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Investigation of thermal and electrical conductivity of graphene based nanofluids

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We report for the first time, the synthesis of highly stable exfoliated graphene based nanofluids with water and ethylene glycol as base fluids with out any surfactant and the subsequent studies on their thermal and electrical conductivities. Graphene was synthesized by thermal exfoliation of graphene oxide at 1050 °C in Ar atmosphere. The as-synthesized graphene has been suitably functionalized and further dispersed it in the base fluids without any surfactant. Thermal and electrical conductivities of these nanofluids were measured for varying volume fractions and at different temperatures. An enhancement in thermal conductivity by about 14% has been achieved at 25 °C with deionized water (DI) as base fluid at a very low volume fraction of 0.056% which increases to about 64% at 50 °C. Electrical conductivity measurements for these nanofluids indicate an enormous enhancement at 25 °C for a volume fraction of 0.03% in DI water. © 2010 American Institute of Physics. [doi:10.1063/1.3516289]

I. INTRODUCTION

The production of heat energy decreases the performance of many of the instruments and machines. Conventional fluids used as heat exchanger in these machines are water, ethylene glycol (EG), silicone oil etc. In the past few decades a large number of investigations have been carried out to improve the thermal properties of these conventional fluids. The use of solid particles as an additive suspended in the base fluid is a technique to augment the heat transfer. Enhancement of the thermal conductivity is the key idea to improve the heat transfer characteristics of conventional fluids. The enrichment of thermal conductivity of conventional fluids by the suspension of solid particles, such as millimeter- or micrometer-sized particles have not been of interest for practical applications due to problems such as sedimentation, erosion, fouling, and increased pressure drop of the flow channel. Choi¹ found that the particles of nanometer size, suspended in conventional fluids, enhance the heat transfer. These Innovative heat transfer fluids consisting of suspended nanometer-sized solid particles are called “nanofluids.” Nanofluids can be considered to be the next-generation heat transfer fluids as they offer exciting new possibilities to enhance heat transfer performance compared to pure liquids. The much larger relative surface area of nanoparticles, compared to those of conventional particles, not only significantly improve heat transfer capabilities, but also increases the stability of the suspensions. Suspended nanoparticles in various base fluids can alter the fluid flow and heat transfer characteristics of the base fluids. Necessary studies need to be carried out before wide application can be found for nanofluids.

Various investigations have been carried out for the physical mechanism and mathematical modeling to describe

and predict the thermal conductivity and heat transfer phenomena. Some models like Maxwell–Garnett² and Hamilton–Crosser,³ do not take particle motion into consideration. Xuan *et al.*⁴ developed a dynamic model that takes into account the effects of Brownian motion of nanoparticles and fractals. But all the static and dynamic models developed with conduction-based mechanisms still fail to predict the magnitude and trends of the experimental data. Even though there are lack of theoretical models to explain the enhancement in thermal conductivity in nanofluid, studies are going on in the experimental side with different nanoparticles to enhance thermal conductivity.

Al₂O₃ and CuO are the most well-known nanoparticles used by many researchers in their experimental works. Even when the size of the particles and type of base fluids are different, all the experimental results showed the enhancement of the thermal conductivity.^{5,6} Eastman *et al.*⁷ reported that the thermal conductivity increased up to 40% for nanofluids consisting of 0.3% (by volume) of Cu nanoparticles of a mean diameter less than 10 nm dispersed in EG. The exceptional electronic transport properties of low dimensional graphitic structures have been extensively demonstrated in carbon nanotubes (CNT).⁸ The CNT-based nanofluids are expected to exhibit superior heat transfer properties compared with conventional heat transfer fluids and other type of nanofluids⁹ due to the very high thermal conductivity of CNT (2000–4000 W/mk).¹⁰

Graphene, a single atomic layer of graphite, which is a two-dimensional form of carbon, is found to exhibit high crystal quality and to have ballistic electronic transport at room temperature.¹¹ Saito *et al.*¹² derived and formulated an equation to calculate the ballistic thermal conductance of a two-dimensional system directly from the dispersion relations of phonons and electrons. Recently, Balandin *et al.*¹³ measured experimentally thermal conductivity of a sus-

