

Supporting Information

Graphene Based Composite Supercapacitor Electrodes with Diethylene glycol as Inter-layer Spacer

Yu Yu,^a YongbinSun,^b Changyan Cao,^a Shuliang Yang,^a Hua Liu,^a Ping Li,^a Peipei Huang,^b Weiguo Song^{*,a}

†Laboratory of Molecular Nanostructures and Nanotechnology, Institute of Chemistry, Chinese Academy of Sciences & Beijing National Laboratory of Molecular Sciences, Beijing, 100190, P. R. China

‡Graduate University of Chinese Academy of Sciences, Beijing, 100049, P. R. China

**E-mail*: wsong@iccas.ac.cn

Experimental section

Preparation of Graphene Oxide. Graphite oxide was prepared by a modified Hummers method. 1.5 g of graphite powder was mixed with 105 mL of 98 wt % sulfuric acid in an ice-bath. After 5 min, 15 mL 85 wt% phosphoric acid was added to undergo another 5-minute agitation. Then, 1 g potassium permanganate (KMnO_4) was slowly added in to stir for 1 h. The flask was transferred into a 35 °C oil-bath for 24 h. A 160 mL portion of deionized water was gradually added into the mixture, and the rate of water addition must be controlled to keep the temperature below 100 °C. The reaction was kept for 30 min, followed by treatment by 10 mL of 30% H_2O_2 solution. The resulting bright yellow suspension was diluted by water or EtOH and ultrasonic-treated intensively, and then centrifugated and washed more than 5 times to clean out remnant salt.

Preparation of DEG/graphene. A 6 mL portion of 3 mg/mL GO aqueous or alcoholic mucus was added into 54 mL diethylene glycol to form a uniform 0.3 mg/mL brown-colored suspension by vigorous stirring and ultrasonication. The suspension was sealed in a 100 mL Teflon-lined stainless steel autoclave to perform solvothermal process at 150 °C for 10 h. After completion of the solvothermal reaction, the product was washed using absolute ethanol and deionized water several times to remove remnant DEG solvent molecules, then dried in a freezer dryer.

Characterization. SEM image was taken on scanning electron microscopy (JEOL-6701F). TEM images and EDS results were taken on transmission electron microscopy (Tecnai G2 F20 U-TWIN). AFM images and cross-section contours were obtained on AFM Nanoscope IIIa. X-ray diffraction (XRD) patterns were recorded on a Rigaku diffractometer (Maxima XRD-7000) using $\text{Cu K}\alpha$ irradiation. TGA analysis was conducted on a Pyris 1 TGA Differential scanning calorimeter under air atmosphere at heating rate of 10 °C/min. IR, Raman spectra, and XPS information were obtained on Nicolet iN10 MX FT-IR Microscope, Thermo Scientific Raman microscope and ESCALab220i-XL photoelectron spectroscopy respectively. The specific surface area and pore size distribution were measured by BET on an Autosorb-1 analyzer.

Electrochemical Measurements. Electrochemical properties of DEG graphene were measured with an alkaline aqueous system (electrolyte: 6 M KOH). For preparing the electrodes of DEG/graphene, 24 mg synthesized materials was mixed with 3 mg acetylene black (Super P) and 3 mg polytetrafluoroethylene (PTFE) binder in a certain amount of ethanol. After an adequate ultrasonication, an obtained uniform suspension was dried to a homogeneous paste to coat on the nickel foam, which was then subjected to a 2 h drying under infrared lamp in the atmosphere. Then the dried electrode was cold-pressed at 4 MPa, followed by a 24 h drying at 80 °C in vacuum to remove ethanol and moisture thoroughly. CV measurement (scanning rates varying from 2 to 200 mV/s) was carried on an electrochemistry workstation (Princeton PARSTAT 2273). In the three-electrode system, a 1 cm \times 1 cm Pt sheet and SCE (saturated calomel electrode) were employed as counter and reference electrodes respectively. GC measurements (current density varying from 0.1 to 20 A/g) and CV measurement (from 2 to 200 mV/s also) were conducted in the form of two-electrode symmetrical coin cell, with a charge-discharge tester (Arbin 2000) and Princeton PARSTAT 2273 respectively. The electrochemical capacitances were obtained both from CV (both two-electrode and three-electrode system) and GC curves. The two-electrode symmetrical coin cells were also used for electrochemical impedance spectroscopy (EIS) measurement on Princeton PARSTAT 2273 in the frequency range of 0.1 – 100 kHz.

