Possible advantages of the hydrothermal method over the other types of crystal growth include the ability to create crystalline phases which are not stable at the melting point. Also, materials which have a high vapour pressure near their melting points can also be grown by the hydrothermal method. The method is also particularly suitable for the growth of large good-quality crystals while maintaining good control over their composition.

- **Chemical Precipitation**

Certain soluble inorganic materials can be removed by the addition of suitable reagents to convert the soluble impurities into insoluble precipitates. These precipitates can be flocculated and removed by sedimentation. The extent of removal depends on the solubility of the product and this is usually controlled by factors such as pH and temperature. Chemicals precipitation can be used in industrial wastewater treatment The solid-state process is the more common and widely used method for production of micron-sized particles. In solid state synthesis of nanoparticles generally heat treatment followed by milling is carried out to get an average particle size of 100nm or less. Mechanical milling is one of the most preferred and earliest technique to produce metallic microcrystalline powder. People claims to get a nanoparticle of very small size of up to 30nm particle size by using media milling of very small size of 200 micro meter. There are other commonly preferred milling methods used by different researchers includes dry milling and ball milling techniques.

- **Microemulsion Technique:**

This is a new technique, which allows preparation of ultrafine metal particles within the size range 5 nm<particle diameter<50 nm. The rate of particle nucleation is a function of the percolation degree of microemulsion droplets. Besides a short introduction into some aspects of the microemulsion types and formation, we mainly focus on the kinetics of metallic particle formation. Effects of stabilizer (emulsifier) type and concentration and the type of continuous phase, reducing agent and additive on the particle formation are summarized and evaluated. The influence of several other parameters such as temperature, the incident light, the nature of metal salts and reaction conditions are also reviewed. These results indicate that the nature of the stabilizer emulsifier, the surface activity of additives and the colloidal stability of microemulsion droplets play decisive role on the particle size and distribution during the preparation of metal particles.

- **Sonochemical Technique:**

In this technique, nanoparticles are prepared by irradiating the aqueous or organic dispersion of precursor materials using an ultrasonic probe at room temperature. The size

of the particles obtained in this method mainly depends on the solution concentration and the time of sonication.

B. Physical Methods

- Laser ablation
- Sputtering
- spray route pyrolysis
- Inert Gas condensation
- **Laser ablation**

In laser ablation, high-power laser pulses are used to evaporate matter from a target surface such that the stoichiometry of the material is preserved in the interaction. As a result, a supersonic jet of particles (plume) is ejected normal to the target surface. The plume, similar to the rocket exhaust, expands away from the target with a strong forward-directed velocity distribution of the different particles. The ablated species condense on the substrate placed opposite to the target. The ablation process takes place in a vacuum chamber - either in vacuum or in the presence of some background gas. In the case of oxide films, oxygen is the most common background gas.

- **Sputtering:**

A technique used to deposit thin films of a material onto a surface ("substrate"). By first creating a gaseous plasma and then accelerating the ions from this plasma into some source material ("target"), the source material is eroded by the arriving ions via energy transfer and is ejected in the form of neutral particles - either individual atoms, clusters of atoms or molecules. As these neutral particles are ejected they will travel in a straight line unless they come into contact with something - other particles or a nearby surface.

- **Spray route pyrolysis:**

Nanometer-sized particles (1–100 nm) are of considerable interest for a wide variety of applications, ranging from electronics via ceramics to catalysts, due to their unique or improved properties that are primarily determined by size, composition and structure. A

simple, rapid and generalizable aerosol decomposition (spray pyrolysis) process is used for the continuous synthesis of nanoparticles with adjustable sizes, narrow size distribution, high crystallinity and good stoichiometry.

- **Inert Gas Condensation**

An inert gas condensation technique has been used to prepare nanometer-sized particles of metallic iron by evaporation and agglomeration in a flowing inert gas stream. It is the most advanced technique, Although the technique is costly, it is considered as a controlled process as by this method the exact shape and size of the nanoparticle can be synthesized. In inert gas condensation technique, the nanoparticle as soon as they formed rapidly collides with inert gas in a low-pressure environment and thus smaller and controlled nanoparticles are formed.

1.8 Applications of nanoparticles:

- **"Green" Packaging with Nanoparticles**

Nanotechnology is being used in the packaging industry as food suppliers are required to use more environmentally friendly plastics for their goods. The quest for green packaging has introduced bioplastics such as PLA, Polylactic acid. Instead of being developed from petroleum like conventional plastics, PLA is developed from corn. Thus, it biodegradable and consumes less fossil fuel to produce than standard packaging. However, it is not without its flaws. Specifically, PLA tends to be weaker than its petroleum-based counterpart. Conventional methods to strengthen the PLA have involved a tradeoff. While the package becomes stronger, it loses its transparency. Now nanoparticles are being used to remedy the process.

- **Use of Nanoparticles in Food Safety**

Researchers are working towards the possible use of nanoparticles for food safety. Byron Brehem-Stecher, an assistant professor in food science and human nutrition is working towards the possible use of silver nanoparticles for improving the safety of food supply.

Although nanoparticles can not be used as food ingredients, however these can be used for developing food related applications. The immediate possible food related applications seems to be microbe - resistant fabrics and non - biofouling surfaces.

- **Nanoparticle and Cleaning Up the Environment**

Many people are concerned about the impact of Nanotechnology in the environment, specifically the toxic effects of nanoparticles as they are leeched into soil or water. However, curiously enough, researchers have discovered that these nanoparticles are automatically cleaned up by the adverse reaction of microbial proteins to the nanoparticles. It turns out that microbial protein tends to cause toxic nanoparticles to aggregate. The bacteria immobilize the nanoparticles and their constituent metals in order to protect the bacteria from potentially toxic effects.

- **Nanoparticles for Pharmaceutical Applications**

Deals with emerging new technologies for developing customized solutions for drug delivery systems. The drug delivery systems should positively impact the rate of absorption, distribution, metabolism, and excretion of the drug or other related chemical substances in the body. In addition, the drug delivery system should allow the drug to bind to its target receptor and influence that receptor's signaling and activity. Drug delivery materials should be compatible, easy to bind with a particular drug, and able to degrade into fragments after use that are either metabolized or driven out via normal excretory routes.

