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Electronic Supplementary Information

A Core/Shell Structured Tubular Graphene Nanoflakes-coated Polypyrrole Hybrid for All-Solid-State

Flexible Supercapacitor

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1. Experimental Section

1.1. Materials

Analytical reagents grade chemicals from Sinopharm Chemical Reagent Co., Ltd. were used throughout, including pyrrole (Py), nitric acid (HNO₃), N,N-dimethylformamide (DMF), ferric chloride hexahydrate (FeCl₃·6H₂O), 4-dimethylaminopyridine (DMAP), methyl orange (MO, sodium 4-[4'-(dimethylamino)phenyldiazo]phenylsulfonate), dicyclohexylcarbodiimide (DCC), and hydrazine hydrate, unless otherwise stated. Py used for the synthesis of PNTs was distilled and kept refrigerated in the dark before use.

1.2. Preparation of small graphene nanoflakes (GNFs)

GNFs were prepared from Vulcan XC-72R carbon black (size 30 nm, Cabot Corporation) by refluxing with concentrated nitric acid as reported in the literature.¹ In the typical procedure, 0.4 g dried VXC-72R carbon black was put into 100 mL 6 M HNO₃ followed by refluxing at 130 °C for 48 h. After cooling to room temperature, the suspension was centrifuged (3000 rcf) for 10 min to obtain a supernatant. The supernatant was ultrasonicated for 1 h and then centrifuged (5000 rcf) for 10 min to obtain another supernatant. The supernatant was heated at 200 °C in an oven to evaporate the water and nitric acid, and then a reddish-brown solid of GNFs was obtained.

1.3. Preparation of polypyrrole nanotubes (PNTs)

PNTs were prepared by a self-degraded template method as reported in the literature.² In the typical procedure, 1.5 mmol (0.41 g) of FeCl₃·6H₂O was added into 30 mL of 5 mM MO aqueous solution and stirred completely with the appearance of a flocculent precipitate immediately. Then 1.5 mmol (105 μ L) of pyrrole monomer was added and the mixture was stirred at room temperature for 12 h. The formed black precipitate, *i.e.* PNTs, was washed with deionized water/ethanol several times until filtrate was colorless and neutral, and finally dried under a vacuum atmosphere at 60 °C for 24 h.

1.4. Preparation of graphene nanoflakes-coated polypyrrole nanotubes (GNFs/PNTs)

GNFs/PNTs were prepared by grafting reaction in the following procedure.^{3, 4} Typically, 3 mg of GNFs and 9 mg of PNTs were mixed in 30 mL DMF under ultrasound for 1 h. Then 1 mg of DMAP and 10 mg of DCC were added into the mixture successively and stirred strongly at room temperature for 24 h. The formed black precipitate was washed using DMF and deionized water with sufficient sonication and centrifugalization for several times to peel off the un-grafted GNFs from PNTs surfaces, and then dried under a vacuum atmosphere at 60 °C for 24 h. Finally, the black precipitate was reduced by hydrazine and then washed to obtain the nanocomposite, denoted as GNFs/PNTs (1:3), where the ratio of 1:3 represents the mass ratio of reactants GNFs to PNTs in the preparation. Adjusting the mass ratios of reactants GNFs to PNTs as 1:9, 1:1, 3:1 and 9:1, the same synthesis procedures were performed to obtain various coating amounts of GNFs onto PNTs.

1.5. Characterizations

Transmission electron microscopy (TEM) was performed using a JEM-2100F instrument. Fouriertransformed infrared spectrum (FT-IR) was recorded on Shimadzu FTIR spectrophotometer using thin KBr disc. X-ray photoelectron spectroscopy (XPS) analysis was performed on a commercial VG Multilab 2000 system to detect the changes in chemical component and structure. The C 1s level spectral decomposition was analyzed using background subtraction and a least-squares fitting program.

