Measurement of Thermal and Electrical Conductivities of Graphene Nanofluids

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Abstract The current work experimentally investigates the thermal and electrical conductivities of nanofluids containing graphene sheets that have very high thermal conductivity. Here, the graphene is prepared from natural graphite by oxidation-reduction process through a single step method. The graphene nanofluid thus obtained exhibited greater stability even after six months of preparation without addition of any surfactants. The detailed characterization process involving TEM, UV absorption and DLS measurements revealed the well dispersed nature of nanofluid with sheets appropriately interconnected and entangled. The DLS measurement indicates a trimodal size distribution of graphene sheet ranging from 5nm to 1500nm. It was also found that the absorption peak of the sample was 269 nm. This reveals the complete reduction of graphene oxide to graphene and the value is in good agreement with the literature. The thermal conductivity is measured using the traditional Transient Hot Wire (THW) method and enhancements are substantial even at lower concentrations while such behaviour is not predicted by the classical Maxwell theory. The thermal conductivity of graphene nanofluids are measured for different concentrations of 0.01 - 0.2 volume % at different temperatures. It is observed that the thermal conductivity increases with increase in concentration of grapheme, which is as expected. The maximum enhancement obtained is 27% at 0.2% concentration. The enhancement also shows a strong temperature dependence which is unlike that of its carbon predecessors like CNT and graphene oxide nanofluids. Electrical conductivity is measured using a 4 cell conductivity meter with inbuilt automatic temperature compensation. Electrical conductivity enhancement is found to be linear with increase in graphene volume fraction.

Keywords: Nanofluids, Dispersion, Transient hot wire measurements, Four cell conductivity meter

1. Introduction

In the pursuit of improving thermal conductivity of liquids for meeting the increasing cooling requirements posed by emerging high heat flux devices, suspensions of nano sized particles in liquids, known as nanofluids, have emerged as potential candidates. What makes a nano fluid different is its anomalous thermal conductivity enhancement reported in literature. In addition to the thermal properties, research has also been conducted on the fluid's electrical performance. Electrical conductivity of a nanofluid is related to the ability of charged particles in the suspension to carry the charges towards respective electrodes when an electric potential is applied. The presence of an Electrical Double Layer (EDL) plays an important role in the stability and dispersion of nano fluids as well as in charge transport. Nanofluids are a class of fluids having stable suspensions of nanoparticles, with sizes typically less than 100nm. Generally nanofluids are classified as: metallic, metal oxide, and carbon based nanofluids. They can also be distinguished based on the shapes- such as spherical, cylindrical and sheet type particles. So far, a large number of studies has been carried out on metallic and metal oxide nanofluids, where the particles are spherical and also on CNT based nanofluids, where the particles are cylindrical. However the decade long research in nanofluids has not come to a definitive conclusion that it is a perfect replacement to the existing coolants. Graphene

is a new entrant in nanofluids which has a two dimensional planar geometry. Graphene sheets have very high thermal conductivity, of the order of 5000W/mK, which is greater than that of CNT (2000 W/mK).

The history of nanofluids dates back to 1995 when Choi et al. (1995) coined the term nanofluids and observed that nanofluids can conduct heat more efficiently than the conventional fluids. There have been a number of research papers reporting the anomalous behaviour of nanofluids with a few contradicting the same. Lee et al. (1999) and Wang et al. (1999) initiated the nano-fluid heat transfer research, reporting thermal conductivity enhancements of 20% for CuO in EG, 12% for CuO in water and 10% for Al2O3 in water. The real breakthrough was from ANL group Eastman et al. (2001) reporting 40% enhancement with only 0.3% copper particles of 10nm size and Choi et al. (2001) reporting a phenomenal 150% increase in thermal conductivity of MWCNT-engine oil nanofluid with just 1% volume fraction of nanotubes. The finding of Das et al. in (2003) showing strong temperature dependence of nanofluids with Al_2O_3 and CuO particles as used by Lee et al. (1999) was a significant milestone in nanofluid research which improved the scope of nanofluid as an alternative for existing coolants. This was later confirmed by Chon et al. (2005) and Li et al. (2006). But the temperature effect on thermal conductivity enhancement of nanofluids was not observed in CNTs. Recently Yu et al. (2009) studied the thermal conductivity enhancement of graphene oxide nanofluids and found no temperature dependence of enhancement. . But the recent observation by Baby et al. (2010) in graphene nanofluid showed a strange behaviour of temperature dependent thermal conductivity enhancement unlike its carbon predecessors and a maximum of 64% enhancement.

