

Supporting Information

Carbonized poly(vinylidene fluoride)/graphene oxide with three-dimensional multiscale-pore architecture as advanced electrode materials

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EXPERIMENTAL SECTION

All materials and chemicals were purchased commercially and used as received. All the chemical reagents were purchased from Sinopharm Chemical Reagent Beijing Co. except where noted. All the SEM images were recorded with JEOL 4600 and 7401 microscope. AFM image was recorded with Dimension 3100. TEM images were recorded with a JEOL JEM-2010F. Raman measurements were performed with a Renishaw Invia Raman Microscope spectrometer. All electrochemical measurements were conducted with a computer-controlled CHI660B electrochemical analyzer (CH Instruments, Shanghai Chenhua Instrument Corporation, China).

Fabrication of GO solutions: GO was prepared by the oxidation of natural graphite powder (325 mesh, Qingdao Huatai Lubricant Sealing S&T Co. Ltd., Qingdao, China) according to a modified Hummer method reported in our previous literatures.[1] The GO aqueous solution was fabricated by dispersing as-prepared GO sheets in water after sonication. GO was first sonicated in mild sonication for 2 h. Then a strong sonication was applied to the presonicated GO solution for 20 min. The resulting GO solution was first centrifuged at 1500 rpm for 2 h. The top layer solution was collected in order to remove most of the large GO sheets, and then centrifuged at 10000 rpm for 2 h to remove the small GO sheets with diameter less than 300 nm.

Fabrication of CPVDFG: PVDF/GO gel were prepared by mixing poly(vinylidene fluoride) (PVDF, Mw = 650,000 g/mol, purchased from Sigma-Aldrich) solution with different concentration of GO ranging from 0.25 wt% to 5 wt% was used for fabricating. The resulting solution was then freeze dried for 24 h after ageing for 4 days and solvent exchanging in water for 5 days to produce dried porous materials. The gel was then put into a tube furnace and heated to the carbonization temperature (600, 700, 800, 850, 900, 950, 1000 °C at 5 °C/min) under nitrogen protection for preparing CPVDFG with porous structures.

Electrochemical measurements: All electrochemical measurements were carried out at room temperature. Cyclic voltammetry and galvanostatic charge/discharge tests were used to characterize the

electrochemical performances of the supercapacitor devices. Different current densities ranging from 0.01 to 50 A/g were applied and a current density of ~ 5 A/g was used for the cycling life tests. CPVDF, CPVDFG with 2% GO amount and CPVDFG with 5% GO amount electrodes were chosen for the parallel test.

The physical property of PVDFG and CPVDFG.

Materials were characterized by x-ray diffraction (XRD) using a PANalytical diffractometer with Cu K α radiation at room temperature. The diffraction peaks of PVDFG (Figure s1a) near $2\theta = 18.3$ (020), 19.9 (110) and 26.5 (021) are appeared to the α phase crystal structure of PVDF. The wide peak shown in Figure s1b represents the low crystalline carbon after thermal treatment.

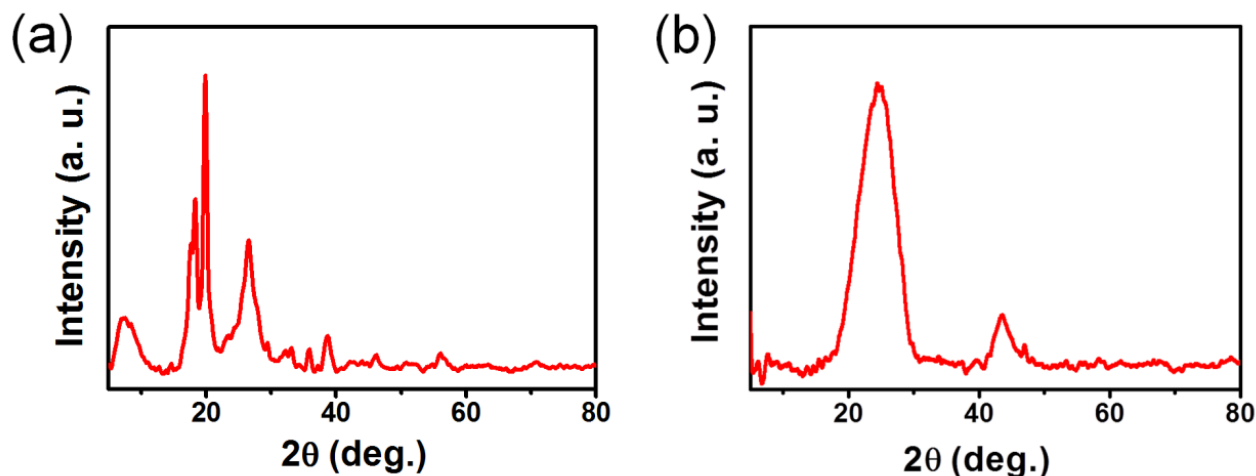


Figure s1. XRD patterns of PVDFG (a) and CPVDFG (b).

The BET results show that the surface areas and the pore sizes of PVDFG and CPVDFG with different amounts of graphene have not changed much. The surface area of the PVDFG and CPVDFG are shown in Table s1.

Amount of GO (%)	0	1	2	3	4	5
S_{BET} of PVDFG (m^2/g)	107.2	110.3	112.7	117.9	118.5	118.3
S_{BET} of CPVDFG (m^2/g)	895.4	893.1	897.7	902.1	902.3	901.3

Table s1. The surface area of the PVDFG and CPVDFG with different amounts of GO.

