Reduced Graphene Oxide Grafted by Polymer of Polybromopyrroles to Nanocomposites with Superior Performance for Supercapacitors

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Electronic Supplementary Information

Table of contents

S1. Preparation of graphene oxide (GO)

1 g of expanded graphite (10–30 μm; Nanjing, China) was added into 10 mL of concentrated sulfuric acid (H_2SO_4, 98.3 wt.%), followed by ultrasonic treatment at room temperature for 2 min. Then, 1 g of potassium persulfate ($K_2S_2O_8$, A. R.) and 1 g of phosphorus pentoxide (P_2O_5, A.R.) were slowly added into the above mixture under constant ultrasonic treatment. The mixture was allowed to stand at room temperature for 12 h after agitation at 80 °C for 6 h.

After that, the mixture was diluted to 500 mL by slowly adding distilled water, followed by filtration to obtain the precipitate. The precipitate was transferred into 50 mL of concentrated H_2SO_4, and dispersed by ultrasonication for 2 min. Then, 6 g of potassium hypermanganate ($KMnO_4$, A.R.) was added into the mixture. The mixture was vigorously stirred at room temperature for 4 h, followed by addition of 20 mL of distilled water to elevate the mixture temperature to be above 95 °C. After incubation for 15 min, 400 mL of distilled water and 10 mL of hydrogen peroxide (H_2O_2, 30 wt.%) were slowly added into the mixture under mild agitation, respectively. The mixture turned out to be saffron yellow after addition of H_2O_2. The saffron-yellow mixture was allowed to stand for 12 h, and then subjected to centrifugal separation several times. The precipitate was thoroughly washed with distilled water until the supernate was neutral. The precipitate was collected by filtration, and finally dried in a freeze-drier to obtain GO.

S2. Synthesis of polybromopyrroles (PBPs)

PBPs were synthesized through electrophilic bromination of pyrrole with bromine

(Br_2) in absolute ethanol, according to previous report.[1] In brief, 60 mL of absolute ethanol and 5 mL of Br_2 were added into a three-neck flask with capacity of 250 mL. The flask was transferred into a low-temperature reaction bath with temperature kept at 0 °C. The flask was bubbled with Ar for 0.5 h, followed by dropwise addition of 30 mL of absolute ethanol containing 1.67 mL of redistilled pyrrole. The reaction was conducted at 0 °C for 4 h with constant agitation under Ar atmosphere to produce PBPs ethanol solution. The components in PBPs ethanol solution were determined to be 2,5-dibromopyrrole (**1**) (86%), 2,3,5-tribromopyrrole (**2**) (7%), and 2,3,4,5-tetrabromopyrrole (**3**) (7%), respectively.[1]

S3. SEM images of the electrode film

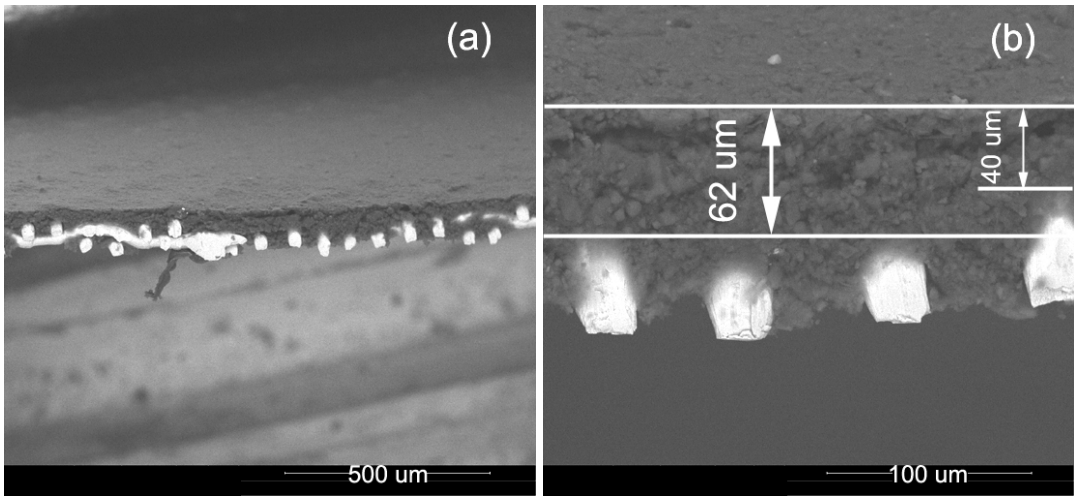


Figure S1. SEM of the electrode film: (a) Low magnification; (b) High magnification.