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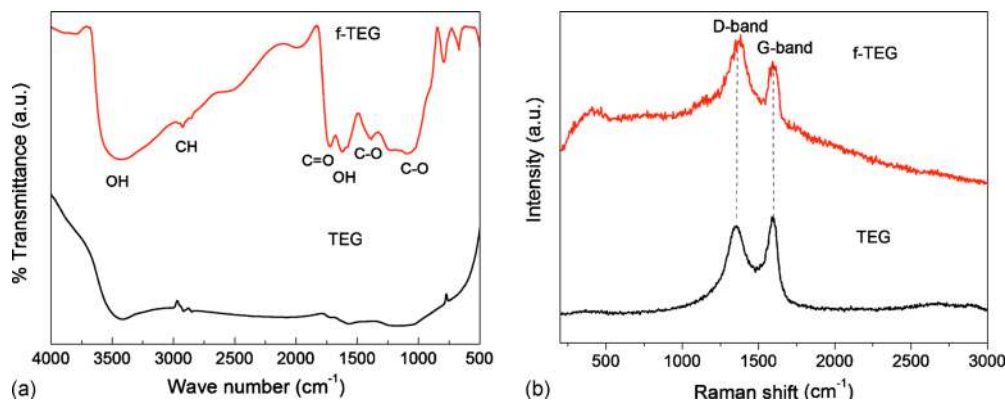


FIG. 1. (Color online) (a) FTIR and (b) Raman spectra of as synthesized TEG and f-TEG.

pendent single-layer graphene at room temperature and was around 5000 W/mK. The extremely high value of thermal conductivity suggests that graphene can perform better than carbon nanotubes. Therefore, it will be interesting to study the thermal conductivity of two-dimensional graphene in base fluids such as deionized water (DI) water and ethylene glycol (EG).

Even though there are different exfoliation methods for the synthesis of graphene, such as thermal exfoliation of graphene oxide (GO),¹⁴ vacuum exfoliation of GO,¹⁵ and chemical exfoliation of GO,¹⁶ the graphene we used for this study was prepared by thermal exfoliation of graphene oxide and we call them as TEG. To the best of our knowledge there is only one paper reporting the thermal conductivity of graphene oxide sheets dispersed EG nanofluids.¹⁷ In the present paper, the functionalized TEG (f-TEG) was prepared and dispersed without any surfactant in DI water and EG in varied concentrations. The thermal conductivity and electrical conductivity for different volume fraction at different temperatures have been studied and the results have been discussed.

II. EXPERIMENTAL DETAILS

The synthesis of graphene nanofluid is a two step method. In the first step we have synthesized graphene via thermal exfoliation of graphene oxide.¹⁴ This graphitic oxide (GO) was prepared by Hummers method.¹⁸ In short, graphite was treated with sulphuric acid, sodium nitrate and potassium permanganate. The suspension was further treated with hydrogen peroxide and was filtered. The filter cake was washed with distilled water and dried in vacuum oven at 40 °C for 8 h. Graphene was synthesized by treating vacuum dried graphene oxide in argon gas atmosphere at 1050 °C for 30 s.

Since the as-synthesized TEG did not disperse in water and EG, they were made hydrophilic by treating with acid. As-prepared graphene was ultrasonicated with mixture of H₂SO₄:HNO₃ in 3:1 ratio for 3 h. After 3 h, the mixture was washed several times with DI water until the pH became neutral and then filtered and dried the sample. The sample was dried at 50 °C in vacuum oven. The functionalised graphene (f-TEG) was dispersed in water and EG in different volume fractions with the help of an ultrasonicator. The fre-

quency of the ultrasonicator was 30 kHz and the time for ultrasonication was 30–45 min. The pH of the fluid is kept around 6–7.

