SYNTHESIS OF COPPER SULPHIDE NANOPARTICLES FOR SOLAR HEATING OF WATER

A Thesis

By

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(Roll. No.- 111CH0096)

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Under the esteemed guidance of

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National Institute of Technology Rourkela

CERTIFICATE

This is to certify that the thesis entitled, "**Synthesis of copper sulphide nanoparticles for solar heating of water**" submitted by **Srashtasrita Das** for the requirements for the award of Bachelor of Technology in Chemical Engineering at National Institute of Technology Rourkela, is an authentic work carried out by her under my supervision and guidance.

To the best of my knowledge, the matter embodied in this thesis has not been submitted to any other University / Institute for the award of any Degree or Diploma.

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DECLARATION

I, Srashtasrita Das, do hereby declare that the thesis entitled "**Synthesis of copper sulphide nanoparticles for solar heating of water**" is an honest attempt to put the entire finding on actual data gathered through reading various research papers and articles. The experimental reporting is from the work carried out in the Interfaces and Nanomaterials laboratory of the Department of Chemical Engineering, National Institute of Technology, Rourkela.

It is an original work and the contents of this report reflect the work done by me during the final year in partial fulfilment for the award of the Degree of Bachelor of Technology in Chemical Engineering in the Department of Chemical Engineering, National Institute of Technology, Rourkela.

Srashtasrita Das

Place: Rourkela

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ABSTRACT

Nanotechnology has gained immense attention in the recent years. Enhanced light absorption of nanomaterials can be used for the purpose of utilisation of solar energy and seem to have profound impact on the many related areas of science and technology. Copper sulphide nanomaterials were developed to determine the effect of nanoparticles for the solar heating of water. Copper sulphide nanomaterials were synthesized by wet chemistry. The molar concentration ratio of copper nitrate to sodium thiosulfate and the reaction temperature play an important role in the synthesis of the nanoparticle. The use of surfactant and its amount is very important in the synthesis to have stable nanoparticles solution and to prevent aggregation or coagulation of the nanoparticles in the solution. For the purpose of characterisation, the formation of the compound was studied in detail using X-ray diffraction (XRD). The zeta potential and the particle size was determined by Dynamic Light Scattering (DLS). The optical property was studied by UV-Vis-NIR spectrophotometer.

The copper sulphide nanoparticles have an optical absorption band in the NIR region that makes it a suitable substance to be used for the experimental purposes to acknowledge the solar heating of water. To determine solar heating of water, a setup has been designed using a metal-halide lamp to emit radiations in the NIR region. After obtaining the results from the UV-Vis-NIR spectrophotometer regarding the optical properties of the nanoparticles, the nanoparticles solution was circulated in the setup to check the solar heating of water.

Keywords: Copper sulphide nanoparticles, X-ray diffraction analysis, UV-Vis-NIR spectrophotometer analysis, Dynamic Light Scattering analysis, NIR absorbance.

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CHAPTER 1

INTRODUCTION

1. INTRODUCTION

1.1 NANOPARTICLES

Nanomaterials can be defined as the substances having particle sizes in the range of nanometers (less than or equal to 100nm), which exhibited novel and significantly improved physico-chemical and biological properties with unique phenomena and processes specifically due to their nanoscale size. It is slowly developing into the promising research field. The nanoparticles seem to have numerous applications and tremendous use in various fields. The nanostructured materials seem to have fascinating optical properties which find important applications in a number of solar energy utilization methods and instruments. Nanotechnology provides methods for fabrication and use of structures and systems with size corresponding to the wavelength of visible light which enables us to utilise many new phenomena, often of resonance character, to be observed when the object size and electromagnetic field periodicity match. Nanoparticles can be found before the evolution of nanotechnology as an emerging topic in the works of both nature and man, although they passed unnoticed by us until recently. The origin of nanoparticles in nature is basically (a) biogenic, (b) geogenic and (c) cosmogenic, while the nanoparticles which have been produced by men come (a) unintentionally from origins as burning wood and oil or (b) unnoticed in crafted stuffs such as cosmetics and colored glass and ceramics[1].

Table 1.1 : The history of inventions [2]

Discovery type	Name	Age	Start date
Industrial	Tools	Stone	2,200,000 BC
Industrial	Metallurgy	Bronze	3500BC
Industrial	Steam power	Industrial	1764
Automation	Mass production	Consumer	1906
Automation	Computing	Information	1946
Health	Genetic Engineering	Genetic	1953

Industrial	Nanotechnology	Nano age	1991
Automation	Molecular assemblers	Assembler age	2020
Health, industrial, automation	Life assemblers	Life age	2050

However, the artificial synthesis of nanoparticles according to need of the experiment has recently gained momentum. There are numerous approaches for developing nanoparticles, but none of them has been accepted as an ideal or generally acceptable tool.

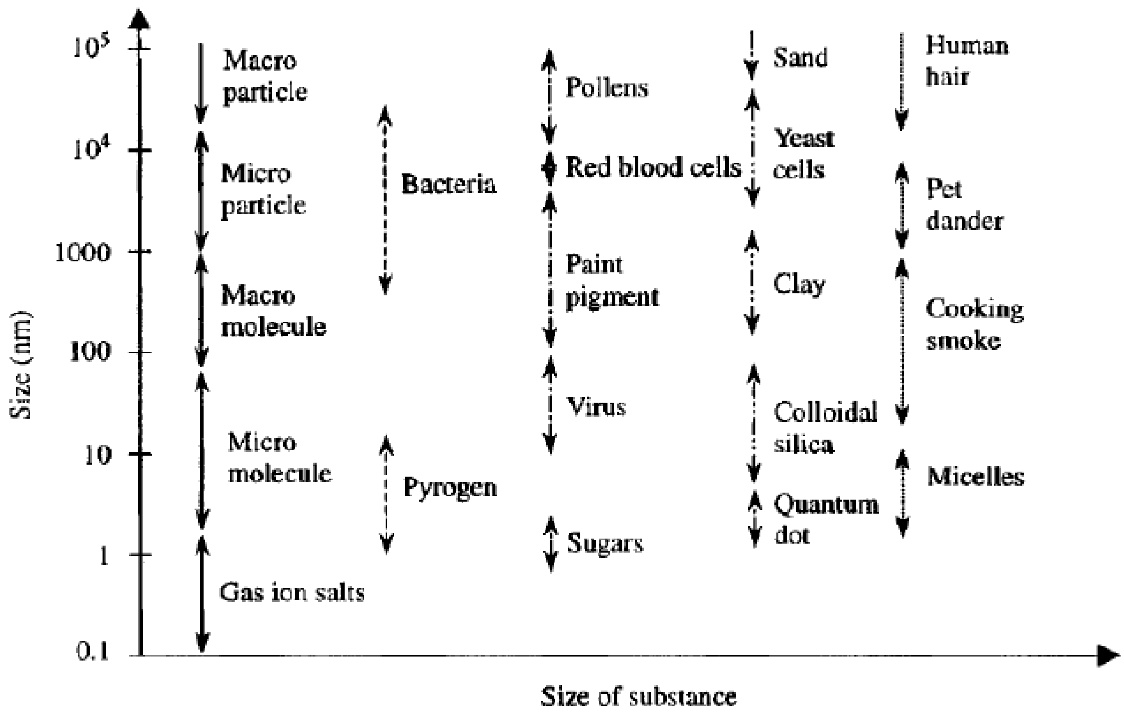

Figure 1.1: Chart representing examples of nanostructures or nanomaterials with their typical ranges of dimension [3]

Imperceptible to the normal eye, these materials suspended in a liquid disperse light without reflecting it, possess certain characteristic colour depending on the shape, size and surroundings. Characterization of nanomaterials is important because it helps in determining the structure, morphology, size of the nanoparticles, porosity, zeta potential, optical characteristics, etc., and enables us to determine the suitable nanoparticles for various applications.

1.2 SYNTHESIS TECHNIQUES

Despite the numerous approaches for the development and synthesis of nanoparticles, the synthesis of nanoparticles can be broadly classified into two categories-

(a) Top Down Approach:

Nanomaterials are created in this technique by breaking down the bulk material. It is traditional method of synthesis or fabrication method in which particles are broken into very small pieces to reach into nano-scale by means of externally-controlled tools used to cut, mill and shape materials into the desired order and shapes, which usually involves application of severe plastic deformations. However, the biggest problem associated with this method is an imperfection of the surface structure. The common techniques involved in the top-down approach are lithographic techniques, attrition, high energy ball milling, mechano-chemical processing, etc. There is no significant difference in physical properties of materials irrespective of the synthesis routes adopted. This process is slow and is usually not recommended for large scale productions. Starting with initial larger structures, another widely used method for this approach is photolithography.

