

Electronic Supplementary Information (ESI) for Chemical Communications

This journal is (c) The Royal Society of Chemistry 2020

Polyaniline functionalized reduced graphene oxide/carbon nanotube ternary nanocomposite as supercapacitor electrode

Chengchao Wang, Yue Yang, Ruijun Li, Datong Wu, Yong Qin and Yong Kong*

Jiangsu Key Laboratory of Advanced Materials and Technology, School of Petrochemical
Engineering, Changzhou University, Changzhou 213164, China

Email address: yzkongyong@cczu.edu.cn

Experimental section

Reagents and apparatus. Natural graphite flakes (325 mesh, purity: 99.95%) were purchased from Qingdao Graphite Co., Ltd. (Qingdao, China). Aniline (purity: 99%), ammonium persulfate (APS) and phosphoric acid (H_3PO_4) were obtained from Aladdin Chemistry Co., Ltd. (Shanghai, China), and aniline was distilled under reduced pressure before use. Multi-walled carbon nanotube (MWCNT, purity: 95%, length: 0.5~2 μm ; outer diameter: 8~25 nm), ammonia water ($\text{NH}_3\cdot\text{H}_2\text{O}$), ascorbic acid, hydrogen peroxide (H_2O_2 , 30 wt%), potassium permanganate (KMnO_4), concentrated sulfuric acid (H_2SO_4) and concentrated hydrochloric acid (HCl) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Ultrapure water (18.2 $\text{M}\Omega\cdot\text{cm}$, Millipore) was used throughout.

FT-IR spectra of different samples were recorded on a FTIR-8400S spectrometer (Shimadzu, Japan). X-ray diffraction (XRD) patterns were recorded on a D/max 2500PC diffractometer (Rigaku, Japan). The morphologies of different samples were characterized with a Supra55 field-emission scanning electron microscope (FESEM, Zeiss, Germany) and a JEM 2100 transmission electron microscope (TEM, JEOL, Japan), respectively. The electrochemical measurements including cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and galvanostatic charge/discharge (GCD) experiments were carried out by using a CHI 660D electrochemical workstation (CH Instruments, Inc., China).

Synthesis of graphene oxide (GO). GO was synthesized from natural graphite flakes by the previously reported method.¹ Briefly, graphite flakes (1.0 g) were mixed with H_2SO_4 (120 mL) and H_3PO_4 (13.3 mL) with continuous stirring in an ice bath for 30 min. Under vigorous stirring, KMnO_4 (6.0 g) was slowly added into the mixture maintaining the temperature below 20 $^\circ\text{C}$. Next, the ice bath was removed and the temperature of the system was increased to ~35 $^\circ\text{C}$ due to the slight exotherm, and the mixture was heated to 50 $^\circ\text{C}$ and continuously stirred for 12 h. After the mixture was cooled to room temperature, it was poured onto ice (~133 mL) with 30% H_2O_2 (1 mL). After 12 h, the mixture was centrifuged, and the residue (GO) was washed with 1 M HCl and water and then dried at room temperature.

Synthesis of PANI-grafted RGO/MWCNT (PANI-RGO/MWCNT). GO (105 mg) and MWCNT (45 mg) were dispersed in 150 mL ultrapure water under sonication for 3 h, and then aniline (1.5 mL) and

$\text{NH}_3 \cdot \text{H}_2\text{O}$ (0.9 mL) were added consequently. The mixture was transferred to a flask of 250 mL and refluxed at 95 °C under stirring for 6 h. Next, ascorbic acid (2.64 g) was added into the mixture at 90 °C with continuous stirring for another 2 h to further reduce GO to RGO,^{2,3} and aniline functionalized RGO/MWCNT (a-RGO/MWCNT) was obtained. The a-RGO/MWCNT was rinsed with ethanol and water, respectively, followed by drying at 60 °C for 24 h.

