

Experimental section and supplementary characterisation data

Experimental Section

Materials

Natural graphite flakes, 3,4-Dihydroxyphenethylamine hydrochloride (DOPA, 98%), tris(hydroxymethyl)aminomethane (TRIS, 99%), 3,4-Epoxy-cyclohexylmethyl 3,4-epoxy-cyclohexanecarboxylate, Epoxy embedding medium hardener MNA, Poly(vinyl alcohol), (99+% hydrolyzed, Mw:146,000~186,000) were purchased from Sigma-Aldrich Chem. Co. and used without further purification. Polydopamine-Coated Graphene Oxide (DGO) was synthesized according to ref. ^[1]

Preparation of DGO/H₂O, DGO/DMF stock solutions

DGO/H₂O stock solution were directly prepared from as prepared DGO filter cakes, typically, wet DGO filter cake (prepared from 1g GO) was added into de-ionized water (400 ml), and this suspension were sonicated for 30 mins to afford a homogeneous dispersion which was used as DGO/H₂O stock solution (0.25 mg ml⁻¹ GO). For DGO/DMF stock solution, the as prepared DGO filter cake (prepared from 1g GO) was washed by acetone and DMF for at least 3 times respectively, then the filter cake was added into DMF (400 ml), and this suspension were sonicated for 30 mins to afford a homogeneous dispersion which was used as DGO/DMF stock solution (0.25 mg ml⁻¹ GO).

Preparation of Poly(vinyl alcohol) (PVA)/TRDGO Nanocomposites

2g PVA were dissolved in 500 ml de-ionized water at 90°C in a bottle to form a transparent aqueous solution (4 mg ml⁻¹). After the PVA/H₂O solution was cooled down, a certain volume of the DGO/H₂O stock solution was poured into the PVA/H₂O solution, and then the mixture was stirred at room temperature for at least 2 hours. At last, the blending was cast into cultural dish and dried at 40~50°C on a hotplate, the formed flat membranes were peeled off and further

annealed at 130 °C in a vacuum oven for 24 hours. The content of graphene in the nanocomposites was calculated according to the initial GO content in the DGO stock solution. For example, if we use 20 ml DGO stock solution (0.25 mg GO per ml stock solution) to mix with 2g PVA, the content of graphene is record as 0.25 wt%. The volume concentration is calculated based on the density of polymer (including PDOPA and PVA) of about 1.05g/cm³ and the density of graphene of 2.2g/cm³.

Preparation of Epoxy/TRDGO Nanocomposites

3,4-Epoxy cyclohexylmethyl 3,4-epoxycyclohexanecarboxylate (12.44 g, 49.30 mmol) and epoxy embedding medium hardener MNA (17.56 g, 98.65 mmol) were pre-mixed by a mechanical stirrer at 800 rpm for 30 mins to form a mixture of epoxy precursors. A certain volume of the DGO/DMF stock solution was poured into the mixture of epoxy precursors, and then the mixture was stirred at room temperature for at least 2 hours. The DMF solvent in the mixture was evaporated by rotary evaporation. The viscous mixture was casted into an Al mould and degassed under 50 °C in a vacuum oven for 60 mins, and then cured at 180 °C in a vacuum oven for 5~10 hours. Corresponding neat epoxy resin was prepared accordingly without the adding of DGO/DMF stock solution, instead, in order to accelerate the curing process, 0.5 wt % catalyst (2-Ethyl-4-methylimidazole) was added into the epoxy resin. The volume concentration is calculated based on the density of polymer (epoxy) of about 1.14g/cm³ and the density of graphene of 2.2g/cm³.

Characterization

X-ray photoelectron spectroscopy (XPS) measurements were conducted on a Kratos Analytical AXIS His spectrometer with a monochromatized Al Ka X-ray source (1486.6 eV photons). Wide-angle X-ray diffraction (WAXD) patterns were recorded on a Bruker GADDS X-ray diffractometer using Cu K α radiation generated at 40 kV and 40 mA. For atomic force microscopic (AFM) studies, the GO and DGO suspensions were spin-coated onto a silica wafer and dried at room temperature. Tapping mode AFM images were obtained at ambient conditions using a Dimension 3100 AFM (Digital Instruments) with Si tips. The field-emission scanning

