A novel, eco-friendly technique for covalent functionalization of graphene nanoplatelets and the potential of their nanofluids for heat transfer applications

Rad Sadri, Maryam Hosseini, S.N. Kazi, Samira Bagheri, Nashrul Zubir, Goodarz Ahmad, Mahidzal Dahari, Tuan Zaharia

Department of Mechanical Engineering, Faculty of Engineering, University of Malaya, Kuala Lumpur 50603, Malaysia
Nanotechnology & Catalysis Research Centre (NANOCAT), IFS Building, University of Malaya, 50603 Kuala Lumpur, Malaysia
Department of Mechanical and Aeronautical Engineering, Clarkson University, Potsdam, NY 13699, USA

Abstract

In this study, a facile and eco-friendly covalent functionalization technique is developed to synthesize highly stable graphene nanoplatelets (GNPs) in aqueous media. This technique involves free radical grafting of gallic acid onto the surface of GNPs rather than corrosive inorganic acids. Raman spectroscopy, X-ray photoelectron spectroscopy and transmission electron microscopy are used to confirm the covalent functionalization of GNPs with gallic acid (GAGNPs). The solubility of the GAGNPs in aqueous media is verified using zeta potential and UV–vis spectra measurements. The nanofluid shows significant improvement in thermo-physical properties, indicating its superb potential for various thermal applications.

1. Introduction

In the last decade, the potential applications of nanoparticle aqueous suspensions with high effective thermal conductivity have gained considerable attention among the scientific community. More recently, there is remarkable enhancement in the thermo-physical and heat transfer properties of carbon-based nanofluids [1–4]. Among various carbon-based nanostructures, graphene nanomaterials are of practical interest because of their favorable thermal, electrical and mechanical properties which can be exploited for various applications [5–10]. Graphene nanoplatelets (GNPs) and nanofluids produced from GNPs are potential candidates for various applications including energy systems. GNPs aqueous suspensions can improve the thermal performance of heat transfer systems by enhancing the thermal conductivity of their conventional working fluids. In this regard, Wei Yu et al. investigated a thermal conductivity of nanofluids containing graphene sheets in ethylene glycol media and reported up to 86% enhancement for 5.0 vol.% graphene dispersion [11]. Moreover, Tessy Theres Boby and Ramaprabhu synthesized exfoliated graphene nanofluids with water and ethylene glycol as base fluids then investigated their thermal and electrical conductivities. They reported 14% enhancement in thermal conductivity for volume fraction of 0.056% at 25 °C with deionized water as base fluids [12]. However, the insolubility of graphene in solvents hinders chemical routes using GNPs. In general, GNPs are extremely hydrophobic and prone to aggregation due to strong p–p interactions and therefore, it is difficult to disperse GNPs homogeneously in aqueous or non-aqueous solvents. This greatly limits the applications of GNPs [13]. Hence, several surface modification techniques have been developed to enhance the stability of GNPs in aqueous and organic media via chemical and physical techniques which involve covalent and non-covalent functionalization of graphene [13]. The most common technique used to treat carbon nanomaterials involves processing of these nanomaterials into a mixture of concentrated sulfuric and nitric acids [14] followed by the functionalization process. However, the use of inorganic and strong acids is undesirable because they contribute towards environmental pollution. In addition, these techniques do not only release hazardous and toxic materials to the environment, but they may also have unfavorable effects on the GNP sheets. Hence, there is a need to develop an efficient, easy to use and environmentally friendly technique which will enhance the dispersion of GNPs in aqueous media, and this is an area that has attracted considerable attention.

