Electronic Supplementary Information

Surface modification of rice husk-derived hard carbon by grafting porous carbon nanosheets for high-performance supercapacitors

Shian Dong,[a] Xiaojun He,[a] Hanfang Zhang,[a] Xiaoyu Xie,[a] Moxin Yu,[a] Chang Yu,[b] Nan Xiao[b] and Jieshan Qiu*[b]*

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1. Experimental Section

Synthesis of PCNS/RHCs: Rice husks were obtained from the suburb of Maanshan City in China. The coal tar pitch (CTP) with a softening point of 110 ^oC was provided by Maanshan Iron & Steel Co. Ltd. of China. Other chemicals were purchased from Aladdin, and used as received. For a typical run, rice husks were put into a box furnace and heated to 500 ^oC for 1 h in Ar atmosphere. The product was washed by 0.5 M NaOH solution and distilled water to remove silicon dioxide. The rice husk-derived carbon (RHC) was obtained after the above mentioned product was dried at 110 ^oC. Subsequently, the mixtures of RHC (1.0 g), CTP (1.0 g), nano-MgO (8.0 g) and KOH (X g) were ground and transferred to a corundum boat, which was put into a tube furnace and heated to 300 ^oC at 5 ^oC min^{-1} for 1 h, then heated to 950 ^oC for 1 h. The products were washed with 2 M HCl solution and distilled water to remove the inorganic impurities, and dried at 110 ^oC for 24 h before use. The obtained materials are named as $PCNS/RHC_X$, where X refers to the mass of KOH. For comparison, the mixtures with RHC (2.0 g), nano-MgO (8.0 g) and KOH (8.0 g) without the presence of CTP were also heated to 950 ^oC for 1 h in Ar atmosphere, and the product was washed by 2 M HCl solution and distilled water to remove the inorganic impurities and dried at 110 ^oC for 24 h. The obtained material is denoted as RHC_{950}. Additionally, the mixtures with CTP (2.0 g), nano-MgO (8.0 g) and KOH (8.0 g) without the presence of RHC were also heated to 950 ^oC for 1 h in Ar atmosphere, and the product was washed by 2 M HCl solution and distilled water to remove the inorganic impurities and dried at 110 °C for 24 h. The obtained material is denoted as $PCNS_{950}$.

Characterization: The Zeta potentials of MgO, CTP and RHC were tested in the deionized water by Nano-ZS90, Malvern. The microstructures of PCNS/RHCs were analyzed by field emission scanning electron microscopy (FESEM, Hitachi, S4800), transmission electron microscopy (TEM, JEOL-2100). The crystallographic structures of PCNS/RHCs were examined by X-ray diffraction (XRD, Philips X, CuKa Radiation, λ=0.15406 nm). Raman spectroscopy analysis was performed with JYLab-RamHR800, excited by a 532 nm laser, and X-ray photoelectron spectroscopy (XPS) was obtained by Thermo ESCALAB250, USA. Fourier transform infrared (FT-IR) spectra were recorded with Thermo-Scientific Nicolet 6700 spectrophotometer. The conductivity of $PCNS/RHC_8$ was measured by a four-wire method using a source measure unit (Keithley 6430). The pore structure of the sample was studied by nitrogen adsorption-desorption technique at –196 °C in an adsorption apparatus (Micrometrics, ASAP2010). The S_{BET} was calculated at a relative pressure from 0.05 to 0.20.

Electrochemical measurements: Active material (PCNS/RHCs) and polytetrafluoroethylene with the mass ratio of 90:10 were mixed together by adding some deionized water and a few drops of ethanol, followed by evaporation of solvent. Then the mixture was rolled into carbon sheet, which was dried at 110 °C under vacuum in drying oven for 2 h and punched into round films with diameter of 12 mm and mass loading of *ca.* 2 mg cm^{-2}. The as-prepared round films were used as electrodes after being pressed on nickel foam for the electrochemical measurement in 6 M KOH electrolyte.

