

## Electronic Supplementary Information (ESI)

# **Partially reduced graphene oxide as a multi-functional sizing agent for carbon fiber composites by electrophoretic deposition**

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### **Experimental**

#### **Preparation of graphene oxide (GO)**

GO was prepared by using the modified Hummers method [S1] and all reagents were purchased from Sigma-Aldrich. In order to achieve the complete oxidation of the graphite powder, the pre-treatment was performed in advance of the oxidation step. Sulphuric acid (50 mL) was added into a 2.0 L flask filled with the graphite powder (10 g), potassium persulfate (10 g), and phosphorus pentoxide (10 g), and the mixture was kept at 80 °C for 4 hrs. And then, the mixture was diluted with 2.0 L of deionized (DI) water and was stirred for overnight. The mixture was filtered using the ester cellulose membrane filter (Millipore, 0.2 µm pore

size), and the pre-treated graphite powder was then obtained by washing with DI water and drying in a vacuum oven.

In the oxidation stage, 80 mL of DI water was added into a 2.0 L beaker filled with phosphorus pentoxide (62 g), and sulphuric acid (480 mL) was slowly poured into the beaker at 0 °C in an ice bath. Then the pre-treated graphite powder (4.0 g) and potassium permanganate (24 g) were added into the mixture, followed by stirring for 12 hrs. Then the mixture was sonicated using a bath-type sonicator (Power Sonic 410, Hwashin Instrument) for 1 hr. And then, 600 mL water was added, followed by drop-wise addition of 35 wt% hydrogen peroxide (8.0 mL). Additional stirring and sonication (2 hrs once a day) were carried out for one week. To dissolve unreacted potassium permanganate particles, 30% hydrochloric acid (300 mL) and ethanol (300 mL) were added into the solution. The mixture was centrifuged at 7,500 rpm for 1 hr and the supernatant was decanted away. Until the supernatant was neutralized, the mixture was washed with methanol/ether solution (3:2), and centrifugation was repeated several times. Finally, the sediments (GO powder) were dried under the vacuum at room temperature for 12 hrs.

#### **Anodic electrophoretic deposition (EPD)**

In EPD stage, the anodic EPD was carried out with a GO suspension. Here, four different concentrations of the GO solution ( $C_i$ ) were considered as  $3.0 \times 10^{-5}$ ,  $3.0 \times 10^{-4}$ ,  $3.0 \times 10^{-3}$ , and  $3.0 \times 10^{-2}$  wt%. Woven fabrics (80 x 80 mm, areal density = 22 mg/cm<sup>2</sup>) of the carbon fibers (TR30, Mitsubishi) and 1.0 mm thick stainless steel plates were connected to anodes and cathodes of the power supply (6035A System DC Power Supply, Agilent Technologies), respectively. Each fabrics and steel plates were placed with 5.0 mm of facing-distance in a fixture. EPD was performed under a constant voltage of 5.0 V for 1 min and the total amount

of the GO solution was 3.5 L (3,500 g). Since a carbon fabric itself is a kind of resistive material, an electrical voltage can decrease along the vertically immersing depth and may lead to non-uniform coating thickness of pRGO. In order to achieve uniform electrical field, conductive copper tape was applied to four edges of carbon fabric so that uniform deposition can be obtained. Furthermore, such copper taping can help the carbon fabric preserve a flat and planar shape during EPD.

### **Preparation of partially reduced graphene oxide (pRGO)**

In order to partially reduce the coated-GO sheets, the GO-coated carbon fabrics were immersed into 10.0% hydroiodic acid in water at room temperature for 10 min [S2]. After reduction, the fabrics were rinsed with sodium bicarbonate solution, DI-water, and acetone, and then dried in an oven at 150 °C for 24 hrs.

### **Preparation of composite samples**

As for the preparation of carbon fiber composite samples, fourteen layers of the pRGO-coated carbon fabric were laminated and an epoxy resin (YD-128, Kukdo Chemicals) was injected with a curing agent (KBH-1089, Kukdo Chemicals) by a vacuum-assisted resin transfer molding (VARTM) process. The composite samples were cured at 120 °C for 2 hrs.

