SYNTHESIS AND CHARACTERIZATION OF GRAPHENE OXIDE BASED NANOFLUIDS & STUDY OF ITS THERMAL CONDUCTIVITY

SUMMARY OF THE DISSERTATION SUBMITTED FOR THE AWARD OF THE DEGREE OF

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by

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SYNTHESIS AND CHARACTERIZATION OF GRAPHENE OXIDE BASED NANOFLUIDS & STUDY OF ITS THERMAL CONDUCTIVITY

This M.Phil. Dissertation research work carried out on the **"SYNTHESIS AND CHARACTERIZATION OF GRAPHENE OXIDE BASED NANOFLUIDS & STUDY OF ITS THERMAL CONDUCTIVITY"** explains the enhanced thermal transport phenomena of graphene oxide based nanofluids. It also provides the strategies for further research work in the field of heat transfer applications. The thesis consists of four chapters. Summary of each chapter is given as under.

CHAPTER-1: INTRODUCTION

The first chapter is focused on the basic introduction of nanoscience and nanotechnology, nanomaterials, the effect of nanoscale on physical and chemical properties of bulk material, an outline for the representation of nanomaterial synthesis approach, and also describes the applications of nanotechnology in the modern world of science to make human life more comfortable. This chapter also includes the basic introduction of graphene- a parent form of all graphitic structures of carbon nanomaterial, along with a literature review of graphene oxide-based nanofluids for thermal management of microelectronics devices. Nanoscience is principally concerned with the study of the phenomena and the manipulation of materials on the length scale of atoms and molecules, and nanotechnology as the design, creation, and utilization of structures, devices, and systems by controlling shape and size at the nanoscale scale, conventionally in 1 to

100 nanometers. The critical aspect of molecular nanoscience is the design and assembly of well-defined molecular architectures, which laid a milestone in the way of possibilities for fundamental research and applications. Nanomaterials refer to substances that have at least one dimension in the order of nanometer scale. A DNA molecule is natural nano-sized objects having a diameter of 25 nm. The advancement of nanotechnology engineering begins with the invention of the Scanning tunneling microscope, in 1981 by IBM researchers Gerd Binning and Heinrich Rohrer, and they observe the properties of the material at the nanoscale. Unlike bulk solids, the features of nanomaterials are considerably different and unusual due to-

I. High surface to volume ratio

II. Quantum confinement

These factors will modify or improve properties such as reactivity due to the large surface area, bonding strength, and optoelectronic properties.

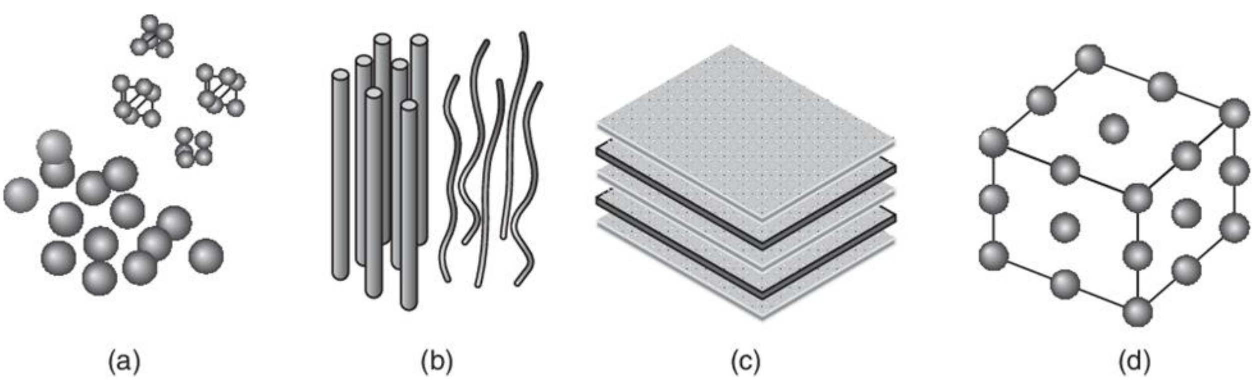

Figure 1: Dimensional classification of nanomaterials

Nanoparticle synthesis methods play a key role in preparing the products and determining the characteristics of synthesized nanomaterial. We can use metal oxides, ceramics, green leaves (for green synthesis) in the synthesis approaches. For the synthesis of nanoparticles, the following two approaches are used:

I. Top-down approach
II. Bottom-up approach

The top-down strategy leads to slicing or continuous flaking of massive matter to get nanosized particles while the bottom-up procedure assigns to the integration of material from the bottom i.e., the two or more atoms or molecules, and smaller particles or monomer are combined to constitute a material from atomic to the nanoscale.

