STUDY OF OPTICAL PROPERTIES OF CHEMICALLY DERIVED SILICA NANOPARTICLES

PROJECT REPORT

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DEPARTMENT OF PHYSICS
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CERTIFICATE

This is to certify that the project report entitled "**STUDY OF OPTICAL PROPERTIES OF CHEMICALLY DERIVED SILICA NANOPARTICLES**" is an authentic work done by **MARY NEHA K L (AM22PHY009)** under my guidance at Department of Physics, St. Teresa's College (Autonomous), Ernakulam for the partial fulfillment of the requirements for the award of the Degree of Master of Science in Physics during the year 2023-24. The work presented in this dissertation has not been submitted for any other degree in this or any other university.

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I, MARY NEHA K L, final year MSc. Physics student of the Department of Physics and Centre for Research, St. Teresa's College (Autonomous), Ernakulam, do hereby declare that the project report entitled "**STUDY OF OPTICAL PROPERTIES OF CHEMICALLY DERIVED SILICA NANOPARTICLES**" has been originally carried out under the guidance and supervision of **Dr. MARIYAM THOMAS,** Assistant Professor, Department of Physics, St. Teresa's College (Autonomous), Ernakulam in partial fulfilment for the award of the Degree of Master of Physics. I further declare that this project is not partially or wholly submitted for any other purpose and the data included in this project is collected from various sources and are true to the best of my knowledge.

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The success and final outcome of this project required a lot of guidance and assistance from many people and we are extremely grateful to have got this along the completion of my project work. Primarily, we thank God almighty for being with us throughout all the days and helping us to complete the project successfully.

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STUDY OF OPTICAL PROPERTIES OF CHEMICALLY DERIVED SILICA NANOPARTICLES

ABSTRACT

Silica nanoparticles also known as silicon dioxide have recently attracted widespread attention due to increasing importance to their use as catalyst, in adsorption, , optical devices, bio-imaging, drug delivery and biomedical applications. The synthesis and study of the optical property of silica nanoparticles is one of the major ongoing research interest. In order to synthesize amorphous silica nanoparticles we have adapted the sol-gel technique. In order to study the optical property of the synthesized silica nanoparticles we have taken the photoluminescence spectrum of the particles. We have also investigated on the nature of defects that contributed to the luminescent property of the synthesized nanoparticles.

CONTENTS

CHAPTER 1

INTRODUCTION

1.1 WHAT IS SILICA?

Silica, scientifically known as silicon dioxide, is mainly used in various fields because of its unique properties. It's commonly found in nature as quartz. Silica nanoparticles can be synthesized through several methods and they are known for their optical, electrical and magnetic properties[10]. The size of the particle, porosity, crystallinity and the form of silica nanoparticles can be controlled and can be used for various industrial and research uses.

Silica, renowned for its hardness since ancient times, exists in amorphous as well as crystalline structures. The crystalline form mirrors the structure of diamond, with silicon atoms arranged tetrahedrally, each surrounded by four oxygen atoms. This results in a three-dimensional poly tetrahedral structure, where oxygen atoms link silicon atoms across SiO2 molecules. In crystalline silica, all silicon atoms are bonded to four oxygen atoms. The orientation of tetrahedra can be random, creating an amorphous structure. The "quality" of the oxide is determined by the ratio of bridging to non-bridging oxygen atoms. A fully bridged structure yields a regular crystal structure, such as quartz [11].

Silica nanoparticles (SNPs) exhibit diverse properties, positioning them as a crucial material in nanotechnology and biomedicine.

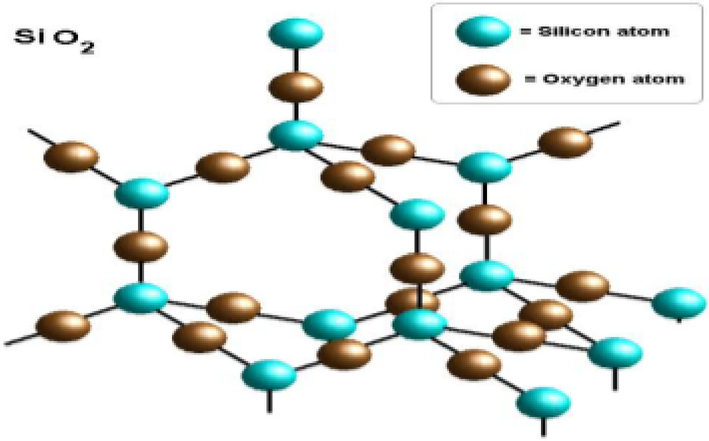


Figure SEQ Figure * ARABIC 1 Structure of silica

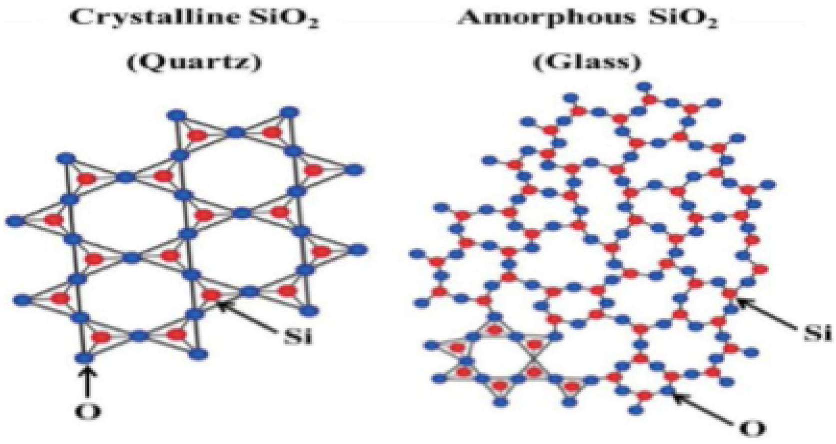


Figure SEQ Figure * ARABIC 2 Crystalline and amorphous structure of silica

1.1.1 Physical and Chemical Properties

The building block of all SiO2 polymorphs is the $[SiO_4]^0$ tetrahedron, that is, the three-dimensional unit formed by a silicon atom and four oxygen atoms bonded to it. Each oxygen atom bridges two Si atoms and form a connection between adjacent tetrahedral units. The Si–O bond has a mixed covalent/ionic character and is described by a wavefunction with both σ[Si(sp3)–O(2p)] and π[Si(3d)–O(2p)] contributions. This determines the shortening of the Si–O bond length (1.605Å), the increase in the SiO–Si angle, and the variability in the intertetrahedral angles . On the other hand, the O–Si–O bond angle (φ) is 109.47°, indicating that the [SiO4]0 unit has a perfect tetrahedral geometry.

In amorphous silica, the flexibility of the Si–O–Si and Si–O–Si–O angles results in a high degree of structural disorder which leads to a quasi-random orientation of the tetrahedral units and a much broader ring-size distribution

The silicon dioxide nanoparticles or silica have large surface area and biocompatibility. Therefore their surface can be modified with various functional groups which enhances their physical and Chemical Properties. Silica can be found polymerization alone or in combination with other metals known as silicates.It can be found polymerized alone or in combination with other metals known as silicates. In nature it commonly occurs as quartz, being the largest constituent of sand. Other crystalline forms of SiO2 are also found such as tridimite and cristobalite and it also exists in amorphous forms[5]. It is also found in the skeleton of some living organisms

Silica nanoparticles find application in biomedical contexts, such as drug delivery systems. They are gaining increased recognition for their potential in diverse biomedical applications, attributed to their distinct characteristics such as a substantial specific surface area, customizable particle size and porosity, excellent biodegradability, and notably, their biocompatibility [6]. These attributes render them suitable for various uses including biosensing, diagnosis, anti-cancer treatments, anti-microbial applications, and so on. The pivotal factor of biocompatibility empowers silica nanoparticles to be applied in biological systems, facilitating the targeted delivery of small molecules, biologics like mRNA, siRNA, antigens, antibodies, proteins, and peptides. The current investigation surrounds SNP toxicity, with factors like size, dose, and surface characteristics influencing safety. Despite the promising applications of SNPs in drug delivery systems and disease diagnosis, their toxicity in both in vitro and in vivo settings continues to be an area of active research.

The structural morphology of the silica nanoparticles can be achieved through several techniques like X-ray diffraction, Transmission electron microscopy and electron diffraction. These methods can be employed to gain information about arrangement of atoms in the nanoparticles and identify whether they are amorphous or crystalline in nature.

