



Role of direct covalent bonding in enhanced heat dissipation property of flexible graphene oxide–carbon nanotube hybrid film

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ARTICLE INFO

Article history:

Received 28 January 2013

Received in revised form 18 July 2013

Accepted 18 July 2013

Available online 24 July 2013

Keywords:

Hybrid materials

Thermal conductivity

Electrical conductivity

Chemical bonding

Phonon scattering

ABSTRACT

The thermal conductivity of graphene oxide/multiwalled carbon nanotube (GO/MWCNT) hybrid films with and without covalent bonding is examined in this study. To fabricate chemically bonded GO/MWCNT hybrid films, chlorinated GO and amino-functionalized MWCNTs are bonded covalently. The mixtures of surface modified GO and MWCNT were filtered and then subjected to hot pressing to fabricate stacked films. Examination of these chemically bonded hybrid films reveal that chlorine-doped GO exhibits enhanced electrical properties because it creates hole charge carriers by attracting the electrons in GO towards chlorine. Enhanced electrical conductivity and low sheet resistance are observed also with increasing MWCNT loadings. On comparing the through-plane thermal properties, the chemically bonded hybrid films were found to exhibit higher thermal conductivity than do the physically bonded hybrid films because of the synergetic interaction of functional groups in GO and MWCNTs in the former films. However, excess addition of MWCNTs to the films leads to an increasing phonon scattering density and a decreased thermal conductivity.

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1. Introduction

Graphene is a two dimensional and one atom thick layer of carbon with excellent electronic, thermal, and mechanical properties. Thus, graphene has focused the significant attention of scientists and engineers in recent years and many potential and promising applications have been considered [1–3]. Graphene based materials can be conveniently synthesized from graphite oxide, which can be readily exfoliated into individual graphene oxide (GO) sheets to yield stable suspensions in water because of the hydrophilic oxygen groups bound to the carbon in the basal plane in the form of hydroxyl and epoxy functional groups, and as carbonyl and carboxyl groups at the sheet edges [4,5].

GO sheets can offer the potential of creating large-scale graphene thin films, which are dense, stiff and strong compared to the porous and fragile property of graphene flake films because of stable and homogeneous colloidal suspensions in aqueous and various polar organic solvents [6,7]. Therefore, GO sheets have been obtained by using well established methods, such as vacuum filtration [8], spin-coating [9,10], layer-by-layer deposition [11], solution casting, and the Langmuir-Blodgett film technique [12,13].

The electrical insulating property of GO sheets due to the disruption of graphitic networks can be turned and recovered to produce reduced GO (r-GO) by chemical reduction [14,15], thermal annealing [16], and ultraviolet excitation [17]. However, these treatments degrade its structural integrity of graphene and aggregated thick layers of r-GO, which

disturb the homogenous suspension in the polar solvent. Therefore, various other types of materials, such as inorganic nanoparticles [18], biomolecules [19], or carbon nanotubes (CNTs) [20] have been used in fabrication of hybridized thin films in the GO sheets to enhance the material properties. Among them, CNTs with quasi-one-dimensional structures possess excellent mechanical properties, low density, high surface area, chemical stability, electrical conductivity and thermal conductivity [21]. Attempts to combine CNTs and graphene or graphene oxide have been made to prepare transparent conductors and electrode materials for rechargeable lithium ion secondary batteries. In order to interconnect between graphene and CNTs, a few methods were introduced. Fan et al. suggested that CNTs are grown in between the graphene by adhering to the catalyst particles [22]. Yu and Dai suggested self-assembled graphene/carbon nanotube films for supercapacitors [23]. Although studies assembled graphene materials and CNTs for electrode materials or supercapacitors, there are very few reports showing the effect of GO and CNTs on the thermal conductivity and the enhancement effect on the electrical properties of composite materials.

