

Electronic Supplementary Information

Three-dimensional graphene oxide/polypyrrole composite electrodes fabricated by one-step electrodeposition for high performance supercapacitors

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Experimental section

Preparation of graphene oxide (GO)

GO used in this work was synthesized by modified hummer method and described in brief as follows: The concentrated 7.5 mL H_2SO_4 in a 100 mL beaker was heated up to 80 °C. $\text{K}_2\text{S}_2\text{O}_8$ (2.5 g) and P_2O_5 (2.5 g) were added in sequence with continuous stirring until the reactants were completely dissolved. Graphite powder (5 g) was then added to above mixture. The resulting mixture was kept at 80 °C for 6 hours, after which the mixture was diluted with distilled water, filtered and washed to remove all soluble substances, and the corresponding pretreated graphite was transferred to a drying dish and left overnight under ambient conditions. Another 115 mL H_2SO_4 was put into a 500 mL Erlenmeyer flask and then cooled in an ice bath. The pretreated graphite and 15 g KMnO_4 were added slowly in sequence and allowed to dissolve completely. The mixture was then allowed to react at 35 °C for 2 hours, after that, 230 mL distilled water was slowly added. After stirring for 15 min, another 700 mL of distilled water was added to the mixture, thereafter 12.5 mL of 30% H_2O_2 was added to the mixture. The mixture was allowed to stand for at least 12 hours then the clear supernatant was decanted. The remaining mixture was washed with 1.1 L 1:10 HCl solution followed by distilled water. Finally, it was purified by dialysis for at least one week to remove any remaining salt impurities for the following experiments.

Calculation

Three-electrode configuration

For three-electrode configuration, the area capacitance (C_A) for the individual electrode (F cm^{-2}) is calculated from the CV curves as follows:

$$C_A = \frac{I}{S\nu(V_c - V_a)} \int_{V_a}^{V_c} I(V) dV$$

(1) where S is the geometric area of the electrode (cm^2); ν is the linear scan rate (V s^{-1}); $V_c - V_a$ is the voltage window (V) during discharging (backward scan), $I(V)$ is the resulting current (A).

C_A based on galvanostatic discharge is calculated as follows:

$$C_A = \frac{I\Delta t}{S\Delta V}$$

(2) where I is the discharge current (A), Δt is the discharge time (s), ΔV is the operating potential/cell voltage range exclude with the IR drop (V).

Specific capacitance (C_S) of the electrode (F g^{-1}) is calculated simply by dividing the

C_A with the loading mass (m) of GO/PPy composite on the electrode (g cm^{-2}):

$$C_S = \frac{C_A}{m}$$

(3)

Two electrode configuration

For two-electrode configuration, the area capacitance (C_A) for the individual electrode (F cm^{-2}) is calculated from the galvanostatic charge-discharge results as follows:

$$C_A = 2 \frac{I\Delta t}{S\Delta V}$$

(4)

Electrochemical impedance spectroscopy (EIS)

The real (C') and imaginary (C'') part of the area capacitance are derived from the impedance data as follows:

$$C' = \frac{-Z''}{S\omega|Z|^2}$$

(5)

$$C'' = \frac{Z'}{S\omega|Z|^2}$$

(6) Where Z is the impedance, S is the geometric area of the electrode, ω is the angular frequency ($\omega=2\pi f$).

The relaxation time τ_0 is deduced from the knee frequency (f_0) as:

$$\tau_0 = \frac{1}{f_0}$$

(7) And f_0 can be accurately defined from the peak frequency on C'' - f plot.

Energy density and power density

The total energy (E) and power (P) of the two-electrode supercapacitor device are first calculated from the galvanostatic charge-discharge results as:

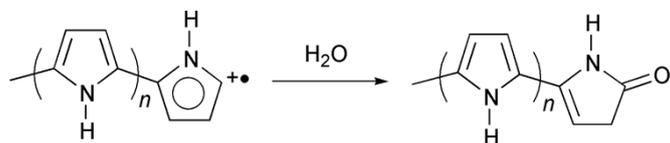
$$E = \frac{1}{2}CV^2 = \frac{1}{2}IV\Delta t \quad (8)$$

