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Electronic Supplementary Information (ESI)

Self-assembled Macroporous Coagulation Graphene Network with High Specific Capacitance for Supercapacitor Applications

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1 Experimental detail

1.1 Materials

The graphite powder used in the experiments was purchased from Sinopharm Chemical Reagent Co. Ltd.. Before use, graphite powder with the size of 300-400 mesh was sieved out. Polyethyleneimine (PEI) with M_w of 10000 was obtained from Sigma-Aldrich. Polytetrafluoroethylene (PTFE) powder (6-10 μm) was purchased from Alfa Aesar. Other chemicals and solvents were all commercially purchased and used without further purification. Ultrapure water (resistivity > 18.0 MΩ·cm) was supplied by a Milli-Q water purification system and used for all experiments.

1.2 Characterization

UV-vis spectra were recorded by using an Agilent 8453 UV-vis spectrophotometer. Thermogravimetric analysis of the samples was carried out in a flowing oxygen atmosphere using a TGA Q5000 apparatus. The heating rate of GO and GO/PEI assemblies was 10 °C/min, while the one

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for PEI was 5 °C/min. Surface area measurements were carried out with a QuantaChrome Autosorb-1 instrument. The sample cell was evacuated to 10^{-5} Torr and heated for 12 h at 250 °C in order to degas the sample before the adsorption study. The scanning electron microscopic (SEM) images were acquired by applying a JEOL JSM-7401F field emission scanning electron microscope (FE-SEM) and EVO MA 25 operated at an accelerating voltage of 20 kV and 15 kV. The transmission electron microscopic observation was conducted on HITACHI S-5500. X-ray diffraction (XRD) patterns of the GO and CGCA samples were recorded at room temperature by a Bruker D8 Advance X-ray diffractometer. The Raman spectra were measured on a Renishaw 1000 microspectrometer using an excitation wavelength of 514.5 nm. The bonding energy of elements was measured by an X-ray photoelectron spectrometer (ESCALAB250Xi) using a monochromatized Al Kα x-ray source of 1486.6 eV under normal incidence and the binding energy of XPS peaks was standardized by the C 1s peak at 284.8 eV. The atom force microscopic (AFM) images of the film surfaces were obtained by using a Nanoscope-IIIa scanning probe microscope in the tapping mode.

1.3 Synthesis of graphene oxide

Graphite oxide (GO) was prepared via a modified Hummers method, which is briefly presented as follows. Graphite (3 g), $K_2S_2O_8$ (2.5 g), P_2O_5 (2.511 g) and H_2SO_4 (12 mL) were added into a 50 mL flask. After reaction at 80 °C for 4.5 h, the mixture was poured into excess of cold deionized water. The pre-oxidized graphite was collected by filtration and then re-dispersed in H_2SO_4 (120 mL). Under the ice bath cooling, $KMnO_4$ (15 g) was added very slowly into the dispersion. After treated at 35 °C for 2 h, the dispersion was diluted with the deionized water (250 mL) and stirred for 4 h. H_2O_2 (12 mL) was then slowly added into the dispersion to remove the excessive oxidant. Crude graphite oxide was collected by filtration using a 0.45 μm filter membrane. The crude product was then washed with HCl (1 M, 1 L), water (1 L) sequentially, and separated by centrifugation. The GO was obtained by drying at 45 °C for 24 h to afford the brown graphite oxide.

1.4 PEI-induced GO coagulation conditions

Fresh samples of GO-water dispersion (0.8 mg/mL) and PEI aqueous solution with different concentrations from 0.1 mg/mL to 100 mg/mL were prepared. The PEI solutions (1 mL) with the concentrations of 0.1, 0.2, 0.4, 0.6, 0.8, 1, 10, 100 mg/mL were poured into a GO dispersion (3 mL) and immediately shaken to ensure sufficient mixing. Coagulation was observed at once. After standing aside for 60 min and centrifuged at 1500 r/min for 3 min, the supernatant were collected and monitored by UV-vis spectroscopy to get the concentration of residual PEI and GO.

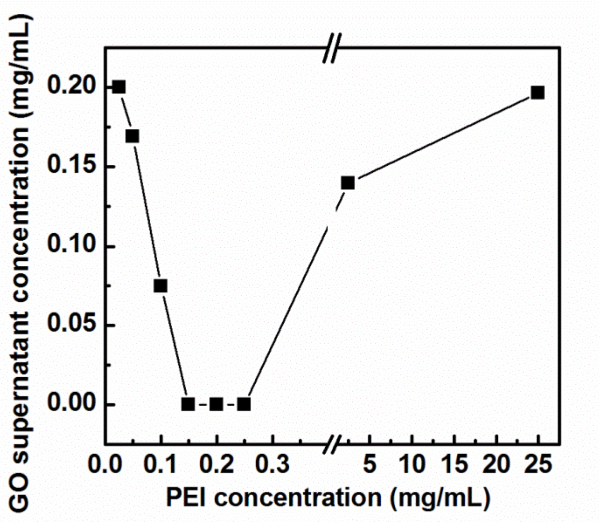


Figure S1. GO concentration in the supernatant verse PEI concentration.