- **Tissue Engineering**

Nanoparticles can help to reproduce or to repair damaged tissue. This so called "tissue engineering" makes use of artificially stimulated cell proliferation by using suitable nanomaterial-based scaffolds and growth factors. Tissue engineering might replace today's conventional treatments like organ transplants or artificial implants. Advanced nanoparticles based tissue engineering can also lead to life extension. On the other hand,

tissue engineering is closely related to the ethical debate on human stem cells and its ethical implications.

- **Catalysis:**

Chemical catalysis benefits especially from nanoparticles, due to the extremely large surface to volume ratio. The application potential of nanoparticles in catalysis ranges from fuel cell to catalytic converters and photo catalytic devices. Catalysis is also important for the production of chemicals. Platinum nanoparticles are now being considered in the next generation of automotive catalytic converters because the very high surface area of nanopartcles could reduce the amount of platinum required. However, some concerns have raised due to experiments demonstrating that they will spontaneously combust if methane is mixed with the ambient air.

1. 9. Objective of the study:

The main objectives of this work are as follows

- ➢ **To synthesize stable and uniform sized iron oxide nanoparticles by hydrothermal method.**
- ➢ **Study on the formation and stability of silica coated iron oxide nanoparticles (Fe$_2$O$_3$@SiO$_2$).**
- ➢ **Surface Characterization of the Fe$_2$O$_3$@SiO$_2$ core-shell nanoparticles**

1.10. Organization of the report

The thesis has been organized in four chapters. The present Chapter 1 is an introductory chapter. Chapter 2 contains a pertinent literature review on silica coated iron oxide /composite nanoparticles synthesis using sol-gel and other synthetic techniques. Chapter 3 deals with synthesis of SiO$_2$ coated Fe$_2$O$_3$ core-shell nanoparticles using hydrothermal and sol-gel method. In Chapter 4, the formation of SiO$_2$ coated Fe$_2$O$_3$ composite nanoparticles has been discussed. The main findings of the work are summarized in Chapter 5 followed by some suggestions for further study.

CHAPTER-2

REVIEW OF BACKGROUND LITERATURE:

This chapter represents a review of the current developments in the area of synthesis and characterization of silica coated metal oxides particles prepared using sol gel technique and also preparation of coreshell nanocomposites. To give a background to discuss the reported studies on this topic, a brief description of the well-known sol gel systems is presented here. The reported studies on the preparation of coated-particles using different synthetic routes and formation of nanocomposites are presented here. Our studies focus on the preparation of silica coated iron oxide i.e. Fe_2O_3 nanoparticles using sol gel chemical and hence a detailed review is presented on core-shell (coated) nanoparticles and nanocomposites.

2.1 Sol-gel Technique:

The sol-gel process is a wet-chemical technique widely used recently in the fields of Materials science and Ceramic engineering. Such methods are used primarily for the fabrication of materials (typically a metal oxide) starting from a chemical solution (*sol*, short for solution) which acts as the precursor for an integrated network (or *gel*) of either discrete particles or network polymers. Typical precursors are metal alkoxides and metal chlorides, which undergo hydrolysis and polycondensation reactions to form either a network "elastic solid" or a colloidal suspension (or dispersion) -- a system composed of discrete (often amorphous) submicrometre particles dispersed to various degrees in a host fluid. Formation of a metal oxide involves connecting the metal centers with oxo (M-O-M) or hydroxo (M-OH-M) bridges, therefore generating metal-oxo or metal-hydroxo polymers in solution. Thus, the sol evolves towards the formation of an gel-like diphasic system containing both a liquid phase and solid phase whose morphologies range from discrete particles to continuous polymer networks. In the case of the colloid, the volume fraction of particles (or particle density) may be so low that a significant amount of fluid

may need to be removed initially for the gel-like properties to be recognized. This can be accomplished in any number of ways. The most simple method is to allow time for sedimentation to occur, and then pour off the remaining liquid. Centrifugation can also be used to accelerate the process of phase separation.
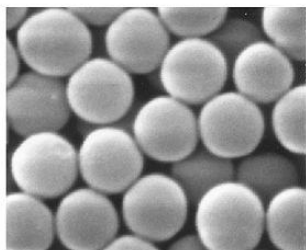
Submicron colloidal silica particles. SEM Micrograph

2.2 Preparation of α-Fe$_2$O$_3$ Hydrosol:

Linua Hua .et al have synthesized α-Fe$_2$O$_3$ hydrosols with FeCl$_3$.6H$_2$O as the raw material and its thin films by dip coating technique .The results showed that uniform α-Fe$_2$O$_3$ monolayer and multilayers could be obtained having pseudo-cubic shaped with mean particle size of nanocubic meter with a certain dip-coating speed. *Ying-Jie Zhu* has reported on the microwave–hydrothermal ionic liquid method for the synthesis of a variety of iron oxide nanostructures such as a-FeOOH hollow spheres, b-FeOOH architectures and a-Fe2O3 nanoparticles. A general thermal transformation strategy is designed to prepare a-Fe2O3 hollow spheres using a-FeOOH hollow spheres as the precursor and template. By thermal treatment of the as-prepared a-FeOOH hollow spheres, a-Fe2O3 hollow spheres showing good photocatalytic activity are obtained.

X.Q. Liu reported α-Fe$_2$O$_3$ ultra-fme powder with an average particle size of 6-26nm has been prepared by a sol-gel process. Thermal analysis, X-ray diffraction and transmission electron microscope were used to study its formation process and micro-structure.

2.3 Preparation of silica gel particles:

(a) By Acid Hydrolysis:

Burtrand I. Lee .et al prepared silica gels by hydrolytic polycondensation of tetraethoxysilane (TEOS) with large amounts of nitric acid as the catalyst have been studied. The molar compositions were TEOS: H20: HNO 3 =1 **:** 10:x . In the presence of

