

Supplementary Information

Pulse electrochemical synthesis of polypyrrole/graphene oxide@graphene aerogel for high-performance supercapacitor

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Experimental Section

Materials

Graphite oxide was prepared according to the modified Hummers method[27]. Ascorbic acid (VC), potassium chloride (KCl) and N,N-dimethylformamide (DMF) were purchased from Tianjin Guangfu Technology Development Co., Ltd. Pyrrole and N-methyl pyrrolidone (NMP) were purchased from Shanghai Macklin Biochemical Co., Ltd. PVDF and acetylene black were bought from Aladdin (Shanghai, China). Distilled water was obtained in Taiyuan University of Technology. All the chemicals were used as received without further purification.

Synthesis of graphene aerogel

VC (37.8 mg) and DMF (0.7 mL) were uniformly dispersed into GO solution (6.3 mL, 3mg mL⁻¹) by ultrasonication. Then the resulting precursor dispersion was transferred to a glass vial with inner diameter of ~1.5 cm, sealed and heated at 100 °C for 4 h to form graphene hydrogel. Finally, the hydrogel was placed in mixed solvent consisting of distilled water and absolute ethyl alcohol for solvent exchange to remove DMF, redundant VC, and byproducts produced in the process of self-assembly. Graphene aerogel (GA) was then obtained after freeze-drying for 48 h

and annealing at 400 °C for 2 h under the protection of Ar.

Preparation of PGO@GA composite

Graphene aerogel, acetylene black and PVDF in 8:1:1 mass ratio were dissolved in NMP to obtain homogeneous slurry by strong ultrasonication. Then the slurry was coated on blank carbon cloth uniformly, which underwent 12 h of vacuum drying at 120 °C to achieve final working electrode. The electrolyte composition contained 0.125 M pyrrole, 0.2 M KCl and 1 mg mL⁻¹ GO. The pulse potential was set at 0.8 V vs. SCE with on/off-time (0.1 s/0.5 s) during 1000 cycles, and the eventually as-obtained material was denoted as PGO@GA.

For comparison, PPy/GO (abbreviated as PGO) was prepared under the same condition using blank carbon cloth as working electrode while PPy was also synthesized on blank carbon cloth under the same pulse condition except for electrolyte containing no GO.

Materials Characterization

The X-ray diffraction (XRD) patterns of samples were recorded using Rigaku D/Max2500 diffractometer with Cu K α radiation ($\lambda=1.5406 \text{ \AA}$). The morphologies and microstructures of samples were tested using field emission scanning electron microscope (FE-SEM, JSM-6700F). Fourier transform infrared (FTIR) spectra were recorded using a Bruker Vector 22 FTIR spectrometer. X-ray photoelectron spectroscopy (XPS) investigations were conducted on a Thermo Fisher ESCALAB 250 xi (England) with an Al K α radiation (1486.6 eV). Raman spectroscopy measurements were performed on LabRAM HR Evolution (HORIBA Scientific, France) with an excitation wavelength of 532 nm.

Electrochemical Measurements

Electrochemical tests were performed in 1 M KCl solution using V3 electrochemical workstation (Princeton, USA) with a conventional three-electrode system of which saturated calomel electrode (SCE) and platinum foil served as reference and counter electrodes, separately. Cyclic voltammetry (CV) tests were performed in the potential window of -0.5 to 0.5 V. Galvanostatic charge-discharge (GCD) was

conducted at current density ranging from 1 to 15 A g⁻¹ in the same potential window. Electrochemical impedance spectroscopy (EIS) measurements were carried out from 0.1 Hz to 100 kHz at open circuit potential with an amplitude of 5 mV. Specific capacitance C (F g⁻¹) was calculated according to the following equation:

$$C = It/(\Delta Vm)$$

where ΔV is referred to as potential window, m (g) the mass of electrode active material, I (A) charging current, t (s) discharging time, m (g).