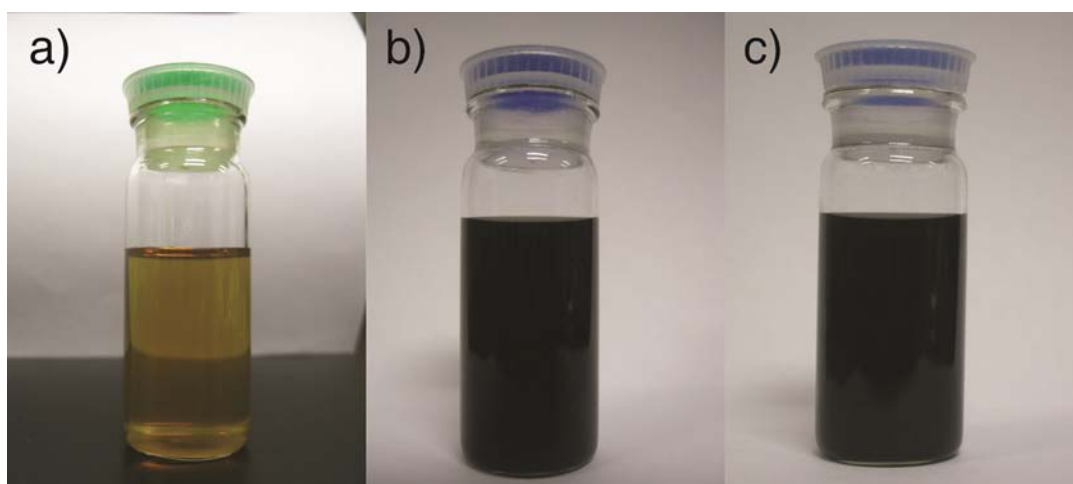


Figure S1. Photograph images of (a) GO disperse in diethylene glycol at a concentration of 0.3 mg/mL, DEG/graphene in H₂O (b) and EtOH (c) at a concentration of 0.2 mg/mL deposited after a month.

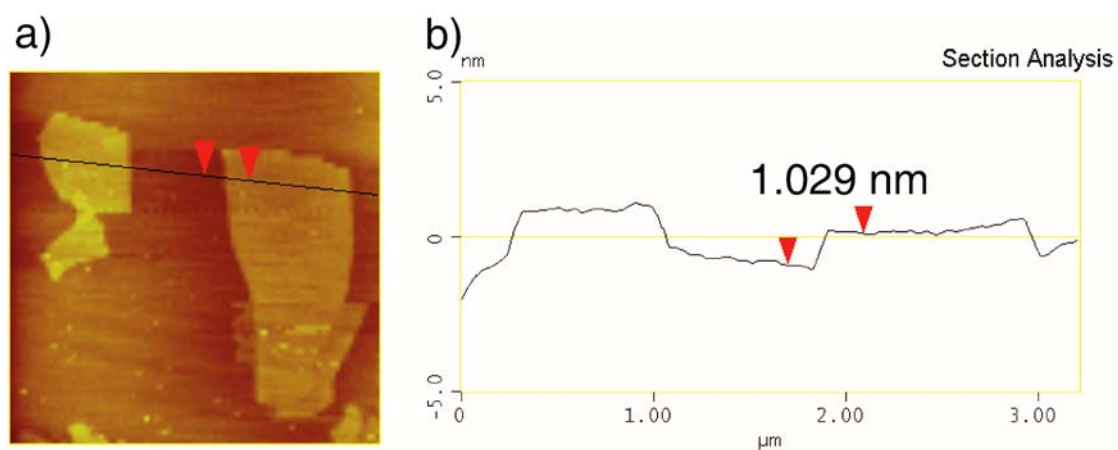


Figure S2. (a) AFM image and (b) cross-section contour of an individual GO sheet.