a large amount of nitric acid, the gels had higher specific surface areas and higher pore volumes as the drying temperature increased from 45°C to 60°C. By increasing the drying temperature is more effective than increasing the acid content in order to increase pore size. *Toshiyasu Kawaguchi* reported Silica gel particles which were obtained from the immiscible mixtures of TEOS and H20 with nitric acid, in which the H20/TEOS molar ratio was less than 2. In the emulsion in which water was dispersed as the droplets in TEOS by stirring, TEOS dissolved into the droplets in proportion to time and was hydrolyzed by an excess of nitric acid water. The hydrolysis and polycondensation reactions of TEOS were restricted inside the droplets, and when the ratio of water to the dissolved TEOS for the droplets reached about 4.5 dense spherical particles were formed in TEOS *Gautam De .et al* prepared silica microspheres from TEOS with acid –water in the ph range 1.35-2.25 with a restriction if water /TEOS molar ration which varied from (1-1.5) for strong acids and 1.5-4.0 for weak acids.
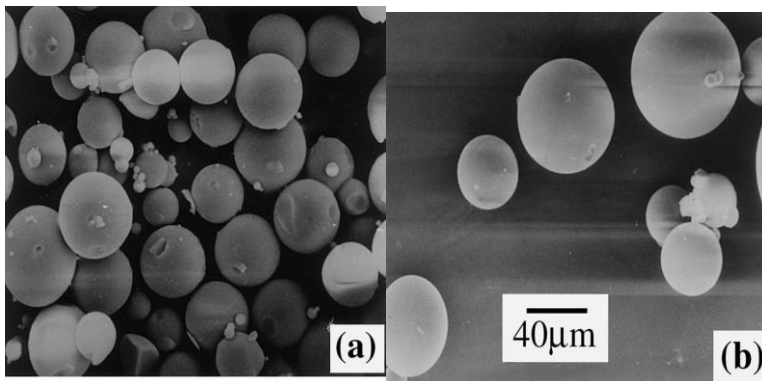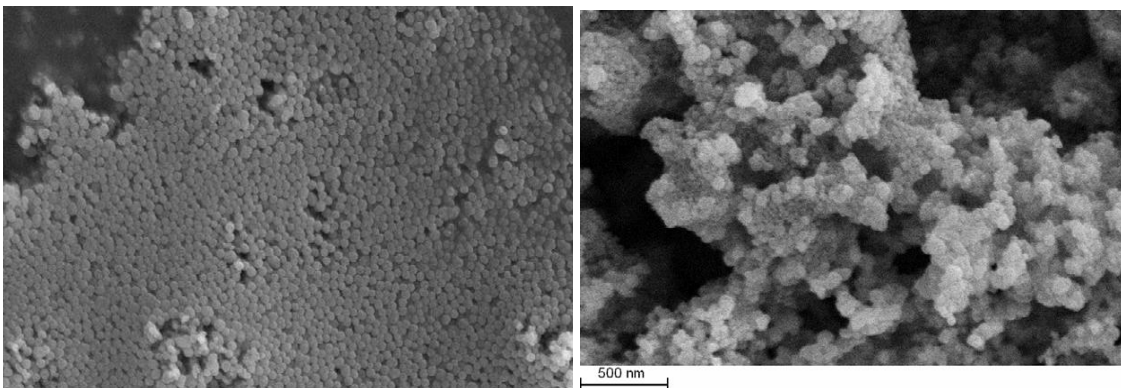

SEM micrographs of silica microspheres obtained by using (a) acetic, and (b) hydrochloric acid.

(b) By Base hydrolysis method: .

Stober and fink.et al has synthesized silica nanoparticle by chemical methods from TEOS, ethanol and deionized water in presence of ammonia as catalyst at room temperature. *Zeev Rosenzweig .et al* developed a simple method to prepare bright and photo stable luminescent silica nanoparticle of different sizes and narrow size distribution in high yield. The method is based on the use of stober synthesis in presence of fluorophore to form bright silica nanoparticles. The study show that digital counting of

the luminescent silica nanoparticle could be used as an attractive alternative to detection techniques involving analogue luminescence detection of bio analytical assays.

SEM micrographs of silica particles obtained from a molar ratio of Water : TEOS : Ammonia : Ethanol = 1 : 4 : 6 : 6;

2.4. Preparation of Core shell Fe_2O_3 nanoparticle:

Chang-chun Wang.et al prepared weakly ferromagnetic iron-oxide nanoparticle with narrow size distribution with a high temperature hydrolysis reaction. *Ho-kun kum* .et al have prepared hollow type silica spheres with controlled cavity size from Fe_2O_3.SiO_2 core-shell composites' particle by using acidic solution. Spherical Fe_2O_3 with a diameter rang of 20-400 nm prepared by hydrolysis reaction. *Manuel Ocaña.et al* reported a simple procedure to coat silica spheres with smooth layers of iron compounds based on the forced hydrolysis (60–85 ∘C) of iron(III) acetylacetonate solutions containing the silica cores and sodium dodecylsulfate (SDS). Finally, the core-shell particles, as prepared, were thermally reduced under hydrogen atmosphere to produce magnetic composites whose magnetic properties were also evaluated as a function of the reduction temperature.
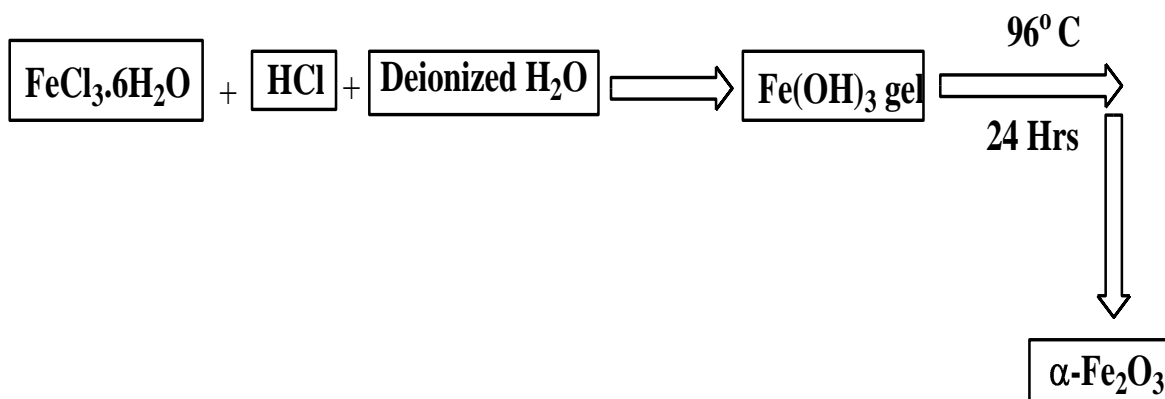
CHAPTER -3

