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Nanofluid based on activated hybrid of biomass carbon/graphene oxide: Synthesis, thermo-physical and electrical properties☆

Hooman Yarmand *, Samira Gharehkhani *, Seyed Farid Seyed Shirazi, Ahmad Amiri, Elham Montazer, Hamed Khajeh Arzani, Rad Sadri, Mahidzal Dahari, S.N. Kazi *

Department of Mechanical Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia

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ABSTRACT

In the present study a mixture of empty fruit bunch (EFB) fiber as a matrix material and graphene oxide (GO) as a guest was activated by processing with KOH. The structural characterization was performed by various techniques such as field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), X-ray diffraction (XRD) and Raman. The as-synthesized hybrid containing activate carbon/graphene (ACG) was dispersed in ethylene glycol (EG) at various mass fractions in order to evaluate the thermo-physical and electrical properties such as thermal conductivity, electrical conductivity, viscosity, density and specific heat capacity of the suspensions at different temperatures. Thermal conductivity of ACG dispersed in EG based nanofluid shows an enhancement of 6.47% at 40 °C and weight fraction of 0.06%.

1. Introduction

Suspension of nanoparticles in a "conventional" working fluid such as water or ethylene glycol is a promising alternative heat exchanging liquid to enhance heat transfer which is called "nanofluid" [1]. In the recent decade researchers have been found that adding nanoparticles to a working fluid introduces a very significant alteration in its thermo physical properties [2–4]. Some remarkable increase in the thermal properties of nanofluid such as thermal conductivity and convective heat transfer capability is due to the positively altered thermal properties of nanoparticles in comparison to the conventional fluid. Nanoparticles can be either metal oxide [5–7] such as Al_2O_3, CuO, ZnO and TiO_2 [8–12] or carbon based particles like carbon nanotube (CNT) [13–16], graphene oxide (GO) [17] and graphene nanoplatelets (GNP) [18,19].

Recently many researchers have been interested to use various types of carbon based nanoparticles such as single-wall and multi wall carbon nanotube [20], graphite [21], graphene [22] and graphene oxide [23,24] to make nanofluids since they are often acknowledged as a miracle nanoparticle which have a large aspect ratio and have very wonder mechanical, thermal and chemical properties. Because of superior thermal conductivity of carbon based nanoparticle, their nanofluids represent extremely higher thermal performance such as heat transfer coefficient and thermal conductivity [25].

Most of earlier researchers worked on a single phase nanoparticle for enhancing thermal conductivity and heat transfer coefficient of working fluid [26]. Recently nanocomposite based nanofluids has become an interesting topic. Generally synthesization of at least two different nanoparticles is named "nanocomposite". Sundar et al. [27] synthesized MWCNT–Fe_3O_4 nanocomposite and prepared hybrid nanofluid and achieved 29% improvement in thermal conductivity with 0.3% volume concentration in the water at a temperature of 60 °C. Baby and Sundar [28] synthesized and prepared hybrid CuO–HEG nanofluid and obtained 28% enhancement in thermal conductivity at 0.05% volume concentration of functionalized graphene without any surfactant. They also reported [29] an enhancement of 8% in thermal conductivity for a volume fraction of 0.04% at 25 °C for Ag/MWCNT–HEG hybrid nanofluids. Amiri et al. [30] investigated the rheological properties of MWCNT–Ag nanocomposite by using covalent and noncovalent functionalization method and found that the covalent procedure is more appropriate for the thermal behavior of nanofluid. New research indicates that graphene nanofluids could provide higher thermal conductivity enhancement in comparison to other tested nanofluids [31]. Graphene particles have better thermal conductivity and also higher mechanical strength, and electrical conductivity. However graphene based materials are acceptable for nanofluid applications, and synthesis of graphene in large batch is difficult and high cost. Moreover, limitation in the surface area of graphene despite its high theoretical surface area (2630 $m^2\ g^{-1}$) reduces its positive points in practice. By considering these facts, it could come to one's mind that the use of graphene as a guest material in an amorphous carbon material could be more efficient and augments the electrical conductivity and thermal conductivity of the composite.

