Transformer oils-based graphene quantum dots nanofluid as a new generation of highly conductive and stable coolant

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A B S T R A C T
Transformer oil-based graphene quantum dots (QGD) nanofluid with superior colloidal stability has great potentials as a new generation of high performance transformer oil. To this end, graphene quantum dots were initially synthesized with a novel and cost-effective exfoliation approach. To eliminate the acidity, a covalently-functionalization process was employed to change GQD to amine-treated graphene quantum dots (AGQD). The morphological analysis confirmed that the diameter and average height of the mono-layered AGQD were mostly in the range of 5–17 nm and ~1 nm, respectively. Transformer oil-based AGQD nanofluid at very low weight fraction has been shown experimentally to have substantially higher positive voltage breakdown, thermal conductivity, natural and forced heat transfer rate, and flash point levels compared to that of pure transformer oil. A comprehensive rheological and electrical analysis of the transformer oil-based AGQD nanofluid showed no significant enhancement in its viscosity compared to pure transformer oil, which is a great advantage of this new generation of transformer oil. Case studies showed that the transformer oil-based AGQD nanofluid has a superior colloidal stability, offering improved high voltage equipment performance and reliability.

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1. Introduction
Transformer oil (TO), a pure mineral oil which are stable at high temperatures, commonly shows low thermal conductivity, which is the main obstacle for upgrading the performance of transformers [1]. Note that a suitable transformer oil should exhibit an outstanding electrical resistance and a superior thermal conductivity [2,3]. According to [1,4], a small enhancement in the thermal conductivity of TO can result in a significant frugality in cost and performance. To this end, researchers synthesized different type of novel TO-based nanofluids with appropriate voltage insulation, thermal and dielectric properties. They concluded that the higher thermal conductivity of TO means the higher rate of heat transfer, leading to smaller size transformers, more desirable lifetime and greater performance [1]. To address this issue, various nanoparticles and carbon nanostructures were used for preparing nanofluids [2,5–7].

Over the last decade, the researches on efficient, scalable and economical ways to produce highly-dispersive TO-based metal or TO-based metal oxide nanofluids have encountered different problems including drop in the breakdown voltage, high level of sedimentation rate, and change in TO acidity. To solve the aforementioned problems, significant efforts have been made on the preparation of TO-based carbon nanostructures nanofluids, which typically employs different covalent and non-covalent functionalizations to overcome the poor stability of additives in TO [3].

Among different carbon nanostructures, graphene (Gr) and carbon nanotubes (CNT) are promising additives for future heat transfer equipment due to the superior thermal and mechanical properties as well as their chemical stability [8–14]. Due to the high specific surface area, superior thermal conductivity, and suitable stability in the presence of covalent and non-covalent functionalization, graphene-based materials have attracted numerous researchers across the globe [3,15–17]. In particular, few layer Grs are the two-dimensional sheets with sp2-hybridized carbons in a hexagonal lattice with unique properties [18–20]. While the graphene-based materials have unique desirable properties including a thermal conductivity of the order of 5000 W/mK [21], the challenge remains on producing long-term colloidal stability of Gr suspension in transformer oil and also the superior electrical conductivity of Gr spoils the insulation property of TO. In this context, it has been highly desirable to develop materials with the capability of functionalization for preparing stable colloidal suspension with high
thermal conductivity while being electrically-semiconductive for use as effective transformer oil. The semiconductor quantum dots (SQD) opened a new gateway to address all the above-mentioned targets. Due to the promising two-dimensional feature, large specific surface area, and favourable electronic properties, graphene quantum dot (GQD) is a promising candidate for use as additives in TO. Applications that require semiconductive additive, superior thermal conductivity and ultra-high electrical resistivity will benefit immensely from GQD, which has been demonstrated to show remarkable thermophysical and physicochemical properties. Note that acidity of additive is also harmful and can be the source of numerous issues in transformers. The more the acidity, the more the solubility of water in the TO, which reduces the insulation property and depreciates transformer [3,22]. So, the synthesized GQD should not include the acidic groups.

In this study, a novel and cost-effective synthesis approach for preparing amine-treated GQD (AGQD) was developed. The morphological study confirmed the presence of AGQD at sub-17 nm sizes. The resulting suspension shows that the TO-based AGQDs nano-fluid is a promising and unique alternative coolant for use in transformer.

