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Study of synthesis, stability and thermo-physical properties of graphene nanoplatelet/platinum hybrid nanofluid☆

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ABSTRACT

In the present study a new synthesis method has been introduced for the decoration of platinum (Pt) on the functionalized graphene nanoplatelet (GNP) and also highlighted the preparation method of nanofluids. GNP–Pt uniform nanocomposite was produced from a simple chemical reaction procedure, which included acid treatment for functionalization of GNP. The surface characterization was performed by various techniques such as XRD, FESEM and TEM. The effective thermal conductivity, density, viscosity, specific heat capacity and stability of functionalized GNP–Pt water based nanofluids were investigated in different instruments. The GNP–Pt hybrid nanofluids were prepared by dispersing the nanocomposite in base fluid without adding any surfactant. The examined nanofluids were stable and no significant sedimentation was observed for a long time (22 days). Thermal conductivity of GNP–Pt nanocomposite dispersed in distilled water nanofluids shows an enhancement of 17.77% at 40 °C and 0.1% weight concentration.

1. Introduction

Dispersion of nanoparticles in a "conventional" working fluid like water or ethylene glycol is performed to manufacture a capable alternative working fluid for improved heat transfer which is named as "nanofluid" [1]. In the new decade researchers have found that adding nanoparticles to a working fluid makes a very remarkable change in its thermo physical properties [2–5]. Some notable enhancement in the thermal properties of nanofluid such as thermal conductivity and convective heat transfer ability is owing to the positively modified thermal properties of nanoparticles in comparison to the conventional fluid. Nanoparticles can be either metal oxide such as Al_2O_3, CuO, ZnO and TiO_2 [6–14] or carbon based particles such as carbon nanotube (CNT) [15–18], graphene oxide (GO) [19,20] and graphene nanoplatelets (GNPs) [21–24].

Currently many scientists have been focused on several kinds of carbon based nanoparticles such as single-wall and multi wall carbon nanotubes [25], graphite [26], graphene [27,28] and graphene oxide [29–31] to prepare nanofluids since they are often known as miracle nanoparticles which have large aspect ratio and have enhanced thermal, mechanical and chemical properties. Since carbon based nanoparticles have superior thermal conductivity, their nanofluids represent extremely enhanced thermal performances such as thermal conductivity and heat transfer coefficient [32].

Majority of the preliminary researches have been conducted on single phase nanoparticle for improving thermal conductivity and heat transfer coefficient of heat exchanging fluid. Lately nanocomposite based nanofluids have become an interesting topic. Synthesis of at least two different nanoparticles into one has been called "Nanocomposite". Sundar et al. [33] had synthesized MWCNT-Fe_3O_4 nanocomposite and prepared hybrid nanofluid where they obtained 29% improvement in thermal conductivity at 0.3% volume concentration in the water at a temperature of 60 °C. Baby and Sundar [34] synthesized 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 [35] an enhancement of 8% in thermal conductivity at a volume fraction of 0.04% and at 25 °C for Ag/MWCNT-HEG hybrid nanofluids. Amiri et al. [36] investigated rheological properties of MWCNT–Ag nanocomposite by using covalent and noncovalent functionalization method and found the covalent procedure is more appropriate for stable thermal behavior of nanofluid. Recent research establishes that graphene nanofluids could provide higher thermal conductivity enhancement in comparison to

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other examined nanofluids [37]. Graphene particles have better thermal conductivity and also higher mechanical strength, and electrical conductivity. However graphene based materials are acceptable for nanofluids applications, since the graphene nanoplatelets is hydrophobic in nature, functionalization method employed in order to make stable suspension of graphene based nanofluids. Functional groups decrease the high theoretical surface area ($2630\ m^2\ g^{-1}$) of graphene and reduces its positive effects in practice. By considering these facts, one could realize that use of platinum as a guest material in GNP nanoparticle could be more efficient and helpful in enhancement of thermal conductivity of the nanocomposite.

In the present work, GNP–Pt nanocomposite powder is synthesized by chemical reaction process. GNP was functionalized by acid treatment method and further decorated with Platinum. After that GNP–Pt/water hybrid nanofluids were synthesized by dispersing the nanocomposite materials in distilled water. The purpose of the present study is to measure experimentally the thermal conductivity, viscosity, density and specific heat capacity of GNP–Pt/Water nanofluids. There has been no reported investigation on the preparation, stability, and thermophysical property of GNP–Pt dispersed nanofluids.

2. Experimental

2.1. Materials

Graphene nanoplatelet (GNP) with purity ~99.5%, maximum particle diameter of 2 μm and specific surface area of 500 m^2/g was purchased from, XG Sciences, Lansing, MI, USA. The rest of the chemicals such as potassium tetrachloroplatinate II (K_2PtCl_4), nitric acid (HNO_3), sulphuric acid (H_2SO_4) and sodium borohydride ($NaBH_4$) were purchased from Sigma-Aldrich Co., Selangor, Malaysia.

