Supporting Information

Continuous fabrication of graphene-confined polypyrrole film for cycling stable supercapacitors

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Experimental Section

Materials: All the reagents were of analytical grade and used as received. GO with average lateral size of 2 μm was purchased from Hangzhou HigherSee Technology Inc. (www.highersee.com).

Preparation of GO-Polypyrrole: First, GO was mixed with pyrrole monomer with different ratios (GO:pyrrole =5:1, 3:1, 2:1, 1:1 in weight). Then, the mixture (15 mg mL^{-1}) was spun into a coagulation bath ($FeCl_3$ aqueous solution, 1% in weight, 1 M HCl) from a designed flattened nozzle, after which the pyrrole was polymerized into polypyrrole. Finally, the hydrogel film was washed with 0.1 M HCl several times and stay in pure water.

Preparation of GP: GO-polypyrrole was reduced in 20 wt% hydrazine hydrate at 95 ^oC for 2 hours as previous reported,[1] followed by washing with ethanol and pure water. The obtained black hydrogel was air-dried and converted to GPx (x equals to the ratio of GO to pyrrole) film.

Preparation of RGO film: The control film of RGO was prepared by wet-spinning of GO liquid crystalline dope (15 mg mL^{-1}) into a coagulation bath ($CaCl_2$ 5 wt %, ethanol:H_2O = 1:3), followed by washing with pure water and then chemical reduction of GO by 20 wt% hydrazine hydrate at 95 ^oC.

Fabrication of flexible supercapacitors: The electrolyte we chosen was H_3PO_4/PVA system. The gel was prepared by mixing H_3PO_4, PVA and water with ratio 1:1:10 in weight. After the mixture stirred at 95°C became clear, the H_3PO_4/PVA gel was dropped onto the GP film as spacer and electrolyte. The flexible all-solid-state supercapacitor was fabricated by assembling two such electrodes that covered with H_3PO_4/PVAgel.

Characterization: POM observations were performed with a Nikon E600POL. SEM and EDS were conducted on Hitachi S-4800. XRD was measured by Rigaku D/max-2500, using graphite monochromatized CuK α radiation. TEM and SAED images were acquired by using a JEM-1200 EX (JEOL). XPS measurements were collected on a PHI 5000C ESCA system (Physical Electronics) operated at 14.0 kV. AFM images of GO sheets were obtained in the tapping mode on a Nano Scope IIIA, with samples prepared by washing with N-Methyl pyrrolidone. Mechanical property tests were carried on a HS-3002C at a loading rate of 10% per minute. Electrochemical measurements were carried out in cells with two symmetrical electrodes, using a mixed cellulose esters membrane as separator (pore size 0.22μm), and 1 M H_2SO_4 as electrolyte. The weight of each electrode material was about 0.5 mg. The effective area of active material was about 0.64 cm^2 for each elctrode. The mass loading of the sample was about 0.78 mg cm^{-2}. CV, GCD and EIS tests were performed using an electrochemical workstation (CHI660e, CH Instruments, Inc.).

Calculations：

(1) The specific capacitance calculated by CV:

$$C_s = \frac{\int I dU}{m \times u \times (U_2 - U_1)}$$

Where C_s (F g^{-1}), m (g), u (V s^{-1}), U_2 and U_1 (V), and I (A) are the gram specific capacitance, the weight of single electrode, scan rate, high and low potential limit of CV tests, and the instant current of CV curves, respectively.

(2) The specific capacitance calculated by GC:

$$C_s = \frac{2 \times I \times t}{m \times \Delta U}$$

Where C_s (F g^{-1}), I (A), t (s), ΔU (V), and m (g) are the gram specific capacitance, the discharge current, the discharge time, the potential window and the weight of single electrode, respectively.

(3) The volume capacitance and area capacitance are calculated as followed:

$$C_{sv} = \frac{C_s \times m}{V}$$

$$C_{ss} = \frac{C_s \times m}{A}$$

Where A (cm^2), V (cm^3), and m (g) are surface area of one electrode, volume of one electrode and weight of on electrode, respectively.