2. Experimental

2.1. Preparation of AGQD

Herein, a modified Hummers method was employed to prepare the graphite oxide sheets from natural graphite powder [23]. For GQD synthesis, the method presented by Zhang et al. [23] with slight modification was used. Typically, 2.0 g of the graphite oxide were oxidized in the concentrated HNO3 (60 mL, 38 wt%) and H2SO4 (180 mL, 98 wt%) for 48 h under mild ultrasonication. After cooling, the mixture was diluted with 1200 mL of deionized water and subsequently was centrifuged at 4000 rpm to separate the un-exfoliated material. The supernatant was then diluted with the deionized water. The colloidal suspension was then dialyzed using a dialysis bag (Mw cut off: 3500 Da) overnight.

To remove the acidic groups decorated on the edge of GQD, 100 mL of colloidal solution was mixed with deionized water (100 mL) and ammonia solution (120 mL) in a vessel. The resulting suspension was sonicated in a 300 W probe-sonicator for 30 min. The mixture was then stirred for 4 h at 100 °C. After cooling to room temperature, the resulting black suspension centrifuged at 25000 rpm and the supernatant was collected. After performing the reaction step, the majority of oxidized GQD changed to the amine-treated GQD (AGQD). Finally, a rotary evaporator was used to concentrate the AGQD solution at 50 °C, which is followed by drying in a vacuum oven to obtain the dried AGQD powder.

2.2. Preparation of nanofluid

In order to prepare TO-based AGQD nano-fluid, the AGQD was sonicated in transformer oil for 30 min. As mentioned before, the AGQD were decorated with the amine groups. Therefore, the easily-miscible amine functionalities on the edges of AGQD may cause great colloidal stability of suspension as well as the superior solubility of the AGQD in transformer oil media.

2.3. Experimental apparatus

Fig. 1 shows a schematic diagram of the experimental setup, which was designed based on an industrial transformer. There is a good agreement between the size and materials of the experimental set-up and the oil-25 KVA transformer. It can be seen that the experimental transformer used in the present study is an oil based-transformer and comprises of a 203 × 100 × 221 mm³ reservoir. To provide input power for heating the working fluid, a cylindrical heating element was installed at the top of reservoir. The average temperatures of working fluids at different locations in the reservoir were measured by PT-100 thermocouples. To provide accurate data on average temperatures of the walls, four thermocouples were installed on the top of the reservoir with another 4 thermocouples installed at different sides of the transformer’s walls. To have force convection heat transfer, a 55 W blower was installed at a constant distance of 5 cm from the transformer. Ammeter, voltmeter and the thermocouples, respectively, had the measurement uncertainties of 0.001 A, 0.1 V and 0.1 °C. According to the Holman technique [24], the total uncertainty for calculating the natural and forced heat transfer coefficients were ~2.1%. Atomic force microscopy (AFM, ScanAsyst mode, frequency 1 Hz, Bruker) was also used to investigate the surface morphology of AGQD.

Brookfield LVDV-III rheometer and KD2 thermal analyzer (Decagon Devices, Inc., USA) were used, respectively, to measure the viscosity and thermal conductivity of resulting nanofluid. Also, the flash point was evaluated experimentally by a seta semi-automatic Cleveland open cup flash point tester, which works on the basis of American Society for Testing and Materials (ASTM) D-92 [25]. Also, Mugger’s automatic laboratory oil tester was used to measure the dielectric breakdown with the setting of ASTM D-92 standard.
2.4. Data processing

As a part of the present study, the effect of AGQD loading on natural & forced convection heat transfer coefficients, breakdown voltage, flash point, pour point, density, electrical and thermal conductivities, and viscosity of suspension was studied. These parameters play the key roles in the overall performance of transformers.

Natural convection heat transfer coefficient and forced convection heat transfer coefficient can be calculated by the following equations.

The input power into transformer is given as,

\[ Q = VI \]  \hspace{1cm} (1)

Using the average temperatures of walls, \( T_c \), and the bulk fluid temperature, \( T_h \), the convection heat transfer coefficients can be obtained from Newton’s cooling law. That is,

\[ h = \frac{Q}{A(T_h - T_c)} \]  \hspace{1cm} (2)

where the heat transfer area, \( A \), was 0.13 m\(^2\).