The crystal structure of silica nanoparticles plays a crucial role in defining their properties and behavior, making it an important aspect to consider in various applications, including catalysis, drug delivery, and nanocomposite materials [5].

1.1.2 Structural Attributes

- Mesoporous Structure: Mesoporous silica are networks with honeycomb porous structure full of empty channels that can encapsulate a large number bioactive molecules [4]. Silica nanoparticles exhibiting mesoporous characteristics, known as MSNs, possess pores ranging from 2 to 50 nm, with a total diameter below 1 µm. Aligned with the IUPAC definition of mesoporous, this diverse range of pore sizes positions MSNs as optimal materials for a spectrum of applications, spanning catalysis, environmental chemical removal, and biomedicine [4]. These nanoparticles (M-SNPs) offer controllable porosity, large surface area, and high thermal stability.

- Pore Structure: Varying pore structures, including numerous nanopores, enhance utility in diverse applications.

1.1.3 Applications

- Drug Delivery: Silica nanoparticles can be used as drugs and genes carriers because of their mesoporous structure and surface functionalization.

- Biomedical Imaging: SNPs encapsulate contrast agents for medical imaging, benefiting from biocompatibility and controllable size.

- Protein Adsorption and Separation: Ideal for protein adsorption and separation due to specific surface area and functionalization options.

- Nucleic Acid Detection and Purification: Silica nanoparticles can be employed in DNA detection, separation, and purification, acting as DNA biosensors.

The physical, chemical, and structural properties in silica nanoparticles presents wide possibilities for applications in drug delivery, imaging, protein separation, DNA detection, and beyond. Their versatile and customizable nature positions them as a promising material for future advancements in scientific and technological fields.

1.2 LITERATURE SURVEY

Undoubtedly, nanoscale materials have garnered extensive attention for their promising applications, with their exceptional features paving the way for innovative technologies. Recent advancements in nanotechnology hold the potential to address numerous challenges in advanced sciences. Silica nanomaterials, in particular, find diverse applications in catalysis, drug delivery, biomedical uses, environmental remediation, and wastewater treatment. Consequently, silica nanomaterials stand out as widely utilized, with the demand for these nanoparticles experiencing a substantial increase, reaching around 2.8 million metric tons in 2016 and exhibiting an annual growth rate of 5.6%.

1.2.1 Silica based nanoparticles in waste water treatment and environmental remediation

Over the past decade, the rise in water scarcity in arid environments, fueled by environmental and water pollution, has emerged as a significant challenge with far-reaching consequences for societies. This has led to environmental degradation and posed serious health risks to both humans and animals. In response, various environmentally friendly nanomaterials have been developed to address and treat such pollution. A novel composite, incorporating magnetic ($Dy_xMnFe_{2-x}O_4$) nanoparticles onto mesoporous silica particles, demonstrated effective removal of diverse organic pollutants [7]. The composite's success is attributed to its eco-friendly and cost-efficient catalytic properties, stemming from its mesoporous characteristics. The remaining dye contents were efficiently degraded through the photocatalytic activities of $Dy_xMnFe_{2-x}O_4$ nanoparticles. This composite exhibits a significant synergistic effect in enhancing both photocatalytic activities and adsorption for environmental waste treatment.

1.2.2 Silica based nanoparticles in drug delivery and biomedical applications

Due to the promising advantages of Mesoporous Silica Nanoparticles (MSNs), including their unique morphology, geometry, and the capability to finely deliver and target specific organs/tissues, they have garnered significant attention in biological and medical fields as carriers for various therapeutic agents [7]. The large pores of MSNs serve as reservoirs for therapeutic drugs, and surface functionalization enables control over drug release in a precise manner, with enhanced biocompatibility achieved through surface modifications. Additionally, the mesoporous structures of MSNs facilitate homogeneous drug distribution compared to other delivery systems. Consequently, efforts have been directed towards functionalizing drug-loaded MSNs using targeting ligands and stimuli-sensitive materials. This approach allows for the delivery of anti-cancer drugs to their targets, responding to multiple stimuli. MSNs also emerge as promising carriers for gene delivery, leading to the development of strategies for creating specific multifunctional nanocarriers.

1.2.3 Silica based nanoparticles in advanced catalysis

Over the past decades, a substantial number of innovative solid catalysts have been employed to enhance the eco-friendly synthesis of various chemicals. Considering nanomaterials suitable for nanocatalysis, silica-based nanomaterials functionalized with diverse catalytic species have been documented across various fields. Catalysts with a core–shell structure and micro/mesoporous size distributions find widespread application in catalytic processes [7]. The metal nanoparticles coated by SiO2, leveraging the favorable properties of silica such as chemical inertness, controlled porosity, and thermal stability, have emerged as crucial catalysts in different domains. Recently, there has been a heightened interest in both academic and industrial circles regarding the design of novel reactions, synthesis, and modification strategies in modern synthetic organic chemistry. This focus aims to enhance the synthesis and fabrication of active materials with potential applications. Specific physicochemical characteristics of strategic materials like platinum (Pt), cobalt (Co), copper (Cu), palladium (Pd), and gold (Au) make them extensively utilized in various modification and synthetic strategies, particularly in catalytic activities, within modern organic synthesis.

1.3 OUTLINE OF THE PROJECT

This project is an attempt to synthesize silica nanoparticles via sol-gel method and to study the structural, morphological and optical properties of the synthesized particles by using the characterization techniques such as X-Ray diffraction, Scanning electron microscopy and UV-VIS spectroscopy. To control the size and morphology of the particles we have adapted tetraethylorthosilicate as a precursor to be used in the sol-gel process. From our findings we have arrived at the conclusion that the synthesized nanoparticles exhibit amorphous nature with an irregular structure. The synthesized amorphous silica nanoparticles also exhibit photoluminescence properties, opening wide applications of their use in bio-imaging, sensors, and optoelectronic devices.

CHAPTER 2

SYNTHESIS AND CHARACTERIZATION TECHNIQUES

2.1 CHARACTERIZATION TECHNIQUES

2.1.1 X-Ray Diffraction

X-ray diffraction (XRD) is a nondestructive technique used for characterizing crystalline materials. The information provided by this technique is used for the identification of the structure of crystalline materials, distribution of electrons within the atoms and throughout the unit cell, orientation of the crystalline planes and other structural parameters such as crystal defects, grain size, strain, crystallinity etc[1].

In the X-ray diffraction experiment, the sample to be analyzed, is placed at the central area of an instrument and illuminated with X-ray beam. A cathode ray tube is used as the source of x-ray, the light from the tube is filtered in order to obtain a monochromatic radiation which is directed towards the sample. A detector is used for sensing the diffracted X-rays. The X-ray tube and detector move in a synchronized manner. The detector sense the resulting signal and it is recorded and graphed. The peaks observed in the obtained graph are related to the atomic structure of the sample.

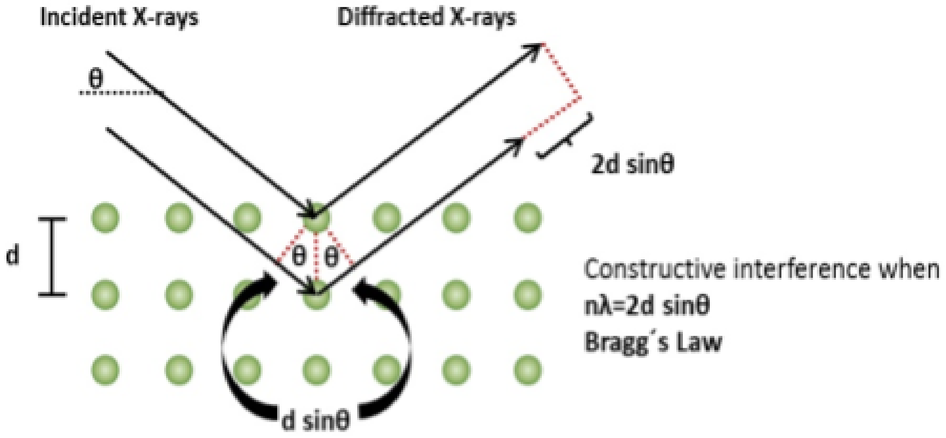


Figure SEQ Figure * ARABIC 3 X-Rays diffracted by atoms within a crystal

The theory of XRD is based on the constructive interference of the incoming X-rays and the crystalline material that is to be analyzed. In a crystal, the repeating arrangements of atoms form distinct planes separated by well defined distances. When the atomic planes are exposed by an X-ray beam, the X-rays are scattered by the regularly spaced atoms. Strong amplification (constructive interference) of the emitted signal occurs at very specific angles θ, known as diffraction angle and thus satisfy the Bragg's law:

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

where n is an integer, λ is the wavelength of the X-rays and d is the interplanar spacing of the atomic planes within the sample.