(b) Bottom-up approach:

Nanomaterials are created in this technique by the method of build-up from the bottom. It utilises the physical forces operating at nano-scale are used to combine basic units into larger stable structures. Nanoparticles are built up in this approach atom by atom or molecule by molecule. There is a spontaneous arrangement of particles into stable structures and aggregates. The defects obtained by bottom-up method are less. The synthesized materials have a homogeneous chemical composition. They also seem to have better short and long range ordering. Some examples of bottom-up approach are colloidal dispersion, chemical precipitation or co-precipitation, hydro-thermal, solvo-thermal synthesis, forced hydrolysis, supercritical hydro-thermal processing or supercritical fluid processing, sol-gel synthesis, microwave heating synthesis, etc. The fabrication techniques are also comparatively cheaper than the top down approach.

CHAPTER 2

LITERATURE REVIEW

2. LITERATURE REVIEW

2.1 INTRODUCTION

Sunlight has by far the highest theoretical potential of the earth's compared to other renewable energy sources. More energy from the sun falls on the earth in one hour than is used by everyone in the world in one year. Harnessing solar energy has recently gained attention in the field of nanotechnology. Researchers have made successful attempts in developing nanoparticles using metals such as gold and copper as well as carbon nanoparticles which can absorb sunlight and result in formation of steam (without the need of any external heating sources), followed by heating of the water. Synthesis of nanoparticles can also be made for this purpose which seems to have the optical property of absorbance in the NIR region.

2.2 SOLAR HEATING

Aqueous solutions containing light-absorbing nanoparticles have recently been shown to produce steam at high efficiencies upon solar illumination, even when the temperature of the bulk fluid volume remains far below its boiling point[4]. Experiment has been conducted on heating of water through light localization using solutions of two different metal-dielectric nanoparticles: nanoshells and nanomatryoshkas. However, nanoshells were found to be more effective for their purpose as the temperature increase at the top of the nanoshell solutions is about greater than 10 °C larger as compared to nanomatryoshka solutions of equal concentration. Also, the steam generation rates for nanoshell solutions are almost a factor of 2 larger than for nanomatryoshka solutions of equal concentration and illumination intensity.[4] This is due to the increased light trapping and localization for nanoshell solutions, which provides an order of magnitude larger maximum heat source density than for nanomatryoshka solutions. It was found that light trapping through multiple scattering could be used to concentrate energy absorption into very small volumes. This can be implemented as a crucially important method which makes the way for further optimization and development of photothermal applications such as light-induced steam production.

Various articles seem to show particle-based approaches for solar energy applications.[5][6] It has been found experimentally that upon solar illumination, the pressure over the solution of SiO_2/Au nanoshells began to increase, indicating steam generation, in less than 5 secs after illumination commenced on the other hand, for carbon nanoparticles the pressure increase was delayed by just over 20 secs. However once started, the steam is generated at a very similar rate for both solutions.[7] Steam generation seemed to occur in microexplosive bursts. A slow and measurable increase in the fluid temperature for the illuminated nanoshell solution was observed, while the carbon nanoparticle solution showed only a negligible increase in temperature for the same illumination conditions during this initial time period. There was no evidence of the chemical breakdown of nanoparticles in the process of the experiment.

Significant work has been done on the design of compact solar autoclave based on steam generation using broadband light-harvesting nanoparticles and showed that with nanoparticle dispersants, temperatures of both the liquid and the steam increase far more rapidly than the temperature of pure water, with the liquid water reaching 100 °C more rapidly with nanoparticle dispersants than water without nanoparticles.[8]

The description of the phenomenon of nucleation of steam on the surface of individual nanoparticles that are heated by means of the solar energy has been described in various research articles. The solar steam nano-bubble generation phenomenon occurs from different phenomena that occur at the nanoscale.[9] Highly tunable nanoparticles fabricated at large volumes using chemical synthesis were made and utilised for the purpose of water vapour generation having applications in an autoclave and other processes such ethanol-water distillation, etc.

2.3 FABRICATION OF NANOPARTICLES

Synthesis of nano-copper and nano-copper sulphide metallic particles by Solanki et al provides insight into the effect of most important operating parameter, water-to-surfactant molar ratio, on the product specification including size as well as size distribution and morphology.[10] The products obtained were analysed using transmission electron microscope imaging, dynamic light scattering with the particle size analyser and absorption spectra using UV-visible spectrophotometer and it was observed that bigger particles were achieved at the higher water-to-surfactant ratio. Dynamic light scattering showed that copper sulphide nanoparticle of bigger size particles of 10 nm to 69.2 nm were achieved by synthesis technique.

Copper nanoparticles have been synthesized copper sulphide nanoparticles by wet chemistry and they seem to show their application in photothermal ablation of tumor cells was tested by irradiation using an NIR laser beam at 808 nm to elevate the temperature of aqueous solutions of CuS nanoparticles as a function of exposure time and nanoparticle concentration. CuS nanoparticles synthesised by them exhibited unique optical property, small size, low cost of production and low cytotoxicity. They also found from results that CuS nanoparticles have an optical NIR range absorption band with a maximum absorbance at 900 nm.[11] Thus the nanoparticles seem to exhibit the required optical property and can be utilised for the purpose of solar heating of water.

The synthesis and formation mechanism of CuS and Cu_2S has been demonstrated by a simple hydrothermal process in the temperature range of 150–250^{o}C.[12] The molar concentration ratio of copper nitrate to sodium thiosulfate precursor was kept in the ratio of 1:2. They also demonstrated that the reaction temperature plays an important role in determining the morphology and composition of the product. The effect of surfactant CTAB was also analysed by them. The optical band gap of the synthesized CuS nanoparticles was found to be 1.7 eV which serves the purpose of its utilisation in applications that require absorption in the NIR region as an important property.

2.4 MOTIVATION

The efficient use of renewable sources of energy is the need of the time and utilisation of novel nanoparticles for solar heating purposes can be a promisingly efficient source of energy for our future. The sun is probably the most important source of renewable energy available today. The utilisation of solar energy for various purposes is a choice with many benefits. It's free. It's clean. It's infinitely renewable. It can reduce your utility costs. It increases the energy self-reliance. It's extremely reliable. However, judicious worldwide use of the solar energy yet needs to be established. Harnessing solar energy has recently gained attention in the field of nanotechnology. Many research efforts have been established towards the use of solar energy in evolving nanotechnologies such as solar heating, solar photovoltaics, solar thermal energy, solar architecture and artificial photosynthesis. The potential of solar energy is well-known to the researchers but new methodologies still need to be invented, and new technologies still need to be implemented for efficient utilisation of solar energy. The use of nanoparticles solution for the purpose of solar heating is a recent topic, and not much work has been done in this field. The experiments that have not been done by many researchers still need to be undertaken so as to follow the path less taken. Sufficient research needs to be done to ensure successful utilisation of nanoparticles solution in solar heating applications that can take use of renewable energy to a higher level.

2.5 RESEARCH OBJECTIVES

Synthesis of the copper nanoparticle by bottom-up approach can be done effectively by the utilisation of suitable precursors and chemicals. Synthesis of copper sulphide nanoparticles from $(CuNO_3)_2$ and $Na_2S_2O_3$ in the presence of the surfactant CTAB (cetyltrimethyl ammonium bromide) has been done. The synthesized nanoparticle was then circulated in the designed solar heater to analyse the heating of water by using copper sulphide nanoparticles. The overall objectives of this research project are:

1. To synthesize copper sulphide nanoparticles.
2. To study the formation of the copper compounds in the nanoparticles
3. To study the size and zeta potential of the nanoparticles.
4. To study the optical characteristics of the nanoparticles.
5. To design a heater to analyse the solar heating of water using nanomaterials

CHAPTER 3

CHARACTERISATION TECHNIQUES

3. CHARACTERISATION TECHNIQUES

The characterisation techniques enable us to probe and measure a material's structure and its properties. Various material analysis processes using a wide range of principles to reveal the various properties such as chemical composition, composition variation, crystal structure and photoelectric properties, optical properties, etc. The synthesised nanomaterial was characterised to determine its properties. With the aid of the characterisation techniques, the properties exhibited by the nanomaterials can be known or verified which shall help in determining the applications of nanomaterials and enhance their utility in various fields of science and technology.