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* Corresponding authors.
E-mail addresses: hooman_yarmand@yahoo.com (H. Yarmand), s_gharahkhani_248@yahoo.com (S. Gharehkhani), salimnewaz@um.edu.my (S.N. Kazi).

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In the present work, for the first time the authors have introduced a 3-D spongy-like structured composite containing carbon derived from the agricultural waste materials and graphene which was synthesized via the simultaneously activation processes. This green, low cost, facile and effective approach was employed to prepare an activated carbon/graphene composite (ACG) which can be served as an extraordinary material for thermal applications. After that ACG–EG nanofluids were made by dispersing the nanocomposite material in pure ethylene glycol. The purpose of the present study is to measure experimentally the thermal conductivity, viscosity, density and specific heat capacity of ACG/EG nanofluids. There has been no remarkable reported investigation on the preparation and rheological property of ACG/EG dispersed nanofluids.

2. Experimental

2.1. Materials

Graphite flakes were purchased from Ashbury Inc. and the rest of the chemicals and materials such as nitric acid (HNO_3), sulfuric acid (H_2SO_4), phosphoric acid (H_3PO_4, 98%), potassium permanganate ($KMnO_4$, 99.9%), hydrogen peroxide (H_2O_2, 30%), hydrochloric acid (HCl, 37%), potassium hydroxide (KOH) and ethylene glycol (EG, 98%) were purchased from Sigma–Aldrich Co., Selangor, Malaysia. The EFB fibers were prepared from the Forest Research Institute of Malaysia.

2.2. Materials synthesis

GO was prepared using graphite flakes by a simplified Hummer's method [32]. Typically, graphite flakes (1 g) were mixed with 120 mL of H_2SO_4 and 13 mL of H_3PO_4 at room temperature. After that, 6 g of KMnO4 was gradually added to the mixture. After 3 days of continuous stirring, the mixture was diluted with 250 mL of ice water. Afterward, H_2O_2 was added until the gas evolution ceased. The suspension was then washed with HCl (1 M) and deionized water until the pH of the solution reached 5. Finally, the product (GO) was separated from the solution using a centrifuge.

A simple heat treatment rout was adopted to produce the final sample. The carbon was prepared via pyrolysis of empty fruit bunch (EFB) fiber at 500 °C with 10 °C/min increment within 2 h in N2 atmosphere. The acceptable tiny powders of carbon were prepared by ball milling (5 min). The GO (3 wt.% of carbon) dispersed in distilled water (50 ml) by sonication for 30 min. GO and carbon samples were added to two beakers containing 100 mL aqueous KOH solution separately and were stirred for 2 h (500 rpm). The mass ratio of KOH/carbon and KOH/GO was 4:1. The carbon sample and GO sample were mixed together, and stirred for 3 h and finally dried at 50 °C. The mixture was put in a ceramic boat and placed in a tube furnace. The mixture was heated at a rate of 5 °C up to 430 °C under N_2 flow and held for 30 min, after that heated up to 800 °C and retained for 75 min. The obtained nanocomposite was washed with distilled water and HCl (0.1 M) several times to remove the impurities and then dried at temperature of 60 °C. This sample was denoted as ACG and used to make a nanofluid.

Since ACG nanocomposite is naturally hydrophobic, it cannot be dispersed in any polar solution like EG. Functionalization by acid treatment is a suitable way to ensure the proper dispersion of ACG in EG. Acid treatment process was performed by dispersing ACG in a 1:3 ratio of HNO_3 and H_2SO_4 solution (strong acid medium) for 3 h under bath-ultrasonication. After 3 h, ACG nanopowder was washed several times with DI water and then dried in an oven at the temperature of 70 °C for more than 24 h. The prepared ACG functionalized sample was used in the next step to make nanofluids at different concentrations. A calculated amount of ACG was dispersed in the EG by ultrasonication. The optimized ultrasonication time was 45 min. The nanofluids prepared by the above mentioned method were stable and no sedimentation of particles was found up to 24 h.

