Graphene Oxide Coated Silica Spheres as Adsorbent

By

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DEPARTMENT OF PHYSICS

FACULTY OF BASIC AND APPLIED SCIENCES

INTERNATIONAL ISLAMIC UNIVERSITY ISLAMABAD

(2017)

Nanotechnology.
Nanomaterials
Silicon Dioxide
Graphene oxide
X-Ray diffraction

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A thesis submitted to

Department of Physics

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INTERNATIONAL ISLAMIC UNIVERSITY ISLAMABAD

FACULTY OF BASIC AND APPLIED SCIENCES

DEPARTMENT OF PHYSICS

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FINAL APPROVAL

It is certified that the work presented in this thesis entitled "**Graphene Oxide Coated Silica Spheres as Adsorbent**" by Ms. Nadia Kiran bearing Registration N0. 327-FBAS/MSPHY/F14 is of sufficient standard in scope and quality for the award of degree of MS Physics from International Islamic University, Islamabad.

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بسم الله الرحمن الرحيم

Declaration

I hereby declare that this thesis work, neither as a whole nor a part of it has been copied out from any source. Further, work presented in this dissertation has not been submitted in support of any application for any other degree or qualification to any other university or institute and is considerable under the plagiarism rules of Higher Education Commission (HEC), Pakistan.

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Nadia Kiran

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List of Abbreviations

nm	nanometer
TEOS	Tetraethylorthosilicate
XRD	X-Ray Diffraction
SEM	Scanning Electron Microscopy
FTIR	Fourier Transform Infra-Red spectroscopy
EDS	Energy Dispersive Spectroscopy
UV-Vis	Ultraviolet-visible spectroscopy
GO	Graphene Oxide
SiO_2	Silicon Dioxide / Silica
MRAM	Magnetic Random Access Memory
GCS	GO Coated Silica
PU	Polyurethane
TGA	Thermal Gravimetric Analysis
EA	Elemental Analyzer
ER	electrorheological
CVD	Chemical Vapor Deposition
SE	Secondary Electrons
BSE	Backscattered Electron
CL	Cathodoluminescence
PVD	Physical Vapor Deposition

List of Symbols

θ	Angle
λ	Wave length
π	Pi
β	Beta
σ	Sigma
ν	Frequency
ε	Epsilon

Preface

The work presented in this thesis has been carried out at laboratory, Department of Physics, Faculty of Basic and Applied Sciences, International Islamic University, Islamabad. The thesis is divided into four chapters. First chapter gives brief introduction of the research work. Chapter two relates to literature review and chapter three discusses fabrication methods and preparation of the samples. Chapter four consists of characterization techniques for investigation of samples and discusses the results. It also describes the effect of coating on structural and chemical properties of Graphene Oxide coated silica spherical nanoparticles and their application as adsorbent. At the end, there is an overall conclusion of the thesis and References to the literature are mentioned.

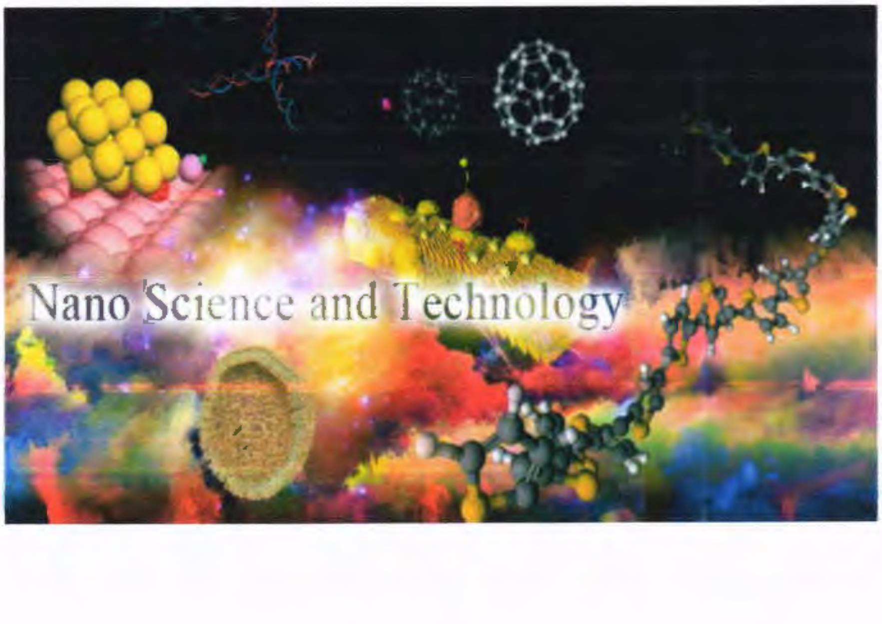
Abstract

The spherical Silica nanoparticles have been synthesized by using modified Stöber Method. In order to enhance the physical and chemical properties of these spherical Silica nanoparticles are coated with Graphene Oxide nanosheets. Whereas Graphene Oxide nanosheets were prepared through modified Hummers method and then used these coated nanospheres as Adsorbent for various types of oils just like diesel and mustard oil.

Characterization of synthesized particles was done by using characterize tools. The morphology of the samples has been checked using scanning electron microscopy (SEM) as well as compositional analysis was described by Energy Dispersive Spectroscopy (EDS). The structural investigation was done by X-Ray Diffraction (XRD). By using UV-visible spectroscopy, band gap is calculated. Fourier transform infra-red spectroscopy (FTIR) confirmed the characteristic energy bands. The observed characteristics and practical applications of Graphene Oxide coated Silica spherical nanoparticles are considered as the rising candidate of Oil adsorbent.

Chapter 1

Introduction



1.1. Adsorbent

It is a solid material which supplies surface for adsorption. Adsorbent is basically a substrate which has following qualities.

- High surface area along with appropriate pore structure and size distribution is necessary
- Good mechanical strength as well as thermal stability are compulsory

It has very long history, first document on it is the report related to adsorption behaviour of charcoal by Fontana and was published in 1777. In 1814, N.T. Saussure had performed a lot of adsorption experiments on charcoal. The adsorption technology nowadays is extensively used in many industrial processes (e.g. gas and vapor separation) and characterization of fine materials. There are some basic terms described here which concerned with adsorbent and helpful to understand it.

1.2. Adsorption

Adsorption is a procedure in which gas or liquid solute gathers on the surface of a solid or a liquid (adsorbent), and form a molecular or atomic film (adsorbate). It is a result of surface energy and can create a layer of the adsorbate on the surface of the adsorbent.

Figure 1.1: Adsorption

1.3. Adsorbate

These are the gas or liquid substances which are to be adsorbed on solids or we can say it as the material being adsorbed.

1.4. Desorption

Desorption is the process to remove the adsorbed substance from a surface of the material.

1.5. Sorption

The phenomenon in which adsorption and absorption occur simultaneously is called sorption.

1.6. Difference b/w Adsorption and Absorption

Mostly people confused with absorb and adsorb. In adsorption, a substance connects to the surface of another solid substance (e.g. paint sticks to the surface of a wall whenever we applied it through a paintbrush). Whereas in absorption, a substance penetrates within another substance (e.g. A sponge soaks up water).

Figure 1.2: Diff. b/w Absorption & Adsorption

1.7. Basic Principle of Adsorption

Adsorption is a surface phenomenon and consequence of surface energy. The surface of a liquid or solid is in a state of strain or unsaturation which results in unbalanced residual force at the surface. These unbalanced residual forces result in higher surface energy. Consequently, the surface of liquids or solids always tend to attract and retain the molecular species with which it comes in contact. This tendency is responsible for the phenomenon of adsorption.

1.8. Classification of Adsorption

There are two principal modes of adsorption of molecules on surfaces Depending upon the nature of force existing between adsorbate molecule and adsorbent

- Physical Adsorption
- Chemical Adsorption

1.8.1. Physical Adsorption

If the forces of attraction existing between adsorbate and adsorbent are **Vander Waal's** forces, the adsorption is called physical adsorption. This type of adsorption is also known as physisorption or Vander Waal's adsorption. It can easily be reversed by heating or decreasing the pressure.

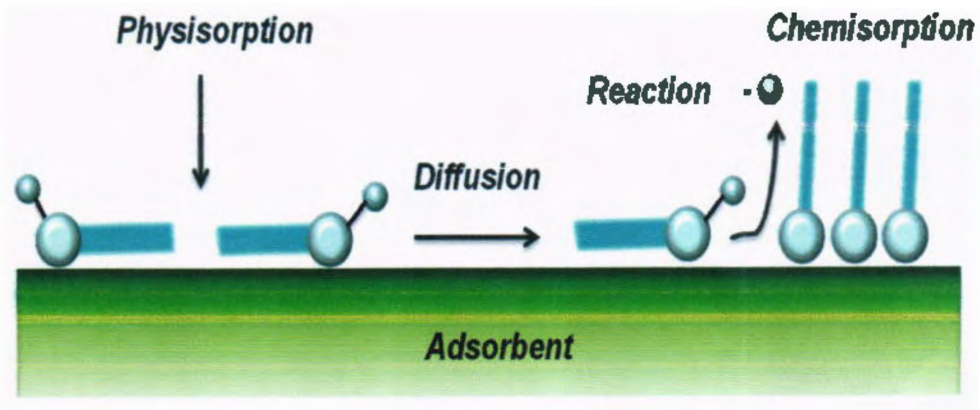


Figure 1.3: Physisorption & Chemisorption

1.8.2. Chemical Adsorption

If the forces of attraction existing between adsorbate particles and adsorbent are almost of the same strength as chemical bonds, the adsorption is called chemical adsorption. This type of adsorption is also called as chemisorption or Langmuir adsorption. This type of adsorption cannot be easily reversed.

1.8.3. Physical Adsorption vs. Chemical Adsorption

Table 1.1: Physical Adsorption vs. chemical Adsorption

Physical Adsorption	Chemical Adsorption
Not very specific	Highly specific
No electron transfer, although polarization of adsorbate	Electron transfer may occur leading to bond formation between adsorbate and adsorbent
Non-activated, rapid & reversible	Activated, may be slow & irreversible
No dissociation of adsorbed species	May involve dissociation
Only significant at relatively low temperatures	Possible over a wide range of temperatures
Physical adsorption decreases with increasing temperature	With increasing temperature, chemical adsorption first increases then decreases
May form multilayers	Limited to monolayer
Heat of adsorption is small (about 5 kcal per mol)	Very large heat adsorption (about 80-400 kcal per mol)
Due to Vander Waal's forces	Due to chemical bonds

1.9. Applications of Adsorption

There are many applications of adsorptions which are enlisted here:

- Chromatographic Analysis
- Production of High Vacuum

- Heterogeneous Catalysis
- Gas Mask
- Removal of Colouring matter from Solutions

The work in this thesis is related to the chemical adsorption. As we know chemical adsorption is related with atomic/ionic or molecular forces, so to do work in this field we must have abundant knowledge about atomic or molecular level. This level in science is called nanotechnology.

1.10.Nanotechnology

Nanotechnology is interlinked with growth and expansion of structures and mechanisms at the middle scale among discrete molecules and around 100 nm where original characteristics emerge as paralleled to bulk materials[1]. As the word '**nano**' defined ahead and '**technology**' indicates the building of beneficial things from scientific principles. Therefore, nanotechnology signifies building helpful objects at the 10^{-9} level[2]. Nanotechnology is a developing technique of the 21st century because scientific aggregation of physics, biology, materials, chemistry and engineering at nanolevel. has excellent importance of the power of materials at nanolevel.

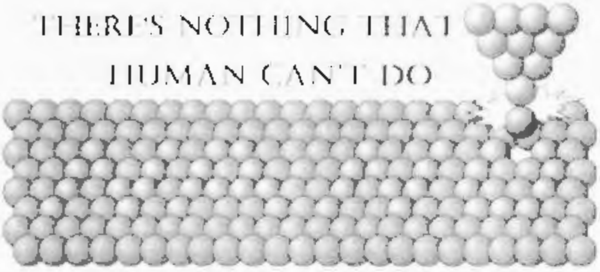


Figure 1.4: Building block of Nano's

Nanotechnology works with the initial level of configuration of atoms and molecules of alive and non-alive things. It is small but it promises that it deals by the whole of manufacturing of small machines and system of molecular size. It has ability to develop those systems that can be used in very valuable applications and productions. In its true sense, nanotechnology signifies to the intended ability to construct items from the bottom up, using tools and techniques being established today to make complete, high performance products[3].

1.11. Importance of Nanotechnology

Nanotechnology is type of science which is [4]chemistry, physics, engineering and electronics. Its impact is very big in our whole world and daily life. Materials are different on the nanometer scale. Changing the size of a material from bulk to nanoscale results in profound changes in properties and behaviour.

Figure 1.5: Importance of Nanotechnology

Mechanical properties of nanoscale materials are often orders of magnitudes higher than their bulk counterparts, because the likelihood of deleterious material defects decreases. This lower likelihood of defects also leads to superior electrical and magnetic properties. Manipulating the shape of a nanomaterial leads to an even higher degree of material property customization[5]. Anisotropic structures such as sheets, tubes and wires can be assembled having different properties from isotropic spheres of the same material. Generally, we can say that it mentioned to as general goals but its advanced version is very beneficial in many industries and all fields of society[6]. These days' scientists and engineers are the leading drivers who can drive this big world very easily in global technologies competition. In this nanotechnology is very useful for both. We would gain the various types of knowledge in this field.

1.12. Applications of Nanotechnology in Different Fields

Materials that show various physical properties causing some changes at the nanoscale have previously unlocked the door to countless new applications. Many of these applications are likewise in different phases of research, but some are already existing commercially. Nanotechnology may be suited to produce many new materials and devices with a great chain of applications, like a nanomedicine in drug delivery, nanocircuits in electronics, biomaterials as energy sources, consumer products in industries[7], etc. Some important applications of nanotechnology in different areas are listed below:

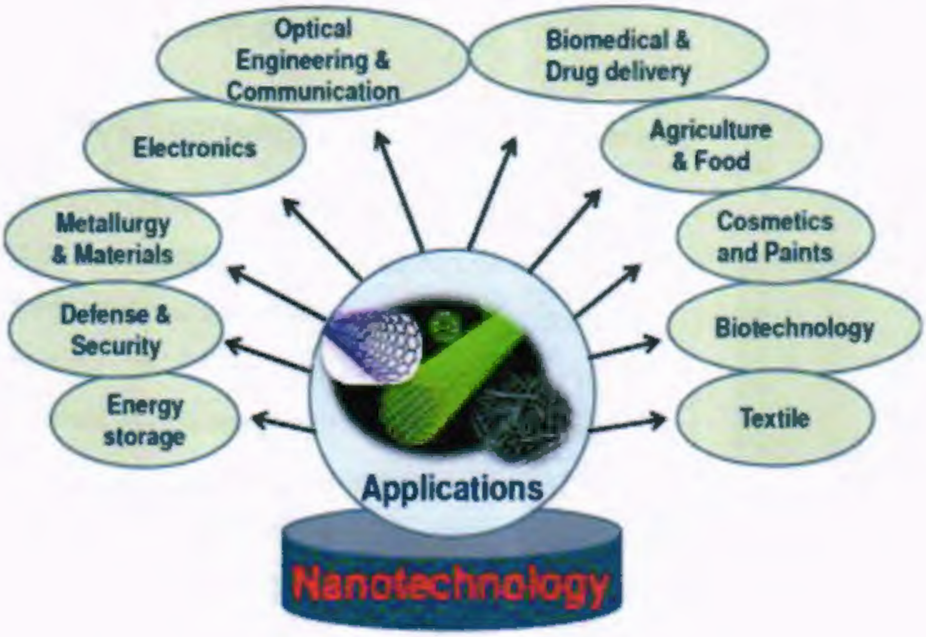


Figure 1.6: Applications of Nanotechnology

1.12.1. Nanomedicine in Biomedical & Drug Delivery

One application of nanotechnology is the nanomedicine that presently being developed includes employing nanoparticles to provide drugs to restricted types of cells such as cancer cells[8]. Nanomedicine associated with medical applications of nanomaterials in biological devices, nanoelectronic in biosensors, and yet achievable applications of molecular nanotechnology in coming age as biological machines[9].

Figure 1.7: Drug Delivery

1.12.2. Energy Storage Devices

Nanotechnology is currently worked to create various new varieties of batteries which have faster-charging capacity, most efficient, lighter weight, greater power density, and store electrical charge longer to fulfil the world's energy demands that are increased day by day. Many scientists are studying ways to acquire unpolluted, reasonable, and renewable energy suppliers, which decrease energy consumption and less toxicity

Figure 1.8: Energy Storage

1.12.5. In Defence as well as in Security

Nanotechnological institutes are developing and winning benefits of nanotechnology to facilitate soldiers persist in battle circumstances. Several types of detecting nanomaterials, like carbon nanotubes, ZnO nanowires or palladium nanoparticles are utilized in nanotechnology-based sensors.

Nanotubes, nanowires, or nanoparticles, a small number of gas molecules are enough due to their small size for the modification of electrical properties of the sensing devices. Military types organizations are not failed to observe that nanotechnology could generate a big change in troops function, move, and stay safe & sound.

Figure 1.11: Defence & Security

1.12.6. Nanoelectronics

Nanotechnology is increasing the capabilities of electronics devices with decreasing their weight and power expenditure. Upcoming information processing devices could require a standard shift in the technique per which calculations are formed. By using electrodes positioned adjacent to one another on a computer chip, the new technique causes electrically charged atoms which ionized the air, leading to an inequality of charges that makes gulps of nano-lightning[13].

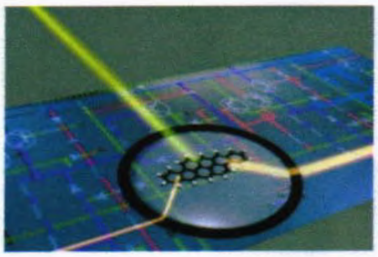


Figure 1.12: Nanoelectronics

1.12.7. Metallurgy and Materials

Several daily commercial products that depends on nanoscale materials and procedures are currently on the market and in regular use. The enhancement of different materials (i.e. steel) comes from the use of nanotechnology rather than the addition of nanoparticles; processes are used that drive out impurities and refine grain boundaries to reduce corrosion or increase strength. Changes can be made to the steel itself, or can be used for coatings that work in a similar way. Composites of nano-enabled steel and ceramics can be used to produce materials with high wear resistance and strength[14].

Figure 1.13: Materials

1.12.8. Agriculture and Food

Figure 1.14: Agriculture & Food

Nanotechnology in agriculture and food shows that despite relates regarding the toxicity hazards of nanomaterials. How food is grownup and how it is packed, nanotechnology impacts on every aspect of food science. Many companies of the world are developing nanomaterials to make a change just not only in the taste, but also in the safety of the food, and as well as the health benefits that we gained from food delivers.

1.12.9. Textile Industry

Nanotechnology offers great durability to fabrics, due to large surface area-to-volume ratio and high surface energy of nano-particles. Therefore, nanotechnology is presenting good affinity for fabrics and leading these to an increase its function. Moreover, fabrics coated nano-particles are not affected the breath ability or hand feel. So, nanotechnology has true commercial potential for the textile industry. Mainly this is due to the conventional methods used to pass on numerous properties to fabrics commonly do not proceed to long lasting effects as well as drop their functions after washing or wearing[7].