$$P = \frac{E}{\Delta t} \quad (9)$$

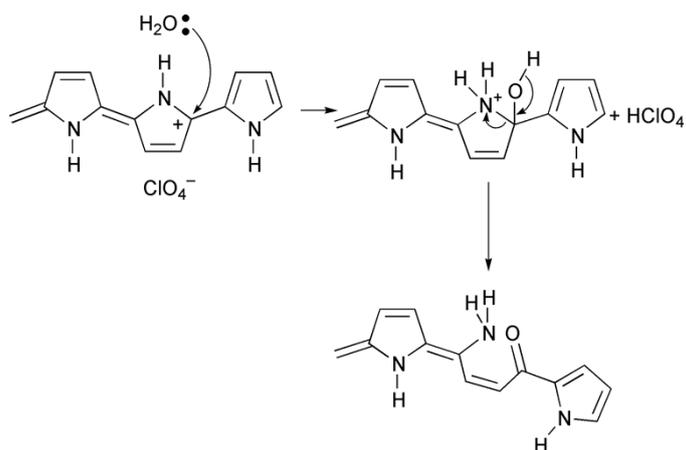
Where C is the total capacitance stored in the device, V is the cell voltage, I is the discharge current, Δt is the discharge time.

Then the energy density and power density are calculated by dividing E and P with the total mass of active materials in the two electrodes, or the geometric area of the supercapacitor (1 cm² in this research).

Supplementary Schemes



Scheme S1 Termination reaction.



Scheme S2 Secondary reaction.

Supplementary Figures

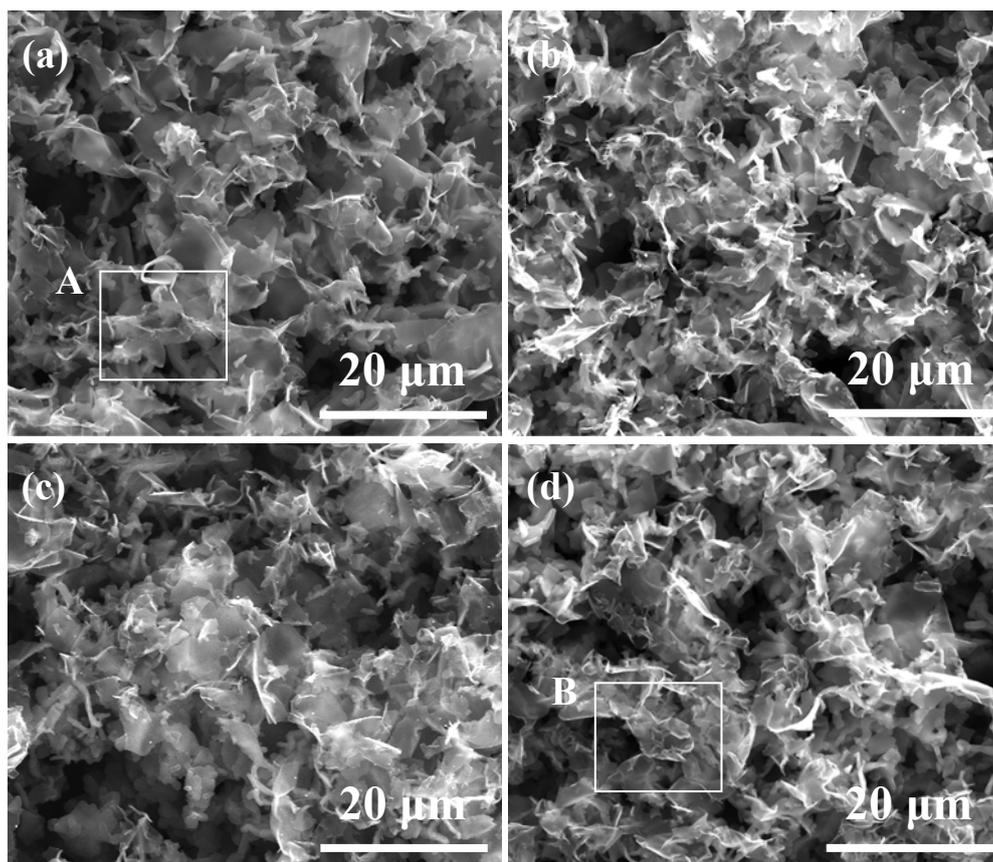


Fig. S1 SEM surface morphologies of the GO/PPy composite electrodes deposited in electrolyte with GO concentration of 0.1 mg mL^{-1} for different times: (a) 1200 s; (b) 1800 s; (c) 2400 s; (d) 2700 s. Enlarged images of area A and B are shown in Fig. S2.