S4. Results of Lorentzian fittings of the Raman spectra

Table S1. Results of Lorentzian fittings of the Raman spectra.

Sample	D_1 (cm^{-1})	D_3 (cm^{-1})	D_4 (cm^{-1})	$G + D_2$ (cm^{-1})	$I_{D1}/I_{(G+D2)}$
RGO/PPBP-1	1347	1484	1250	1585	0.798
RGO/PPBP-2	1344	1473	1243	1584	0.797
RGO/PPBP-3	1345	1493	1219	1587	0.783
RGO	1348	1502	1229	1589	0.866

S5. XPS analysis

Table S2. XPS results of the samples.

Sample	C (at.%)	N (at.%)	O (at.%)
RGO/PPBP-1	84.65	9.06	6.29
RGO/PPBP-2	81.61	9.66	8.73
RGO/PPBP-3	81.29	11.66	7.04

	C				N				O		
	Component (eV)/content (at.%)				Component (eV)/content (at.%)				Component (eV)/content (at.%)		
RGO/PPBP-1	284.7/46.6	285.7/42.9	287.0/10.5	–	398.5/25.3	400.3/49.4	401.0/10.3	405.4/15.0	531.4/48.1	533.4/38.7	536.1/13.2
RGO/PPBP-2	284.5/12.8	285.1/43.3	286.7/32.0	290.9/11.9	398.4/22.4	400.4/59.5	401.9/4.4	403.9/13.7	530.2/30.6	532.3/62.2	536.6/7.2
RGO/PPBP-3	284.7/42.0	285.8/31.8	286.3/26.2	–	398.5/19.8	400.5/53.4	402.6/11.3	404.0/15.5	531.2/44.9	533.3/44.3	536.0/10.8
Assignment	C=C	C–C	C–O/C–N	O–C=O	N-6	N-5	N-Q	N-X	C=O	COH/C–O–C	O_2/H_2O
refs.	2,3				1,2,4				4		

