Supplementary Information

Tuning PANI Nanostructure by Driving Force for Diverse Capacitance Performance

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Contents:

(a) Experiment Section

Materials. Aniline (99.5%) was purchased from Tianjin Jinke Fine Chemical Institute, and was distilled under reduced pressure before use. Dodecylbenzenesulfonic acid (DBSA, 99.5%) was obtained from Chongqing Golute Chemical Co.,Ltd. Ammonium peroxydisulfate (APS, 98%) was purchased from Xilong Chemical Co.,Ltd.

Synthesis of the PANI nanostructures. PANI nanostructures were synthesized by emulsion polymerization using DBSA and APS as dopant and oxidant, respectively.[1-2] 0.03 mol of DBSA was dispersed into 75 mL of deionized water and mixed for 1 h. Then aniline (AN) dissolved in methylbenzene and n-butanol was added to the DBSA solution in sequence with mixing for 1 h. The polymerization was then initiated by adding APS dissolved in 30 mL deionized water with the mixing way used of mechanical stirring (1000 rpm with stirring rod), magnetic stirring (500 rpm with magneton) and sonication (200 W). The whole reaction is kept in 15 ℃ and the polymerization time is 30 min for using mechanical stirring, 2 h for magnetic stirring and 4 h for sonication until the reaction system is dark green. The molar ratio of DBSA, APS and AN was 1:1:1, while the molar ratio of methylbenzene, n-butanol, deionized water was 1:1:70. The as-product was washed with deionized water and ethanol for several times by centrifuge, and then was dried at 40 ℃. The as-prepared PANI was compressed into pellets for conductivity measurement by four-probe method.

Capacitance Properties Measurement. Electrochemical measurements were carried out using two-electrode sandwich-type construction cells with a glassy fibrous separator between the two symmetrical working electrodes. A gold grid was used as current collector. The mixture containing 85 wt% active material, 10 wt % conducting carbon black, and 5 wt % polytetrafluoroethylene (used as a binder, PTFE 60% dispersion in H_2O) was well mixed and then pressed onto the gold grid. The electrochemical performances of the prepared electrodes were characterized by cyclic voltammeter (CV), galvanstatic charge/discharge, electrochemical impedance spectroscopy (EIS) and cycling life measurement. The used electrolyte was 1 mol/L aqueous H_2SO_4 solution.

Characterization. The morphology of the product was examined using scanning electron microscope (SEM) (Hitachi, S-4300, Japan). The molecular structures were characterized by

Fourier Transform Infrared Spectroscopy (FTIR) (Varian Excalibur 3100), Ultraviolet-visible spectrophotometry (UV-vis) (Varian Cary 5000) and X-ray diffraction (XRD) (Bruker D8 FOCUS, Germany). The conductivity of PANI was measured by a four-probe method with a digital multimeter (Keithley 2750). The doped degrees were calculated based on the results of X-ray Photoelectron Spectroscopy (XPS) (British Kratos Company). All the capacitence experiments were performed by VMP3 Potentiostat/Galvanostat (EG&G, Princeton Applied Research).

(b) Capacitance characterization of the PANI nanostructures

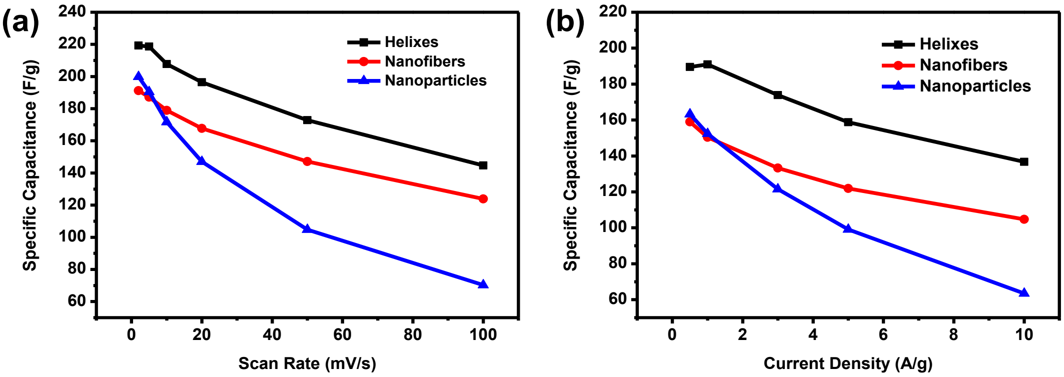

Figure S1 Capacitance characteristics of PANI helixes, nanofibers and nanoparticles electrodes for supercapacitors in 1 M H_2SO_4 aqueous solution. (a) The specific capacitance plots with various scan rates. (b) The specific capacitance plots with various current densities.