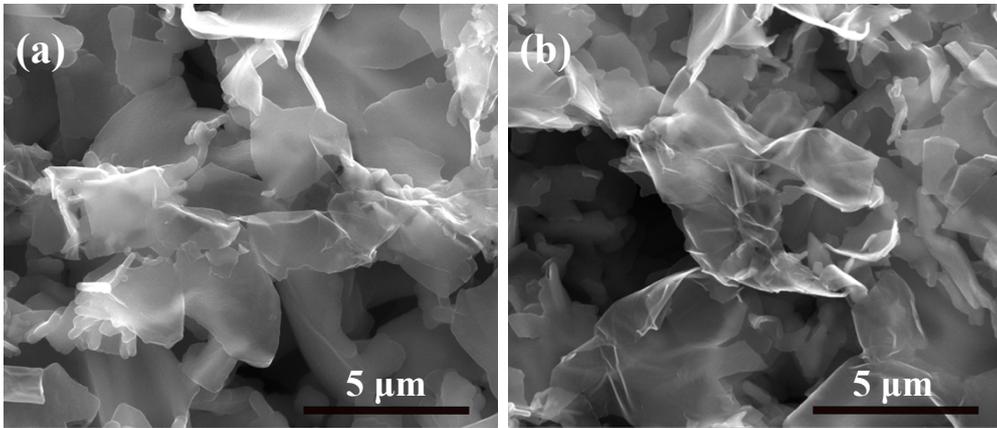


Fig. S2 High magnification SEM surface morphologies of the GO/PPy composite electrodes deposited in electrolyte with GO concentration of 0.1 mg mL^{-1} for different time: (a) 1200 s; (b) 2700 s.

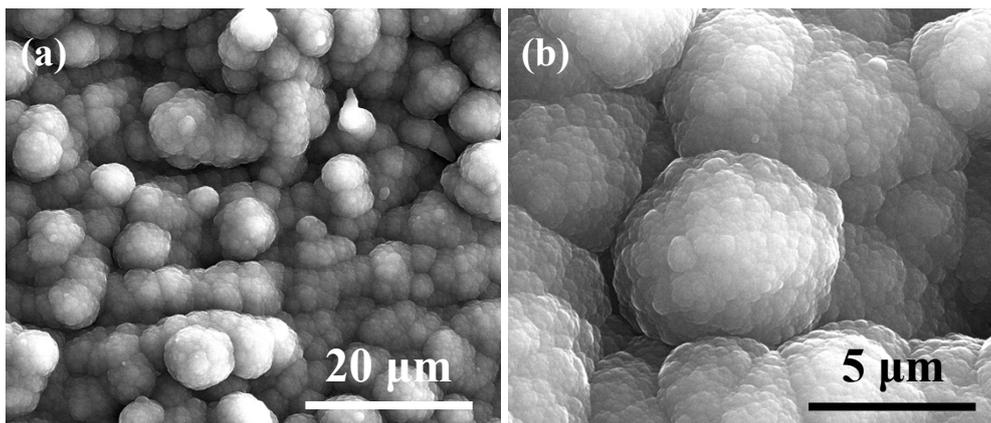


Fig. S3 SEM surface morphology of the pure PPy-1200 s electrode deposited in 5 vol.% (72 mmol L⁻¹) pyrrole aqueous solution containing 20 mmol L⁻¹ LiClO₄ as supporting electrolyte: (a) low magnification; (b) high magnification.