(4) The energy density and power density are calculated as followed:

$$E = \frac{1}{3.6 \times 8} C_s U^2$$

$$P = \frac{E}{t}$$

Where E (W h kg^{-1}), C_s (F g^{-1}), U (V), P (W kg^{-1}), t (h) are the energy density, the gram specific capacitance, the potential window, the power density and the discharge time, respectively.

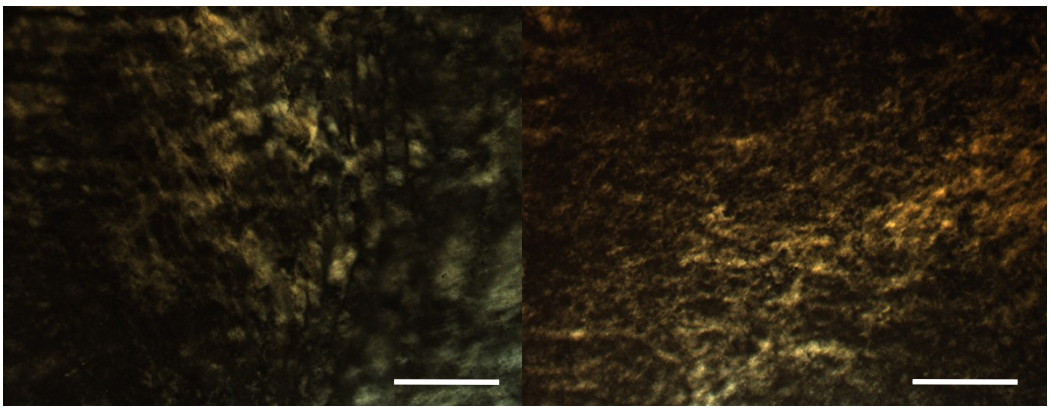

Fig.S1 POM images of GO (left) and the mixture of GO and pyrrole (right). Scale bar: 100 μm.

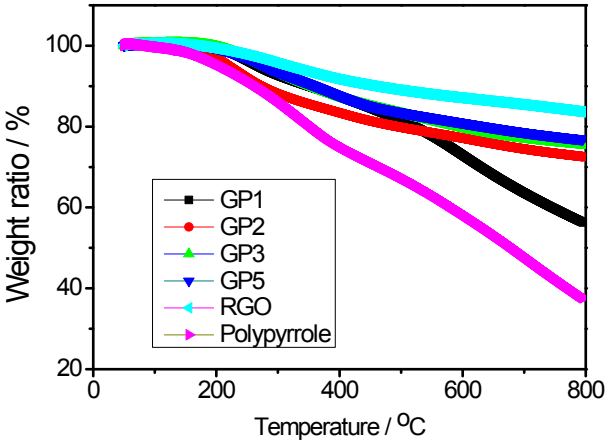

Fig.S2 TGA curves of PPy, GP1, GP2, GP3, GP5 and RGO.

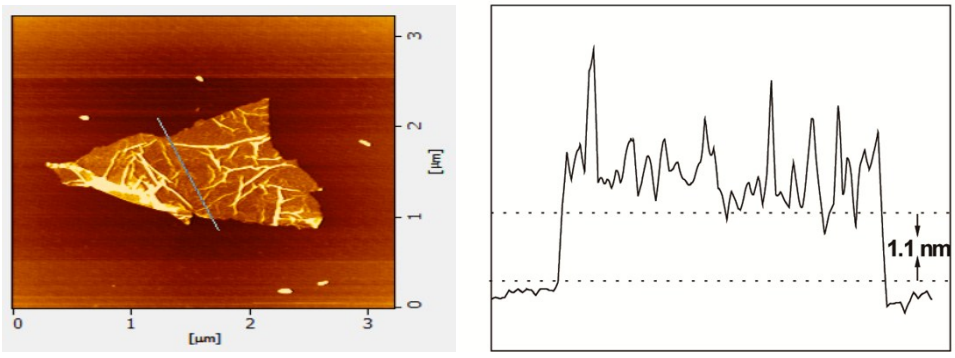

Fig.S3 AFM profiles of RGO.