The electrochemical measurements were carried out in two-electrode system on an electrochemical workstation (CHI760C, Shanghai, China). The charge-discharge performance of supercapacitors was measured on a supercapacitance test system (SCTs, Arbin Instruments, USA). The electrochemical impedance spectroscopy (EIS) measurement was performed with an amplitude of 5 mV over a frequency range from 100 kHz to 0.001 Hz using a Solartron impedance analyzer (Solartron Analytical, SI 1260, UK) with a Solartron potentiostat (SI 1287).

The gravimetric specific capacitance of the electrodes, C (F g^{-1}), is calculated according to galvanostatic charge-discharge (GCD) curve based on Eq. (1).

$$C = \frac{4I}{m\frac{\Delta V}{\Delta t}} \qquad (1)$$

where I is the discharge current (A), $\Delta V/\Delta t$ is the average slope of the discharge curve after the voltage drop (V s^{-1}), and m is the total mass of active materials in two electrodes (g).

The energy density (E, Wh kg^{-1}) and power density (P, W kg^{-1}) based on the total mass of active materials in supercapacitors, are calculated according to Eqs. (2) and (3).

$$E = \frac{1}{2 \times 4 \times 3.6} CV^2 \qquad (2)$$

$$P = \frac{E}{\Delta t} \qquad (3)$$

where *V* is the usable voltage after voltage drop (V) and *Δt* is the discharge time (s).

2. Supplementary Figures and Tables

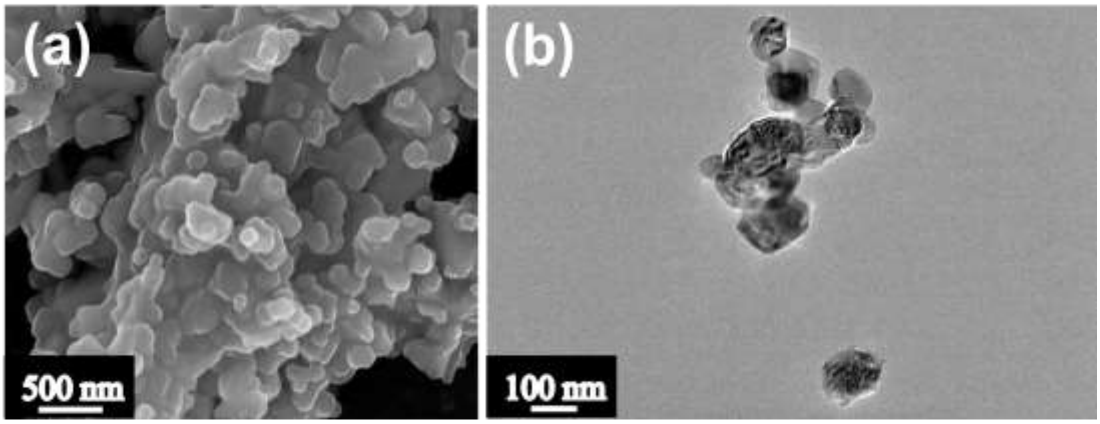

Fig. S1 FESEM and TEM images of MgO particles.