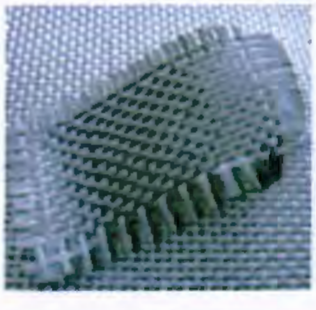


Figure 1.15: Textile Industry

Applications of nanotechnology have broad range and there are many other disciplines of life in which we used it. Therefore, we can say that it is a multidisciplinary science which has its branches in all fields of life such as colloidal science, material science, physics and supramolecular chemistry, biology etc.

1.13. Future of Nanotechnology

Nanotechnology is in constructive phase these days and it is maturing rapidly. Continuously efforts are made in the different areas of nanotechnology to grow, it is certain that various new materials, characteristics, and applications in different fields will be discovered. Combinations of different nanomaterials and their functional characteristics will also continue to progress. Hence, nanomaterials in the form of nanocomposites, nanopowders, or nanoparticles should be available for more extensive applications in all fields of life even at better and cheaper rates[15].

Figure 1.16: Future of Nanotechnology

Moreover, nanotechnology offers the assurance of improving multifunctional nanocomposites or nanomaterials that will contribute to construct and maintain simpler, protected, quicker, and more inexpensive means of transportation, like aircraft, spaceships, and ships, vehicles etc. In addition, it proposes numerous means to enhance the infrastructure of transportation.

Around the fields of information technology and nanoelectronics & devices, nanotechnology will make the possibility for manufacturing of smaller circuits and processors. These tiny devices will proceed much quicker to enable further greater computer speeds. Latest nanocircuits will mean that these computers have much longer life. In future, nanotechnology will be used to challenge environmental issues and help us to keep the environment safe.

There are many other future applications of nanotechnology those will come to light when development further proceeded. In fact, presently more over 370 outcomes of the nanotechnology are available in the market. It ranges from vehicles & sports tools to electronic devices & cosmetics as mentioned above.

1.14.Nanomaterials

Nanostructure materials are generated by strictly controlling the morphology at nanoscale measurements of particles. To get knowledge about specific molecule's characteristics, we can set them collectively in very well-defined ways to fabricate new materials with different and amazing characteristics. The size limit is often set at about 100 nm, but that is not a highly agreed-upon value. Size alone does not make this distinction. Manipulating the shape of a nanomaterial leads to an even higher degree of material property customization. Anisotropic structures such as sheets, tubes and wires can be assembled having different properties from isotropic spheres of the same material[7].

Nanostructures are fundamentally different forms of matter than simple chemicals. Their size and organization frequently take advantage of the quantum mechanical properties of these structures to have unique properties. Molecular construction includes the manipulation of specific atoms (i.e. the bottom up) and ultra-miniaturization outcomes in smaller and more smaller tools (i.e. the top down). On the other hand, physical properties of nanomaterials depend on how much larger extent on their exterior and interfacial atmosphere than perform bulk materials.

Figure 1.17: Nanomaterials

Assemblage and breaking of bonds b/w atoms or collections of atoms is the key point of nanomaterials. The rapid improvements in synthetic methods for nanomaterials has caused it feasible to construct nanostructures with ranges from 1 to 100 nm. These nanostructures have new and many different shapes just like as spheres, wires, rods, half shells, or cubes and the compositions of these nanostructures are metals, organics, oxides, and semiconductors. Examples of these include nanocrystals, block copolymers, nanowires, and nanotubes. Most famous and abundant nanomaterials have been used in this research work are:

1) Silica
2) Graphene Oxide

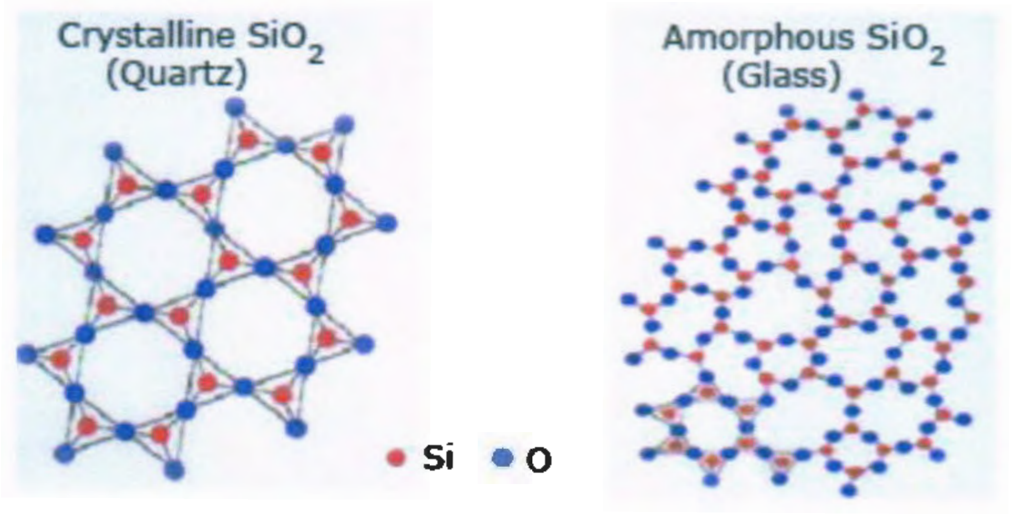


Figure 1.19: Structure of Silica

When all oxygen atoms are in bridging style, then a uniform crystal structure developed–quartz otherwise non-bridging style makes amorphous structure which tends to glass.

1.14.3. Properties of Silicon Dioxide

Both physical and chemical properties of silicon dioxide involve hardness, colour, melting & boiling point, and reactivity. Under normal environment of temperature and pressure silica is solid, crystalline mineral. Generally, it is hard, brittle and colorless to white, but if contaminants are present then it may be colored. Its melting & boiling point is very high so big hot furnace is required to make glass by melting silica sand. It does not solvable in water, and act as an insulator for electricity[16]. Silica reacts only with hydrofluoric acid and this reaction is used to etch quartz in the semiconductor industry. The properties of the silica can be generalized by listing them in the tabular form. The table is given below:

Table 1.2: Properties of Silica

Properties of Silicon Dioxide	
Chemical Formula	SiO_2
Color	Transparent / White
Glass Transition Temperature	1475 K

Magnetic Susceptibility	$-29.6 \cdot 10^{-6}$ cm^3/mol
Melting Point	1,610 °C
Boiling Point	2,230 °C
Molar Mass	60.08 g/mol
Density	2.648 (quartz), 2.196 (amorphous) gm/cm^3
Dielectric Constant (at low frequencies)	3.9
Refractive Index (at optical wavelength)	1.5

1.14.4. Uses of Silicon Dioxide

Nowadays there are countless industrial uses of silica which are applicable in different ways to help our lives. We have enlisted these uses step by step:

- The first and foremost important industrial usage of crystalline silica was related to metallurgical and glass manufacturing from three to five thousand years BC. It has continued throughout human history and played a main role in the advancement of the world specifically in glass, foundry and ceramics. Whenever you picked a glass to take a drink, you are dealing with silica. It is also utilized in grinding & polishing glass and stones.
- One another common mineral referred to silica is quartz. It has occurred in countless materials which are frequent on construction places: including soil, concrete, sand, portland cement, mortar, sand stone, masonry, rock, granite, and landscaping materials.
- Silica is used as a food additive, (i.e., anti-caking agent), to clarify beverages, as an excipient in vitamins & drugs[19] and control viscosity, as an anti-foaming agent. In supplements, it's used to prevent the various powdered ingredients from sticking together.
- Silica contributes to the reliability and flexibility of connective tissues which found in skin, nails, bones, and arteries. It is vital for the growth of skin, hair, and nails. Silicon is found safe in cosmetics and pharmaceutical manufacturing.
- Silica has great impacts in microelectronics as semiconductor devices[20] and in the field information technology as silicon chips & in plastics of computer mouses.

- Melting point of silica is 1610°C, which is greater than copper, iron, and aluminium, that's why it is used in mouldings and metal castings.

The work in this thesis focuses mainly on amorphous type of silica materials that is well utilized and studied class of porous silica materials. There are numerous potential and future applications for porous silica which can be unlocked through continuous research and development.

1.14.5. Introduction to Graphene Oxide (GO)

Nowadays there is an extreme significance of graphene oxide has noticed to all fields of science. Thin sheets of GO have recently developed as a new carbon-based material that gives another route for graphene too. Graphene is just one atomic layer of graphite - a layer of sp^2 bonded carbon atoms organized in hexagonal or honeycomb pattern[21]. It is expensive and comparatively hard to produce[22].

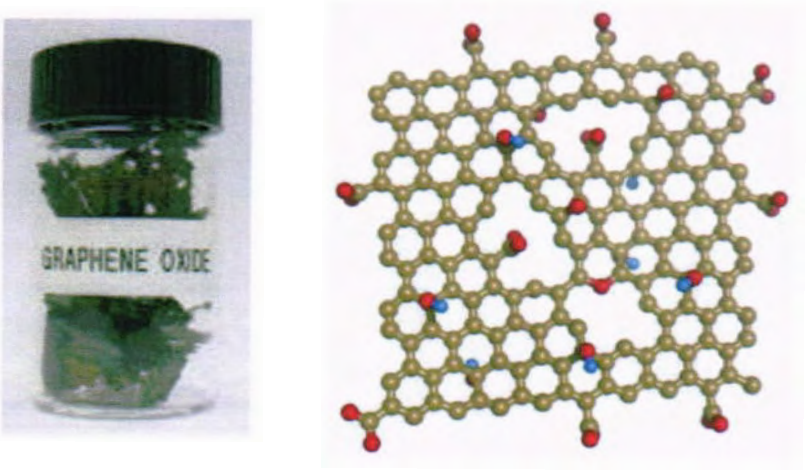


Figure 1.20: GO

Graphene oxide is synthesized by powerful oxidation of graphite (that is inexpensive and abundant), laced with oxygen-containing functional groups. It is supposed easy to synthesized and dispersible in water as well as in other solvents[23].

Basically, GO is not a conductor or an insulator however its properties can be controlled through oxidation. It is normally sold in the form of powder, dispersed, or as a coating on different substrates. The solubility of graphene oxide in organic and inorganic solvents is of great interest to researchers[24]. Graphene oxide possesses intrinsically hydrophilic properties due to its water loving ability. This was imparted due to the presence of the oxygen groups which increase the interlayer spacing of GO. Thus, water molecules can intercalate the sheets of GO rendering solubility and further increasing interlayer distance while sonicated in water.

1.14.6. Structure of Graphene Oxide

Graphene Oxide structure is basically depended on the synthesis technique and level of oxidation. As GO is an oxidized form of graphene which is laced with oxygen-comprising atoms on both sides of sheets and edges[25]. The precise atomic structure of GO remains largely unknown. The oxygen-containing groups (carboxyl, epoxy and hydroxyl) in GO can intensely affect its chemical, mechanical, as well as electric characteristics and give potential benefits for utilizing GO in several applications[26].

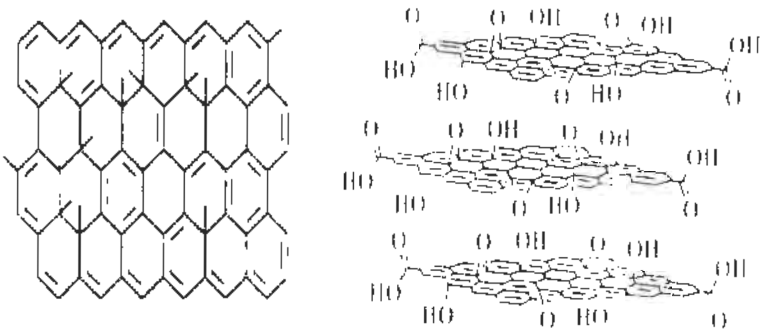


Figure 1.21: GO structure

These functional groups of oxygen reduce the van der Waals forces and increase the interlayer spacing b/w sheets. By sonication, these expanded sheets are easily pulled-out using an external force. Generally, GO is synthesized from graphite powder by means of these basic techniques: Staudenmaier, Hofmann, Brodie and Hummers. There are many variations exist in these techniques with gradually improvements to attain better results and low-cost procedures.

1.14.7. Properties of Graphene Oxide

Recently growth rate of interest in graphene oxide's applications has caused thousands of publications and a fast-tracking step of research. GO is strongly hydrophilic and easily dispersible in water, organic solvents, and other different solutions due to the existence of oxygen-containing groups. This is the main advantage of GO when combining it with polymer or ceramic materials to improve their electrical and mechanical properties[27]. Graphene Oxide is very strong and can thus be processed into sheets as thin as paper. It is commonly called an insulator but this is not true. The conduction capability of graphene oxide depends on the ratio of oxidization in the compound and the synthesized method. GO can be easily merged with different types materials & polymers, and improved the properties of composites such as elasticity, tensile strength, conductivity and many more[28].

1.14.8. Uses of Graphene Oxide

The scientists and researchers' interest for graphene oxide is due to amazing properties of this material and potential for applications. It is low-cost and easy to synthesized than graphene that's why may go in mass production and use more quickly[29].

Due to high surface area, graphene oxide can be deposited effectively on any substrate, and then converted into a conductor[30]. Therefore, it can be appropriate for batteries, capacitors, chemical sensors, flexible electronics, solar cells and touch screens[31]. GO is also suitable for countless medical applications such as disease detection, bio-sensing, drug-carriers and antibacterial materials.

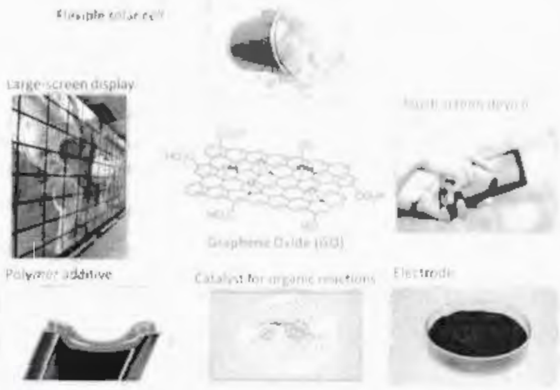


Figure 1.22: Applications of GO

Graphene Oxide with polymer nanocomposite materials is used as filler which have shown amazing improvements in properties such as tensile strength, elastic modulus, thermal stability, and electrical conductivity. It works as a base material in support of the upcoming applications in super capacitors, water purification, coatings, drop-casting, and spraying. Furthermore, GO-based materials have control over the local microenvironment[26].

1.15. Coating of Nanomaterials

Scientific concepts related to control the characteristics of materials at nano-scale have been about half a century. But, strong research efforts are made nearly twenty-five years ago, and during this period we have seen tremendous growth of nanomaterials as well as their products based on these. Currently, there are many techniques used to develop nanostructured and nanocomposite coatings for a broad range of products[32].

Coating or surface modification of nanoparticles is basically a wrapping which is applied to the surface of a nanoparticle, typically mentioned as the substrate[33]. The main objective for applying the coating material might be functional, decorative or both. The coating might be an all-over (totally cover the substrate), or only cover some portion of the substrate[34].

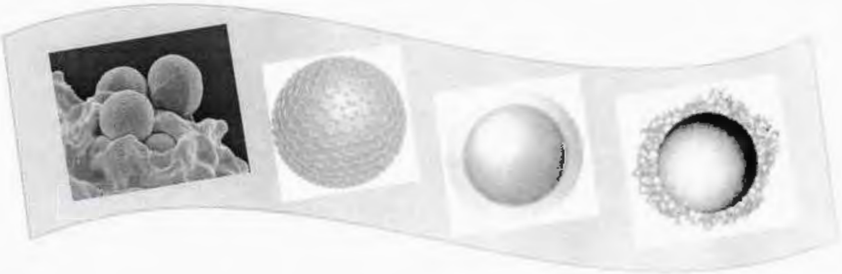


Figure 1.23: Coated Nanomaterials

The surface modification of nanomaterials is divided into different types which are based on its principles. These types include partial chemical modification, chemical & mechanical modification, high-energy surface modification, external membrane modification (i.e. capsule), esterification, surface modification by precipitation, coupling and grafting reactions[35]. Surface structure and states of nanomaterials are modified by the chemical reactions b/w the nanoparticles of material's surface and modifier[36].

1.15.1. Graphene Oxide Coated Silica Spheres

In this era, nanoparticles coating with a variety of modifier nanomaterials is a common practice to make new and beneficial innovations. Nanomaterials can be modified with organic or inorganic molecules, irrespective of their synthesis in aqueous or non-hydrolytic solutions[37]. Similarly, silica nanoparticles which are basically hydrophilic (water-loving), want to be chemically modified to become more hydrophobic (water-repellent). Likewise, Graphene oxide (GO) is a novel material with excellent adsorptive properties[38]. It results from large surface area of graphene oxide and its hexagonal arrays of carbon atoms with different functional groups that are perfect for strong interactions of nanoparticles with other molecules[39]. However, very small particles of GO can cause adsorbent loss through pores of frit. This problem can be overcome by covalently binding GO nanosheets to a support. In thesis, GO was covalently bonded to spherical silica and these GO Coated Silica (GCS) nanoparticles can be successfully applied as adsorbents[40] for different types of oils.

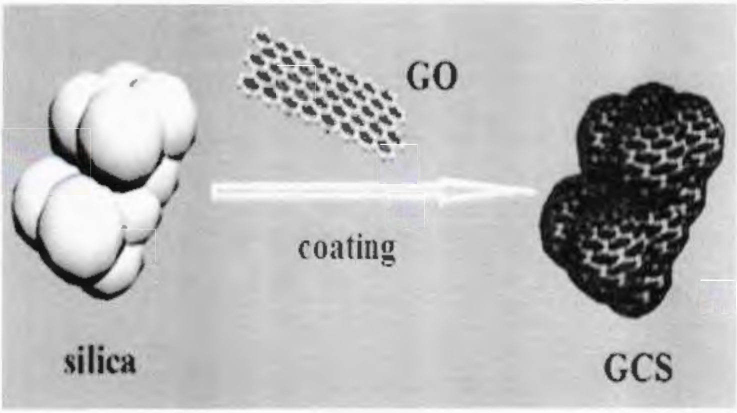


Figure 1.24: GO coated Silica

The most commonly used synthesis method of growing nanoparticles is in a liquid means composed of numerous reactants. To control the final shape of the nanoparticles, "**sol-gel**" method is used because chemical methods are usually better as compared to vapour condensation methods[41]. As the name indicates "**sol-gel**", involves the establishment of an inorganic setup of colloidal suspension (sol) supported by gelation of the sol solution to make it into liquid phase (gel)[37].

1.16. Application as adsorbents

According to a famous quote,

> " **Where nature finishes producing its own species, man begins, using natural things and with the help of this nature, to create an infinity of species** ".