### **Characterization**

The optimal pH condition of GO solution for EPD was determined by measuring the Zeta potential using an Electrophoretic Light Scattering Spectro-photometer ELS-8000, Otsuka Electronics). The absorbance of GO solution before and after EPD was measured by a ultraviolet–visible (UV-Vis) spectroscopy (Cary 5000, Agilent Technologies) at 400 nm

wavelength. The chemical structure analysis was studied using Fourier-transform infrared (FT-IR) spectroscopy (Nicolet iS10, Thermo Scientific) and the X-ray photoelectron spectroscopy (XPS) using a Theta Probe AR-XPS System (VG ESCALAB MKII spectrometer) equipped with a monochromatic Mg K $\alpha$  ( $h\nu = 1486.6$  eV) source at a power of 150 W (15 kV  $\times$  10 mA). For FT-IR and XPS measurements, GO sample was prepared from the GO powder. Especially for pRGO, the sample was prepared by gently scraping off the pRGO-coated carbon fiber surface. The micro-structure and size of a single GO sheet were observed using the transmission electron microscopy (TEM, JEOL JEM-1010). The pRGO-coating morphology and crack patterns in the fractured composite samples were investigated by the scanning electron microscopy (SEM, JEOL JSM-5800) observation.

#### **Measurement of surface energy of pRGO-coated carbon fibers**

To examine the interfacial property of pRGO-coated carbon fiber surface, the surface free energy was measured from the advancing contact angle by the Wilhelmy method (K100SF tensiometer, Krüss). Five individual fibers (5.0 mm length) were placed parallel to each other (1.0 mm distance) onto a platinum holder and the contact rate was 0.005 mm/sec. To determine the polar and dispersive components of the surface energy, the purified water and diiodomethane were used as probe liquids, and the following the Owens-Wendt equation was used.

$$W_a = \gamma_L (1 + \cos \theta) = 2\sqrt{\gamma_S^p \gamma_L^p} + 2\sqrt{\gamma_S^d \gamma_L^d}$$

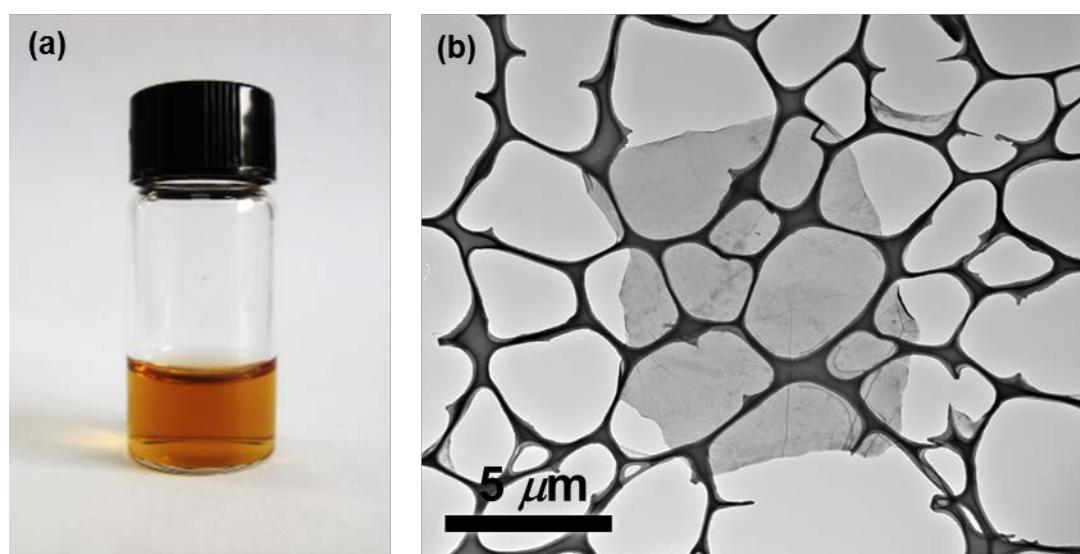
where  $W_a$  is the work of adhesion,  $\gamma$  is the surface energy, and  $\theta$  is the contact angle, respectively. The subscripts  $L$  and  $S$  are corresponding to testing liquids and a solid (carbon fiber), and the superscripts  $p$  and  $d$  mean polar and dispersive components, respectively. In addition, the wettability between the carbon fiber surface and epoxy resin was investigated by observing the contact angle for a micro-droplets of epoxy resin on the carbon fiber using an optical microscope .

