Supporting Information

Extraordinary Rate Capability Achieved by a 3D "Skeleton/Skin" Carbon Aerogel - Polyaniline hybrid with Vertically Aligned Pores

Mingkai Liu,[a*] Bomin Li,[c] Hang Zhou,[a] Cong Chen,[a] Yuqing Liu,[a] Tianxi Liu[a,b*]

[a]*School of Chemistry and Chemical Engineering, Jiangsu Key Laboratory of Green Synthetic Chemistry for Functional Materials, Jiangsu Normal University, Xuzhou 221116, China;*
[b]*State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Materials Science and Engineering, Donghua University, Shanghai 201620, China;*
[c] *State Key Laboratory of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, China;*

Experimental section

Materials

Graphite (100 mesh) was purchased from Qingdao Henglide Graphite Co., Ltd. Carbon nanotubes (20 - 30 nm, 5 μm in length) were obtained from Sigma Aldrich. Triethylamine (TEA), N,N-dimethylacetamide (DMAc), 4,4'-oxidianiline (ODA) and pyromellitic dianhydride (PMDA), coupling with some reagents like H_2SO_4 (98%), $KMnO_4$, H_2O_2 (30%) and HCl (35%) were purchased from Sinopharm Chemical Reagent Co., Ltd. Aniline and ammonium persulfate (APS, 98%) were obtained from Shanghai Chemical Reagent Co. Ultraclean water was used throughout the experiments.

Fabrication of CA-PANI aerogel film

Graphene oxide (GO) sheets were prepared according to a modified Hummers' method.[S1] CNTs (60 mg) with bundle morphology were dispersed in to GO solution (200 mL, 1 mg/mL) under mild sonication to achieve a homogeneously dispersed mixture of GO/CNT. The GO/CNT mixture was added into PAA solution (4 wt%), which was prepared by ODA and PMDA.[S2] Then, the mixed solution of PAA/GO/CNT was placed above the liquid nitrogen, which led to the formation of a uniaxial thermal gradient and vertically aligned ice pillars were formed. Then the resulted PAA/GO/CNT hybrid film was freeze-dried under vacuum (~ 10 Pa) for 24 h before being thermally treated at 800 ºC in Ar for 3 h, resulting in the formation of CA materials. Here, the thickness of the CA materials can be easily controlled by adjusting the volume of PAA/GO/CNT solution in the foil container. CA-PANI film was prepared by polymerization of aniline monomers on the CA matrix. Typically, 200 mg CA matrix were dipped into 100 mL of 1 M H_2SO_4 solution. Aniline (720 mg, 7.72 mmol) was added to the above solution which was maintained in a NaCl-ice bath for 30 min. APS (443 mg, 1.92 mmol) was dissolved in the above solution under continuously stirring for 10 h. The obtained hybrid film was washed by ultraclean water and acetone for several times. The final CA-PANI film with PANI nanorods anchored on the surface of CA materials was obtained after being dried in a vacuum oven at 60 ºC for 24 h. In addition, pure PANI materials were prepared in the same way without the addition of CA materials.

Characterization and measurements

Morphologies of the prepared samples were observed on a field-emission scanning

electron microscopy (FE-SEM, SU8010, Hitachi) equipped with an X-ray energy dispersive spectrometer (EDS). X-ray diffraction (XRD) patterns were recorded on a diffractometer (D8, ADVANCE, Bruker).

Cyclic voltammetry (CV) and galvanostatic charge/discharge testings were performed on an ARBIN cell workstation (BT2043) with a scan range of -0.2 to 1.0 V in 1 M H_2SO_4 solution. For three-electrode system, CA-PANI pressed on nickel foam was used as working electrode. Platinum foil and Ag/AgCl electrodes were employed as counter and reference electrodes. The specific capacitance (C) of the active CA-PANI materials was calculated from the discharge curve according to the following equation:

$$C = \frac{I \cdot \Delta t}{\Delta V \cdot m} \tag{1}$$

where I is the current density (A), Δt represents the discharge time (s), m is the weight of the electroactive materials (g), ΔV is the potential except for the IR drop.

Asymmetric supercapacitor of CA//CA-PANI was assembled with CA as the negative electrode and CA-PANI hybrid as positive electrode. The mass ratio of the two electrodes was estimated by the following equation:

$$\frac{m_+}{m_-} = \frac{C_- \times V_-}{C_+ \times V_+}$$

Where m (g) is the mass of the electrode materials, C (F/g) represents the specific capacitance of each electrode, and V (V) is the discharge potential.