3. Experimental Details

3.1. Materials:

The chemicals used in this experiment are Ferric chloride ($FeCl_3$)(Nice),
Tetraethylorthosilicate (TEOS) (Merck), concentrated NH_4OH, ethanol solution, 25%
ammonia (Merck), concentrated Hydrochloric Acid (HCl), All the chemicals are used as
received, without further purification. Double distilled water was used throughout the
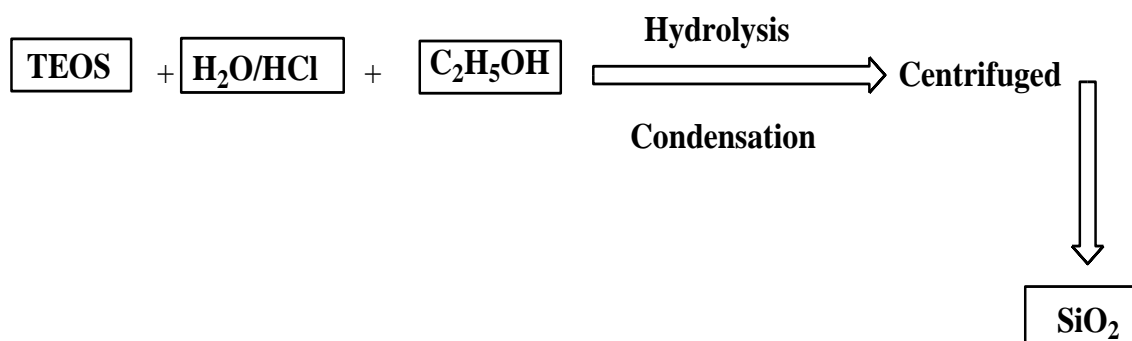experiment.

3.2 Synthesis of iron oxide nanoparticles:

The α-Fe_2O_3 hydrosol was synthesized by using hydrolysis method with a little
improvement: predetermined amounts of stock solutions of $FeCl_3$ (3 mol dm−3) and HCl
(0.2 mol dm−3) were mixed in a flask at the ratio of 1:3 (v/v), and the deionized water
was added till the final concentration of Fe3+ is 0.01 mol dm−3. This mixture was
preserved in water bath at 96 ∘C for 24 h, and then quenched to room temperature. The
resulting orange-red solution was the α-Fe_2O_3 nanoparticulate hydrosol (pH = 2.2).

$$\boxed{\text{FeCl}_3, 6\text{H}_2\text{O}} + \boxed{\text{HCl}} + \boxed{\text{Deionized H}_2\text{O}} \Longrightarrow \boxed{\text{Fe(OH)}_3 \text{ gel}} \xrightarrow[\text{24 Hrs}]{\text{96}^0\text{ C}} \boxed{\alpha\text{-Fe}_2\text{O}_3}$$

3.3 Base Hydrolysis of TEOS for Silica nanoparticle by stober's synthesis:

Silica particles were prepared by a simple one-step protocol which involves the condensation of tetraethylorthosilicate (TEOS) in ethanol: water mixture under alkaline conditions at room temperature. First 20 ml of ethanol was taken in a 50ml beaker, and then 2ml of TEOS was added followed by 4ml of concentrated NH_4OH. After that it was stirred for 8 hour .Then the mixture thus obtained was centrifuged, finally a white color powder was formed which was named as silica nanoparticle.

Schematic representation:

$$\boxed{\text{TEOS}} + \boxed{\text{H}_2\text{O/HCl}} + \boxed{\text{C}_2\text{H}_5\text{OH}} \xrightarrow[\text{Condensation}]{\text{Hydrolysis}} \text{Centrifuged} \longrightarrow \boxed{\text{SiO}_2}$$

3.4 Synthesis of silica nanoparticles by Acid Hydrolysis:

For a silica sol-gel process of TEOS, the influence of acid concentration in the acid step is maintained. A mixture of TEOS, ethanol and water with a final molar ratio of 1:4:2.5 was used. The amount of water in the acid step was chosen so as to permit a complete hydrolysis –condensation. The HCl concentrations in the acidic water fraction was selected as 0.2ml as per its molar ratio. The initial TEOS –ethanol mixture was prepared at room temperature .The acidic water –ethanol fraction was added drop wise in about 1 min to the well stirred mixture. The temperature was maintained at 50°C, throughout the reaction. In case of low acid concentration, long hydrolysis times have to be used. During this reaction, evaporation of the components in the hydrolyzing mixture was avoided. To exclude the influence of moisture, CO_2 and air pollution upon the hydrolysis-condensation reaction, the reaction was carried out in a closed system.

3.5 Fe2O3–SiO2 composites obtained by sol–gel synthesis:
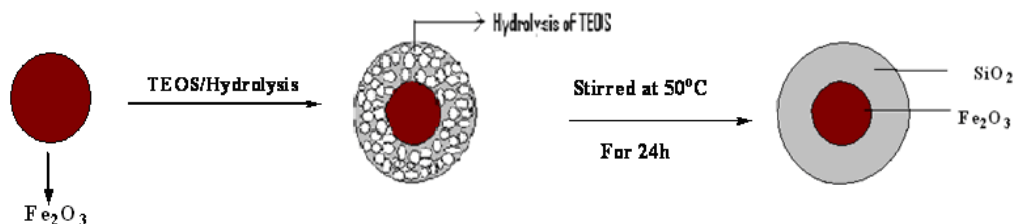
In order to establish the optimum conditions to deposit uniform layers of iron compounds on monodispersed silica spheres, we first studied the influence of the nature of the iron chloride on the coating characteristics. Ethanol was used as solvent since the solubility of iron compound in water is very low. The prepared dispersions were then aged under stirring at constant temperature 50 °C for 24 h in tightly capped bottle after which, the solids obtained were centrifuged and washed with doubly distilled water. The so purified solids were finally collected by filtration and dried at 50 °C

CHAPTER-4

4.1. Characterization techniques

There is various characterization techniques used for characterizing different nanoparticles. Here we have discussed the basic principles of few techniques that have been used in the experimental part of this project work. They are Absorption spectrophotometer (UV-VIS), X-Ray diffraction (XRD), Scanning electron Microscope (SEM)/EDAX and Particle size analyzer.

A. Absorption spectroscopy

A spectrophotometer is an instrument, which is used to determine the percentage of transmittance light radiation when light of certain frequency is passed through the samples.

The spectrophotometer records the intensity of absorption (A) or optical density (O.D) as a function of wavelength. If suppose I_t and Io are the intensities of incident and transmitted rays of light respectively.