### **Measurement of interlaminar shear strength (ILSS) and electrical conductivity**

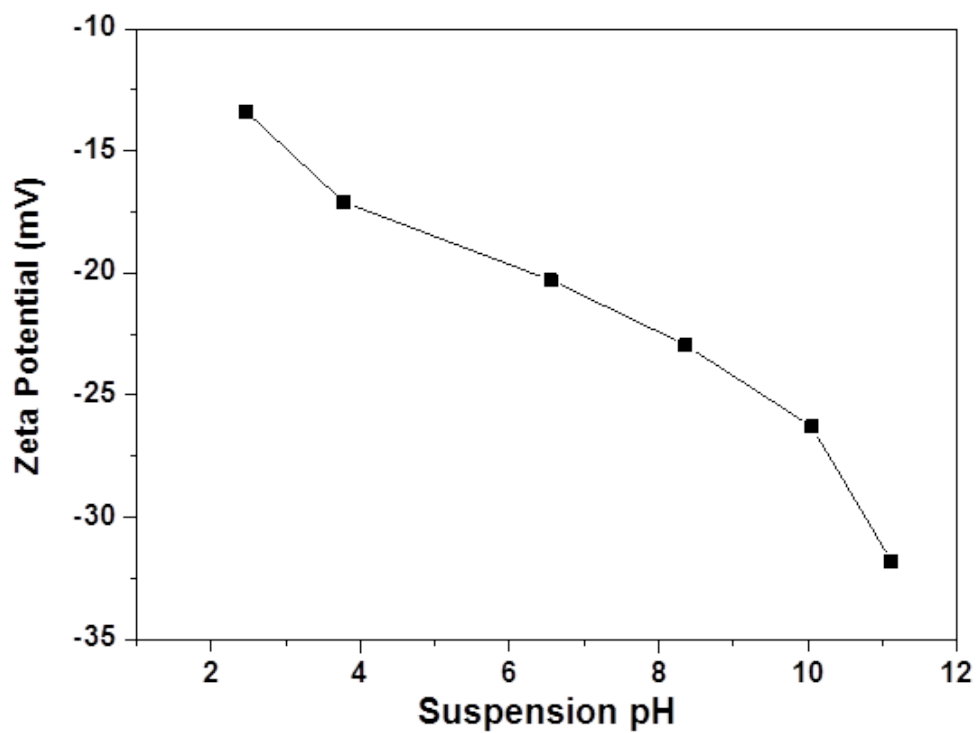
The ILSS of the composite samples were measured by the short beam tests based on the ASTM D2344. Both in-plane and out-of-plane electrical conductivities were also measured for 15.0 x 15.0 x 3.0 mm (width x length x thickness) specimens using a Keithley 2100 multimeter. For both ILSS and electrical conductivity, the average value was determined from the six different samples.