GRAPHENE – BASIS OF CARBON NANOMATERIAL

Graphene, a 2-D form of a crystalline single-layered atomic layer of sp^2 covalent bonded carbon atoms that are arranged into a hexagonal crystal mesh. A graphene is a parent form of all graphitic structures of carbon nanomaterial. Graphene, an allotrope of carbon in which atoms are regulated in a hexagonal crystal lattice with an atomic bond length of 0.142 nm in between carbon atoms with an average span of 0.335 nm in between two graphene layers. Graphene has attracted notable attention in the current decade due to its novel physicochemical, mechanical, high thermal conductivity, and superior optical transparency and furthermore, graphene has inherent strength in the fabrication of optoelectronic devices like-photodetectors, light-emitting diodes, and also can be adopted for the fabrication of biosensors. When the graphene sheet is distorted then the geometry of distortion creates edges on the periphery of the graphene sheet and this edge configuration determines the distributions of electrons in graphene structure which are responsible for enhanced electronic (which includes tunable bandgap & high charge carrier mobility) and magnetic properties.

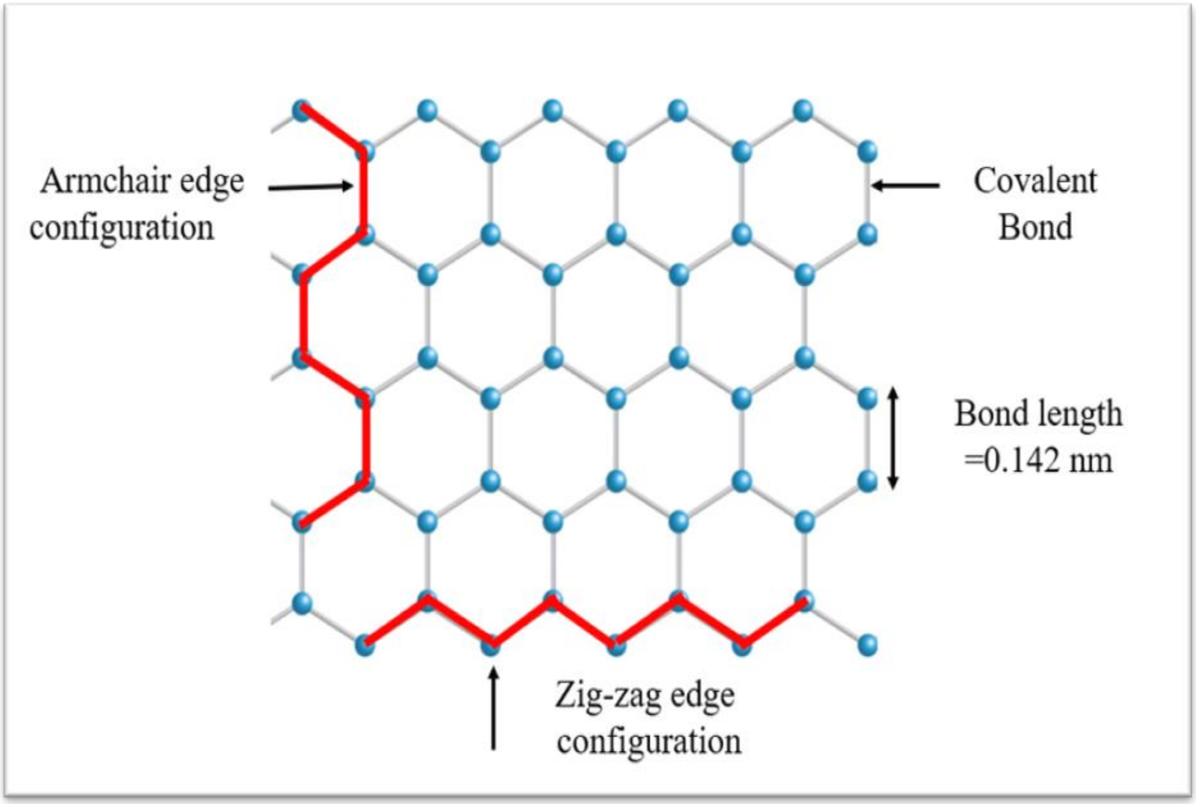

Figure 2: Atomic structure of graphene layer

Graphene is a zero-bandgap material because valance and conduction band in graphene, intersect each other at Dirac points where energy dispersion relations are linear concerning momentum. So, it cannot be used for nano-electronics applications because the energy band gap is crucial to control charge carrier density, which is efficient for switching device applications so it is necessary to turn an energy bandgap in graphene which is attained by the following manner.

I. Substrate – interaction
II. Quantum confinement
III. Chemical functionalization
IV. External electric field

Graphene is a zero-bandgap semimetal material because valance and conduction band in graphene converge to each other & derivatives of graphene possess extended-spectrum of attributes, due to its large relative surface area, optical transparency, biocompatibility, ballistic electron passage have procured excellent engagement in electronic, optoelectronics & biological health monitoring devices for the well-being of social culture.