1.6. Electrochemical measurements

All electrochemical measurements were carried out using an Autolab electrochemical workstation (PGSTAT, 128N, Metrohm). 10 mg of electrode material was dispersed in 1 mL of solution containing 0.98 mL of ethanol and 20 µL of Nafion 117[®] solution, followed by ultrasonication for 30 min. Then a certain volume of sample suspension was pipetted onto a gold electrode to give a 3 mg cm⁻² loading as a working electrode after drying in 50 °C oven. Cyclic voltammetry (CV), galvanostatic charging/discharging and electrochemical impedance

spectroscopy (EIS) measurements were performed in 3 M KCl electrolyte in a three-electrode cell ^{5, 6} using a saturated calomel reference electrode (SCE) and a Pt wire counter electrode. Capacitance value (C) could be calculated from the CV curve using Equation (1) or galvanostatic charging/discharging curve using Equation (2):⁷

$$C = \int I_1 \mathrm{d}U / 2vmU \tag{1}$$

$$C = I_2 t / m U \tag{2}$$

where I_1 (A) is the response current of CV, U (V) is voltage window (voltage drop IR_{drop} has been considered for galvanostatic charging/discharging), v (V s⁻¹) is the scan rate, m (g) is the mass of electrode material, I_2 (A) is the discharging current, t (s) is the discharging time.

1.7. Assembly of flexible all-solid-state symmetric supercapacitor (SSC)

A 3 mg cm⁻² loading of above GNFs/PNTs (1:3) suspension was deposited onto two pieces of aluminum foils and dried in 50 °C oven. The gel electrolyte was prepared using 2 g of polyvinyl alcohol (PVA), 20 ml of distilled water, and 4.25 g of LiCl at 95 °C with vigorous stirring.⁸ The resulting gel was as the solid-state electrolyte and separator between two GNFs/PNTs (1:3) loaded aluminum foils, which was further dried in 50 °C oven. Finally, the assembled device was sealed using Parafilm[®] to prevent the gel electrolyte from absorbing moisture. The electrochemically capacitive properties of the assembled SSC were investigated in a two-electrode configuration. Ragone plot with areal energy and power densities (*E* and *P*) is obtained by Equations (3) and (4), respectively.⁷

$$E = CU^{2} / (2 \times 3600)$$
(3)
$$P = E \times 3600 / t$$
(4)

The LED light used in the test is a cap-shape red LED lamp bead with a diameter of 5 mm. The working potential is 1.8-2.2 V, the working current is 15-20 mA, and the rated power is 0.04 W, we also added this part into the revised manuscript.

2. Supplementary Figures



Figure S1. (a) Estimated size distribution of GNFs from TEM image. (b) AFM image and (c) corresponding height profile of GNFs.



Figure S2. TEM images of (a, b) GNFs/PNTs (1:9), (c, d) GNFs/PNTs (9:1), and (e, f) product without DCC/DMAP involved (mass ratio of reactants GNFs to PNTs as 1:3) (Inset is corresponding amplified HRTEM image of the local area).



Figure S3. XPS survey spectrum and high resolution spectra of C 1s for (a, b) PNTs and (c, d) GNFs.



Figure S4. XPS high resolution spectra of C 1s for (a) GNFs/PNTs (1:9), (b) GNFs/PNTs (1:1), (c) GNFs/PNTs (3:1), and (d) GNFs/PNTs (9:1).



Figure S5. (a) Capacitances at various scan rates and current densities of GNFs/PNTs (1:3). (b) CV at a scan rate of 200 mV s⁻¹ of GNFs/PNTs hybrids and the product (mass ratio of reactants GNFs to PNTs as 1:3) without DCC/DMAP involved. (c) Capacitances of GNFs/PNTs hybrids at various mass ratios of reactants GNFs to PNTs. (d) Comparison of capacitances of conductive polymer/graphene nanocomposites among some literatures data.⁹⁻¹⁸



Figure S6. Electrochemical capacitance performance of the supercapacitor device: (a) Areal capacitances at various scan rates and current densities. (b) Electrochemical impedance spectroscopy (EIS). (c) Comparison of areal capacitances of SC devices among some literatures data.^{8, 19-26} (d) Capacitance retentions under flat, bent and twisted conditions (Inset photo shows flexibility of the device).