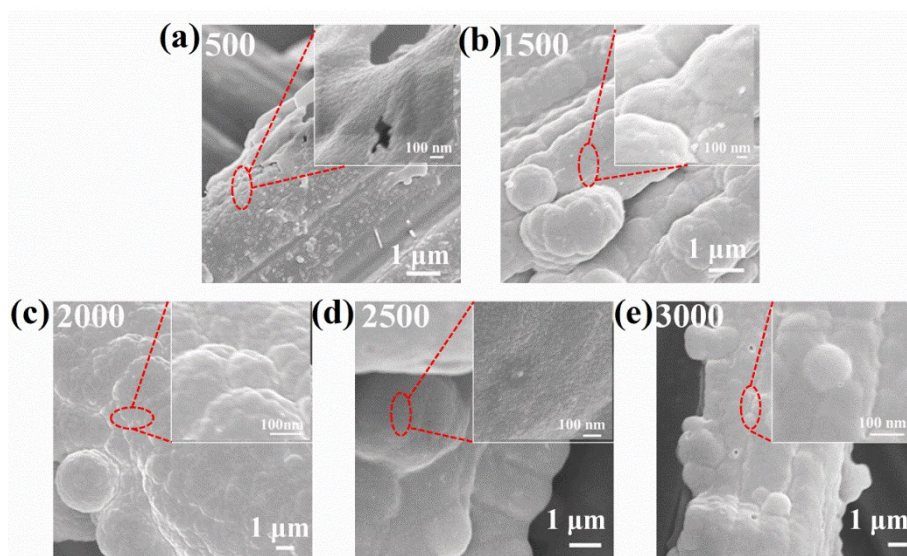


Fig. S1. SEM images of PPy synthesized at different pulse cycles

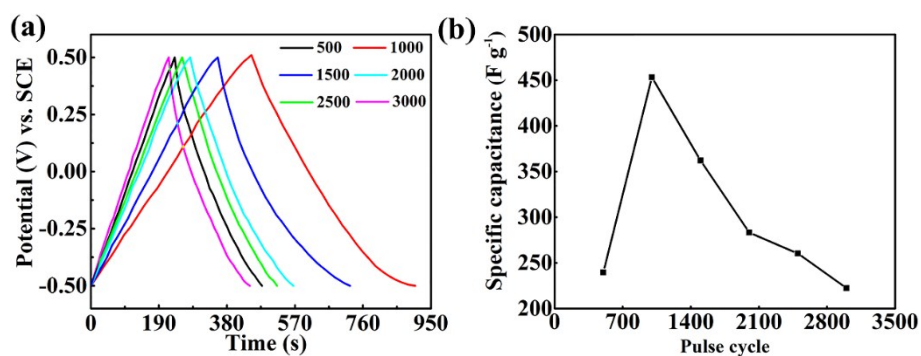


Fig. S2. GCD curves at 1 A g⁻¹ tested in 1 M KCl for PPy synthesized at different pulse cycles (a), and the relationship between specific capacitance value and pulse cycle (b)

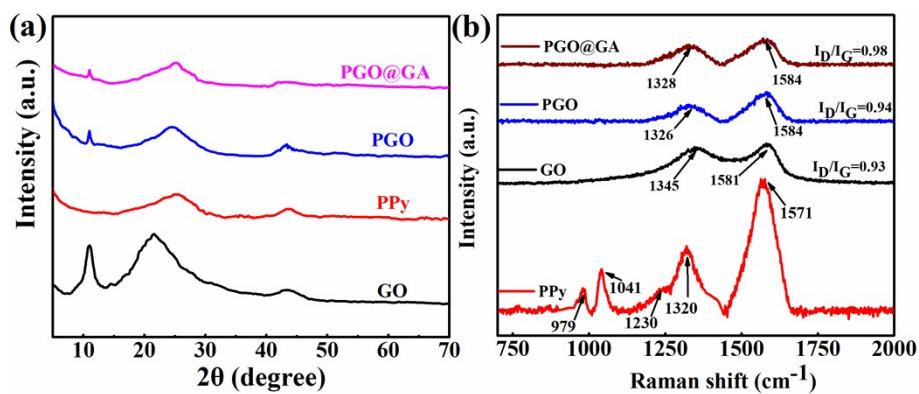


Fig. S3. X-ray diffraction patterns (a) and Raman spectra (b) of GO, PPy, PGO and PGO@GA