Engineered Properties of Graphene Material

Engineered Properties	Experimental Value
Charge carrier mobility	20000 $cm^2\ V^{-1}\ S^{-1}$
Transparency	~99.7%
Bandgap	Zero
Thermal conductivity	4800-5300 $Wm^{-1}\ K^{-1}$
Specific Surface Area	2630 m^2 /g
Tensile strength	130 GPa
Young’s modulus	1 TPa

CHAPTER- 2: SYNTHESIS & CHARACTERIZATION TECHNIQUES

A nanoparticle is a fundamental component of nanomaterials and serves as a junction between the microscopic structures and nanomaterials. So, the synthesis of nanoparticles plays an important role, in their physicochemical, structural, and morphological attributes, which yields a variety of dimensions and chemical composition of nanoparticles. We have overviewed the current trend in the material synthesis that includes high temperature & pressure, vacuumed environment & gives better control of structure, phase purity, and craved dimension of nanomaterial. This chapter includes various physical and chemical nanomaterial synthesis methods. Among these physical synthesis methods are environment-friendly strategies because these methods do not involve hazardous chemicals. Chemical methods can be used for bulk scale production with uniform deposition of nanomaterial on a substrate surface. These methods provide high quality synthesized nanomaterial for a potential application.

The chemically integrated sample is investigated through multiple experimental techniques to explore the crystalline structure, surface morphology, specific surface area, and average pore size distribution. The XRD spectrum gives the average crystallite size of the sample. UV-visible spectroscopy unveils about optical absorbance of the sample. Raman spectroscopy is employed to study anatomical information of carbon-based nanomaterials. FTIR spectrum unveils oxygen-containing functional groups assigned to the surface of the sample. A field emission scanning electron microscope with EDS (FESEM) was inquired to perceive the surface morphology and chemical composition of the synthesized sample. The transmission electron microscope (TEM) micrographs were used for the interpretation of invaluable information on the inner structure of the sample.

CHAPTER- 3: SYNTHESIS AND CHARACTERIZATION OF GRAPHENE OXIDE BASED NANOFLUIDS & STUDY OF ITS THERMAL CONDUCTIVITY

Thermal management and cooling of electronic and photonic technologies are extremely vital for better operational execution and need innovative cooling technology. The conventional base fluids (water, ethylene glycol, transformer oil) which are employed for cooling purposes owns moderate heat transfer properties. Therefore, to increase the thermal conductivity of the base fluid, carbon-based nanomaterials were dispersed into the base fluid, consequently the enhanced thermal conductivity of resultant nanofluids. Nanofluid-a solid-liquid suspension of nanometer-sized particles less than 100 nm with large relative surface area, performs a crucial function in the energy and power transfer processes in multiple industries because nanofluid has an enhanced thermal conductive profile associated with the traditional base fluid.

Graphene oxide (GO), a heterogeneous oxidized product, concerned by chemical oxidation of graphite powder is a non-conductive hydrophilic material due to the carriage of ample oxygen functional groups. Due to the excellent intrinsic thermal conductivity, graphene oxide has potential applications as a heat transfer fluid. The chemical functionalization of graphene oxide alters the properties and become more adaptable for optoelectronics, biodevices, and as a drug-delivery material. The electronic energy bandgap of graphene oxide is tunable by manipulating the chemical composition and atomic structure and also bandgap is associated with oxygen functionalization and bandgap increases with the order of oxidation. The electronic structure and attributes of graphene oxide depend on the surface edges and the width of the nanosheet.