The energy density (E) and power density (P) of the symmetric supercapacitors were calculated based on the following equations:

$$E = \frac{1}{2} C V^2 \tag{2}$$

$$P = \frac{E}{t} \tag{3}$$

where C is the specific capacitance (F/g), V represents the voltage (V), t is the discharge time (s).

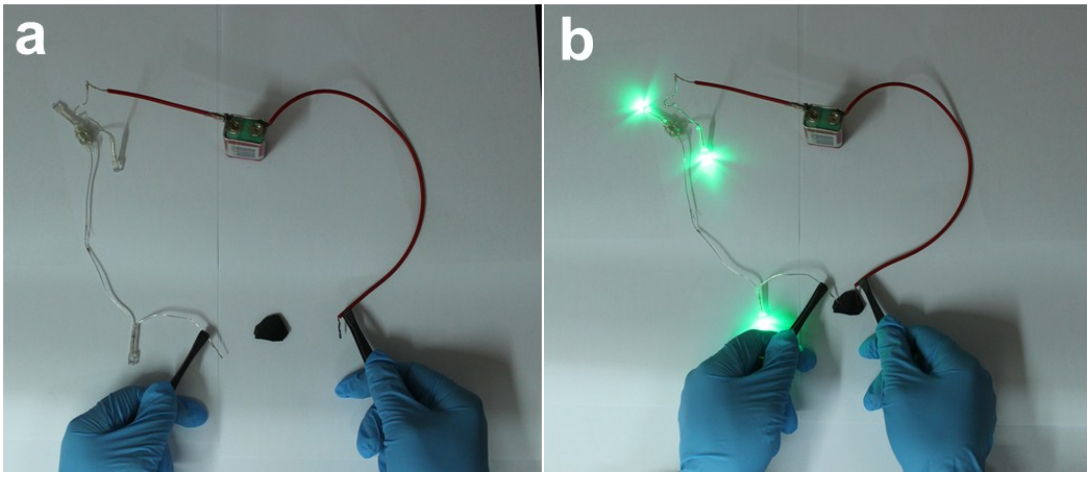

Fig. S1 Green LED lights can be lit up in a closed circuit with CA materials replacing of copper wire.

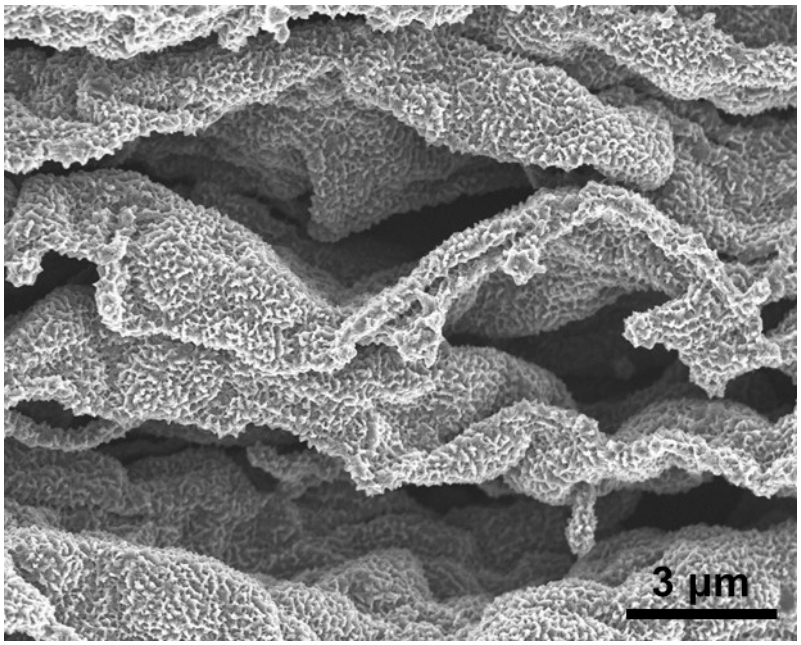

Fig. S2 SEM images exhibits the homogeneous deposition of PANI nanorods on the side of vertically aligned pores.