The various techniques used for characterisation of the synthesis of the nanoparticle involved:

3.1 SPECTROPHOTOMETRIC ANALYSIS

UV-Vis spectroscopy is the measurement of the attenuation of a beam of light after it passes through a sample or after reflection from a sample surface in which absorption measurements can be obtained at a single wavelength or over an extended spectral range which may cover the visible range or ultraviolet range or near infrared range. The region beyond red is called infrared while that beyond violet is called as ultraviolet part of the spectrum. It works on the principle that when a sample is exposed to light energy such that the energy difference between possible electronic transitions within the molecule matches with it, a small amount of the light energy would be consumed by the atom and the electrons would be elevated to the higher energy state orbital. A spectrophotometer records the degree of absorption by a sample at different wavelengths and plots the absorbance (A) versus wavelength (λ), which is known as a spectrum, where λ_{max} is the wavelength at which there is a maximum absorption and the intensity of maximum absorption can be known. The band gap can be then calculated from the Tauc plot using Kubelka munk function.

3.2 DYNAMIC LIGHT SCATTERING ANALYSIS

Dynamic Light Scattering (DLS), also called as photon correlation spectroscopy, is a spectroscopic technique used in various fields related to science and technology, primarily to characterize the hydrodynamic radius of polymers, proteins, and colloids in solution in the field of nanotechnology. It can also be used to inspect the behaviour of complex fluids. It can help in determining the size distribution of nanoparticles in a suspension. DLS analysis takes into consideration the Brownian motion of particles, which causes laser light to be scattered at different intensities, and utilises the Stokes-Einstein equation to relate the velocity of a particle in solution to the hydrodynamic radius of the particle which states that $D = kT / 6\pi\eta a$, where D is the diffusion velocity of the particle, k is the Boltzmann constant, T is the temperature, η is the viscosity of the solution and 'an' is the particle's hydrodynamic radius. At the point when light hits little particles, the light diffuses in all directions (Rayleigh scattering) when the particles are small as contrasted with the wavelength (below 250 nm). When the light source is a laser, and in this manner, is monochromatic and coherent, the dissipating power varies with time. This fluctuation is because of the way that the small molecules in arrangements are experiencing Brownian movement. Thus the separation between the scatterers in the solution is continually changing as time progresses. This scattered light then experiences either constructive or destructive interference by the encompassing particles, and inside this intensity fluctuation, data is contained about the time scale of scattering particles movement.

3.3 ZETA POTENTIAL ANALYSIS

Zeta potential, a scientific term for electrokinetic potential in colloidal dispersions, is the measure of the magnitude of the electrostatic or charge of repulsion or attraction between particles. It can also be stated as a parameter characterizing electrochemical equilibrium on interfaces which depends on the properties of liquid as well as on properties of the surface of the particles, thereby describing the nature of the electrostatic potential near the surface of a particle. Zeta potential analysis can be done from the same instrument during the dynamic light scattering analysis.

3.4 X-RAY DIFFRACTION ANALYSIS

XRD is an analytical technique which is specifically used for phase analysis of a crystalline structure. It relies on the dual wave or particle nature of X-rays to obtain information about the structure of materials which are usually crystalline in nature. It can be utilized to take a look at different qualities or properties of the single or polycrystalline materials. It can help in identification of fine-grained minerals such as clays and mixed layer clays that are difficult to determine optically, help to determination of unit cell dimensions and measurement of sample purity, along with the identifying of the atomic or molecular structure of the crystalline material. The X-ray diffraction works on the principle of Bragg's Law which states that $n\lambda = 2d \sin\theta$, where d is the diffraction spacing between planes, θ is the incident angle, n is any integer, and λ is the wavelength of the beam incident on the nanoparticles. XRD, requiring a large volume of sample, is time-consuming technique. A crystallographer can produce a 3-D picture of the density of electrons within the crystal by measuring the angles and intensities of the diffracted X-ray beams. X-rays are directed at the sample, and the diffracted rays are collected after detection, processed and then counted to make calculations. From the intensity, the chemical bonds can also be determined.

CHAPTER 4

SOLAR THERMAL ACTIVITY

4. SOLAR THERMAL ACTIVITY

The microscopic mechanism of this nanoparticle-catalysed steam formation is intriguing. As the nanoparticles are heated by the incident light, they rapidly transfer heat to the water in the immediate surroundings. Since the nanoparticles are strong absorbers of NIR light, the thin shell of H_2O that is in direct contact with the nanoparticle suspension rapidly heats above its boiling point and transforms into steam. Then, because steam is a very poor thermal conductor, heat transfer from the heated particle to the water is strongly inhibited.

As the nanoparticle is further heated by the sunlight, the thickness of the steam shell continuously grows. Once the steam shell reaches a thickness of several 100 nm, the weight of the steam/nanoparticle assembly becomes less than that of an equivalent volume of water and, as a consequence, it buoys toward the surface of the nanoparticles. Finally, the steam bubble annihilates at the surface and steam escapes from the water. In this way, steam is generated without heating the entire water volume to the boiling point.

Surface plasmon resonance is a prominent spectroscopic feature of noble metal nanoparticles, which gives rise to a sharp and intense absorption band in the visible range. The physical origin of the absorption is a collective resonant oscillation of the free electrons in the conduction band of the metal. The localized surface plasmon polaritons are collective electron charge oscillations in metallic nanoparticles that are excited by light. They exhibit enhanced near-field amplitude at the resonance wavelength. The materials which exhibit this property in the NIR region are Gold, Silver, Copper, etc.

Chalcogenides, such copper sulphide (CuS), also seem to exhibit peculiar optical property in the NIR region, that have found potential uses in catalysis, environment remediation, energy storage and conversion, and optoelectronic devices. Thus, such materials exhibiting properties in the NIR region can also be used as strong absorbers of light an utilised in the same manner as metals exhibiting SPR for the purpose of solar heating of water.

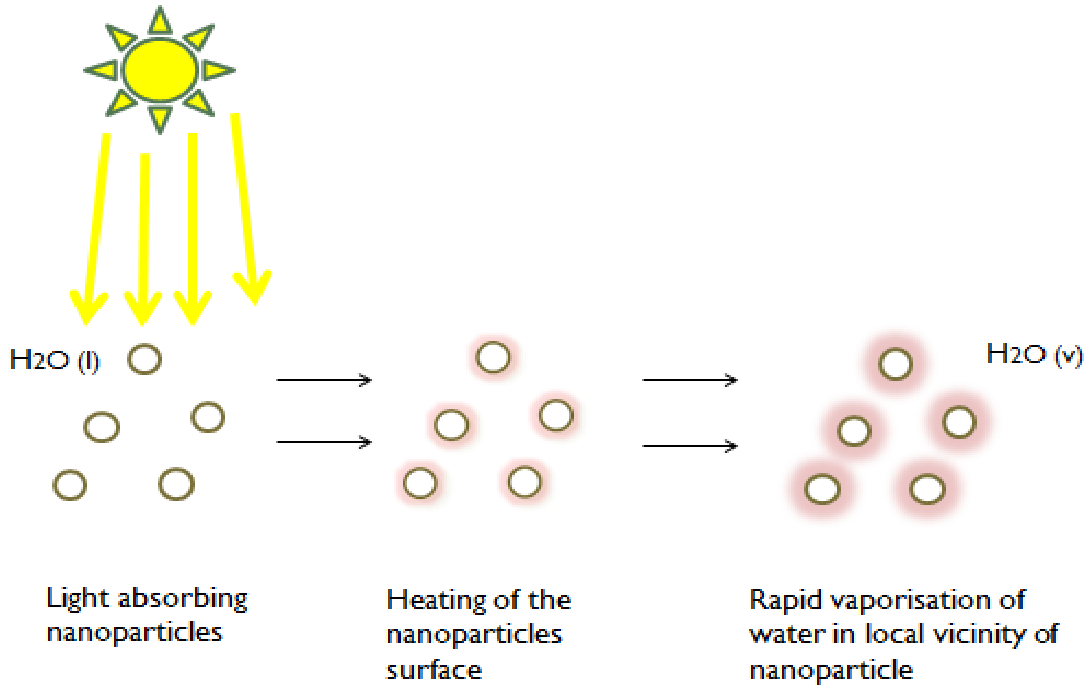

Figure 4.1: The mechanism of localised steam generation by using nanoparticles

CHAPTER 5

EXPERIMENTAL WORK

5. EXPERIMENTAL WORK

5.1 INTRODUCTION

There are numerous methods available for the synthesis of copper sulphide nanoparticles. However, the bottom-up approach for the synthesis of nanoparticles by wet chemistry method is one of the widely used methods for the synthesis of nanoparticles. One of the efficient and simplest experimental procedures for the synthesis of copper sulphide nanoparticles involves the utilisation copper nitrate and sodium thiosulphate as precursors in the molar concentration ratio of 1:2 in the presence of CTAB as a surfactant to obtain a stable suspension of the synthesised particles. The stock solutions of the chemicals to be used were prepared. From the stock solutions, a solution of copper nitrate (having concentration = 1mM) and sodium thiosulphate (having concentration = 2mM) was prepared in the presence of CTAB (having concentration = 3mM)

5.2 MATERIALS AND INSTRUMENTS USED

The following chemicals used in the process of synthesis were: Copper Nitrate (Chemical name: Copper nitrate extra pure trihydrate, $Cu(NO_3)_2.3H_2O$) (1mM, Loba Chemie Pvt. Ltd), Sodium Thiosulphate (Chemical name: Sodium thiosulphate pentahydrate, $Na_2S_2O_{3.}$ $5H_2O$) (2mM, Ranbaxy Fine Chemicals Ltd.), CTAB (Chemical name: Hexadecetyltrimethyl ammonium bromide) (3mM, Sigma Aldrich), and milli pore water. All the chemicals were used without further purification. Some of the instruments used were: UV-Vis-NIR spectrophotometer, Malvern zeta sizer, X-ray diffraction, and peristaltic pump. Metal halide lamp was used which would emit radiations in the NIR region. All the testtubes and flasks were properly cleaned and rinsed with millipore water before use, and then dried in air oven to remove existent moisture.

