SUPPORTING INFORMATION

Nitrogen-doped Activated Carbon for High Energy Hybrid-type Supercapacitor

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Experimental Section

Synthesis of Nitrogen-doped Activated Carbon (NAC)

Nitrogen-doped nanoporous carbon monoliths were prepared by a modified NH3 activation using corncob as a carbon source and NH_3 as a nitrogen source. Corncobs were grounded and sieved into powders with typical size of more than 880 μm, after drying for 12 h at 120 °C. The powders were mixed with KOH in a 3:1 mass ratio. The mixture was then transferred to ceramic boats and heated to desired temperature under N_2 flow of 1.5 L/min in a horizontal quartz tube furnace. The N_2 was then switched to NH_3 gas with a flowrate of 1.5 L/min. The powder mixture was heated with a desired time. Then NH_3 was switched back to N_2 while activation was completed and temperature was reduced to room temperature. The as-prepared products were denoted as NAC-x (NH_3 Activated Carbon),

which x is activation temperature

Preparation of Carbon-coated Si nanoparticles (Si/C)

Nanosized Si powder were purchase from MTI. Carbon coating was proceed by thermal decomposition of acetylene at 700 °C based on previous reports.

Chemical analysis and textural characterization

The scanning electron microscopy (SEM, FEI SIRION 200/INCA, OXFORD) and transmission electron microscopy (TEM, JEM-2100F, JEOL) were employed for the morphologies and texture of the samples. Elemental analysis (Elementar, vario ELIII) and X-ray photoelectron spectroscopy (XPS, UlVAC-PHI PHI 5000 VersaProbe) were used to study the element contents and surface functional groups. The Raman spectra were collected with 532 nm excitation and 20X objective on a Thermo Nicolet Almega system. The laser power was < 2 mW.

Nitrogen sorption isotherms and textural properties of all samples were determined at -196 °C using nitrogen in a conventional volumetric technique by a Micromeritics ASAP 2020 sorptometer over a wide relative pressure range from about 10-6 to 0.995. The surface area was calculated using the Brunauer–Emmett–Teller (BET) equation based on adsorption data in the partial pressure (P/P_0) ranging from 0.02 to 0.25 and the total pore volume was determined from the amount of nitrogen adsorbed at a relative pressure of 0.98. Pore size distributions were calculated by using the Density Functional Theory (DFT) Plus Software (provided by Micromeritics Instrument Corporation), which is based on calculated adsorption isotherms for pores of different sizes. All of the samples were degassed at 300 °C for 600min prior to the measurements.

Electrochemical testing

All electrochemical measurements were carried out in a three-electrode system. For half-cell testing, NACs and Si/C electrodes were used as working electrodes and Li metal as the counter and reference electrode. The NAC electrodes were prepared by mixing 80 wt. % active material, 10 wt. % Super-P carbon black and 10 wt. % Na-Alginate binder in de-ionized water to form homogeneous slurry, and then coated onto the aluminum foil. The Si/C electrode was prepared by mixing 70 wt. % active material, 15 wt. % Super-P carbon

black and 15 wt. % Na-Alginate binder on coated copper foil. The mass loadings of the active materials in both cathode and anode are 4 mg and 2 mg, respectively. 1.2 M $LiPF_6$ dissolved in a mixture of ethylene carbonate, diethyl carbonate and dimethyl carbonate (EC:DEC:DMC=1:1:1 by vol.) and 10 wt% fluoroethylene carbonate (FEC) electrolyte was employed as the electrolyte. The hybrid supercapacitors were also assembly in coin cells with pre-cycled Si/C anode (charge-discharge for 3 cycles) and NAC cathode in the same electrolyte, and the optimized mass ratio of cathode and anode was 2:1. All the electrochemical tests were carried out at room temperature. The voltage range of Si/C electrode was 0.01 V - 1.5 V. The NAC electrodes and the hybrid supercapacitor were measured at the same voltage range of 2.0 V - 4.5 V. The energy density and power density were calculated based on the total mass of active materials on both the anode and cathode. Cyclic voltammetry (CV, scan rate ranging from 5 to 20 mV s^{-1}) and electrochemical impedance spectroscopy (EIS, frequency ranging from 0.1 Hz to 100,000 Hz with potential amplitude of 10 mV) were performed on a by-logic electrochemical workstation.

Energy and power density calculation

As we use galvanotatic charge/discharge process for the half-cell measurement, the capacity (mAh) was obtained directly from the instrument reading. The specific capacity was calculated by the mass loading of the electrode.