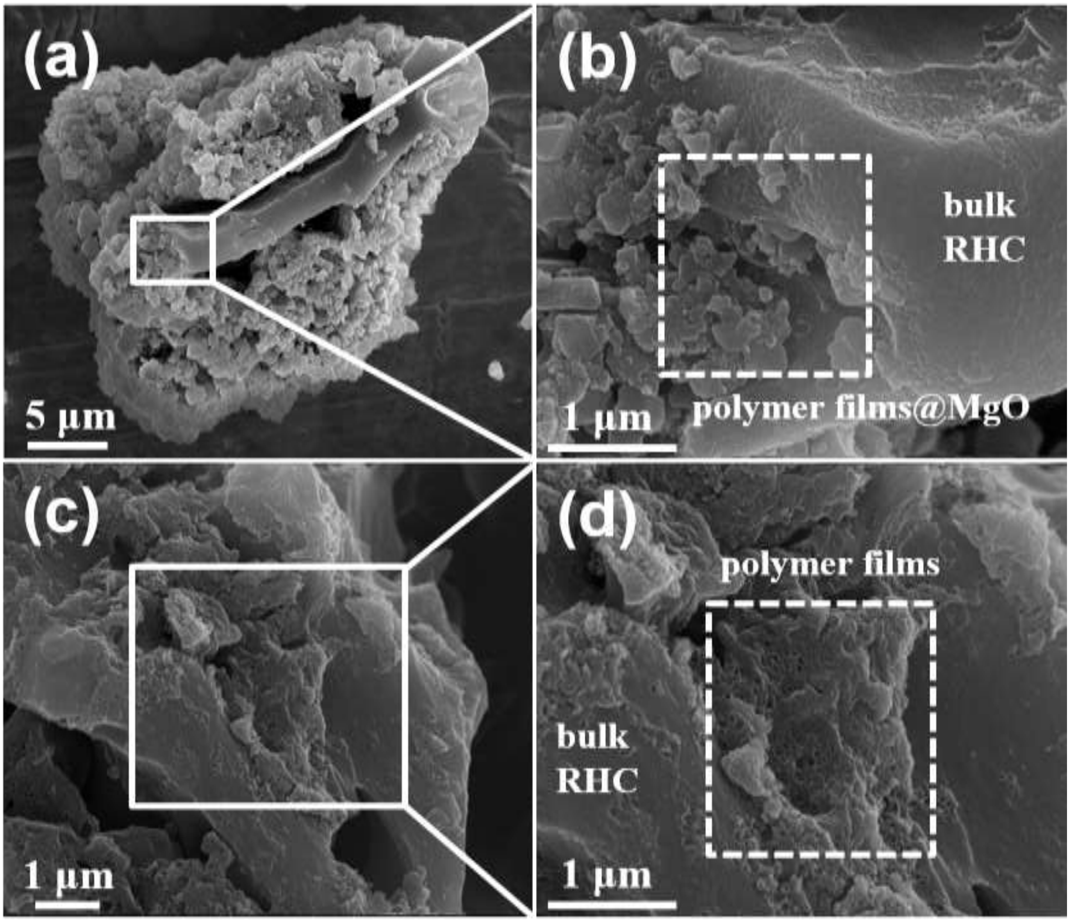

Fig. S2 FESEM images of intermediate product of PCNS/RHC_8 at 500 °C: (a, b) Unwashed samples; (c, d) Samples washed by acid and distilled water.

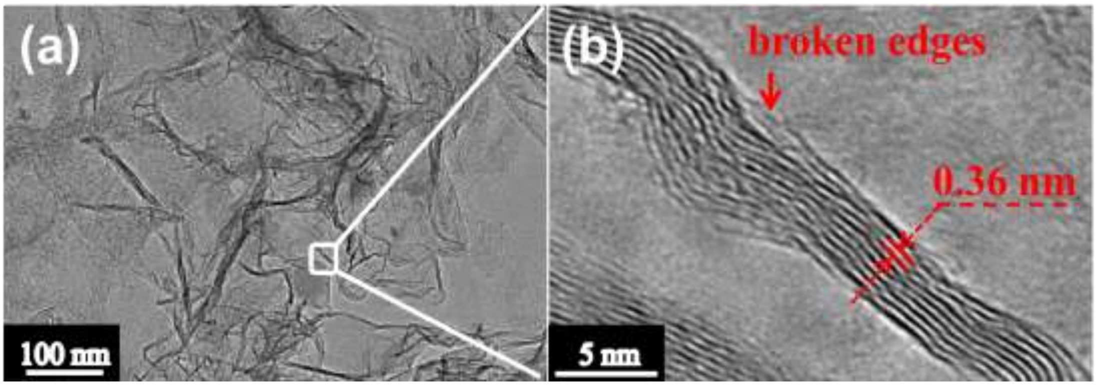

Fig. S3 TEM images of PCNS/RHC_8.