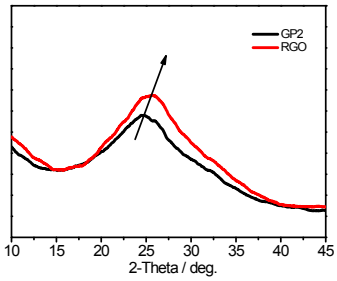

Fig.S4 XRD of GP2 and RGO.

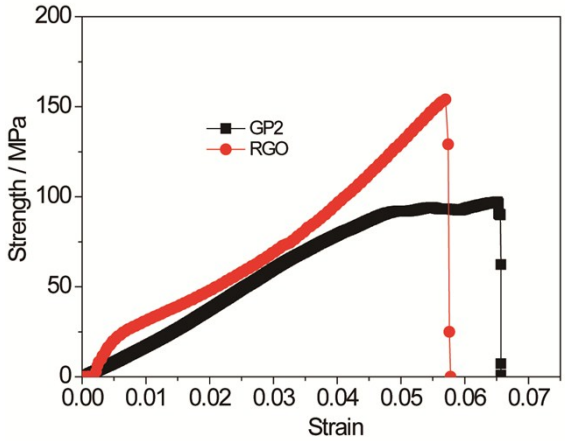

Fig.S5 Mechanical tests of GP2 and RGO.

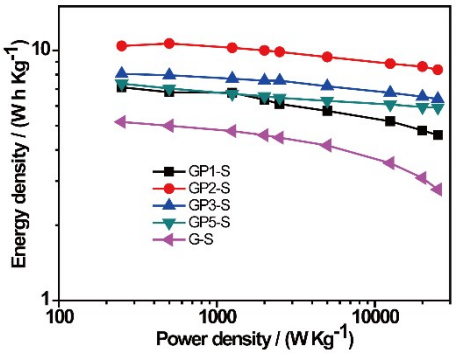

Fig. S6 Ragone plots for GP1-S, GP2-S, GP3-S, GP5-S and G-S.

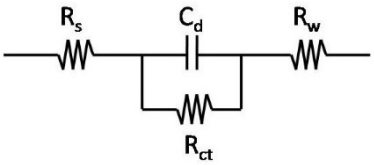

Fig. S7 The equivalent circuit of the Nyquist plots.