2.2. Materials synthesis

Since GNP is not naturally hydrophilic and it cannot be dispersed in polar base fluid such as distilled water. Functionalization by acid treatment is an appropriate method to make it hydrophilic. This functionalization process helps to introduce functional groups such as hydroxyl and carboxyl groups on the surface of GNP. Acid treatment process was conducted by dispersing GNP in a 3:1 ratio of H_2SO_4 and HNO_3 solution (strong acid medium) for 3 h under bath-ultrasonication. After 3 h, GNPs were washed several times by DI water and then dried in an oven at the temperature of 70 °C for more than 24 h. The functionalized GNPs were then decorated with platinum by a chemical reaction process. The brief procedure of synthesis is stated here for reference. The functionalized GNP (30 mg) was dispersed into 10 mL of distilled water. This process was continued by the addition of 0.035 M K_2PtCl_4 to the dispersed functionalized GNP suspension with continuous stirring for 2 h at room temperature, then 2 mL of sodium borohydride (0.1 M) was added to the solution drop wisely at 60 °C. The irradiation of final solution was done under vigorous stirring for 4 h. Then GNP–Pt nanocomposites were collected after centrifuge at 11,000 rpm for 40 min. The obtained composite was washed well with distilled water several times to remove reactants. The prepared rich sample was used in the next step to prepare nanofluids at different concentrations by adding specific amounts of distilled water. The resulting nanofluids were stable and the sedimentation of GNP–Pt hybrid nanofluid was less than 5.7% after 22 days. Fig. 1 shows the schematic of molecular structure of synthesized GNP–Pt nanocomposite.

2.3. Experimental techniques

To explore the morphological characteristics of the sample, the Transmission electron microscope (TEM) and field emission scanning electron microscopy (FESEM,) analyses were performed by SU 8000 (Hitachi) and HT 7700 (Hitachi) respectively. For 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) with Cu–Kα radiation over a 2θ range from 20° 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).

As stated before, nanofluids are prepared by dispersing specific amount of GNP–Pt hybrid nanocomposite in distilled water. Thermal conductivities of nanofluids were measured by the KD-2 pro instrument (Decagon, USA), where KS-1 probe sensors of diameter 6 mm and 1.3 cm length were used. The accuracy of the measured thermal conductivity is 5%. To ensure the equilibrium of nanofluids, an average of 16 measurements were recorded for 4 h for each temperature and weight concentrations. Calibration of instrument with DI water was performed before starting of the measurements of thermal conductivities of the nanofluids. Thermal conductivity of DI water at 30 °C was measured as 0.61 W/mK, which is in agreement with the previous investigations [38,39]. The viscosity of base fluid and GNP–Pt hybrid nanofluids was measured by 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 between them. The densities of distilled water and hybrid nanofluids were measured by Mettler Toledo DE-40 density meter. The accuracy of the measured density is $\pm 10^{-4}\ g/cm^3$. For each of the sample and temperature the measured data were recorded 3 times. Specific heat capacities of the base fluids and the hybrid nanofluids 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. 2 shows the XRD patterns of Pt coated GNP. The peak at around 26.6° represents the structure of GNP. The XRD profile of the sample shows three diffraction peaks at 40°, 46.5° and 67.8°, which are attributed to the (111), (200) and (220) lattice planes of cubic Pt (JCPDS card no. 00-001-1194). XRD patterns confirm that no unexpected reaction happened during acid treatment, chemical reduction and Pt coating processes. Moreover it can be clearly concluded that Pt nanoparticles has been successfully decorated on the GNPs.

The morphological characterizations of the Pt coated GNP nanopowders are presented in Fig. 3. The uniform distribution of Pt attachment on the graphene sheets can be noticed in FESEM image (Fig. 3). Pt nano-particles attachment with GNP can be the evidence of a successful acid treatment ensuring reduction of functional groups which finally provides appropriate uniform attachment of Pt on GNP sheets.

Fig. 4 shows the TEM image of Pt coated GNP sheet. The uniformity of Pt nano-particles distribution due to proper functionalization of GNP is more visible in TEM images. From the image it could also be figured out that the wrinkled surface and folding at the edges of GNP sheets are produced during the acid treatment and the attachment of Pt particles.

3.2. Stability

The uniformity of nanoparticles dispersion in water could be observed by a UV–visible Spectrophotometer which could correlate the absorbance with the homogeneity of suspension. Fig. 5(a) illustrates the UV–vis spectrum of the functionalized GNP–Pt based water nanofluids. UV–vis spectroscopy is generally considered for the investigation of the stability of the coolant and the sedimentation with time as estimated from the change of absorbance of the suspension with time. According to the Beer–Lambert's law, the absorbance of a solution is