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Supplementary information

Facile electrodeposition of reduced graphene oxide hydrogel for high-performance supercapacitors

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1. Graphene oxide synthesis

A small amount of expandable graphite was charged into a 1 L beaker and heated for 10 s in a microwave oven. The graphite expanded to about 150 times its original volume. Graphene oxide was synthesized from the expanded graphite according to a modified Hummers method.[S1] Typically, 1 kg of concentrated H_2SO_4 (95 wt%) was charged into a 2 L beaker equipped with a mechanical stirrer (Teflon impeller). The beaker was then placed into an ice bath and chilled to 0 °C. Seven grams of expanded graphite were gradually added under stirring to make a suspension. Next, 45 g of $KMnO_4$ was slowly added so that the temperature did not exceed 20 °C. The temperature was then raised to 35 °C and the suspension was stirred for 2 h. The beaker was subsequently chilled again in an ice bath and 1.5 L of deionized water was slowly added so as to maintain a temperature below 70 °C. The mixture was stirred for 1 h and then diluted with 10 L of deionized water. Fifty milliliters of H_2O_2 (30 wt%) was slowly added, and vigorous bubbles appeared as the color of the suspension changed from dark brown to yellow. The suspension was centrifuged and washed four times with a 1 M HCl solution, followed by centrifuging at 10,000 rpm and washing with deionized water to completely remove the acid until the pH of the GO dispersion reached 6. In its as-synthesized form, the GO dispersion was a paste. After drying the GO dispersion at 80 °C under vacuum for 24 h, the concentration of GO was determined to be approximately 1.0 wt%.

2. Characterizations

To determine the mass of ERGO deposited on stainless steel mesh substrate and water content in ERGO hydrogel, the mass of substrate (m_s) was determined using by microbalance with an accuracy of 0.01 mg. After electrodeposition, mass of ERGO hydrogel on stainless steel substrate ($m_{ERGO\ hydrogel} + m_s$) was weight with microbalance. Then, ERGO hydrogel on stainless steel substrate was dipped in large amount of DI water for 24h to completely remove H2SO4 trapped in ERGO hydrogel and subsequently dried at 100 oC for 12 h. The mass of ERGO on stainless steel substrate ($m_{ERGO} + m_s$) was determined again with microbalance. Water content in ERGO hydrogel was calculated following formula:

$$Water\ content = \frac{(m_{ERGO\ hydrogel} - m_{ERGO}) * 100\%}{m_{ERGO\ hydrogel}}$$

The morphology of the freeze-fried ERGOs was examined by scanning electron microscopy (SEM, Hitachi 4800). The UV-vis spectra of GO and ERGO were measured using UV-VIS-NIR spectrophotometers (Perkin Elmer, Lamda 950). X-ray photoelectron spectroscopy (XPS) analysis was performed on X-ray photoelectron spectrometer (SPECS Phoibos 100 MCD analyzer) using a non-monochromatized Al-Kα X-ray source (SPECS XR 50). Raman spectra were measured with a confocal Raman microscope (Thermo Scientific) utilizing incident laser light with a wavelength of 532 nm. Thermogravimetric analysis (TGA) was performed on thermogravimetric analyzer (Perkin Elmer) under a nitrogen atmosphere at a heating rate of 10 °C/min.

3. Fabrication of ERGO supercapacitor and electrochemical measurement

After electrodeposition, ERGO hydrogel on stainless steel substrate was exchanged electrolyte by dipping in 1M H_2SO_4 or 1M H_2SO_4 + 0.2M HQ solution for 5 hours. Subsequently, the uncoated substrate was removed except two wires, which were then connected to measurement devices for electrochemical characterization. Next, two identical electrode was assembled with a cellulose filter paper sandwiched in between, served as separator. The supercapacitors were sealed in polyethylene bag and infiltrated with electrolytes (Fig. S1).