Identification and characterization of functional groups on the surface of TEG and f-TEG were carried out using PerkinElmer FT-IR spectrometer in the range 500–4000 cm⁻¹. UV absorption spectra of the samples in deionized water were recorded on JASCO Corp., V-570 spectrophotometer. The Raman spectra were obtained with a WITTEC alpha 300 Confocal Raman system equipped with a Nd:YAG laser (532 nm) as the excitation source. The intensity was kept at minimum to avoid laser induced heating. The morphology of the samples was characterized by field emission scanning electron microscopy (FESEM, FEI QUANTA). Transmission electron microscopy (TEM) was carried out using a JEOL JEM-2010F microscope. For TEM measurements, the graphene powder was dispersed in absolute ethanol using mild ultrasonication and casted onto carbon coated Cu grids (SPI supplies, 200 mesh). Leica DM IL LED phase contrast optical microscope was used for the optical imaging and to see the movement of particles in base fluid. Thermal conductivity of the suspension was measured using KD2 pro thermometer (decagon, Canada). The probe sensor used for these measurements are of length 6 cm and of diameter 1.3 mm. In order to study the temperature effect on thermal conductivity of nanofluid a thermostat bath was used. All the measurements were taken after calibrating the KD2 Pro instrument with glycerol. With glycerol the error in measurement was less than 1%. The overall uncertainty in thermal conductivity was less than 4% including temperature variation. The thermal conductivity measurements of the nanofluids were cross checked using another instrument, Lambda 01/L (Flucon GmbH), which has a reproducibility of 1%. This is attached to LabTemp 30190 (PSL Systemtechnik GmbH), which is having a resolution/accuracy of 0.1 °C/0.1 °C and reproducibility of 1%.

III. RESULTS AND DISCUSSION

A. FTIR and Raman spectroscopy analysis

Figure 1(a) shows the FTIR of TEG and f-TEG. It is very clear from the spectra that oxygen and water containing functional groups are almost removed from the GO during thermal exfoliation process. The peaks at around 3442 and

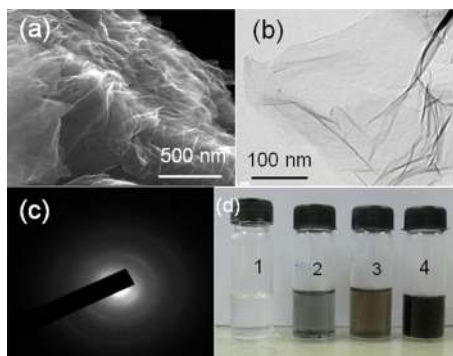


FIG. 2. (Color online) (a) FESEM, (b) TEM, (c) SAED pattern of as synthesized TEG. (d) Digital photograph of different nanofluids.

1625 cm^{-1} are due to OH functional groups. A small doublet peak of CH_2 (2922 and 2860 cm^{-1} and carboxyl groups (CH at 1365 cm^{-1}) are present in TEG and f-TEG. The peaks at 1720 and 1380 cm^{-1} can be assigned to the $\text{C}=\text{O}$ and $\text{C}-\text{O}$ stretching vibrations of COOH . These functional groups are from the carboxylic acid. The functional groups help graphene sheets to interact with water molecules and disperse properly. The proper dispersion of nanoparticles helps to improve the thermal and electrical conductivity of fluid.

Raman spectra of as synthesized TEG and f-TEG are shown in Fig. 1(b). In TEG the peak around 1592 cm^{-1} is due to the translational vibration of carbon atoms in sp^2 hybridized state. The peak around 1352 cm^{-1} is due to sp^3 defects formed in the structure. An increase in the D-band intensity is taken as a fingerprint for successful functionalization. The G-band and D-band are present in f-TEG also but with a small blueshift. Moreover one can see a slight increment in the relative intensity of D-band in f-TEG. In TEG, the D-band intensity is lesser than that of G-band but in f-TEG the D-band intensity is slightly higher than G-band. All these changes in f-TEG can be due to defects and chemical doping formed in the sheet due to acid treatment by ultrasonication. A universal observation is that higher disorder in graphite leads to a broader G band, as well as to a broad D band of higher relative intensity compared to that of the G band.^{19,20}

B. Electron microscopy and digital images

Figures 2(a)–2(c) shows the FESEM, TEM, and diffraction image of TEG. From FESEM image of TEG we can see the exfoliated wrinkled and layered structure of graphene. The image reveals that most of the GO exfoliated to form individual sheets. TEM image clearly shows the transparent graphene sheets with folding at the edges to avoid the dangling bonds at the edges. Figure 2(c) shows electron diffraction (SAED) performed on a selected area of the graphene sheets along with TEM. The diffraction rings can be fully indexed to the hexagonal graphitic structure, confirming the crystalline nature of the graphene sheets and was compared with previously published SAED pattern of graphene.²¹

Figure 2(d) is the digital photograph of (1) DI water, (2) As synthesized TEG in DI water, (3) f-TEG (low concentration) in DI water, and (4) f-TEG (high concentration) in DI water with out any surfactants. The as synthesized TEG start settling at the bottom of the bottle whereas complete dispersion is achieved with f-TEG (different concentration) in DI water with out any surfactants. The formation of stable dispersion allows the reaction to be monitored by UV-visible absorption spectroscopy.