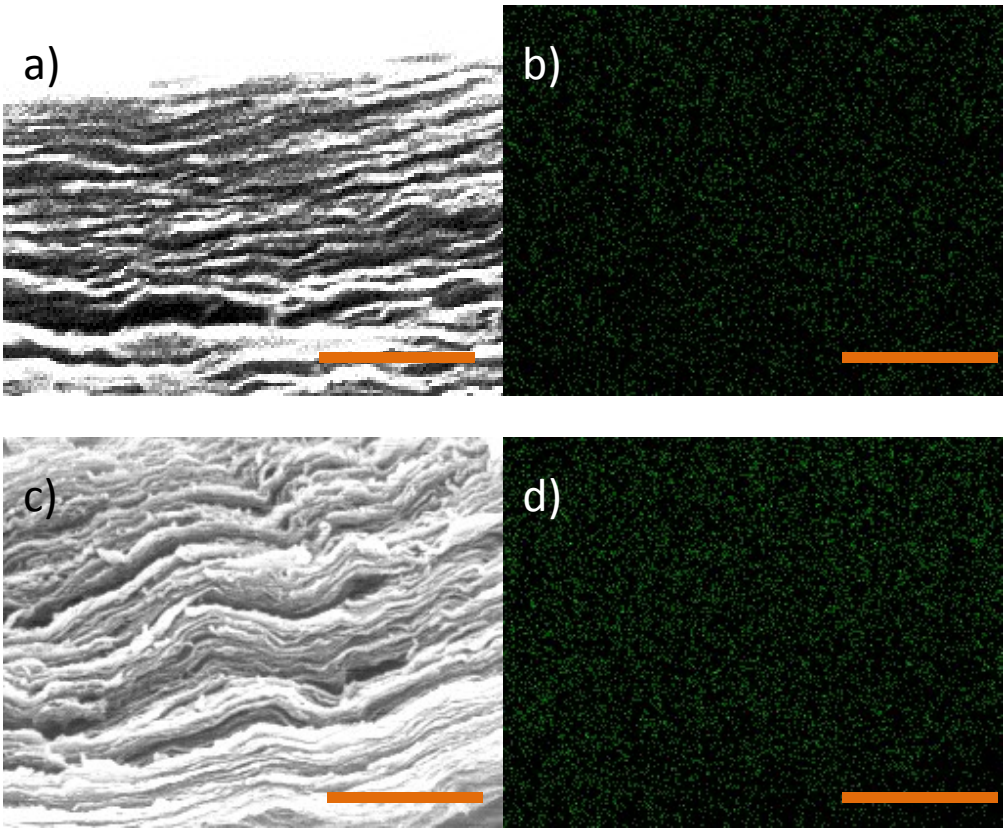

Fig.S8 a) The SEM image of initial GP2 and b) its corresponding EDS maping of N element. c) The SEM image of GP2 after 50,000 cycles and d) its corresponding EDS maping of N element. Scale bar: 1 μm.

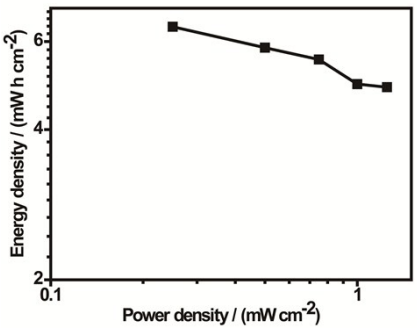

Fig. S9 Ragone plots for GP2-FS.

Table S1 Comparison of specific capacitances based on graphene / polypyrrole system.

