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An experimental investigation of the physical properties of the graphene/multi-walled carbon nanotubes composite

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ABSTRACT

In this present work, the physical characteristics of the graphene/MWCNTs composite have been studied. Surface modification has been done by grinding process and acid treatment where planetary ball milling (PBM) machine for grinding in aqueous circumstance and a mixture of HNO_3 and H_2SO_4 for acid treatment have been executed. Though, there are many researches of GN and MWCNTs nanoparticles based on individually as well as combined with other nanoparticles have been accomplished, reports on the combination of these two nanoparticles are negligible. In this paper, IR thermography, morphological and structural characteristics of modified GN–MWCNTs by field emission scanning electron microscopy, Raman spectroscopy and dispersibility analysis by sedimentation, UV–Vis spectroscopy, electric conductivity and thermal conductivity measurements have been presented in order to report the characteristics of GN/MWCNTs composite. Acid treatment as well as wet grinding of GN/MWCNTs composite at 500 rpm for 2 h gives the highest thermal conductivity enhancement which is 4.29% at 40 °C.

1. Introduction

Nanoparticles based fluid with a high thermal conductivity enhancement [1] is potentially applicable in the heat sink applications such as heat exchangers, evaporators and industrial cooling applications [2]. In order to get more stable suspensions [3,4], within a few years, many researches and projects have been conducted based on the advantages of nanofluids compared with those fluids containing millimeter or micrometer size particles [3] in base fluid. In this field of investigation, since their discovery, both graphene (GN) and carbon nanotubes (CNTs) have been promising reinforcements for nanofluids due to their exceptional mechanical and physical properties. It is well known that graphene (GN) has two-dimensional extended honeycomb network of sp^2 hybridized carbon atoms [5], excellent mechanical and chemical properties [6], high electron mobility [7], high thermal conductivity (5000 W/m K) [8] and twice particular surface area compared with SWCNTs [9]. On the other hand, carbon nanotubes (CNTs), first experimental observation were made in the early 1990s [10,11], have attracted great interest for their some extraordinary properties such as one of the lightest [12], strongest [13], stiffest [13], electrically conductive [14] nanoparticles with high thermal conductivity (3500 W/m K) [15], have very large aspect ratio [16], have mobilities in excess of 100,000 cm^2/Vs [17], current carrying capacity of 10^9 A/cm^2 [18] which is three orders of magnitude higher current than copper [19] and ON/OFF current ratios higher than 10^5 [20].

Since, GN and CNTs share very similar carbon chemistry and, therefore, the methods and understanding for CNTs can be transferred to GN research and vice versa [20]. However, the fundamental difference between these two nanoparticles is that GN is reflective with little absorption while CNTs is the darkest material with significant optical absorption [20] and CNTs can be considered as the roll of the two dimensional plain sheet of graphene. The dispersibility and thermal conductivity of various classes of nanofluids, such as (i) metallic particles [21], (ii) nonmetallic particles [22], and carbon allotropes [23,24] have been under investigation which is leading the considerable attention to the synthesis of nanocomposites by incorporating different nanoparticles owing

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to their exceptional properties [25]. However, the intrinsic tendency to agglomerate [26] in water due to the hydrophobic surface [27] is the chief obstacle to prepare GN and CNTs based nanofluids that are under research with a significant challenge. Commercially available raw CNTs contain different impurities such as amorphous carbon and metallic nanoparticles [28], entanglement due to long and winding shapes [16], existence of van der Waals forces [24] and weak interfacial interactions between CNTs and their surrounding matrix due to the hydrophobic surfaces of CNTs [24] hinder their well dispersion in base fluid. Munkhbayar et al. [29] reported in their experiment that purification of MWCNTs by acid treatment shows complete elimination of amorphous carbon and carbon particles from MWCNTs. They also reported in their another experiment [30] that grinding of GN can significantly improve its dispersibility in base fluid. In the field of composite synthesis, there are very few reports are available on GN–MWCNTs nanocomposite. For example, Bhattacharya et al. [31] reported the bi-functional polymer nanocomposite based on graphene and MWCNTs which gives excellent microwave absorption and electrochemical property where TiO_2, Fe_3O_4 and polyaniline (PANI) were used. Another author Yen et al. [32] prepared graphene and multi-walled carbon nanotube composite by oxidizing of graphite by Staudenmaier's method and acid treatment of MWCNTs by nitric acid in order to use this as photoanode of dye-sensitized solar cell. He reported a greater degree of dye adsorption and lower levels of charge recombination by this nanocomposite in DSSC system. This paper reports the graphene–MWCNTs composite by following a mixture of sulfuric acid and nitric acid based acid treatment and the grinding process. The objective of this study was twofold: (i) to get a better composition of GN and MWCNTs nanoparticles by acid treatment as well as grinding process and (ii) to analyze the properties by IR images of microwave treatment (Section 3.1), FESEM (Section 3.2.1), TEM (Section 3.2.2), Raman spectra (Section 3.2.3), sedimentation (Section 3.3.1), UV–Vis spectra (Section 3.3.2), electric conductivity (Section 3.3.3), thermal conductivity and thermal conductivity enhancement (Section 3.3.4) of this nanocomposite. Here, it should be noted that the results of this paper are only for comparison and do not indicate the optimum conditions for this process.