Then the absorbance A is defined as $A = \log I_t/I_0$

$$Or, A = \varepsilon cx$$

Where, x=sample path length (cm)

c=concentration (mol lit^{-1})

ε =molar extinction coefficient ($mol^{-1}cm^{-1}$)

This technique usually gives the preliminary concept of particle size and size distribution such as mono or polydispersity. Usually a blue shift (decrease in wavelength) is associated with a decrease in particles size and vice-versa.

B. X-Ray Diffraction

The identification of phases has now turned into multifaceted probe for materials analysis and characterization. Powder diffraction (PD) has now become an important and indispensable method in materials science, physics and chemistry. This method can yield a greater deal of structural information about materials under investigation.

The random diffraction orientations of the individual crystal in a powder specimen are equivalent to the solution of a single crystal about all possible axes during the X-ray exposure.

The reciprocal lattice therefore takes an all possible orientations relative to the incident beam but its origin remains fixed at the end of the incident beam vector.

Condition for diffraction :

It should satisfy Bragg's diffraction. To satisfy Bragg's equation, it is necessary to adjust d, θ, λ in such a way that

$$2dSin\theta= n\lambda$$

Where,

d= perpendicular distance between lattice planes of miller indices.

λ= wavelength of the incident X-ray.

Θ=glancing angle

Bragg's law

When a chromatic intense beam of light falls on a parallel lattice plane of crystal, the incident beam reflected secularly from various planes of crystal. In this case, the phenomenon of reflection is known as crystal diffraction of scattering. Diffraction is essentially a scattering phenomenon in which large numbers of atoms co-operate.

C. Scanning Electron Microscope (SEM)

SEM is a type of electron microscope that creates various images by focusing a high energy beam of electrons onto the surface of a sample and detecting signals from the interaction of the incident electron with the sample's surface. SEM images have greater depth of field (curved surfaces are resolved properly) yielding a characteristic 3D appearance useful for understanding the surface structure of a sample. Magnification is of order 10,000 X and resolution 10 nm.

Scanning process

- A stream of electrons is formed by electron surface and accelerated towards the specimen using positive electric potential.

- The stream is confined and focused using metal apertures and magnetic lenses into a thin focused monochromatic beam.

- The beam is focused onto the sample using a magnetic lens. Interactions occur inside the irradiated sample affecting the electron beam.

- **Particle size analysis:**

The **particle size distribution (PSD)** of a powder, or granular material, or particles dispersed in fluid, is a list of values or a mathematical function that defines the relative amounts of particles present, sorted according to size PSD is also known as **grain size distribution**. The method used to determine PSD is called particle size analysis, and the apparatus a particle size analyzer.

4.2. Results and Discussions

A. UV-visible measurements:

Iron oxide nanoparticles prepared by hydrothermal method are characterized by UV-visible spectrometer. Fig 1 shows the UV_VIS spectra of Iron oxide nanoparticles. Its shows an absorption peaks at around 340 nm and 230 nm respectively. These peaks are due to charge transfer spectra and are characteristic peaks of Iron oxides. Figure2 represents the UV-VIS spectra of SiO2 particles prepared by stobber sythesis and by acid hydrolysis of TEOS.
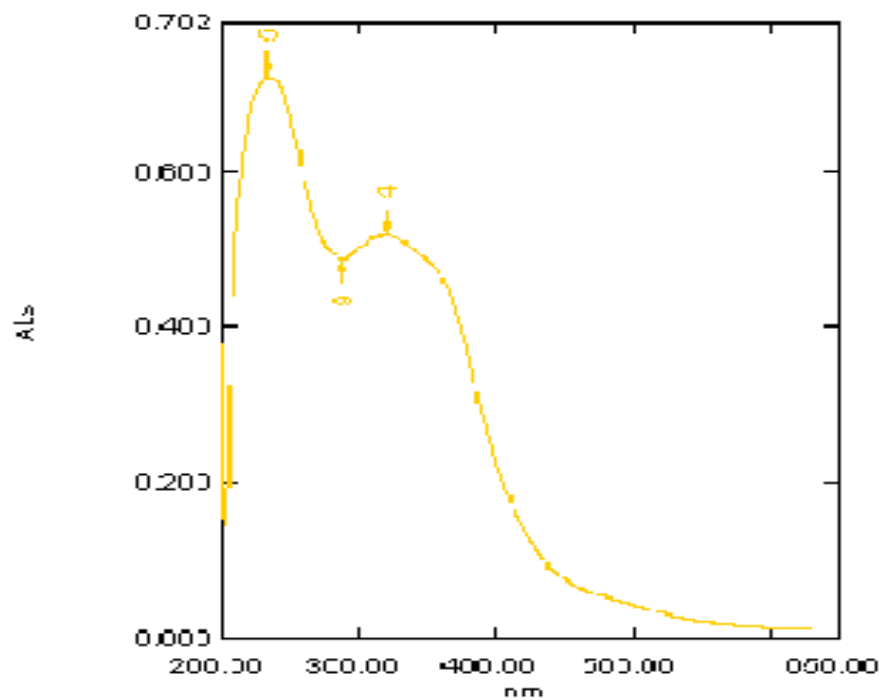
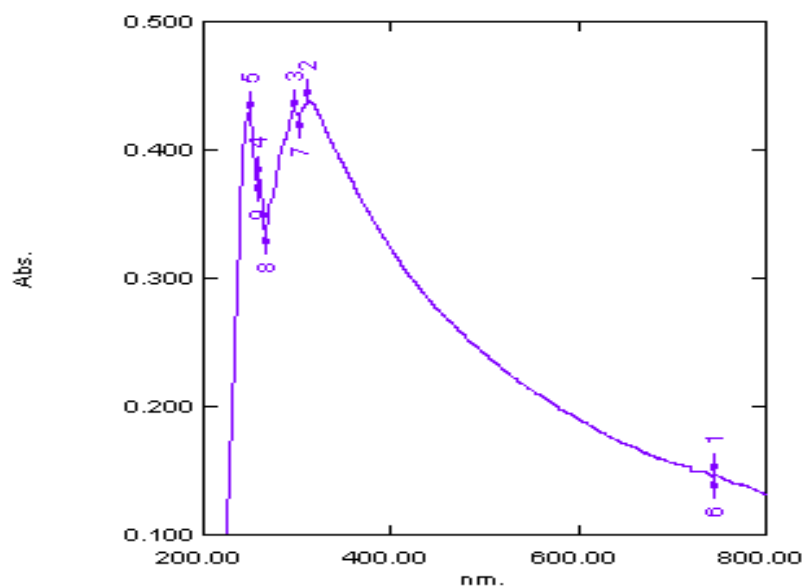**Fig. 1 UV-vis spectra of Fe$_2$O$_3$-nanoparticles, prepared by hydrothermal method**