3. Results and discussion

3.1. Morphology

To check the morphological properties of AGQD such as size and thickness, the atomic force microscopy (AFM) was used and the results are shown in Fig. 2. AFM ichnography and cross-section contour of AGQD are shown in Fig. 2. In fact, using a dialysis process, the size of the AGQD was controlled. The AGQD size were mostly in the range of 5–17 nm. Also, the topographic results showed the average thickness of < 1 nm, which is similar to mono layer of functionalized graphene quantum dots or chemically treated graphene nanoribbons with one layer [26,27]. A majority of the AGQD have only one layer. Also, the 3D AFM images confirmed the production of uniform AGQD with the almost same thickness.

Fig. 2. AFM image, 3D image and cross-sections of AGQD.
3.2. Colloidal stability

Fig. 3a illustrates the absorption spectra of the pure TO and TO-based AGQD sample. Obviously, the UV–Vis absorption spectra of pure TO shows two peaks at ca. 216 and 268 nm, which are similar with spectrum of pure transformer oil reported by other researchers [28,29]. Contrary to the UV–Vis spectrum of the pure oil, the TO-based AGQD sample absorbs significantly visible light in the wavelength range of 200–350 nm. This figure shows also a sharp absorption band at ca. 233 nm, which is corresponded to the π → π* transition of aromatic sp² domains [27,30]. Also, there is another absorption band at ca. 321 nm, which is due to the presence of AGQD.

The colloidal stability of AGQD in transformer oil is shown in Fig. 3b. It is seen that the AGQD suspension is stable under UV–vis irradiation. In fact, the degradation rate of AGQD in TO is <0.5% after 1 month, indicating effective colloidal stability of the suspension under visible light irradiation. Compared with the other nanoparticles and carbon nanostructures [31], the present study suggests that the AGQD shows almost no sedimentation in transformer oil. It is conjectured that large surface-to-weight ratio and easily-miscible amine functionalities on the edge graphene nano-sheets are the reason for the superior stability of AGQD dispersion in transformer oil.

3.3. Physical properties

3.3.1. Electrical resistivity

As one of the important factors that influences the transformer performance, the electrical resistivity of TO-based AGQD nanofluid and pure transformer oil was studied in this section. Fig. 4(a) and (b) illustrate the measured electrical conductivity and resistivity of the TO-based AGQD nanofluid and pure transformer oil as functions of temperature. It is seen that the electrical conductivity increases somewhat with the addition of AGQD into the pure oil, representing an enhancement <5% of the range of temperatures investigated. This means that the electrical resistivity drops in the range of 2–5% with the 0.001 wt% loading of AGQD. The observed slight enhancement is due to the intrinsic electrical transfer capacity of AGQD. It is also seen that the electrical conductivity was not undergone a considerable change after loading AGQD.

3.3.2. Thermal conductivity

The transformer oil typically has a low thermal conductivity, which is considered a significant drawback. In addition, the thermal conductivity of TO decreases markedly as the temperature increases, which is one of the main factors for the decrease of the transformers performance and lifetime [3]. To improve the poor thermal conductivity of TO, different nanoparticles were employed as the additives. Many parameters such as size, shape, specific surface area, rate of sedimentation, concentration and thermal conductivity of additives influence the effective thermal conductivity of the resulting nanofluids.

Fig. 5a shows the measured thermal conductivity of pure transformer oil and TO-based AGQD nanofluids in the operating temperature range of 30–70 °C. This figure clearly shows that the thermal conductivity of pure transformer oil has a decreasing trend with an increase in the temperature. Interestingly, the measured data for the suspension shows
a changed to the slightly upward trend with the addition of AGQD. It is conjectured that the change in the variation of thermal conductivity of suspension with temperature is due to the increase in the intensity of Brownian motion. When particles move randomly due to the Brownian motion, they drag the nearby fluids with themselves and increase the transport of heat in the suspension. As the temperature increases, the Brownian motion increases and the associated transport of heat accelerates, leading higher effective thermal conductivity. Large surface-to-volume ratio intensifies the Brownian motion. Beheshti et al. [1] performed a similar study on TO-based oxidized CNT nanoparticles. They reported an increasing trend of thermal conductivity for their samples up to 60 °C, but noticed a sharp decrease in trend at higher temperatures. They reported a sharp increase in the particle aggregation for temperature > 60 °C. Fig. 5a shows that the enhancements in thermal conductivity of TO-based AGQD nanofluids are about 4% at 30 °C and 10% at 70 °C. It means the main thermal problem with TO, which is a significant decrease with temperature, can be solved by loading AGQD.