S6. SEM images of individual RGO and PPBP

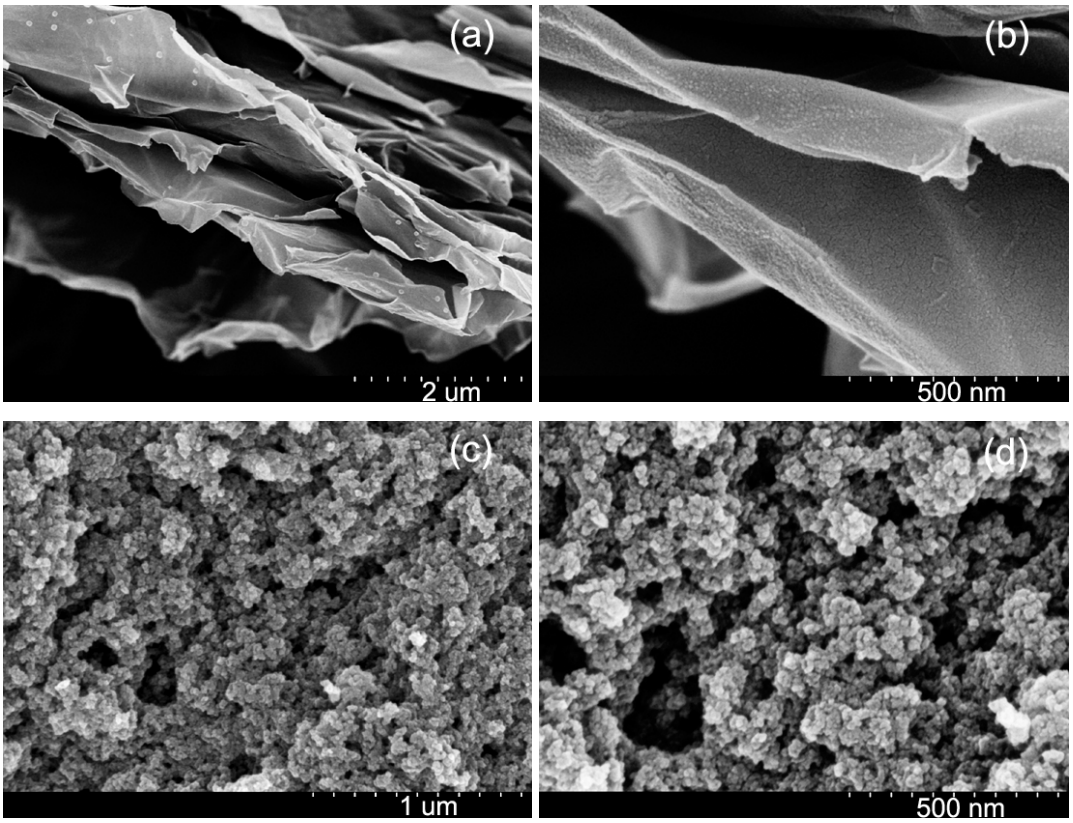


Figure S2. SEM images of : (a,b) RGO; (c,d) PPBP. a and c are the low-magnification images; b and d are the high-magnification images corresponding separately to a and c.

S7. Scanning probe microscopy images of RGO/PPBP-2

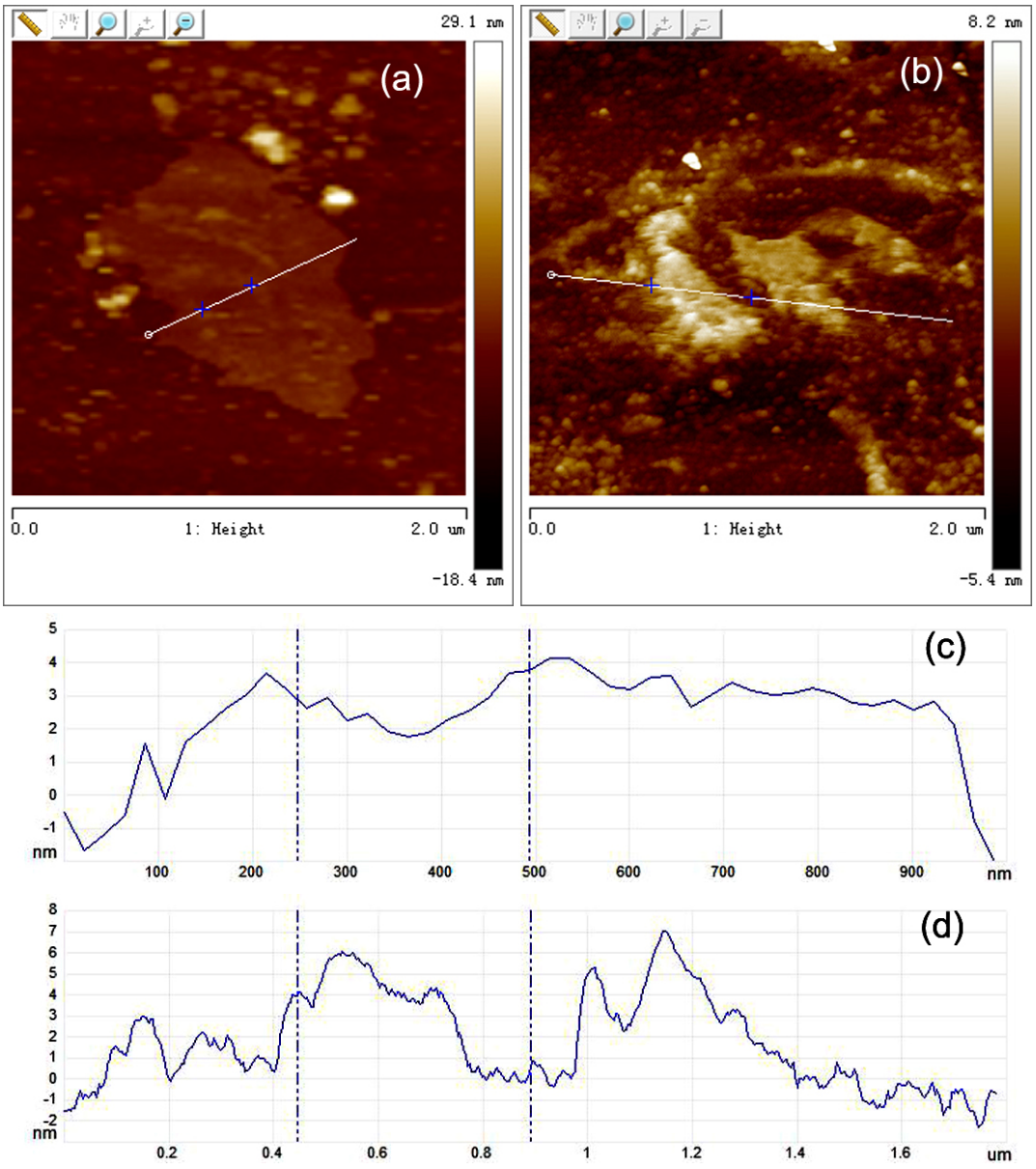
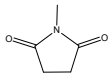


