



# Alumina-coated graphene nanosheet and its composite of acrylic rubber



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## ABSTRACT

A graphene was coated with a thin alumina layer to prepare a novel nanosheet which had high thermal conductivity but low electrical conductivity. The nanosheet with minimal aggregation was prepared effectively by first coating it with aluminum tri-*sec*-butoxide in anhydrous dimethylformamide, followed by rapid calcination in an inert atmosphere after the hydrolysis of the alkoxide. The morphology observed by scanning electron microscopy and elemental mapping by energy-dispersive X-ray spectrometry showed that the alumina layer coated on the graphene surface was uniform and ultra-thin. Thermogravimetry demonstrated that the uniformly coated alumina protective layer substantially improved the thermal stability of the graphene and that the electrically-insulative alumina layer effectively reduced the electrical conductivity of the graphene. The enhanced polar nature of surface as well as the increased surface roughness due to the coated alumina improved the dispersion of the graphene in the polar acrylic rubber matrix and the interaction at the interface. This led to an effective improvement of the thermal conductivity but marginal increase in electrical conductivity by the filler. Tensile modulus increased drastically to as high as 470% for the composite reinforced with the 5 phr (about 2.5 vol%) loading of the alumina-coated graphene.

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## 1. Introduction

Graphene, a single-atom-thick sheet of hexagonally arrayed  $sp^2$ -bonded carbon atoms, has attracted great attention because of its extraordinary electronic, thermal, and mechanical properties, large surface area and high aspect ratio, making it potentially valuable for a variety of applications, such as in microelectronic devices, catalysis, sensors, biomedicines, and composite materials [1–7]. Graphene can be prepared by various methods, such as micromechanical exfoliation of graphite [8], epitaxial growth on silicon carbide [9], chemical vapor deposition on metal substrates [10], thermal or chemical reduction of exfoliated graphite oxide (GO) [11,12], and exfoliation of graphite intercalation compounds [13]. Thermal exfoliation of GO can produce bulk quantities of graphene in which GO is reduced and exfoliated simultaneously upon rapid heating due to the thermal decomposition of oxygen-containing groups of GO and the pressure of the gas products (mainly  $CO_2$ ) that builds up instantaneously at the gallery between the sheets [14,15]. This method is economical and eco-friendly because it does not require the use of a solvent. Having the capacity to produce bulk quantities of thermally-exfoliated graphene will facilitate various applications such as the fabrication of graphene-based polymer composites.

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Although graphene possesses various advantageous properties as a promising nanofiller in the preparation of polymer nanocomposites, graphene has practical limitations such as problematic dispersion and poor interfacial interaction with the polymer matrix, which impairs the performance of the final composite [16,17]. Graphene has high thermal and electrical conductivities. Therefore, it can be used as a filler for the fabrication of polymer composites that require the high conductivities. However, high electrical conductivity can be a drawback in some applications where electrical insulation is essential to prevent short-circuit and electric leak [21]. Thus, appropriate modifications of graphene are necessary in order to optimize its performance [18–20].

Alumina is one of the most widely used materials because it has high mechanical strength and hardness, good electrical insulation properties, good dielectric properties, high thermal conductivity and stability, and high corrosion resistance to a broad range of chemicals [22,23]. Therefore, a thin alumina layer coated on a graphene sheet can reduce effectively the electrical conductivity of the graphene. However, thermal conductivity and mechanical strength of the hybrid nanosheet must be sufficiently high for the nanosheet to be used in various applications such as the fabrication of electrically-insulative but thermally conductive high strength polymer composites. The polar and hydrophilic nature of the coated alumina can enhance the compatibility and interfacial interaction of the modified graphene with polar polymer matrices in the fabrication of polymer composites. The combination of the special electronic property of graphene and the dielec-

tric property of the coated alumina layer can pave the way toward various promising applications such as in energy storage, electronic devices and sensors [24,25].

In order to prepare such a high performance hybrid nanosheet, a uniform, continuous, stable and sufficiently thin alumina coating on the graphene surface is necessary. To our knowledge, there have been no studies examining the benefits of coating graphene with alumina. Herein, we present a simple method to coat graphene with an ultra-thin, uniform and stable alumina layer. The process involves first coating it with aluminum tri-*sec*-butoxide (ASB) in an aprotic polar solvent such as anhydrous dimethylformamide to form a thin, continuous alkoxide layer on the dispersed graphene surface, followed by hydrolysis of the alkoxide and calcination in an inert atmosphere (Fig. 1). We also demonstrate here the possible utilization of modified graphene as a nanofiller for fabrication of an electrically-insulative acrylic rubber composite with greatly improved performance.

## 2. Experimental

### 2.1. Materials

Expandable graphite (ES350 F5, average particle size: 280  $\mu\text{m}$ ) purchased from Qingdao Kropfmuehl Graphite Co., Ltd. (China) was used for the preparation of graphene. Aluminum tri-*sec*-butoxide (ASB) (Aldrich), anhydrous dimethylformamide (DMF) (Aldrich), acetone (Aldrich), acrylic rubber with epoxide cure sites (AR-740, TOA ACRON), and hexamethylenediamine carbamate (Dowhon, China) were used as received.

