Electronic Supplementary Information

High-performance and flexible electrochemical capacitors based on graphene/polymer composite films

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Synthesis of GO: GO was prepared from natural graphite powder by a modified Hummers method.^[S1] The details are described as follows. Graphite (3.0 g) was added to concentrated H₂SO₄ (70 mL) under stirring at room temperature, then NaNO₃ (1.5 g) was added, and the mixture was cooled to 0 °C. Under vigorous agitation, KMnO₄ (9.0 g) was added slowly to keep the temperature of the suspension lower than 20 °C. Successively, the reaction system was transferred to a 40 °C water bath and stirred for 30 min. Then, 150 mL of water was added, and the solution was stirred for 15 min at 90 °C. Additional 500 mL of water was added and followed by a slow addition of 15 mL of H₂O₂ (30%), turning the color of the solution from dark brown to yellow. The mixture was filtered and washed with 1:10 HCl aqueous solution (250 mL) to remove metal ions followed by washing with 200 mL of water to make a GO aqueous dispersion. And then it was purified by dialysis for one week to remove the remaining metal species. Finally, it was centrifuged at 4000 rpm to remove the unoxidized or uncompletely oxidized graphite powder.

Preparation of polymer gel electrolyte: The polymer gel electrolyte was prepared according to the method reported previously.^[S2] Briefly, polyvinyl alcohol (PVA) (5g, molar mass = 80,000 g, 99% hydrolyzed, Sinopharm Chemical Reagent Co. Ltd. Shanghai, China) was mixed with distilled water (50 mL). The mixture was heated at 90 °C under continuous

stirring until the solution turned clear. Then, concentrated phosphoric acid solution (3.491 mL, 85% aqueous solution) was added and the solution was stirred for additional 1 h.

XPS and Raman spectroscopic characterizations of GO and rGO_{55}/PVP_{45} . The XPS spectra of GO and rGO_{55}/PVP_{45} are shown in Fig. S1a. The C/O atomic ratios of GO and rGO_{55}/PVP_{45} were measured to be 0.56 and 5.15, respectively. Accordingly, the C/O atomic ratio of rGO was caculated to be about 4.5. The Raman spectrum of GO or rGO_{55}/PVP_{45} has two prominent bands around 1348 and 1585 cm⁻¹ (Fig. S1b), and they are assigned to the D and G bands of carbon, respectively. The G band is related to graphitic carbon and the D band is associated with the structural defects or partially disordered structures of graphitic domains. The I_D/I_G value of GO was calculated to be 0.78, while that of rGO_{55}/PVP_{45} was higher, 1.40. This result indicates that the oxidized areas of GO sheets were partly restored upon reduction with hydrazine, forming small conjugated domains.

Fabrication of scotch tape supported graphite foils: Graphite foil $(30 \text{ cm} \times 30 \text{ cm}, 0.13 \text{ mm thick})$ was purchased from Alfa Aesar. A strip of scotch tape was pasted on the surface of graphite foil and then peelled off. Consequently, a thin layer of graphite was adhered onto scotch tape.

Calculations: The capacitance of each device was calculated from the galvanostatic charge/discharge curves at different current densities using the formula:

C = i/(-dV/dt)

Where i is the current applied, and dV/dt is the slope of the discharge curve. Specific capacitances for each individual electrode were calculated based on the area of the device, the weight or the volume of each electrode according to the following formulae:

Areal capacitance : $C_a = 2 C/A$

Gravimetric capacitance: $C_g = 2 C/m$

Volumetric capacitance: $C_v = 2 C/V_1$

where A is the area of the device, m is the weight of rGO in each electrode and V_1 is the volume of each electrode.

The power and energy density were calculated from the galvanostatic curves at different charge/discharge current density using the following formulae:

$$\mathbf{P} = (\mathbf{V}_{\text{max}} - \mathbf{V}_{\text{drop}})^2 / (4\mathbf{R}_{\text{ESR}}\mathbf{V})$$

$$E = C \times (V_{max} - V_{drop})^2 / (2 \times 3600 \times V)$$

Where P is the power density (W/cm³), V_{max} and V_{drop} are the voltage and voltage drop at the begining of discharge, respectively. R_{ESR} is the internal resistance of the device and V is the total volume of the device excluding the current collectors. E is the energy density in Wh/cm³, and C is the capacitance of the device.

Supporting Tables and Figures

Table S1 Electrical conductivities of rGO/PVP composite films with different rGO contents.

rGO content (wt%)	38	55	65	71
Conductivity (S/m)	4.2	247.9	609.2	815.9



Fig. S1 (a) X-ray photoelectron spectroscopy (XPS) of GO and rGO_{55}/PVP_{45} . (b) 514 nm excited Raman spectra of PVP, rGO_{55}/PVP_{45} and GO.



Fig. S2 SEM images of the cross-section (a) and the surface (b) of a scotch tape supported graphite foil.



Fig. S3 Configurations of the ECs with solid polymer gel (a) and liquid (b) electrolytes.



Fig. S4 Capacitance retention of a solid-state flexible rGO_{55}/PVP_{45} EC tested at a high

current density of 100 A/g versus cycling numbers.



Fig. S5 The performance of an rGO₅₅/PVP₄₅ EC with 1.0 M H₃PO₄ liquid electrolyte: (a) CV curves recorded at various scan rates, (c) Nyquist plot with a magnification for the high-frequency region as the inset, (c) C_v s measured at different charge/discharge current densities.



Fig. S6 Digital photographs showing the flexibility of the rGO₅₅/PVP₄₅ ECs.



Fig. S7 The capacitance changes of a solid rGO_{55}/PVP_{45} EC during the process of bending to 180° with a radius of 2.5 mm for 1,000 cycles.



Fig. S8 A red LED lighted by three solid ECs connected in series.



Fig. S9 Capacitance retention of rGO_{71}/PVP_{29} ECs with organic electrolyte tested at a high current density of 100 A/g versus cycling numbers.

References:

[S1] W. S. Hummers Jr and R. E. Offeman, J. Am. Chem. Soc., 1958, 80, 1339–1339.

[S2] M. F. El-Kady, V. Strong, S. Dubin and R. B. Kaner, Science, 2012, 335, 1326-1330.