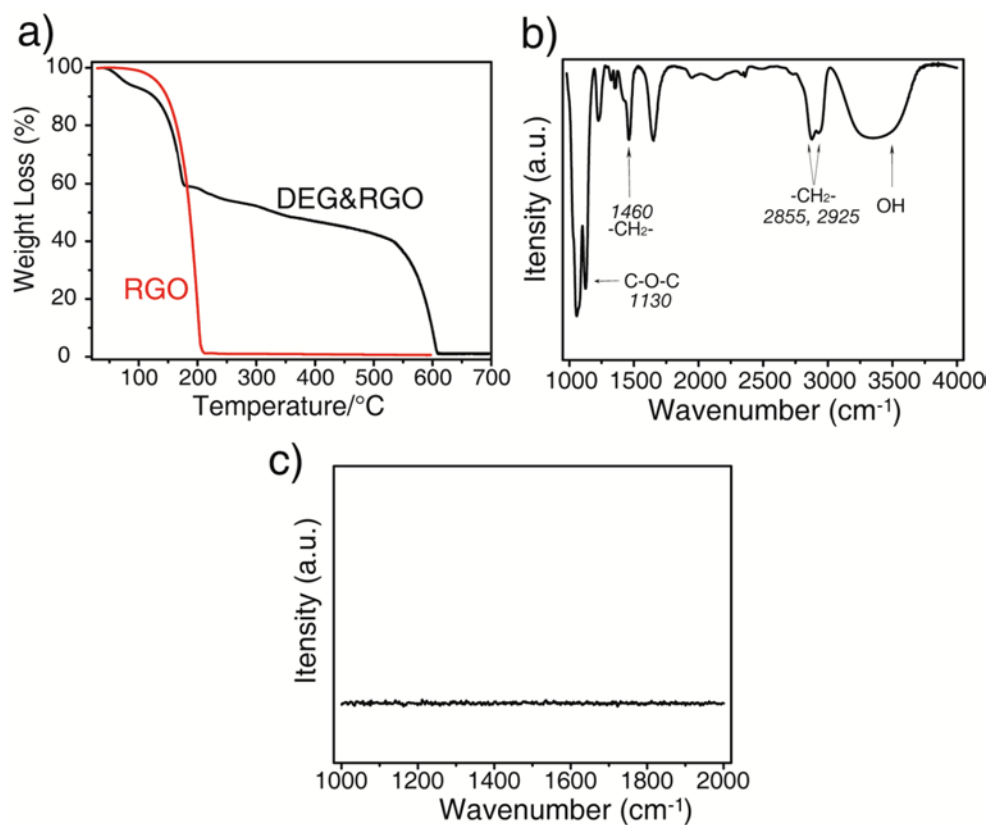


Figure S3. (a) TGA results of DEG and DEG-RGO physically mixed DEG&RGO, (b) FTIR spectra and (d) Raman spectroscopy of DEG.

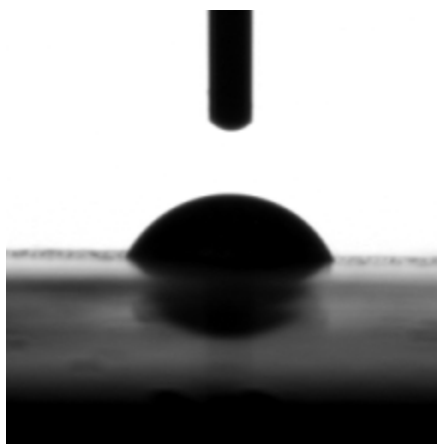


Figure S4. The static contact angle of DEG/graphene film and the water shape according to the film