Keywords:
Green functionalization
Graphene nanoplatelets (GNPs)
Eco-friendly synthesis
Thermal conductivity
Nanofluids

http://dx.doi.org/10.1016/j.cplett.2017.02.077
0009-2614/© 2017 Elsevier B.V. All rights reserved.
attention from the scientific community [15]. In this study, a facile, eco-friendly and non-corrosive technique is developed for covalent functionalization of GNPs for the first time using gallic acid (GA) to improve the solubility of GNPs in aqueous media. The technique proposed in this study involves free radical grafting of GA onto the surface of GNPs. This technique is particularly advantageous due to the non-toxic, non-corrosive and anti-oxidation properties of GA (GA is a natural antioxidant typically found in green tea, berries, grapes and wines [16]), as well as its stabilizing nature [17]. In order to verify the success of the functionalization method, the GNPs covalently functionalized with GA are characterized by Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), zeta potential and UV–vis spectra measurements. Following this, GAGNP-water nanofluid is prepared by dispersing 0.05 vol.% of covalently functionalized GNPs in distilled water (i.e. base fluid). The thermal conductivity, dynamic viscosity, specific heat capacity and density of the GAGNP-water nanofluid is measured with respect to variations in the fluid temperature to determine the potential of this nanofluid as a heat transfer liquid for thermal applications.

2. Materials and methods

In order to synthesize the covalently functionalized GNPs, 1 g of pristine GNPs (XG Sciences Inc., Lansing, Minnesota, USA) and 3 g of gallic acid (3,4,5-trihydroxybenzoic acid) (Sigma-Aldrich (M) Sdn. Bhd., Selangor, Malaysia) were poured into a vessel filled with 200 ml of distilled (DI) water and then stirred for 15 min at 80 °C to attain a homogeneous black suspension. Following this, 7 ml of concentrated hydrogen peroxide (30%) (Sigma-Aldrich (M) Sdn. Bhd., Selangor, Malaysia) was poured dropwise into the vessel as an initiator throughout the sonication time. The mixture was then ultrasonicated with a probe sonicator for 20 min. After sonication, the reaction mixture was heated at 80 °C under reflux condition for 12 h. The oxidized GNPs were centrifuged and washed several times with large amounts of DI water until the pH was neutral. The covalently functionalized sample (GAGNPs) was dried overnight in a vacuum oven set at 60 °C. The GAGNPs were much more soluble in water compared to the pristine GNPs, which was due to strong covalent functionalization. Fig. 1 shows the schematic diagram of the covalent functionalization of GNPs with GA. The significant enhancement in dispersion of the GAGNPs in water can be attributed to the miscibility of GA. The GAGNPs (0.05 vol.%) were sonicated in DI water for 15 min in order to synthesize the GAGNP-water nanofluid. Fig. 1 shows the proposed free radical grafting reaction of graphene nanoplatelet in aqueous media. In the initiation step, hydrogen peroxide (as a free-radical oxidizer that generates non-toxic by-products and leaves no chemical residue) at high temperatures becomes unstable and decomposes spontaneously into hydroxyl radicals [18]. These hydroxyl radicals will attack gallic acid and GNPs to produce free radicals on the gallic acid and GNPs structure, which leads to linkage of the activated molecules onto the surface and edges of GNPs. In addition, the hydroxyl radicals can attack the GNPs directly, leading to formation of hydroxyl groups on the surface of GNPs [14]. Experimental apparatus details are described in the supplementary material.

3. Results and discussion

Raman spectroscopy was used to provide insight on the covalent functionalization of GNPs with GA and the results are shown...
in Fig. 2(A). It can be observed from the Raman spectra that both pristine GNPs and GAGNPs have D, G and 2D band at a wavenumber of 1342, 1574 and 2713 cm\(^{-1}\) respectively. The blue shift in G and 2D band of GAGNPs is related to a sufficient concentration of defects [19]. The G band is associated with graphitic carbon (sp\(^2\)) whereas the D band is associated with amorphous or disordered carbon (sp\(^3\)). The increase in the Raman intensity ratio \((I_D/I_G)\) is due to changes in the hybridized carbon from sp\(^2\) to sp\(^3\) as a consequence of covalent functionalization. The \((I_D/I_G)\) ratio is found to be 0.64 and 0.74 for the pristine GNPs and GAGNPs, respectively.