2.3. Experimental techniques

To investigate the morphological characteristics of the sample, the field emission scanning electron microscopy (FESEM,) and transmission electron microscope (TEM) analyses were performed by SU 8000 (Hitachi) and HT 7700 (Hitachi) respectively. For the TEM analysis the sample was prepared by ultrasonically dispersing the material in ethanol prior to collection on carbon coated copper grids.

Phase compositions were determined by using an X-ray diffractometer (XRD, EMPYREAN, PANALYTICAL, the Netherlands) with Cu–Kα radiation over a 2θ range from 10° to 70°. The "PANalytical X'Pert HighScore" software was employed to compare the XRD profiles with the standards compiled by the Joint Committee on Powder Diffraction and Standards (JCPDS). Raman spectra data were collected by using a Renishaw Invia Raman Microscope with laser excitation at 514 nm.

As mentioned earlier, nanofluids are prepared by dispersing a specific amount of ACG nanocomposite in EG. Thermal conductivities of the nanofluids were measured by the KD-2 pro device (Decagon, USA) where KS-1 probe sensors were used having 6 cm and 1.3 mm length and diameter, respectively. The accuracy of the measured thermal conductivity is 5%.To ensure the equilibrium of the nanofluids, an average of 16 measurements were recorded during 4 h for each temperature and weight concentrations. Calibration of instrument with DI water was performed before starting of the measurements of nanofluids. The thermal conductivity of DI water at 30 °C was measured and a value of 0.61 W/mK was found, which is in agreement with the previous investigations [33,34]. The electrical conductivity measurements of the samples were measured by conductivity meter (AB 200, Fisher scientific, USA). The viscosity of EG and ACG/EG hybrid nanofluids was measured by a rheometer (Physica, MCR, Anton Paar, Austria). The rotational rheometer consists of a moving cylindrical plate and a stationary cylindrical surface which are parallel with a small gap. The densities of EG and hybrid nanofluids were measured experimentally by Mettler Toledo DE-40 density meter. The accuracy of density measurement is 10^{-4} g/cm^3. For each temperature and sample the measurements were recorded 3 times. Specific heat capacities of the base fluid and the hybrid nanofluid were measured with a differential scanning calorimeter (DSC 8000, Perkin Elmer, USA) with an accuracy of ±1.0%.

3. Results and discussion

3.1. Material characterization

Fig. 1 (a and b) shows the FESEM images of AC and ACG respectively. The image presents an appropriate contribution of GO in the carbon structure which is confirmed further by TEM image (Fig. 1 (c)). Moreover the chemical composition of the ACG sample is presented in Table 1.

Raman and XRD analysis of the carbon materials are two powerful methods for structural characterization. The XRD analysis results for AC and ACG are shown in Fig. 2(a). The samples exhibit a very weak and broad peak in the range of 20°–30°, indicating that the samples are in amorphous state. The Raman spectra of ACG and AC are presented in Fig. 2(b). The Raman spectra of the prepared sample display the D-band at ~1340 cm^{-1} and the G-band at ~1598 cm^{-1}. One of the important parameters in the Raman studies is the peak intensity ratio of the D and G bands, (I_D/I_G) which is attributed to the disordered crystal structures of the carbon. The I_D/I_G value is 0.51 for ACG, and 0.36 for AC.

3.2. Nanofluid properties

3.2.1. Thermal and electrical conductivity

The thermal conductivity of three different ACG/EG weight percentage nanofluid samples is measured in the range of 20 °C to 40 °C temperature. Low values of weight percentage are selected to avoid increase of effective viscosity and sedimentation. Fig. 3(a) presents the