Similarly, the researchers or scientists find the new ways and materials to unlock the hidden properties and then utilized these in different as well as easy ways for the services of mankind. In this thesis, we have chosen the basic nanomaterials in coated way to use as adsorbents. Adsorbent is the material which has the ability to extract certain elements from solids, liquids or gases by causing them to stick its surface without modifying the physical characteristics of that material[42]. For the application of this coated nanomaterial, fabricated Polyurethane sponges have been used. These sponges were fabricated with a thin layer of GO/SiO_2 nanomaterial through very easy way, which were then used to adsorb different kinds of oils (i.e. diesel, olive oil, mustard oil, beans oil etc) from the surface of water in the sea.

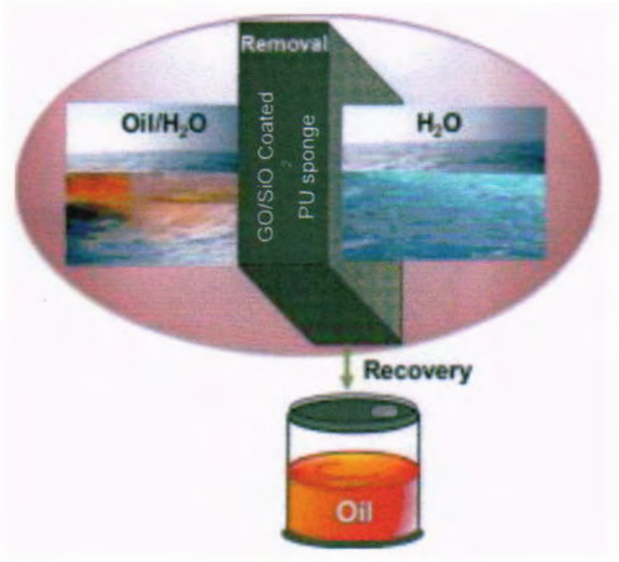


Figure 1.25: Adsorption of oil

Furthermore, these GO/SiO2 PU sponges can be reused many times even more than 50 cycles and their adsorption capability is not deteriorated. The coating of GO/SiO_2 nanomaterials are not only create hydrophobic sponges but also increased the compressive strength of these . Thus, an arrangement of high hydrophobicity, elasticity and strength made the GCS sponges highly efficient and reusable adsorbents for oil leakage[43]. There are various commercial applications of this technology to clean water from oils.

Chapter 2

Review of Literature

2.1 Overview

Silica is well known and most abundant occurring element of this planet. It has normally excellent stability with flexible bonding properties for other elements. Due to these magical properties, silica has become most important element in technologies almost from ancient glassware to latest supercomputers. Among various organic/inorganic hybrid nanomaterials, silica coated nanomaterials are highly reported in literature. Silica has capability to make broad range of nanomaterials: single or as a component of greater material structures. This may be lead to their broad use and the easiness of particle synthesis.

This chapter signifies a review of the existing growth in the field of synthesis and characterization of Graphene Oxide coated Silica spheres which were prepared using "**sol-gel**" method. It also told about the preparation of GO/SiO_2 coated Polyurethane sponges as an oil adsorbents. The reported research results on the topics of Silica, Graphene Oxide, famous "**sol-gel**" methods and preparation of nanoparticles coated polyurethane sponges by simple methods are presented here.

- Antonio B et al. in 2012 had work out for novel, flexible and simple one-step method to develop uniform silica nanospheres. This was the first time to synthesized uniform silica nanospheres by one-step method and great results had been achieved. This successful approach was based on joining the synthesis processes of silica and resorcinol-formaldehyde under Stöber conditions (i.e. an ethanol-water medium and the presence of ammonia). He found that the diameter of silica nanospheres could be modified ranging from 150 nm to 500 nm by changing ethanol/water ratio or the intensity of silicon alkoxide. His silica nanospheres established a great platform to produce hollow uniform nanoparticles of carbon or resorcinol-formaldehyde. These capsules' diameter range was about 130 nm to 450 nm that depended on the precursor which was silica. He offered so many advanced materials, which had extensive significance due to their capability as catalysis, drug delivery, selective adsorption electrochemistry, and nanocasting[44].
- In 2008 Flores, J. C., et al. prepared silver coated silica nanospheres by simple and fast method: silver nanoparticles (around 2 ± 4 nm in diameter) and silica nanospheres (around 10 ± 50 nm in diameter). He had followed the modified Stöber method and involved the production of uniform silica nanospheres at room temperature, mixed with deposition of silver nanoparticles in single-pot wet chemical method with no more coupling agent for the formation of nanospheres. He also presented the preparation and characterization of bare

silica spheres without silver, he also proposed a reaction procedure to make core–shell structure[45].

- Ibrahim et al. in 2010 reported that the effects of TEOS (Tetraethyl orthosilicate) and Ammonium hydroxide (NH_3) concentrations on the resulted silica nanoparticles' size. He prepared the spherical silica nanoparticles by following the Stöber rout and named that silica particles as "Stober Silica". His results also showed that these silica particles' size become larger to increase the TEOS and Ammonia ratio wherever both the degree of hydrolysis and condensation turn out to be faster and effect on the solubility of midway [Si (OC2H5)4-X(OH)X]. The surface modification of the silica nanoparticles by silane coupling agent have given good dispersion in hydrophobic mediums.
- In 2007 Rahman, I. A., et al. synthesized silica nanoparticles via hydrolysis in addition to condensation of tetraethyl orthosilicate (TEOS) under the influence of low frequency ultrasound. He got homogeneous and settled silica nanoparticles (around 7.1 ± 1.9 nm in diameter). He found that the particles size was enlarged by raising the concentration of NH_3 and TEOS whereas raising concentration of H_2O, temperature, and decreased ratio of NH_3 extensively decreased the particle size. When optimum terms are applied, he achieved slim dispersed and ultra-fine silica particles with a high yield of ~75% in a primary size range or reproducible. These silanol assemblages were great responsive towards high temperature and fractional restoration was achieved by ageing the sample material at room temperature. He also stated that silanol groups concentration was inversely proportional to their particle size[46].
- Jianguo Song et al. in 2014, was successfully prepared Graphene Oxide with two-dimensional structure by modified Hummer's method. It was proven that redox method was a promising way to synthesize GO on a large scale. He confirmed his results by different characterization techniques and these techniques fully supported his results for the synthesized GO. Such as his XRD results showed the crystal structure, TEM & DFM confirmed microscopic morphology, FTIR certified the presence of oxygen-containing functional groups, Elemental Analyzer (EA) & XPS described the components of synthetic material as well as chemical structure of the GO sheets and TGA & UV-Vis spectroscopy results indicated that GO sheets possessed excellent optical response and outstanding thermal stability. He told that these oxygen-containing functional groups specified many opportunities for beneficial applications of GO in different areas.

- Recently in 2016 Usama Zulfiqar, et al. reported the synthesis of hydrophobic silica nanoparticles of different diameter ranges from 48 to 260 nm by sodium silicate solution. He was achieved different mean sizes of nanoparticles by varying the concentration of the precursor (sodium silicate solution) in methanol. He was investigated that the size of the nanoparticles increased by increasing the amount of the precursor and resulted particles showed superhydrophobic properties owing to their hierarchical structure with maximum water contact angle of 158° and lowest roll off angle of $<5^{\circ}$[47]. Then he deposited silica nanoparticles with bi-modal size distribution on cotton fabric and fibres to prepare superhydrophobic composites for oil-water separation. The composites containing cotton fabric and fibres displayed excellent oil-water separation efficiency under the influence of gravity and absorption respectively. He investigated that his super hydrophobic nanocomposites are efficient candidate materials for large -scale oil-water separation.
- In 2015 Yoon, Chang-Min, et al. successfully synthesized a chain of density-controlled GO coated silica spheres by the surfactant template technique with amine surface modification to examine the effect of particle density at electrorheological (ER) activity. They controlled the density of silica spheres through generating different sized pores with surfactant template along with swelling agent incorporation approach. Further this they fabricated the ball-milled GO on to the surface of various silica spheres to enhance ER, specifically towards low density particles showed favourable ER functioning as compare to high density particles including synergetic effect of dielectric feature. He examined the ER performance by Stokes' law with practical sedimentation observation and said these low-density particles with high ER performance can be used as promising candidate for fluids by the reason of amplified particle mobility and dielectric feature[48].
- About the year 2012 Sobon, Grzegorz, et al. demonstrated comprehensive research with Er-doped fibre laser mode-locked through two saturable absorbers that were depended on Graphene Oxide (GO) & reduced GO. They described the successful production of saturable absorbers together with specified contrast of their parameters as well as they did not find any considerable change in the laser performance obtained in both inspected set-ups. Their results also showed that their described technology, from the oxidation of graphite to GO, was reproducible and synthesized GO may be effectively consumed as a useful saturable absorber exclusive of its reduction to rGO. The GO formed stable aqueous dispersion that did not required any organic composites or could be affected straightforwardly on the fused silica windows while rGO combines in water and should be passed on properly in toxic

organic solution due to its hydrophobic properties. Hence they concluded that GO appears to be good applicant as an economical substance for saturable absorbers to Er-doped fibre lasers[49].

- Kou, Liang, and Chao Gao. et al. in 2011 reported the synthesis of silica (SiO_2) nanomaterial coated Graphene Oxide (GO) nanocomposites by facile one-step liquid solution procedure at room temperature with no additional templates or surfactants. During their synthetic approach, a water-alcohol mixture was used as the reaction agent because that was environmental friendly in addition to nontoxic. They claimed that their synthesized hybrid (GO-SiO_2) layers can be constructed into paper film via filtering method then that film works at great conductivity of 10^3-10^4 Sm^{-1} after reduction. Interestingly, these GO-SiO_2 nanohybrid sheets showed outstanding hydrophilic behaviour plus it concerned with commonly types of building blocks for the construction of big area superdrophilic surfaces for different types of substrates (e.g., polypropylene, ceramic tile, and lotus leaf) by simple drop coating technique. Thus, these coated large area superhydophilic surfaces flatten the treatments combined with spoiling the internal structure of substrates without any extra process[50].
- In 2013 Liu, Yue, et al. fabricated coated Polyurethane (PU) sponges with reduced Graphene Oxide (rGO) by a facile method and characterized their properties as well as their structure by Fourier Transform Infrared Spectroscopy (FTIR), X-ray Diffraction (XRD). Thermal Gravimetric Analysis (TGA), and Scanning Electron Microscopy (SEM). Their prepared rGO coated PU sponges had high compressive strength as compared with the simple PU sponges and showed extremely high absorption for organic liquids from water surfaces due to their superhydrophobic and superoleophilic characteristics. They got the absorption capacities for all the liquids and were found tested values more than 80 gg^{-1} and maximum value 160 $gg^{-1}$was achieved for chloroform. Moreover, they claimed that the absorption capacity of rGO coated PU sponges did not deteriorate when they were reused for 50 times even the weight of the dry coated sponges did not change. So, these rGO coated PU sponges has excellent recyclability and much more cost effective for the treatment of oil spills as well as for oil water separation.
- Yang, Kaijie, Baoliang Chen, and Lizhong Zhu. Et al. in 2015 reported that the considerable accumulation of the graphene nanosheets could be casily overwhelmed by loading graphene on the silica (SiO_2) nanoparticles because it decreased its powerful adsorption capacity. With the help of silica nanoparticles, the stacked interlamination of graphene was exposed

towards the adsorption spots in the interlayers and enhanced its adsorption capacity. Adsorption capacity of these graphene coated nanomaterials was enhanced by increasing the loading quantity of the graphene sheets and radically reduced by introducing the oxygen containing functional groups in the graphene sheets. Strong π-π stacking interactions and high hydrophobic effect of the graphene sheets had great contribution towards the excellent adsorption of graphene coated silica materials. That's why the substitution of water droplets was enclosed to the graphene sheets by ineffectual non-hydrogen bonding along with phenanthrene composites while effective π-π stacking interfaces was assumed to be an extra adsorption procedure on behalf of graphene coated materials. These coated particles acted as a framework for environmental applications such as economical and highly proficient adsorbents to remove aromatic pollutants from water surface[51].

Chapter 3

Materials and Methods

3.1 Overview

This section provides information on to what place I retrieve the materials that are treated in my research. It further includes information on at which point approached my research work – and why. It is a notable component of my obstinate lab report. This section gives a studied account of the matter of form that was followed in completing my experiments.

3.2 Materials:

The materials that second-hand are a significant part of my completely effort to boost a schedule of action or involve a suited research question.

3.3 Methods:

The methods that are used to gain information and ratiocinate an end-argument or uphold a merger is furthermore important.

3.4 Formation of Nanoparticles

The term 'nanoparticle' is general and is regularly used to deal with materials that are better illustrated for other terms. Nanoparticles are often crystalline and bring to a close up considering referred to as nanocrystals. The changeover from microparticles to nanoparticles can control to several changes in physical properties. There are two main factors in this

- surface area to volume ratio,
- particle's size proceeding to the state on the way to what place quantum effects prevail[52].

Generally, two approaches are used in the preparation of nanoparticles from ancient times.

- Top-down approach
- Bottom-up approach

These approaches involve the reduction of nanomaterial constituents (approaches to sub atomic level) by additional self-assembly method preceding towards the foundation of nanostructures.

3.4.1 Top-down approach

The first one is breakdown (top-down) approach in which an outward force is directed towards solid or bulk material to precedes for its break-up and directed towards into nanoparticles. General examples of Top-down approach include ball milling, simple plastic deformation and etching through the mask.

3.4.2 Bottom-up approach

The second one is the build-up (bottom-up) approach that creates Nanoparticles by assembling them from building blocks of Atom-by-atom (atoms of gas or liquids based on atomic transformations), molecule-by-molecule (molecular condensations), or cluster-by-cluster. Typical examples of Bottom-up-approach are formation of nanoparticles from colloidal dispersion and quantum dot formation during epitaxial growth.

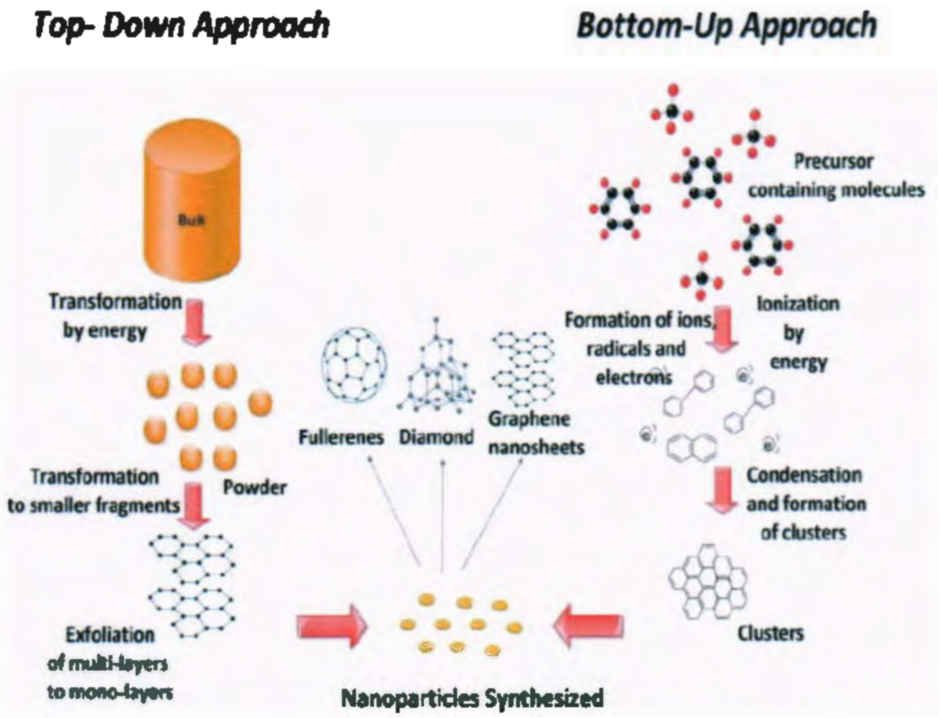


Figure 3.1: Approaches for nanoparticles

Each approach has its own limitations. For example, in top-down approach by nature, are not low-priced and rapid to manufacture-slow and not acceptable for large scale fabrication. Whereas in bottom-up, fabrication is mostly less expensive when sizes of nanoparticles fall below nanometer scale. Because bottom-up approach empowers one the concede nanostructure with less defects and preferably homogeneity. On the other hand, top-down approach generally creates surface defects and impurities[53].

Thus, a device or procedure which is used for the synthesis of nanoparticles accomplished the following situations: • aggregation control • tuneable particle size, shape, crystal structure, size, and composition distribution • progress in the purity of nanoparticles • stabilization of structures, physical properties, and reactants • greater reproducibility • cost effective, scale-up, along with greater mass production. Similar results can be achieved through bottom-up and top-down approaches.

3.5 Synthesis of Silica Spheres

The synthesis of silica has been a research field of rapid development, attracting great interest due to wide variety of potential applications. Many fields of science and industry target silica as a material of intense interest. The properties of nanoparticles are highly size-dependent so the synthesis of nanoparticles with desire size and uniform composition is of great importance. These properties are of interest in applications such as adsorption, separation, catalysis, drug delivery and purification. Silica nanoparticles can be produced using a wide variety of synthetic methods[54] with precise control over their physical (size) and chemical characteristics (uniform composition). Some of these are dry methods (solid state method) and some are wet methods (chemical method). Spherical silica particles can be synthesized by these several different methods:

- Spray Drying
- Chemical Co-Precipitation
- Sol-gel Method
- Microemulsion Method
- Vapor-Phase Synthesis
- Acid Hydrolysis
- Thermal Treatment Method

In this thesis, silica nanoparticles were obtained from a modified Stöber method[55].

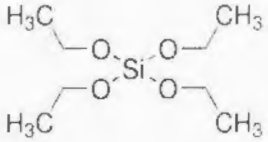
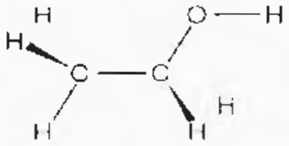
3.5.1 Synthesis of Silica Spheres by modified Stöber method

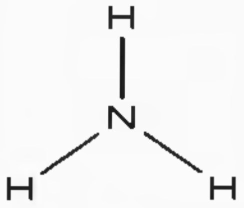
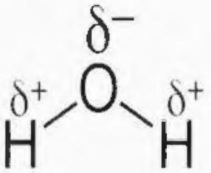
The formation of spherical silica can be controlled through control of the reaction system. There are numerous factors that determine the final form of the spherical silica. The first successful synthesis of spherical silica particles with controlled particle size was the Stöber method in liquid phase through "bottom-up" procedure[56]. The Stöber method, continues to be a widely employed for synthesizing silica nanoparticles, was developed in 1968. This is an example of "**sol-gel**" procedure wherein a composite precursor (usually tetraethylorthosilicate) reacted along with water molecules which are in alcoholic suspension, so that the resultant composite materials joined simultaneously to make greater structures[57].