![Raman spectra and XPS spectra](image-url)

**Fig. 2.** (A) Raman spectra and (B) wide-scan O1s and C1s XPS spectra for pristine GNPs and GAGNPs.

![C1s and O1s XPS spectra](image-url)

**Fig. 3.** C1s XPS spectra for (A) pristine GNP and (B) GAGNP, and O1s XPS spectra for (C) pristine GNP and (D) GAGNP.
The higher ID/IG ratio obtained for the GAGNPs is attributed to the higher number of sp³ carbons present and the occurrence of electrophilic addition reaction. The Raman spectra can be considered as one of the solid proofs in examining the covalent functionalization of GNPs. Raman spectroscopy can distinguish a single layer from a few layers by focusing on the shape, size, and intensity of the 2D bands, as the layer of graphene increased, the 2D band becomes much smaller and broader. A single, sharp 2D peaks of GAGNPs compare with GNPs can verify the presence of single layered- or few layered-graphene [20]. Full Raman spectra analysis data is given in Table S1 of the Supplementary material.

X-ray photoelectron spectroscopy (XPS) was used to examine the surface of the graphene sheets before and after covalent functionalization with GA. The wide-scan O1s and C1s XPS spectra for pristine GNPs and GAGNPs are shown in Fig. 2(B). The peaks at a binding energy of 284.6 and 533 eV were generated by photoelectrons emitted from the C1s and O1s core level, respectively. The oxygen-to-carbon (O/C) ratio increases from 0.04 (pristine GNPs) to 0.14 (GAGNPs) [21], indicating that the free radical grafting of GNPs was successful in oxidizing amorphous carbon impurities and grafting different oxygen functional groups onto the GAGNPs. Full XPS analysis data is given in Table S2 of the supplementary material.

Fig. 4(A) and (B) shows the transmission electron microscopy (TEM) image of the pristine GNPs and GAGNPs, respectively. It can be seen from Fig. 4(A) that the GNP flakes have a relatively smooth surface as well as edges. In contrast, the surface of the GAGNP sheets appears rough with the presence of wrinkles and defects, particularly at the edges, as a consequence of covalent functionalization with GA, as evidenced from Fig. 4(B). The surface wrinkles can be attributed to the inherent instability of the two-dimensional structures and improved flexibility of the GNP flakes during the functionalization process which involves ultrasonication and heat.

Fig. 4(C) shows the measured zeta potential values of the GAGNP-water nanofluid as a function of pH. It can be seen that the GAGNP-water nanofluid has high negative zeta potential values (−30.6 to −50.7 mV) within a pH of 3.10–9.69, which are far

![Fig. 4. (A, B) TEM images of pristine GNPs and GAGNPs, (C) zeta potential values of GAGNP-water nanofluid as a function of pH, and (D) colloidal stability of GAGNPs dispersed in DI water.](image-url)
from the isoelectric point (i.e., point of zero charge). This indicates that the GAGNP-water nanofluid has strong electrostatic repulsion forces within this pH range and resists aggregation via non-covalent interactions such as π-π interactions or H-bonding. This property can be attributed to the oxygen functionalities at the surface of the GNPs. The GAGNP-water nanofluid is stable when the pH is more than 3.1. The zeta potential value of the nanofluid is around ∼30.6 mV at this pH. The results indicate that the GAGNP-water nanofluid is stable even in slightly acidic conditions.

In highly acidic solutions (pH < 3.1), the GAGNP-water nanofluid tends to aggregate and undergoes intermolecular dehydration catalyzed by H⁺, which leads to the coupling of GNPs via ether linkages. It can be clearly seen from Fig. 4(C) that the GAGNP-water nanofluid becomes more stable upon the addition of alkali, which leads to the generation of additional negative charges in the nanoparticles.

Fig. 4(D) shows the colloidal stability of the aqueous suspensions with respect to the number of the days after preparation. It is clear that the relative concentration of the nanofluids reduces with the number of days. However, the nanofluids have a fairly constant concentration after Day 34. The maximum magnitude of sedimentation is ∼10%, which confirms the colloidal stability of the nanofluids containing GAGNPs.

