



REGULAR ARTICLE

Thermal Conductivity and Dielectric Studies of Graphene Quantum Dots for Heat Transfer and Electrical Applications

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The synthesis of graphene quantum dots (GQDs) has been established in a two-step method from graphite powder using a hydrothermal reactor. The present research explores experimental analysis of the thermal conductivity of water-based GQDs nanofluids as a new generation of heat transfer medium. The thermal conductivity of water-based GQDs nanofluids has been measured at different temperatures (20 – 80 °C) and for different mass fractions (0 – 0.053 wt%). At low concentrations, the thermal conductivity of GQD/water nanofluid increases significantly in comparison with pure water. Thermal conductivity enhancement reaches up to 77.64% for the nanofluid containing 0.053 wt% of graphene quantum dots at 80°C and the volumetric heat capacity of the nanofluid decreases with an increase in mass fraction of GQDs, and increases with temperature. Hence, heat transfer of nanofluid based on GQDs shows better performance than base fluid and the impact of mass fraction in the water has been found at different temperatures. Additionally, dielectric properties of synthesized GQDs pellets have also been studied as a function of frequency in the range of 0.01 – 10⁵ Hz. Dielectric permittivity decreases with frequency due to dipole rotation and charge orientation, and electrical conductivity increases with frequency because of the highly conductive nature of GQDs.

Keywords: Synthesis, Graphene quantum dots, Thermal conductivity, Dielectric permittivity, Electrical conductivity.

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1. INTRODUCTION

Conventional heat transfer fluids like water, ethylene glycol (EG), and engine oil pose a significant challenge in high heat transfer applications due to their low thermal conductivity. This is especially important in mechanical equipment and engineering processes. Dispersing nanoparticles with sizes less than 100 nm in conventional fluids results in a novel fluid technology known as nanofluids. These fluid techniques have the potential to improve the stability and high thermal conductivity properties [1] while also reducing equipment size. Choi first used the term 'nanofluid' in 1995 [2]. Numerous studies have shown that there is an increasing interest in utilizing nanofluids to enhance their stability, heat conduction abilities, and thermophysical characteristics [3-4]. Many additives have been identified in the research communities including metals, metal oxides such as aluminum oxide (Al₂O₃) and titanium oxide (TiO₂), and carbon-based nanostructures such as graphene and carbon nanotubes. Metal and metal oxide-based nanoparticles tend to sediment in the base fluid, which is the main issue associated with them. However, carbon-based nanostructures provide a solution to this problem as they can be functionalized both covalently and non-covalently, making them transform from hydrophobic to hydrophilic structures. In recent times, researchers have

shown an increased interest in improving different carbon-based nanostructures such as graphene, graphene nanoplatelets, graphene oxide (GO), graphene quantum dots (GQDs), single, double, and multi-walled carbon nanotubes to prepare nanofluids [5-6]. Dielectric materials with high permittivity and low losses are utilized in capacitors to store additional electrical energy. GQDs offer significant potential for improving unique logical techniques for electronic applications due to their small size, which is typically less than 10 nm and can be less than 5 nm for certain applications [7, 8]. Graphene has been ascribed to highly optical, thermal, mechanical, and excellent electrical conductivity properties [8, 9]. Many characteristics of graphene have been wide applications in various areas such as supercapacitors, catalysis, electronic devices, flexible touch screens, sensors, energy storage, and energy conversion [10-15]. Concerning the excellent properties, current analysis has identified the graphene-based thermal conductivity and dielectric properties which could explore its application in the thermal and electrical field [8-11].

In this research work, GQDs have been synthesized by hydrothermal treatment methods using starting raw material graphite powders which were further oxidized to GO by the modified hummers' method. GQDs nanofluids were prepared at 0.013 wt%, 0.026 wt%, 0.039 wt%, and

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0.053 wt% mass fractions using distilled water. Thermal conductivity and volumetric heat capacity properties of each nanofluid sample were analyzed at various temperatures and mass fractions. Additionally, the dielectric properties of graphene quantum dot pellets, such as dielectric permittivity and electrical conductivity, were studied as a function of frequency for various thickness samples. The reported methodologies show the thermo-physical properties of the GQD/water-based nanofluids and conductivity applications of GQD nanoparticles.