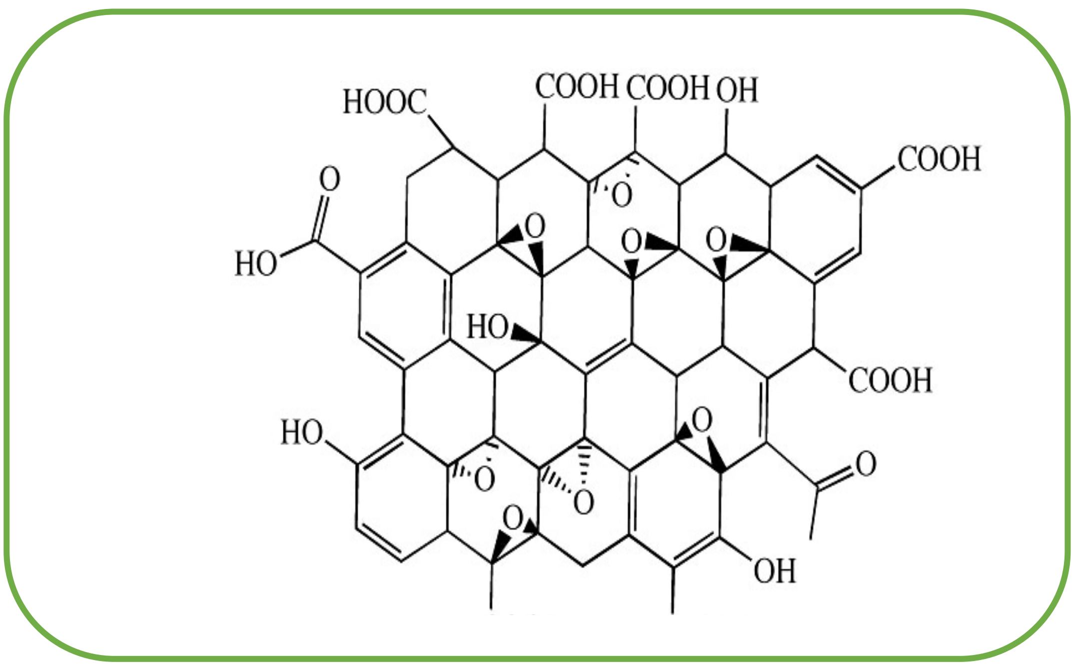

Figure 3: Structure of Graphene Oxide

The synthesis of GO was carried out by modified Hummer's method by using $KMnO_4$ as an oxidizing agent, and $NaNO_3$ in the carriage of H_2SO_4. Modified Hummer's method has great success over Brodie's method because it advances the reaction safety by replacing explosive ClO_2 with $KMnO_4$ and the use of $NaNO_3$ instead of fuming HNO_3 eliminates the accumulation of acid smoke throughout the reaction. The prepared Graphene oxide (GO) sample was investigated through multiple experimental techniques to explore the crystalline structure, surface morphology, surface area, and average pore size distribution.

X-ray diffraction spectrum analysis gives the average interplanar spacing, average crystallite size, and crystalline structure of nanomaterial. The X-ray diffraction pattern of incorporated graphene oxide (GO) shows a most intense peak at $2\theta = 11.43°$. The average crystallite size was found to 7.09 nm using the Scherer equation ($D_p = 0.94\lambda / \beta\cos\theta$) with stacking height ($L_c = 0.89\lambda / \beta\cos\theta$) of 4.75 nm and the crystalline layers are 8. Raman spectra were investigated to inquire about structural information of carbon-based nanomaterial. The disorder parameter I_D/I_G (i.e., intensity ratio of D band and G band) is 0.91, measures the presence of localized sp^3 imperfections within the hexagonal mesh. The UV- visible absorption spectrum of processed GO, shows an acute absorption peak at the 243 nm associated with (π-π*) transition of aromatic C-C bonds and the shoulder peak assigned to 332 nm (n-π*) transition of aromatic C=O bonds. GO have an optical band gap of 3.48 eV using Tauc's plot. FTIR spectrum validates the intercalation of oxygen-bearing groups upon chemical oxidation of graphite powder that is accountable for the chemical reaction. From the FESEM micrographs, it can be concluded that graphene oxide has multiple sheet-like structures that are stacked together and EDS elemental analysis reveals that there is 63.3

wt% of carbon content and 36.7 wt% oxygen content is present in the synthesized graphene oxide sample.

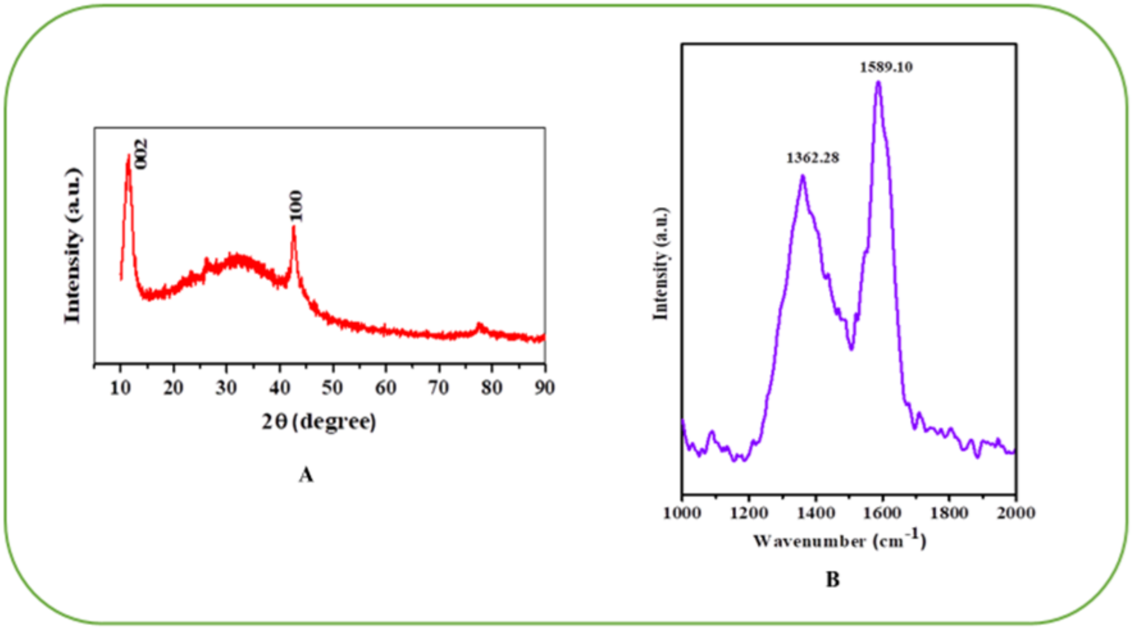

Figure 4: (A) XRD spectra, (B) Raman spectra of synthesized GO

BET surface analysis addresses the relative surface area of 72.65 m2/g and average pore diameter (4V/A) is 1.9054 nm and the material is microporous (<2 nm). BJH adsorption aggregate volume of pores was estimated by about 0.006254 cm^3/g in the pore diameter expanse of 17-3000 Å.