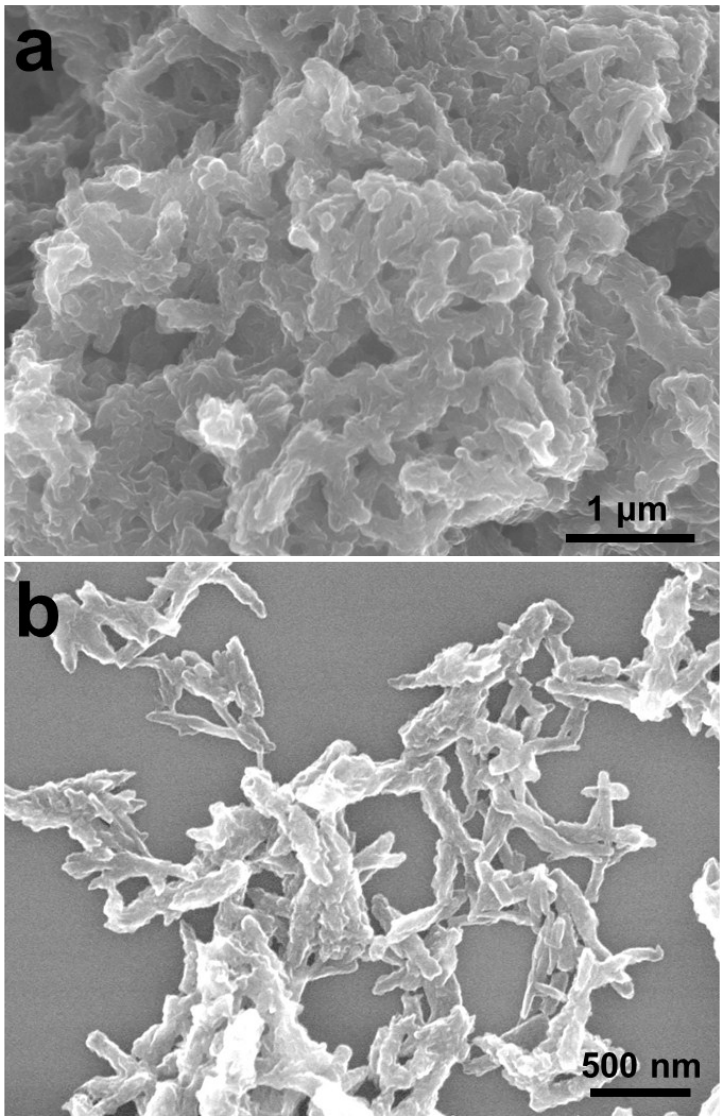

Fig. S3 SEM images of pure PANI nanorods at low and high magnifications.

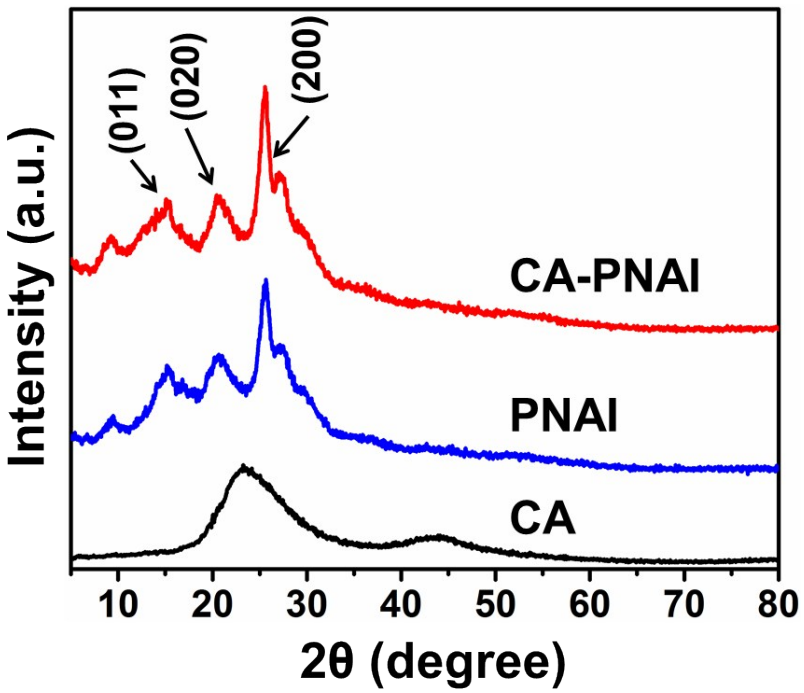

Fig. S4 XRD patterns of CA materials, pure PANI and CA-PANI hybrids.