3.5.2 Chemicals

The chemicals and their specifications which used in the Stöber method to produce silica spheres are listed in the given table:

Table 3.1: Chemicals used for Silica

Chemicals	**Chemical Formula**	**Chemical Structure**
tetraethyl-orthosilicate (TEOS)	$SiC_8H_{20}O_4$	
absolute ethanol	C_2H_6O	

ammonia	NH_3	
de-ionized water	H_2O	

All these chemicals were purchased from Sigma Aldrich and the purity of all these used chemicals was 99.9%.

3.5.3 Experimental setup

- Heating plate with automatic temperature regulation
- Glass beakers
- Magnetic Stirrer
- Centrifuge Machine
- Petri Dish
- Stirring Plate
- Weighing Balance

3.5.4 Experimental Procedure

Silica nanoparticles were synthesized by hydrolysis along with condensation of TEOS in ethanol, combined with presence of ammonia as catalyst. First of all, solution having sufficient amounts of absolute ethanol, ammonia along with deionized water and then stirred for 5 minutes to ensure complete blending. Then an appropriate quantity of TEOS in absolute ethanol was added to the obtained solution and after that reaction continued at ambient temperature for 24 hours as per reactants concentrations. Subsequently the colloidal solution was centrifuged by high-speed, and separated silica particles through three times washings of absolute ethanol form undesired particles[44]. Keep on by drying in oven at 100 °C for 2 hrs to avoid continuous reaction.

3.5.5 Schematic representation:

The schematic representation of the Stöber method for the synthesis of spherical silica is as:

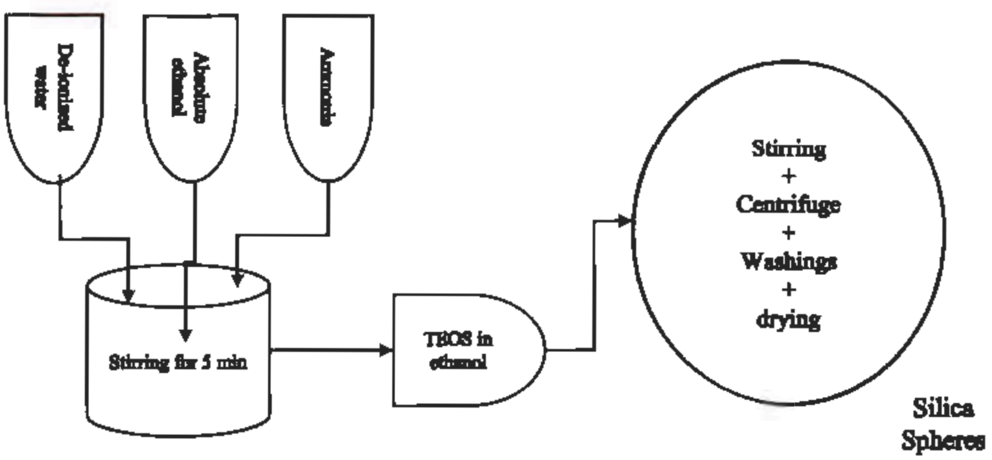


Figure 3.2: Procedure for Silica nanoparticles

The usage of silica nanoparticles with a specific particle size along with tremendously narrow distribution, is always wanted, for the applications in different fields. Diameter of the silica nanoparticles by Stober procedure is handled through the contribution after nucleation and growth procedures. That's why, we can say that particles' diameter influenced via TEOS plus NH_3 ratio. [45]The nanoparticle's size increases by raising TEOS and ammonia ratio at which both the condensation and hydrolysis' rate as well as condensation turn out to be quicker, affect the intermediate solubility affect and hence influence the supersaturation for the nucleation procedure.

3.6 Synthesis of Graphene Oxide (GO)

Graphene oxide is an oxidized derivative of graphene and is obtained from the severe oxidation of graphite powder. This process introduces oxygen-containing functional groups to the surface of GO[58].

Graphene Oxide can be prepared by these several different methods:

- Electrochemical synthesis of graphene oxide

- Morphological synthesis of graphene oxide
- Graphene oxide nanosheets synthesized by using graphite nano-fibers
- Chemical Vapor Deposition (CVD)
- Total Organic Synthesis
- Chemical Methods

Here we have used the modified Hummers method to synthesize graphene oxide.

3.6.1 Synthesis of Graphene Oxide by modified Hummers Method

Graphene oxide, a chemically altered graphene, is synthesized from the chemical exfoliation of natural graphite powder following the most commonly used modified Hummers method[59]. Graphite consists of stacked graphene layers with a plane distance of 0.335 nm.

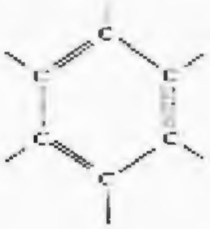
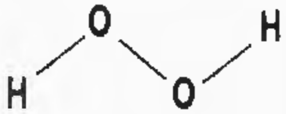
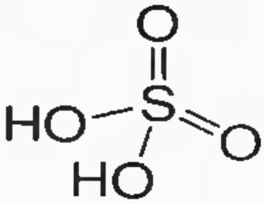
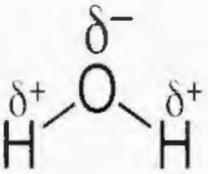
Briefly, graphite powder was oxidized in the presence of H_2SO_4, $NaNO_3$ and KMnO4. Oxidized graphite was washed with HCl, H_2O_2 and warm distilled water, followed by exfoliation induced by sonication. Severe oxidation process in modified. Hummers method separates these stacked graphene layers (into single and few sheets) and introduces many oxygen-containing functional groups to the basal planes and edges[60]. This oxidized product is referred to as graphene oxide. In addition, this process results in a layer distance of 0.74 nm. As-prepared GO readily exfoliates into individual nano sheets in polar solvents upon a simple sonication and forms a suspension which is stable for a long period[61].

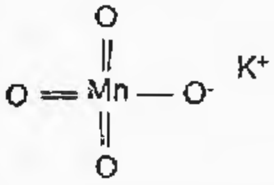
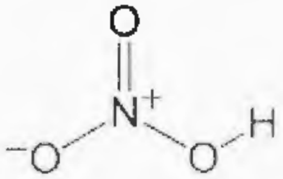
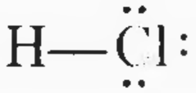
3.6.2 Chemicals

The chemicals and their specifications which used in the modified Hummers method for Graphene Oxide are listed in the given table:

Table 3.2: Chemicals used for GO

Chemicals	**Chemical Formula**	**Chemical Structure**

Graphite Powder	C	
Hydrogen Peroxide	H_2O_2	
Sulfuric Acid	H_2SO_4	
Distilled Water	H_2O	

Potassium Permanganate	KM_nO_4	
Nitric Acid	HNO_3	
Hydrochloric acid	HCl	

All these chemicals were purchased from Sigma Aldrich and the purity of all these used chemicals was 99.9%.

3.6.3 Experimental setup

- Heating plate with automatic temperature regulation
- Heating bath ((beaker with water)
- Glass beakers
- Cooling bath (beaker with ice)
- Petri Dish
- Magnetic Stirrer
- Centrifuge Machine
- Stirring Plate
- Weighing Balance

3.6.4 Experimental Procedure

Before going to the procedure of graphene oxide we have to get expanded graphite from naturally graphite powder. Synthesis of expanded graphite by chemical method with sulfuric and nitric acids is summarized. Expanded graphite was prepared at room temperature by mixing of sulfuric acid (H_2SO_4) and nitric acid (HNO_3) with natural graphite powder. The mixture was placed for 1h and 30min in a magnetic stirrer and then soak for 3 days. The mixture which was prepared was washed with distilled water to achieve pH in the range of 5-7. After that centrifuge this and then dried at 60°C to get expanded graphite.

By using modified Hummer method in detail, expanded graphite was added in intervals to the sulfuric acid (H_2SO_4) which was magnetically stirred for 10 min. $KMnO_4$ was slowly added in it with continuously stirring in an ice bath for 45 min to keep the temperature below 10 °C. Afterwards, the suspension was then stirred for 2h in water bath at 40°C. Then the temperature of mixture was set at constant 90°C for 60min whereas deionized water was continuously added to it. Further H_2O_2 was mixed into this solution after 5min. The outcome solution of the reaction was centrifuged then washed it with HCl and deionized water mixture repetitively. Lastly, the final product was dried with hot plate at 60°C[62].

3.6.5 Schematic representation:

The schematic representation of the Hummers method for the synthesis of graphene oxide is as:

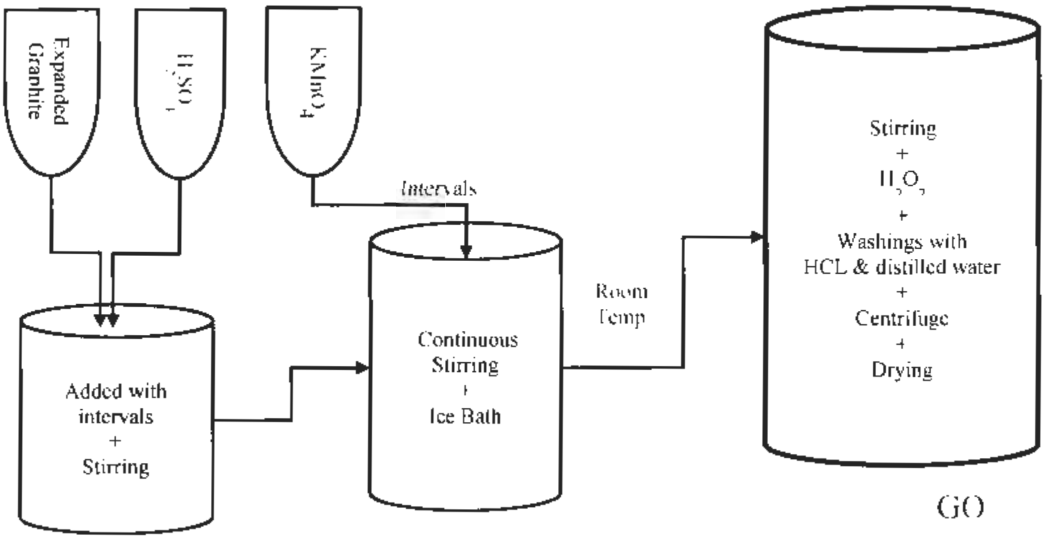


Figure 3.3: Procedure for GO sheets

The most important point for the synthesis of graphene oxide is to choose the appropriate oxidizing agents for oxidation of graphite. Graphene oxide has many oxygen-containing functional groups after chemical modification., which make its possibility to use in several applications.

3.7 Coating and Chemical Modification of Nanoparticles

There are limitations in the applications of nanomaterials due to their limited behaviour in various solvents. Surface modifications of nanomaterials assist to modify their properties to suitable in different applications nanotechnology, because surface properties reveal the interaction among the components, as well as the solubility and agglomeration behaviour in various solvents[63].

To improve or exchange the dispersion of the nanoparticles, the compatibility between the nanoparticles with other materials, physical or chemical methods are required to modify the physical, chemical, mechanical prozperties, as well as the surface structure of nanoparticles[64].

These are different techniques used for coating and surface modification of nanoparticles.

- Thermal Spraying
- PVD Techniques
- CVD Techniques
- Sol-gel Technique
- Plasma Assisted Coatings
- Liquid Phase Oxidative Treatments

While here we adopted the sol-gel method for coating of silica spheres with graphene oxide nanosheets.

3.7.1 Graphene Oxide (GO) coated Silica Spheres by Sol-gel method

Basically, "**sol-gel**" method is a wet-chemical procedure that works either with colloidal particles or chemical solution[65] since after 1800s to produce integrated networks (gel). It offers a wet method to dope materials on behalf of improved performance. "**Sol-gel**" method could be managed to get desired particle shape, size, and size distributions. It also provides new approaches and a better control at molecular level.

3.7.2 Materials

The materials which used in the Sol-gel method for Graphene Oxide coated Silica spheres are given:

- Silica
- Graphene Oxide
- Deionized Water
- Ethanol

3.7.3 Experimental setup

- Heating plate with automatic temperature regulation
- Glass beakers
- Petri Dish
- Magnetic Stirrer
- Centrifuge Machine

3.7.4 Experimental Procedure

Coated Silica spheres were prepared by dispersing Silica spheres into ethanol solution and vigorously stirred for 12h to get template solution. Subsequently in another beaker GO nanosheets were dispersed in deionized water then added this dropwise to the obtained modified solution. Mixed solutions were continuously stirred for overnight then washed with deionized water as well as with ethanol. Resulting Graphene Oxide coated Silica spheres in powder form were collected by centrifugation and dried by heating plate at 60°C. Further sonication will reduce the particle size of the GO coated Silica spheres.

3.7.5 Schematic representation:

Overall scheme for surface modification of silica nanoparticles with GO wrapping procedure is explained by below fig.

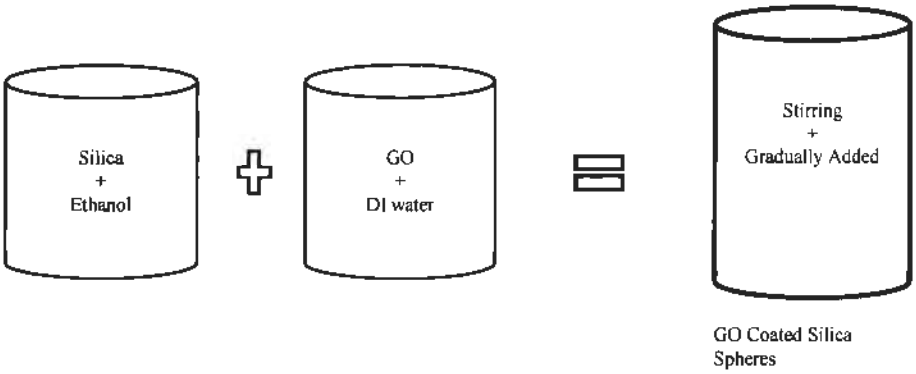


Figure 3.4: Coating procedure

The approach that we used for surface modification to enhance functionalization of nanoparticles based on the particular atomic structures of the materials and their collaborations towards ligands[66].

4 Chapter 4

Characterization and Results

4.1 Overview

The basic purpose of this chapter is to briefly discuss the experimental results of the work that is performed on SiO_2 nanoparticle synthesis and decoration it with carbon support sheets. These experiments, involving the simultaneous synthesis and coating of GO sheets on spherical Silica nanoparticles were performed in the presence of water and ethanol by following wet chemical methods. Every material has its own particular properties. Different techniques can be used to fathom the properties of nanoparticles. Each technique gives some specific information: some are allied to chemical and others may be associated with physical properties. Different tools of characterization have been used to study structural and chemical properties of materials.

4.2 Characterization Techniques

There are various characterization techniques used to analyze and determine the particle size of the spherical silica particles and their coatings with GO sheets. We have enlisted and briefly discussed the basic principles of some techniques which are used in our experimental work that is done for this thesis. For sample characterization, the following techniques were used:

- SEM - Scanning Electron Microscopy
- EDS - Energy Dispersive X-ray Spectroscopy
- XRD - X- Ray diffraction
- FTIR - Fourier – Transform Infrared Spectroscopy (FTIR)
- UV-VIS - Absorption Spectrophotometer (UV-VIS)

In this chapter, SEM analysis confirmed SiO_2 spheres were decorated with GO sheets as well as the morphology of the silica spheres and graphene oxide sheets. Then the successful development of GO/SiO_2 nanocomposites was verified by UV-Vis absorption spectroscopy. Conversely, XRD provided report about the degree of crystallinity of nanocomposites which were established at altered concentration. Its analysis confirmed that the decorated SiO_2 matches that of amorphous structure. SEM, XRD and simultaneous FTIR analyses were performed to verify the characteristics of GO/SiO_2 nanocomposite material samples that were synthesized by using new approach.

induced current, environmental electron microscopy, acoustic thermal-wave microscopy, and imaging with X-rays. Specific X-rays are produced when electron beam eliminates an inner shell electron of the sample, a higher-energy electron fulfil the shell and emit energy. These typical X-rays are utilized for the identification nanocomposites and also compute the plenty of elements in the given sample.

There are different types of signals (photon and electrons) produced when the incident electron beam strikes the sample in SEM. These signals and their specifications are as under:

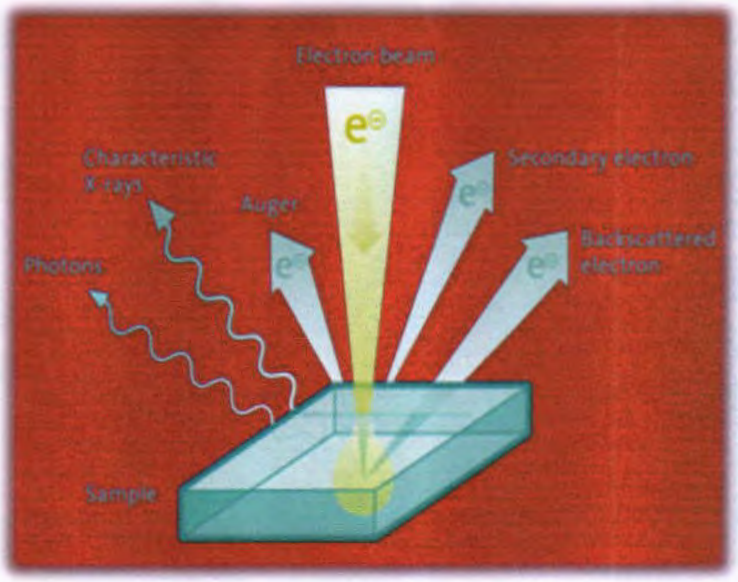


Figure 4.2: Basic principle of SEM

- **Secondary Electrons (SE)**

It gives topographical information.

- **Backscattered Electron (BSE)**

It gives atomic number and topographical information.

- **Auger Electron**

It gives surface sensitive compositional information.

- **X-rays**

It gives through thickness compositional information.

- **Photons/Cathodoluminescence (CL)**

It gives electrical information.

- **Specimen Current**

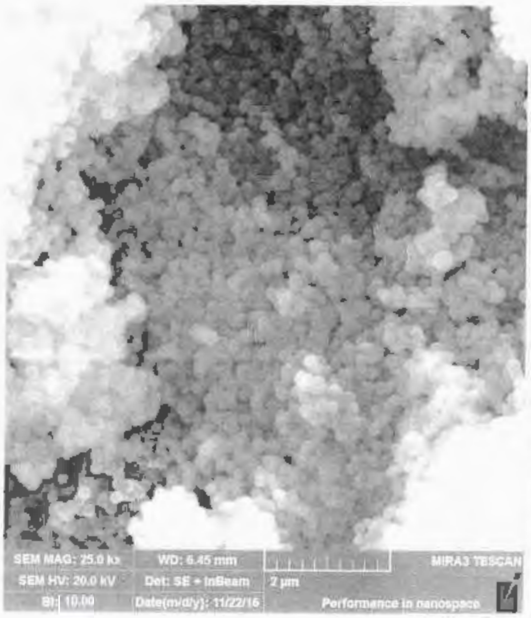
It gives electrical information.