### **References**

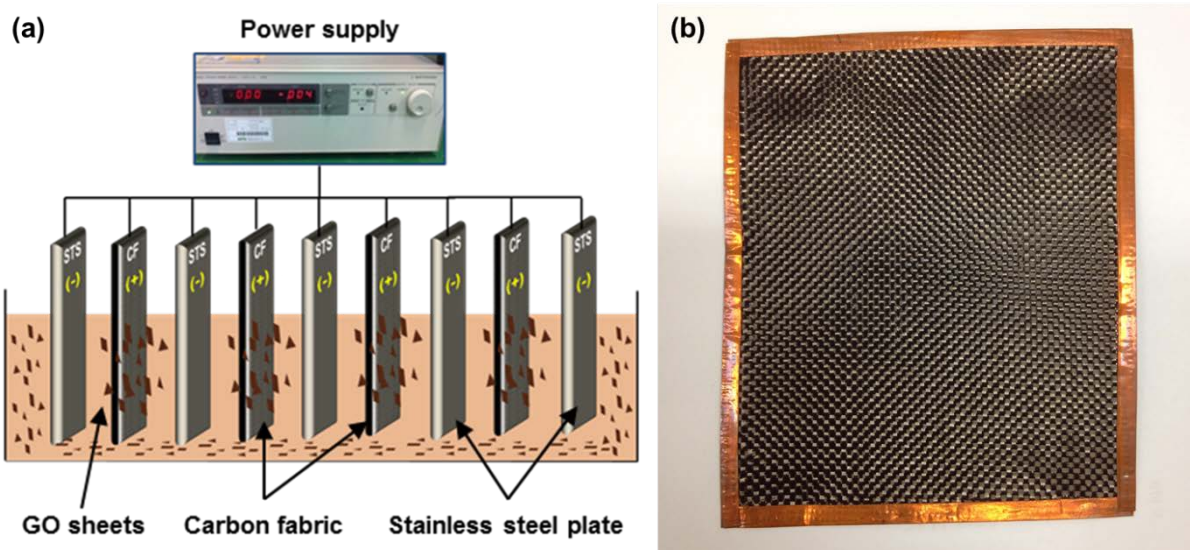
- [S1] D. C. Marcano, D. V. Kosynkin, J. M. Berlin, A. Sinitskii, Z. Sun, A. Slesarev, L. B. Alemany, W. Lu and J. M. Tour, *ACS Nano*, 2010, **4**, 4806.
- [S2] I. K. Moon, J. Lee and H. Lee, *Chem. Commun.*, 2011, **47**, 9681.