electron microscopic (FE-SEM) images of the materials were obtained on a JEOL 7600F SEM. TEM were examined using a JEOL 2010 microscope with LaB₆ filament at an acceleration voltage of 200 kV. Raman spectra were recorded with a WITec CRM200 confocal Raman microscopy system at an excitation wavelength of 488 nm and an air-cooling charge-coupled device (CCD) as the detector (WITec Instruments Corp, Germany). The electrical conductivity of TRDGO paper was measured by a Hewlett Packard 4140B pA Meter/DC Voltage source. The I-V curves were measured at ambient condition, over a range of 3 to -3V with a step of -0.1V across the pair of Au electrodes with a channel length of 100 μm. The electrical conductivity of the PVA/TRDGO nanocomposites and epoxy/TRDGO nanocomposites with low resistance were measured by a MCP-T610 low resistivity meter (Mitsubishi Chemical Analytech) with a standard four point probe, the electrical conductivity of the nanocomposites with high resistance were measured by a MCP-HT450 high resistivity meter (Mitsubishi Chemical Analytech).

Reference

1. Yang, L. P.; Yee, W. A.; Phua, S. L.; Kong, J. H.; Ding, H.; Cheah, J. W.; Lu, X. H. *Rsc Advances* 2012, **2**, 2208-2210.

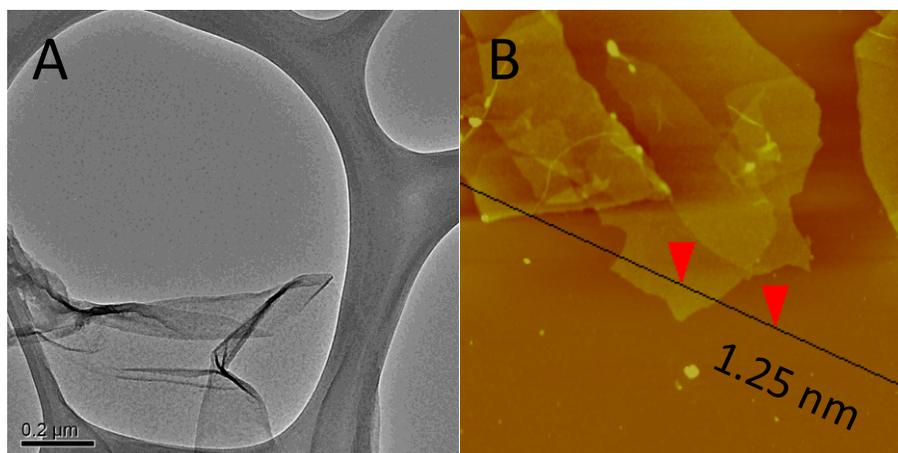


Figure S1 Transmission electron microscopy (TEM) image and Atomic Force Microscopic (AFM) height images of DGO.