C. UV-visible and optical spectroscopy studies

UV-visible spectra of TEG and f-TEG were taken by dissolving equal amount of each sample in DI water, 0.3 mg in 10 ml [Fig. 3(a)]. Since the as-synthesized TEG was not dispersing properly and due to the nonhomogeneity of particles in water, it was showing absorption flattening. But in the case of 0.3 mg of f-TEG in 10 ml of water, there was an absorbance peak around 265 nm . This is due to $\pi \rightarrow \pi^*$ absorption in ($\text{C}=\text{C}$). For GO, this peak will be around 230 nm .^{22–24} For a comparative study, UV-visible spectrum for a little high concentration, 7.5 mg in 10 ml , was taken [Fig. 3(b)]. In the case of high concentration, a high value of absorbance is observed and got saturated after a particular concentration.

Optical image of the nanofluid was taken by putting a drop of fluid on a cleaned glass slide to see the Brownian motion of particles in the base fluid. Figure 4(a) shows the optical image of as-synthesized TEG wherein the particles

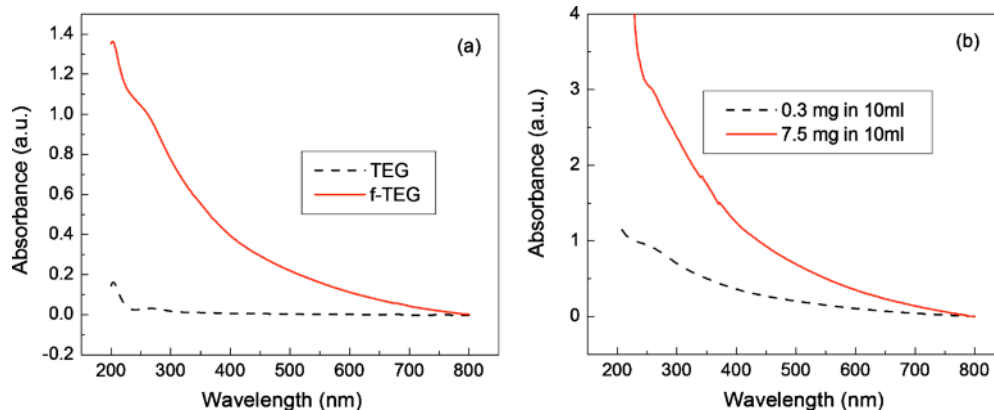


FIG. 3. (Color online) UV-visible spectrum of (a) as synthesized TEG and 0.3 mg f-TEG in 10 ml water (b) 0.3 mg f-TEG in 10 ml water and 7.5 mg f-TEG in 10 ml water.

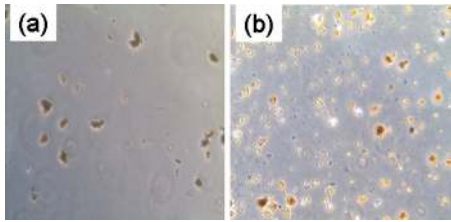


FIG. 4. (Color online) Optical micrographs of (a) TEG and (b) f-TEG dispersed water based nanofluid.

were not well dispersed and the nonhomogeneity of particles was visible. The image in Fig. 4(b) shows uniform dispersion and distribution of f-TEG nanosheets in DI water. Compared to TEG nanofluid, f-TEG nanofluid was homogeneous and was stable for long time.