5.3 EXPERIMENTAL PROCEDURE

The experiments were carried out in the laboratory. The procedure followed for the synthesis of the copper sulphide was:

1. Stock solution of 50 mM concentration and 10 ml volume was prepared for copper nitrate, sodium thiosulphate and CTAB by weighing the required amounts of the chemicals and then adding water to them to have individual stock solutions of 10 ml each.
2. The product was synthesized by initially adding 1.5 ml of CTAB from stock solution to 22 ml water in a beaker to obtain a concentration of 3mM.
3. 0.5 ml of copper nitrate was added from stock solution to the 3mM CTAB solution to obtain a concentration of 1mM.
4. 1 ml of sodium thiosulphate was added from stock solution the 3mM CTAB solution to obtain a concentration of 1mM.
5. The final solution of the 25ml volume in the beaker was then placed on a magnetic stirrer and was stirred for 12 hours.
6. The product obtained was then centrifuged at 25000 rpm for 15 mins to obtain the synthesized nanoparticles.
7. It was then further washed with water twice to obtain the synthesized nanoparticles free from excess ions or surfactants present along with the synthesised nanoparticle.

Figure 5.1: The synthesised nanoparticles

The reaction occurs as follows:

$$Cu(NO_3)_2 + 2Na_2S_2O_3 = Na_2[Cu(S_2O_3)_2] + 2NaNO_3$$

$$Na_2[Cu(S_2O_3)_2] + H_2O \rightarrow CuS \downarrow + H_2SO_4 + Na_2SO_4$$

The product (copper sulphide nanoparticles) was thus successfully synthesised by using copper nitrate and sodium thiosulphate in the previously mentioned molar concentration ratio of 1:2 in the presence of CTAB as a surfactant.

5.4 DESIGNING OF SETUP IN THE LABORATORY

A setup was designed in the Interfaces and Nanomaterials laboratory to determine the application of synthesised nanoparticles in solar heating of water. A metal halide lamp was used which emits rays in the near-infrared or NIR region since solar rays are not available throughout the day. The use metal halide lamp also makes the use of setup feasible for its use for experimental purposes inside the laboratory. The light rays from the lamp were focused on the capillary tube by means of a cuboidal reflector at the top of the capillary tube and a parabolic reflector at the bottom of the capillary tube so that the capillary is illuminated from top as well as from bottom.

For the purpose of heat exchanger, a copper tube was coiled and placed in a plastic beaker of 500ml volume containing water which is to be heated by the circulating nanoparticles in the designed setup

According to the literature (since the setup was designed before the experimental work), the residence time of the nanoparticles in the capillary tube was approximated at t=5 secs.

The outer diameter of the capillary used in the design = 1.3 cm
the inner diameter of the capillary used in the design = 1.1 cm

The length of the capillary is 12.5 cm.

Using the formula of $Vp = \pi(D^2/4)v$, where Vp is the volumetric flowrate of the nanoparticles in the capillary, D is the inner diameter of the capillary tube, and v is the velocity of nanoparticles at which they are circulated in the setup.

On the basis of above formula, the flowrate was calculated for different rpm and the volumetric flowrate was kept in the range of 2 ml/s – 6 ml/s. Thus the rpm of the pump was set according to the desired flowrate.

For such a small flowrate, a peristaltic pump was used to pump the nanoparticles solution from the beaker through the capillary tube and the coiled tube was used which acts as heat exchanger to enable heat transfer from the nanoparticles solution to the water to be heated. Temperature sensors have been used to read the temperature of the solutions.

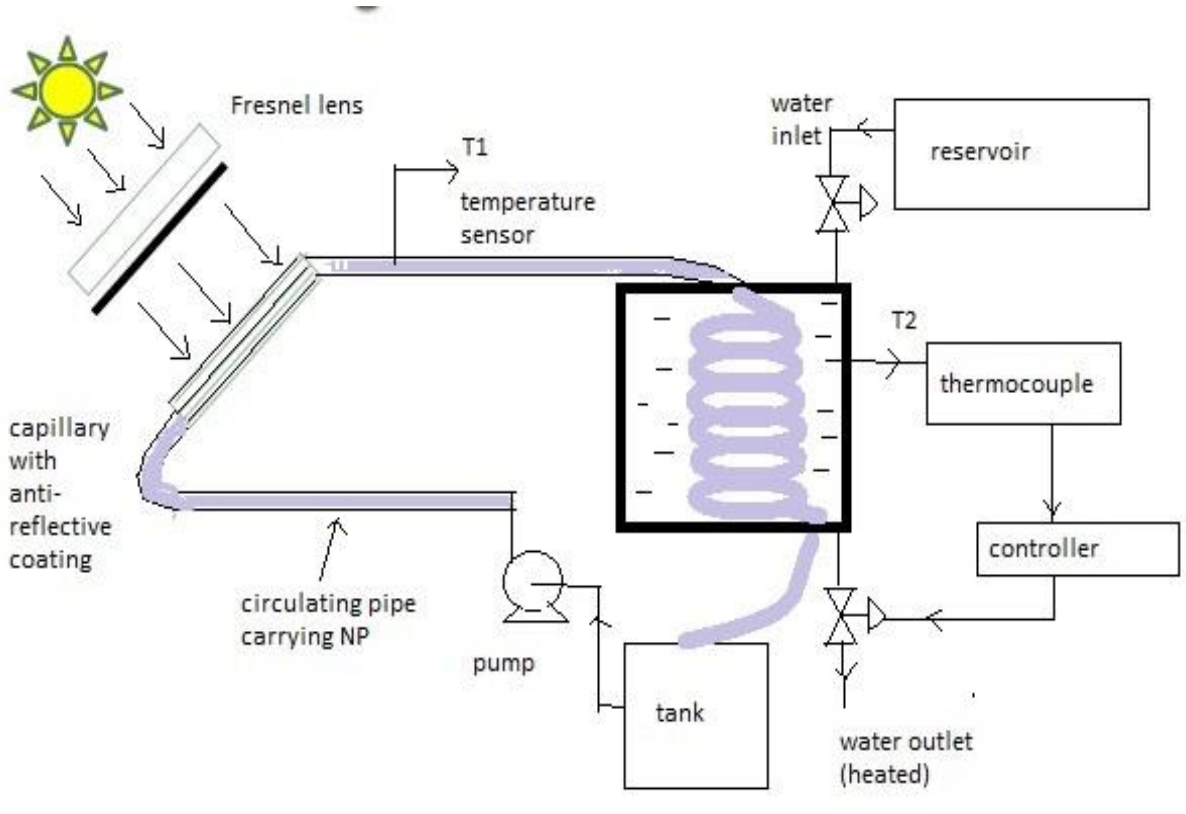

Figure 5.2: Setup layout or prototype

Figure 5.3: Setup designed in the laboratory

CHAPTER 6

RESULTS AND DISCUSSION

6. RESULTS AND DISCUSSION

6.1 OPTICAL PROPERTY

The optical property of the synthesised nanoparticles was analysed in Shimadzu UV-3600, UV-Vis-NIR spectrophotometer. In the presence of CTAB as a surfactant, the particles were not agglomerated, and a stable suspension was obtained. The data obtained from the UV-Vis-NIR spectrophotometer was used to plot a graph. The graph was plotted using the software OriginPro and the following plot was obtained for CuS nanoparticles prepared in the presence of CTAB with precursor molar ratio of 1:2 [$Cu(NO_3)_2$: $Na_2S_2O_3$] being used:

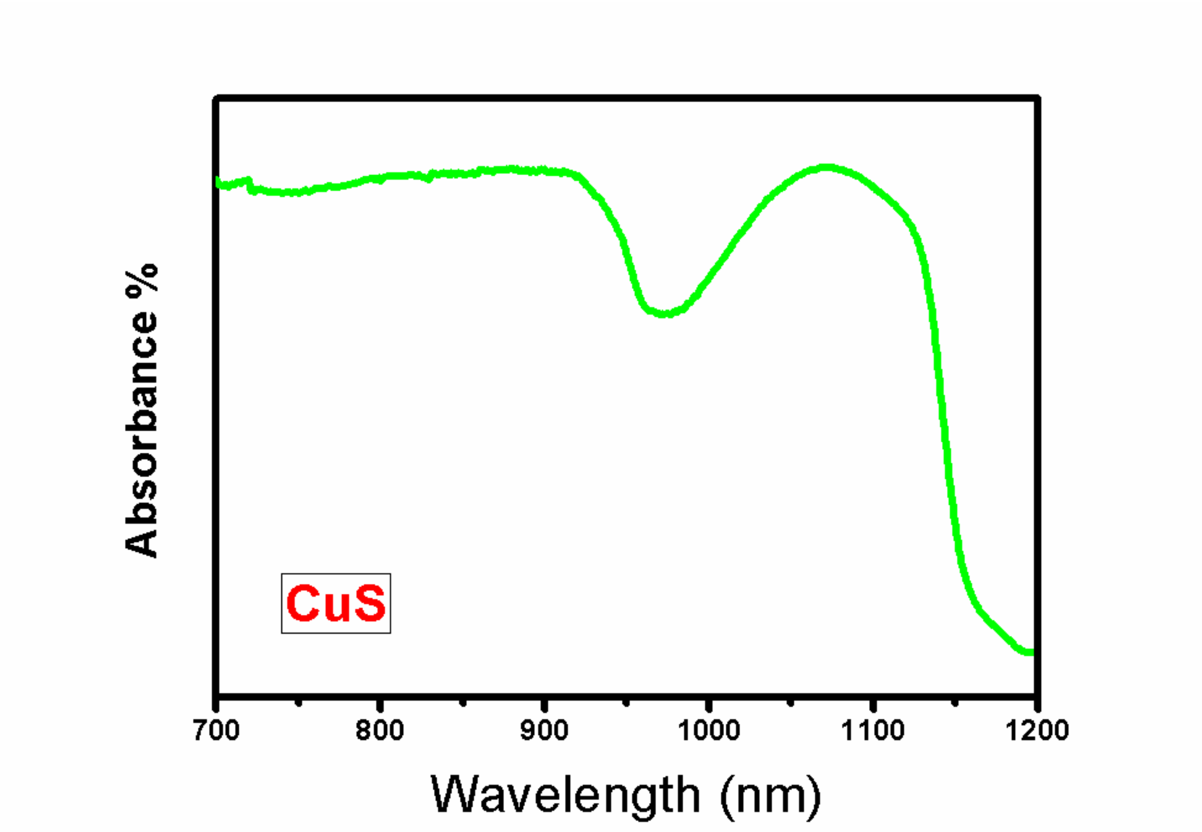

Figure 6.1: The plot obtained before the centrifuge of the nanoparticles solution

A broad peak was observed in the region of 1000nm-1150nm, which lies in the NIR region (750nm-1400nm)

This shows that the nanoparticles synthesised exhibit the required optical properties. This also encourages us to proceed further with the experimentation work as the synthesised particle seems to have the optical property required for solar heating of water using the nanoparticles.

The CuS nanoparticles solution prepared in the presence of CTAB with precursor molar ratio of 1:2 [$Cu(NO_3)_2$: $Na_2S_2O_3$] was further centrifuged and then washed with water to obtain the nanoparticles solution after the removal of the excess ions or surfactant present in the form of supernatant from the nanoparticles solution. The precipitate obtained was further analysed in the UV-Vis-NIR spectrophotometer. The data obtained from UV-Vis-NIR spectrophotometer was used to plot a graph. The graph was plotted using the software OriginPro, and the following plot was obtained after the synthesised product was centrifuged and washed:

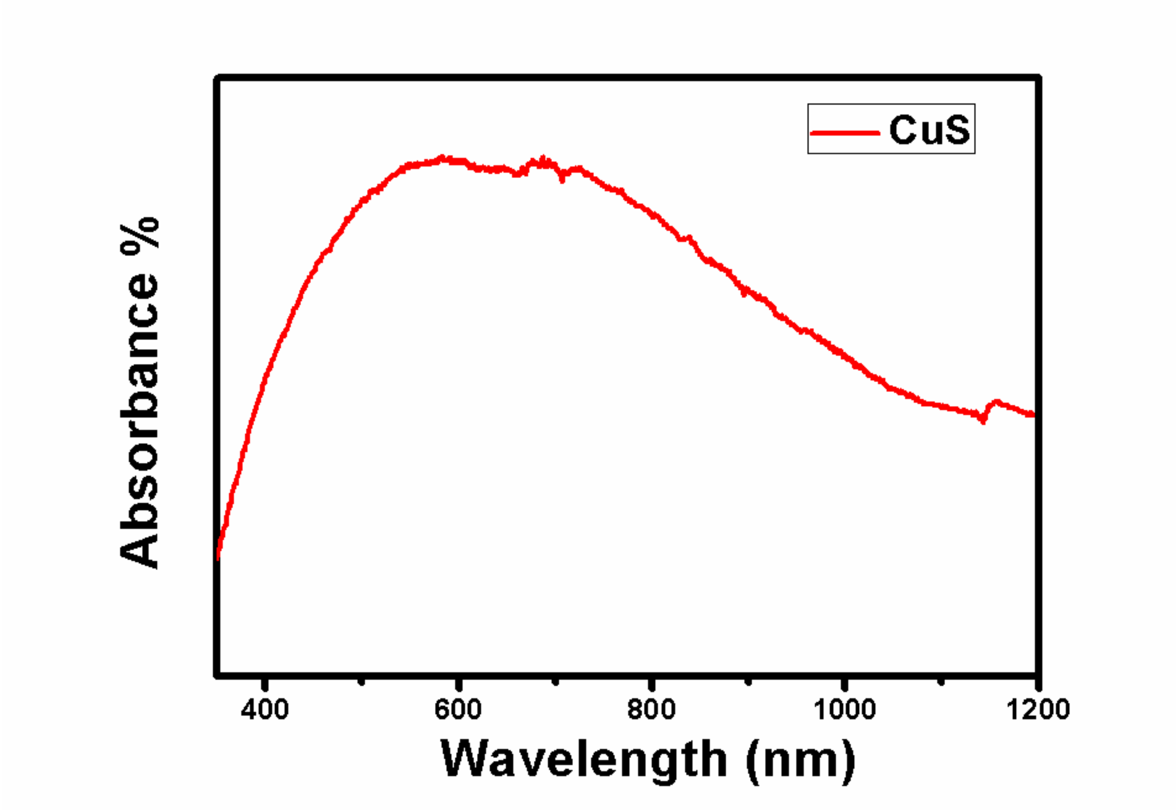

Figure 6.2: The plot obtained after the centrifuge of the nanoparticles solution

A broad peak was obtained from the graph in the region of 500nm-800nm, which lies partly in the visible range and partly in the NIR range.

Tauc plot is a method that is widely used to obtain band gap. After the absorbance % vs. wavelength plot had been obtained, the data used to obtain the Tauc plot. Using the Kubelka Munk function, $(ahv)^{1/2}$ vs (hv) graph was plotted, where a is the absorbance, h is the Planck's constant and v is the frequency of the wave which can be also written as v = c/ (wavelength). Thus, for the absorbance and wavelength data, the following plot was obtained in excel sheet by plotting $(ahv)^{1/2}$ in the y-axis and (hv) in the x-axis.