The above equation relates the wavelength of the incoming X-rays to the diffraction angle and the interplanar spacing within the sample to be analyzed.

The diagrammatic representation of the XRD technique is shown below

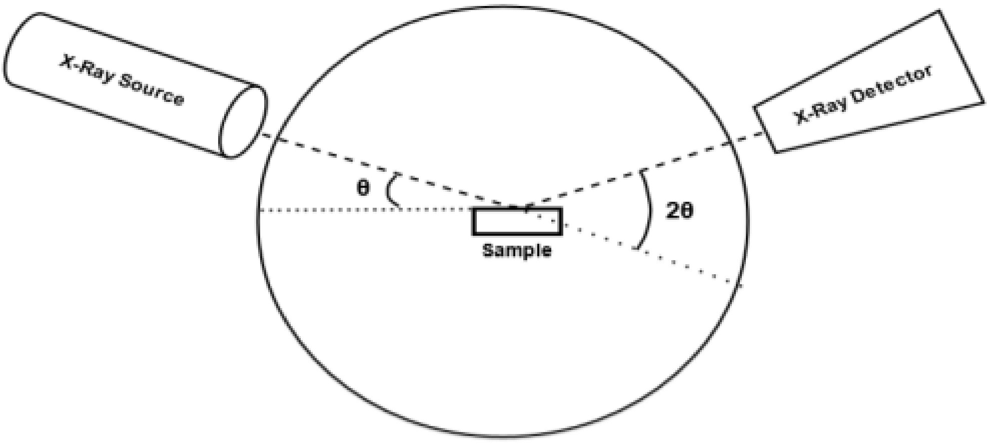


Figure SEQ Figure * ARABIC 4 XRD instrumentation

These diffracted rays are then detected, processed and counted. In order to attain all the possible diffraction directions of the lattice, the sample is scanned through a range of 2θ, since the powdered material exhibits random orientation. Since a set of unique d-spacing is attributed to each compound, the diffracted peaks are converted to d-spacings which allows the identification of the compound.

X-ray diffractometers has three basic elements: X-ray tube, sample holder, and detector. X-rays are produced by heating a filament, which leads to the production of electrons, by applying a voltage, the emitted X-rays are accelerated towards the target and electrons are made to strike on the target material. Characteristic X-ray spectra are emitted, when high energy electrons displace the inner shell electrons of the target material. The spectra consist of two components Kα and Kβ. Kα further consists of Kα1 and Kα2. The main difference between these two is that the Kα1 has a slightly shorter wavelength and its intensity is twice than that of Kα2. These wavelengths represents the characteristic of the target material used (Cu, Fe, Mo, Cr). In order to produce monochromatic X-rays needed for diffraction, filtering using foils or by crystal monochromators is required. The mean of the wavelengths of Kα1 and Kα2 is used, since they are sufficiently close.

For single crystal diffraction copper is the most commonly used target material with CuKα radiation = 1.5418Å.After collimation, these X-rays are directed onto the sample.The sample and the detector is rotated in order to record the intensity of the reflected X-rays. Constructive interference is occurred when the X-rays incident on the sample satisfies Bragg's equation and as a result, a peak is obtained. This X-ray signal is recorded and processed by a detector and changes the signal to a count rate which is then applied as an output to a device such as a printer or computer monitor.

The sample is made to rotate in the path of the collimated X-ray beam at an angle θ, and an X-ray detector collect these X-rays, which is mounted on an arm and rotates at an angle of 2θ. The angle and the rotation of the sample is controlled by an instrument called goniometer.

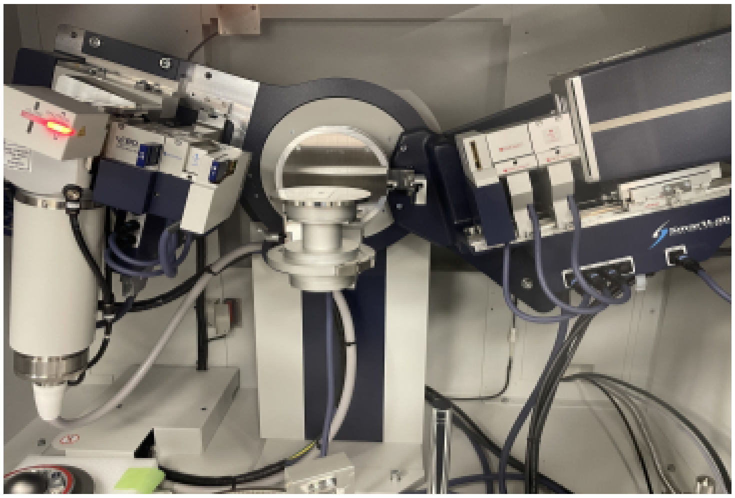


Figure SEQ Figure * ARABIC 5 X-Ray diffractometer

2.1.2 Scanning Electron Microscopy

Scanning electron microscopy (SEM), which is also recognized as SEM analysis or SEM technique, can be regarded as an effective technique in analysis of organic and inorganic materials on a nanometer to micrometer scale.

A scanning electron microscope (SEM) is a type of microscope that creates the images of a sample by making use of high energy beam of electrons for scanning in a raster scan pattern. The generation of signals that contains information about the sample's surface topography, composition and other properties, is resulted from the interaction between electrons and the atoms within the sample [3].

Components and Working System of SEM:

Main Components

1. Electrons of high energy are generated using a source called electron gun

2. Column down for traveling the electrons through two or more electromagnetic lenses (condenser lenses).
3. Objective aperture
4. Deflection system consists of scan coils.
5. A chamber for the sample.
6. Electron detector for backscattered and secondary electrons.
7. A computer hardware and software system consisting of a viewing screen to display the scanned images and keyboard to control the electron beam.

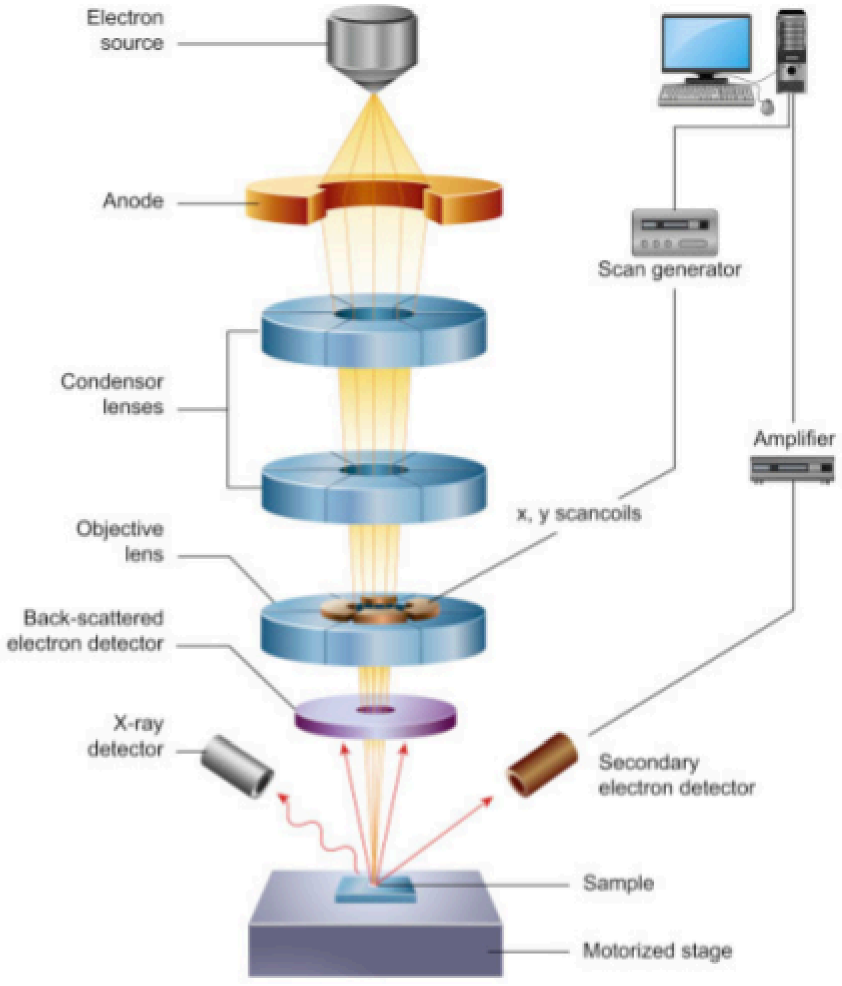


Figure SEQ Figure * ARABIC 6 SEM instrumentation

2.1.3 SEM Analysis Process

SEM is a tool at which invisible worlds of microspace and nanospace can be seen [3]. This is all can be achieved through the following processes,