D. Thermal conductivity measurements

Thermal conductivity of f-TEG dispersed water samples were measured with different volume fraction ranging from 0.005% to 0.056%. Figure 5(a) shows the graph of thermal conductivity versus temperatures ranging from 25 to 50 °C for different volume fractions. Thermal conductivity increases with increasing volume fraction in a nonlinear manner. The nonlinearity in thermal conductivity of carbon based nanofluids was already reported.¹ We have selected very low volume fraction for the present study such that the viscosity of the nanofluid is not increased which is undesirable for application point of view. The thermal conductivity increases with volume fraction for 25 and 50 °C (Fig. 1S).²⁷ The percentage of enhancement in thermal conductivity is calculated using $[(k-k_0) \times 100]/k_0$, where “ k_0 ” is the thermal conductivity of base fluid and “ k ” is that of nanofluid. The enhancement of thermal conductivity for water based nanofluid at 25 °C for a volume fraction of 0.056% is about 14% where as at 50 °C, the enhancement is about 64%. This is a considerably good enhancement for such a small volume fraction probably due to the extremely high surface area of graphene sheets. The present results are much superior to what Yu *et al.*¹⁷ had reported for 5% volume fraction of graphene oxide in EG. With multi walled carbon nanotubes (MWNT), the maximum thermal-conduction enhancement

observed by Xie *et al.*¹⁰ is only about 7% for 1% MWNT by volume, and that observed by Assael *et al.*²⁵ is 20%–40% for 0.6% by volume in DI water.

In fluid the movement of nanoparticles is random and influenced by different forces like Brownian motion.⁴ According to the Brownian theory, the smaller the sizes of the colloid particles, the faster the particles move, so that energy transport inside the liquid becomes stronger. In the case of graphene, they interact well with each other at much lower concentrations in the base fluids, which results in the ease with which an electron can hop from one graphene to other in nanofluid. The increase in thermal conductivity in nanofluids can be explained by the main mechanism of Brownian motion of the suspended particles as it is one of the most dominating functions of temperature. There are different reports on the enhancement of thermal conductivity with respect to temperature. Yu *et al.*¹⁷ did not find any considerable enhancement in thermal conductivity with respect to temperature using graphene oxide nanosheets dispersed EG nanofluid. But there are other reports^{9,26} of nanofluids where thermal conductivity of fluid increases with increasing temperature. So independent of the base fluid, the thermal conductivity will vary with respect to temperature. These results suggest that one can still expect more enhancements in thermal conductivity if volume fraction is high. To minimize the error in the experimental values, eight readings for each temperature were taken and the average was taken as the thermal conductivity at that temperature.

Further we have dispersed f-TEG in EG and studied the thermal conductivity. The enhancement in thermal conductivity is very low in low volume fractions compared to enhancement of water based fluid. The plot for thermal conductivity versus temperature for different volume fractions is shown in Fig. 5(b). We can see that there is a small enhancement in thermal conductivity for 0.05% volume fraction, which was around 3%–4% at 25 °C and 6%–7% at 50 °C due to the high viscosity of EG which in turn affects the thermal conductivity of nanofluids.¹⁷ The trend in the variation in thermal conductivity of f-TEG in EG with different volume fractions at 25 and 50 °C was almost same what was there in the case of f-TEG in DI water (Fig. 2S).²⁷

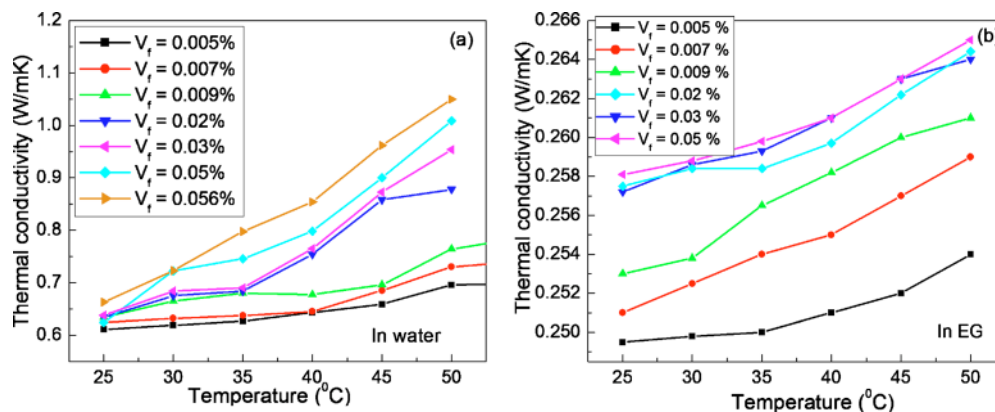


FIG. 5. (Color online) (a) Thermal conductivity of f-TEG dispersed in water based nanofluid at varying temperature for different volume fraction and (b) thermal conductivity of f-TEG dispersed in EG based nanofluid at varying temperature for different volume fraction.