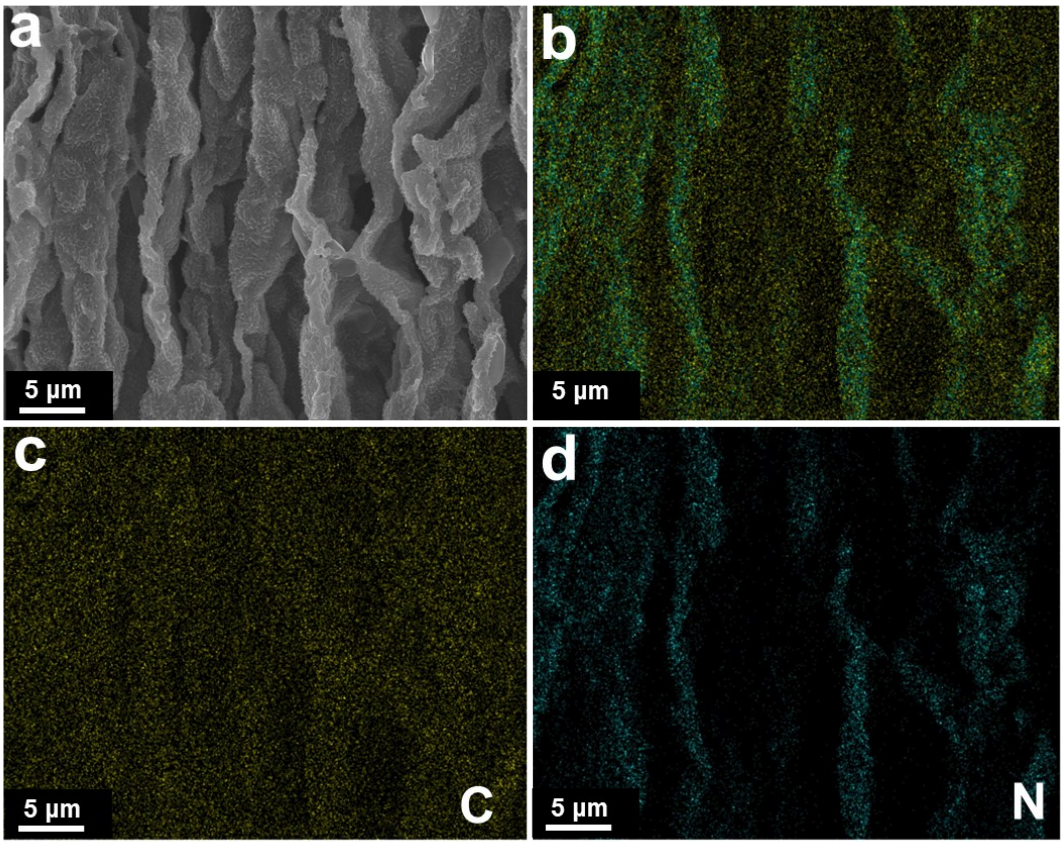

Fig. S5 (a) SEM image and EDS mapping images including (b) survey, (c) C element and (d) N element of CA-PANI hybrid.

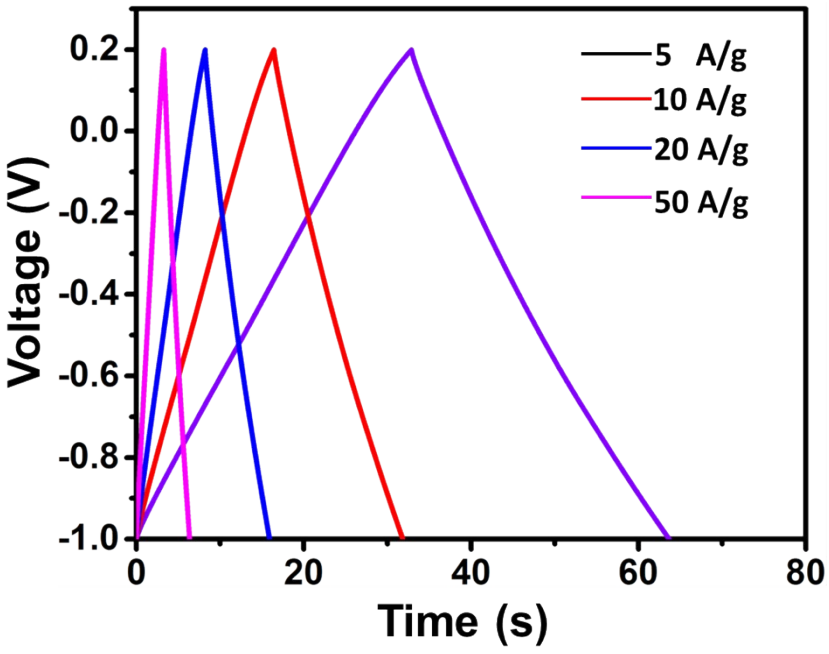

Fig. S6 Charge/discharge curves of CA electrode from 5 to 50 A/g.