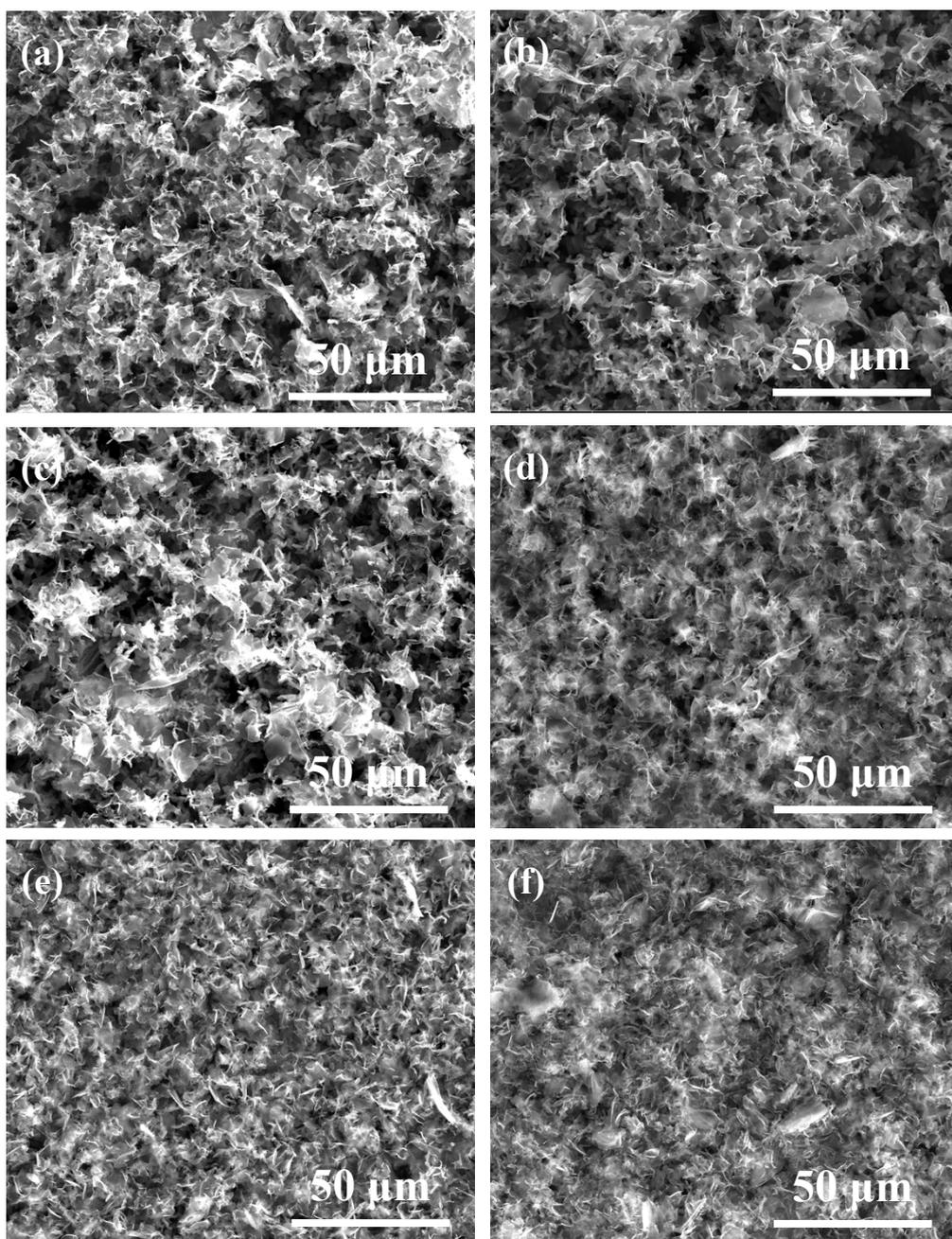


Fig. S4 SEM surface morphologies of the GO/PPy composite electrodes deposited with various GO concentrations (the deposition time is 1200 s for all the electrodes): (a) 0.05 mg mL⁻¹; (b) 0.1 mg mL⁻¹; (c) 0.2 mg mL⁻¹; (d) 0.4 mg mL⁻¹; (e) 0.8 mg mL⁻¹; (f) 1.2 mg mL⁻¹.

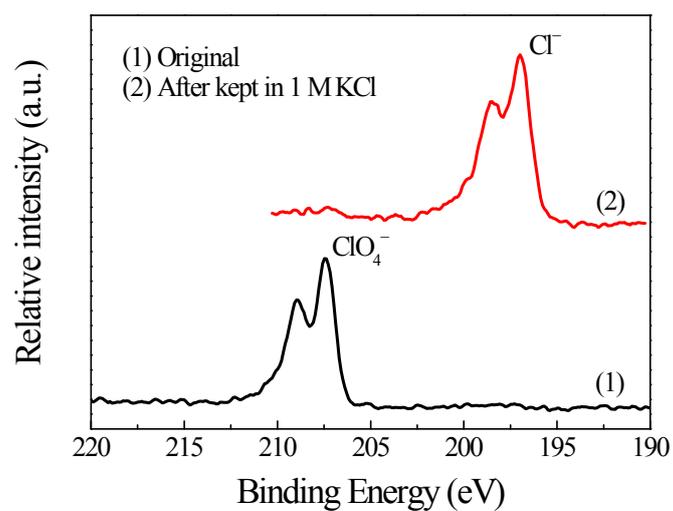


Fig. S5 Cl2p spectra of the original GO/PPy composite and GO/PPy composites after keeping in 1 M KCl solution for at least one day.