Fig 2. a. UV- vis spectra of SiO$_2$ nanoparticle prepared by stober's method.
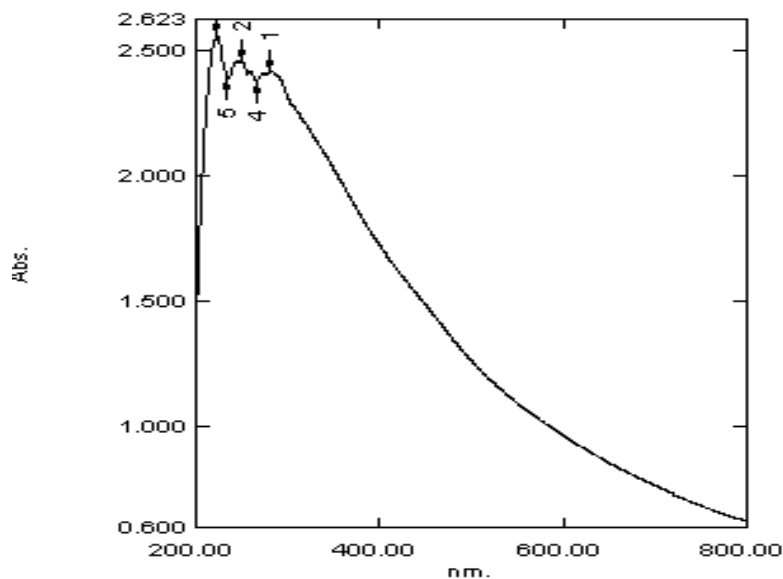
Fig 2.b. UV-vis spectra of SiO$_2$ with HCl nanoparticle prepared by acid-hydrolysis method.

B. XRD Analysis:

Iron-oxide nanoparticles prepared by hydrothermal method and silica nanoparticle prepared by stober's method are characterized by X'Pert Philips Analytical X Ray Diffractometer.
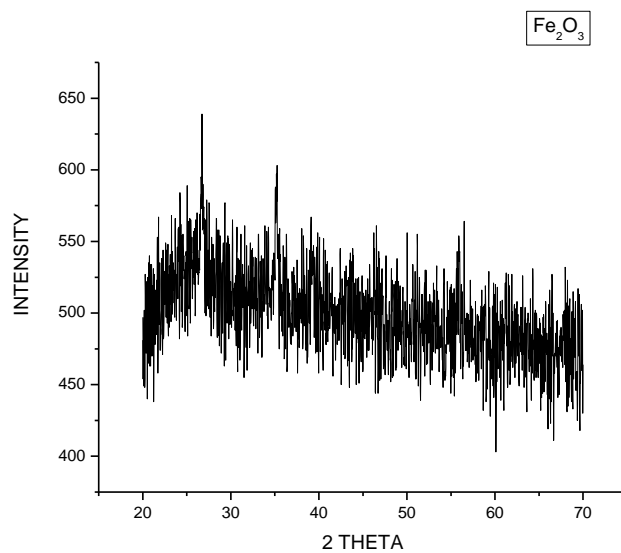
Fig 3.A XRD of Fe_2O_3 Particles prepared by Hydrothermal Method.

Fe_2O_3 particles separated out from the solution and XRD has been taken. Figure 3 represents the X-ray diffraction spectra of iron oxides and Silica particles prepared by hydrothermal method and stobber synthesis. The 2θ value of iron oxide sample was found to match with JCPDS-33-0664, confirming the formation of α-Fe_2O_3.
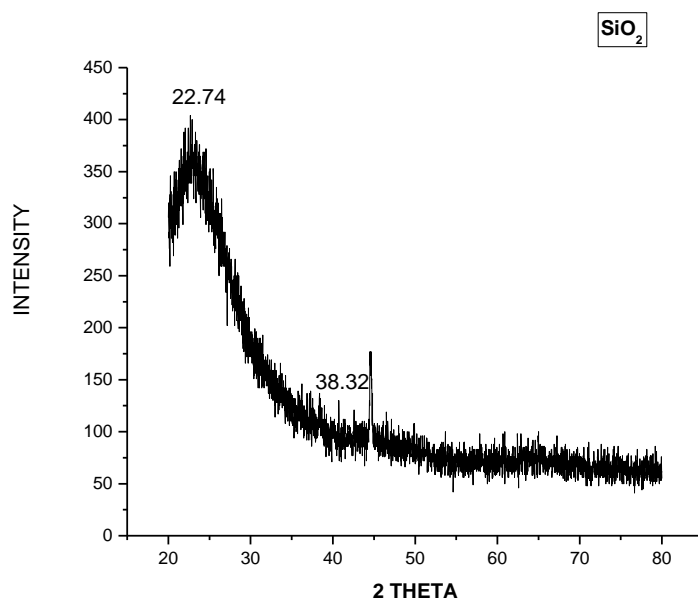

Fig. 3.B. XRD of SiO_2 Particles prepared by stobber Method

The silica sample does not show any well defined peaks indicating amorphous nature of the sample. The 2θ value of sample was found to match with JCPDS file (79-1711) confirming the formation of SiO_2.

C. SEM Analysis

The surface morphology of the iron oxide and silica particles have been studied by scanning electron microscopy method. Figure 4 represents the SEM and EDAX images of Fe_2O_3 nanoparticles. This figure (Fig. 4A) suggests the aggregation of the particles and small grains are present at the surface. However