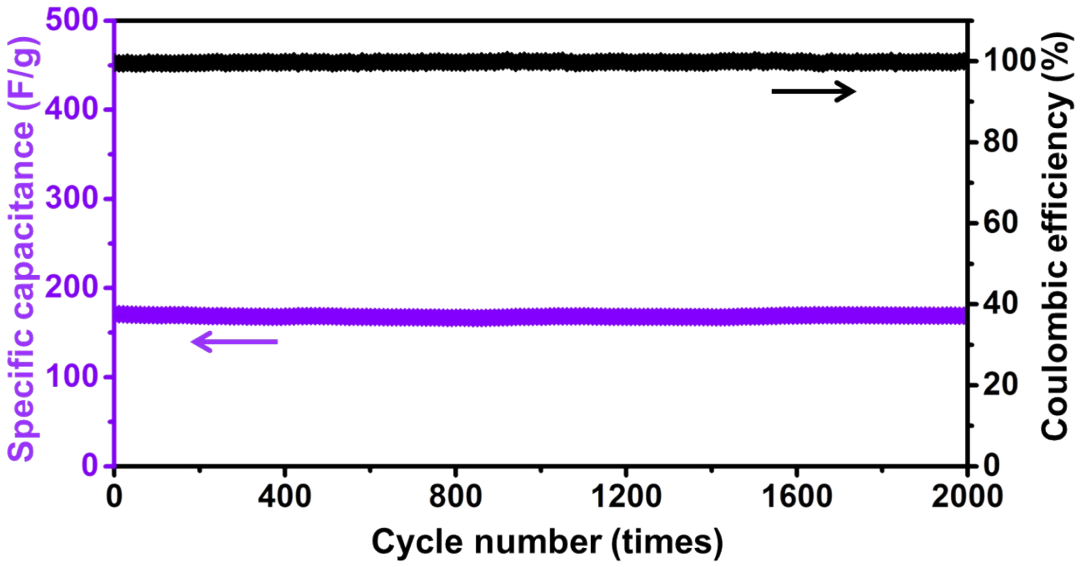

Fig. S7 Long-term cycling stability of CA electrode at 1 A/g and corresponding Coulombic efficiencies.

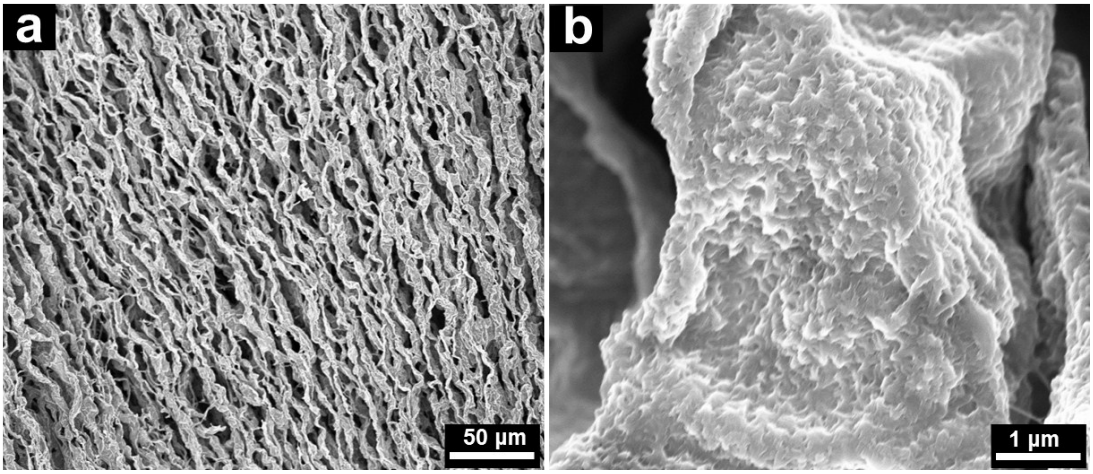

Fig. S8 SEM images of CA-PANI hybrid after being cycled at 5 A/g for 5000 times.