### 3.3.3. Convective heat transfer coefficient

In addition to the thermal conductivity, the convective heat transfer rate is an important factor for high performance transformer fluids. A simple analogy of $h=k/\delta t$ clearly shows that there is a direct relationship between the convective heat transfer rate and thermal conductivity. It should be mentioned that $\delta t$ is the thickness of thermal boundary layer. Therefore, natural and forced heat transfer coefficients for pure transformer oil and TO-based AGQD nanofluid were measured and the results are presented in this section.

Fig. 5b shows the natural convective heat transfer coefficient of pure transformer oil and TO-based AGQD nanofluid for different input powers. (Natural convection is due to the buoyancy forces caused by temperature gradients, which result in density variations and subsequent fluid movement.) The natural convective heat transfer coefficient of pure transformer oil increase from 55.56 W/m² K at input power of 49.76 W to 64.13 W/m² K at input power of 149.83 W, representing 15.4% enhancement. The corresponding enhancement for TO-based AGQD nanofluid is 23.9%. As compared with the earlier results obtained for TO-based CNT nanofluids [1], the present AGQD suspension shows significantly higher natural heat transfer coefficient.

Forced convection is commonly used to transport large quantities of heat. As mentioned above, a blower was employed to provide the forced convection heat transfer. Forced convective heat transfer coefficient for pure transformer oil and TO-based AGQD nanofluid were measured and the results are shown in Fig. 5c as a function of input power. Like the natural convection case, the forced convection heat transfer coefficient of the both samples show an increasing trend with the input power. It is also seen that the forced convection heat transfer coefficient of TO-based AGQD nanofluid was significantly higher than the pure TO, indicating the enhancement in the range of 21–32% at very low concentration of 0.001 wt%. Comparison of Fig. 5b and c shows the forces convection heat transfer coefficients of the transformer oil with and without AGQD are much higher than those under natural convection condition.

### 3.3.4. Breakdown voltage

Breakdown voltage is related to the dielectric strength of transformer oil which is an important indicator of the transformer performance. Breakdown voltage is measured by detecting the generation of spark between two electrodes with a specific gap filled with the transformer oil. Recent results concluded [32] that a small increase in the moisture content or a small acidity can cause a significant drop in the breakdown of TO. Impurities reduces the breakdown voltage by decreasing the electrical resistivity [1,32]. So, very low weight fraction of AGQD was selected herein. In addition, in order to avoid acidic suspension, the amine-treated GQD was used. For temperature of 25 ± 2 °C, the measured breakdown voltages of pure transformer oil and TO-based AGQD nanofluid are presented in Fig. 6. To minimize the uncertainty in the measurements of the dielectric breakdown voltage, the test was repeated 60 times for each sample including pure transformer oil and TO-based AGQD nanofluid with and without sonication. Also, the mean breakdown voltages along with the corresponding standard deviation are listed in Table 1. All the tests were performed with a device including the mushroom electrodes set at a constant gap of 1 mm at the same conditions. As noted before, the key factors for deteriorating the dielectric strength of transformer oil is the presence of water and other contaminants. Although Malaysia typically has high humidity, sonication procedure introduces insignificant amount of moisture to the transformer oil and results in an insignificant deterioration of the breakdown voltage of pure TO. The difference between panel (a) and panel (b) in Fig. 6 illustrate that only a short sonication time (30 min sonication) is sufficient to change the dielectric properties of TO. Thirty minutes is the sonication time needed for preparing stable suspension of AGQD. However, breakdown voltage decreases about 0.6% after a 30-min sonication, which is negligible.
On the other hand, from Fig. 6 panel (c), loading AGDQ in TO leads to an enhancement in positive breakdown voltage (ca. 2.2%), increasing from 58.03 to 59.31 kV. Hwang et al. [33] has also reported higher positive voltage breakdown levels than that of pure transformer oil. This paradoxical superior electrical breakdown performance compared to that of pure oil is due to the electron charging of the nanoparticles to convert fast electrons from field ionization to slow negatively charged nanoparticle charge carriers with effective mobility reduction by a factor of about $1 \times 10^5$.