The as-prepared a-RGO/MWCNT (50 mg) and aniline (0.5 mL) were dispersed in 1 M HCl (30 mL) under sonication for 30 min, and then mixture was cooled in an ice bath and continuously stirred for another 10 min. After that, 0.755 g APS was also dissolved in 1 M HCl (20 mL), which was slowly added into the above solution maintaining the temperature at 0 °C. The mixture was stirred overnight, and the resultant products (PANI-RGO/MWCNT) were collected, washed with ethanol and water, and dried at 60 °C for 24 h. Schematic illustration showing the preparation of PANI-RGO/MWCNT is depicted in Fig. S1.

Synthesis of RGO, PANI and RGO/PANI. For control experiments, RGO, PANI and RGO/PANI were synthesized as follows. For the synthesis of RGO, 105 mg GO was dispersed in 150 mL water and refluxed at 95 °C under stirring for 6 h, followed by the addition of 2.64 g ascorbic acid. After continuous stirring for 2 h at 90 °C, the products were collected, washed with ethanol and water, dried at 60 °C for 24 h. For the synthesis of PANI, 0.5 mL aniline was mixed with 30 mL HCl solution (1 M) with continuous stirring in an ice bath for 10 min, and then an aqueous solution of APS (0.755 g APS dissolved in 20 mL 1 M HCl) was added dropwise. The reaction was allowed to proceed for 24 h at 0 °C, and the precipitates were filtered and rinsed with ethanol and water, followed by drying at 60 °C for 24 h. For RGO/PANI, 50 mg RGO and 0.5 mL aniline were mixed with 30 mL HCl (1 M) under sonication for 30 min, and then the mixture was cooled in an ice bath and stirred for another 10 min. 0.755 g APS was dissolved in 20 mL HCl (1 M), which was slowly added into the above solution maintaining the temperature at 0 °C. After continuous stirring for 24 h at 0 °C, the products, RGO/PANI, were collected, washed with ethanol and water, respectively, followed by drying at 60 °C for 24 h.

Electrochemical testing. All electrochemical measurements were performed in a conventional three-electrode cell consisting of a glassy carbon electrode (GCE, 3 mm in diameter) modified with different materials as the working electrode, a platinum foil as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode, and the electrolyte was 1 M H₂SO₄ aqueous solution. The working electrode was fabricated as follows. 20 mg of different materials was dispersed in 10 mL water, and then 10 μ L of the dispersion (2 mg mL⁻¹) was dropped onto the surface of GCE and allowed to dry in ambient air. Cyclic stability of different samples was investigated by repeating the GCD testing for 1000 cycles at the current density of 10 A g⁻¹. EIS was carried out in the frequency range from 10⁵ to 0.01 Hz with an alternating sinusoidal signal of 5 mV, and the equivalent circuit was simulated by the ZSimpWin software. The specific capacitance (C_s) was calculated from the GCD curves based on the following equation^{4,5}:

$$C_s = \frac{I \times t}{m \times V}$$

where C_s represents the specific capacitance (F g⁻¹), I is the charging-discharging current (A), t is the discharging time (s), m is the mass of the materials modified on the surface of GCE (g), and V represents the voltage change during the discharging process (V).

FT-IR spectra of RGO, PANI and RGO/PANI

The FT-IR spectra of RGO, PANI and RGO/PANI confirm the successful synthesis of these materials for control experiments (Fig. S2). The characteristic bands of oxygen-containing groups at around 3425, 1731, 1222, 1047 and 1404 cm⁻¹ almost disappear completely on the spectrum of RGO, indicating successful reduction of GO. The characteristic bands of PANI are observed at around 1573 and 1490 cm⁻¹ for both PANI and RGO/PANI,⁶ implying successful formation of PANI via chemical oxidative polymerization of aniline.