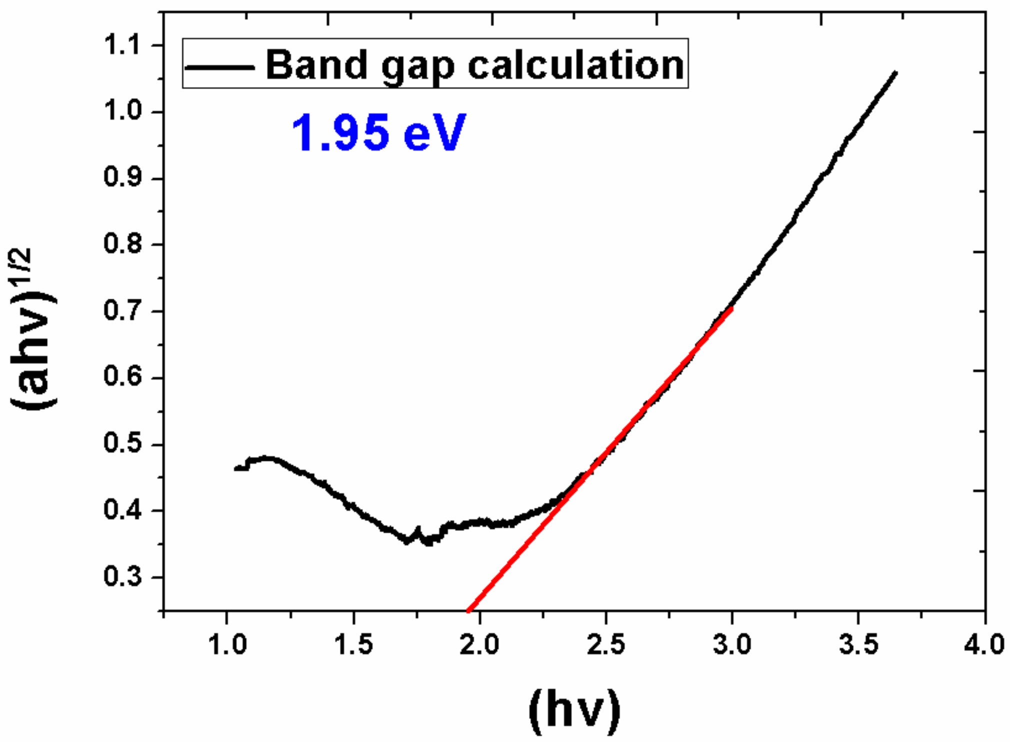

Figure 6.3: The plot for band gap

To obtain the band gap from the plot, a line was drawn as tangent at the point of inflection in the graph as shown in the above figure and the band gap was found at the intersection of the tangent and x-axis to be 1.95 eV. From the literature, it was seen that the band gap of CuS was found to be in the range of 1.68eV-1.75eV which is close to the value obtained by the synthesis of the CuS nanoparticle in the laboratory.

It was seen that a peak was obtained in the NIR region for the copper sulphide synthesised obtained before the centrifuge of the nanoparticles solution as well as obtained after the centrifuge of the nanoparticles solution.

The band gap of copper sulfide promises that it has potential applications in the field of photovoltaics and solar heating.

6.2 PARTICLE SIZE

The Malvern zeta sizer was used for dynamic light scattering analysis for the purpose of determining the size distribution of nanoparticles in the suspension. The data obtained from the Dynamic Light Scattering (DLS) analysis was tabulated and the intensity vs. size graph was plotted for the 1st run below.

The following graph was obtained:

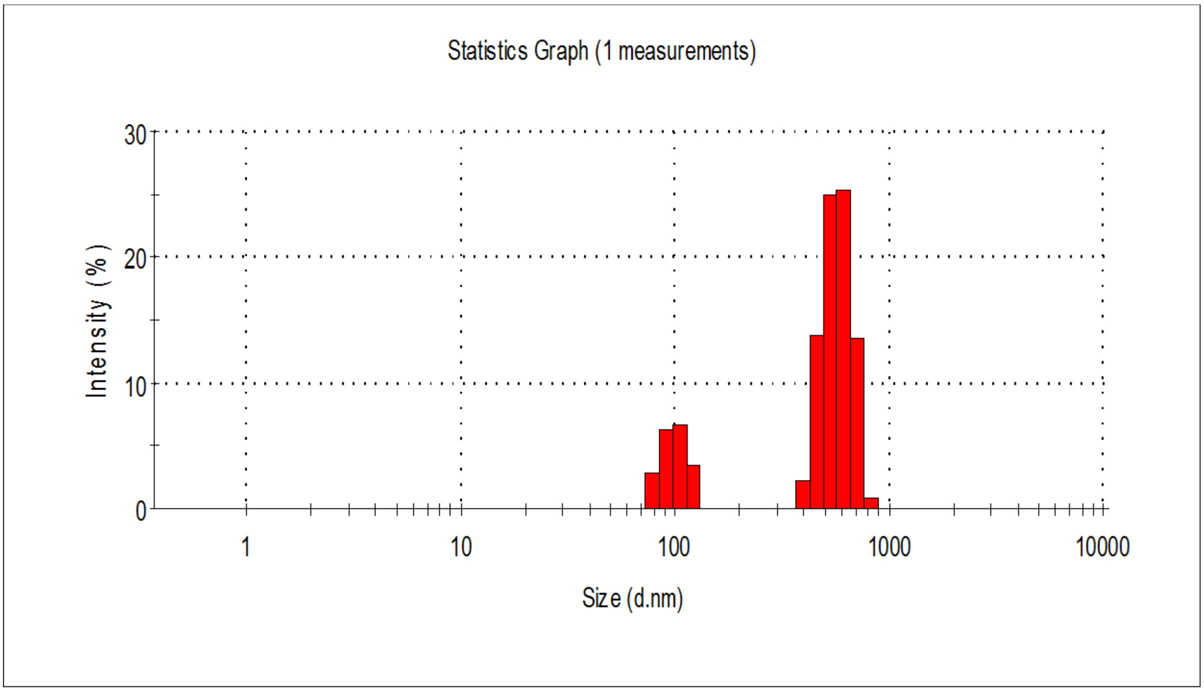

Figure 6.4: The bar graph of intensity vs. size for 1st run

Sample Name:	Cus size 1		
SOP Name:	Sulphur.sop		
File Name:	rahul.dts	**Dispersant Name:**	Water
Record Number:	49	**Dispersant RI:**	1.330
Material RI:	1.50	**Viscosity (cP):**	0.8872
Material Absorbtion:	0.010	**Measurement Date and Time:**	Thursday, December 13, 2007

Temperature (°C):	25.0	**Duration Used (s):**	80
Count Rate (kcps):	139.6	**Measurement Position (mm):**	4.65
Cell Description:	Disposable sizing cuvette	**Attenuator:**	7

			Size (d.nm):	**% Intensity**	**Width (d.nm):**
Z-Average (d.nm):	1251	**Peak 1:**	574.6	80.9	89.93
PdI:	0.834	**Peak 2:**	100.0	19.1	13.87
Intercept:	0.933	**Peak 3:**	0.000	0.0	0.000
Result quality :	**Refer to quality report**				

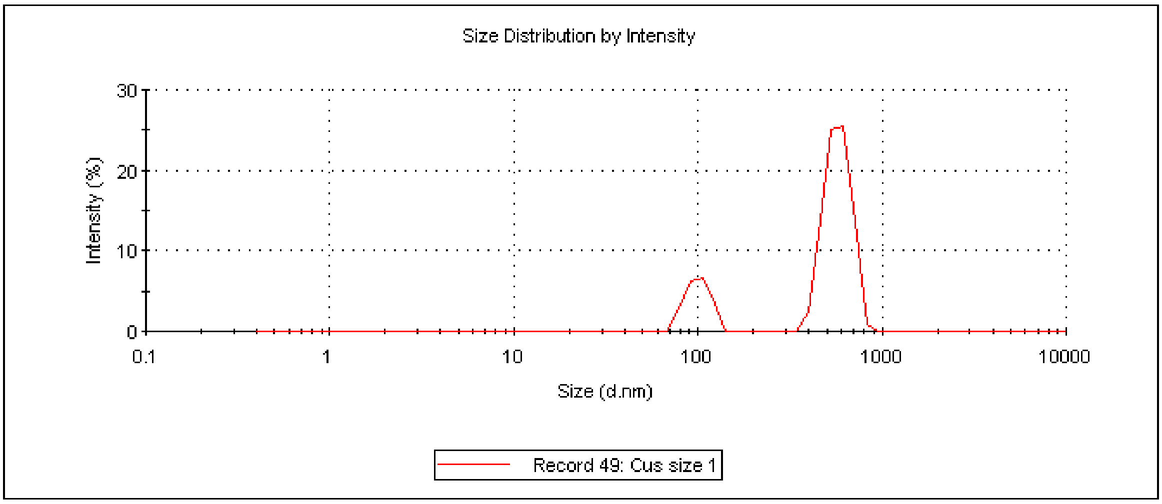

Figure 6.5: The graph of intensity vs. size for 1st run

From the graph, two peaks of particle size were found:

a) First peak was obtained at 100 nm

b) Second peak was obtained at 574.6 nm

The dynamic light scattering analysis was done for second time to obtain more precise values. The data obtained from the Dynamic Light Scattering (DLS) analysis was tabulated and the intensity vs. size graph was plotted for the 1st run below

The following graph was obtained:

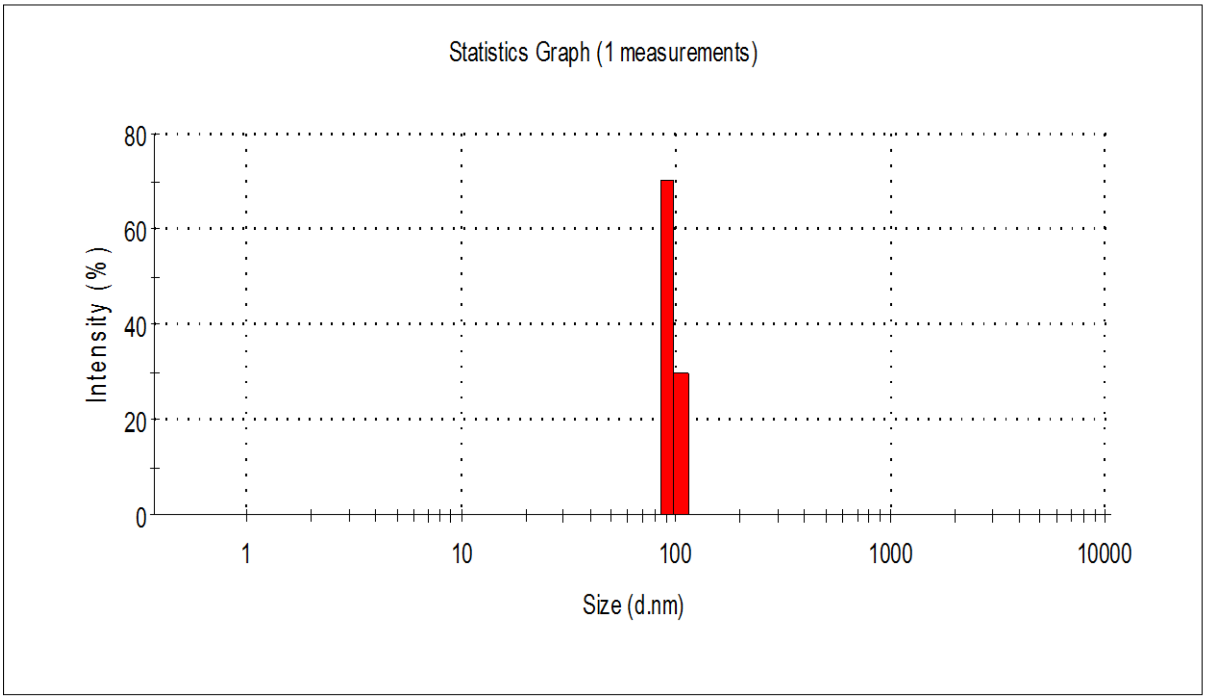

Figure 6.6: The bar graph of intensity vs. size for 2nd run

Sample Name:	Cus size 1		
SOP Name:	Sulphur.sop		
File Name:	rahul.dts	**Dispersant Name:**	Water
Record Number:	51	**Dispersant RI:**	1.330
Material RI:	1.50	**Viscosity (cP):**	0.8872
Material Absorbtion:	0.010	**Measurement Date and Time:**	Thursday, December 13, 2007

Temperature (°C):	25.0	**Duration Used (s):**	80
Count Rate (kcps):	149.4	**Measurement Position (mm):**	4.65
Cell Description:	Disposable sizing cuvette	**Attenuator:**	8

			Size (d.nm):	**% Intensity**	**Width (d.nm):**
Z-Average (d.nm):	1597	**Peak 1:**	95.58	100.0	6.599
PdI:	1.000	**Peak 2:**	0.000	0.0	0.000
Intercept:	1.26	**Peak 3:**	0.000	0.0	0.000
Result quality :	**Refer to quality report**				

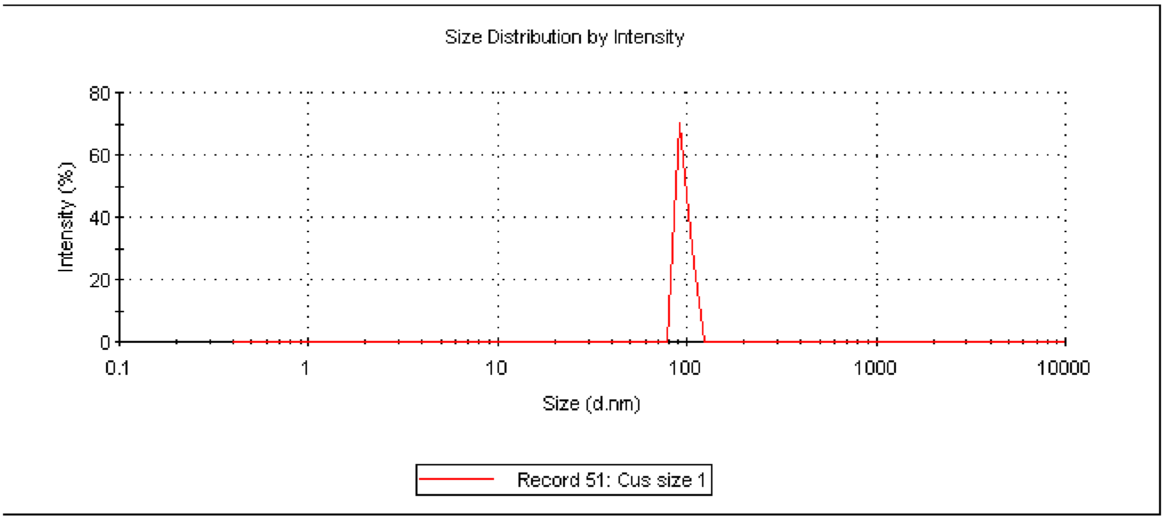

Figure 6.7: The graph of intensity vs. size for 2nd run

From the graph, the peak of particle size was found to be 95.58 nm

6.3 ZETA POTENTIAL

The Malvern zeta sizer was used for zeta potential analysis

Sample Name:	cus 1		
SOP Name:	TiO2 ZETA.sop		
File Name:	rahul.dts	Dispersant Name:	Water
Record Number:	48	Dispersant RI:	1.330
Date and Time:	Thursday, December 13, 2007 1:05:41 AM	Viscosity (cP):	0.8872
		Dispersant Dielectric Constant:	78.5

Temperature (°C):	25.0	Zeta Runs:	12
Count Rate (kcps):	69.8	Measurement Position (mm):	2.00
Cell Description:	Clear disposable zeta cell	Attenuator:	7

			Mean (mV)	Area (%)	Width (mV)
Zeta Potential (mV):	16.0	Peak 1:	16.0	100.0	4.07
Zeta Deviation (mV):	4.07	Peak 2:	0.00	0.0	0.00
Conductivity (mS/cm):	0.214	Peak 3:	0.00	0.0	0.00

Result quality : Good

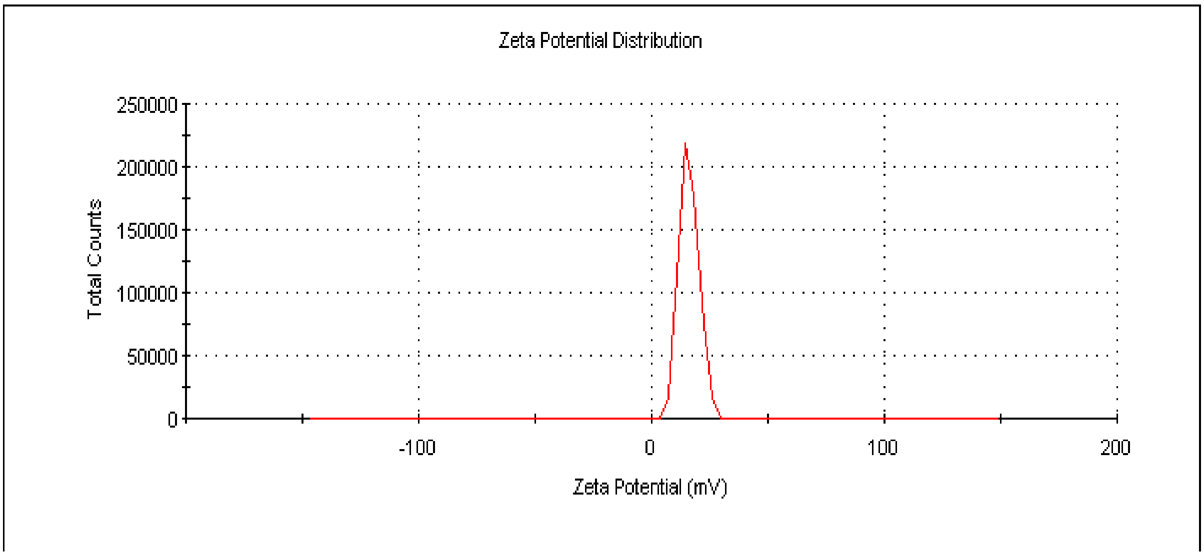

Figure 6.8: The zeta potential distribution graph

The zeta potential was found to be 16 mV. The positive charge found on the surface of nanomaterials shows that the solution obtained was a stable suspension.