Very few experimental investigations have been reported on the electrical conductivity of water based nanofluids. Ganguly et al. (2009) studied the change in electrical conductivity of alumina based fluids with particle fraction and temperature. It shows that electrical conductivity rises linearly with particle fraction, but remains almost constant with temperature. Modesto et al. (2010) observed a linear rise in electrical conductivity of TiO2 suspensions with particle fraction of low ionic strength and no significant impact for high ionic concentrations. Electrical and thermal conductivity of multiwalled-CNT based fluids have been studied by Glory et al. (2008) and electrical conductivity of graphene nanofluids by Baby et al. (2010). Fang et al. (2005) studied the electrical conductivity of gold (Au) nanoparticles in toluene and chloroform.

In this study, homogeneous stable well characterized graphene nanofluids were prepared, and the effects of particle volume fraction and temperature on thermal conductivity and effect of particle volume fraction on electrical conductivity were investigated to explore the temperature dependent behaviour of graphene nanofluids.

2.   Graphene   Synthesis   and Characterization

Since it is difficult to utilize mechanically exfoliated small graphene flakes for mass production of functional devices, there have been intense efforts to develop methods for synthesis of large-area, high-quality graphene. There are many synthetic routes to prepare graphene, such as micromechanical cleavage, intercalation, solvo-thermal synthesis and chemical vapour deposition. The chemical route to prepare graphene sheets in large quantities is followed here. The raw materials for bulk production of graphene sheets by the chemical method are usually graphite powders, and graphite is inexpensive. In addition, the chemical methods are versatile in terms of being well suited to chemical functionalization. Therefore, in this paper, the chemical method was applied to produce graphene nanosheets (GnS), which is well dispersed in water without any need of surfactants.

Graphene is prepared from natural graphite (sp1 hybridized, 30-μm nominal particle size) by oxidation-reduction process through one step method. The graphite sheet is first

exfoliated and oxidized to graphene oxide using Hummer's method. Later the oxide is reduced to water soluble graphene in three steps: 1) Pre-reduction 2) Sulfonation 3) Post reduction. Pre-reduction of graphene oxide with sodium borohydride at 80 °C for 1 hour removes the majority of oxygen functionality from graphene oxide. The stoichiometrically controlled sulfonation with the aryl diazonium salt of sulfanilic acid in an ice bath for 2 hours enables water solubility with minimal impact on the unique properties of graphene. Post reduction with hydrazine (100 °C for 24 h) removes any remaining oxygen group present. Thus a graphene nanofluid of required volume concentration is obtained and it was observed that the sample is very much stable even after 6 months of preparation without addition of any surfactants. This can be explained by sedimentation ratio, from Stokes-Einstein theory (1897), which is given by

$$v = \frac{2r_p^2 |\rho_p - \rho_m| g}{9\varepsilon_m}$$

(1)

Lower the value of sedimentation ratio higher the stability of the suspension. In this case the density of graphene is comparable to the density of water and the sedimentation ratio is close to zero. This results in the higher stability of the suspension.
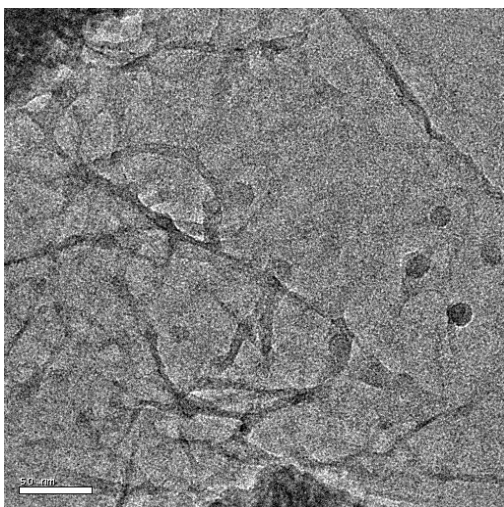

