Supporting Information

Revisiting the capacitance of polyaniline by using graphene hydrogel as a substrate: the importance of nano-architecturing

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Experimental section

Fabrication of PANI@OGH film

OGH films were prepared by vacuum filtration of chemical converted graphene colloid using the procedure reported previously.[21, 22] The OGH film was cut to the desired size (about 1*1 cm^2), followed by immersion in 5 ml of 1.0 M HCl aqueous solution containing 0.15 ml of aniline monomer. The mixture was stored at 0 ^oC for 2 hours. 5 ml of 1.0 M HCl aqueous solution containing 0.09 g ammonium peroxydisulfate (pre-cooled to 0 ^oC) was then poured into the above mixture, and the mixture was left at 0 ^oC for another 0.5 hours. The resultant films were thoroughly rinsed by HCl aqueous solution, ethanol, ammonia and milli-Q water subsequently. To measure the weight fraction of PANI in PANI@OGH film, both the OGH film and PANI@OGH films with the same sizes were dried at 50 °C overnight before weighing and calculation. Following the above procedure, for the same size of 1*1 cm^2, we measured the weight of OGH film and PANI@OGH film of 0.55 mg and 0.72 mg, respectively, resulting in the weight fraction of PANI of 24 wt% in this PANI@OGH film. In the present work, the polymerization time was controlled to achieve different loading amount of PANI within the PANI@OGH film. As a result, for the same size of 1*1 cm^2, we measured the weight of PANI@OGH films of 1.06 mg, 1.31 mg and 1.67 mg for polymerization time increased to 1 hour, 2 hours and 4 hours, respectively. The weight fraction of PANI in these PANI@OGH films was thus found to be 48 wt%, 58 wt% and 67 wt%, respectively.

Structural and Properties Characterization

SEM images were obtained using a JEOL JSM 7001F scanning electron microscope. XRD spectrum was obtained by Philips 1130 X-ray diffractometer (40 kV, 25 mA, Cu Kα radiation, λ = 1.5418 Å) at room temperature with the 2θ angle ranging from 5° to 50°. The scan rate was 2° min^{-1} and scan step was 0.02°. FT-IR spectra were collected by PerkinElmer Spectrum 100 (Universal ATR Sampling Accessory), and the strain-stress curves were obtained by the use of dynamic mechanical thermal analyzer (Rheometrics Mark IV DMTA).

Electrochemical Testing

Supercapacitors using the PANI@OGH film as the electrodes were assembled in a symmetrical two-electrode configuration.[18] To assemble the supercapacitor, two pieces of PANI@OGH films with the same sizes (about 1*1 cm^2) were attached to Pt foils respectively, followed by sandwiching a filter paper containing 1.0 M H_2SO_4 (as electrolyte) between them. Then the resultant device was fully wrapped by parafilm and tightly clamped. The Pt foils were connected with platinum wires by a toothless alligator clip, allowing electrochemical testing by Versastat-4 potentiostat. CV tests were carried out at a scan rate ranging from 10 mV/s to 1 V/s under the potential between -0.1 V and 0.9 V. The galvanostatic charge/discharge tests were carried out at the same potential range at current densities ranging from 0.1 A/g to 100 A/g. The gravimetric capacitance of PANI@OGH film was calculated as follows:

$$C\text{s} = 2i/[(\Delta U/\Delta t)\cdot m] = 2i\cdot t/(\Delta U\cdot m) \quad \text{(Equation 1)}$$

where i is the applied current, t is the discharging time, ΔU is the voltage drop upon discharging (excluding the iR drop), and m is the net mass of both CCG and PANI in a single electrode.