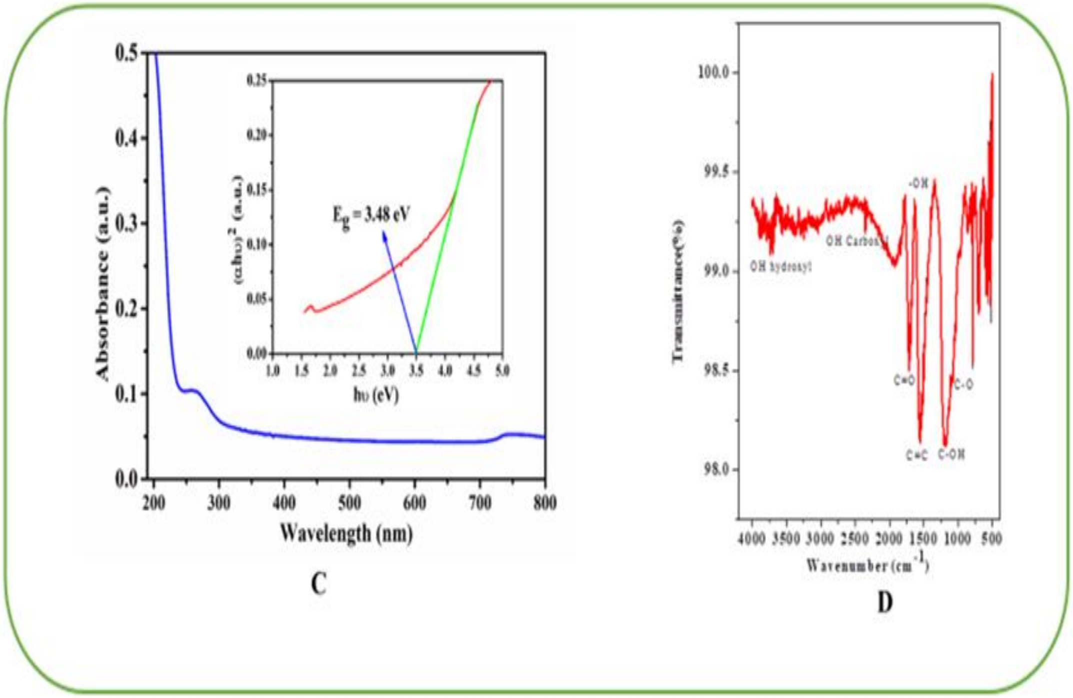

Figure 5: (C) UV-visible spectra, (D) FTIR spectra of synthesized GO

TEM-SAED micrographs of synthesized GO which depict the layer formation of the GO sheets which shows a non-uniform wrinkled structure with an average particle size below 15 nm. The micrographs show a semi-transparent multilayered structure of stacked GO.