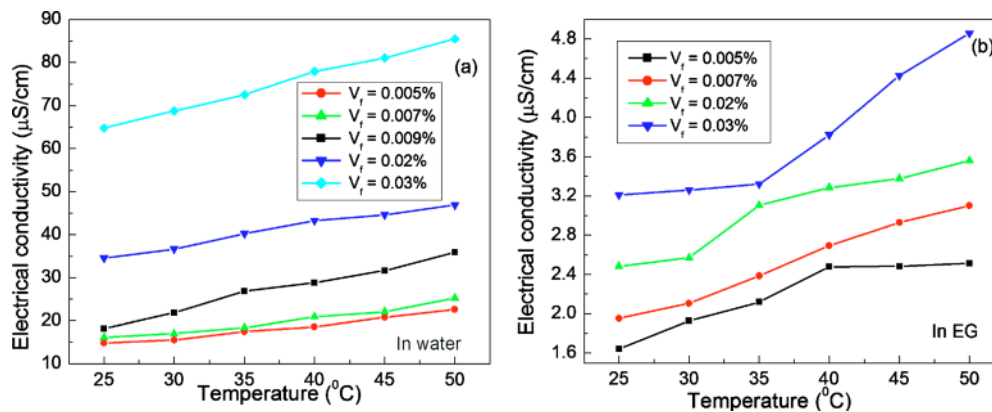


FIG. 6. (Color online) (a) Electrical conductivity measurement of water based f-TEG nanofluid at different temperature for different volume fraction and (b) Electrical conductivity measurement of water based f-TEG nanofluid at different temperature for different volume fraction.

In order to check the credibility of the measurements, the thermal conductivity of the nanofluids was measured using another instrument (Lambda) and the variations in the values were less than 2%.

E. Electrical conductivity measurements

We have also measured the electrical conductivity for the present nanofluids with respect to volume for different temperature. The electrical conductivity for different volume fraction in varying temperature with respect to water and EG are shown in Figs. 6(a) and 6(b). In nanofluids with DI water as base fluid, electrical conductivity of f-TEG increases to about 60 μS/cm for a volume fraction of 0.03%, whereas electrical conductivity of water was around 4 μS/cm. The percentage enhancement in electrical conductivity was calculated using the formula $[(\sigma - \sigma_0) \times 100] / \sigma_0$ where “ σ_0 ” corresponds to electrical conductivity of base fluid and “ σ ” that of nanofluid. An enhancement of about 1400% was observed for a volume fraction of 0.03% at 25 °C. In the case of EG as base fluid, the normal value of electrical conductivity is ~ 1 μS/cm and which increases to 3.2 μS/cm for 0.03% volume fraction of f-TEG in EG base fluid. In both the cases, the electrical conductivity is increases with increasing volume fraction as well as increasing temperature.

The trend of enhancement of electrical conductivity with respect to increase in volume fraction as well as increase in temperature is same for DI water (Fig. 3S)²⁷ and EG (Fig. 4S)²⁷ based nanofluids, even though there is difference in the order of the corresponding values.

IV. CONCLUSION

Graphene was prepared by thermal exfoliation and functionalized with acid treatment. The functionalized graphene was successfully dispersed in base fluids using ultrasonication. Thermal conductivity and electrical conductivity measurements of f-TEG dispersed nanofluids were carried out. An enhancement in thermal conductivity of 14% for a volume fraction of 0.056% has been observed for water based nanofluid at 25 °C and 64% enhancement for the same volume fraction at 50 °C. Similarly the electrical conductivity also shows an enhancement compared to the base fluid. In order to check the credibility of the measurements, the ther-

mal conductivity and electrical conductivities of nanofluids were repeated several times. The overall uncertainty in measurements was less than 4%. These results suggest that the cost effective graphene based nanofluids can find potential applications as coolants.

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²⁷See supplementary material at <http://dx.doi.org/10.1063/1.3516289> for thermal conductivity and electrical conductivity of f-TEG dispersed nanofluid in DI water (and EG) with respect to volume fraction for different temperatures are given in supplementary information (Figs. 1S, 2S, 3S, 4S).