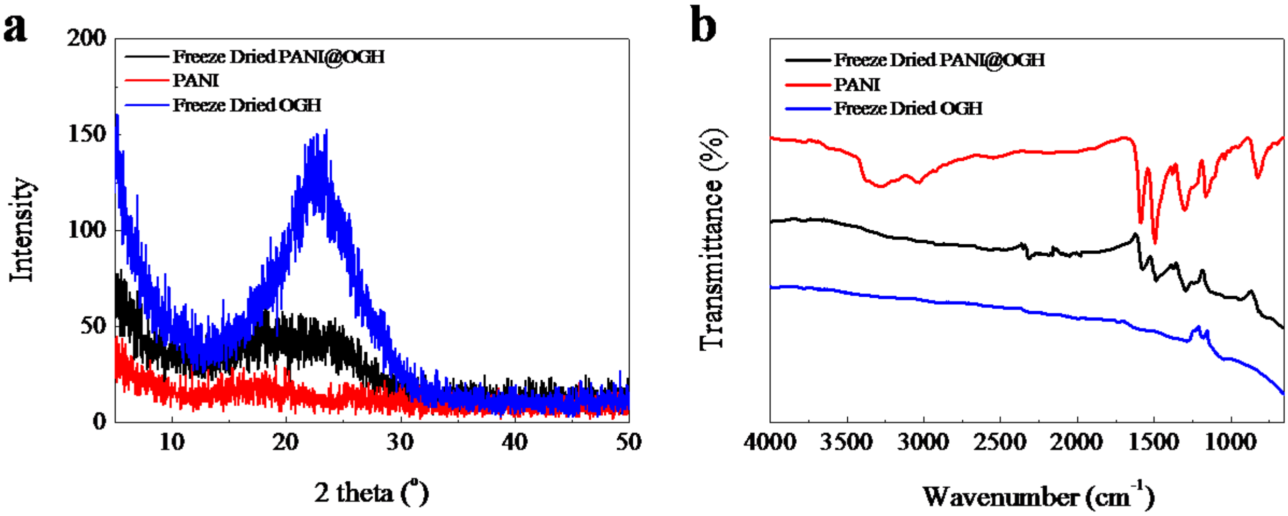

Figure S1 (a) XRD spectrum and (b) FT-IR spectrum of freeze dried PANI(48wt%)@OGH, freeze dried OGH film and pure PANI.

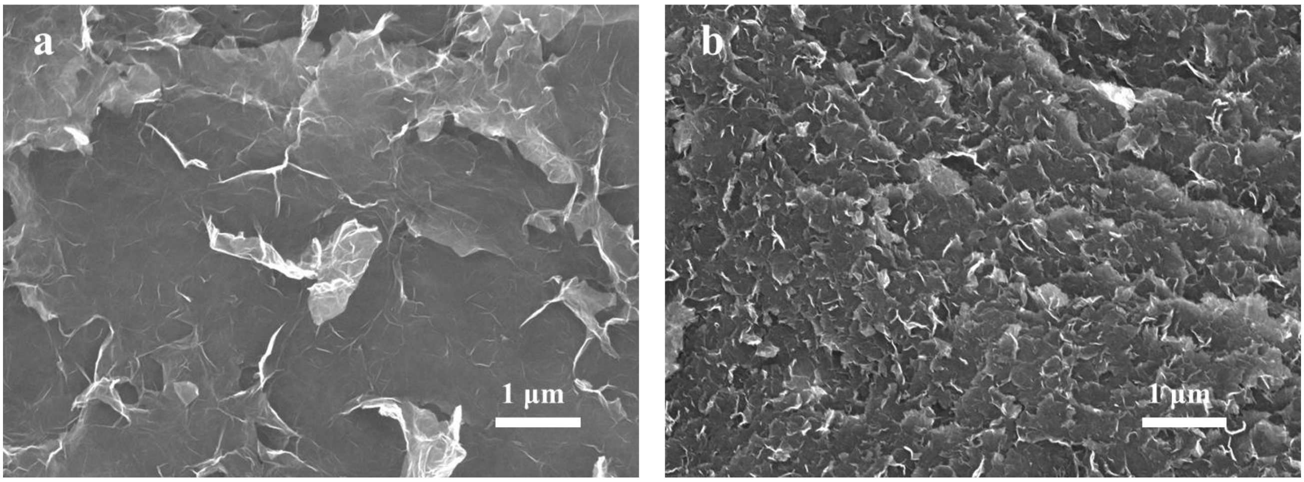

Figure S2 SEM images of the top view of interior structure of (A) freeze dried OGH film and (B) freeze dried PANI@OGH film. The different morphologies indicate a successful and uniform coating of PANI within OGH film.