2. MATERIALS AND EXPERIMENTAL

2.1 Synthesis of GQDs

The syntheses of GQDs were carried out by two-step modified hummers' and hydrothermal treatment methods as shown in the Fig. 1 [8, 10].

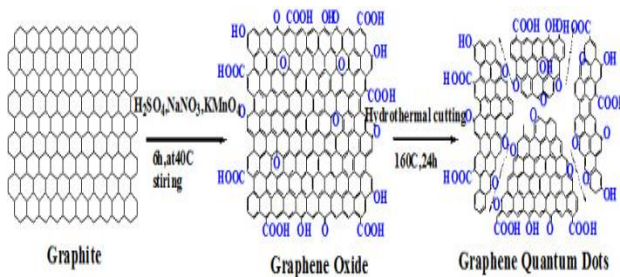


Fig. 1 – Synthesis reaction of Graphene Quantum Dots from Graphite powder

2.2 Preparation of GQDs/Water Nanofluids

GQDs were dispersed on base fluid distilled water with different mass fraction. The prepared nanofluids should be an agglomerate-free stable suspension without sedimentation of GQDs for long time [5]. GQDs were dispersed in distilled water through ultrasonic vibration for 30 minutes at various temperatures 25, 30, 40 and $50^\circ C$. The mass fraction concentration of nanofluids was maintained at 0.013, 0.026, 0.039 and 0.053 wt% for thermal conductivity studies.

2.3 Preparation of Graphene quantum dots Pellets

GQDs pellets of 10 mm diameter and 1, 2, 3, and 4 mm thickness were prepared from synthesized GQDs powder using Wabash hydraulic press and stainless steel die for dielectric studies.

2.4 Measurements

2.4.1. Thermal Conductivity Studies

The KD-2 Pro-thermal property analyzer (KD2, Decagon Devices, WA, USA) was used to conduct a thermal evaluation of GQDs/Water nanofluids using the transient hot-wire technique. The thermal conductivity of the nanofluids was measured using a long single-needle (KS-1) probe sensor (6 cm long, 0.13 cm diameter). The

volumetric heat capacity nanofluids were also measured using a dual-needle (SH-1) probe sensor (3 cm long, 0.13 cm diameter, 0.6 cm gap between the two needles). Before use, the analyzer was standardized with distilled water. The influence of mass fraction and temperature on thermal conductivity, and volumetric heat capacity of nanofluids have been studied using an isothermal bath.

2.4.2. Dielectric Studies

The dielectric properties of GQD pellets were investigated using a computer-operated Tester LCR metre, Hioki 3533, in the frequency range 10^{-2} to 10^5 Hz, with silver foil working as a blocking electrode. The dielectric studies have been examined as a function of frequency and temperature. The tested GQD samples were in cylindrical form with diameter of 10 mm and thickness of 1, 2, 3 and 4 mm. The AC conductivity (σ_{AC}) was calculated using dielectric data and the following relation:

$$\sigma_{AC} = \omega \epsilon_0 \epsilon' \tan \delta \tag{1}$$

Hence ω is $2\pi f$ (f is frequency), ϵ_0 is vacuum of permittivity and ϵ' is dielectric constant or dielectric permittivity

$$\epsilon' = C_p / C_0 \tag{2}$$

C_p is observed capacitance of the sample (GQDs), C_0 is the vacuum capacitance of the cell

$$C_0 = \epsilon_0 \cdot (A/d) \tag{3}$$

Here A – area of GQDs pellets and d – thickness of GQDs pellet and $\tan \delta$ is the measured dielectric loss tangent [7-8].

3. RESULT AND DISCUSSION

3.1 Thermal Conductivity of GQDs Nanofluids

KD-2 pro-thermal property analyzer has been used for the measurements of thermal conductivity, this technique is based on transient hot-wire method. The vessel is filled with the GQDs/water nanofluid sample and the probe is inserted in the middle of the vessel.