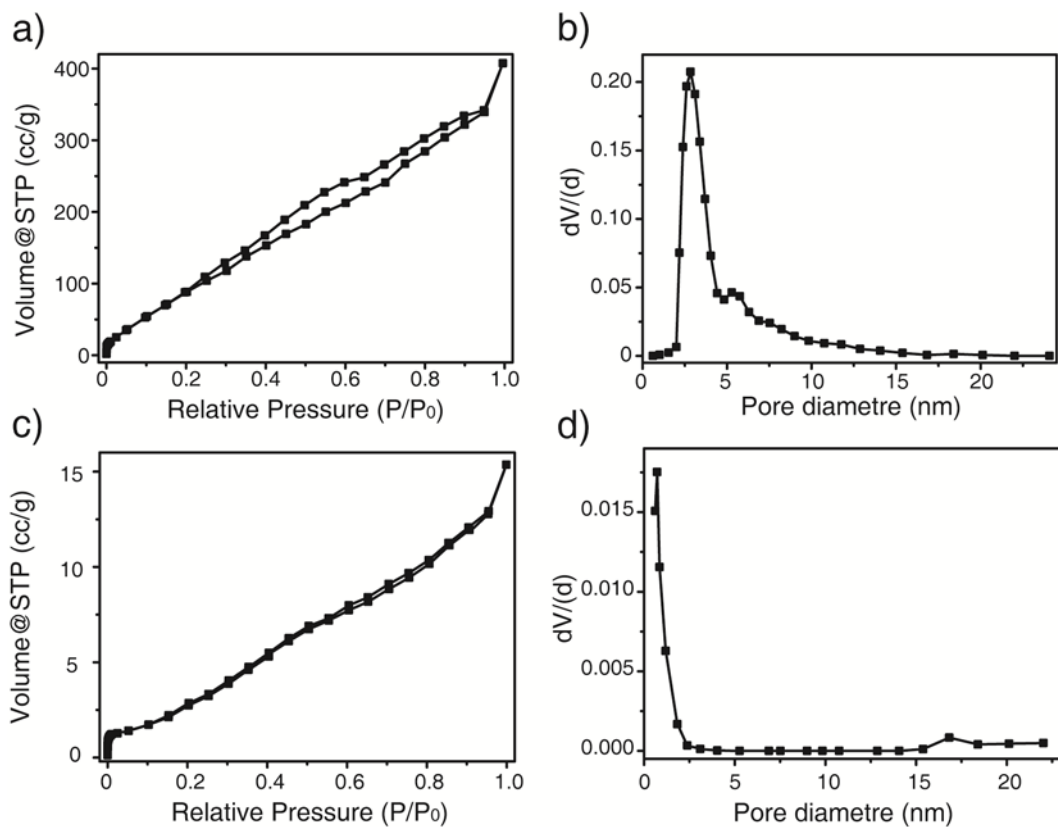


Figure S5. N₂ adsorption-desorption isotherm and pore distribution of DEG/graphene (a, b) and pristine GO (c, d) by freeze drying.

