Supporting Information

Controlled Growth of Whisker-like Polyaniline on Carbon Nanofibers and Their Long Cycle Life for Supercapacitor

Junyi Wei, Jianan Zhang, Yang Liu, Guiheng Xu, Zhimin Chen, and Qun Xu*

Electrochemical measurement by three-electrode system in 1 M H₂SO₄

The capacitance performances of the samples were also evaluated in three-electrode system for reference. The preparation of thin film electrode is similar to that described in the experimental section. A slurry of PANI/CFs was prepared by thoroughly mixing PANI/CFs, carbon black and poly(tetrafluoroethylene) (60% in dispersion in H₂O) in a mass ratio of 80:10:10. The slurry was then pasted onto stainless steel ($0.7 \times 0.7 \text{ cm}^2$) to form the tested electrode and then dried at 60 °C for 24h. The prepared electrode, Ag/AgCl electrode and platinum wire were connected to a CHI 660D workstation (CH Instrument, Inc.) and served as working, reference and counter electrodes, respectively. The electrochemical measurements were carried out in 1 M H₂SO₄.

The CV curves of PANI/CFs with different initial ANI concentration: 5, 10, 25, and 50 mM are presented in Figure S1a. Each CV curve presents two pairs of redox peaks (O_1/R_1 and O_2/R_2) implying the pseudocapacitance characteristic and the reversible charge-discharge behaviors. The current density response of PANI/CFs evidently increases with the ANI concentration, indicating a growth of specific capacitance of PANI/CFs with increase of the ANI concentration.

Figure S1b shows the specific capacitance of PANI/CFs with different ANI concentration at different scan rate 5, 10, 20, 50, and 100 mV/s. The specific capacitances were calculated according to Equation 1(See the main text). The specific capacitances of PANI/CFs with 5 mM ANI remained steady from 245, 238, and 229 to 213 F g-1 and had a reduction to 185 F g⁻¹ with the increase of scan rate. The specific capacitances of PANI/CFs with 10 mM ANI are in the same trend, decreasing from 273, 263, 250, and 216 to 134 F g⁻¹. The leveling out of specific capacitance with the increase of scan rate indicates that the electrochemical stability of PANI/CFs with 5 and 10 mM. The specific capacitance of PANI/CFs with 25 mM declined from 581, 554, and 507 F g-1 to 301 and slump down to139 F g⁻¹. The specific capacitance of PANI/CFs with 50 mM ANI is very close to that with 25 mM, in agreement with the trend revealed by the two-electrode system. Interestingly, the specific capacitance of PANI/CFs with 50 mM ANI dramatically goes down to 72 F g⁻¹ at 100 mV/s. According to the SEM and TEM images of PANI/CFs, we know that it is due to the self-aggregation of ANI. This result further confirms the conclusion that the ordered whisker-like nanostructure and the synergistic effect of the two composites are responsible for the electrochemical stability.

Figure S1c and S1d show the charge-discharge curves in the potential window -0.2 to 0.8 V

of PANI/CFs with different initial ANI concentration at the current density of 0.2 and 1 A g^{-1} . The curves are nearly linear and symmetric, indicating an ideal capacitor behavior, in agreement with the results of two-electrode system (in the main text).



Figure S1 The electrochemical capacitance performance of PANI/CFs nanocomposites with different concentration of aniline: 5, 10, 25, and 50 mM. a) Cycle voltammetry within the potential window -0.2 to 0.8 V at the scan rates of 10 mV/s; b) Specific capacitance of PANI/CFs prepared with different initial aniline concentration: 5, 10, 25, and 50 mM at different current densities; c) Galvanostatic charge-discharge tests within the potential window -0.2 to 0.8 V at the current density of 0.2 A g⁻¹; d) Galvanostatic charge-discharge tests within the potential window -0.2 to 0.8 V at the current density of 0.8 V at the current density of 1 A g⁻¹. The electrolyte is 1 M H₂SO₄.



Figure S2. SEM images of the PANI/CFs nanocomposites with different concentration of aniline: (a) 5 mM; (b) 10 mM; (c) 25 mM; and (d) 50mM. Other conditions: aniline/APS=1/1 (molar ratio), CF =0.3 mg ml⁻¹, and the reaction was carried out 0 $^{\circ}$ C for 7 h.



Figure S3. The Cyclic voltammetry curves of PANI/CFs with different aniline concentration at different scan rate: 5, 10, 20, 50, and 100 mV/s: (a) 5 mM; (b) 10 mM; (c) 25 mM; and (d) 50 mM.

Table S1 The amount of PANI/CFs coated on stain steel and percentage of CFs and PANI in the resulting PANI/CFs composites

Samples	Weight percentage of CFs in the composite (%)	Weight percentage of PANI in the composite (%)	Amount of PANI/CFs coated on stainless (g)
5 mM	58.94	41.06	0.00602
10 mM	41.96	58.04	0.00423
25 mM	16.20	83.80	0.00560
50 mM	9.11	90.89	0.00602