The specific capacitance (F g^{-1}) was calculated by the equation listed below:

$$C_m = \frac{Q_m}{V}$$

$$Q_m = \text{Specific Capacity (Ah)} * 3600 \text{ s/h}$$

Where Q_m is calculated from the specific capacity of the NAC material. V is the full voltage range, which is 2.5 V (2.0 – 4.5 V) or 2.0 V (2.0 – 4.0 V).

The energy density (E_m, Wh g^{-1}) and power density (P_m, W g^{-1}) were calculated from the galvanostatic charge/discharge process curve by the equation:

$$E = \int_{t2}^{t1} IV dt$$

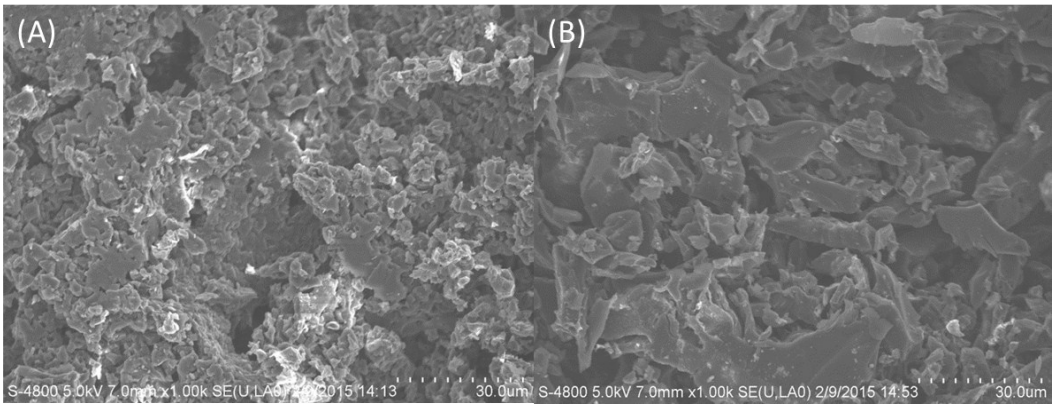
$$Em = \frac{E}{m_c + m_a}$$

where E (Wh) is total energy, I is the constant current density (A g^{-1}), V is the voltage, m_c and m_a are the mass of cathode and anode material, and t1, t2 is the start time and end time in the discharge process, respectively.