Figure S3. (a,b) SPM images of different regions for RGO/PPBP-2; (c,d) Height distribution diagrams corresponding to a and b, respectively.

S8. GC/MS analysis

Table S3. GC/MS results of the resulting products after microwave irradiation of individual NMP.

Intermediate	t_R (min)	M_W	Structure	Main fragment ions (m/z)
Pyrrolidone (**1**)	8.0	85		85, 57/56, 29/28
1-methyl-1*H*-pyrrol-2(5*H*)-one (**2**)	9.7	97		97, 69/68, 40, 29/28
N-methylsuccinimide (**3**)	11.2	113		113, 85/84, 57/56, 29/28

S9. BET analysis

Table S4. BET analysis results of the samples.

sample	BET analysis					
	S_{BET} (m^2 g^{-1})	V_{total} (cm^3 g^{-1})	V_{micro} (cm^3 g^{-1})	V_{meso} (cm^3 g^{-1})	S_{micro} (m^2 g^{-1})	S_{micro}/S_{BET}
RGO/PPBP-1	378.4	0.4375	0.0171	0.4204	–	–
RGO/PPBP-2	390.6	0.3448	0.0114	0.3334	174.1	44.6%
RGO/PPBP-3	259.6	0.1846	0.0054	0.1792	104.1	40.1%
RGO	173.1	0.1669	0.0000	0.1669	–	–

S10. EIS spectrum fitted with Zsimpwin software

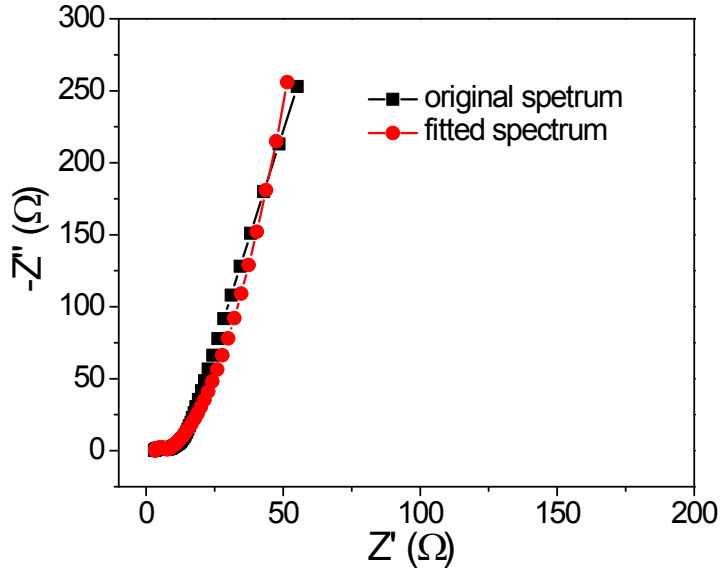


Figure S4. Fitted EIS spectrum obtained by Zsimpwin software using the data from the original EIS spectrum of RGO/PPBP-2‖RGO/PPBP-2 supercapacitor cell.

Table S5. Fitting report of Figure S4 based on a R(C(RW))C equivalent circuit.

index	fixed	symbol	start	end	% error
1	0	R	3.32	3.32	1.47
2	0	C	0.7756	7.756E-5	5.963
3	0	R	3.989	3.989	3.111
4	0	W	0.06378	0.0638	3.674
5	0	C	0.07506	0.07505	3.114

References

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3. Fang, Y.; Luo, B.; Jia, Y.; Li, X.; Wang, B.; Song, Q.; Kang, F.; Zhi, L. Renewing Functionalized Graphene as Electrodes for High Performance Supercapacitors. *Adv. Mater.* **2012**, *24*, 6348–6355.

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