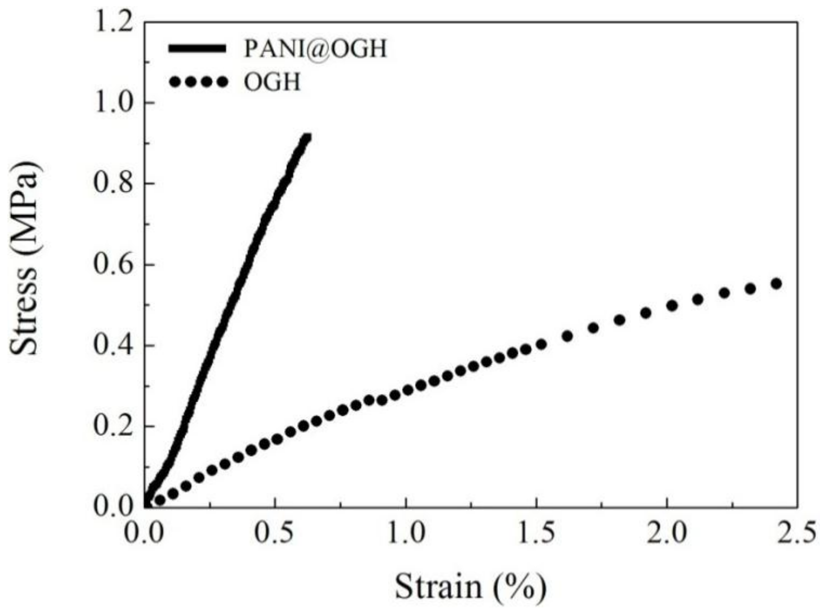

Figure S3 Strain-stress curves of the PANI@OGH film. The data for the PANI-free OGH film was presented for comparison. The result reveals a Young's modulus of 140±10 MPa of PANI@OGH film, about 4 times as that of the OGH film. Remarkably, this value is highly comparable to that of conventional rubbers.

Table S1 Conductivity determination of OGH, dedoped and doped PANI@OGH films

	OGH	**Dedoped PANI@OGH**	**Doped PANI@OGH**
Thickness (μm)	91±2	102±3	95±2
Sheet resistance (Ω/square)	518±22	461±42	100±27
Conductivity (S/m)	21±2	20±3	105±3

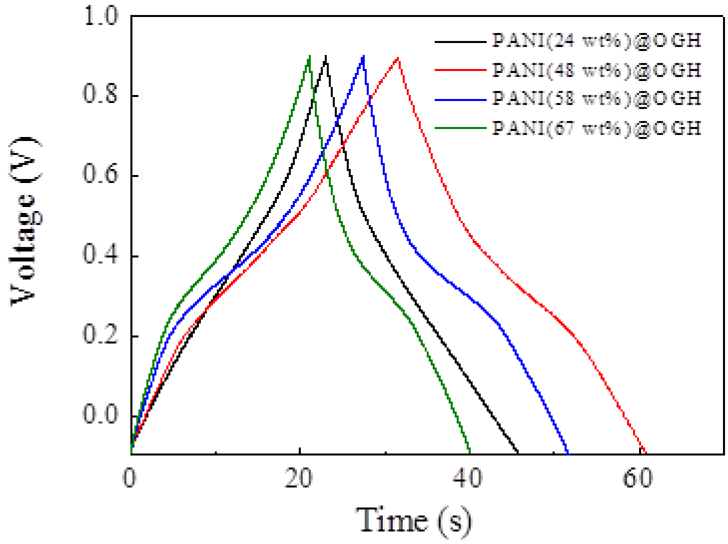

Figure S4 Galvanostatic charge/discharge curves of PANI@OGH films with different PANI contents obtained at a current density of 10 A/g,