- Instead of light SEM uses high energy electrons for the formation of an image.
- A metallic filament is heated to produce a beam of electrons at the top of the microscope.
- The vertical path followed by the beam is along the column of the microscope.
- Once it hits the sample, other backscattered electrons are discharged from the sample.
- The backscattered electrons are collected by the detector and are transformed into a signal and is sent to the computer and thus creates an image.

Some of the characteristic information that we obtain from SEM are:

- ❖ Topography: The surface features of a sample, its texture (direct relation between these features and material properties).
- ❖ Morphology: The shape and size of the particle making up the sample (direct relation between these structures and material properties).
- ❖ Composition: The sample is composed of elements an compounds in their relative amounts (direct relationship between composition and material properties).
- ❖ Crystallographic Information: Pattern of arrangement of the atoms within the sample (direct relation between these arrangements and material properties).

2.1.4 UV-Visible Absorption

UV-VIS spectroscopy serves as an instrumental method for chemical analysis, finding utility in both qualitative and quantitative assessments. This approach finds diverse applications across a broad spectrum of compounds, enabling the observation of the optical characteristics of chemical substances, identification of different species, and the precise quantification of specific analytes [2].

UV-Visible spectroscopy relies on the wave-like behavior of electrons and their interaction with electromagnetic radiation. UV-vis spectrometers are instrumental in the identification, characterization, and quantification of a remarkably diverse range of molecular compounds.

When a material is exposed to electromagnetic radiation, various phenomena like transmission, absorption, reflection, and scattering can manifest. Absorption takes place when the energy of incoming light matches the energy difference (ΔE) between a molecule's ground and excited states. The transition of an electron from the ground state to an excited state is referred to as an electronic transition.

The relationship between energy difference and wavelength is explained by Planck's equation, which can be represented as,

$$E=h\nu=hc/\lambda.$$

In this equation, E represents the energy required to move an electron from its ground state to an excited state, h is Planck's constant, ν is the wavenumber, c is the speed of light, and λ stands for the wavelength.

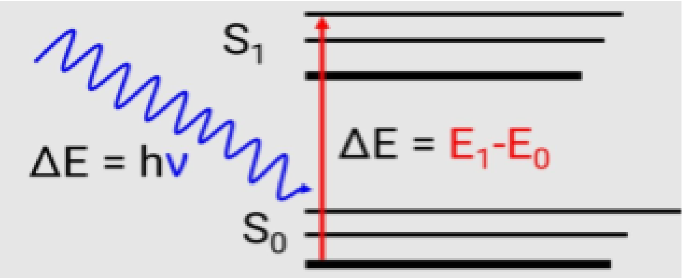


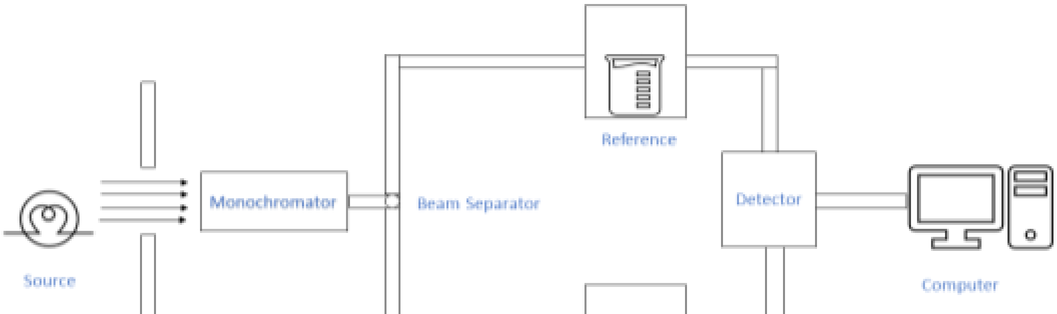
Figure SEQ Figure * ARABIC 7 Schematic representation of absorption

Planck's equation illustrates that when less energy is needed to excite electrons, the corresponding absorption band will have a longer wavelength. These absorption bands serve as indicators of the molecular structure of a sample and can shift in both wavelength and intensity depending on the molecular interactions and environmental conditions. Typically, these bands appear broad and lacking distinctive features due to the multitude of molecular vibrational levels associated with electronic energy levels.

Instrumentation:

A UV-Vis spectrophotometer consists of a light source, a monochromator, a detector, and a data recorder. The light source can provide illumination at one or more specific wavelengths. A monochromator, also known as a wavelength selector is used to select a particular range of wavelengths of the radiation from the light source to illuminate the sample. And the detector measures the intensity of the light that passes through the sample.The data recorder records the absorbance or transmission of light at each wavelength.

The sample is illuminated with the light beam from the monochromator and the wavelength of the light after passing through the sample is measured using the detector. Chemical structure and number of molecules can be obtained from the information provided by the detected signal. This, enables both quantitative and qualitative information regarding the sample. Information may be obtained as transmittance, absorbance or reflectance of radiation in the 190 to 1100 nm wavelength range. By absorbing the incident energy, electrons get excited to higher energy states. The energy difference between the ground and excited state of the electrons should match with



the energy of photons, for the occurrence of transition. This is the basic operating principle of absorption spectroscopy.

The energy of the transmitted light from a sample is measured using a photodetector and records the absorbance of the sample. The absorption or transmission spectrum of the light absorbed by the sample is plotted against the wavelength. Beer-Lambert law is the basic principle for the quantitative analysis of the absorption spectrum and it states that the absorbance of the solution is directly proportional to the sample concentration.

2.1.5 Photoluminescence

Photoluminescence spectroscopy is a nonintrusive and nondestructive technique used to investigate the electronic properties of materials. It involves the illumination of sample using light, which is followed by absorption resulting in photoexcitation.

When certain energy is absorbed by a molecule, it becomes excited and its electrons

Transfer to excited states. The electrons do not remain there for a longer time and return to lower and more stable energy levels. This can occur by non-radiative process or through a radiative process. The radiative process involves the emission of electromagnetic radiations. This process of emitting radiation is called luminescence. Photoluminescence is caused when a sample is irradiated with a light, which results in the emission of light with a particular wavelength, which is different from that of the incident light. Photoluminescence consist of both fluorescence and Phosphorescence, which differ in the lifetime after irradiation over which the luminescence occurs. The radiated light is often visible but can also be in the ultraviolet or infrared spectral region.

PL originates from an absorption/emission process between the electronic levels having different energy[8].

Fluorescence is the phenomenon in which a material absorbs light of a particular wavelength followed by a short-lived emission of light of a longer wavelength [8]. This process involves a light source to excite the molecule, which is then transformed from a ground to an excited state. As the molecules return to the ground state, energy is released in the form of heat and light. The phenomenon of fluorescence is instantaneous and the fluorescent materials generally emit the radiation within $10-6$ to $10-4$ seconds of absorption. Thus, the lifetime of fluorescence is generally small. Also, no change in Spin state of the electron involved during the process of fluorescence.

Phosphorescence is the process in which the radiations are incident on certain substances, they absorb them and then emit light continuously for a long time even after the incident light is cut off [8]. In this process the direction of the electron Spin may change when the electrons move to a lower energy state. In Phosphorescence the molecule does not return immediately to the ground state. Instead, it goes through a metastable state, a state where electrons stay for a longer period of time. This transition is known as intersystem crossing. The life-time of Phosphorescence is therefore much longer.