In this study, in order to achieve enhanced thermal conductivity, chemically converted GO and multi-walled carbon nanotube (MWCNT), which were bonded covalently, are proposed and compared with physically combined pristine GO and acid-treated MWCNTs. Also, filtered hybrid films were pressed to fabricate high-packed films, which show paper-like structure. Chemically bonded GO/MWCNT hybrid films revealed the enhanced electrical properties due to enhanced electron channel. The chemical bonds allowed the MWCNTs to act as effective interconnectors between GO layers and thus showed enhanced heat conductive properties compared to the physically bonded hybrid films. Also,

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the morphologies of the fabricated films provided clear evidence with regard to the MWCNT dispersion in the GO layers.

2. Experimental details

2.1. Materials

Graphite with a mean particle size of $<20\ \mu\text{m}$, phosphoric acid (H_3PO_4 , 85%), thionyl chloride (SOCl_2), and potassium permanganate (KMnO_4) were purchased from Aldrich Chemical. Sulfuric acid (H_2SO_4 , 95.0%), hydrochloric acid (HCl, 35.0–37.0%), anhydrous tetrahydrofuran (anhydrous THF, 99.5%), hydrogen peroxide (H_2O_2 , 34.5%), methanol (MeOH, 95.0%), and acetone were purchased from Samchun Chemicals. MWCNT (Hanwha Nanotech, Seoul, Korea) had diameters ranging from 40 to 60 nm and an average purity of 95%. To prepare the surface-treated graphene oxide (GO) and MWCNTs, concentrated sulfuric acid (H_2SO_4 , Samchun Chem., Pyungtaek, Korea), nitric acid (HNO_3 , Aldrich, Seoul, Korea), and ethylenediamine ($\text{C}_2\text{H}_8\text{N}_2$, Aldrich, Seoul, Korea) were used without further purification. Thionyl chloride (SOCl_2 , Aldrich, Seoul, Korea) and tetrahydrofuran (THF, HPLC grade, Aldrich, Seoul, Korea) were used as received.

2.2. Preparation of surface-treated GO nanosheet

GO was synthesized using the modified Hummers method [24]. All reagents were used without further purification. In a typical synthesis, 3 g of graphite powder was placed into a mixture containing 360 mL of concentrated sulfuric acid and 40 mL of concentrated phosphoric acid. The resulting mixture was stirred in an ice bath for 4 h. After homogeneous dispersion of the graphite powder in the solution, KMnO_4 (18 g) was added slowly to the solution over 1 h in an ice bath at 273 K. The mixture was then stirred for 12 h at 323 K in an oil bath. After the reaction, the mixture was poured into 400 mL of deionized (D.I.) water containing 3 mL of H_2O_2 . The mixture was washed several times and purified with HCl and D.I. water, respectively. The collected graphite oxide was dispersed in D.I. water by ultrasonication to exfoliate the graphite oxide to GO, which was dried in a vacuum oven at 323 K for 2 days. The obtained GO had particles with average lateral dimensions of several micrometers and thicknesses of 4.5 nm.

GO with carboxylic acid groups were dispersed in SOCl_2 using an ultrasonicator for 1 h at room temperature to form a suspension. Chlorinated GO was then filtered through a $0.4\ \mu\text{m}$ membrane after refluxing and stirring for 12 h at 338 K. The filtered powders were then washed with THF and dried for 12 h under vacuum at ambient temperature.

2.3. Preparation of surface-treated MWCNTs

The as-received MWCNTs were purified and functionalized with carboxylic acid groups by heat treating the MWCNTs (1 g) in 800 mL of H_2SO_4 and HNO_3 (3:2 by volume) in an ultrasonicator bath (Bransonic, MT-1510, 42 kHz) for 8 h at room temperature to form a suspension. The suspension was then heated to 323 K and stirred for 24 h and filtered through a nylon membrane. The filtered cake was washed thoroughly with water, and this process was repeated several times until the filtrate was neutral. The HNO_3 treatment produced carboxylic groups on the surfaces of the MWCNTs without greatly decreasing the length of the MWCNTs. This reaction also eliminated impurities that could impart unexpected thermal properties to the composite. Carboxylated MWCNTs were then immersed into SOCl_2 using an ultrasonicator at room temperature for 1 h and stirred for 12 h at 338 K to convert the carboxylic acid groups on the surface of MWCNTs to acid chlorides. The suspension was vacuum-filtered through a polytetrafluoroethylene membrane, washed with THF, and dried for 12 h under vacuum at ambient temperature. Then, the acid-chloride-activated MWCNTs were added to ethylenediamine in dimethylformamide and refluxed

at 398 K for 24 h with stirring. Finally, the reaction mixture was filtered through a nylon membrane and washed with D.I. water, and the remaining solvent was dried in a vacuum oven at 373 K for 5 h.