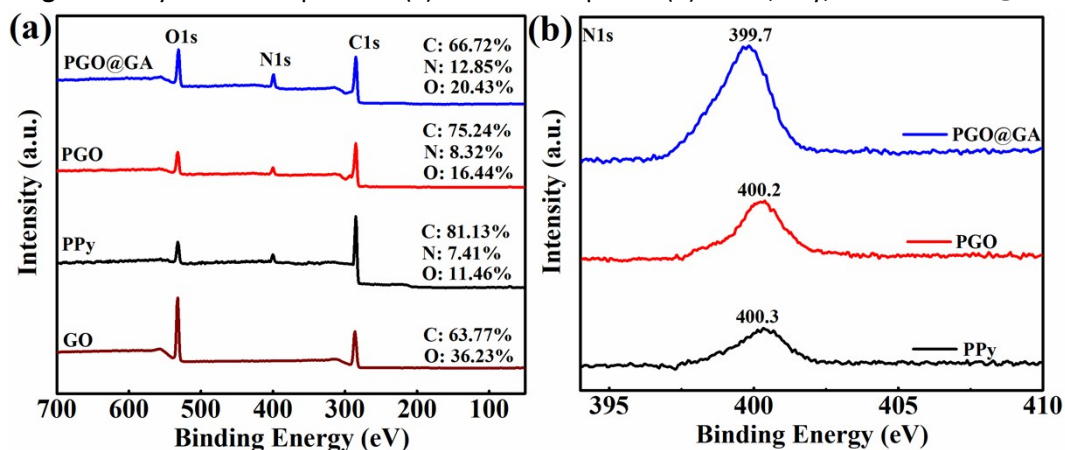


Fig. S4. (a) XPS survey spectra of GO, PPy, PGO and PGO@GA; (b) N 1s spectra of PPy, PGO and PGO@GA

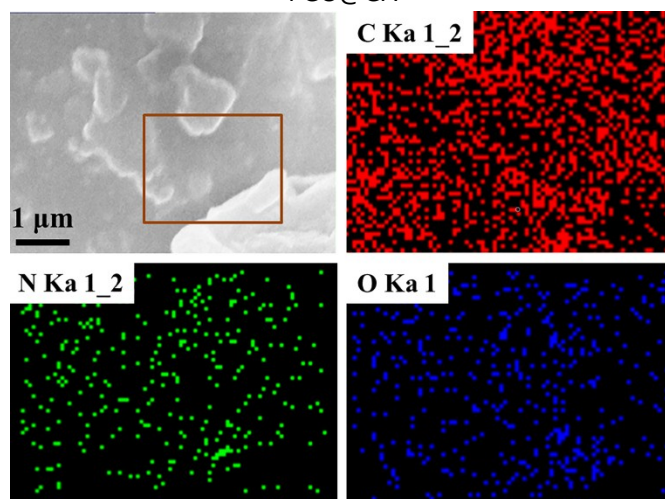


Fig. S5. EDS image and elemental mapping of PGO@GA

Table S1. Capacitive property of PPy-based composites

Electrode material	Capacitance ($F g^{-1}$)	Cyclic stability	Electrolyte	Testing system	Ref.
HGPNA-0.75	418 ($0.5 A g^{-1}$)	($50 mV s^{-1}$, 2000 cycles, 74%)	1.0 M KOH	Three-electrode	1

PPy/GO	660 (4 mA cm ⁻²)	(10 mA cm ⁻² , 1000 cycles, 90%)	1.0 M KCl		2
GO-PPy/PEOT	568.35 (0.1 A g ⁻¹)	(0.1 A g ⁻¹ , 500 cycles, 83.4%)	2.0 M NaCl		3
GPPy hydrogels	295 (1 A g ⁻¹)	(10 A g ⁻¹ , 5000 cycles, 80%)	1 M H ₂ SO ₄		4
PPy/rGO	290 (0.2 A g ⁻¹)	(2 A g ⁻¹ , 20000 cycles, 97.5%)	3 M KCl		5
rGO/PPy	361 (0.2 mA cm ⁻²)	(10 mA cm ⁻² , 5000 cycles, 80%)	1.0 M KCl		6
PGO@GA	625 (1 A g ⁻¹)	(10 A g ⁻¹ , 5000 cycles, 85.7%)	1.0 M KCl		This work

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