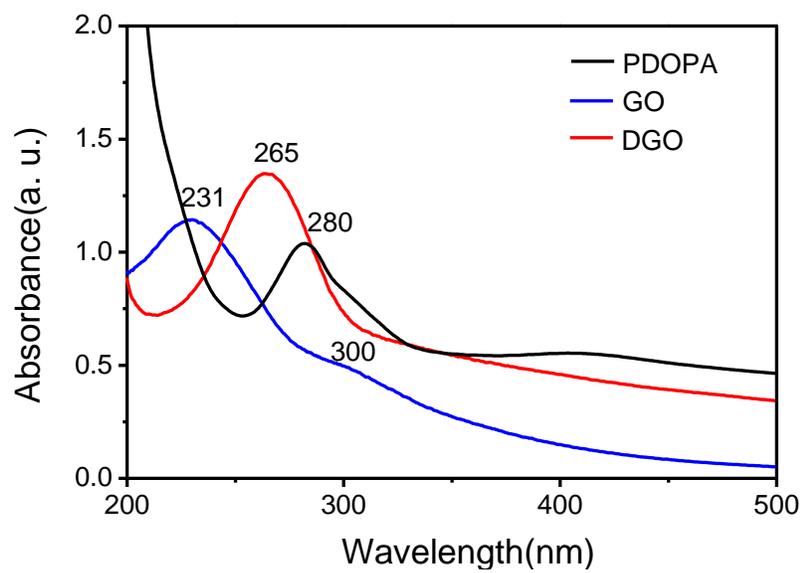


Figure S2 UV-vis spectrum of GO, PDOPA and DGO

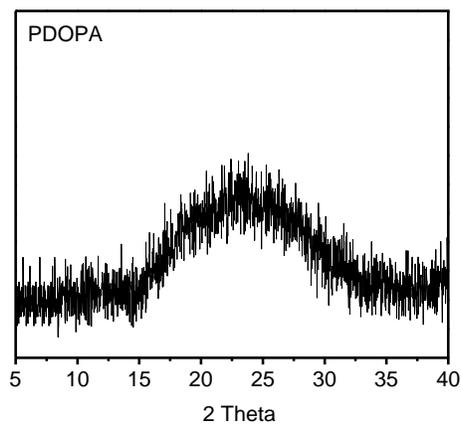


Figure S3 Wide-angle X-ray diffraction (WAXD) patterns of PDOPA powder.

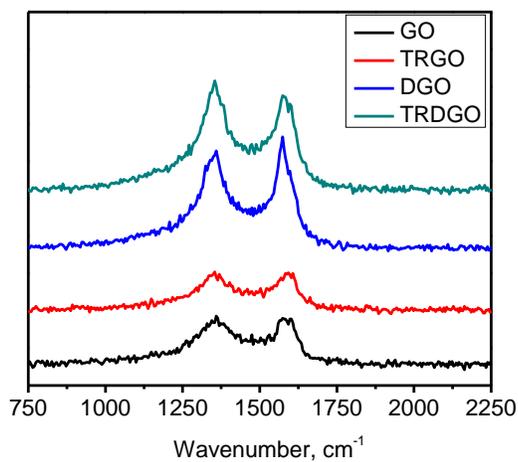


Figure S4 Raman spectrum of graphene oxide derivatives

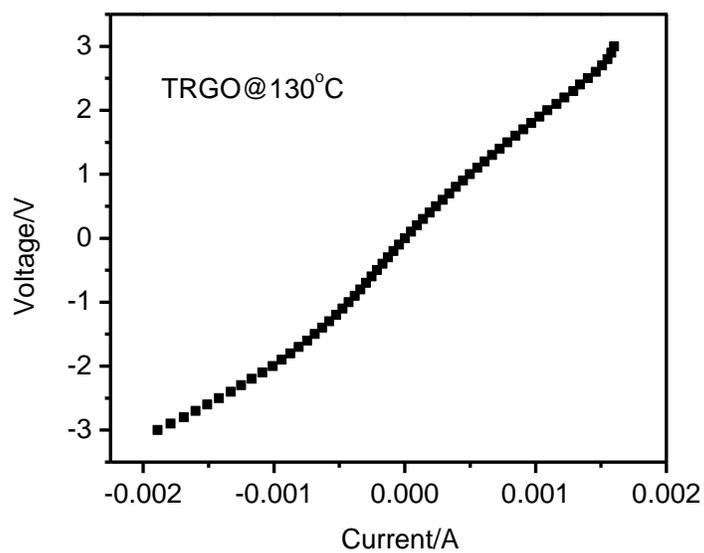


Figure S5 I-V curve of the TRGO film thermally treated at 130 °C

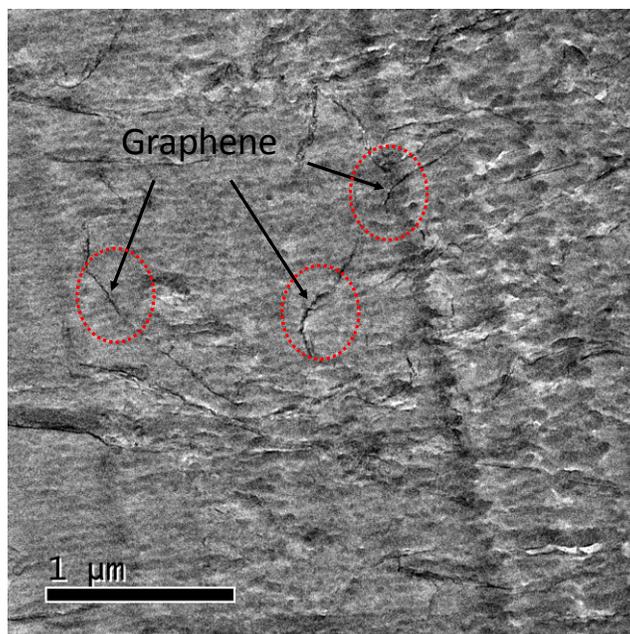


Figure S6 TEM image of epoxy/graphene nanocomposite(0.74 vol% DGO).