4.2.1.2 Results Analysis

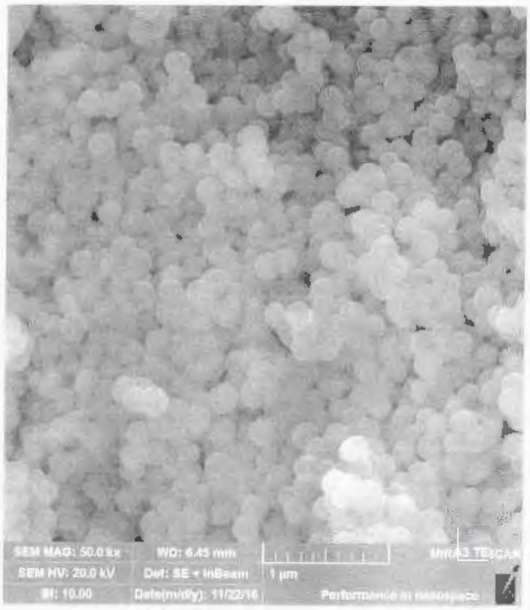
SEM - Scanning Electron Microscopy was operated on our sample to observe the structures and morphologies of the prepared nanoparticles. The SEM tests were accomplished on the dry powder of the nanomaterials. Because of very low resolution of SEM, we can even imagine the surface of the particles and macroscopic morphology changes.

4.2.1.2.1 Pure SiO_2 Spheres

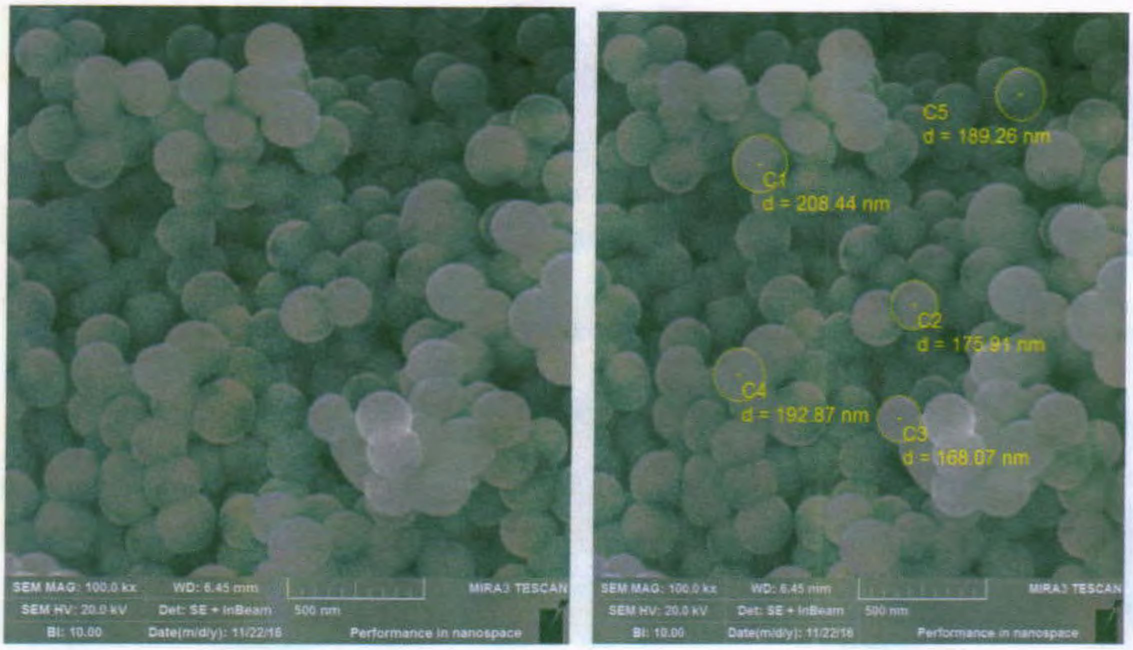
Figure represents the SEM images of pure SiO_2 nanoparticles. The morphology in these images is approximately uniform and sizes of the particles seem to be similar.



(a)



(b)



(c) (d)

Figure 4.3: SEM results of pure Silica (a) at 2µm (b) at 1µm (c) at 500 nm (d) at 500 nm with diameter sizes

This well-ordered morphology reveals that the nanoparticles are spherical and the phase pure formation of SiO_2 particles without presence of unnecessary impurities. The average diameter of these SiO_2 spheres is 186nm. These SEM images also exposed that spherical nanoparticles are randomly dispersed as well as agglomerated.

4.2.1.2.2 GO Nanosheets

SEM – scanning electron microscopy was investigated the morphological characteristics of the graphene oxide, even single flakes of GO nanosheets were observed. The flakes of graphene oxide have comparatively large surface area or its morphology looks like the wafers or curtain. These characteristics signify excellent exfoliation of graphite powder through oxidation procedure.

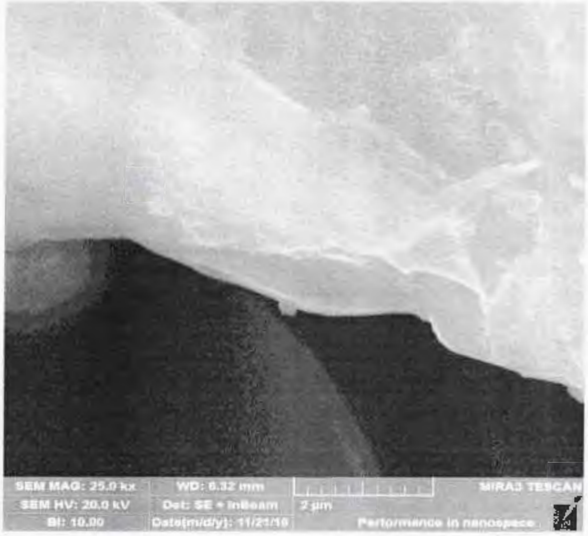
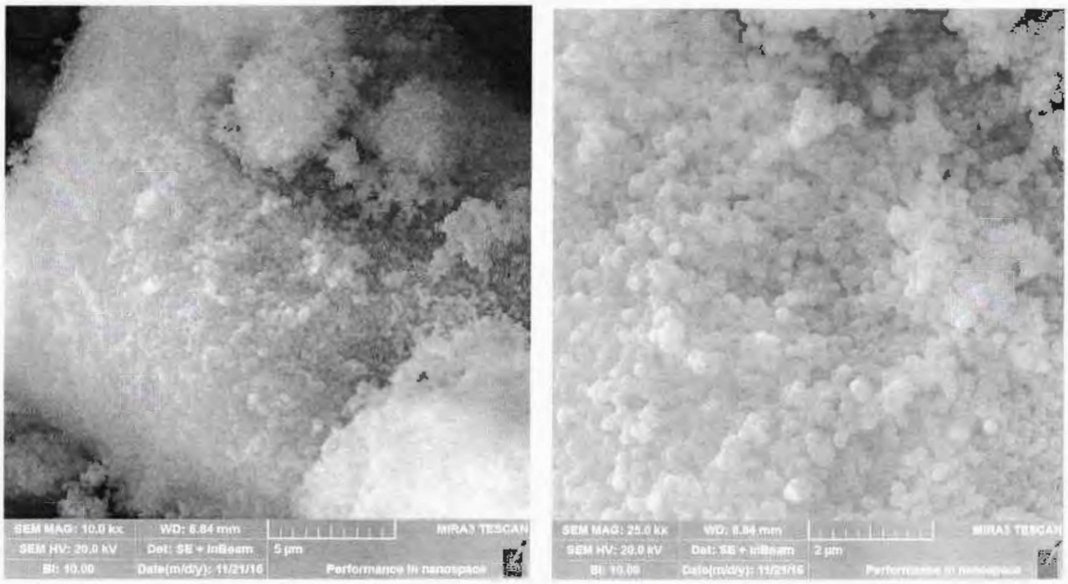


Figure 4.4. SEM result of GO

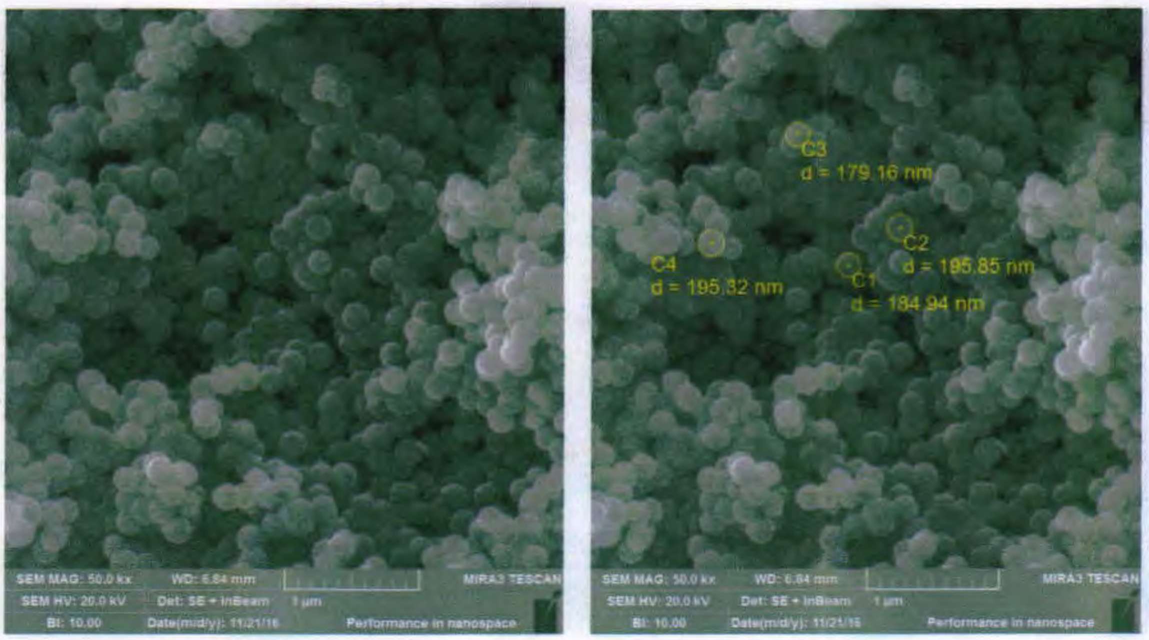
Morphology of GO nanosheets is noticed as flaky surface revealing its layered microstructure which is shown in fig. The interspaces b/w the layers with thinner layer edges of GO have clearly observed[67].

4.2.1.2.3 20% GO coated SiO_2 Spheres

To study the macroscopic morphology of SiO_2 spheres with graphene oxide, SEM test were done after composing SiO_2 with GO.



(a) **(b)**



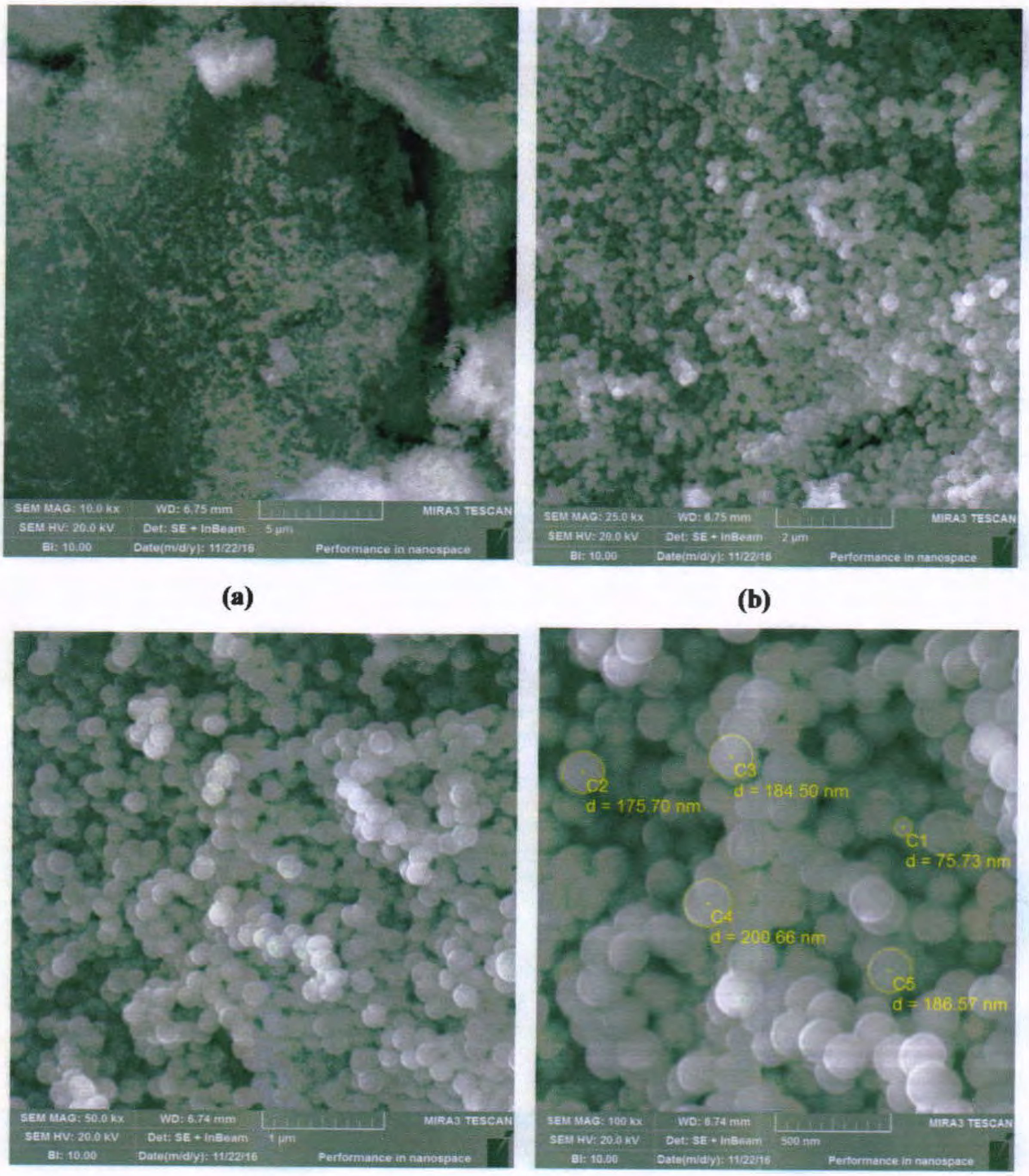
(c) (d)

Figure 4.5: SEM results of Silica with 20% GO (a) at 5μm (b) at 2μm (c) at 1μm (d) at 1 μm with diameter sizes

The spherical structure was the same after coating due to very small amount (20%) of GO was coated on SiO_2. The presence of graphene cannot be seen in these images because GO nanosheets are ultra-thin, and the coated amount was so low to be noticed by such a low-resolution as SEM. Fig. shows the SEM images of GO/SiO_2 composite particles with 20% GO coating.

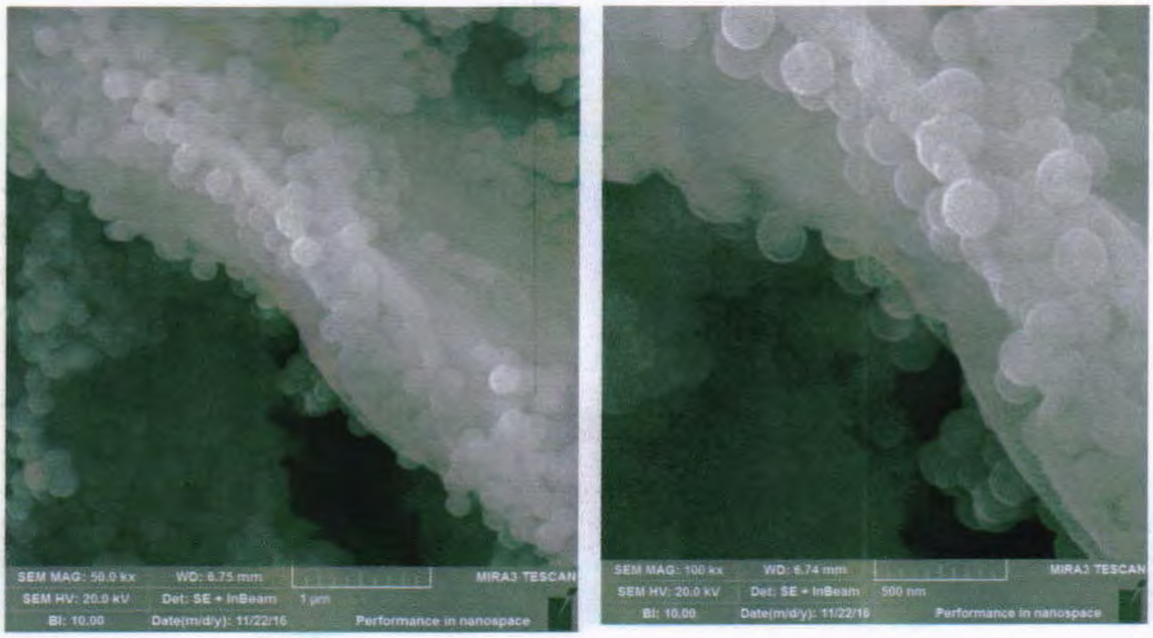
4.2.1.2.4 60% GO coated SiO_2 Spheres

Successful fabrication of the GO/SiO2 nanocomposite with a silica spherical structure was confirmed by 60% GO by these SEM images. The figure tells us about the aggregation of nanoparticles in addition with small layers are observed at the surface.


SEM MAG: 10.0 kx
WD: 6.75 mm
MIRA3 TESCAN
SEM HV: 20.0 kV
Det: SE + InBeam
5 µm
BI: 10.00
Date(m/d/y): 11/22/16
Performance in nanospace
SEM MAG: 25.0 kx
WD: 6.75 mm
MIRA3 TESCAN
SEM HV: 20.0 kV
Det: SE + InBeam
2 µm
BI: 10.00
Date(m/d/y): 11/22/16
Performance in nanospace
SEM MAG: 50.0 kx
WD: 6.74 mm
MIRA3 TESCAN
SEM HV: 20.0 kV
Det: SE + InBeam
1 µm
BI: 10.00
Date(m/d/y): 11/22/16
Performance in nanospace
C2
d = 175.70 nm
C3
d = 184.50 nm
C1
d = 75.73 nm
C4
d = 200.66 nm
C5
d = 186.57 nm
SEM MAG: 100 kx
WD: 6.74 mm
MIRA3 TESCAN
SEM HV: 20.0 kV
Det: SE + InBeam
500 nm
BI: 10.00
Date(m/d/y): 11/22/16
Performance in nanospace

(a) (b)

(c) (d)



(e) (f)

Figure 4.6: (a) SEM results of Silica with 60% GO (a) at 5μm (b) at 2μm (c) at 1μm (d) at 1μm with diameter sizes (e) at 1μm (f) at 500 nm

Surface of GO/ SiO_2 was rough and somewhat wrinkled. It was more obvious at the later SEM images of GO/SiO2 (Figure 4.6), ultrathin graphene oxide sheets coated the SiO_2 particles. In addition, it can be also observed that the GO is nearly uniformly spread over the SiO_2 spheres surface[68].

