Electronic Supplementary Information for:

Electrochemical Supercapacitors based on a novel Graphene/conjugated polymer composite system

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Materials and Reagents

Graphite powder flakes from Sigma-Aldrich was used to prepare GO. 3,4-dimethoxythiophene, thiophene and 1,1,1-tris(hydroxymethyl)ethane were purchased from Sigma-Aldrich and used as received. Tetrahydrofuran (THF) from Junsei, Japan was distilled over sodium prior to usage. Thionyl chloride (Duksan Pure Chemical, Korea) was freshly distilled before use. All other solvents were used as received unless otherwise stated.

Preparation of Graphene Oxide Nanosheets

Graphite oxide (GO) was prepared using the Hummer's and Offeman's method by reacting commercially obtained graphite flakes (Aldrich) in a mixture of H_2SO_4, $NaNO_3$, and $KMnO_4$. In a typical reaction, briefly, 3 g of graphite powder was mixed with 1.5 g of $NaNO_3$ and introduced to 50 mL of concentrated H_2SO_4, and the mixture was cooled down to 0 ºC in an ice bath. Then, 9 g $KMnO_4$ was added slowly while stirring and maintaining the temperature below 5 ºC. The cooling bath was then removed and the suspension was brought down to room temperature. After that, 100 mL of distilled water was added and the temperature was increased to 90 ºC. The mixture was further diluted with 300 mL of water, stirred for 30 min and then treated with 50 mL of 5% H_2O_2, filtered and washed with deionized water until the pH was 7. The GO powder was dried by vacuum obtaining a final mass of 4 g with a greyish appearance. The GO was readily dispersed in water via ultrasonication to form stable colloids. The GO powder was examined by X-ray diffraction (XRD) and FTIR spectroscopy.

Synthesis of 3-methyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-3-yl)-methanol (ProDOT-OH) monomer.

In presence of catalytic amount of p- toluenesulfonic acid (*p*-TSA) in dry toluene, ProDOT-OH monomer was synthesized from 3,4-dimethoxythiophene and 1,1,1-tris(hydroxymethyl)ethane by a trans-esterification route by previously established method.[35] Briefly, to a 500 mL RB flask outfitted with a magnetic stir bar and a condenser, 3,4-dimethoxythiophene (2.0 g, 13.9 mmol), 1,1,1-tris(hydroxymethyl)ethane (2.5 g, 20.8 mmol), *p*-TSA (0.26 g, 1.39 mmol) and 200 mL of toluene was added. The reaction was heated to 100 °C

for 12 hours in argon atmosphere and the pale green solution was cooled to room temperature, extracted with ethyl acetate, washed with deionized water, dried over sodium sulphate and concentrated via rotary evaporator. The crude mixture was then purified by silica gel column chromatography (*n*-hexane/ethyl acetate, 1/1, v/v) to give a colourless liquid. ^{1}H NMR (400 MHz, CDCl$_3$) d: 0.94 (s, 3H), 1.97 (t, 1H), 3.71 (s, 1H), 3.73 (d, 4H), 4.07 (d, 2H), 6.48 (s, 2H).