2.4. Composite fabrication

The composite was fabricated by solvent mixing and hot-pressing to obtain sheet type-hybrid films in this study. 0.05 g of surface-treated GO was suspended in 10 mL of THF with various amounts of surface-treated MWCNTs under ultrasonication for 1 h and stirred for 3 h at 338 K. The suspension was then filtered through a $0.4\ \mu\text{m}$ membrane and hot-pressed at 100 psi at 353 K for 2 h. The chemical reaction between GO and MWCNT surfaces was achieved during the hot-pressing. The synthesis route of the entire procedure for the chemical reaction of GO and MWCNTs is shown in Fig. 1.

2.5. Characterization

The characterization on the crystal structure of GO was carried out using an X-ray diffractometer (XRD, New D8-Advance/Bruker-AXS) at a scan rate of $1\ ^\circ\text{s}^{-1}$ with a 2θ range of $5\text{--}60^\circ$ with $\text{Cu K}\alpha_1$ radiation ($\lambda = 0.15406\text{nm}$). Field emission scanning electron microscopy (FE-SEM, SIGMA, Carl Zeiss) and high-resolution transmission electron microscopy (HR-TEM, JEM-3010, Japan) were used to examine the morphology of the fabricated hybrid films. The surface-treated GO and MWCNT hybrid film was characterized by X-ray photoelectron spectroscopy (XPS, VG-Microtech, ESCA2000) using a $\text{Mg K}\alpha$ X-ray source (1253.6 eV) and a hemispherical analyzer. During curve fitting, the Gaussian peak widths were constant in each spectrum. The inner resistance of the GO and MWCNT hybrid films was measured by AC impedance spectroscopy (IM-6ex, Zahner) between 0.1 kHz and 1 MHz. The samples were sandwiched rapidly between two Pt electrodes. The conductivity of all samples was measured using a two-point method. The electrical conductivity (σ) was calculated using the equation, $\sigma = h / (R \times S)$, where h is the thickness of the conducting films, R (Ω) is the inner resistance, and S (m^2) is the surface dimension of the films. The sheet resistance of the hybrid films was determined by ex situ four-point resistivity measurements (Cascade Microtech, Inc.). Thermal diffusivity of all films was measured by laser flash analysis (Netzsch 447 NanoFlash) at room temperature. The films were cut into samples of 10 mm diameter and put on the metal holders. The transferred signal initiated a thermal equilibration process in the composite specimen, which was recorded using a difference detector at the rear surface and used to evaluate the thermal diffusivity following a method described in the literature [25,26]. The heat capacity (C , $\text{J/g}\cdot\text{K}$) at room temperature ($25\ ^\circ\text{C}$) was measured using the same samples by differential scanning calorimetry (Netzsch 200F3) and then, density of the specimens was measured by the water displacement method. The thermal conductivity (k) was calculated using the equation, $k = \alpha \times \rho \times C_p$, where k , α , ρ , and C_p are the thermal conductivity [$\text{W}/(\text{m}\cdot\text{K})$], thermal diffusivity (mm^2/s), density (kg/m^3), and specific heat capacity [$\text{J}/(\text{kg}\cdot\text{K})$] of the composite, respectively.

3. Results and discussion

3.1. Characterization of GO

The fabricated GO was characterized by HR-TEM and XRD. The results are summarized in Fig. 2.

It is well known that the GO has large amounts of hydroxyl, carboxyl, carbonyl, and epoxide functional groups attached onto the basal or edge plane, and shows a number of tiny wrinkles over a surface with mountainous peaks at the reaction sites involved in oxidation [27]. Fig. 2(a) shows a large-scale, magnified HR-TEM image, which displays a number of tiny wrinkles over the entire surface caused by the formation of surface functional groups. The X-ray diffractogram features of graphite and

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