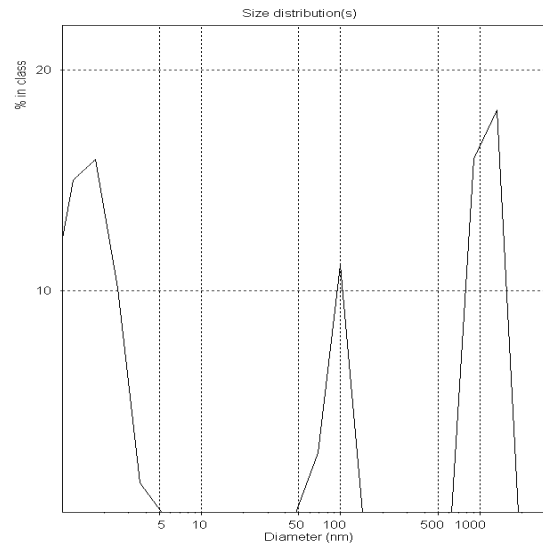Figure 1: TEM of graphene flakes

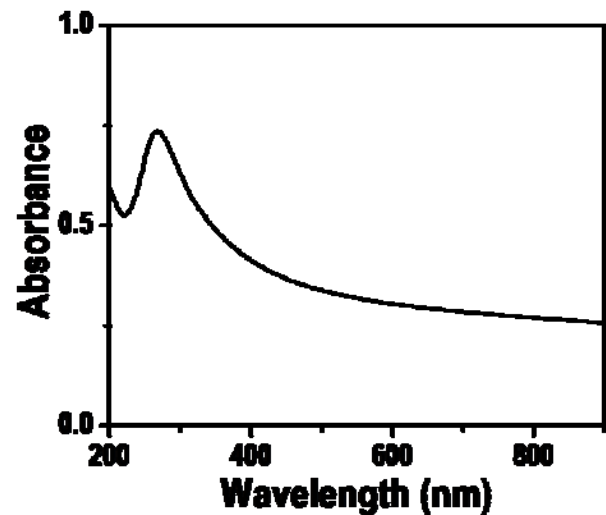
Figure 2: DLS measurement of graphene flakes

Figure 3: UV absorption spectrum of graphene flakes

The TEM images of graphene (Figure 1), reveals that the sheets are interconnected and entangled. This shows that the graphene is likely to form networks which might act as conduction paths. The Dynamic Light Scattering measurement indicates a trimodal distribution of size of graphene sheet (Figure 2) showing the presence of graphene sheet lengths from as low as 5nm to 1500nm. About 52% of the particles are in the size range close to 5nm, about 34% near 1500nm and the remaining in the range of 100nm.

In order to ensure the purity of graphene nanofluids, UV visible absorption spectrum

analysis is carried out (Figure 3). Absorption spectrum measurements are taken after the preparation of graphene nanofluids from graphene oxide. It was found that the absorption peak of the sample is 269 nm. The values are in good agreement with the absorption spectrum data of graphene in the literature24. Also the non existence of absorption peak at 229 nm which is that of graphene oxide ensures the complete reduction of graphene oxide to graphene.

3. Experimental method

3.1 Thermal conductivity measurement

Thermal conductivity was measured by the apparatus built on the principle of traditional transient hot-wire (THW) method in a temperature-controlled bath with operating limits 250C to 600C. In this method, a thin metallic wire is used as a line heat source as well as temperature sensor and it forms an arm of a Wheatstone bridge. The wire is surrounded by the liquid whose thermal conductivity is to be measured. The wire is then heated by sending current through it. Higher the thermal conductivity of the surrounding liquid, lower will be the temperature rise of the wire. This principle is used to measure thermal conductivity of the liquid. The experiment lasts for a maximum of 2 – 5 seconds and hence this is a very fast method. Also, within such small time duration, natural convection of liquid does not set in. In conjunction with an advanced electronic data acquisition system, the method gives a very accurate measurement of thermal conductivity. The experimental setup has been validated by measuring the thermal conductivity of de-ionized water, and the error in measurement is within 1.2%. Further details of the experimental setup can be found in Patel et al. (2010). The thermal conductivity measurements were carried out eight times for each sample of graphene nanofluid for temperatures between 300C and 500C in steps of 50C which ensured the repeatability of the experiment. The average value of measured thermal conductivity is reported in the paper.