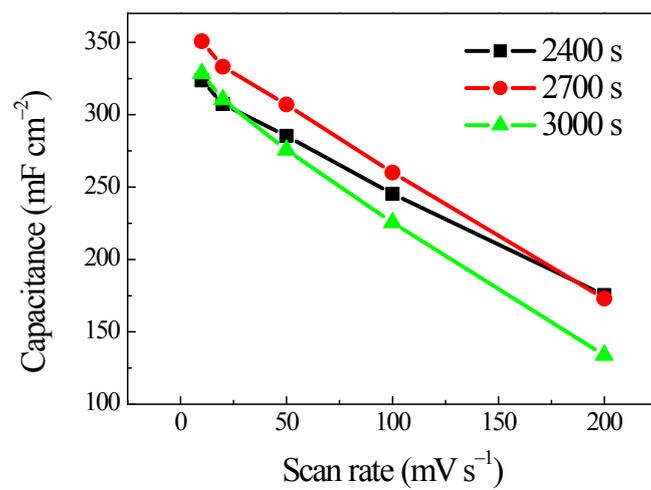


Fig. S6 Comparison of plots of area capacitance vs. scan rate for GO/PPy-2400, -2700 and -3000 s composite electrodes.

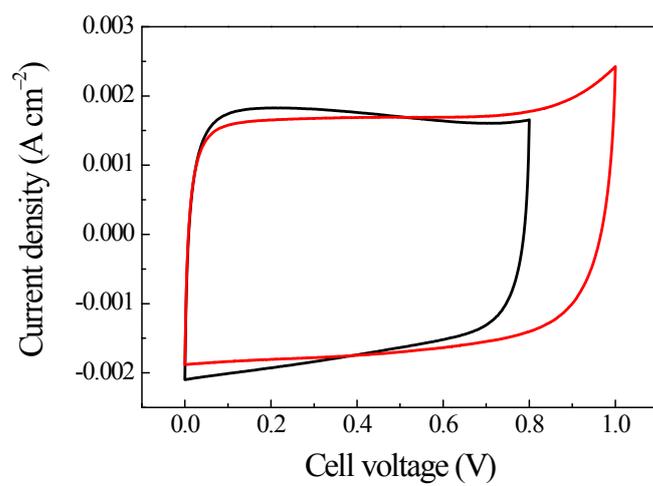


Fig. S7 CV curves of aqueous supercapacitor with cell voltage of 0.8 and 1.0 V (scan rate: 10 mV s⁻¹).