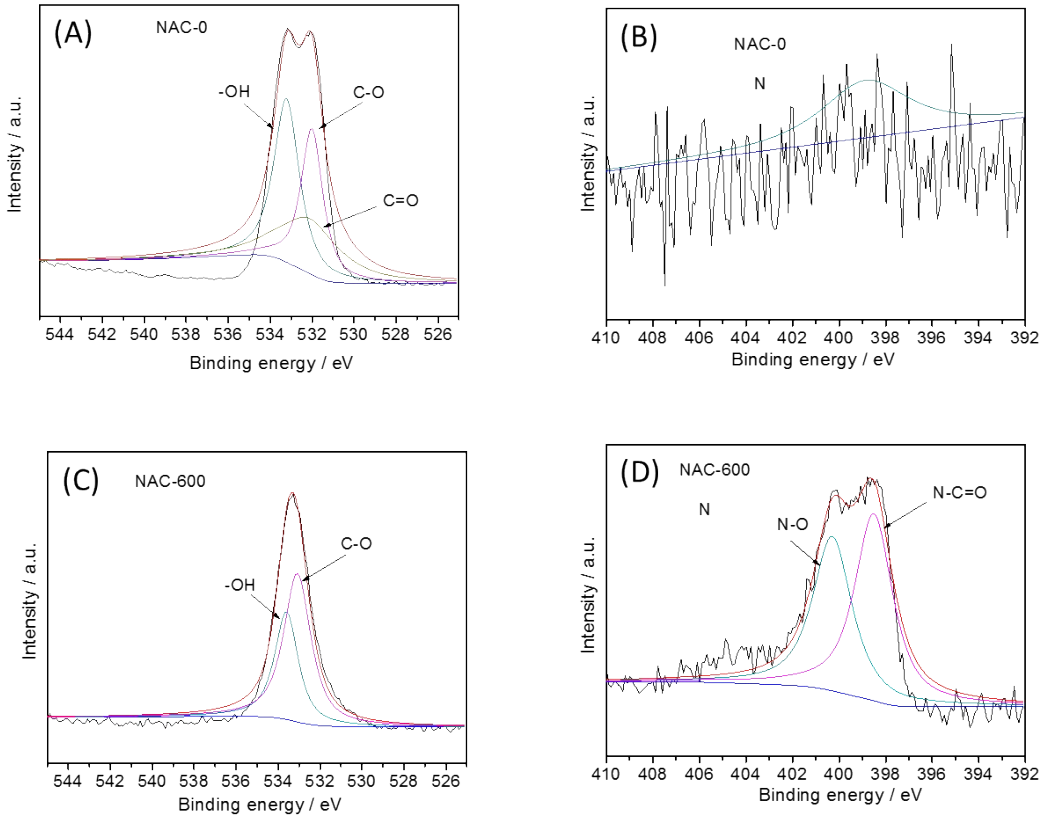
$$P = \frac{E}{\Delta t}$$

$$Pm = \frac{P}{m_c + m_a}$$

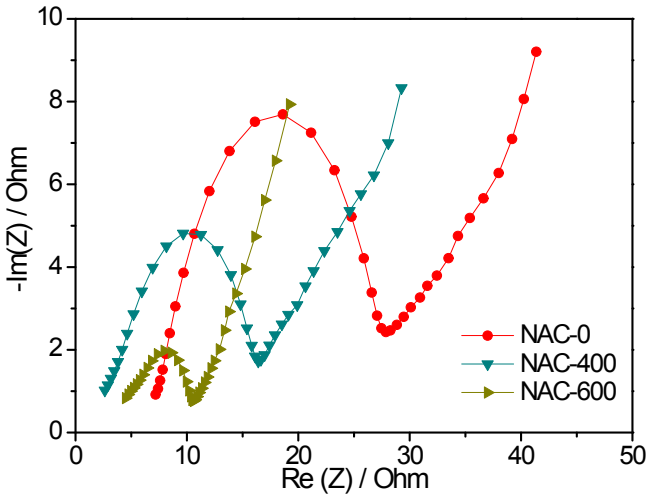
where P is total power (W), and Δt is discharge time (s).



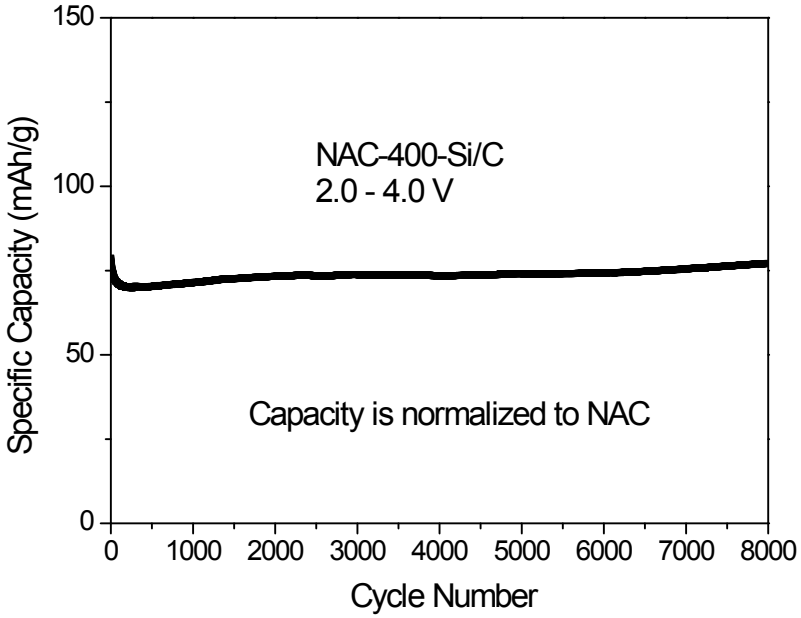
Supplementary Figure S1



Supplementary Figure S2



Supplementary Figure S3



Supplementary Figure S4

Table S1 Calculated power and energy density at different current density for HS

Current density (A g^{-1})		**0.4**	**0.8**	**1.6**	**3.2**	**6.4**	**12.8**
Power density (W kg^{-1})	2-4.5V	867	17467	3507	7100	14507	31027
	2-4.0V	802	1611	3244	6580	14026	29369
Energy density (Wh kg^{-1})	2-4.5V	237	230	219	202	176	141
	2-4.0V	169	164	158	146	105	67

Table S2. Energy and power density comparison with literature reported hybrid devices

Positive electrode	**Negative electrode**	**Voltage window**	**Energy density (Whkg-1)**	**Power density (Wkg-1)**	**Ref.**
PSNC-3-800	PSOC-A	1.5 - 3.5	30 - 38	~ 7000	34
		1.5 - 4.2	50-75	~8000	
CNS	MnO/CNS	0 – 4.0	83	18000	9
3D graphene	Fe3O4 graphene	1.0 – 4.0	86	2587	7
AC	LTO	1.0 – 3.0	69	~ 500	33
AC	soft carbon	0 – 4.0	48	9000	32
AC	hard carbon	1.5 - 3.9	60	~ 2200	31
AC	B-Si/SiO2/C	2.0 – 4.5	89	9704	8
NAC	Si/C	2.0 – 4.5	141	30127	this work
			230	1747	