3.2 Electrical conductivity measurement

The electrical conductivity is measured by a 4-Cell conductivity electrode meter (CYBERSCAN CON 11) with built in Automatic Temperature Compensation (ATC). The electrode meter gives both temperature and conductivity values simultaneously for the given instant. The conductivity (K) and the inverse of resistivity (R) are determined by using Ohm's law.

$$K = 1/R = I / V \qquad (2)$$

Since the charge on ions in solution facilitates the conductance of electrical current, the conductivity of a solution is proportional to its ion concentration. The accuracy for conductivity and temperature measurement is ± 1 % (Full scale + 1 digit) and the conductivity range is 19.9μS/cm to 199.9mS/cm.
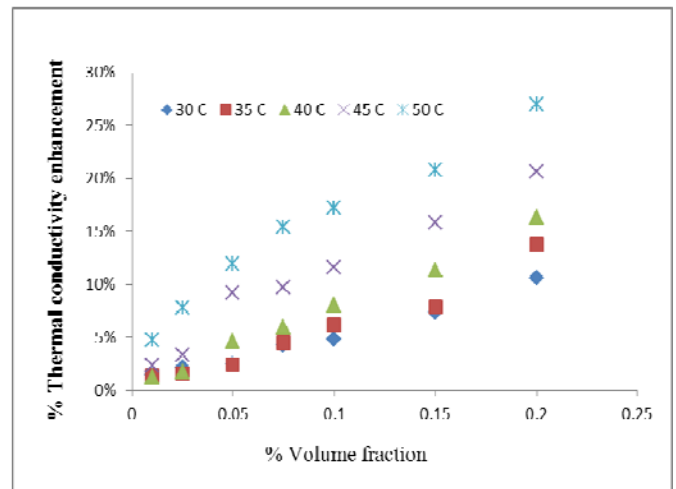

Figure 4: Thermal conductivity enhancement Vs volume fraction

4. Results

The dependence of thermal conductivity of graphene nanofluids on temperature and concentration has been investigated thoroughly. The thermal conductivity of graphene nanofluids shows enhancement which depends on concentration and temperature, which is unlike its carbon predecessors of graphene oxide and CNT nanofluids, where the thermal conductivity

does not vary significantly with temperature.

The importance of particle size is stressed in Das et al. (2003) where stochastic motion of nanoparticles is predicted and in Sastry et al. (2009) where aspect ratio of nanotube is identified as playing an important role to enhance thermal conductivity by the formation of chain like structures.

Figure 4 depicts the dependence of thermal conductivity of graphene nanofluids on concentration in the range 0.05 - 0.2 volume percentage at different temperatures. It is observed that the thermal conductivity increases with increase in concentration of graphene which is as expected. The maximum enhancement obtained was 27% at 0.2% concentration.

The thermal conductivity values were compared with effective medium theory by Maxwell where it is assumed that the particles are non-interacting. Figure 5 shows the thermal conductivity values compared at different concentrations with the Maxwell theory. It is observed that at lower concentration the Maxwell theory is able to predict the thermal behaviour but as the concentration increases it fails to do the same, which needs to be investigated.