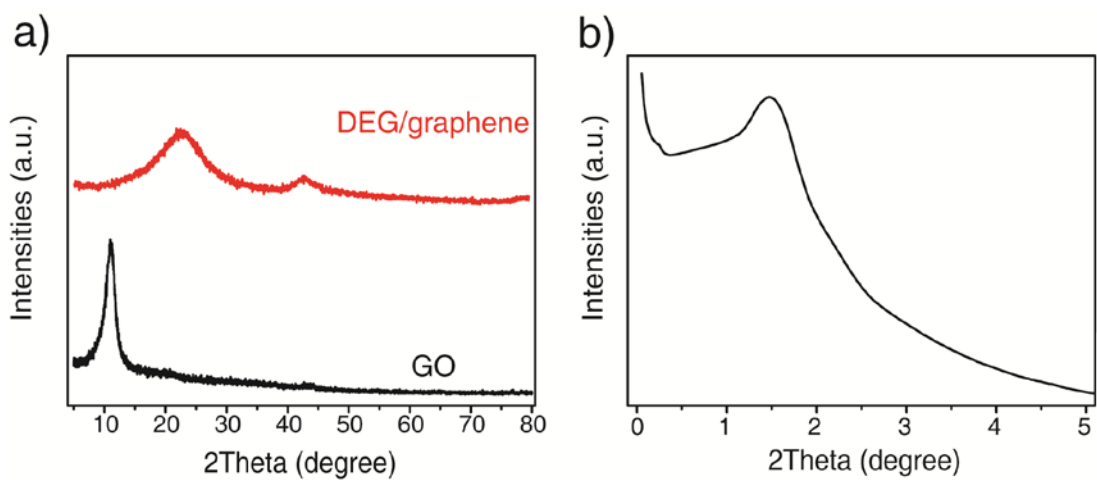


Figure S6. (a) WAXRD patterns of DEG/graphene (top) and GO (bottom). (b) SAXS patterns of DEG/graphene.

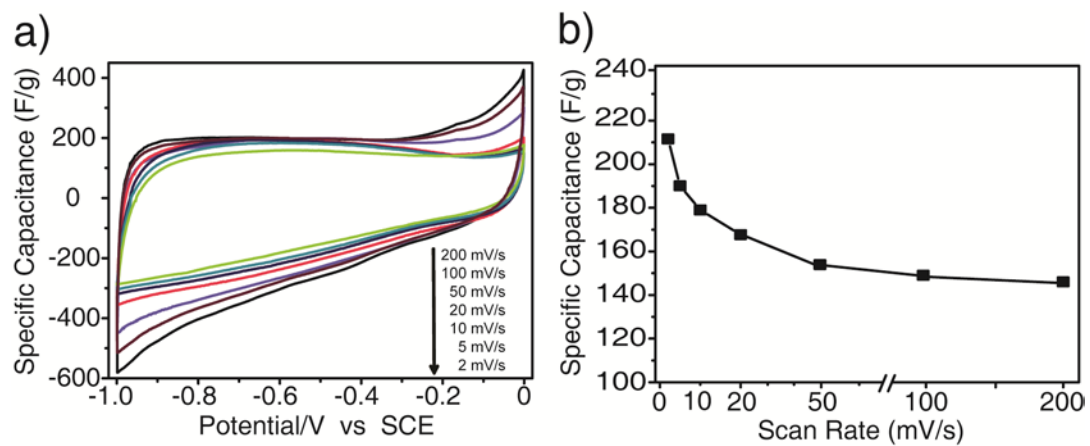


Figure S7. CV curves (a) and the specific capacitances calculated by CV of DEG/graphene at the scanning rate of 2-200 mV/s in the three-electrode system.

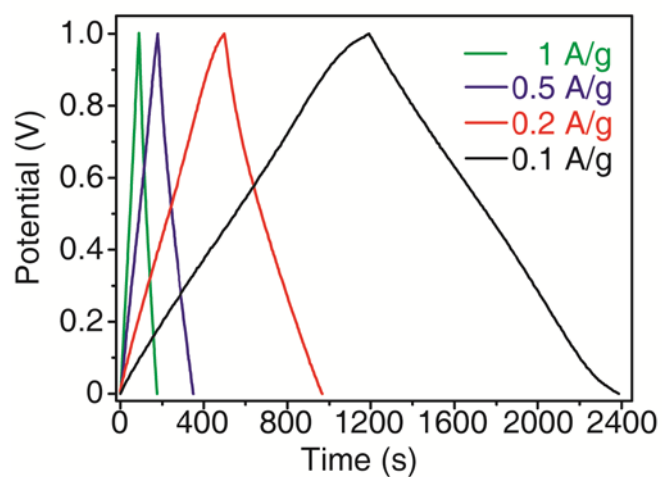


Figure S8. GC curves of DEG/graphene at the current densities of 0.1, 0.2, 0.5, and 1 A/g.