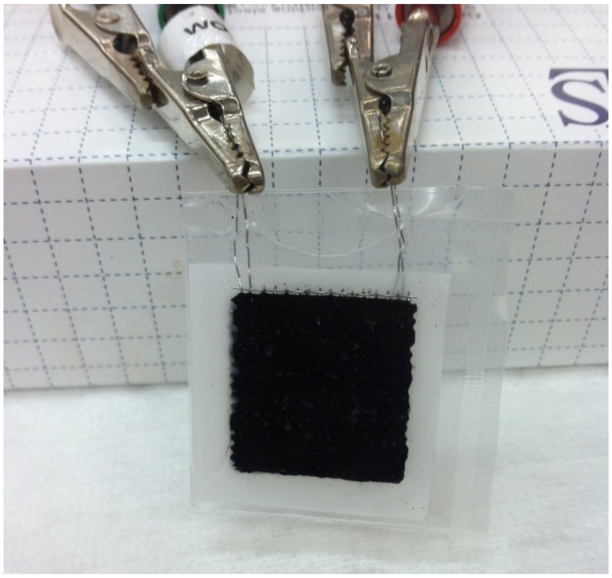

Fig. S1 Photograph of ERGO supercapacitor cell

The cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were carried out using potentiostat/galvanostat PARSTAT 2273 (Princeton Applied Research). The EIS measurements were performed at open circuit potential with a sinusoidal signal over a frequency range from 100 kHz to 10 mHz at an amplitude of 10 mV. The galvanostatic charge – discharge measurements were carried out using Arbin battery tester BT2000 (Arbin Instrument). The specific capacitance (C_{sp}) of ERGO derived from galvanostatic discharge curves were calculated based on the following formula:

$$C_{sp} = 4(I\Delta t)/(m\Delta V)$$

where I is the constant discharge current, Δt is the discharge time, m is the net mass of two electrode and ΔV is voltage drop on the discharging (excluding the IR drop).