The electrical property of the base fluid gets altered, when the nanoparticles are dispersed into the base fluid. It is observed that the electrical conductivity of graphene nanofluid increases linearly with volume fraction (Figure 6). The electrical conductivity of the base fluid (DI water) is measured as 6 x 10-6 S/cm. It can be seen observed that the electrical conductivity of water based nanofluid rises linearly with particle volume concentration. The dispersed nanoparticles in the fluid develop surface charges. Less availability of free ions in DI water produces a net charge density on the particles surface. Like charges repel each other and thus the particles are stable in the fluid. Surfactants are not added to the suspension. Thus the enhancement of electrical conductivity of water nanofluids with particle fraction is purely attributed to the presence of particles with electrical double layer.
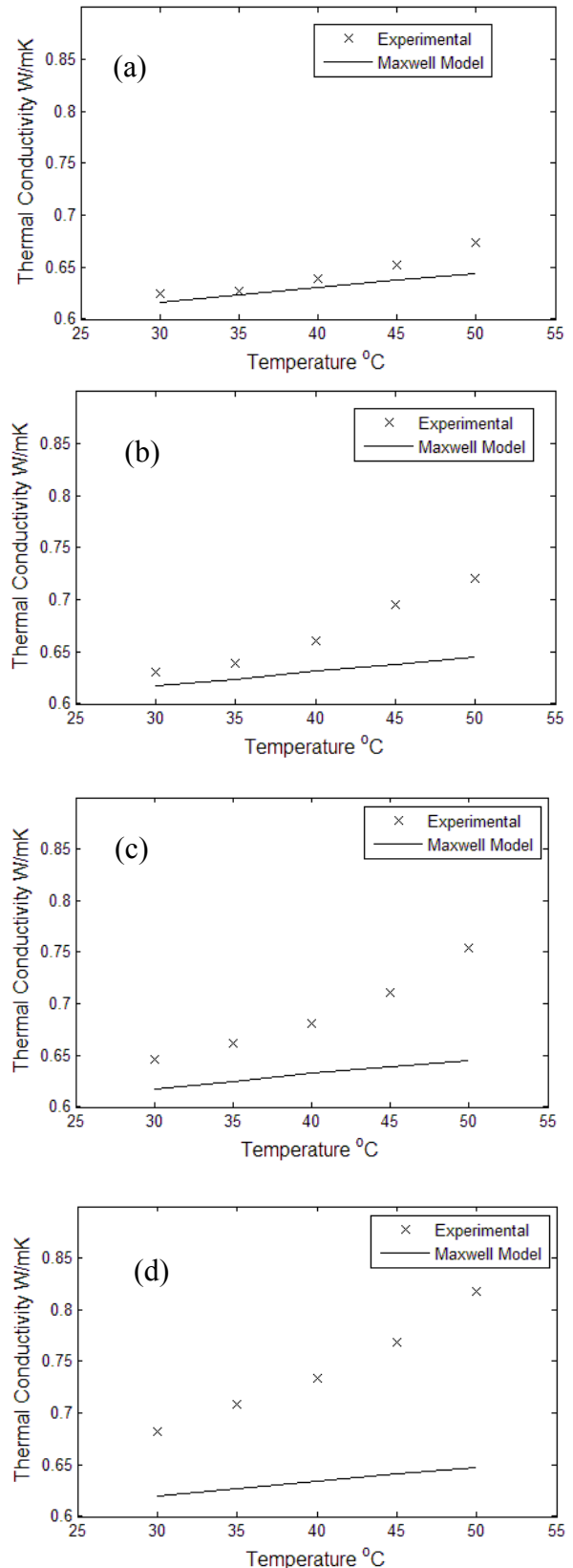

Figure 5: Comparison of experimental data with Maxwell model prediction at different concentrations (a) 0.01%, (b) 0.05%, (c) 0.1%, (d) 0.2%
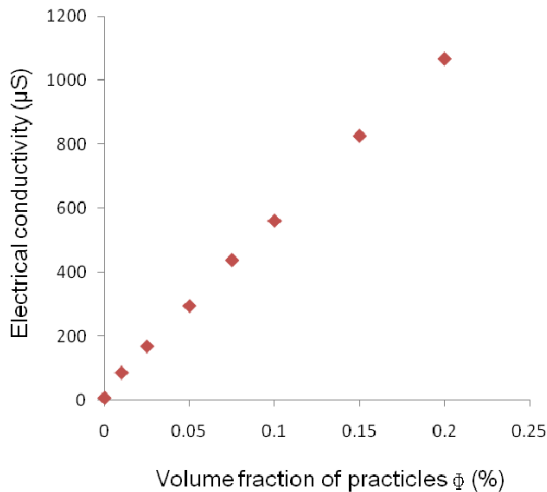
Figure 6: Variation of electrical conductivity
Vs volume fraction

5. Conclusions

Experiments have been performed to study the thermal and electrical properties of graphene nanofluids at various concentrations and temperatures. It is observed that the thermal conductivity of a graphene nanofluid increases with increase in volume concentration and has a strong temperature dependence, which is unlike its carbon predecessors of CNT and graphene oxide nanofluids. . It is also shown that there is a linear rise in electrical conductivity of graphene nanofluid with particle volume fraction which is similar to the trend observed in water based nanofluids.

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