6.4 STRUCTURAL PROPERTIES

The nanoparticle solution was sent for x-ray diffraction analysis

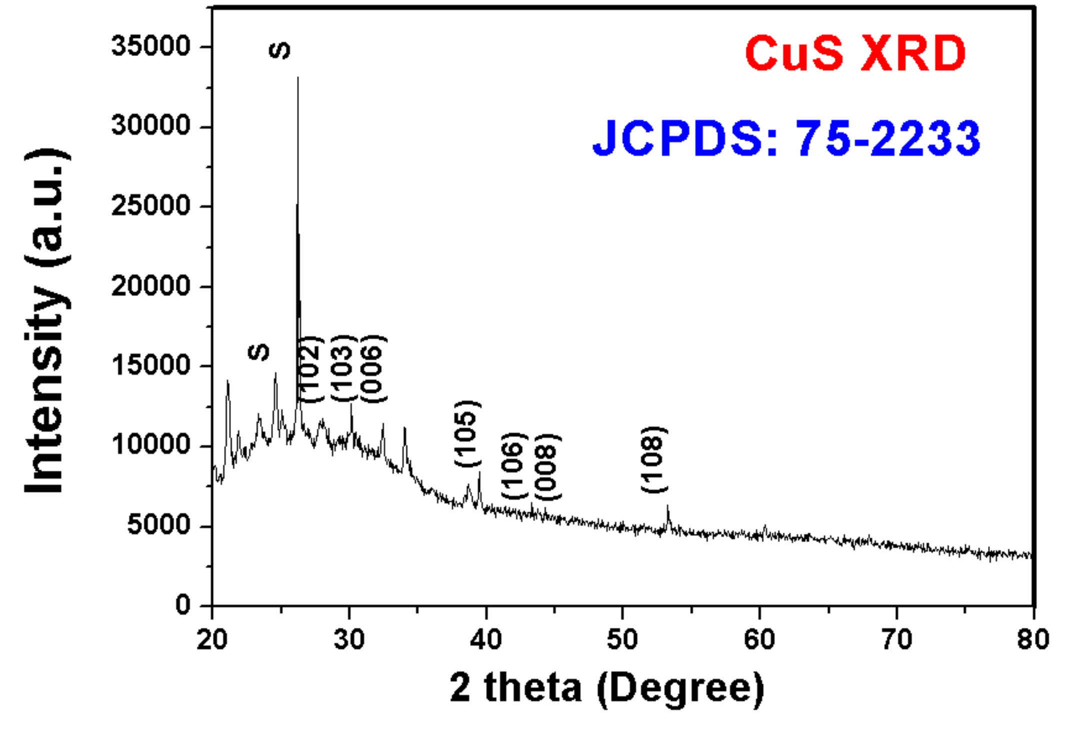

Figure 6.9: The graph of intensity vs. (2θ) plotted from data obtained from XRD analysis

The peaks obtained from the XRD patterns of the product obtained with a $[Cu(NO_3)_2{:}Na_2S_2O_3]$ = 1 : 2 molar ratio were found to be similar and well-matched to pure hexagonal CuS [JCPDS card No. 75-2233]. From those peaks, it was found that CuS particles were present in the solution, thus confirming the formation of copper sulphide nanoparticles.

However, it was also seen that along with copper sulphide nanoparticles, peaks of sulphur particles were obtained near the value of $2\theta = 25^o$, thereby exhibiting that orthorhombic sulphur particles were also formed during the synthesis. These sulphur particles remained suspended in the nanoparticles solution.

6.5 HEATING OF WATER

Since the copper sulphide nanoparticles exhibited desired optical properties and structural properties, the material was used in the setup. The copper sulphide nanoparticles solution was circulated through the capillary using peristaltic pump. The rate of circulation was determined by setting the rpm of the pump at the value of 7. The metal halide lamp was used to illuminate the thin capillary tube with the intensity of light irradiated in the NIR region so that the nanoparticles can absorb the light energy and heat the nanoparticles solution.

The heated nanoparticles solution was circulated through the copper coil so that heat can be transferred from the heated nanoparticles solution to the water kept in the beaker surrounding the copper coils. The system was left for an hour to observe the rise in temperature of the water to be heated.

It was seen that there was a rise in temperature of the water which was to be heated. After running the setup for two hours, a temperature rise of 3^oC was observed in that time duration showing that the nanoparticles can be utilised for solar heating of water.

The system was left undisturbed for another 1 hour, and it was found that the temperature rise of 7^oC was achieved in the total time duration.

For further comparison, two beakers were kept under the metal halide lamp, one beaker contained water without nanoparticles added to it, and the other contained nanoparticles solution. It was seen that after 1 hour, the beaker containing nanoparticles solution had an increase in temperature of 5^oC, whereas the beaker containing water without nanoparticles solution had an increase in temperature of 2^oC.

CHAPTER 7

CONCLUSIONS

7. CONCLUSIONS

In the project carried out, the particles were synthesised using the wet chemical method. Copper sulphide nanoparticles were prepared in aqueous media in the presence of surfactant by taking copper nitrate and sodium thiosulphate in the molar concentration ratio of 1:2. The synthesised material was then characterised for its optical property by using the UV-Vis-NIR Spectrophotometer, and the CuS nanoparticles showed absorbance in the NIR region which makes it suitable for utilisation in the solar heating of water. The band gap of the copper sulphide nanoparticles was calculated to be 1.95 eV. The dynamic light scattering analysis or DLS was performed to obtain the particle size, and it was found that the nanoparticles were in the desirable size range. The zeta potential was found to be 16mV which shows that a stable nanoparticles solution was formed. X-ray diffraction analysis of the material was performed which confirmed the formation of CuS nanoparticles, along with the formation of sulphur particles. After the characterisation and analysis techniques, the material was used to determine the solar heating of water by circulating the nanoparticles in the setup made for the purpose of determining the heating of water. The increase in temperature showed that the nanomaterial synthesised can be utilised for solar heating of water.

REFERENCES

7 REFERENCES

1) Nanoparticles before Nanotechnology, nanowiki.info, ebook series #3, Barcelona, 2013.
2) Wilson, M., Kannangara, K., Smith, G., Simmons, M., Raguse, B.; Nanotechnology: basic science and emerging technologies. Chapman & Hall/CRC. New York. 2002.
3) He, C., Zhao, N., Shi, C., Du, X., Li, J., Cui, L.; A practical method for the production of the hollow carbon onion particle; Journal of Alloys and Compounds. 2006, 425, 329 – 333.
4) Hogan, N. J., Urban, A. S., Orzoco, C. A., Pimpinelli, A., Nordlander, P., Halas, Naomi J; Nanoparticles Heat through Light Localization. Nano letters. 2014. 14, 4640-4645
5) Otanicar, T. P.; Phelan, P. E.; Golden, J. S. Optical Properties of Liquids for Direct Absorption Solar Thermal Energy Systems. Solar Energy 2009, 83, 969–977.
6) Otanicar, T. P.; Phelan, P. E.; Prasher, R. S.; Rosengarten, G.; Taylor, R. A. Nanofluid-Based Direct Absorption Solar Collector. J. Renewable Sustainable Energy 2010, 033102.
7) Neumann, O., Urban, A. S., Jared, D., Lal, S., Nordlander, P., Halas, Naomi J.; Solar Vapour Generation Enabled by Nanoparticles. ACS Nano. 2012, 7, 42-49.
8) Neumann, O., Feronti, C., Neumann, A. D., Dong, A., Schell, K., Lu, B., Kim, E., Quinn, M., Thompson, H., Grady, N., Nordlander, P., Oden, M., Halas, Naomi J.; Compact solar autoclave based on steam generation using broadband light-harvesting nanoparticles. PNAS. 2013, 110, 11677–11681.
9) Polman, Albert; Solar steam nanobubbles. ACS Nano. 2013, 7, 15–18.
10) Solanki, Jignasa N., Sengupta, R., Murthy, Z.V.P.; Synthesis of copper sulphide and copper nanoparticles with microemulsion method. Solid State Sciences. 2010, 12, 1560-1566
11) Li, Y., Lu, W., Huang, Q., Huang, M., Li, C., Chen, W., Copper sulfide nanoparticles for photothermal ablation of tumor cells. Nanomedicine. 2010, 5, 1161-1171.
12) Kundu, J. and Pradhan, D.; Influence of precursor concentration, surfactant and temperature on the hydrothermal synthesis of CuS: structural, thermal and optical properties. New J. Chem., 2013, 37, 1470-1478.