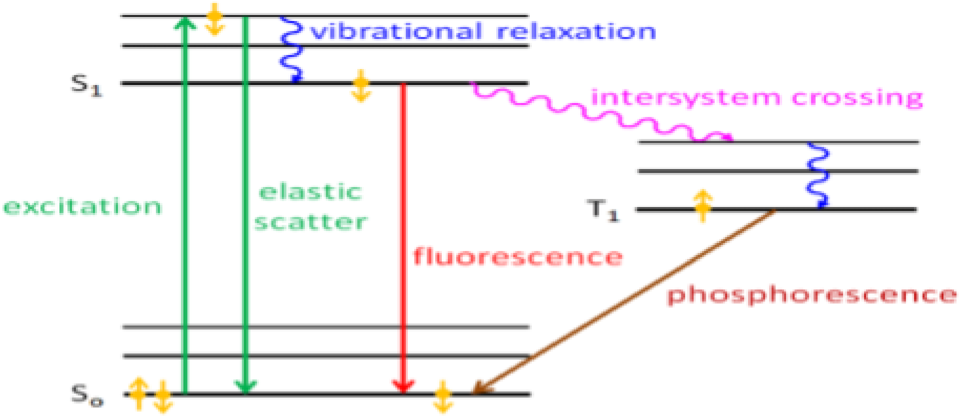


Figure SEQ Figure * ARABIC 9 Schematic representation of photoluminescence

Instrumentation:

Spectrofluorometer is the instrument used to record fluorescence from a sample. In order to record the fluorescence, scanning of the excitation, emission or both wavelengths is done. Through extra attachments, study of signal deviation with respect to time, temperature, concentration, polarization, or other variables is observed.

Block diagram of fluorescence spectrometer is represented in the figure below

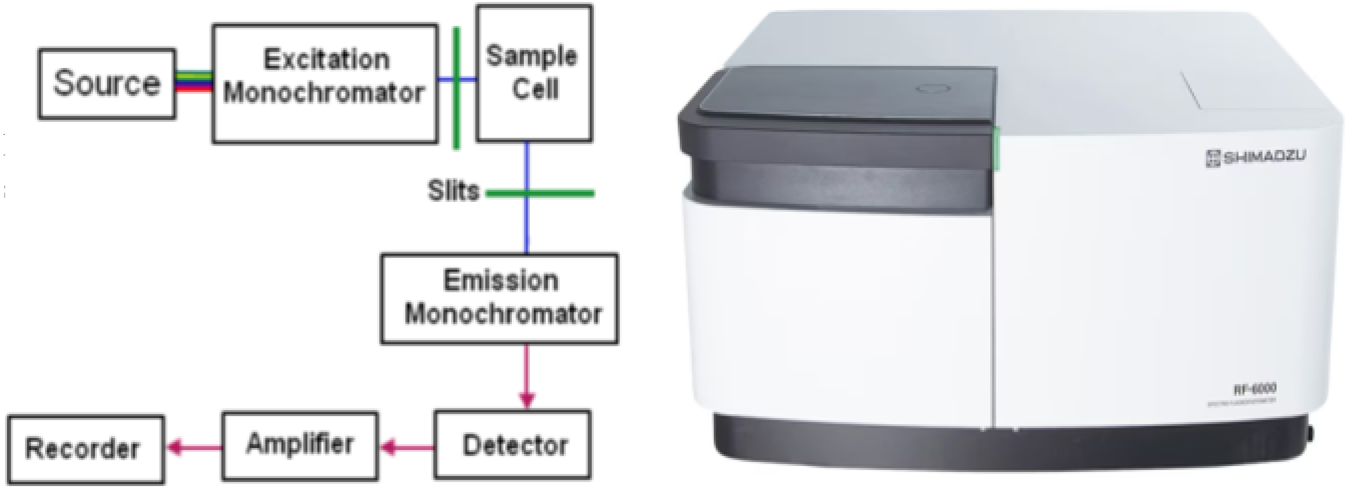


Figure SEQ Figure * ARABIC 10 Block diagram and a real picture of spectrophotometer

- **Monochromators:** Monochromators can be classified into two, Excitation and Emission monochromators. The entire reflective optics is used by a monochromator to keep great resolution as well as to reduce aberrations and re-diffraction.
- **Gratings:** The purpose of a reflection grating is to disperse the incident light through the vertically positioned grooves. The grating contains 1200 grooves per mm and it is coated with a protective layer of MgF_2 to prevent the oxidation of the grating.
- **Slits:** A monochromator usually consists of an entrance slit and an exit slit. The wavelength range of the radiation incident on the sample depends on the width of the exit slit.
- **Detectors:** There are 2 types of detectors, Signal and reference detector. The signal detector is based on photon counting, which is a photomultiplier tube that directs the signal to a photon counting module. The time dependent output and the correction of wavelength of the Xenon lamp is monitored by a reference detector. This detector is based on UV radiation which enhances silicon photodiodes, placed just prior to the compartment of the sample.

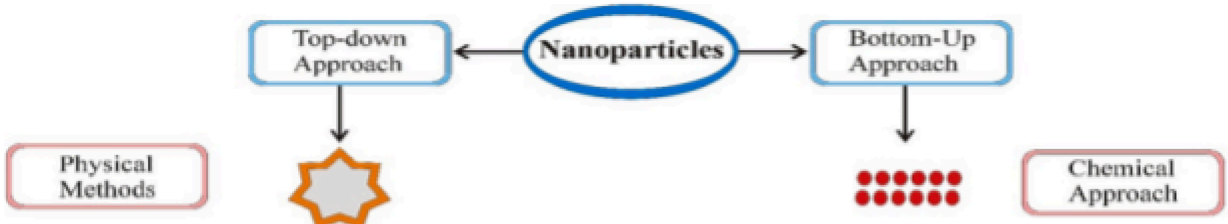
2.2 SYNTHESIS METHODS

Over the past few decades, many highlighting works have been done on novel processing methodologies to prepare silica nanoparticles (SNP), which have resulted in the establishment of methods that allowed better control over the size, shape, porosity and improvements in their physio-chemical properties.

Since silica nanoparticles are highly dependent on structural characteristics such as size, shape, and so forth, perfect control of the structure and quality of manufactured silica nanoparticles has emerged as an essential goal of nanoscience research. As a result, several ways for controlling nanoparticle synthesis have been devised by the researchers, including the template method, microemulsion method, sol–gel method, and many others. Among them, Microemulsions are one of the most convenient and widely used methods for the synthesis of silica nanoparticles [13].

As illustrated in the figure given, the different methodologies used to synthesize silica particles can be divided into two categories: top-down and bottom-up [13]. The preparation methods of silica nanoparticles can be divided into physical, chemical and green synthesis methods. In this paper we mainly focus on the chemical methods used to synthesize silica nanoparticles.

Chemical methods include sol–gel method, microemulsion method, electrolysis method, chemical vapor deposition method, precipitation method, hydrothermal reaction method, solvent evaporation method and so on.



2.2.1 Sol-gel method

This method is one of the so-called “bottom-up” nanoparticle preparation methods, that is solid silica nanoparticles are prepared from small molecules [13].

This method is renowned for its ability to produce monodisperse nanoparticles with a narrow size distribution, which is particularly advantageous for the development of silica-polymer nanocomposites. The sol gel process allows for precise control over the nanoparticle size, and distribution, making it a preferred method for many researchers.

Sol gel process involves the formation of networks throughout colloidal suspension which is followed by gelation to form a system in continuous liquid phase (gel). A sol is a dispersion of colloidal particles (1–100 nm) in a liquid and a gel is an interconnected rigid network which contains pores of sub-micron dimensions and polymeric chains. Depending upon the nature of the precursors that is, inorganic and alkoxide precursors the sol-gel process can be classified into two. In this process, the reaction of metal alkoxides and water, will form a one phase solution, in the presence of acid or base, that goes through a solution-to-gel transition to form a rigid, two-phase system composed of solid metal oxides and solvent filled pores. The type of catalyst used in the reaction largely influences the physical and electrochemical properties of the resultant materials. The acid catalyzed reaction results in weakly crosslinked linear polymers in the case of silica alkoxides. These polymers entangle and form additional branches leading to gelation. Whereas in the case of base catalyzed reaction highly branched clusters are formed, due to rapid hydrolysis and condensation of alkoxysilanes.