**Fig. S1** (a) Stable and homogeneous GO solution and (b) TEM image of a well-exfoliated single GO sheet

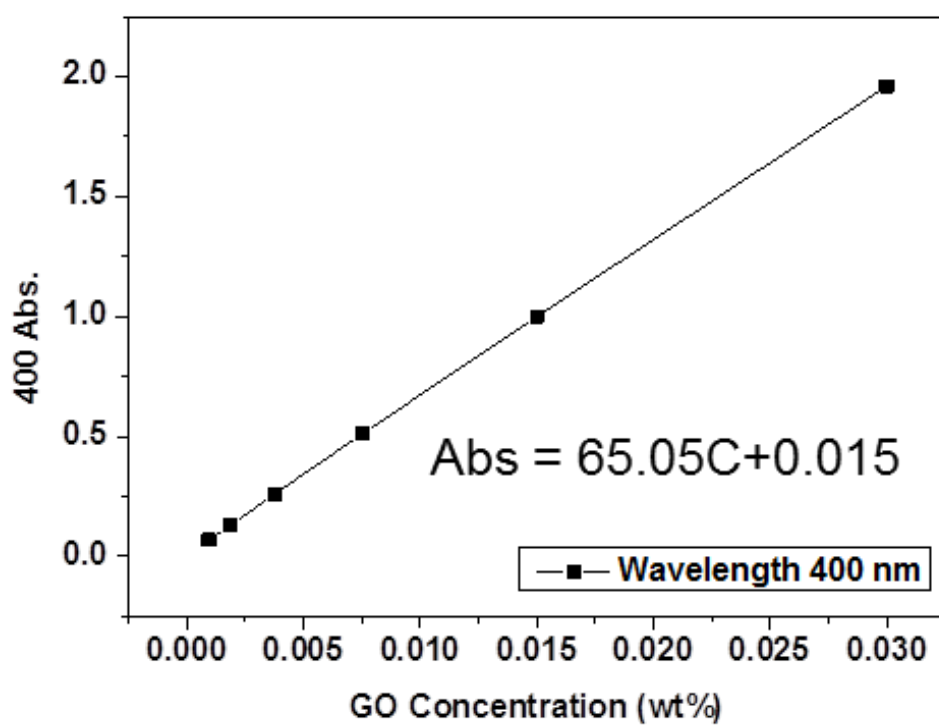


**Fig. S2** Zeta potential of the prepared GO solution

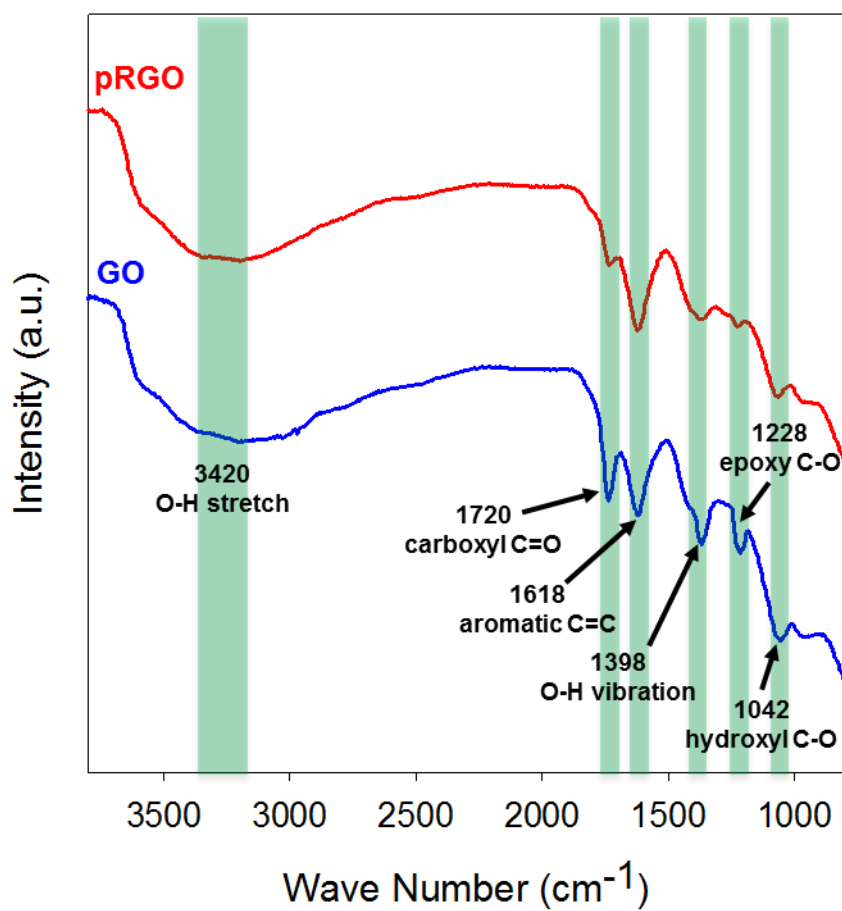


**Fig. S3** (a) Schematic illustration for EPD of GO sheets onto carbon fabric and (b) a carbon fabric with copper taping along four edges

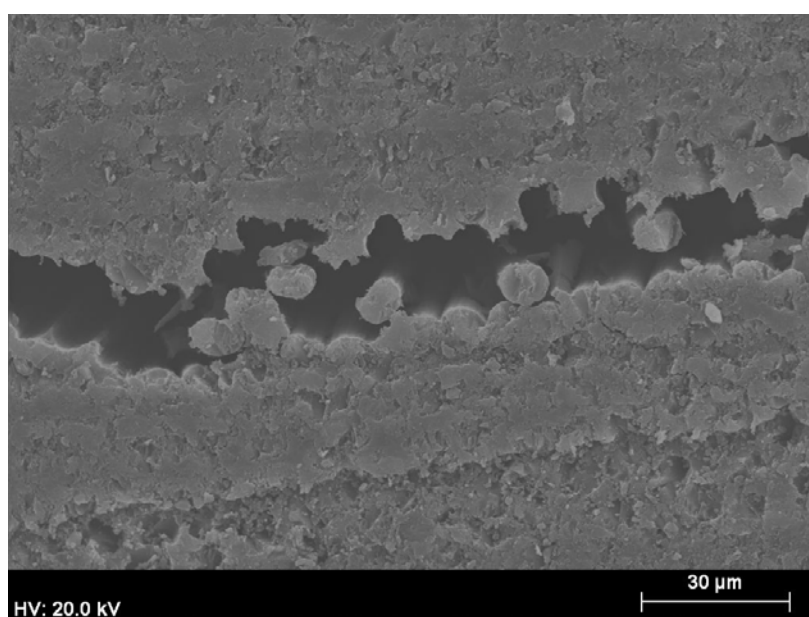




**Fig. S4** Plots from the UV-vis analysis for different concentration of GO solution with their linear relationship



**Fig. S5** FT-IR spectra of GO and pRGO with characteristic bands



**Fig. S6** SEM image of a crack pattern for the sample SA4 which represents the intra-fiber bundle fracture