1.5 Preparation of CGCA and supercapacitor electrode fabrication

As indicated in section 1.4, 20 mL PEI solution (0.6 mg/mL) was poured into 80 mL GO dispersion (0.8 mg/mL), shaking and standing aside for 1 min to allow the GO/PEI assemblies to deposit to the container bottom. The sediment was collected through filtration and then freeze-drying for 48 h. The sample was heated at 400 °C for 4 h in a horizontal tube furnace (50-mm diameter), with a nitrogen flow of 50 sccm under atmospheric pressure. The temperature was increased from room temperature to 400 °C at 10 °C/min. For the preparation of the CGCA electrode, a certain amount of CGCA powder was mixed with 10% conductive carbon black and 5% PTFE (60 wt% dispersion in water) in ethanol and grinding using a mortar. After ethanol was volatilized, the obtained homogeneous paste was coated on the foam nickel as 1×1 cm size, which was then dried at 130 °C for 1 h. The corresponding mass loading of active material was 0.53 mg. The dried electrode was cold-pressed at 2 MPa, followed by a 24 h drying at 130 °C in vacuum to remove ethanol and moisture.

Electrochemical performances of the prepared supercapacitor electrode were measured using a three-electrode system, where CGCA electrode worked as the working electrode, Pt wire as the counter electrodes and Hg/HgO as the reference electrode. A KOH solution (6 M) was used as the measured electrolyte. Cyclic voltammetry and galvanostatic charge–discharge tests were carried out in the potential range between -0.8 and 0 V on a commercial instrument (Arbin Instruments Corp., Model SCTS) at room temperature. Electrochemical impedance spectroscopic (EIS) measurement was performed by using a commercial instrument (Biological Science Instrument, VSP-300), measured in the frequency range from 200 kHz to 100 mHz at a 5 mV AC amplitude.

From charge-discharge measurements, the gravimetric specific capacitances, surface areal specific capacitances, energy density and power density of the CGCA supercapacitor electrode were obtained from the acquired data using following equation:

$$C_g = I\Delta t/m\Delta V$$

$$C_{sc} = C_g/S_a$$

$$E = \frac{1}{8}C_g\Delta V^2$$

$$P = E/\Delta t$$

where I is the constant current, Δt is the discharging time, m is the mass of the electrode material , ΔV is the voltage drop during the discharging process and S_a is the specific surface area from BET.

2. Characterization results

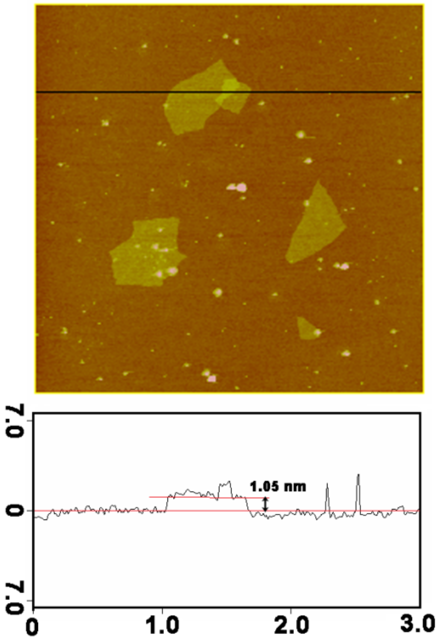
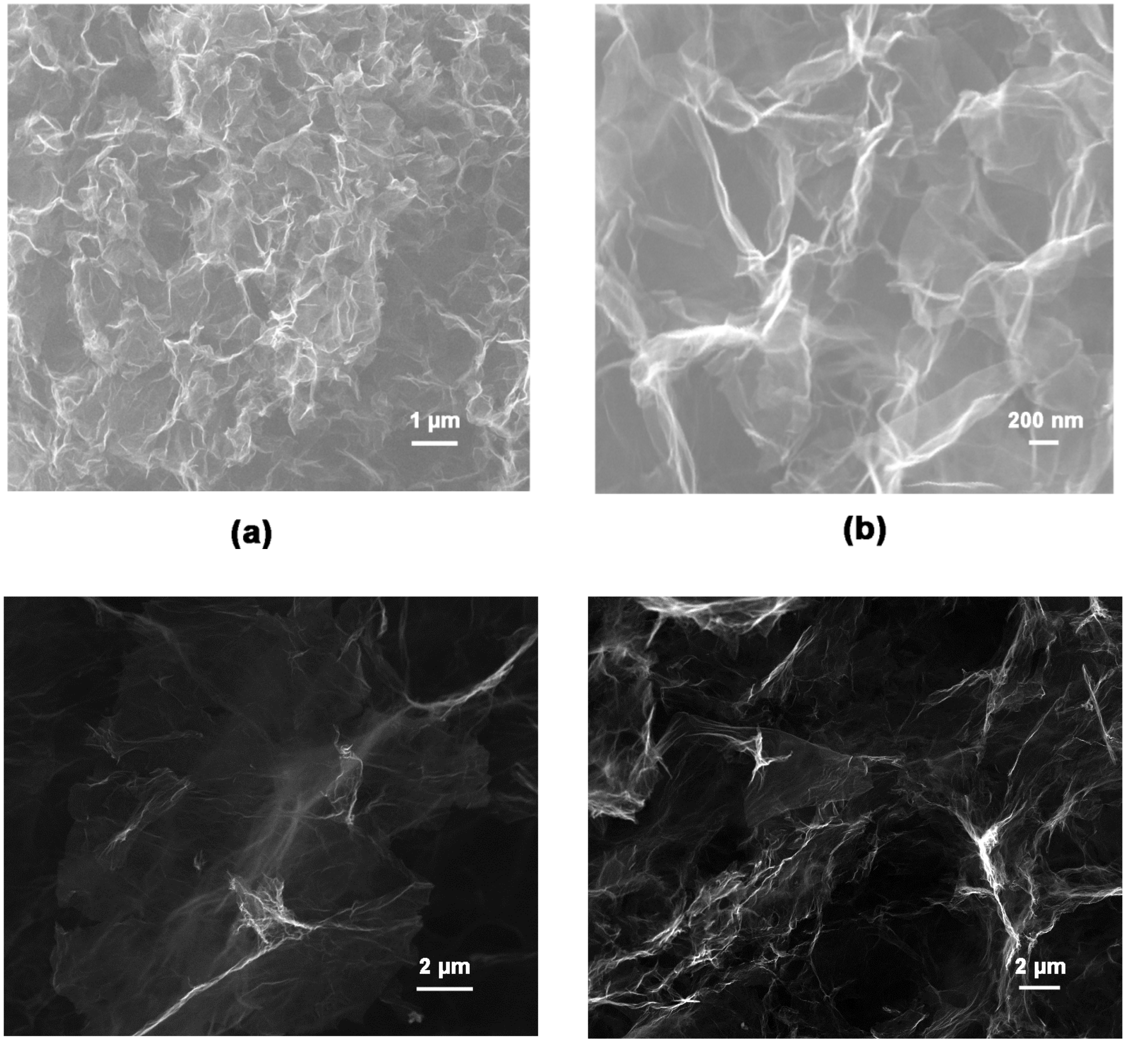