4. SEM images of GO

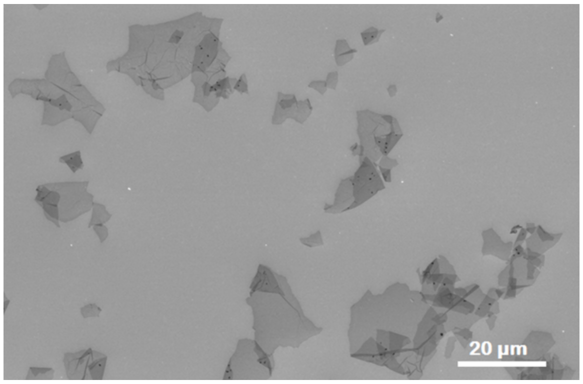

Fig. S2. SEM image of GO

5. Elemental composition of GO and ERGO

Table S1. Elemental composition of GO and ERGO

	C (at.%)	**O (at.%)**	**C/O**
GO	66.9	30.4	2.2
ERGO	86.6	13.4	6.5

6. Thermogravimetric analysis

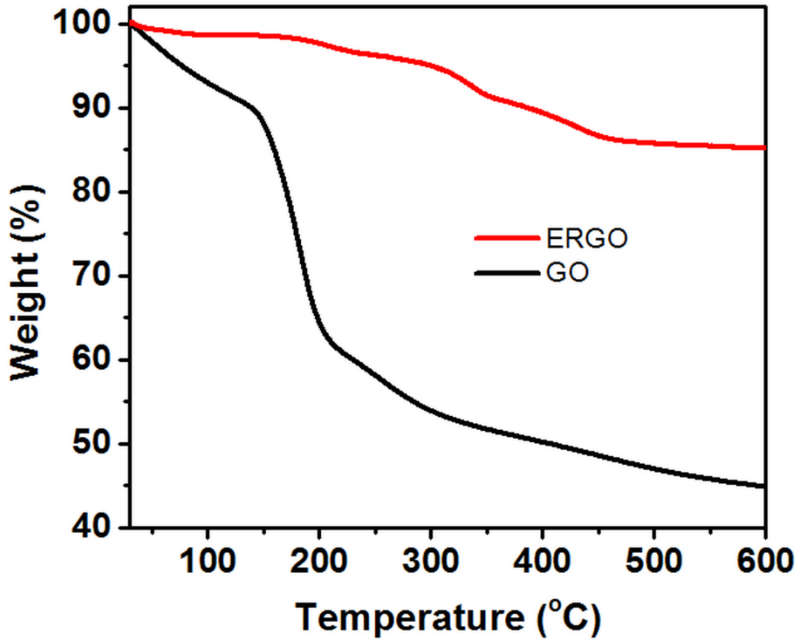

Fig. S3 TGA curves of GO and ERGO

7. X-ray diffraction

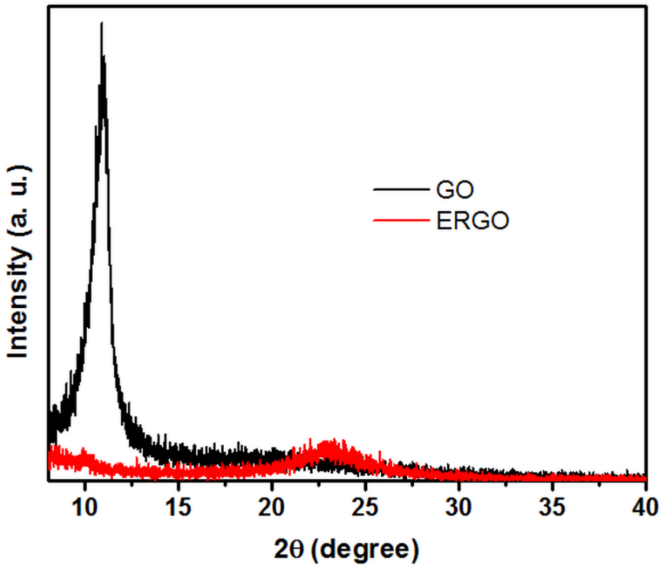

Fig. S4 XRD of GO and ERGO

8. CV and impedance spectra of ERGO after 10000 cycles

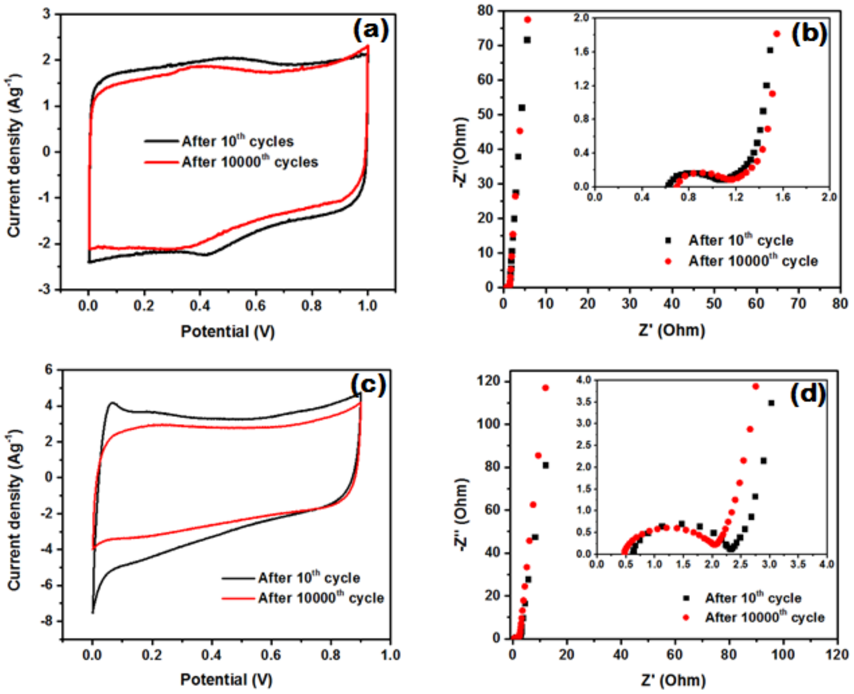

Fig. S5: CV at scan rate of 20 mV s^{-1} and Nyquist plot of ERGO supercapacitors using (a,b) H_2SO_4 and (c,d) H_2SO_4 + HQ electrolytes, respectively

Fig. S5 shows the CV curves and impedance spectra of ERGO supercapacitors after 10 and 10000 charge-discharge cycles. The CV curve of ERGO in H_2SO_4 electrolyte after 10000 charge-discharge cycles was still quasi-rectangular, indicating the electrical double layer capacitive behaviour (Fig. S5(a)). Interestingly, the broad redox peaks in range of 0.0-0.7 V of CV curves, which were attributed to the reversible redox reaction of remained oxygen functional groups such as hydroxyl, carbonyl and carboxyl groups, shifted to smaller potential range of 0.0-0.5 V, implying that some of these oxygen functional groups would be removed during the charge-discharge process. The Nyquist plot of ERGO in H_2SO_4 electrolyte after 10000 charge-discharge cycles was almost identical to that after 10 cycles, indicating that the diffusion of electrolyte and charge transfer resistance was almost unchanged after 10000 charge-discharge cycles.

The CV curves of ERGO in H_2SO_4 + HQ after 10000 charge – discharge cycles became more rectangular and the redox peaks of HQ was significantly suppressed, indicating the degradation of HQ during charge-discharge process (Fig. S5(c)). The ESR of ERGO in H_2SO_4 + HQ after 10000 charge – discharge cycles was slightly decreased, implying better ion diffusion and smaller charge transfer resistance (Fig. S5(d)).