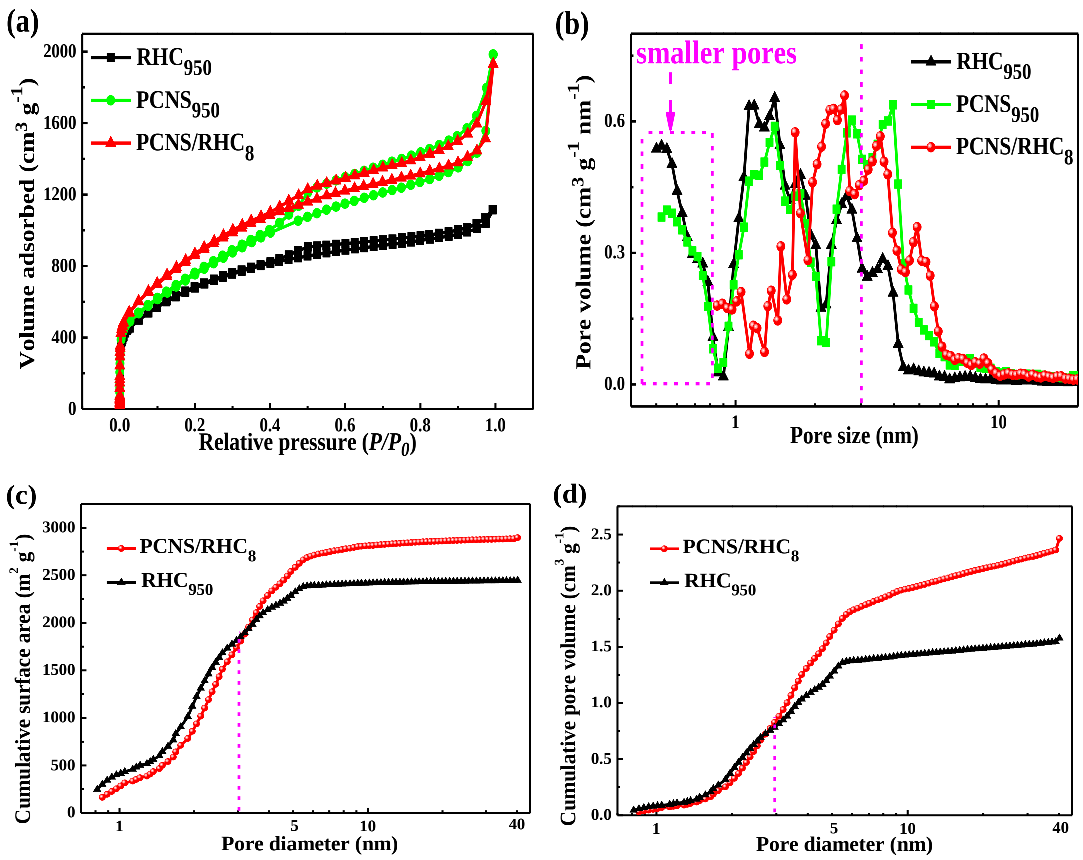

Fig. S4 (a) N_2 adsorption-desorption isotherms of $PCNS_{950}$, RHC_{950} and $PCNS/RHC_8$; (b) Pore size distribution of $PCNS_{950}$, RHC_{950} and $PCNS/RHC_8$; (c) Cumulative surface area of $PCNS/RHC_8$ and RHC_{950}; (d) Cumulative pore volume of $PCNS/RHC_8$ and RHC_{950}.