4.2.2 EDS - Energy Dispersive Spectroscopy

EDS - Energy Dispersive X-Ray Spectroscopy or (EDX) is a characteristic technique worked in combination along with SEM - scanning electron microscopy. It is a powerful, fast and non-destructive tool for microanalysis of elemental composition or chemical characterization of a sample having atomic number 4 to 92 (U). It gives both qualitative as well as quantitative analysis of the material.

In SEM, backscattered electron images show compositional distinction that outcomes out from distinctive atomic number elements plus also their distribution. EDS permits each to recognize what those specific elements are and their comparative ratios (e.g. atomic %). Every element has its own atomic structure with a unique set of peaks in electromagnetic emission spectrum, which is the basic principle of EDS.

4.2.2.1 Basic Principle of EDS - Energy Dispersive Spectroscopy

Elemental investigation was taken with the electron beam focused to the material atoms. When the incident radiation is bombarded, electrons are emitted from the atoms involving the surface of the sample. These electron vacancies are occupied with electrons coming from a higher state, an x-ray is released to cover up the energy difference b/w two electrons' states. This x-ray energy is representative of that specific element from which it was released.

Figure 4.7: Basic principle of EDS

A solid-state detector collected these X-rays whose energy range is about 0-40 Kev and showed on computer screen. Peaks will display on the spectrum, and the area involved within a peak is generally proportional to the quantity of the concern element of the sample. The efficiency of the detector is decreasing with increasing energy values.

4.2.2.2 Results Analysis

With the help of EDS - Energy Dispersive Spectroscopy chemical investigation of the processed particles was done. This can be possible by SEM - Scanning Electron Microscopy with the help of a detector which compared with gained x-ray energy values to verify the elements present in that sample.

4.2.2.2.1 Pure SiO_2 Spheres

The EDS spectrum of SiO_2 is shown in figure. This spectrum displays peaks of silicon as well as oxygen. It confirms the establishment of SiO_2 spheres.

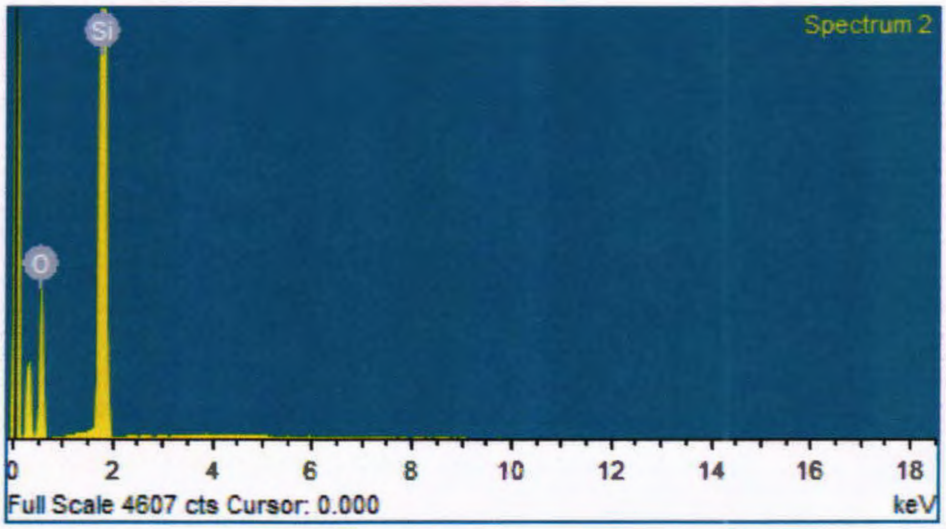


Figure 4.8: EDS results of pure Silica

Measured quantities of silicon and oxygen are shown in the given table.

Table 4.1: Atomic% & Weight% of pure Silica elements

Element	Weight%	Atomic%
O K	40.20	54.13
Si K	59.80	45.87
Totals	100.00	

4.2.2.2.2 20% GO coated SiO_2 Spheres

Figure indicates the EDS spectrum of 20% GO coated SiO_2 spheres that sanction the occurrence of oxidized carbon elements. The Si nanoparticles shows optical absorption band peak at 1.8 keV.

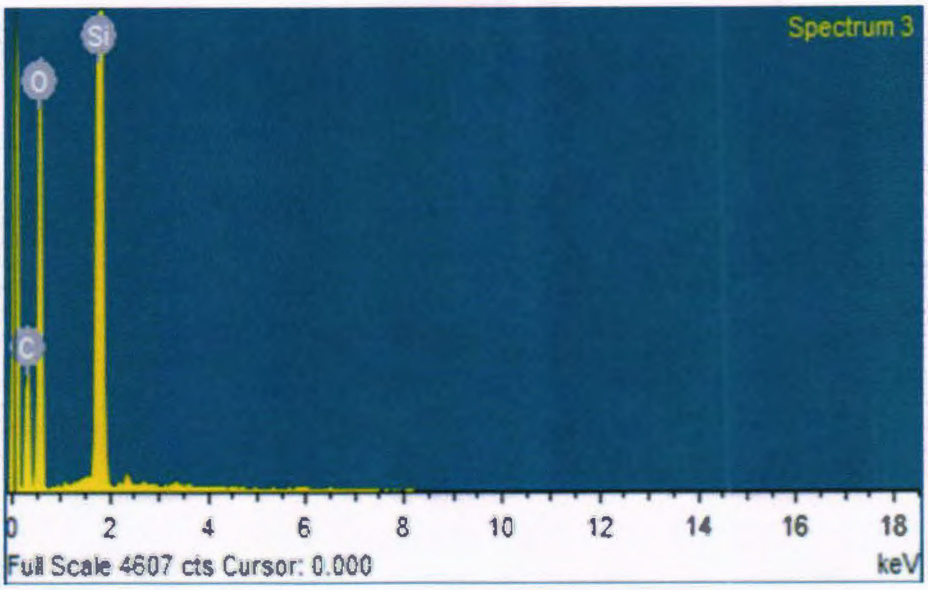


Figure 4.9: EDS results of Silica with 20% GO

The chemical compositional data of our coated material (20% GO coated SiO_2) is shown in table.

Table 4.2: Atomic% & Weight% of 20% GO coated Silica elements

Element	Weight%	Atomic%
C K	28.52	38.73
O K	48.50	48.94
Si K	22.98	12.33
Totals	100.00	

4.2.2.2.3 60% GO coated SiO_2 Spheres

The EDX spectrum of 60% GO coated silica is shown in figure. This spectrum shows the peaks of Silicon, Oxygen, and carbon while there is no impurity detected in the sample.

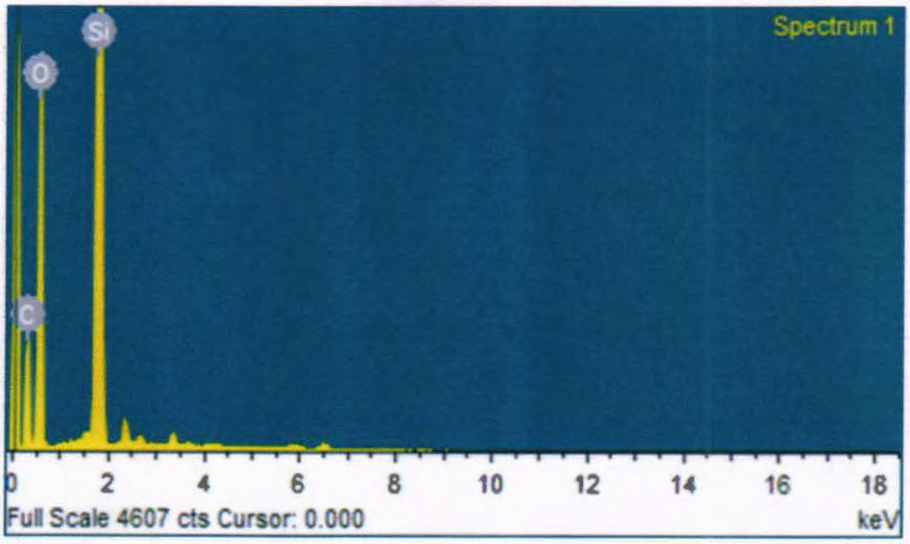


Figure 4.10: EDS results of Silica with 60% GO

The chemical compositional data of our coated material (60% GO coated SiO_2) is shown in table. The elemental analysis indicates the existence of Si, C, and O elements while atomic percentage, signifies the development of spheres.

Table 4.3: Atomic% & Weight% of 60% GO coated Silica elements

Element	Weight%	Atomic%
C K	29.56	39.99
O K	49.48	49.43
Si K	20.96	10.58
Totals	100.00	

4.2.3 XRD - X-ray Diffraction

XRD – X-ray Diffraction is a rapid, effective and non-destructive investigative method, that is primarily use up the for characterization of the crystal parameters such as crystalline structures, crystal size and other crystallographic information of a sample. It also gives info about average spacing, b/w sheets or layers of atoms, crystal defects, crystal structure, alignment of a single crystal or grains, and little crystalline regions internal stress. So XRD - X-ray Diffraction is responsive only towards crystalline structures, homogenous and inhomogeneous both types of materials can be applied.

Figure 4.11: XRD – X ray Diffraction

4.2.3.1 Basic Principle of XRD - X-ray Diffraction

The basic principle of XRD – X-ray Diffraction is constructive interference in conjunction with Bragg's law. Bragg's law was established by Bragg in 1914 and stated that a definite relationship between the lattice spacing of crystalline material and the wavelength of electro-magnetic radiation of diffraction angle.

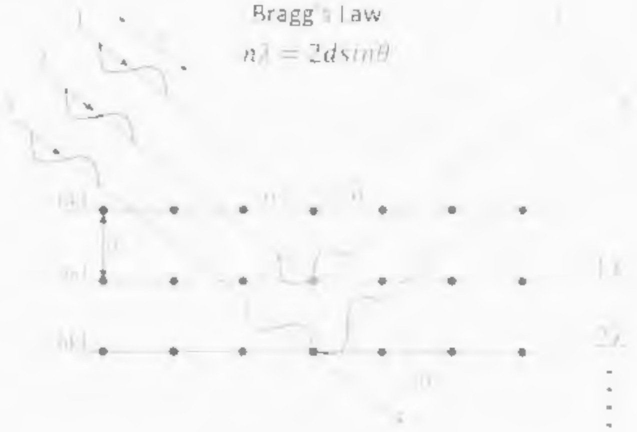


Figure 4.12: Basic principle of XRD

The Bragg's relation is shown in below equation.

$$n\lambda=2d\sin\theta$$

Here,

n = an integer order of diffraction,

λ = incident wavelength of X-ray beam,

d = spacing b/w atomic layers

θ = angle of incidence and reflection

There are different methods used for XRD of the sample. These methods are as under:

- Laue Method
- Debye-Scherrer Method
- Bragg's crystal rotating Method
- Bragg's Powder Diffraction Method

4.2.3.2 Bragg's Powder Diffraction Method

Nowadays powder diffraction has become most significant and critical method in nanomaterials. This method produced great results about structural information of nanomaterials during investigation process. The sample in powder form is exposed to X-rays of known wavelength. According to Bragg's law when an intense beam of monochromatic light has fallen on a crystal, incident beam reflected secularly from different planes. Diffraction is basically a scattering phenomenon; many atoms co-operate in it. Bragg's reflection will occur by their (1 1 1) plans, other particles will be rightly oriented for reflection by (1 0 0) planes and so on. In this method, no actual rotation of the crystal system occurs but the distribution of the number of crystallites in every possible direction is equating to single rotted about all possible direction of 2θ.

4.2.3.3 Particle Size

The term 'Particle Size' is used to refer crystals having size less than 1000 angstrom. For the calculation of average crystallite size of nanoparticles, **Debye Scherrer** formula is used from the broadening of diffraction peaks.

$$D = \frac{k\lambda}{\beta\cos\theta}$$

Here D is crystallite size, k is a shape factor (~0.8-1.39), λ is an incident radiation wavelength, θ is the Bragg's angle and β is full width by half of its highest intensity and it is calculated in radians.

The decreased crystallite size is the reason for increasing the width of diffraction. Broadened peaks are noticed in very small crystallites because there are not sufficient planes are present which produced complete destructive interference. Crystallites smaller than ~120nm create broadening of diffraction peaks.

4.2.3.4 Results Analysis

The XRD patterns for all samples were observed by X-ray powder diffractometer procedure. The data assemblage then analysis was conducted by using the software provided to the diffractometer.

4.2.3.4.1 Pure SiO_2 Spheres

The crystal structures and the purity of the pure SiO_2 spheres (prepared by Stöber method) were characterized by XRD - X-ray diffraction along with a diffractometer. The samples of silica have not shown any well-defined peaks in the figure representing that it has an amorphous nature. The characteristic wide halo peak has appeared at $2\theta=23^\circ$ which confirms the formation of SiO_2 spheres[69].

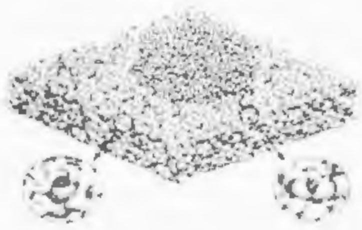


Figure 4.13 SiO_2 spheres

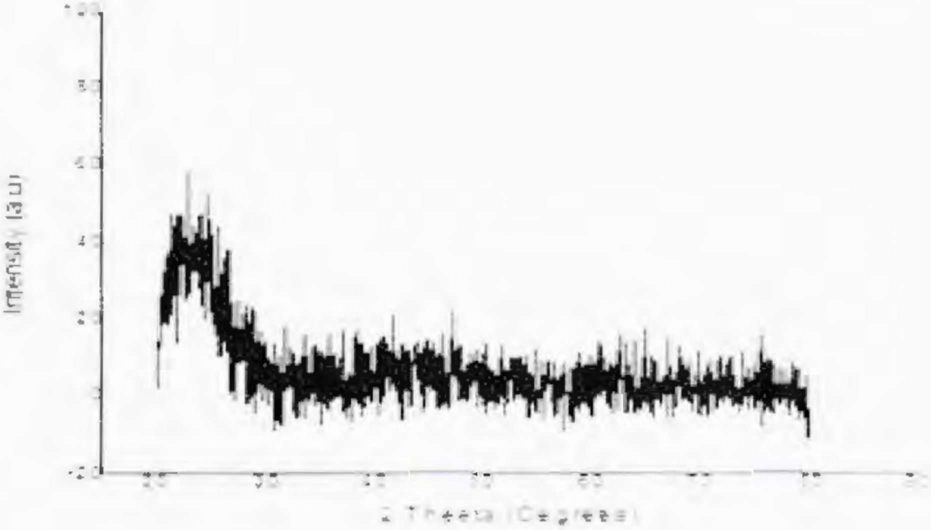


Figure 4.14: XRD results of pure Silica

Yang et al. synthesized silica nanoparticles indicated a characteristic peak at $2\theta=23^\circ$.Chen et al. approved that x-ray diffraction result of silica spheres was amorphous having 2θ fluctuating from 15° to 30°. Sausa et al. noticed that the XRD results of spherical silica nanoparticles and concluded that there is no reflection at higher angles for spherical silica nanoparticles. This indicates that spherical silica nanoparticles are not crystalline at the atomic level.

4.2.3.4.2 Comparison b/w GO coated Silica Spheres and different Concentrations (20% & 60%)

To prove the adsorbance property of nanomaterials, pure SiO_2 and its coatings with 20% & 60% concentration were characterized by XRD (Figure 4.15).

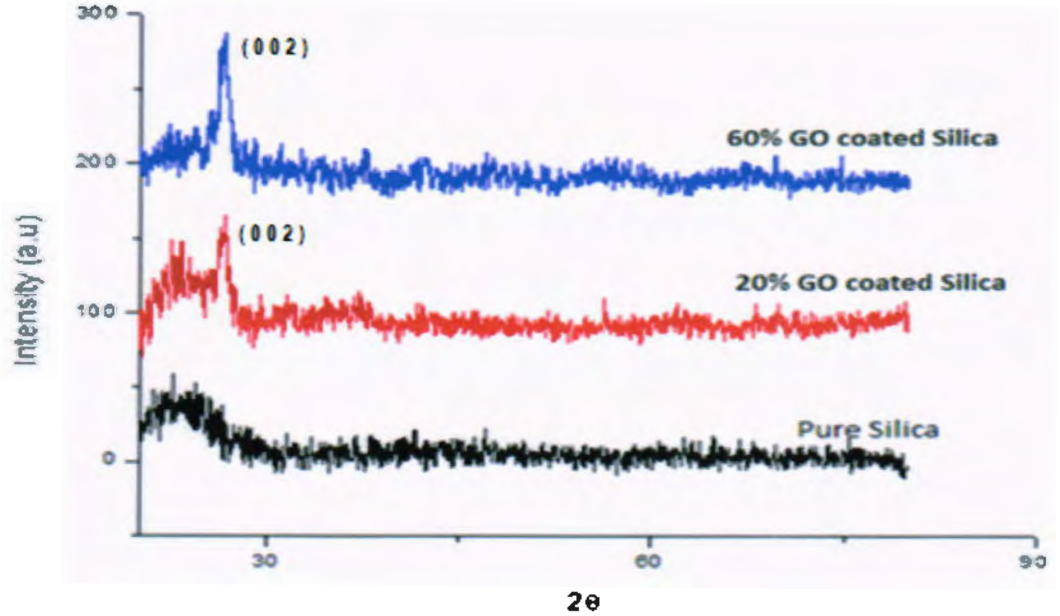


Figure 4.15: XRD results of pure Silica compared with 20% & 60% GO

Figure shows the XRD - X-ray diffraction pattern for our samples (pure SiO_2 and GO/SiO_2 coated spheres with 20% & 60% concentrations). With comparing the results of our samples to the pure SiO_2 XRD curve, we cannot evaluate the crystallization degree towards our coated samples. The broad diffraction peak in XRD curve for coated samples was indexed at $2\theta = 26°$due to Graphene Oxide, anyhow GO has such a small impact on Silica because GO crystallinity is not good as many crystals (Ying et al). The shape of pure SiO_2 peak did not change with amorphous characteristic peak. The GO/SiO_2 coated spheres showed a broad peak at 26° with both concentrations because of the major effect of silica. This indicates that the synthesized GO coated SiO_2 spheres had not a good crystallinity level, so was supposed to have appropriate adsorbents.

4.2.4 FTIR - Fourier Transform Infra-Red Spectroscopy

FTIR is an advance, speedy accurate, non-destructive and the preferred method of infrared spectroscopy which uses the mathematical process-Fourier transform to convert raw data to actual spectrum. IR - Infrared spectroscopy is basically most significant and critical technique accessible for scientists to recognise unknown materials by utilizing the interactions of infrared light with matter.

Figure 4.16: FTIR – Fourier Transform Infra-Red Spectroscope

In IR - infrared spectroscopy, radiation is go through a sample. Some portion is absorbed by the sample and some is forwarded (transmitted). The interactions of radiation with materials make changes in molecular dipoles which relate to vibrations as well as rotations. The subsequent spectrum signifies the molecular absorption with transmission, that create a molecular fingerprint of the material. Due to this reason, infrared spectroscopy is very beneficial for various kinds of analysis. Infrared spectroscopy is comparatively easy approach to get spectra from samples which are in solution, pastes, powders, films, fibres, or in the gaseous states. Infrared spectroscopy can also be linked with other analytical techniques like chromatography or thermal analysis.