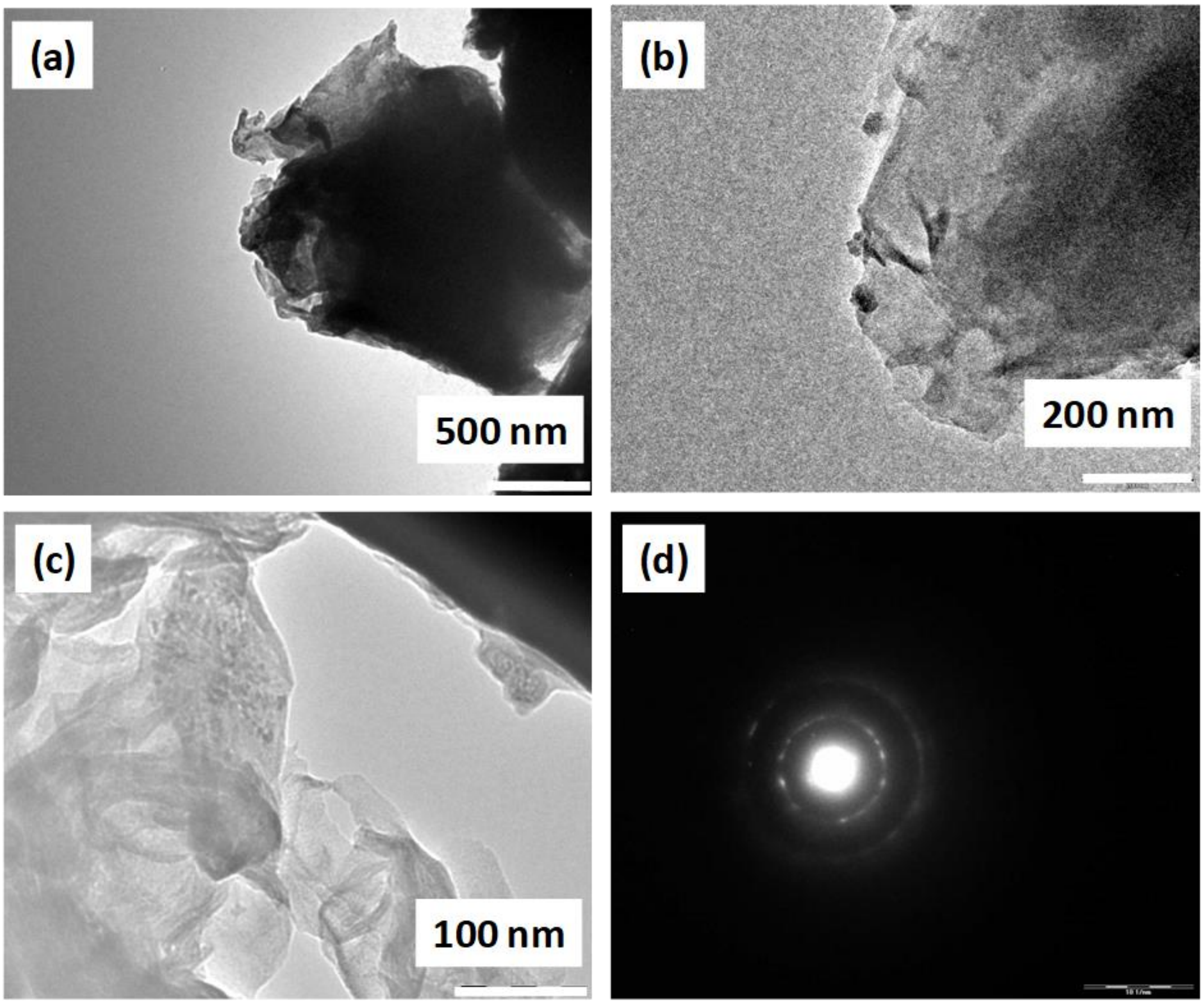

Figure 6: TEM micro images of graphene oxide

NANOFLUID PREPARATION

Nanofluid is a suspension of the solid-liquid phase of nanometer-sized particles dispersed in a base fluid (ethylene glycol) with high thermal stability. Graphene oxide-based nanofluids are prepared with varying mass concentrations (0.05, 0.15, and 0.25 wt%) are dispersed in ethylene glycol base fluid. The mixture was stirred so that it can get disperse well, and the mixture is subjected to sonication for 2 hours at 24°C by digital ultrasonic cleaner Axiva (40 kHz) with a power capacity of 80W obtain the well-dispersed uniform GO-EG based nanofluid sample.

Description of GO-EG based NFS

Name of sample	**Weight percentage (%)**	
	Graphene oxide	Ethylene glycol
GO-1	0.05	99.95
GO-2	0.15	99.85
GO-3	0.25	99.75

STABILITY OF NANAOFLUIDS

The experimental stability of GO-EG nanofluid was investigated by Dynamic light scattering (DLS) instrument since GO has good hydrophilic nature because of the intercalation of hydroxyl groups through the oxidation process.