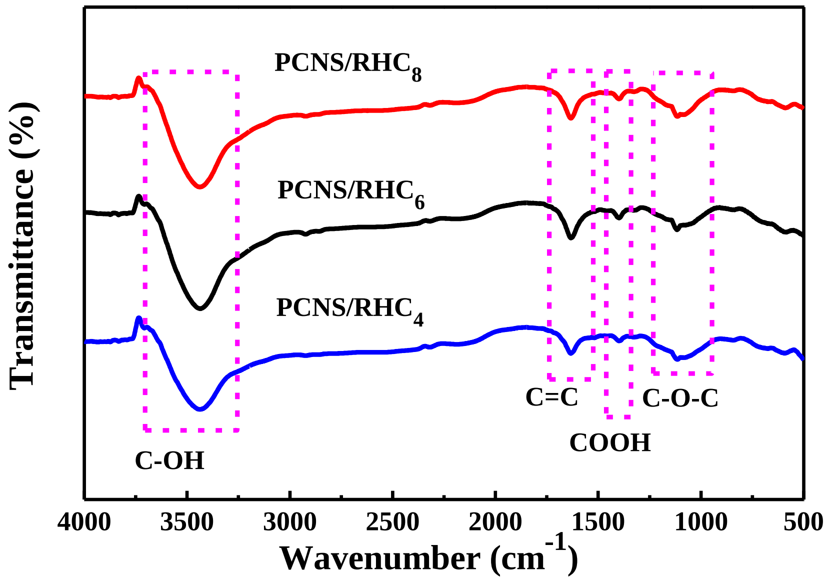

Fig. S5 FT-IR spectra of PCNS/RHC composites.

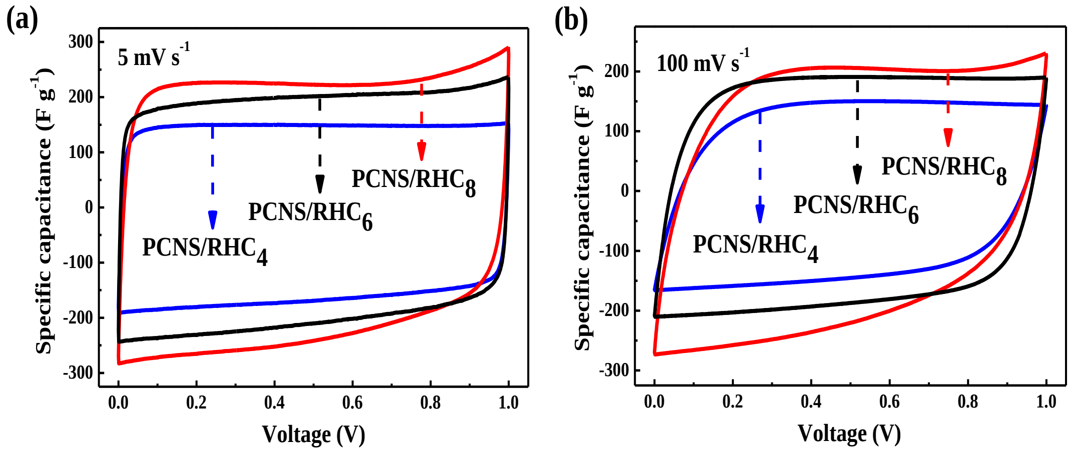

Fig. S6 (a) CV curves of PCNS/RHCs at 5 mV s^{-1}; (b) CV curves of PCNS/RHCs at 100 mV s^{-1}.