This difference in cluster formation is due to the solubility of resultant metal oxides in the reaction medium. The solubility of the silicon oxide is more in alkaline medium which results in the inter-linking of silica clusters. A general procedure of the sol-gel method includes four stages namely hydrolysis, condensation, growth and aggregation.

Hydrolysis: The hydrolysis reaction involves the reaction of metal alkoxides with water to form metal hydroxides and alcohols. The general chemical equation for the hydrolysis of metal alkoxides, such as tetramethoxy silane ($Si(OMe)_4$) or tetraethoxysilane ($Si(OEt)_4$), can be represented as follows:

$$\mathrm{Si\text{-}(OR)_4 + H_2O \rightleftarrows Si\text{-}(OR)_3\,(OH) + R(OH)}$$

Complete hydrolysis to form $M(OH)_4$ is often challenging to achieve, and instead, partial hydrolysis occurs leading to the formation of hydroxylated metal species.

Condensation: The condensation reaction involves the formation of metal-oxygen-metal (M-O-M) bonds by the reaction between hydroxylated metal species. The condensation reaction can be represented by the following general chemical equation:

$$(OR)_3\text{-Si-}(OH) + HO\text{-Si-}(OR)_3 \rightarrow [\ (OR)_3Si\text{-O-}Si(OR)_3\ ] + H\text{-O-}H$$

The condensation reaction leads to the formation of bridging oxygen atoms between metal species, resulting in the growth of the metal oxide network.

2.2.2 Microemulsion method

This method is mainly used to prepare the nanomaterials having unique properties [13]. This method involves the use of stable colloidal nano-droplets known as microemulsions, which act as nano-reactors for the formation of nanomaterials. The nanoparticles of SiO_2, CdSe, TiO2, ZnS, $CaCO_3$ etc. with different size and shapes have been successfully synthesized by employing micro-emulsion techniques. Two main types of emulsions are commonly used in the microemulsion method: water-in-oil (W/O) and oil-in-water (O/W) emulsions. These emulsions are stabilized by surfactant films, creating thermodynamically stable colloidal systems suitable for nanoparticle synthesis.

The microemulsion system provides a confined environment for the nucleation and growth of nanoparticles, allowing for precise control over their size and shape. The size and shape of the resulting nanoparticles are influenced by factors such as the composition of the emulsion, reactant concentrations, type of surfactant used, and the presence of capping agents. Surfactants play a crucial role in stabilizing the microemulsion system by reducing interfacial tension between oil and water phases. The surfactant molecules form a protective layer around the nano-droplets, preventing coalescence and ensuring the stability of the emulsion.

The microemulsion method offers advantages such as precise control over reaction conditions, uniformity in nanoparticle size distribution, and the ability to synthesize a variety of nanoparticles including pure, bimetallic, and multi-metallic nanoparticles. By adjusting parameters such as reactant concentrations and surfactant types, researchers can tailor the properties of the synthesized nanoparticles for specific applications. Nanoparticles synthesized using the microemulsion method find applications in various fields, including catalysis, drug delivery, sensors, and nanocomposites, due to their well-defined properties and enhanced reactivity.

2.2.3 Chemical Vapor Deposition

Chemical vapor deposition is a widely used method for depositing thin films and synthesizing nanostructured materials by introducing chemical precursors in the vapor phase onto a substrate surface [13]. In CVD, a solid material is deposited on a heated surface through a chemical reaction, leading to the formation of a thin film or nanostructured material. The CVD process requires an activation energy to initiate the chemical reaction between the precursor gases in the vapor phase.

Different types of CVD methods, such as thermal CVD, plasma CVD, laser CVD, and photo laser CVD, utilize various mechanisms to provide the necessary activation energy for the reaction.

- **Thermal CVD**: In thermal CVD, the reaction is initiated at high temperatures (around 1000 °C), where thermal energy is used to drive the chemical reactions leading to the deposition of the material on the substrate.
- **Plasma CVD**: Plasma CVD involves using plasma to activate the chemical reactions at lower temperatures (300-700 °C) compared to thermal CVD. The plasma provides the energy required to break chemical bonds and facilitate the deposition of the material onto the substrate.
- **Laser CVD and Photo Laser CVD**: Laser CVD methods utilize laser energy to heat the absorbing material, leading to pyrolysis and the deposition of the material on the substrate. In photo laser CVD, ultraviolet radiation with sufficient energy is used to break chemical bonds and initiate the chemical reactions necessary for material deposition.

Chemical vapor deposition offers advantages such as precise control over film thickness, composition, and properties, making it suitable for producing nanostructured materials with tailored characteristics.

CHAPTER 3

EXPERIMENTAL

By using the sol-gel method, the silica nanoparticles were synthesized. All the reagents used are of analytical grade without any further purification. Tetraethylorthosilicate (TEOS), absolute ethanol, acetic acid, polyvinylpyrrolidone (PVP) are the reagents used in this project.

TEOS (2.2 ml) was added to acetic acid(2.3 ml) and the solution was stirred for 10 minutes. To the above stirred solution 12 ml of 5 wt% of PVP in ethanol is slowly added and the resultant mixture was allowed to stir for 1 hour in order to form sol. After aging for 24 hours the sol was transformed into gel. The gel was then dried at 100^0C for 2 hours to remove the water and excess solvent. After drying the gel at 100^0C temperature, we obtain a white granule like substance, which is then subjected to calcination at 500^0C for 4 hours to remove the organic compounds. The powder was then grinded to obtain the silica nanoparticles. A schematic representation of the steps involved in the synthesis process is shown in the figure.

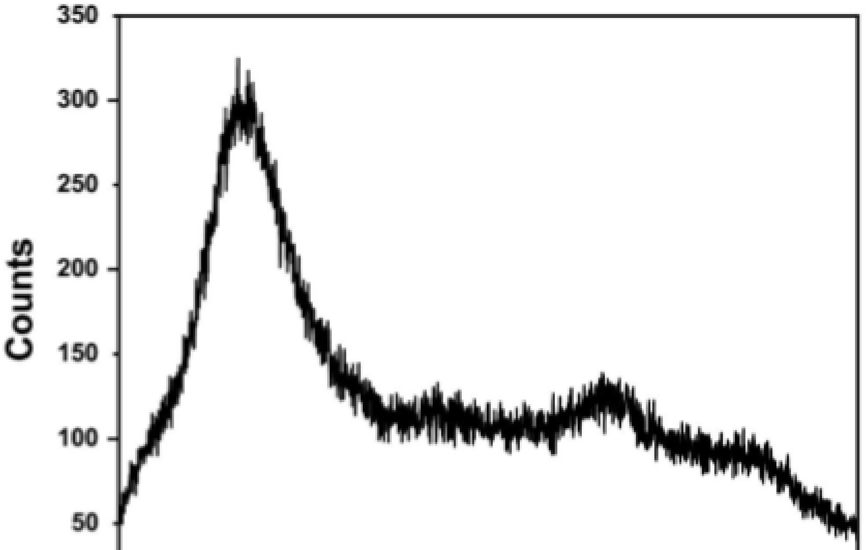
Figure SEQ Figure * ARABIC 12 (a) gelation (b) after heating at 100 degree celcius for 2 hours (c) after calcination at 500 degree celcius for 4 hours