Reference	Method	Capacitance	Rate performance
This work	wet spinning py + GO + Fe^{3+}	302 F/g @ 1 A g^{-1}	80% to 100 A g^{-1}
1[2]	py+surfactant+GO self-assembling Fe^{3+}	440 F/g @ 1 A g^{-1}	79% to 5 A g^{-1}
2[3]	pulse-electropolymerization	175 F/g @ 1 A g^{-1}	
3[4]	py+CTAB+GO APS	366 F/g @ 10 mVs^{-1}	25% to 200 mV s^{-1}
4[5]	py+PSS+GO Fe^{3+}	417 F/g @ 10 mVs^{-1}	64% to 100 mV s^{-1}
5[6]	electrochemical polymerization	275 F/g @ 1 A g^{-1}	76% to 5 A g^{-1}
6[7]	py+GO Fe^{3+}	330 F/g @ 1 A g^{-1}	68% to 5 A g^{-1}
7[8]	py+GO Fe^{3+} interfacial polymerization	92 F/g @ 1 A g^{-1}	
8[9]	electrochemical polymerization	352 F/g @ 1 A g^{-1}	
9[10]	PPy NT + RGO	400 F/g @ 0.3 A g^{-1}	81% to 1.5 A g^{-1}
10[11]	PPy NT + RGO + CNT	205 F/g @ 1 A g^{-1}	85% to 10 A g^{-1}
11[12]	PPy NP + RGO + CNT	325 F/g @ 1 A g^{-1}	79% to 8 A g^{-1}
12[13]	py + RGO + SDS + APS	294 F/g @ 10 $mAcm^{-2}$	
13[14]	py + RGO + APS	204 F/g @ 1 A g^{-1}	
14[15]	py + GO electrodeposition	231 F/g @ 2 A g^{-1}	
15[16]	py + CTAB + GO + APS + citric acid	696 F/g @ 1 A g^{-1}	86% to 8 A g^{-1}
16[17]	py + GO Fe^{3+} reduced by EG	370 F/g @ 1 A g^{-1}	65% to 5 A g^{-1}
17[18]	PPy sphere + RGO composite	430 F/g @ 1 A g^{-1}	93% to 10 A g^{-1}
18[19]	py + Graphene + APS + NaOH	466 F/g @ 10 mVs^{-1}	35% to 200 mV s^{-1}
19[20]	PPy + GO + HCl	181 F/g @ 10 mVs^{-1}	40% to 200 mV s^{-1}
20[21]	py + RGO hydrogel + Fe^{3+} + TSA	316 F/g @ 5 A g^{-1}	79% to 50 A g^{-1}
21[22]	hollow PPy sphere + RGO	340 F/g @ 1 A g^{-1}	85% to 5 A g^{-1}
22[23]	py + GO hydrogel + electropolymerization	350 F/g @ 1.5 A g^{-1}	
23[24]	GO + TSA + py + APS	302 F/g @ 1 A g^{-1}	93% to 2 A g^{-1}
24[25]	electrochemical polymerization on exRGO	351 F/g @ 1 A g^{-1}	79% to 20 A g^{-1}
25[26]	RGO + CNT // CF + PPY	76 F/g @ 1 A g^{-1}	75% to 10 A g^{-1}
26[27]	PPy nanotube + RGO hydrogel	226 F/g @ 1 A g^{-1}	57% to 10 A g^{-1}
27[28]	PPy + RGO hollow tube based on Ni foam	420 F/g @ 1 A g^{-1}	77% to 20 A g^{-1}

Table S2 Comparison of the C_{Sv} for the reported supercapacitors

Reference	Electrode materials	Electrolyte	Test condition	C_{Sv} / (F cm^{-3})
This work	GP2	1 M H_2SO_4	1 A g^{-1}	513
[29]	PaGMs	$BMIMBF_4$	20 mV s^{-1}	150

[30]	CDC	1 M H_2SO_4	20 mV s^{-1}	350
[31]	PANI-graphene	1 M H_2SO_4	0.1 A g^{-1}	802
[32]	Ti3C2Tx	1 M H_2SO_4	2 mV s^{-1}	900
[33]	EM-CCG	1 M H_2SO_4	0.1 A g^{-1}	260
[34]	Evaporation-induced graphene hydrogel	6 M KOH	0.1 A g^{-1}	376

Table S3 Comparison of the C_{SS} for the reported flexible planar supercapacitors

Reference	Electrode materials	Electrolyte	Test condition	C_{SS} / (mF cm^{-2})
This work	GP2	PVA-H_2SO_4	1 mA cm^{-2}	185
[35]	Paper – CNT - MnO_2	6M KOH	1 mA cm^{-2}	123
[36]	Activated carbon cloth	5M LiCl	6 mA cm^{-2}	756
[37]	Activated carbon cloth	1M H_2SO_4	10 mV s^{-1}	76
[38]	RGO gelation	1M H_2SO_4	1 mA cm^{-2}	33.8
[39]	Carbonized cotton mat	1M Na_2SO_4	0.0112 mA cm^{-2}	0.7
[40]	Graphene hydrogel film	PVA-H_2SO_4	1 A g^{-1}	372
[41]	VOPO4-graphene film	PVA-LiCl	0.02 mA cm^{-2}	8.36
[42]	Electrochemical rgo films	25% KOH	0.8 mA cm^{-2}	0.283
[43]	Graphene - Ni foam	5 M KOH	0.67 mA cm^{-2}	45.6
[44]	Graphene - cellulose paper	1M H_2SO_4	1 mV s^{-1}	120

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