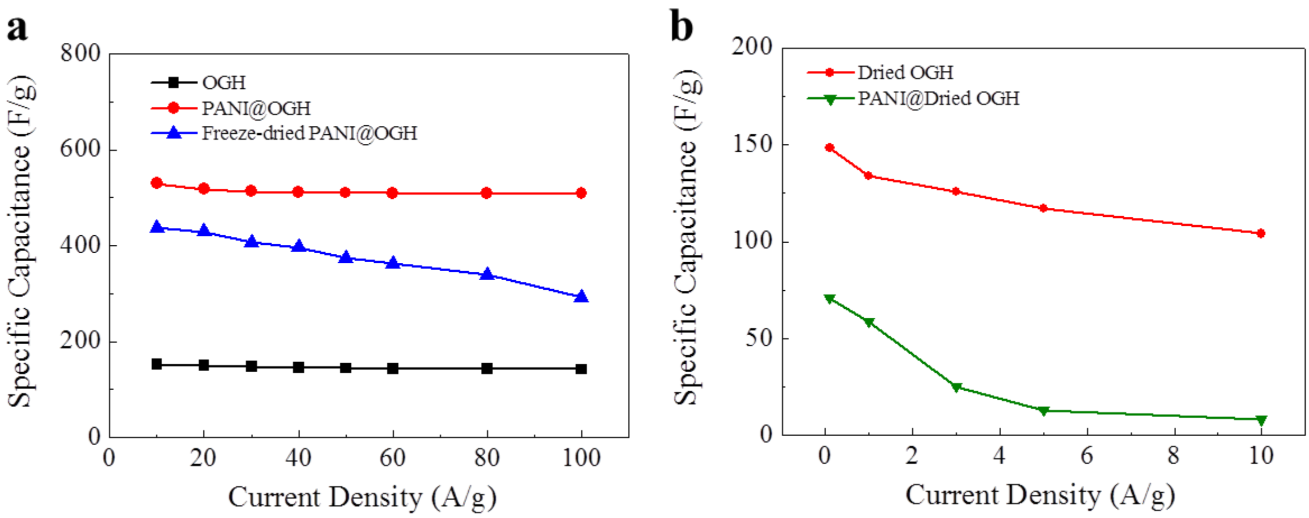

Figure S5 Specific capacitance of (a) OGH film, PANI(48wt%)@OGH film and freeze-dried PANI(48wt%)@OGH film, and (b) Dried-OGH film and PANI@Dried-OGH.

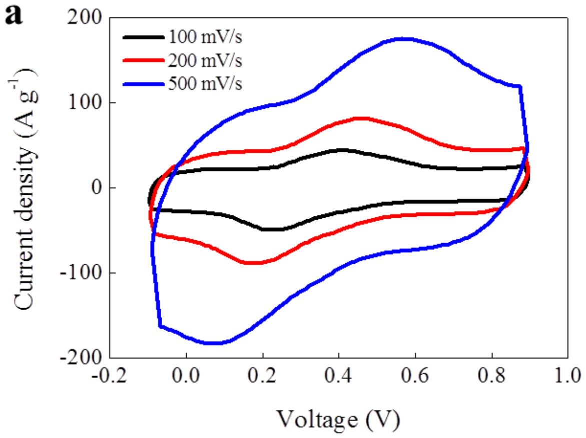

Figure S6 (a) CV curves of PANI(48wt%)@OGH film at a scan rate of 100, 200 and 500 mV/s respectively; and (b) galvanostatic charge/discharge curves of PANI(48wt%)@OGH film at a current density of 20, 50 and 100 A/g, respectively.

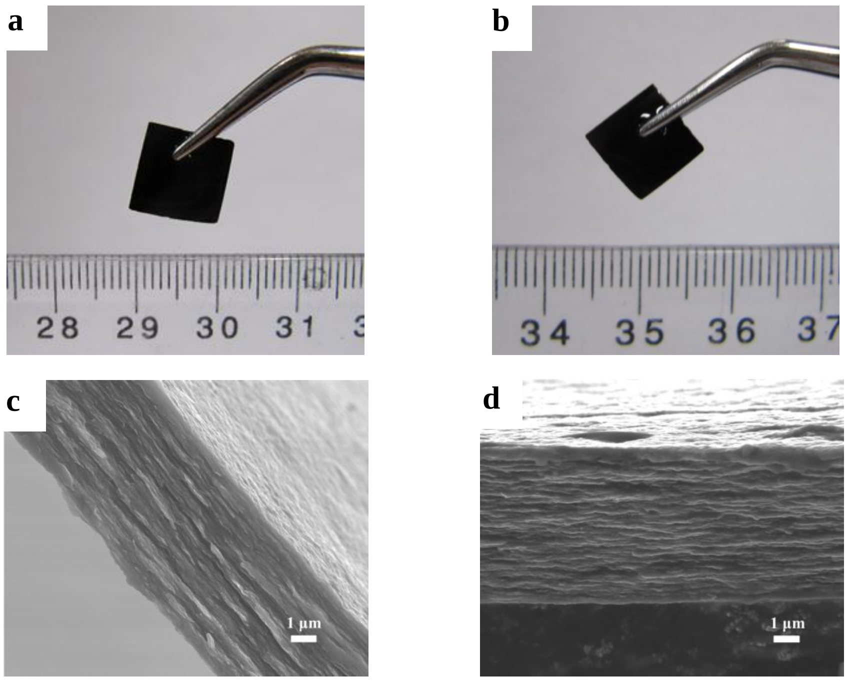

Figure S7 Photographs of PANI@OGH film and SEM images of freeze-dried PANI@OGH film (a, c) before and (b, d) after 10,000 times of electrochemical test operated at a current density of 100 A/g. These images reveal no obvious change in the morphology of PANI@OGH film before and after the test, indicating that the PANI@OGH film is mechanically stable with long cycling life.