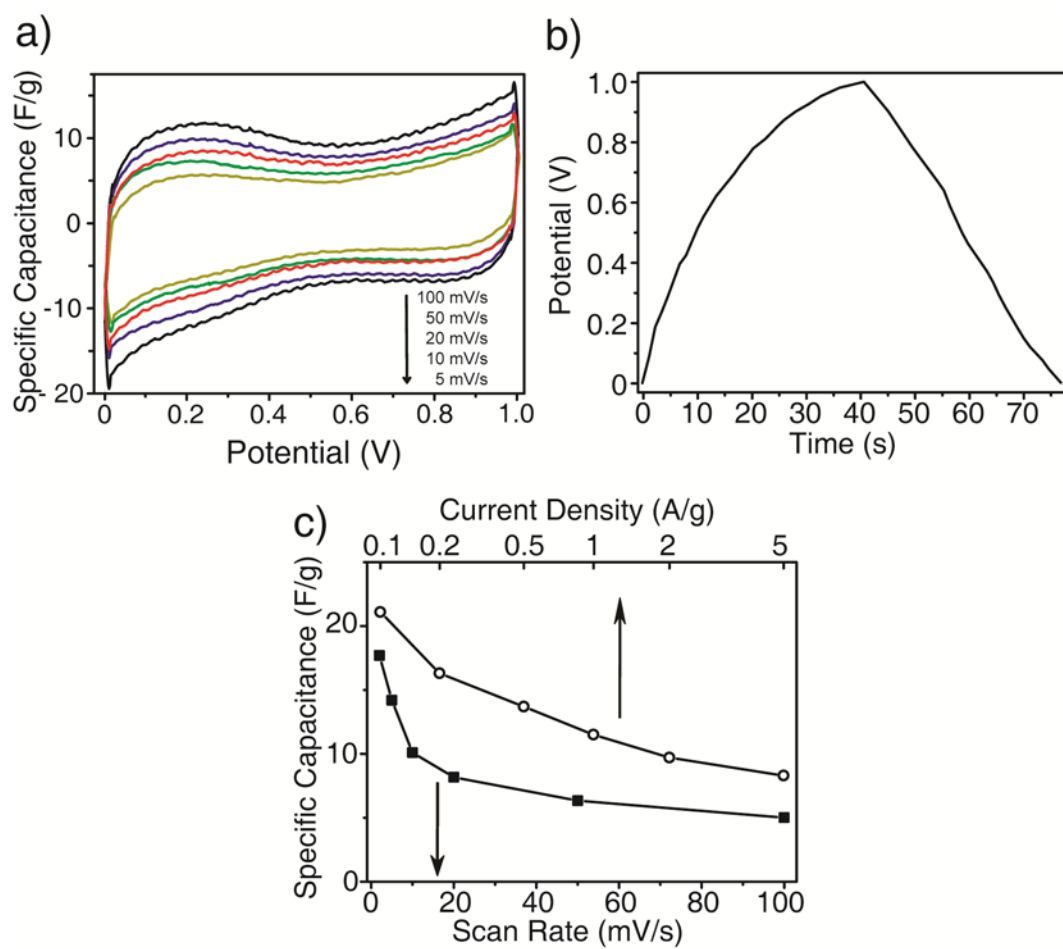


Figure S9. (a) CV curves (at the scanning rate of 5-100 mV/s), (b) GC curve at 0.2 A/g, and (c) the specific capacitances of pristine GO calculated by CV (bottom axis) and GC method (top axis).