3. References

- 1. Y. Dong, C. Chen, X. Zheng, L. Gao, Z. Cui, H. Yang, C. Guo, Y. Chi and C. M. Li, *J. Mater. Chem.*, 2012, 22, 8764-8766.
- 2. X. Yang, Z. Zhu, T. Dai and Y. Lu, Macromol. Rapid Commun., 2005, 26, 1736-1740.
- 3. M. V. Rosenthal, T. Skotheim and J. Warren, J. Chem. Soc., Chem. Commun., 1985, 342-343.
- 4. T. Darmanin, M. Nicolas and F. Guittard, *Langmuir*, 2008, 24, 9739-9746.
- 5. K. Qi, Y. Qiu and X. Guo, *Electrochim. Acta*, 2014, 137, 685-692.
- 6. X. Zhong, S. Yu, L. Chen, J. Hu and Z. Zhang, J. Mater. Sci.: Mater. Electron., 2016, 28, 2279-2289.
- V. T. Le, H. Kim, A. Ghosh, J. Kim, J. Chang, Q. A. Vu, D. T. Pham, J.-H. Lee, S.-W. Kim and Y. H. Lee, *ACS Nano*, 2013, 7, 5940-5947.

- 8. G. Wang, X. Lu, Y. Ling, T. Zhai, H. Wang, Y. Tong and Y. Li, ACS Nano, 2012, 6, 10296-10302.
- 9. S. Biswas and L. T. Drzal, *Chem. Mater.*, 2010, 22, 5667-5671.
- 10. X. Wang, T. Wang, C. Yang, H. Li and P. Liu, *Appl. Surf. Sci.*, 2013, 287, 242-251.
- N. A. Kumar, H.-J. Choi, Y. R. Shin, D. W. Chang, L. Dai and J.-B. Baek, ACS Nano, 2012, 6, 1715-1723.
- 12. S. Zhou, H. Zhang, Q. Zhao, X. Wang, J. Li and F. Wang, *Carbon*, 2013, 52, 440-450.
- 13. S. Ye and J. Feng, ACS Appl. Mat. Interfaces, 2014, 6, 9671-9679.
- 14. J. Liu, J. An, Y. Ma, M. Li and R. Ma, J. Electrochem. Soc., 2012, 159, A828-A833.
- J. Liu, J. An, Y. Zhou, Y. Ma, M. Li, M. Yu and S. Li, ACS Appl. Mat. Interfaces, 2012, 4, 2870-2876.
- 16. L. Mao, H. S. O. Chan and J. Wu, RCS Adv., 2012, 2, 10610-10617.
- 17. J. Xu, K. Wang, S.-Z. Zu, B.-H. Han and Z. Wei, ACS Nano, 2010, 4, 5019-5026.
- W. Fan, C. Zhang, W. W. Tjiu, K. P. Pramoda, C. He and T. Liu, *ACS Appl. Mat. Interfaces*, 2013, 5, 3382-3391.
- 19. H. Gao and K. Lian, J. Power Sources, 2011, 196, 8855-8857.
- 20. G. Zheng, L. Hu, H. Wu, X. Xie and Y. Cui, *Energy Environ. Sci.*, 2011, 4, 3368-3373.
- 21. M. F. El-Kady, V. Strong, S. Dubin and R. B. Kaner, *Science*, 2012, 335, 1326-1330.
- P. Yang, X. Xiao, Y. Li, Y. Ding, P. Qiang, X. Tan, W. Mai, Z. Lin, W. Wu, T. Li, H. Jin, P. Liu, J. Zhou, C. P. Wong and Z. L. Wang, *ACS Nano*, 2013, 7, 2617-2626.
- 23. D. Fu, H. Zhou, X.-M. Zhang, G. Han, Y. Chang and H. Li, *ChemistrySelect*, 2016, 1, 285-289.
- L. Wang, X. Feng, L. Ren, Q. Piao, J. Zhong, Y. Wang, H. Li, Y. Chen and B. Wang, J. Am. Chem. Soc., 2015, 137, 4920-4923.
- B. Yao, L. Yuan, X. Xiao, J. Zhang, Y. Qi, J. Zhou, J. Zhou, B. Hu and W. Chen, *Nano Energy*, 2013, 2, 1071-1078.
- L. Yuan, X.-H. Lu, X. Xiao, T. Zhai, J. Dai, F. Zhang, B. Hu, X. Wang, L. Gong, J. Chen, C. Hu, Y. Tong, J. Zhou and Z. L. Wang, *ACS Nano*, 2012, 6, 656-661.