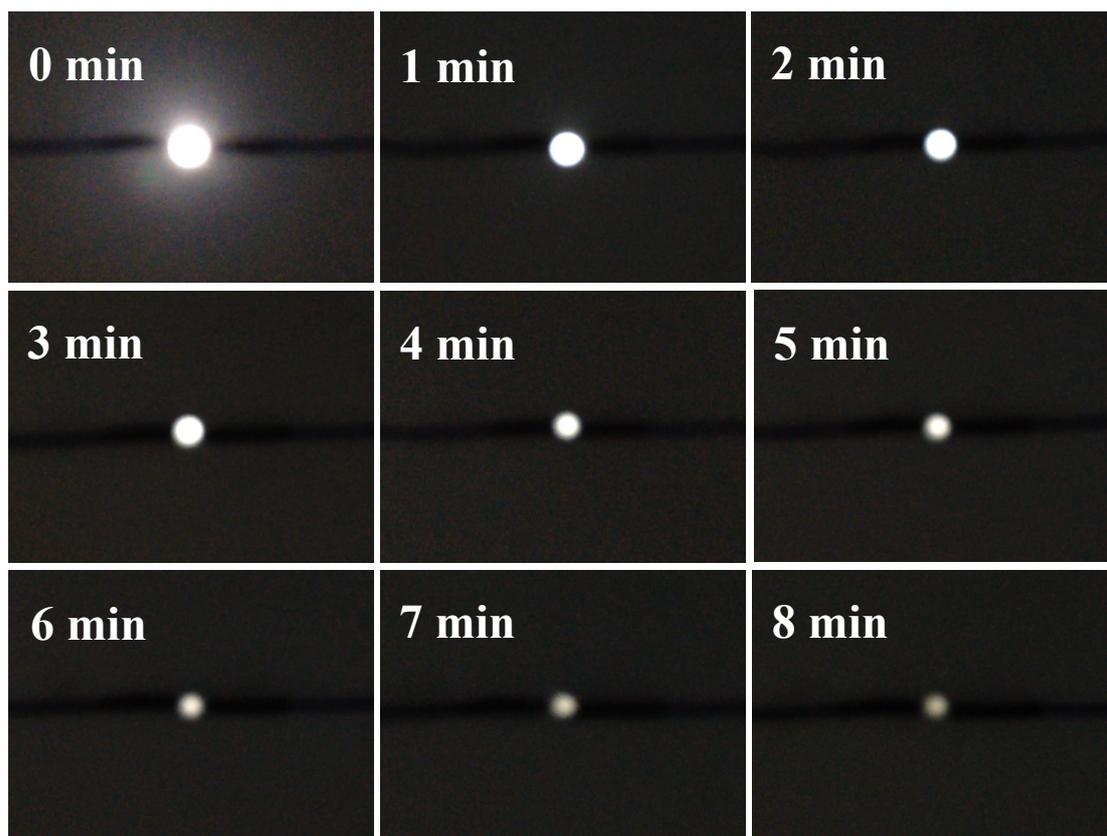


Fig. S8 Photos for the LED powered by four unit solid-state capacitors in series at different times.

Supplementary Tables

Table S1 Comparison of the mass loading, area and specific capacitances of various graphene/PPy composite electrodes.

Composites	Mass loading (mg cm ⁻²)	Area capacitance (mF cm ⁻²)	Specific capacitance (F g ⁻¹)	Reference
Graphene/PPy	-	-	165 at 1 A g ⁻¹	1
Graphene/PPy	0.16	-	424 at 1 A g ⁻¹	2
Graphene/PPy	-	-	248 at 0.3 A g ⁻¹	3
Graphene/PPy	1.7	175 at 10 mV s ⁻¹	-	4
Graphene/PPy	-	-	345 at 1 A g ⁻¹	5
GO/PPy	-	-	332.6 at 0.25 A g ⁻¹	6
GO/PPy	-	-	356 at 0.5 A g ⁻¹	7
GO/PPy	-	152.5 at 10 mV s ⁻¹	-	8
GO/PPy	0.26	116 at 10 mV s ⁻¹	481.1 at 0.77A g ⁻¹	Present study
		94 at 200 mV s ⁻¹	410.4 at 38.5 A g ⁻¹	
	1.02	350 at 10 mV s ⁻¹	380.0 at 0.2 A g ⁻¹	
		173 at 200 mV s ⁻¹	315.9 at 10 A g ⁻¹	

All the capacitances are single electrode capacitance.

Table S2 Elemental analysis results of GO/PPy composite electrodes deposited in electrolyte with different GO concentration (the deposition time is 2100 s).

Concentration of GO (mg mL ⁻¹)	Wt.%					
	N	C	H	O	PPy	GO
0.1	15.31	53.05	3.400	28.24	72.90	27.10
0.4	14.56	50.16	3.166	32.11	69.33	30.67
0.8	14.43	50.07	3.172	32.32	68.71	31.29

References

1. S. Biswas and L. T. Drzal, *Chem. Mater.*, 2010, **22**, 5667-5671.
2. H.-H. Chang, C.-K. Chang, Y.-C. Tsai and C.-S. Liao, *Carbon*, 2012, **50**, 2331-2336.
3. J. Zhang and X. S. Zhao, *J. Phys. Chem. C*, 2012, **116**, 5420-5426.
4. J. Zhang, P. Chen, B. H. Oh and M. B. Chan-Park, *Nanoscale*, 2013, **5**, 9860-9866.
5. S. Li, C. Zhao, K. Shu, C. Wang, Z. Guo, G. G. Wallace and H. Liu, *Carbon*, 2014, **79**, 554-562.
6. L.-Q. Fan, G.-J. Liu, J.-H. Wu, L. Liu, J.-M. Lin and Y.-L. Wei, *Electrochim. Acta*, 2014, **137**, 26-33.
7. C. Zhu, J. Zhai, D. Wen and S. Dong, *J. Mater. Chem.*, 2012, **22**, 6300.
8. H. Zhou, G. Han, Y. Xiao, Y. Chang and H.-J. Zhai, *J. Power Sources*, 2014, **263**, 259-267.