4.2.4.1 Basic Principle of FTIR - Fourier Transform Infra-Red Spectroscopy

The major components of an FTIR – Fourier Transform Infra-Red spectrometer are presented schematically in Figure. The radiations coming out from the source have passed through Michelson interferometer towards sample before touching the detector. High frequency contributions are eradicated by using a filter when these radiation signals are amplified. Then data is converted in digital form by using an analog-to-digital converter plus send it to the computer for Fourier-transformation.

Figure 4.17: Basic principle of FTIR

Output of the instrument is in the form of a spectrum. Mostly industrial instruments offer a spectrum with the wavenumber reducing from left to right. The infrared spectrum is distributed into three major regions:

- near-infrared (13000 – 4000 cm−1)
- mid-infrared (4000 – 400 cm−1)
- far-infrared (<400 cm−1).

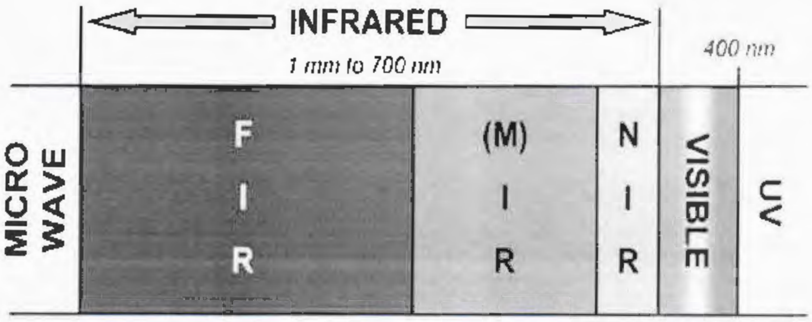


Figure 4.18: Infrared spectrum

4.2.4.2 Results Analysis

The characteristic results of FTIR are excellent, normally a minor quantity of the material will be produced superb spectrum in short interval of the time. Generally, three methods are used to examine solid samples: alkali halide discs, films or mulls. In alkali halide discs, a solid sample is mixed with dry alkali halide powder[70]. Normally, potassium bromide (KBr) is used because of complete transparency in mid-infrared region. The spectra were recorded from KBr pellets by using FTIR spectroscopy, which is attached with a computer.

Figure 4.19: FTIR using KBr pellet

4.2.4.2.1 Pure SiO_2 Spheres

The FTIR spectra of Silica spheres prepared by Stöber method is represented in figure (4.20).The FTIR spectra of spherical Silica shows the absorbance bond at 857cm^{-1} is due to Si-O bond, the strongest IR absorption band is at 1514 cm^{-1} indicated the existence of Si-O-Si bonding while absorption band at 993 cm^{-1} also shows Si-O-Si bonding[46]. The absorption band at1790 cm^{-1} is because of OH group.

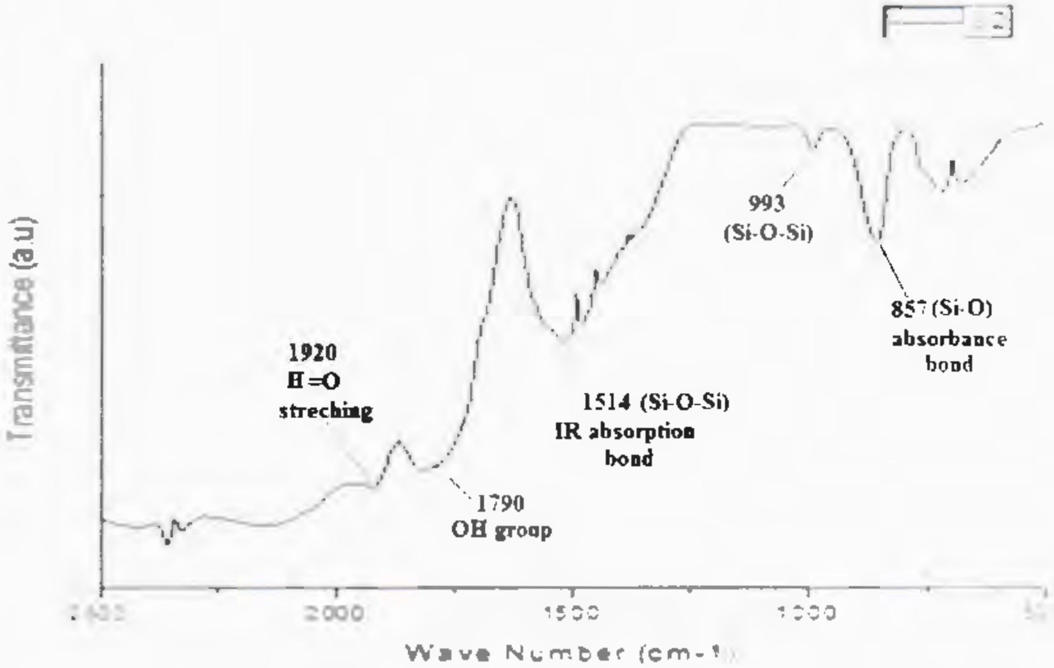


Figure 4.20: FTIR results of pure Silica

4.2.4.2.2 GO Sheets

As, a modified Hummers method was used to oxidize as well as exfoliate graphite by the treatment of $KMnO_4$ and concentrated H_2SO_4 into GO[71]. The GO has a brown colour and could be easily dispersed in H_2O with the help of oxidized functional groups. The GO was characterized by FTIR in transmittance mode. The typical FTIR spectrum of GO in Figure (4.21) corresponds to prior work.

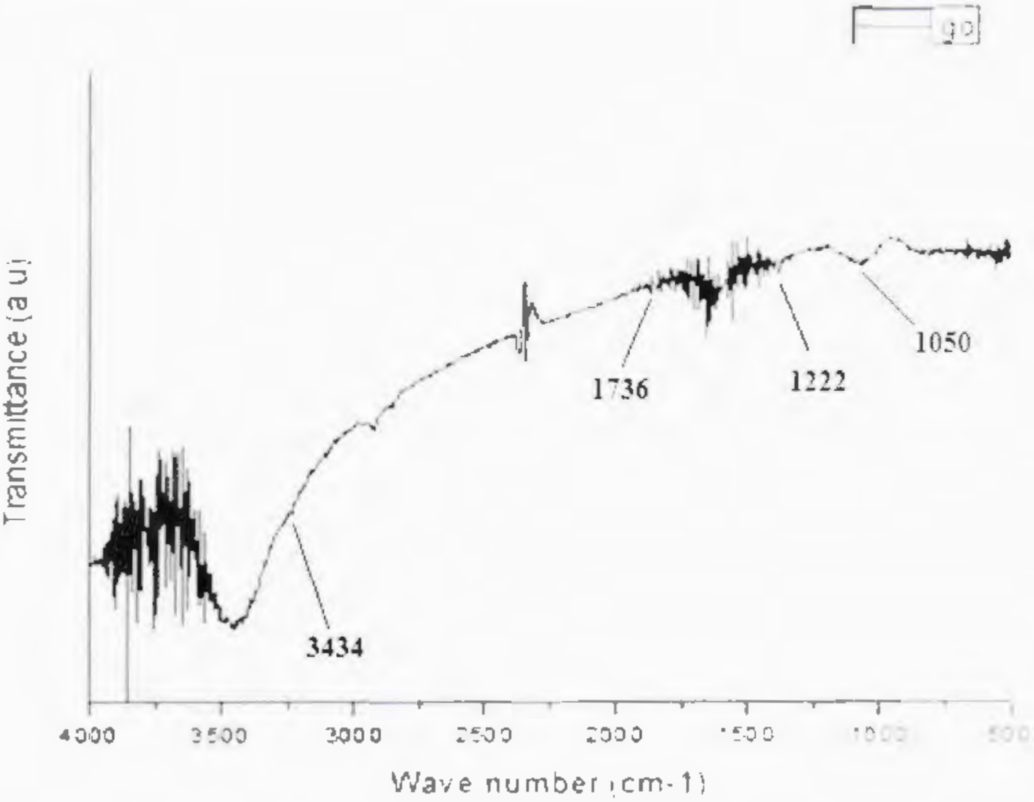


Figure 4.21: FTIR results of GO

The FT-IR spectrum of GO revealed characteristic peaks at around 3434 and 1736 cm-1 corresponding to O–H and C=O stretching frequencies of the –COOH group, respectively (Fig. 5). The peaks corresponding to aromatic C=C bending, phenolic C–O stretching and epoxy C–O–C stretching were identifed at 1222 and 1050 cm-1, respectively[72].

4.2.4.2.3 60% GO coated SiO_2 Spheres

Since graphene oxide has many oxygen-functional groups and chemical modification can lead to structural changes in these functionalities, FTIR will be a useful technique in analyzing the structure of graphene oxide and structural evolutions resulted by surface modifications of silica. To prove the coating of GO on Silica spheres in GO/SiO_2 nanocomposite. FTIR - Fourier transform infrared spectra were inspected[73] to the given below Figure (4.22).

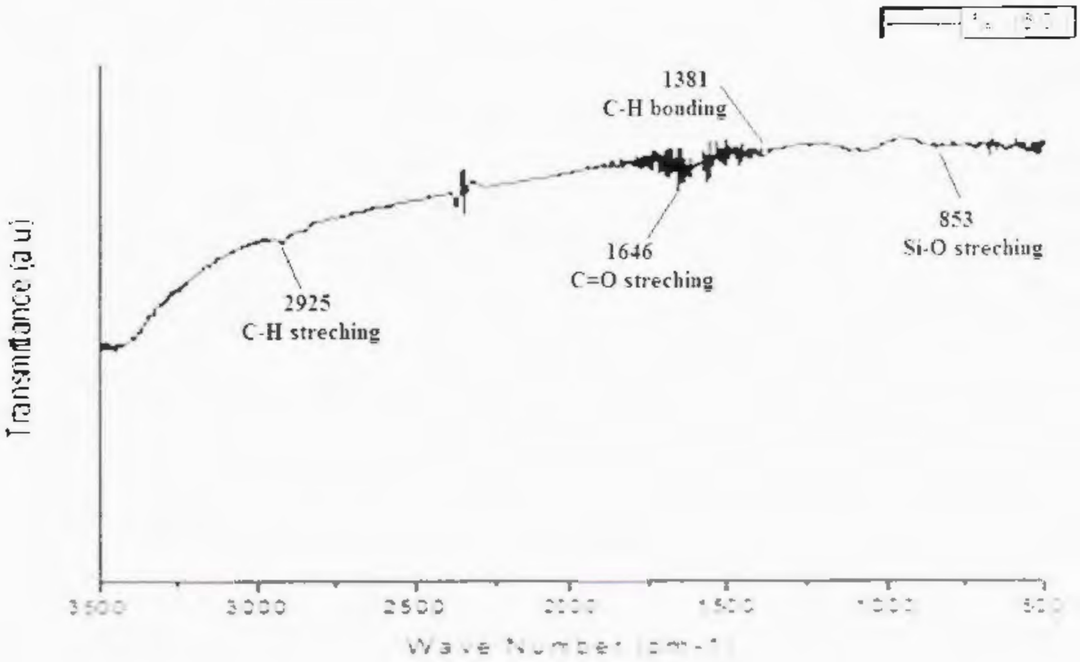


Figure 4.22: FTIR results of Silica with 60% GO

The FTIR spectra of GO coated Silica Sphere shows the absorbance band at 853cm-1 is due to Si-O bond, the strongest IR absorption band is at 1646cm-1 shows the presence of C-O bonding whereas absorption band is at 1381cm-1 due to C-H bonding. The absorption band at 2925cm-1 is because of existence of C-H streching.

4.2.5 UV-Visible Spectroscopy

Colour is most significant feature of a material. Different materials have various colours depending on the structures of ligands. Human eyes act as spectrometers in examining the reflected light which reflects from the solid surface or passes through a liquid when differentiating matter by colour. Sunlight or white light is comprised with a broad range of radiations in the infrared, visible and ultraviolet regions for electro-magnetic spectrum.

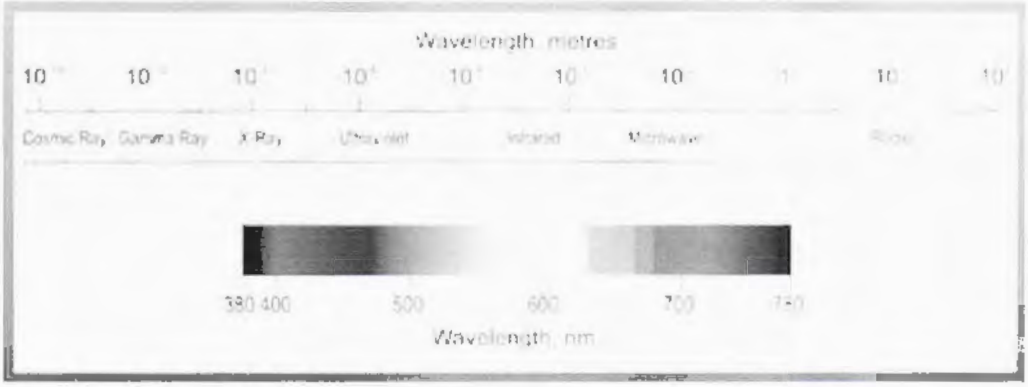


Figure 4.23: Electro-magnetic spectrum

Electromagnetic spectrum is very broad ranging from short wavelengths (including cosmic ray, gamma ray) to long wavelengths (including sonic, infrared sonic). The ultraviolet (10-400 nm) and visible radiations (400 nm-800 nm) constitute only a small portion of it. Ultraviolet radiations which are less than 200 nm are tough to control and rarely used for structural analysis of matters. The energies of UV-Vis light range from 1.55 eV to 6.20 eV corresponding to wavelengths of 800 nm and 200 nm, respectively. The energy of electro-magnetic radiation is stated through the following equation:

$$E = h\nu$$

Here E denotes for energy, h for Planck's constant and v for frequency. Such energies are sufficient to cause electronic transitions from low energy orbitals to high energy orbitals in molecules. When the energy of light matches the gap between two energy levels, the light is absorbed and electronic transition or promotion occurs.

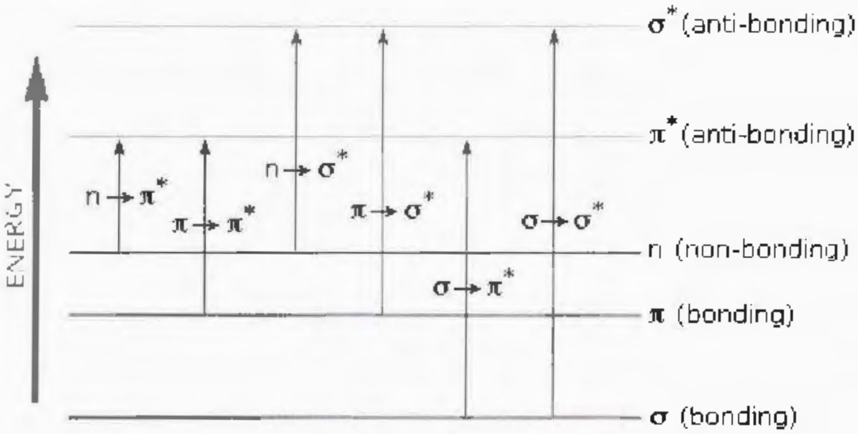


Figure 4.24: Electronic Transitions

Generally, in UV-visible spectra, we deal only with absorbance and it usually exhibits few broad absorbance bands. UV-visible spectroscopy also gives information about many physicochemical properties of compounds which help us to identity a specific compound.

4.2.5.1 Basic Principle of UV-Visible Spectroscopy

A spectrophotometer is a device used to calculate the percentage of transmittance of light radiation when light of specific frequency (range of UV-Vis) is passed through the samples (liquids or clear solutions). The spectrophotometer detects the intensity differences between the transmitted and incident light that is named as absorption (A) or optical density (O.D) which is a function of wavelength. A schematic diagram of a UV-Vis spectroscopy system is exposed in Figure (4.25).

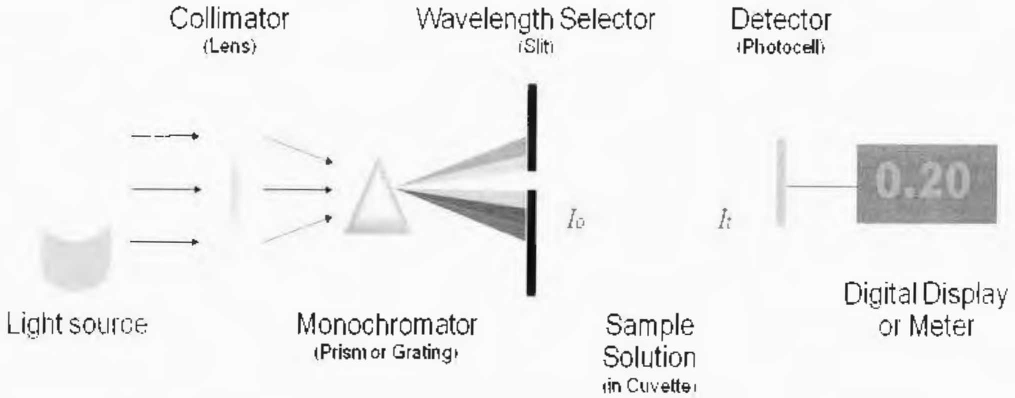


Figure 4.25: Basic principle of UV-Visible Spectroscopy

The main components are as: a light source, collimator, monochromator, wavelength selector, sample cuvette, detector and digital display. If I_o and I_t are the incident and transmitted rays of light, then the absorbance A can be defined,

$$A = \log I_t / I_0$$

or,

$$A = \varepsilon c x$$

or,

$$\log I_t / I_0 = \varepsilon c x$$

Here, x is sample path length, c is concentration, and ε is molar extinction coefficient. A UV-Vis spectrometer can determine the wavelengths at which absorption maxima occurs which can be used to identify certain chromophores and conduct quantitative analysis of the number of molecules based on the Beer-Lambert law.

4.2.5.2 Results Analysis

UV-visible spectroscopy is mainly used to examine both liquids or solutions. In this technique, a cell has liquid or solution in the area of spectrophotometer sample. The UV-Vis spectra are generally computed in very dilute solutions and the ideal solvent for the sample solutions should dissolve all kinds of compounds, non-flammable plus nontoxic, and completely transparent for all wavelengths.

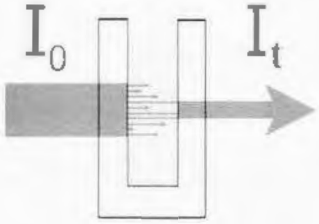


Figure 4.26: Light aborbance of the solution in cuvette

The solvents most commonly used, are water, 95% ethanol, and n-hexane and all these transparent in the range of UV-Vis spectrum. For accurate results, the analyzed sample must have the absorbing component for which the standardization has performed. The difference b/w initial (I_o) and final absorbance (I_t) is directly proportional to the amount of substrate.