Figure S2. AFM image and corresponding cross-section profile of GO sheets deposited on silicon wafer.



(a) (b)

(c) (d)

Figure S3 (a)-(d). SEM images of CGCA with different magnitudes.

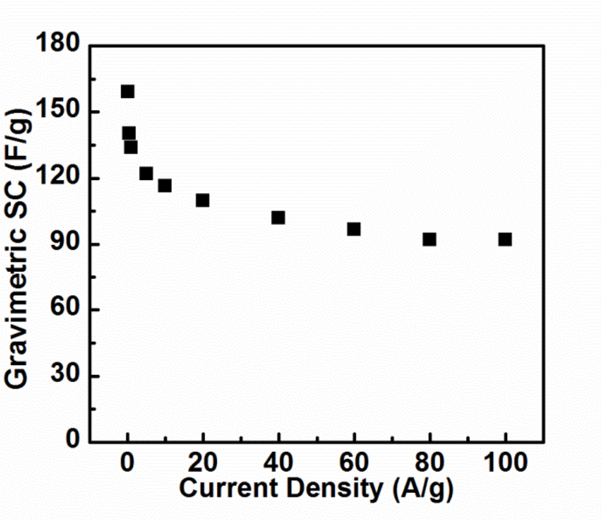


Figure S4. Gravimetric specific capacitance of CGCA electrode under different current densities.

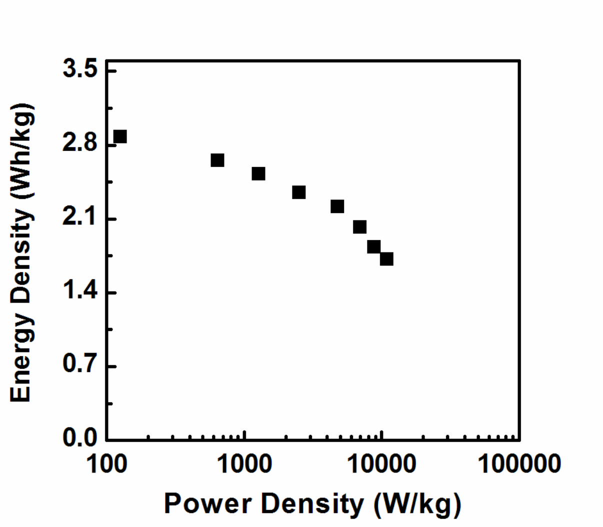


Figure S5. Ragone plot of the electrode based on CGCA.

Table 1. The atomic ratios of GO/PEI assemblies before and after carbonization from XPS

Atom	C (%)	O (%)	N (%)
Ratio before carbonization	65.67	25.78	7.15
Ratio after carbonization	87.84	7.4	4.62