The electrochemical characteristics of the CPVDFG with different GO amounts are shown in Figure s2. Figure s2a shows the cyclic voltammetry curves of the CPVDFG electrodes with different GO amounts recorded in the potential range of -0.1 and 0.6 V. All the CV curves of the different CPVDFG electrodes exhibit a relatively ideal rectangular shape and near mirror-image current response on voltage reversal, and no obvious redox peak was observed, indicating a typical EDLC

capacitive behavior and excellent electrochemical reversibility. The rectangular areas haven't really changed which represents the specific capacities are increased slightly. This result is consistent with the variation of surface areas. Figure s2b and s2c show the stability and rate capability of CPVDFG electrodes with different GO amounts. The result shows that specific capacitance values and maintenance capabilities of the CPVDFG electrodes increase with the GO amount. As shown in Figure3c, the porous CPVDFG electrode exhibits a superior charge/discharge cycle characteristics, with only a minor capacitance loss (less than 3%) observed after 9000 cycles at 5A/g. CPVDF, by contrast, has poor cycle performance (loss around 4% after 500 cycle), as shown in Figure s2b. The specific capacitance of different porous-CPVDFG-based electrodes at different charge/discharge current densities are compared in Figure s2c. These curves indicate that the power density and high-rate discharge characteristic of CPVDFG electrodes increase with the GO amount. In sum, the as-fabricated CPVDFG shows outstanding electrochemical performance with superior characteristics of stabilization, specific capacitance and rate capability. The addition of GO into CPVDF leads the small percentage increase of specific capacitance and make a greater enhancement on high-rate discharge characteristic and cycle performance.

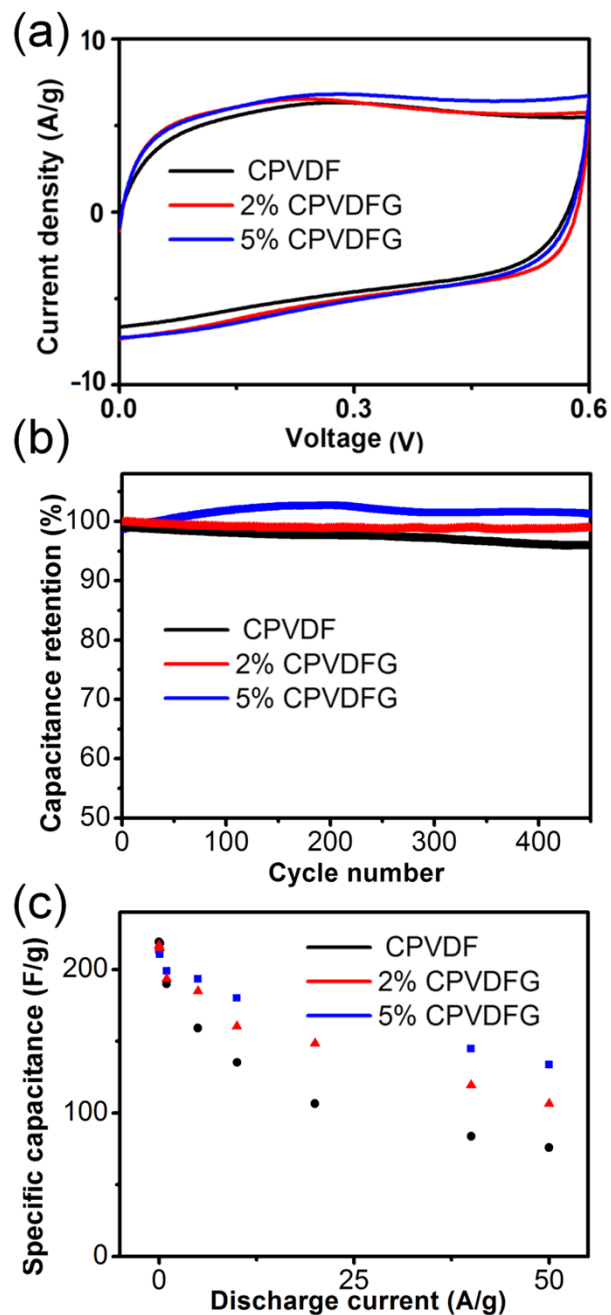


Figure s2. Electrochemical characteristics of CPVDFG with different GO amounts. (a) CV curves of CPVDF, CPVDFG (2% GO) and CPVDFG (5% GO). (b) Cycle performance of the different CPVDFG electrodes with the current density at 5 A/g. (c) Specific capacitances of different CPVDFG in supercapacitor calculated from the corresponding discharge curve in galvanostatic charge/discharge curves at different charge/discharge current densities ranging from 0.01 to 50 A/g.

1. a) Xue, M.; Li, F.; Zhu, J.; Song, H.; Zhang, M.; Cao, T. *Adv. Funct. Mater.* **2012**, *22*, 1284-1290; b) Li, F.; Xue, M.; Ma, X.; Zhang, M.; Cao, T. *Anal. Chem.* **2011**, *83*, 6426-6430; c) Liu, H.; Gao, J.; Xue, M.; Zhu, N.; Zhang, M.; Cao, T. *Langmuir* **2009**, *25*, 12006-12010.