The effective thermal conductivity and dynamic viscosity of the GAGNP-water nanofluid (GNP concentration: 0.05 vol.%) and DI water (base fluid) were measured experimentally and the results are shown in Fig. 5(A) and (B), respectively. The thermal conductivity data for DI water obtained from the National Institute of Standards and Technology (NIST) database was also plotted in Fig. 5(A) for comparison and it is evident that there is excellent agreement between the measured thermal conductivity and those obtained from the NIST database [25], with an error less than 1%. In addition, it is apparent from Fig. 5(A) that the thermal conductivity of the GAGNP-water nanofluid is significantly higher than that for DI water and the thermal conductivity increases with an increase in the fluid temperature. This thermal conductivity enhancement is due to the Brownian motion of the nanoparticles suspended in the base fluid [26]. The maximum thermal conductivity enhancement for the GAGNP-water nanofluid (containing 0.05 vol.% GAGNPs) is 24.18% at 45 °C. It can be seen from Fig. 5(B) that the effective viscosity of the GAGNP-water nanofluid is only slight higher than that for DI water. The viscosity of the GAGNP-water nanofluid and DI water decreases with an increase in the fluid temperature. This decreasing trend is due to weakening of the intermolecular forces with increasing fluid temperature [26]. The minor difference in dynamic viscosity between the GAGNP-water nanofluid and DI water is an important advantage of the GAGNP-water nanofluid since a high dynamic viscosity will result in increased pumping power and this will undermine the overall positive impact of thermal conductivity enhancement [27]. The density of the GAGNPs aqueous suspensions and DI water also measured as a function of temperature and the data is shown in Fig. 4(C). It is clear that the density of the GAGNPs nanofluid and base fluid decreases slightly with increasing temperature, which is due to the thermal expansion of the liquid. The density of the nanofluid decreases by approximately 0.6% when the temperature

![Variation of (A) thermal conductivity, (B) dynamic viscosity, (C) density, and (D) specific heat capacity for the GAGNPs aqueous suspensions and DI water (base fluid) as a function of temperature.](image-url)
increases from 20 °C to 40 °C. There is also a small increase in the density of the GAGNPs aqueous suspension compared to that of DI water. In addition, it can be seen from Fig. 4(D) that the specific heat capacity of the GAGNPs colloid and base fluid increases in response to the increase in fluid temperature. The slope is similar for both of the specific heat capacity curves, which conform to the findings of Pak and Cho [28].

4. Conclusion

A simple, eco-friendly technique is proposed in this study to covalently functionalize graphene nanoplatelets (GNPs). This technique involves free radical grafting of gallic acid onto the GNP sheets in order to enhance the dispersion of GNPs in aqueous media. The success of the covalent functionalization process is verified using Raman spectroscopy, X-ray photoelectron spectroscopy and transmission electron microscopy. Based on the UV–vis absorption spectra, the GAGNP-water nanofluid has remarkable stability over the course of 63 days. Zeta potential measurements provide additional proof of the hydrophilic functionalized groups in the GAGNPs. One of the key findings of this study is the superior thermal conductivity enhancement (i.e. 24.18% at 45 °C) over the base fluid obtained for the GAGNP-water nanofluid which contains only a low loading of nanoparticles (0.05 vol%) in the base fluid. Another key finding is that the viscosity of the low volume concentration of GAGNP-water nanofluid is close to that of distilled water, which is highly desirable since a high fluid viscosity will result in increased pumping power. This novel, facile and eco-friendly functionalization method can pave the way for mass production of hydrophilic GNPs which can be used for various thermal applications.

Acknowledgment

The authors gratefully acknowledge the financial support provided by University of Malaya under the University of Malaya Research Grant Scheme (Project no.: GC001D-1AET) and Fundamental Research Grant Scheme (Project no.: FP060-2015A). The authors also appreciate the assistance provided by the technical and administrative staff of Faculty of Engineering, University of Malaya, in carrying out this study.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cplett.2017.02.077.

References