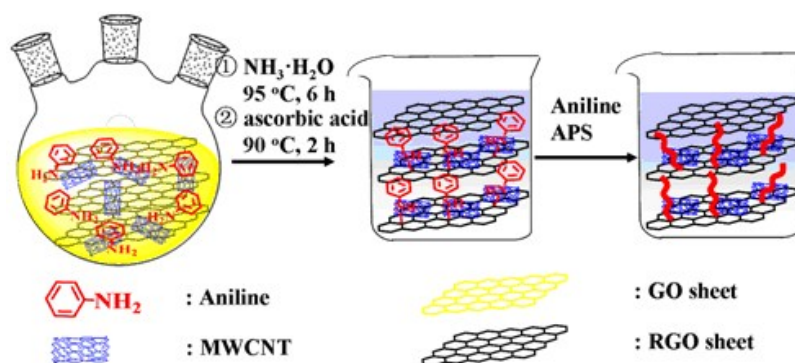


Figure S1. Schematic illustration showing the preparation of PANI-RGO/MWCNT.

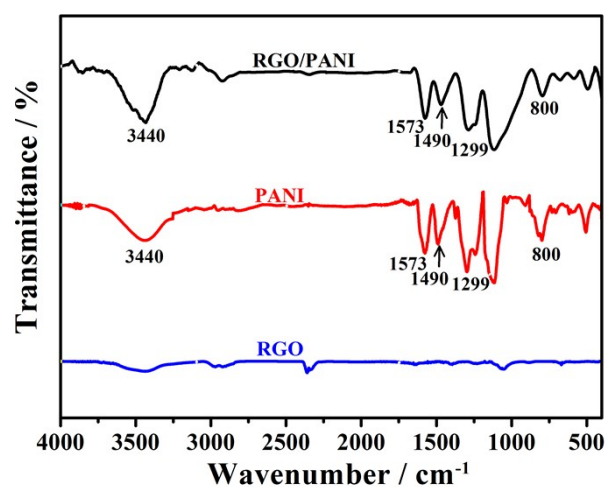


Figure S2. FT-IR spectra of RGO, PANI and RGO/PANI.

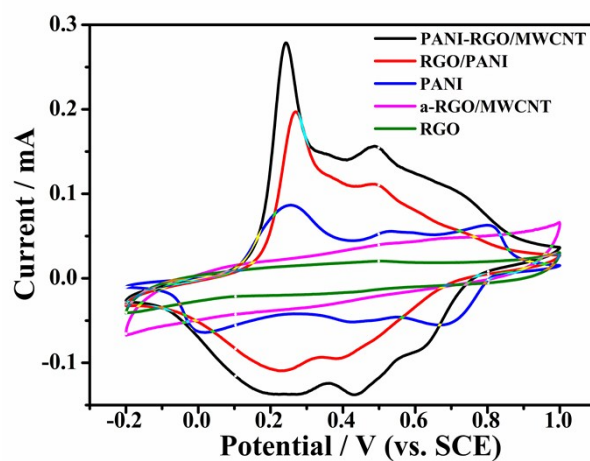


Figure S3. Cyclic voltammograms of RGO, a-RGO/MWCNT, PANI, RGO/PANI and PANI-RGO/MWCNT in 1 M H_2SO_4 at a scan rate of 5 mV s^{-1} .

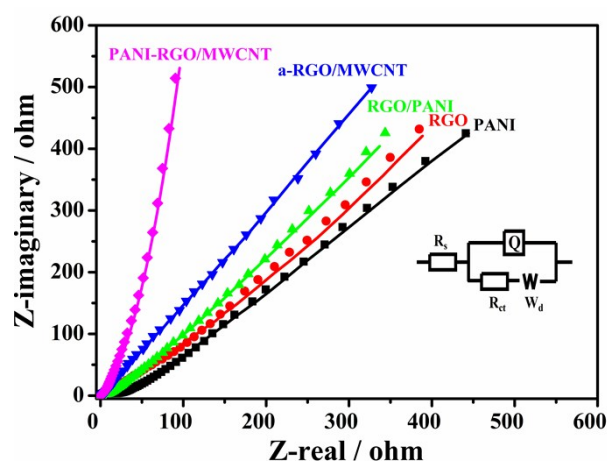


Figure S4. Nyquist plots of RGO, a-RGO/MWCNT, PANI, RGO/PANI and PANI-RGO/MWCNT in 1 M H_2SO_4 . Inset is the corresponding equivalent circuit, where R_s represents the ohmic resistance of electrolyte and the internal resistance of electrode, R_{ct} represents the interfacial charge transfer resistance, W_d represents the Warburg resistance, and Q represents the constant phase element.