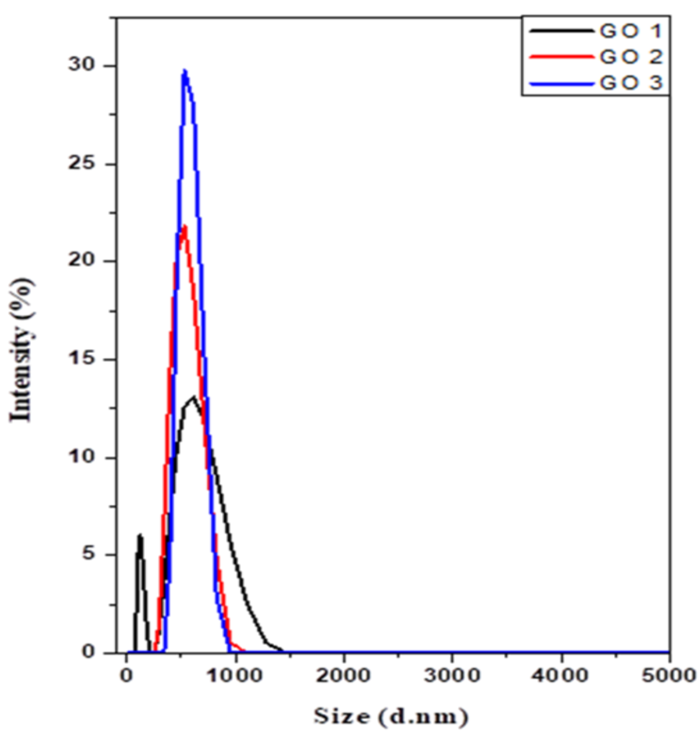

Figure 7: DLS particle size distribution of GO-EG NFS

UV-VISIBLE SPECTRA OF NANOFLUIDS

The UV-visible absorption spectrum of GO-EG nanofluid with different mass concentration was obtained to measure the colloidal stability of the nanofluid. There is a slight intensity change in the absorption spectrum of GO-EG nanofluid with increasing mass concentration of dispersed graphene oxide when spectra were recorded after 21 days.

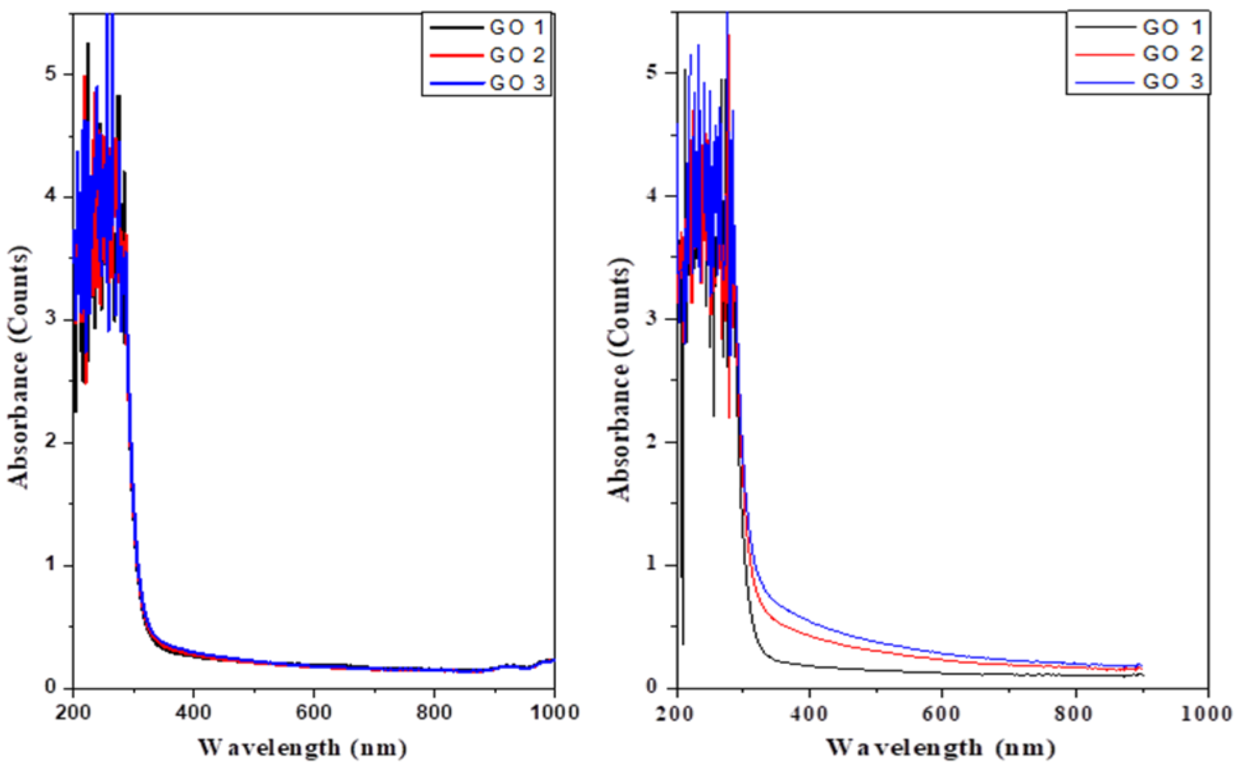

Figure 8: UV-visible spectra of nanofluids (a) initially, (b) after 21 days

THERMAL CONDUCTIVITY OF NANOFLUIDS

The dependence of thermal transport phenomena of GO-EG nanofluids was investigated with different mass concentrations (0.05%, 0.15%, and 0.25%). **Fig. 9** depicts the variation of thermal conductivity (TC) of different nanofluids with variable mass concentration. The thermal conductivity of nanofluids shows enhancement with increasing mass concentration in a non-linear manner and enhanced thermal conductivity is given by

TC enhancement % = (knf-ko)/ko * 100

where knf, ko is thermal conductivities of nanofluid and base fluid respectively. From **fig. 9** it can be observed that the thermal conductivity of nanofluid has a temperature-dependent relationship and the thermal conductivity will also increase with increasing mass concentration and sample no 3 shows maximum thermal conductivity enhancement with 36.72% for 10°C. So, with the enhanced thermal conductivity nanofluid can be used as a potential candidate for the cooling applications.