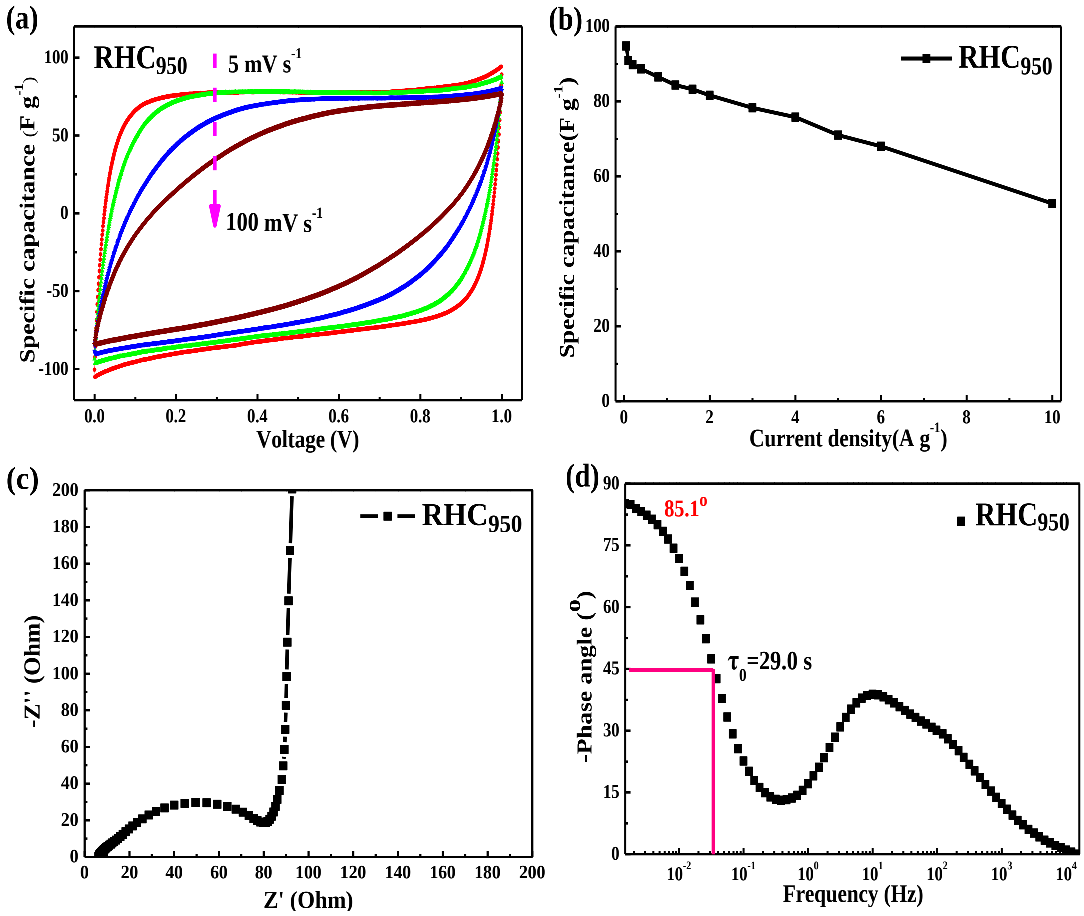

Fig. S7 (a) CV curves of RHC_{950} at different scan rates; (b) Specific capacitances of RHC_{950} at different current densities; (c) Nyquist plot of RHC_{950}; (d) Bode plot of RHC_{950} electrodes.

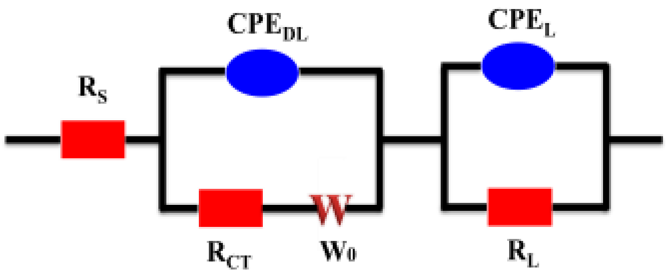

Fig. S8 The equivalent circuit of Randle's model.

R_S: equivalent series resistance. CPE_{DL}: double layer capacitance. CPE_L: pseudocapacitance. R_{CT}: charge transfer resistance. W_0: Warburg element. R_L: leakage resistance.

Table S1 The Zeta potential of raw materials.

Samples	Zeta potential (mV)
RHC	–21.2
CTP	–28.8
MgO	21.5

Table S2 The contents of C, O, N elements and oxygen-containing functional groups in PCNS/RHCs.

Samples	C1s (%)	O1s (%)	N1s (%)	O1s		
				C=O (%)	C–O (%)	O–H (%)
PCNS/RHC_4	95.06	3.32	1.62	1.36	0.86	1.10
PCNS/RHC_6	91.93	6.70	1.37	2.21	2.08	2.41
PCNS/RHC_8	88.28	10.71	1.01	2.37	5.16	3.18

Table S3 Fitted equivalent circuit elements of PCNS/RHC_8 and RHC_{950}.

Samples	R_S (Ohm)	R_{CT} (Ohm)	CPE_{DL}		W ($S\ s^{0.5}$)	CPE_L	
			Q ($S\ s^n$)	n		Q ($S\ s^n$)	n
PCNS/RHC_8	0.43	0.62	0.32	0.96	$1.5*10^{-16}$	0.0006	0.85
RHC_{950}	6.20	87.13	0.0054	1	$3.8*10^{-4}$	0.0016	0.68