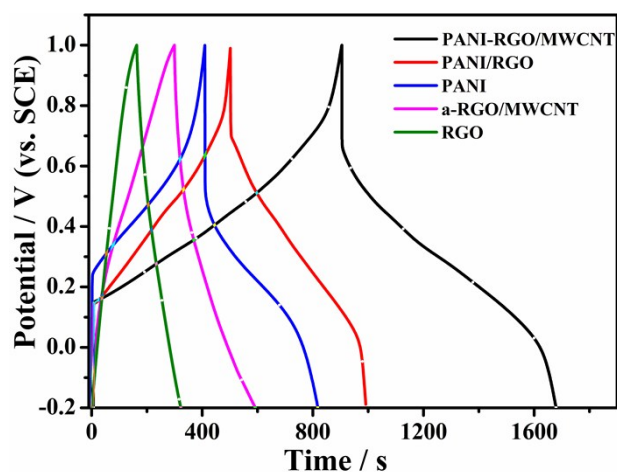


Figure S5. GCD curves of RGO, a-RGO/MWCNT, PANI, RGO/PANI and PANI-RGO/MWCNT in 1 M H_2SO_4 at a current density of 1 A g^{-1} .

Table S1. Performance comparison with the previously reported results at the current density of 1 A g⁻¹.

Sample	Capacitance	Mass loading	Reference
Graphene/PANI	448 F g ⁻¹	0.36 mg cm ⁻²	7
RGO/PANI	410 F g ⁻¹	1.5 mg cm ⁻²	8
Graphene/PANI	497.9 F g ⁻¹	1~1.33 mg cm ⁻²	9
RGO-PANI	553 F g ⁻¹	0.283 mg cm ⁻²	10
PANI-RGO/MWCNT	645 F g ⁻¹	0.283 mg cm ⁻²	This work

References

- 1 D. C. Marcano, D. V. Kosynkin, J. M. Berlin, A. Sinitskii, Z. Sun, A. Slesarev, L. B. Alemany, W. Lu and J. M. Tour, *ACS Nano*, 2010, **4**, 4806.
- 2 X. Pu, L. Li, M. Liu, C. Jiang, C. Du, Z. Zhao, W. Hu and Z. L. Wang, *Adv. Mater.*, 2016, **28**, 98.
- 3 K. X. Sheng, Y. X. Xu, C. Li and G. Q. Shi, *New Carbon Mater.*, 2011, **26**, 9.
- 4 W. J. Wang, Q. L. Hao, W. Lei, X. F. Xia and X. Wang, *RSC Adv.*, 2012, **2**, 10268.
- 5 A. De Adhikari, R. Oraon, S. K. Tiwari, J. H. Lee and G. C. Nayak, *RSC Adv.*, 2015, **5**, 27347.
- 6 J. Xu, K. Wang, S. Zu, B. Han and Z. Wei, *ACS Nano*, 2010, **4**, 5019.
- 7 M. Hassan, K. R. Reddy, E. Haque, S. N. Faisal, S. Ghasemi, A. I. Minett and V. G. Gomes, *Compos. Sci. Technol.*, 2014, **98**, 1.
- 8 H. Qiu, X. Han, F. Qiu and J. Yang, *Appl. Surf. Sci.*, 2016, **376**, 261.
- 9 R. Wang, M. Han, Q. Zhao, Z. Ren, X. Guo, C. Xu, N. Hu and L. Lu, *Sci. Rep.*, 2017, **7**, DOI: 10.1038/srep4456.
- 10 R. Li, Y. Yang, D. Wu, K. Li, Y. Qin, Y. Tao and Y. Kong, *Chem. Commun.*, 2019, **55**, 1738.