the elemental analysis suggests the presence of Fe, and Oxygen atomic percentage, indicates the formation of iron oxides.
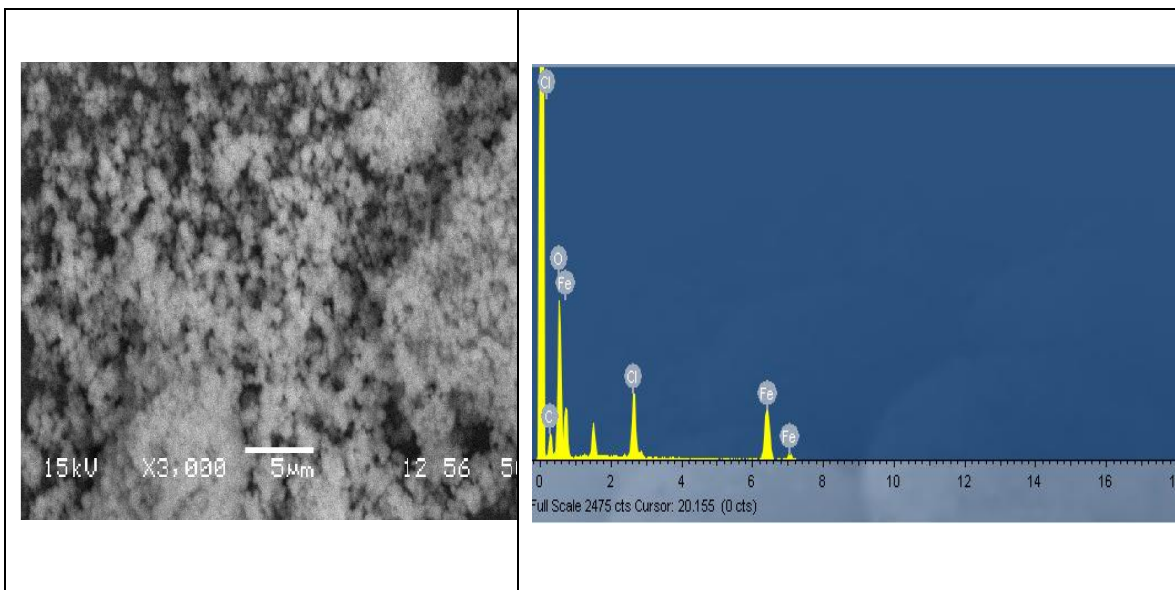

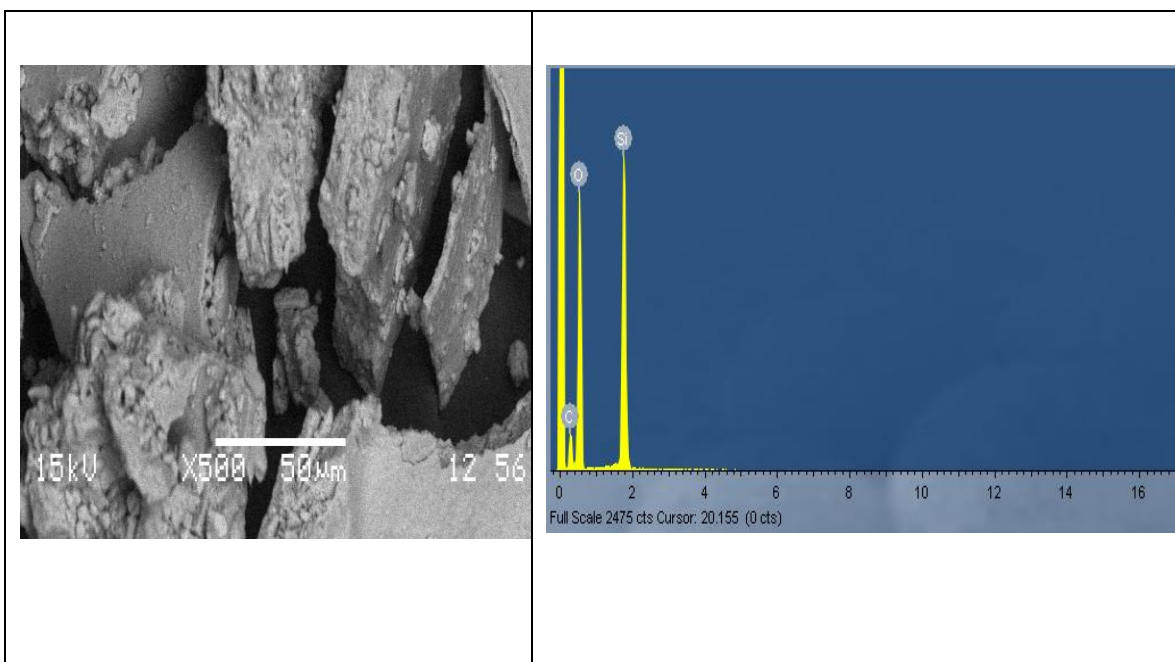**Fig. 4.A. SEM and EDAX Image of Fe$_2$O$_3$ nanoparticles prepared by hydrothermal method.**

Figure 4. B. SEM and EDAX Image of SiO₂ nanoparticles prepared by hydrothermal method.

The silica particles synthesized by stobber method have been separated out by ultracentrifugation and SEM has been studied. The SEM and EDAX image of SiO_2 particles has been shown in Fig. 4 B. The particles seem to be bigger in size and in aggregated form. EDAX results suggest the presence of Si and oxygen elements, confirming the formation of SiO_2 particles.