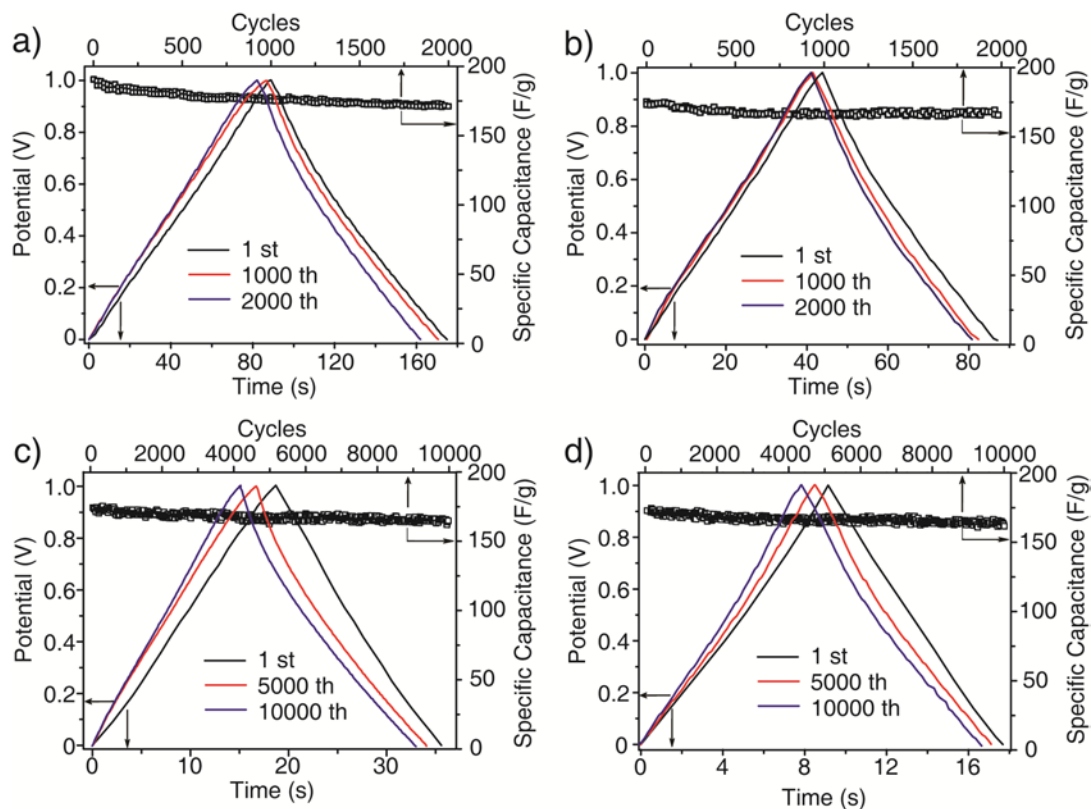


Figure S10. GC curves (left and bottom axes) of the 1st, 1000th, and 2000th at 1 A/g (a), 2 A/g (b), or 1st, 5000th, and 10000th at 5 A/g (c), and 10 A/g (d), and the retention of Cs at the corresponding current densities, respectively.

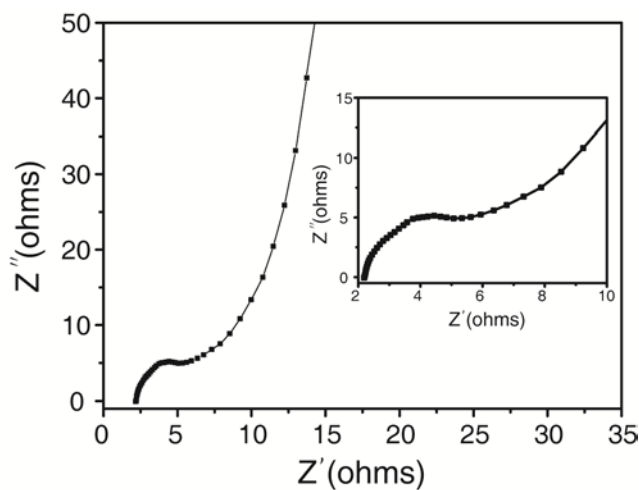


Fig. S11 Nyquist plots of two-electrode symmetrical coin cells of pristine GO supercapacitors electrodes. The inset is the close-up EIS image in the high frequency region.