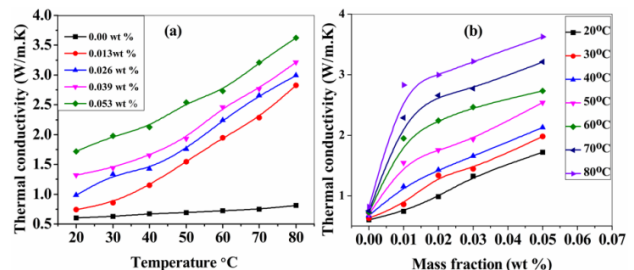


Fig. 2 – Thermal conductivity of GQDs/water nanofluids: (a) Effect of Temperatures and (b) Effect of mass fraction

Fig. 2 shows the variation in thermal conductivity of GQDs for different concentration of nanofluid (0 – 0.053 wt %) at different temperature (20 – $80^\circ C$).

The figure shows that thermal conductivity increases with increasing concentration of GQDs in nanofluid as well as increasing temperature from 0.743 W/m K to 2.827 W/m K at the concentration of 0.013 wt% and from 1.714 W/m K to 3.623 W/m K at 0.053 wt% concentrations.

Table 1 – Thermal conductivity enhancement (TCE) of GQDs/water nanofluid as a function of temperature

Temperature (°C)	TCE of GQDs/water nanofluid (0.013%)	TCE of GQDs/water nanofluid (0.053%)
20	19.24	65
30	26.25	68.15
40	41.80	68.39
50	55.15	72.76
60	63.04	73.83
70	67.16	76.63
80	71.34	77.64

Table 1 gives the enhancement percentage of the thermal conductivity of GQDs/water nanofluids as a function of temperature at 0.013 – 0.053 wt%. It can be observed that the enhancement of the thermal conductivity of the nanofluids depends on various factors, such as the Brownian motion, a solid-liquid interface layer, effect of nanoparticle clustering and the inherent nanoparticles of heat transfer [5, 16]. The mass fraction of nanofluids also affected thermal conductivity, for all of the nanofluids; a significant rise in thermal conductivity is observed when the mass fraction of GQDs increases. The maximum increase in the thermal conductivity coefficient related to water based GQD nanofluids at concentration of 0.053 wt% and at 80°C is it is 3.623 Wm⁻¹K⁻¹. Similarly, the thermal conductivity ratio of nanofluid is increased with the mass fraction of GQDs and reaches a maximum up to 77.64% at 80°C with 0.053 wt% have been observed (Table 2).

Table 2 – Thermal conductivity enhancement (TCE) of GQDs/water nanofluid as a function of mass fraction

Mass fraction (wt %)	TCE of GQDs/water nanofluid (%) with 20 °C	TCE of GQDs/water nanofluid (%) with 80 °C
Base Fluid (Water)	0	0
0.013	19.24	71.34
0.026	38.94	72.91
0.039	54.58	74.81
0.053	65	77.64

3.2 Volumetric Heat Capacity of GQDs Nanofluids

Volumetric heat capacity refers to how much heat is necessary to raise the temperature of one gramme of a substance by one degree Celsius. The heat capacity of the water based GQDs nanofluid for various mass fraction (0 – 0.053 wt %) and at different temperature (30 – 80 °C) is shown in Fig. 3.

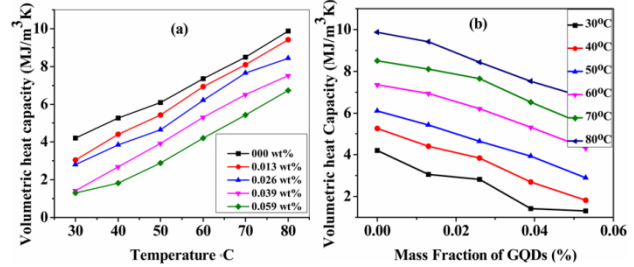


Fig. 3 – Volumetric heat capacity of GQDs/water nanofluid: (a) effect of temperatures, (b) effect of mass fraction