D. Particle size analysis

The particles size of iron oxides, silica and silica coated iron oxides nanoparticles prepared by hydrothermal and sol-gel method has been characterized by light scattering experiments. The results are shown in Figure 5.
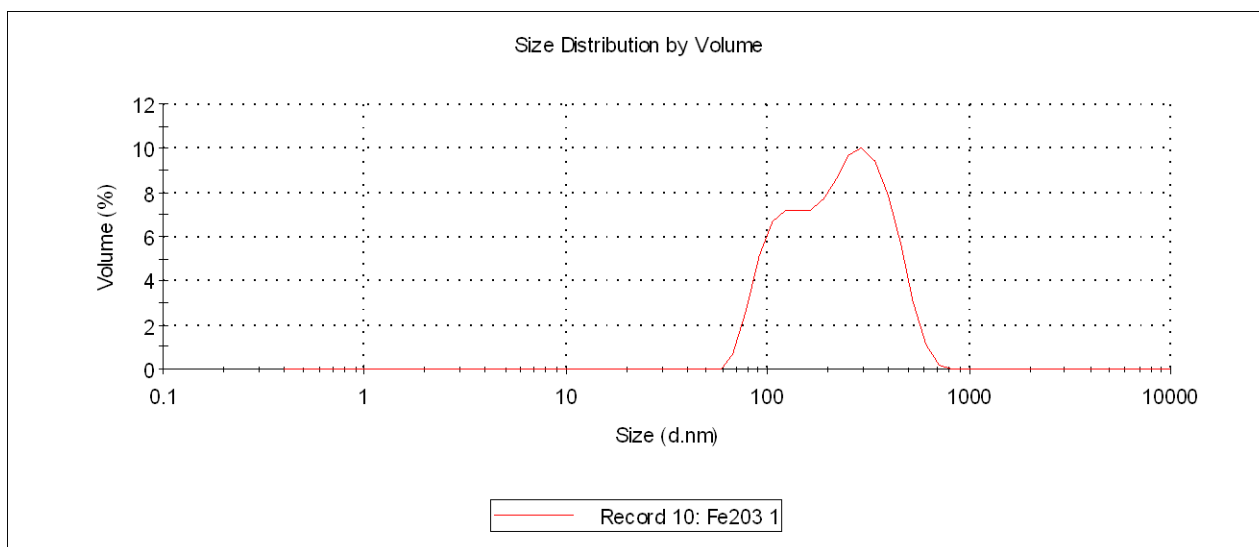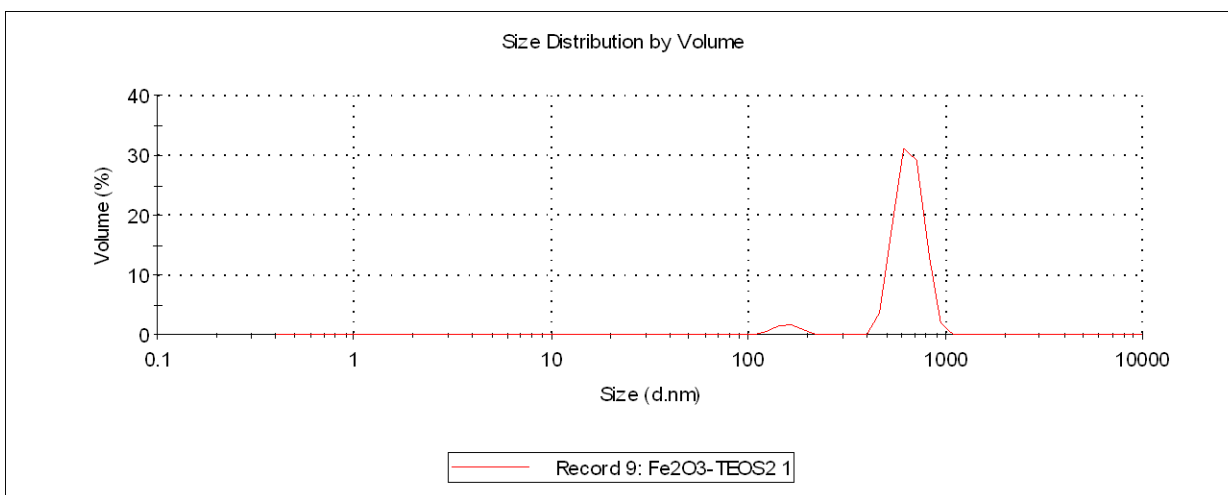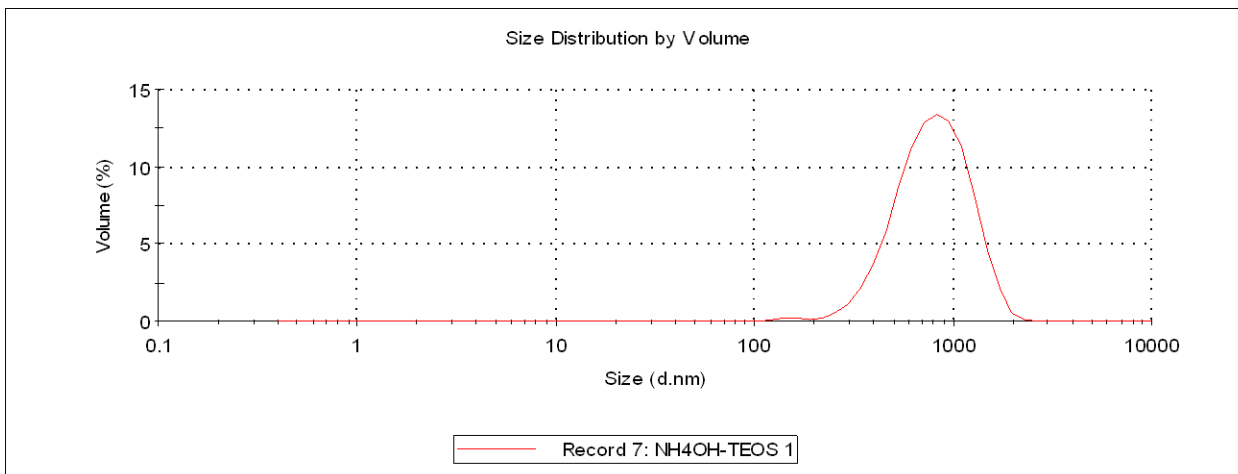
Figure 5. Particle size distribution curve of (a) Iron oxide (b) Silica and Silica coated Iron oxide nanoparticles.

Figure 5 reprsents the size distribution curve of iron oxide, silica and the Silica coated Iron oxide nanoparticles. In the case of the pure oxide nanoparticles a bimodal particle distribution curve was observed where as in case of the coated particles the particle distribution is more unifirm with a narrow range distribution range. The particle size distribution range for iron oxide particles are in the range of 60-200 nm and 100-500nm with peak maxima arround 120 and 550 nm. Where as in case of the coated particles the range is 100-200 nm and 500-900 nm with peak maxima arround 120 and 550 nm.

4.3. Conclusions

The main conclusion of the study is summarized below

1. We have successfully synthesised α-Fe_2O_3 particles by Hydrothermal method.
2. Silica Coated Fe_2O_3 Particles has been synthesised by both acid & base hydrolysis of TEOS
3. The Core Shell Particles has been characterized by SEM, XRD, and Particle size analysis.
4. From particle size analysis, it was seen that, the distribution maxima of Fe_2O_3 and $Fe_2O_3@SiO_2$ coated nanoparticle were of 120 & 350 nm, 150nm & 550 nm respectively.
5. From XRD analysis, it was confirmed that silica sample nanoparticles is amorphous in nature.
6. The SEM/EDAX analysis data represents the presence of $Fe_2O_3@SiO_2$ and show only the compositions of Si, O & Fe peaks.

4.4. Future Plans

1. Selective removals of iron oxide nanoparticles from the core to form the silica nanocapsules.
2. To study the magnetic properties of the prepared core-shell particles .

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