Characterization techniques

High resolution transmission electron microscopic (HR-TEM) images were recorded using Joel Japan JEM 2010 instrument, to observe the nanoscale structures of the polymer functionalized GNS hybrids. The morphology and elemental analysis of the polymer-GNS hybrids were carried out by using field emission scanning electron microscopy (FESEM) equipped with *in-situ* energy dispersive X-ray (EDX) spectra (Hitachi, S-2700 model microscope, Japan). The changes in the surface chemical bonding of the GNS as well as the grafting behaviour of the hybrid were recorded by attenuated total reflection Fourier transform infrared spectrophotometry (ATR-FTIR, Perkin-Elmer Spectrum GX, USA). Raman spectra and images for the samples were obtained with a micro-Raman system (Alpha 300s, WITec GmbH) with 532 nm lasers. In order to avoid the laser-induced thermal effects or damage to the samples, the incident laser power was controlled to be less than 4 mW. The absorption spectra of the hybrid randomly dispersed in ethanol were obtained using a Perkin Elmer Lambda 40 ultraviolet-visible spectrophotometer. Thermogravimetric Analysis (TGA), thermal decomposition properties of the unmodified graphene, polymer and the conjugates, were recorded on a Perkin-Elmer (USA) Pyris 1TGA, Thermogravimetric analyser at a heating rate of 10 °C min^{-1} under continuous nitrogen flow. Composite pressed to tablets under a hydraulic press to mirror finishing were subjected to the standard four point probe method at ambient temperature (Advanced Instrument Technology (AIT) CMT-SR1000N with Jandel Engineering probe) which provided information on sheet resistance and the electrical conductivity. Factory recommended correction factors were used to calculate the conductivity values which were the averages of a few measurements of the same pressed film

Electrochemical Testing

Electrochemical measurements were conducted in a divided three-electrode cell controlled using a VersaSTAT3 AMETEK Model (Princeton Applied Research TN) potentiostat/galvanostat. The three-electrode electrochemical cell consisted of a composite loaded glassy carbon as the working electrode, an Ag/AgCl as the reference electrode, and platinum gauze as the auxiliary counter electrode were used throughout the work. Glassy carbon electrodes (GCE) of 3.0 mm in diameter were polished with finer emery-paper and 0.3 μm Al_2O_3 powder. This working electrode was cleaned in an ultrasonic bath for 1 minute and dried in air for use. Capacitive performances of the resultant hybrids were obtained in 1 M $H_2SO_{4\,(aq)}$. All potentials are reported relative to an Ag/AgCl (sat. KCl) reference electrode at different scan rates and the potential window for cycling were confined between -0.5 V and 1 V.

Specific Capacitance Calculation

The capacitance values (C) of the GO/Polymer hybrids were obtained from the cyclic voltammetry. To quantitatively evaluate the charge storage capacity, the specific capacitance of the composites is determined by the expression

Voltammetric charge/(potential window $\times$ composite loading mass) [1,2]

1   C. C. Hu, T. W. Tsou, *Electrochem. Commun.* 2002, **4**, 105.
2   B. E. Conway, *Electrochemical Supercapacitors: Scientific Fundamentals and Technological Applications*, Kluwer, New York, 1999, p21.
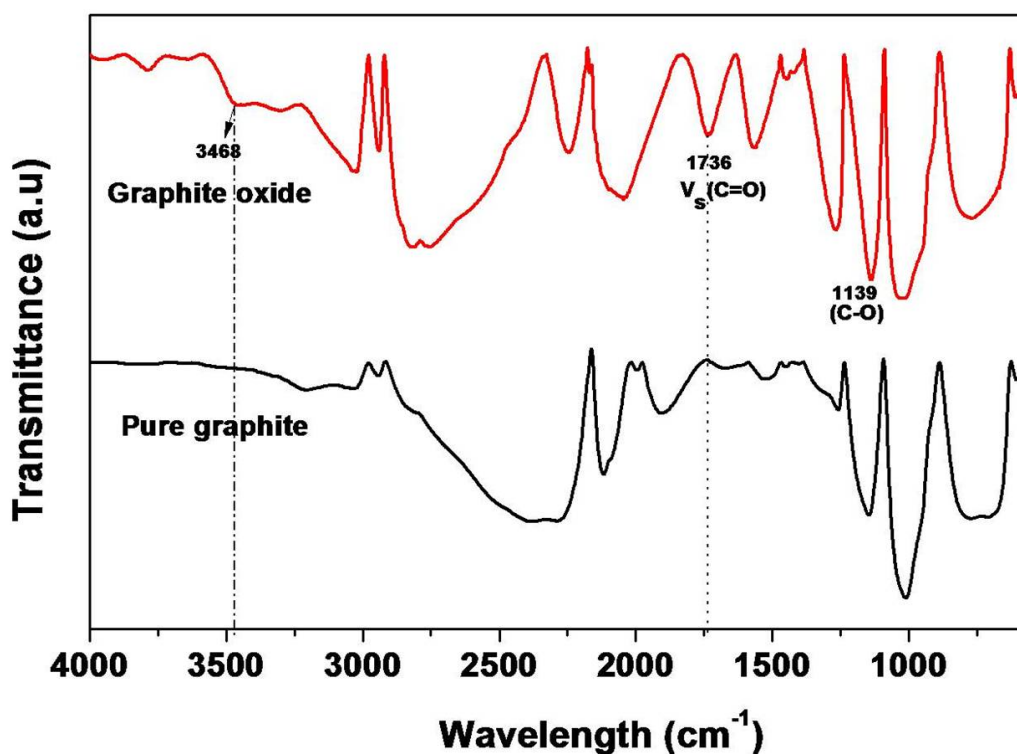
A. Characterization of GO substrates:

Fig. S1 ATR-IR spectra of the as received pristine graphite powder and graphite oxide samples.

A weak shoulder at 3468 cm^{-1} is attributed to the hydroxyl stretching vibrations of the C-OH groups. The characteristic band of the carboxylic acid groups in GO appears at around 1736 cm^{-1} which are assigned to the C=O stretching vibrations of the -COOH groups. The spectrum also shows a strong band at 1618 cm^{-1}, which can be assigned to the C=C stretch. A band at around 1400 cm^{-1} could possibly be due to the O-H deformations of the C-OH groups, while the band at 1139 cm^{-1} is attributed to C-O stretching vibrations, which confirm that GO contains some epoxy groups in the samples.[38]
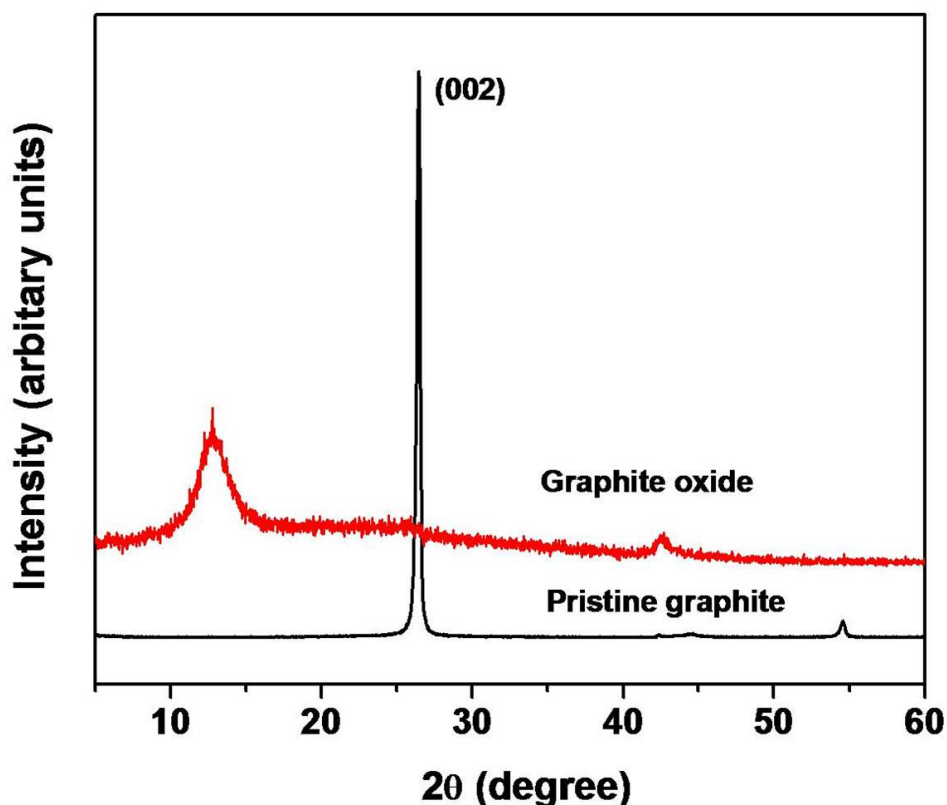
Fig. S2 XRD patterns of pristine graphite powder and GO. The (001) diffraction peak of graphite oxide appears around 2θ 11°.