The effect of temperature on the heat capacity of water-based GQDs nanofluid is shown in Fig. 3(a). From the figure, it can be observed that heat capacity of the GQDs nanofluid is increasing with temperature. At higher temperature, the slope is much better, that means the heat capacity is greatly influenced. The effect of mass fraction on the heat capacity of the water based nanofluid is shown in Fig. 3(b). Figure shows that the volumetric heat capacity of the nanofluid decreases with an increase in GQDs concentration. Fig. 3 shows that the volumetric heat capacity decreases with a steeper slope for higher mass fractions. Physical interactions in the nanofluid environment are only responsible for the negative changes in volumetric heat capacity caused by higher GQDs concentration. The heat capacity is decreased up to 1.257 (MJ/m³K). As the number of GQDs in the base fluid increases a considerable fall in the heat capacity of the nanofluid is observed due to Brownian motion so the thermal energy is transported easily and less energy is required for excitation of the nanofluid.

3.3 Dielectric Permittivity of GQDs

Dielectric permittivity (ϵ') represents the degree of electrical polarization of a material. Fig. 4(a) and Fig. 4(b) shows the variation in dielectric permittivity of synthesized GQDs pellets as a function of frequency for various thicknesses (1 mm, 2 mm and 4 mm) and at different temperature 25, 50, 75, and 100 °C.

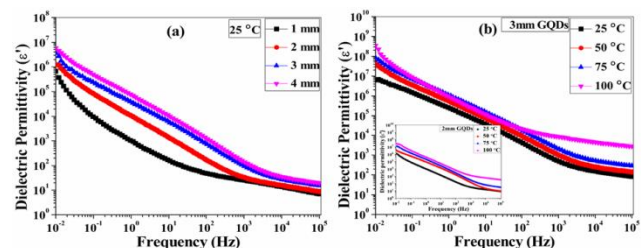


Fig. 4 – Dielectric permittivity of synthesized GQDs measured as (a) different thicknesses, (b) different temperatures

The dielectric permittivity of graphene quantum dots (GQDs) shows a continuous decrease as the applied frequency increases up to 10⁵ Hz. This decline is attributed to the reorientation of charges and alterations in the dipole moment of functional groups present on the GQDs in response to the changing frequency of the applied electric

field. At lower frequencies, there is more time for charges and dipoles to align, resulting in higher dielectric permittivity, whereas at higher frequencies, the limited time for orientation leads to a reduced dielectric permittivity [5, 8]. Dielectric permittivity also increases as temperature rises (Fig. 4(b)). This is due to GQDs' extremely capacitive and conductive properties, along with the positive temperature coefficient effect, the conductive particles within GQDs exhibit ferroelectric properties. These properties are related to higher dielectric permittivity at low frequencies and high temperatures.

3.4 Electrical Conductivity of GQDs

Electrical Conductivity (σ) measures the material ability to conduct electrical current. Fig. 5(a) and Fig. 5(b) show the variations in electrical conductivity of GQDs pellets with frequency for different thicknesses and at different temperature. The figure shows that the electrical conductivity of synthesized GQDs pellets increases continuously with increasing thickness as a function of frequency. It can be also seen that electrical conductivity of GQDs increases continuously with increases temperature (Fig. 5(b)), due to positive temperature co-efficient (PTC) effect as well as negative temperature co-efficient of resistance [8]. But with increasing temperature all the curves show only AC conductivity region and at higher frequency, beyond 10^4 Hz all curves merged together like dielectric permittivity. The rise in temperature generally leads to an increase in electrical conductivity due to the enhanced thermal activation of charge carriers [7-8, 17].