CHAPTER 4

RESULTS AND DISCUSSION

4.1 X-RAY DIFFRACTION

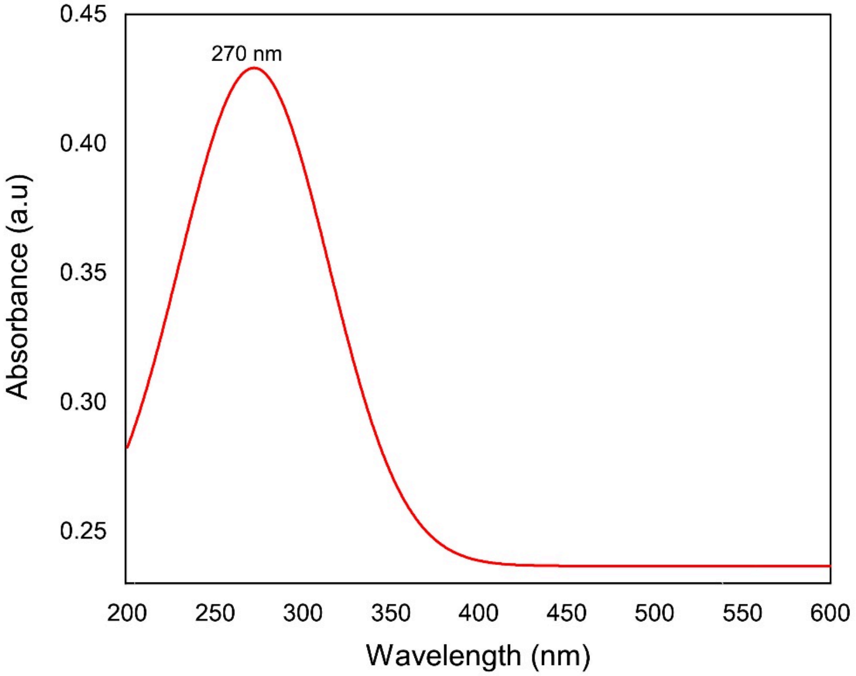
The synthesized silica nanoparticles were studied using X-ray diffraction measurement. The synthesized silica nanoparticles were characterized by X-ray Diffractometer (XRD) using CuKα (λ = 1.54 Å) as a radiation source. The XRD pattern shows a broad peak that corresponds to the amorphous phase of silica nanoparticles. The presence of a broad peak centered at 2θ = 22.88° confirms the existence of silica. The broadening of peak around 2θ =20° – 24° usually occurs for the amorphous nature of silica. The absence of any sharp peaks indicates the absence of impurities in the synthesized amorphous silica powder sample.



4.2 UV-VIS ABSORPTION SPECTRUM

The UV-VIS absorption spectrum obtained from the synthesized sample is shown in the figure. The maximum wavelength is observed at 270 nm. Depending upon the size of the particle, the maximum wavelength may shift.

The optical properties of the synthesized silica nanoparticles are attributed to surface defects which are related to the large surface to volume ratio. These structural defects can be classified into two, paramagnetic and non-paramagnetic, which can be characterized by optical absorption in a broad range of wavelengths: near-infrared, visible, and ultraviolet. According to R Tohman *et al* The optical absorption band near 5eV is due to oxygen vacancy and this band is caused due to singlet to triplet transition [14]. Therefore, we were able to validate that the optical absorption exhibited at 270 nm was due to silica nanoparticles.



4.2.1 Tauc Plot

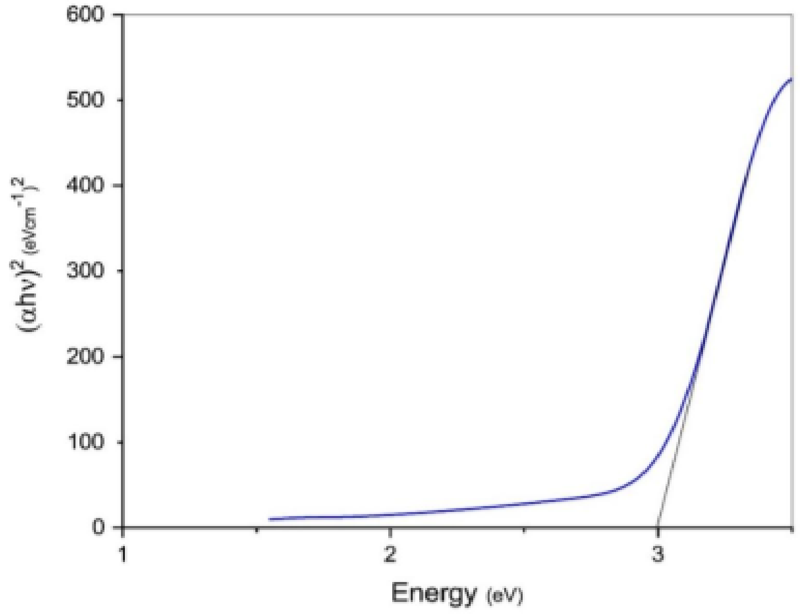


Figure SEQ Figure * ARABIC 15 Tauc plot of the synthesized nanoparticles showing a 3eV bangap energy

The specific wavelength of 270 nm indicates the energy difference between the quantized energy levels that the electrons can absorb. From the Tauc plot we have evaluated the energy bandgap of the synthesized particles to be 3 eV. In semiconductor nanoparticles like silica, the energy difference between valence and the conduction band can range from 1 to 4 eV.

4.3 SCANNING ELECTRON MICROSCOPY ANALYSIS

The SEM images of the synthesized silica nanoparticles in a 1 µm resolution is shown in figure16. The synthesized particles did not exhibit any particular structure i.e., the have an irregular structure. This further verify the fact that the synthesized silica nanoparticles are amorphous in nature.

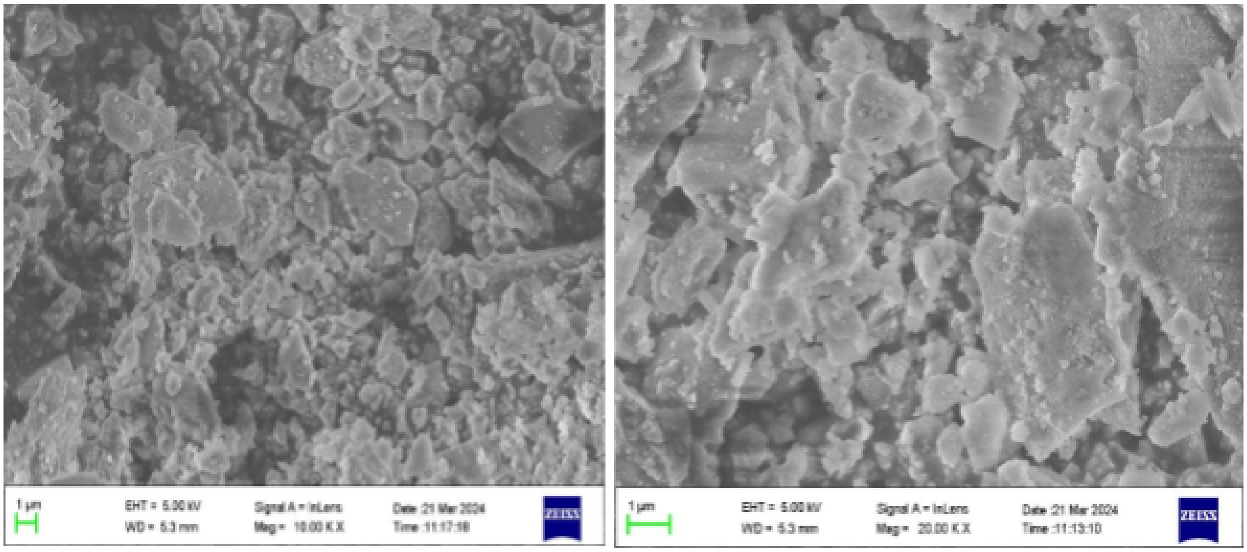


Figure SEQ Figure * ARABIC 16 SEM image obtained for the synthesized amorphous silica nanoparticles

4.4 PHOTOLUMINESCENCE STUDY

The excitation and emission spectrum of the synthesized amorphous silica nanoparticles are shown in the figure. The excitation peak of the sample was obtained at 213 nm (5.8 eV) and 233 nm (5.3 eV), for which we have obtained the emission peak at 430 nm (2.9 eV) and 470 nm (2.6 eV) respectively.