### 2.2. Preparation and modification of graphene

GO was prepared using the Brodie method as described in our previous paper [26]. Briefly, a reaction flask with 200 mL fuming nitric acid was cooled in an ice bath to 0  $^{\circ}\text{C}$ , and 10 g of graphite powder was added with stirring. Over a 1-hour period, 85 g of potassium chlorate was then slowly added with stirring at 25  $^{\circ}\text{C}$ . After 24 h, the mixture was poured into 3 L of distilled water. The GO was filtered and washed with distilled water until the pH of the filtrate was neutral. It was then dried in a vacuum oven at 100  $^{\circ}\text{C}$ . Elemental analysis showed that the GO composition was  $\text{C}_{10}\text{O}_{3.45}\text{H}_{1.58}$ .

To obtain the thermally-exfoliated graphene, the dried GO was charged in a quartz tube and flushed with nitrogen for 5 min. The quartz tube was then quickly inserted into a furnace preheated at

1100  $^{\circ}\text{C}$  and was left there for one minute for thermal exfoliation and reduction of GO [14,15]. The graphene is designated as PG. Elemental analysis showed that the graphene composition was  $\text{C}_{10}\text{O}_{0.78}\text{H}_{0.38}$ .

One part of PG was dispersed in 200 parts anhydrous DMF by sonication for 1 h. A predetermined amount of ASB was then added to the dispersion, followed by agitation for 1 h to allow ASB to coat on the graphene surface by adsorption. A stoichiometric amount of water with respect to ASB was added to the above dispersion and the mixture was agitated for an additional 1 h to ensure the complete hydrolysis of ASB. The colloidal dispersion of aluminum hydroxide-coated graphene was aged for 1 day at room temperature and then filtered through 1  $\mu\text{m}$ -pore size filter paper, washed with acetone and dried in a vacuum at 80  $^{\circ}\text{C}$  for 1 day. The dry powder was charged in a quartz tube and flushed with nitrogen for 5 min. The quartz tube was then quickly inserted into a furnace preheated to 1100  $^{\circ}\text{C}$  and was kept there for 25 min with a continuous flow of nitrogen to convert the coated aluminum hydroxide to alumina (Fig. 1). Three modified graphene samples were prepared with different ASB/graphene weight ratios. The sample designation codes in Table 1 give information about the ratio of the weight of alumina calculated from the ASB feed to the weight of graphene. For example, the weight ratio is 30:100 for AG30.

### 2.3. Preparation of graphene/acrylic rubber composite

The graphene/acrylic rubber composites were prepared with a 30 mL Brabender mixer (W30) connected to a Plasti-Corder (Plasti-Corder PL2100) at 50  $^{\circ}\text{C}$  with a mixing speed of 50 rpm. Two types of fillers (PG and AG30) were used for composite preparation. The acrylic rubber (100 parts) was mixed with hexamethylenediamine carbamate (curing agent, 1.3 parts) and an appropriate amount of filler for 10 min using the mixer. The mixtures were then press cured at 170  $^{\circ}\text{C}$  under 5 MPa for 20 min, followed by a post-curing at 170  $^{\circ}\text{C}$  in an oven for an additional 240 min. The composite's designation provides information about the composition of the composite. For example, AG/AR-2 is the composite containing 2 parts AG30 per 100 parts acrylic rubber (2 phr). The AR is the cured acrylic rubber itself containing no filler.

### 2.4. Characterization

Morphology, elemental analysis and elemental mapping of graphene were observed and recorded using a field emission scanning electron microscope (FE-SEM; Quanta 200, FEI Co.) equipped with an energy-dispersive X-ray spectrometer (EDX).

Thermogravimetric analysis (TGA) was performed with a Q50 (TA Instrument) at a heating rate of 10  $^{\circ}\text{C}/\text{min}$  with 6 mg of sample in a platinum crucible under  $\text{N}_2$  atmosphere.

X-ray diffraction (XRD) patterns were acquired with an X-ray diffractometer (Ultima IV, Rigaku) using  $\text{Cu K}\alpha$  radiation ( $\lambda = 0.1542 \text{ nm}$ ) as the X-ray source.

The electrical conductivity of pressed graphene powder (density of about 0.6  $\text{g}/\text{cm}^3$ ) and composite films were measured by a two-probe method using a Keithley 237 source-measure unit at room temperature. In the case of the rubber composite, silver paste was used to ensure good contact between the specimen and the electrodes.

Composite films approximately 10  $\mu\text{m}$ -thick were imaged using an Eclipse LV100 (Nikon) optical microscope equipped with an Artcam-300MI-DS digital camera.

Tensile properties were examined with a tensile tester (OTU-2, Oriental TM Co., Korea). The acrylic rubber composite film was cut into a micro-tensile specimen 25 mm in length, 5 mm in width, and 0.5 mm in thickness. The specimen was elongated at a rate of 100 mm/min.

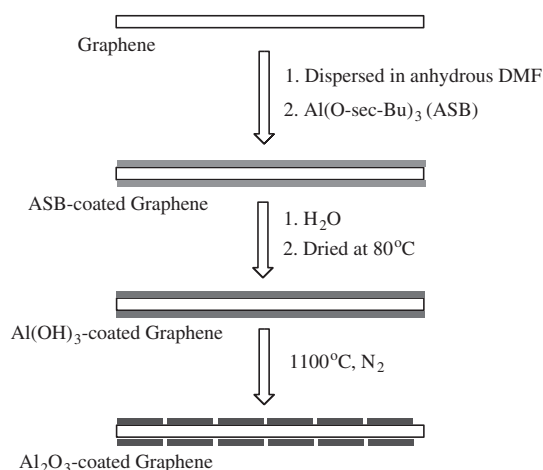


Fig. 1. Schematic representation of the process of coating graphene with alumina.

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