The oxidation process was further confirmed using the XRD patterns of pristine graphite and GO shown in Figure S2. The traces for graphite show the characteristic peak of graphite at 2θ of 26° with a d-spacing of 0.35 nm. GO shows a diffraction peak at 2θ of 11° corresponding to a d-spacing of 0.8 nm. It has been reported that the d-spacing of GO depends on the method of preparation and also on the number of layers of water trapped in the structure of the material.39 Albeit the presence of traces of pristine graphite in the sample, the GO was highly dispersible in water after introduction to ultra-sonication for around 20 min giving slightly brownish solutions.
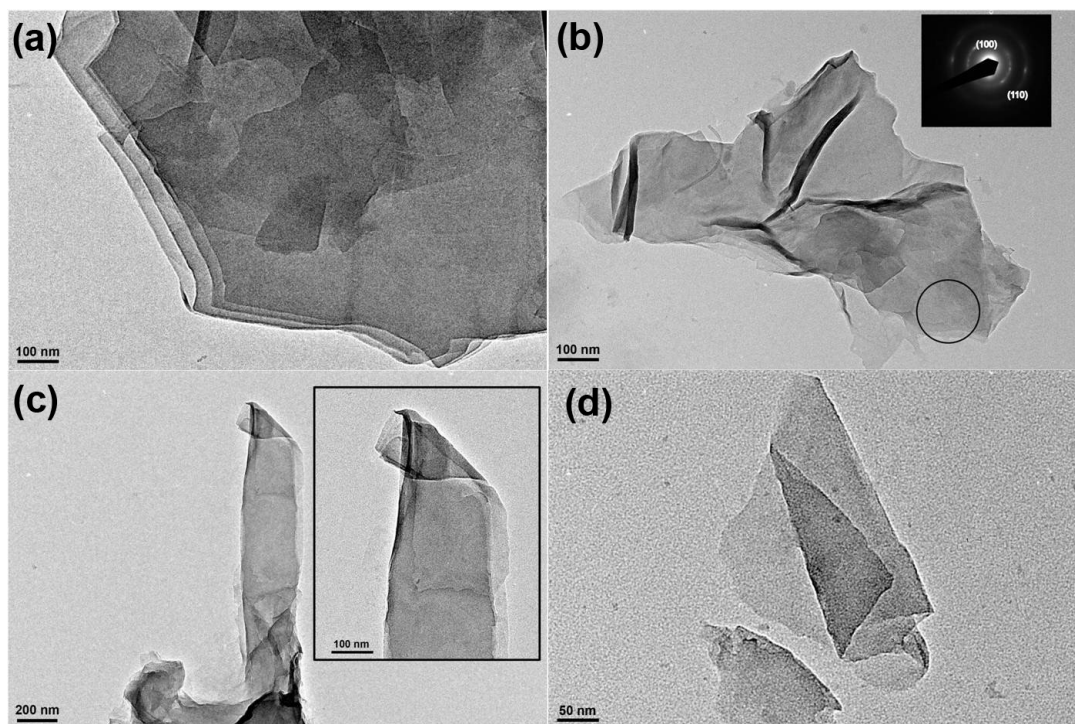
Fig. S3 High resolution TEM images of graphene oxide (GO) nanosheets showing a mixture of few layer graphene (FLGS) and their amorphous structure (a). The inset shows the corresponding selected area electron diffraction pattern (SAED). Bilayer (b) and a few single layer graphene sheets were also noticed (c and d).
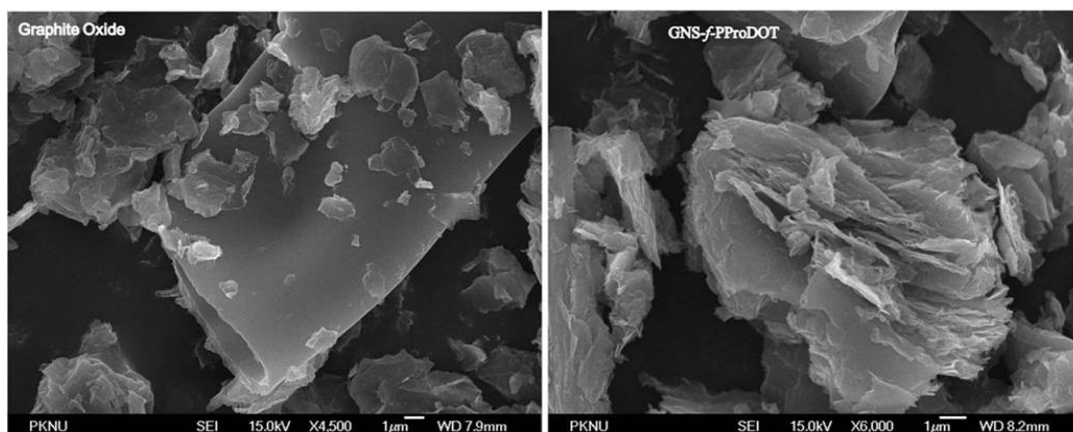
Fig. S4 FESEM images of graphene oxide (GO) nanosheets and the polymer composite hybrids showing the fracture surfaces.
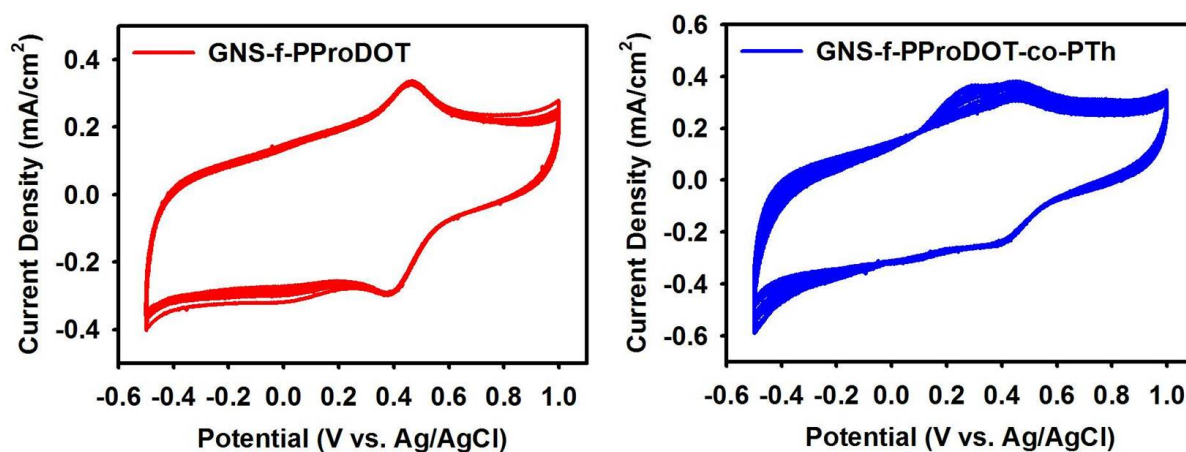

Fig. S5 Cycling stability of the polymer and co-polymer hybrids obtained at 10 mV/s. Scans collected every tenth cycle.