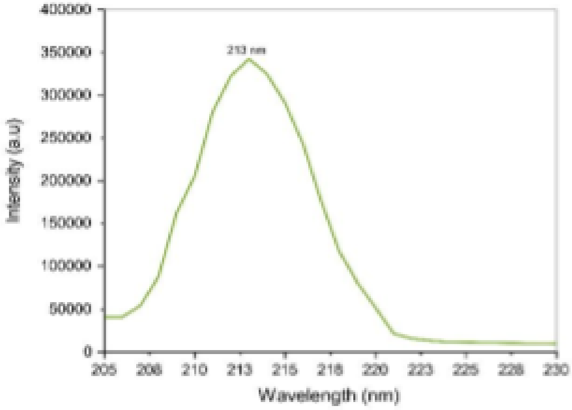


Figure SEQ Figure * ARABIC 18 Excitation spectrum with a peak at 213 nm

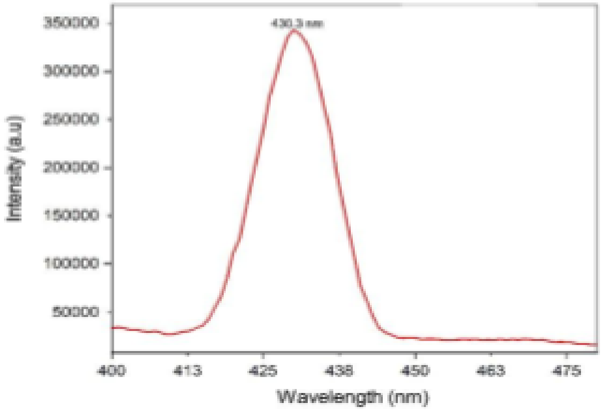
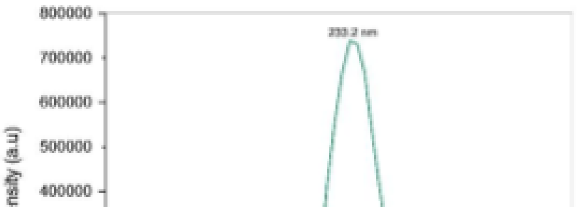


Figure SEQ Figure * ARABIC 18 Emission spectrum with a peak at 430 nm when excited at a 213 nm wavelength



According to Hiroyuki Nishikawa *et al.* the presence of oxygen deficiencies can lead to the formation of specific defect centres such as oxygen vacancies, which can influence the optical and luminescent properties of the material.

Therefor an emission peak at 430 nm and 470 nm may be due to the presence of hydroxyl (OH) groups and the neutral oxygen vacancy. The hydroxyl (OH) groups can be present in silica due to the presence of water or other sources of hydroxyl ions during the synthesis process or as impurities in the raw materials used to make the silica nanoparticles. The concentration of hydroxyl groups in silica can vary depending on the production methods and the purity of the starting materials.

L. Skuja *et al* in his paper 'Optically active oxygen-deficiency-related centres in amorphous silicon dioxide' mentioned that, an absorption or excitation band at 5.7eV to 5.8eV is characteristics of irradiated silicas, particularly the oxygen deficient ones, due to the presence of E'_{Υ} centre that is, the asymmetrically relaxed oxygen vacancy with an unpaired electron localized in a sp3-like orbital of a single Si atom. And the excitation band at 5.3 eV maybe due to the presence of an OH group in the neighbourhood of the E' center [16].

What is an E'_{Υ} center?

In stochiometric SiO_2, two silicon atoms are always connected by one bridging oxygen atom. When this oxygen atom is removed (what we imply as an oxygen defect), the connection of silicon atoms via oxygen is broken and an unpaired electron will remain with one of the silicon atoms, that is what we call a silicon dangling bond whose basic structure is $\bullet Si \equiv O_3$ thus the silicon atom acquires a negative charge. And the remaining positive silicon atom can bond to the back oxygen, that is what we define as asymmetrically relaxed oxygen vacancy and there is also

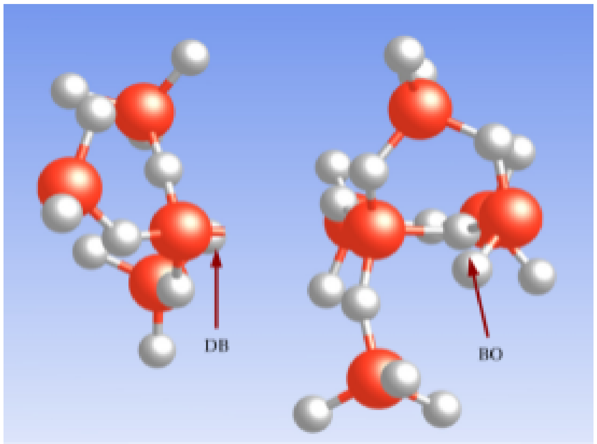


Figure SEQ Figure * ARABIC 21 Diagrammatic representation of silicon dangling bond and oxygen back bonding a chance for the two silicon atoms to bond together which we define as metastable ‘Si-dimer’ configuration. The diagrammatic representation of the above mentioned defects are shown in the figure [16].

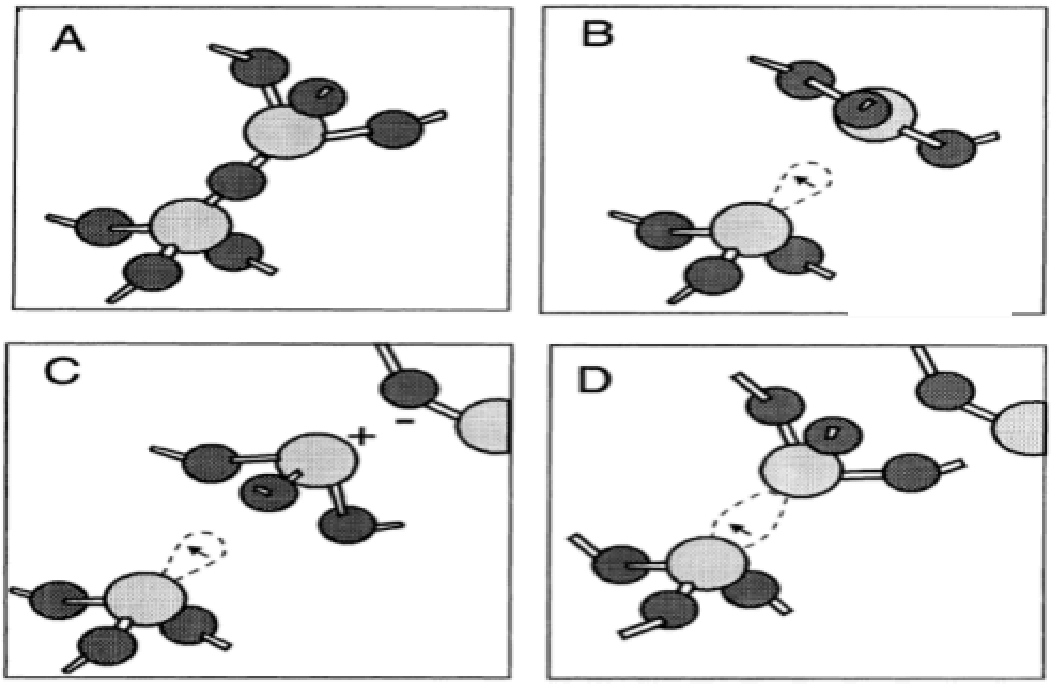


Figure SEQ Figure * ARABIC 22 (A)Fragment of a perfect lattice (B)Asymmetrically relaxed oxygen vacancy with a localized unpaired electron in a sp3-like orbital of a silicon atom (C)and(D)Two different types of bonding that the two separated silicon atoms can form

CHAPTER 5

CONCLUSION AND FUTURE SCOPES

Amorphous silica nanoparticles have been synthesized using solgel method. The precursor used for the synthesis of the silica nanoparticles was tetraethylorthosilicate, and PVP was used as a surfactant. In the XRD spectra obtained a single broad peak at 22.8° confirmed the amorphous nature of the synthesized silica nanoparticles. In the UV-VIS absorption spectrum an absorption peak at 270 nm wavelength have been obtained and the bandgap energy of the synthesized silica nanoparticles have been found out using Tauc plot method and it was found to be 3 eV. From the Photoluminescence study of the synthesized particles two excitation peaks at 213 nm and 233 nm have been observed for emission bands at 430.3 nm and 470 nm respectively. The absorption peak and the excitation peaks in the photoluminescence study have confirmed the presence of oxygen defects within the synthesized silica nanoparticles.

As a future study, the synthesized silica nanoparticles can be used for various applications which includes using silica nanoparticles as a antibacterial agent [15]. Various studies shows the absence of antibacterial activity in raw silica nanoparticles. However, significant antibacterial activity was observed when the nanostructures were treated with nitric and sulphuric acids. The silica nanoparticles can be used as a drug delivery vehicles due to their biocompatibility. Rhodamine-b loaded into the silica nanoparticles as a model drug can be utilized for tracking drug release[17]. The optical properties of silica nanoparticles can be attained with respect to surface defect related to large surface to volume ratio.

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