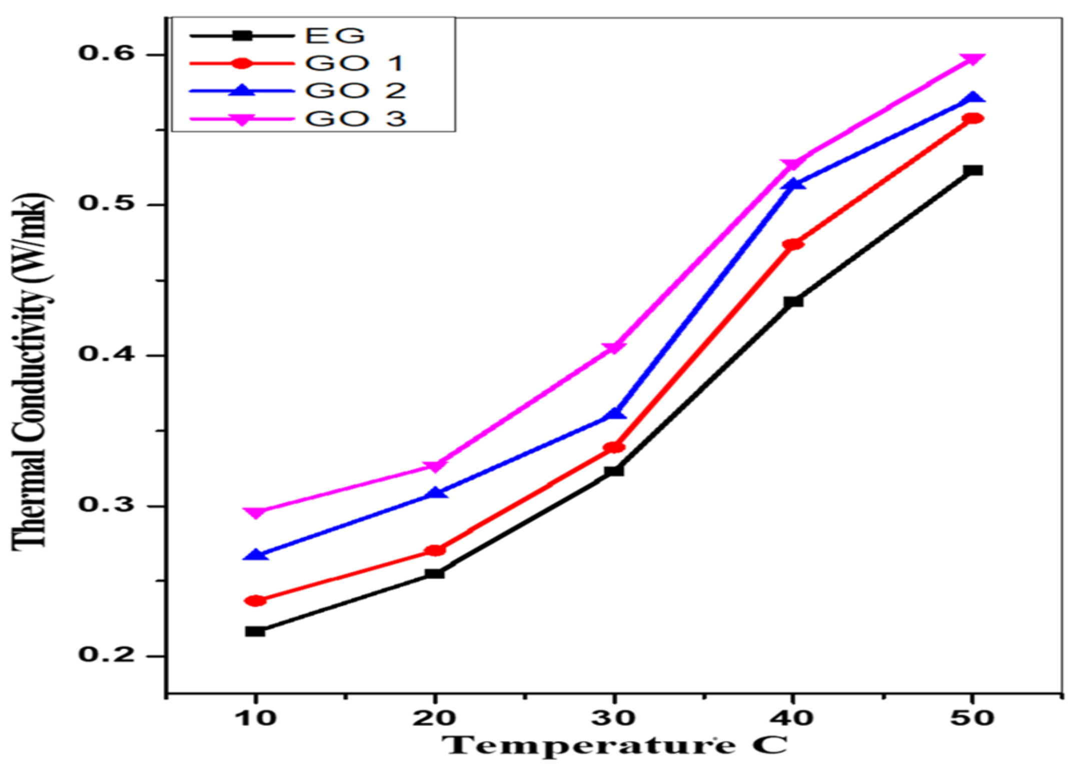

Figure 9: Thermal conductivity of nanofluids

CHAPTER– 4: CONCLUSION AND FUTURE SCOPE

This chapter focuses upon the conclusions drawn from the investigations carried out on the synthesis and characterization of graphene oxide based nanofluids & study of its thermal conductivity. It also provides the strategies for further research work in the field of heat transfer applications. The concluding remarks made and the recommendations suggested for future works are as follows

CONCLUSION

1. Graphene oxide was successfully synthesized by modified Hummer's method.
2. The surface morphology was examined by FESEM and TEM analysis which confirms the layered structure of graphene oxide.
3. The average crystallite size, stacking height, and the number of graphene layers is investigated by XRD spectra.
4. The order of oxidation of graphite flakes was confirmed by Raman spectroscopy and intercalation of oxygen-containing functional groups was examined by FTIR analysis.
5. The optical bandgap of graphene oxide was investigated by UV-visible spectroscopy and the obtained bandgap is 3.48 eV.
6. The relative surface area of graphene oxide was estimated by BET surface analysis and measured the area of 72.65 m^2/g.
7. The homogeneous and stable nanofluids were prepared with different mass concentrations and their thermal stability and thermal conductivity were measured.
8. An increase in temperature led to enhanced thermal conductivity and shows a semi-linear relationship in the range of 10 to 50°C.

9. Enhanced thermal conductivity is observed with increasing mass concentration in the base fluid.
10. Among all samples of nanofluids sample, 3 shows the highest thermal conductivity with increasing temperature.
11. The heat transfer profile of GO is a favorable combination of degree of oxidation, high aspect ratio, particle size and geometry, and low thermal interface resistance between graphene oxide sheets.

FUTURE SCOPE

1. Cooling efficiency can be increased by applying nanoparticles in host fluids
2. The addition of nanoparticles in fuels (nano fuels) can improve combustion in IC engines and reduce the emission of harmful gases during combustion.
3. The enhanced heat transfer profile of nanofluids makes them suitable for the next generation heat transfer fluids for microelectronics industries.
4. Nanofluids can be used as a targeted drug-delivery method.

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