4.2.5.2.1 60% GO coated SiO_2 Spheres

UV-Vis spectroscopy will be useful in monitoring the structural changes during chemical reduction or modification. The simple method for multicomponent investigation is based on the measurements at several wavelengths as same as the number of elements in the mixture.

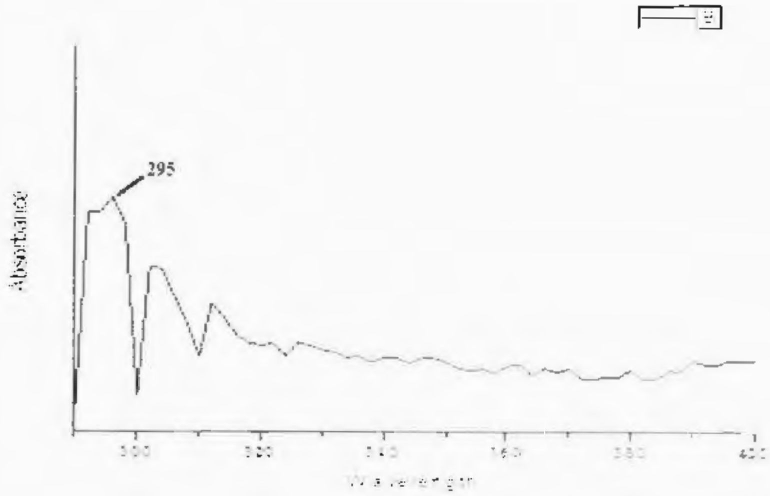


Figure 4.27: UV-Vis results of Silica with 60% GO

The UV-vis spectra of GO coated Silica Sphere shows the Maximum absorbance peak is about 295 nm. The band gap is calculated by using the following relation

$$\text{Band gap energy } (E) = (h*c)/\lambda$$

Where

h = Plank's constant

c = Speed of light

λ = wave length

So, we get the band gap of GO coated silica sphere is 4.2 eV

4.3 Applications

With the development of world oil production and the increase of transportation, oil spills as well as chemical leakage from industrial mishaps on seawater have had devastating impacts on marine, aquatic ecosystems and as well as on environment. Due to this, various sea birds or mammals have been died and has a serious threat to people's health. Therefore, a material is urgently required which is cheap, reliable, and environment friendly that can remove these oily pollutants from water surfaces with high adsorption ability, high selectivity, low cost, low density, scalable fabrication, and excellent recyclability.

In this thesis, we prepared Graphene Oxide coated Silica spheres and then used these GO/SiO_2 nano particles as adsorbent for different oils[74] with the help of a Polyurethane Sponge. Polyurethane (PU) sponge is commercially available 3D porous material with high absorption capacity, good elasticity and low density. Oil adsorbent PU sponges was coated with GO/SiO_2 nanoparticles by a simple method and then used these for different kinds of oils (diesel, lubricate oil, pump oil, bean oil, olive oil, mustard oil etc.). The coating of GO/SiO_2 nanoparticles makes PU sponges more hydrophobic and increase their compressive strength. Hence, a combination of great elasticity, hydrophobicity as well as strength creates highly efficient plus reusable adsorbent PU sponges for oil spilling[43].

4.3.1 Preparation of GO/SiO_2 coated Polyurethane Sponges

First of all, polyurethane sponges were cut into small pieces and cleaned ultrasonically with ethanol. After that these small blocks were washed with deionized water and dried at 60 °C in oven. Then these PU sponges were soaked in GO/SiO_2 solution for 1 h and dried in oven for 24 h at 30 °C to obtain the coated sponges.

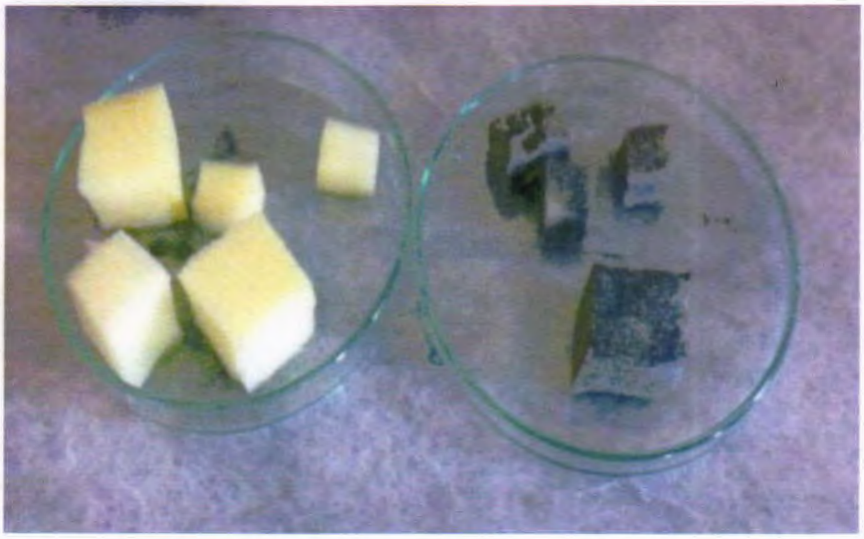


Figure 4.28: Simple and coated polyurethane sponges

These PU sponges are basically hydrophilic but modifications with GO/SiO_2 nanoparticles altered their properties from hydrophilic towards hydrophobic[43].

4.3.2 Adsorption of Different Oils

The results presented in this thesis might be provided a quick and easy procedure towards oil adsorption purely as well as from the surface of water. The attachment of GO/SiO_2 nanoparticles has decreased hydrophilicity of PU sponges by increasing their surface roughness along with modifying the chemical composition[68]. Two samples of diesel oil in graduated cylinders are presented for the experimental work in figure below. Observe, the level of diesel oil in both these graduated cylinders is the same.

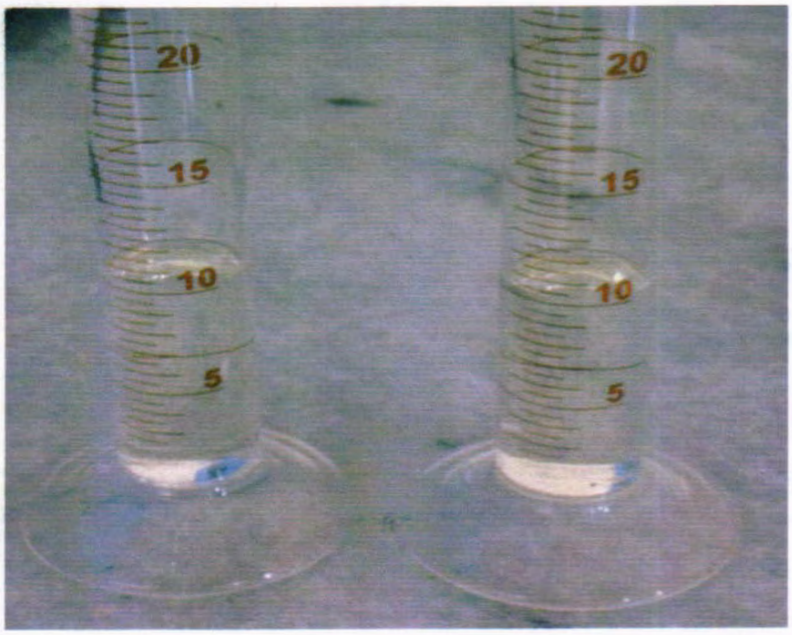


Figure 4.29: Diesel Oil

Dip the simple and modified GO/SiO_2 coated PU sponges in the diesel oil in the equally filled graduated cylinders with diesel oil. Picture is shown below.

Figure 4.30: Adsorption of diesel oil

Adsorption of the pure diesel oil with simple and coated PU sponges are shown. By looking carefully, we have observed that the ratio of the adsorption with GO/SiO_2 coated PU is much more than the simple one.

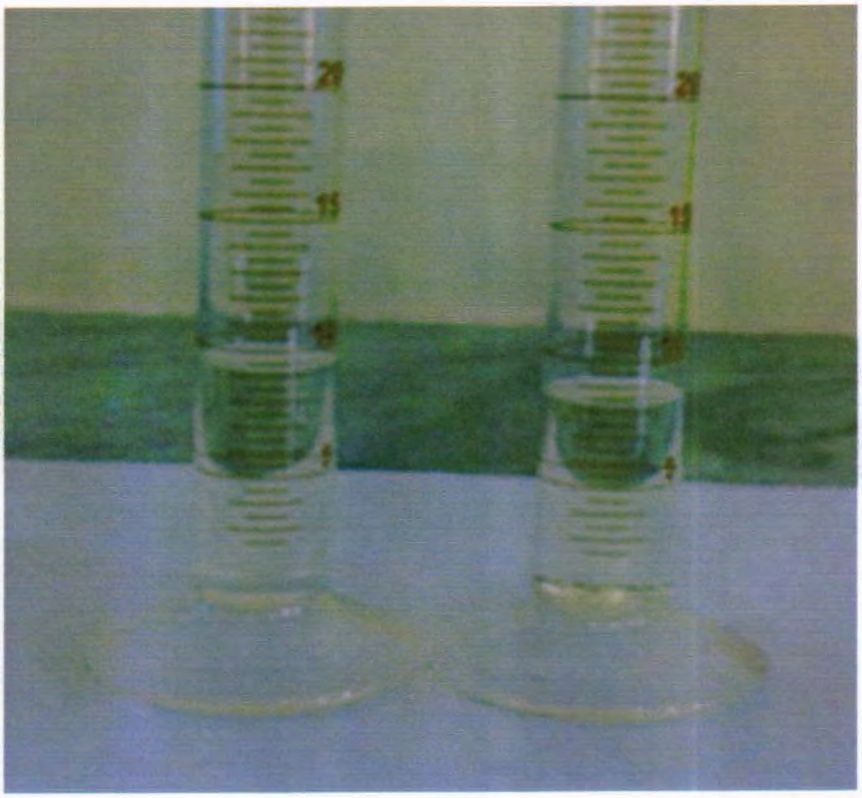


Figure 4.31: Diesel oil after adsorption

Now our next experimental work is related with mustard oil layer on the surface of water. We have taken two beakers with equal amount of water as well as thick layer of mustard oil on it.

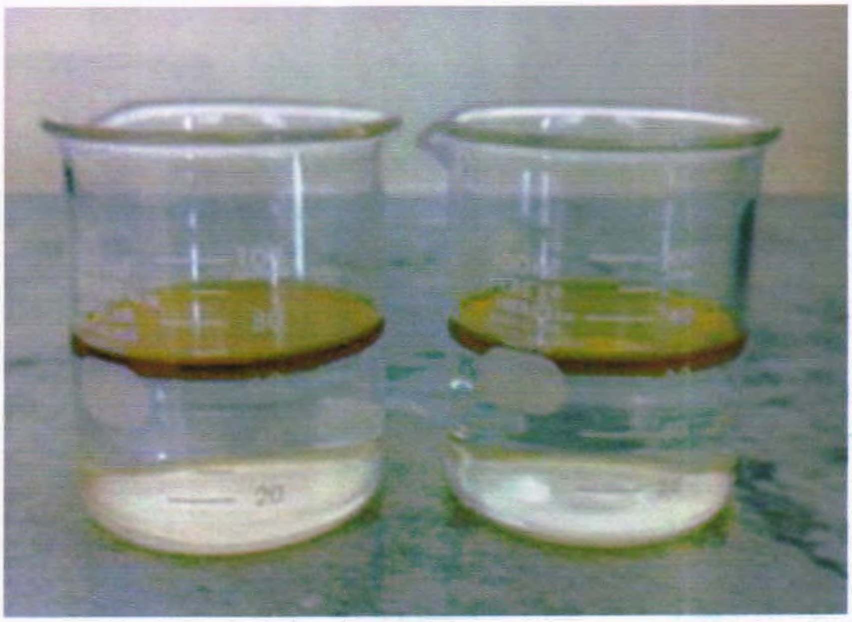


Figure 4.32: Mustard oil in water

We have dipped both type of PU sponges (simple and modified) in beakers. The given figure shows the relevant step of the experiment.

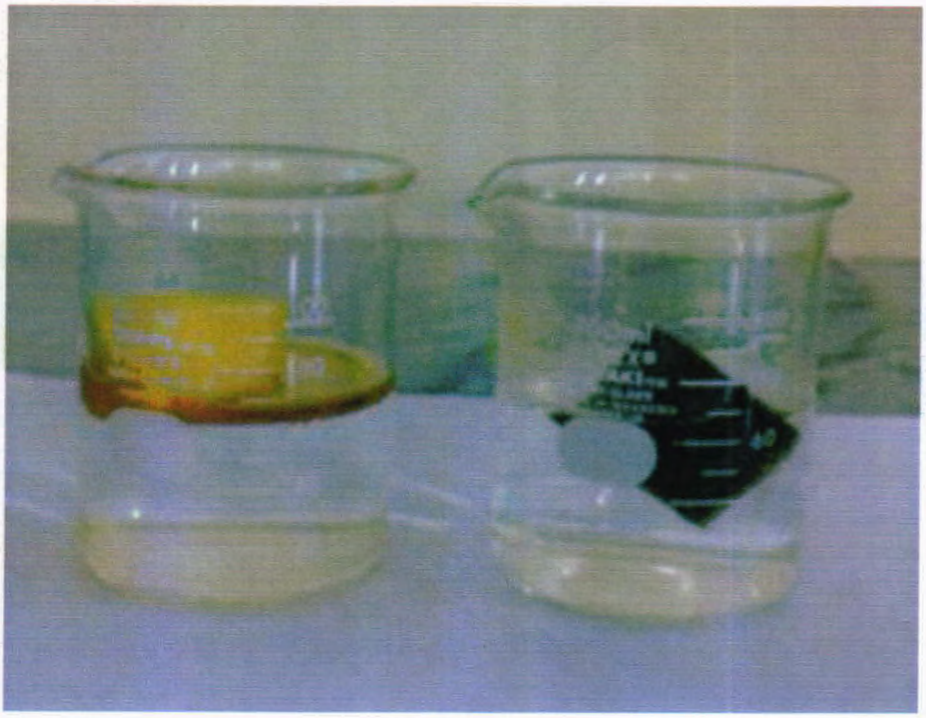


Figure 4.33: Adsorption of mustard oil from water surface

In above figure we have clearly seen that all of the mustard oil is adsorbed by the GO/SiO_2 coated PU sponge from the surface of water. Not even a single drop of mustard oil is left on the water surface. We can check it from the vertical view of the beakers.

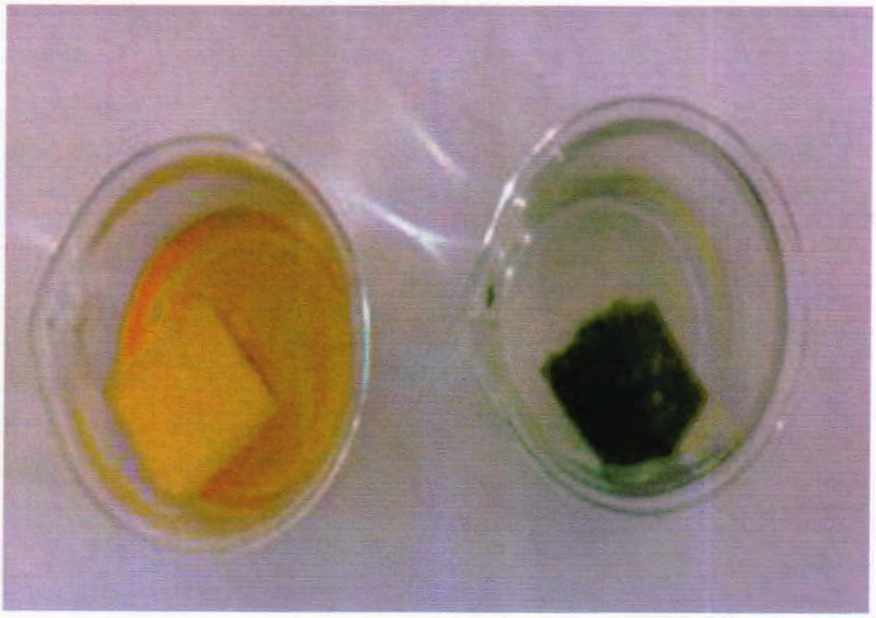


Figure 4.34: : Adsorption of mustard oil from water surface (Vertical view)

This shows that GO/SiO_2 coated PU sponge is acted as an adsorbent material for different types of oils and can be used these sponges for the oil-water separation or filtration of oil from water.

4.3.3 Recyclability

These adsorbed oils were easily accumulated by simple mechanical squeezing procedure. The squeezed sponges can be recycled in oil–water separation for numerous cycles whereas keeping highly separation capability[75]. The coated PU sponges were discovered reusable up to 50-60 cycles by owning 80% of its initial capacity[76].

4.4 Conclusions

When GO is co-used with silica as coated material for PU sponges, main outcomes of this research work are summarized here:

There are three different synthesis techniques have been used to make successfully graphene oxide coated silica spheres for the adsorption of the oily pollutants from the surface of water with the help of polyurethane sponges.

- Modified Stöber Method is used for the synthesis of Silica Spheres
- Modified Hummer's Method is used for the synthesis of graphene oxide sheets
- Graphene Oxide coated Silica spheres are synthesized by Sol-gel Method

The SiO_2 nanoparticles are formed when GO is synthesized. Then a wet-chemical technique is used to produce particles of the coating material. On behalf of these experiments, it can be concluded that GO/SiO_2 nanospheres produced possessed great absorptivity for oily pollutants, low cost, reliability, and high recyclability which can be efficiently used for water filtration in sea or industries.

The synthesized GO/SiO_2 nanospheres samples were characterised by using different techniques such as SEM, EDS, XRD, FTIR or UV-Vis spectroscopy to gain morphology, compositional investigation, structural analysis, chemical bonding and optical studies respectively. Scanning electron microscopy results confirmed that the silica particles are spherical and the average size of ~ 186 nm was obtained. It also clearly showed the proper coatings of GO (20% & 60%) on Silica spheres. EDS analysis data of the pure silica and coated material showed the compositions of Si, O & C peaks which describe the purity of the samples. From XRD results, it was proved that silica nanoparticles are naturally amorphous and the coating of GO (20% & 60%) did not much disturb the structure of SiO_2.

The FTIR results revealed the molecular bonding's of the coated materials. UV-Visible absorption spectroscopy outcomes tell us that the GO

All above characterization results supported the nanocomposites to be modified towards a certain application, as exhibited by our experimental work to the adsorption. The GO/SiO_2 composites coated with PU sponges prepared in this investigation are efficient candidate materials for large-scale oil-water separation.

4.5 Future Works

To accomplished this thesis work, it should be observed that there are still abundant chances for future research in this arousing field of the study. This thesis results can be applied for future researchers. Future inquiries may focus on quality control (i.e. particle size, more adsorption and recyclability, etc) of the GO/SiO_2 nanoparticles during the process of adsorption. The analysis of SiO_2 with carbon or graphene based nanocomposites and boost their practical applications in several environmental issues are also future directions.

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