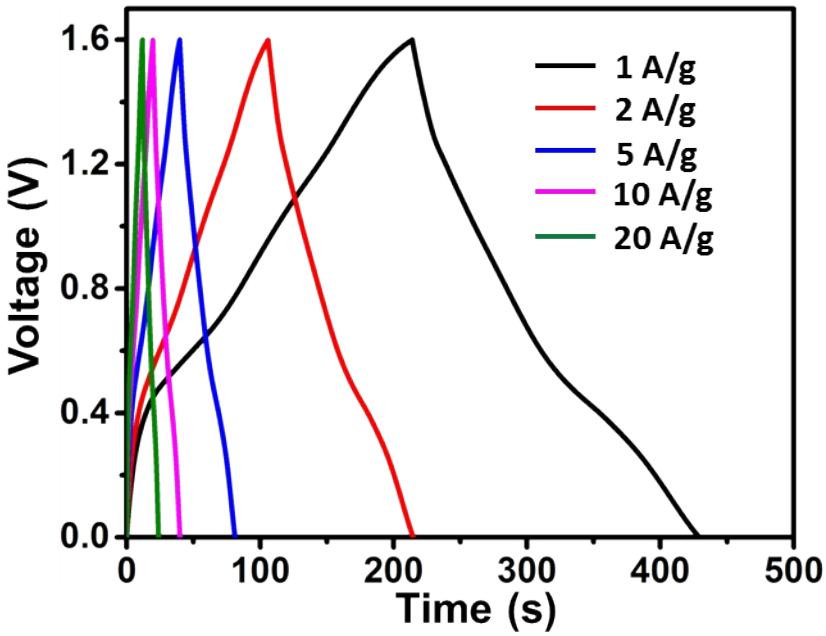

Fig. S9 Charge/discharge curves of CA//CA-PANI asymmetric cell under different current densities from 1 to 20 A/g

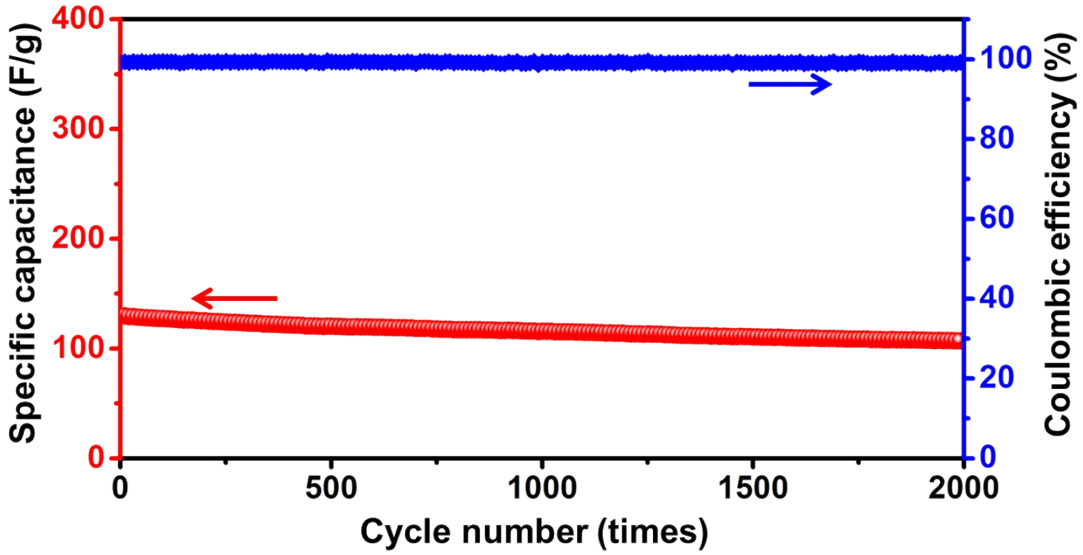

Fig. S10 Long-term cycling stability of CA//CA-PANI asymmetric supercapacitor.

Notes and references

1 Z. B. Yang, H. Sun, T. Chen, L. B. Qiu, Y. G. Luo and H. S. Peng, *Angew. Chem. Int. Ed.*, 2013, **52**, 7545.

2 (a) D. Chen, H. Zhu and T. X. Liu, *ACS Appl. Mater. Interfaces*, 2010, **2**, 3702; (b) Y. E. Miao, G. N. Zhu, H. Q. Hou, Y. Y. Xia and T. X. Liu, *J. Power Sources*, 2013, **226**, 82.