According to the CV curves (Fig 2a), the specific capacitance plots with various scan rates could be calculated (Fig. S1a). With the scan rate increased, the specific capacitance decreased correspondingly. There is the same trend for the specific capacitance with different current densities (Fig. S1b). From the two plots above, it could be concluded that the rate capabilities of PANI helixes and nanofibers are better than nanoparticles, which is manifested by a big decrease with the increase of scan rate and current density. Furthermore, PANI helixes showed better capacitance performance for its higher specific capacitance.

(c) Doped degree characterization of the PANI nanostructures

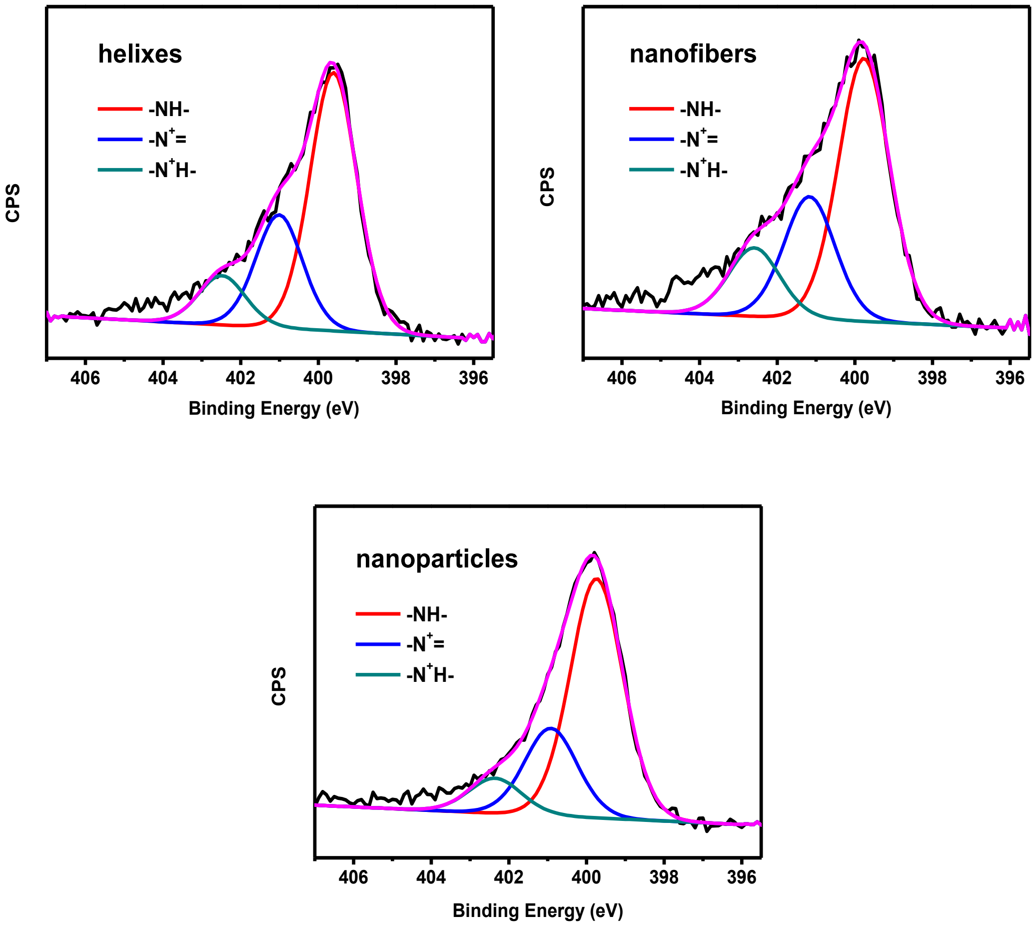

Figure S2 XPS spectra of PANI with different morphologies

Figures S2 represents the deconvoluted N 1s XPS spectra of all the PANI salts examined in the present study. The N 1s spectrum of PANI-base could be resolved into three peaks centered at 399.6, 401.1, and 402.6 eV, which were attributed to –NH–, $–N^+=$ and $–N^+H–$, respectively. [3-6]

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