2. Experimental details

2.1. Materials

Graphene nanopowder with 8 nm (average flake thickness) flakes, average particle size ~550 nm, specific surface area 100 m^2/g, and 99.9% purity (purchased from Graphene supermarket) and MWCNTs measuring ~20 nm diameter and ~5 μm length and with greater than 95% purity, less than 3% impurities and a specific surface area of 40–300 m^2/g (purchased from Carbon Nanomaterial Technology Co. Ltd., South Korea) were used in this experiment. Distilled water (DW) was used as the base fluid of the nanofluids. Surfactant sodium dodecyl benzene sulfonate (SDBS, $C_{18}H_{29}NaO_3S$) with hard type, 348.48 molecular weight (Tokyo Chemical Industry Co. Ltd.) was used for better dispersion of ground GN, ground MWCNTs and ground but not purified GN–MWCNTs composite in the base fluid.

2.2. Preparation of samples

2.2.1. Microwave oven

A domestic microwave oven (magic oven, MWO-20M7) with 2.45 GHz frequency was used to execute microwave treatment. The microwave oven was slightly customized for temperature measurements. The details of the microwave treatment procedure were described in our previous work [33]. Then raw GN, raw MWCNTs and mixture of GN and MWCNTs were taken under microwave heat treatment. Portable infrared camera (Ti45, Fluke Inc.) was applied in order to capture the infrared images as well as check the original temperature profile of the heated samples which could not be determined by infrared thermometer.

2.2.2. Purification by acid treatment

A simple method for purification by using nitric acid (HNO_3) and sulfuric acid (H_2SO_4) was employed which has been explained in details elsewhere [34,35]. Briefly, purification was performed by ultrasonication (1510E-DTH, Branson Ultrasonic Corporation, USA) for 5 h to remove the impurities and amorphous carbon and to improve exterior activity. The output power and frequency of the applied ultrasonic vibration were determined to be 63 W and 42 kHz, respectively. After performing ultrasonication, anhydrous ethanol was used to neutralize the acids. The presence of hydrophilic functional groups such as C—O—C,C=O,O—H and —COOH onto the surface of the purified nanoparticles has been investigated in previous many reports [36,32]. Next, the acidic mixture of GN/MWCNTs containing carboxyl radicals was diluted by adding distilled water. This dilution and filtration process was conducted using a vacuum filter. The moisture was removed by placing the purified nanoparticles composite in a vacuum oven for 5 h at 80 °C. Then, the temperature was set at 200 °C and purified GN/MWCNTs sample was placed in that oven for more 5 h. The total purification process has been shown in Fig. 1.

2.2.3. Grinding process by PBM

A planetary ball mill (PBM) (HPM-700, Haji Engineering, Korea) was used to shorten the length of the nanoparticles. Mono-sized (3.0 mm) spherical zirconia (ZrO_2) balls were used as the collision medium. The agitator-applied rotation speed was 500 rpm and the grinding time under wet grinding was 2 h. During the grinding, the nanoparticles were subjected to high energy inter-particle and milling ball collisions. The details of the grinding process were described elsewhere [22]. The ball milling can significantly change the shape of particles from spherical to flat which affects the aspect ratio of the nanoparticles. The direction of the pot rotation was set counter to that of the disk revolution. A significant grinding rate obtained by counter-directionally rotation of mill pot to the disk revolution has been reported by Mio et al. [34]. The reason for choosing wet grinding is that Tang et al. [37] reported that wet-grinding could improve the water wet-ability of ground MWCNTs ultrasonically dispersed in chitosan solution. And, the reason for choosing 500 rpm is that Munkhbayar et al. [29] conducted their wet grinding of MWCNTs at various rotation speeds (200–500 rpm) and reported that the best dispersion characteristics were observed for the grinding process in wet condition at a

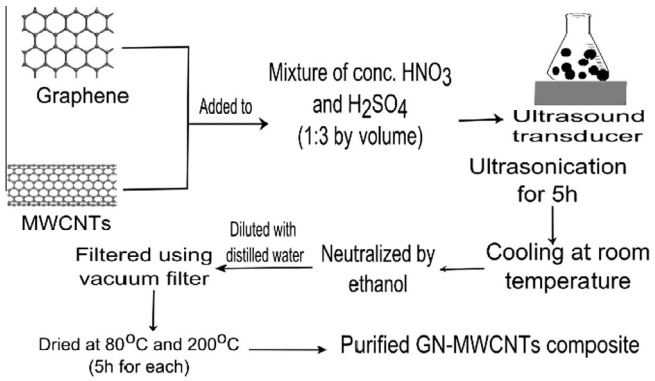

Fig. 1. Purification procedure.