### 3.3.5. Density

Natural convection heat transfer depends on the buoyancy force generated by density variation due to temperature. Therefore, the temperature dependence of transformer oil density plays an important role in natural convection heat transfer. Fig. 7 shows the measured density of TO-based AGQD nanofluids as well as pure transformer oil at different temperatures. As expected, the densities of pure transformer oil and TO-based AGQD nanofluid decrease significantly as temperature increases, which is due to the thermal expansion of oil. It is also seen that the 0.001 wt% loading of AGQD in the transformer oil has no noticeable effect on the density. The maximum difference is about 0.23% at 40 °C, which is negligible.

### 3.3.6. Flash point

Flash point is a critical temperature for which the transformer oil generates sufficient vapor for producing a flammable mixture with air. Therefore, the flash point is the temperature that identifies the probability of fire hazard in the transformer. Accordingly, the transformer oil with higher flash point is more desirable [22].

Fig. 8 shows the flash points of pure transformer oil with and without sonication and TO-based AGQD nanofluid. It is seen that the flash point increased from 150.1 to 150.9 after sonication, representing 0.5% enhancement in flash point with the introduction of slight amount of oxygen or moisture into the transformer oil. This figure also shows a significant increase in flash point when 0.001 wt% of AGQD was loaded into the transformer fluid, indicating an increase of almost 13 degrees in the volatility of the TO. This enhancement is attributed to the superior chemical stability of AGQD and homogenous covalent bonds with TO.

### Table 1

Breakdown voltage of TO-based AGQD nanofluid and pure TO with and without sonication for 30 min.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Mean breakdown voltage (kV)</th>
<th>S.D. (kV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure TO</td>
<td>58.03166667</td>
<td>1.137174</td>
</tr>
<tr>
<td>Sonicated Pure TO</td>
<td>57.65333333</td>
<td>1.311039</td>
</tr>
<tr>
<td>0.001-TO-based AGQD nanofluid</td>
<td>59.30666667</td>
<td>1.239354</td>
</tr>
</tbody>
</table>
molecules. A higher flash point temperature means safer operational condition for the transformers. The rate of enhancement in the flash point of TO-based AGQD nano fluid to pure transformer oil is about 8.8%, which is quite high compared to those obtained in other studies [1.3].

3.3.7. Viscosity

The viscosity of oil (resistance to flow) in transformers is an important parameter as it affects the convection and fluid circulation and thereby the transformer performance. Therefore, the viscosity of pure transformer oil and the TO-based AGQD nano fluid as functions of temperature was measured and the results along with the amount of enhancement are shown in Fig. 9. It is seen that the viscosity of both transformer oils decrease sharply with the increase in temperature. However, there is no noticeable changes in the viscosity after loading the 0.001 wt% AGQD additive. The axis on the right shows that the maximum of enhancement of viscosity due to the loading AGQD is <1.3%. Therefore, the synthesized transformer oil with the use of AGQD provides enhanced conductivity with almost no penalty in viscosity.

Conclusion

Experimental data for the thermophysical properties of suspension of AGQD in conventional transformer oil was provided. The hot-wire method showed that the thermal conductivity of the prepared sample is markedly increased at very low weight fraction of AGQD, while the effective viscosity remained roughly the same with the maximum increase of about 1.3%. The variations of electrical resistivity, flash point and voltage breakdown of the suspension versus temperature were also measured. The presented data showed that the transformer oil-based AGQD nano fluid has a great potential in enhancing the natural and forced convection heat transfer rate in transformers. In addition, the suspension exhibits long-term colloidal stability, superior thermal conductivity, and higher positive voltage breakdown, with only slight penalties in rheological properties. The test results also indicated that AGQD is effectively dispersed in the transformer oil with long term colloidal stability. Therefore, the transformer oil-based AGQD nano fluid has significant potential as a new generation of high performance coolant for use in transformer.

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