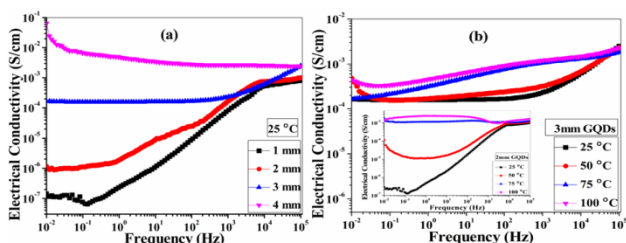


Fig. 5 – Electrical Conductivity of synthesized GQDs measured as (a) different thicknesses, (b) different temperatures

4. CONCLUSION

This research aimed to explore the thermal and electrical conductivity of graphene quantum dots (GQDs), focusing on the measurement of thermal conductivity in a GQDs/water nanofluids. The results revealed that the nanofluid exhibited higher thermal conductivity

compared to the base fluid (pure water). Additionally, a direct relationship was observed, indicating that the enhancement in thermal conductivity was proportional to the increase in the mass fraction of graphene quantum dots. This implies that as the concentration of GQDs in the nanofluid rises, so does its thermal conductivity. The study suggests the potential of GQDs in enhancing heat transfer properties in applications where improved thermal conductivity is desired. The maximum thermal conductivity enhancement reaches up to 77.64% for the nanofluid containing 0.053 wt% of GQDs at 80°C in water as base fluid. Thermal conductivity also depends on temperature and shows an increasing trend. Based on recent findings regarding the thermal conductivity and stability of GQDs/water nanofluids, can be used as a capable working fluid in heat transfer industrial applications. In addition to above, Dielectric properties of synthesized graphene quantum dots (GQDs) have been studied as function of frequency in the range between of 0.01 – 10^5 Hz. Dielectric permittivity increases with thickness up to 4 mm due to highly capacitive and conductive nature of GQDs. The decrease in dielectric permittivity with rising frequency is attributed to the rotation of dipoles and charge orientation. Conversely, an increase in temperature leads to a rise in dielectric permittivity, mainly due to the highly conductive nature of graphene quantum dots. Electrical conductivity of graphene quantum dots increases exponentially with frequency showing more AC conductivity and less DC conductivity. This behavior is attributed to the inherent conductivity of GQDs, stemming from the graphene structure, and the quantum effects that manifest at the nanoscale. The electrical conductivity of the synthesized GQDs also increased with thickness up to 4 mm, due to a decrease in resistivity. The electrical conductivity and dielectric permittivity of materials often increase with temperature due to the influence of thermal activation and positive temperature co-efficient impact on charge carriers. These results show that the synthesized GQDs can be used as a potential candidate for high dielectric base electrical applications; energy storage devices (fuel cells and solar cells as well as double-layer capacitors and batteries), super electronic device, capacitors, chemical sensors and heat transfer applications.

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Дослідження теплопровідності та діелектрики графенових квантових точок для теплопередачі та електричних застосувань

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Синтез графенових квантових точок (GQDs) був встановлений двоетапним методом з графітового порошку за допомогою гідротермального реактора. У цьому дослідженні досліджується експериментальний аналіз теплопровідності нанофлюїдів GQD на водній основі як середовища теплопередачі нового покоління. Теплопровідність нанофлюїдів GQD на водній основі вимірювалася при різних температурах (20–80 °C) і для різних масових часток (0–0,053 мас.%). При низьких концентраціях теплопровідність нанофлюїду GQD/вода значно збільшується порівняно з чистою водою. Підвищення теплопровідності досягає 77,64% для нанофлюїду, що містить 0,053 мас.% графенових квантових точок при 80°C, а об'ємна теплоємність нанофлюїду зменшується зі збільшенням масової частки GQD і збільшується з температурою. Таким чином, теплопередача нанорідини на основі GQD показує кращу продуктивність, ніж базова рідина, і вплив масової частки у воді було виявлено при різних температурах. Крім того, також були вивчені діелектричні властивості синтезованих гранул GQD як функція частоти в діапазоні 0,01 – 105 Гц. Діелектрична проникність зменшується з частотою через обертання диполя та орієнтацію заряду, а електрична провідність зростає з частотою через високу провідність GQD.

Ключові слова: Синтез, Графенові квантові точки, Теплопровідність, Діелектрична проникність, Електропровідність.