Electronic Supplementary Information

Flour food waste derived activated carbon for high-performance supercapacitors

Changzhen Zhan,[a] Xiaoliang Yu,[a] Qinghua Liang,[a] Wei Liu,[a] Yanbo Wang,[c] Ruitao Lv, [b] Zheng-Hong Huang*[a,b] and Feiyu Kang[b]

[a] State Key Laboratory of New Ceramics and Fine Processing, School of Materials Science and Engineering, Tsinghua University, Beijing 100084, China

[b] Key Laboratory of Advanced Materials (MOE), School of Materials Science and Engineering, Tsinghua University, Beijing 100084, China

[c] The High School Affiliated to Renmin University of China, Beijing 100080, China

E-mail: zhhuang@tsinghua.edu.cn (Z.-H Huang).

1. Experimental section

1.1 Materials

Flour food waste residue (waste Chinese steamed buns residue in this work) was used as carbon source, and potassium hydroxide (KOH, Aladdin Ltd., China) was used as activation agents.

A typical recipe of Chinese steamed buns: First, making the dough with mixing flour, warm water and yeast. Second, let the dough rest for 1-2 hours. And last, divide the dough into pieces and steam it for about half an hour.

1.2 Synthesis of flour-based porous carbon

The flour porous carbon samples was synthesized by two steps. Firstly, flour-based carbon (FBC)

was prepared by the carbonization of flour-based leavening food waste residue. Then the obtained FBC was chemical activated using KOH as an activation agent. In a typical process, waste Chinese steamed buns residue was dried in an oven at 120°C for 24 h and was carbonized at 500 °C for 1 h to obtain the FBC sample. Afterwards, the FBC sample was disintegrated in an agate mortar and then carefully mixed with the activating agent KOH. The mixture was grinded adequately and then placed in a tube furnace with a nickel boat. The activation was performed by heating the mixture at 800 °C for 1 h under nitrogen atmosphere. After washing with 1 M HCl solution to remove any inorganic impurities, and washed thoroughly with deioned water until the pH value reached 7, the resultant samples were dried at 120 °C and was designated as CKmn, where m:n is the mass ratio of FBC and KOH (C/K ratio). The FBC800 sample was obtained by further carbonization of FBC at 800 °C for 1h. The samples named with "DN" were prepared using the de-nitrogen flour as initial material for the steamed buns following a same subsequent heat treatment and activation. The de-nitrogen flour was obtained by washing the dough in DI water. Protein, the nitrogen source of flour, was difficult to disperse in water. Consequently, the de-nitrogen flour was obtained by filtrating the washed water.

1.3 Characterization

Scanning electron microscopy (SEM, LEO1530) and transmission electron microscopy (TEM, Tecnai G20, 200 kV) were used to characterize the samples. N_2 sorption isotherms were measured by using a volume adsorption apparatus (autosorb-1) at 77 K. The total pore volumes were estimated from single point adsorption (P/P_0 = 0.995), the specific surface area was calculated by Brunauer-Emmett-Teller (BET) method, the micropore surface area and micropore volume were determined by t-plot method, and the pore size distributions (PSD) were derived from density functional theory

(DFT) method. The phases were examined by X-ray diffraction (XRD, Bruker D8 ADVANCED) operating at an acceleration voltage of 40 kV. PHI Quantera Imaging X-ray photoelectron spectroscopy (XPS) was used to investigate the surface chemistry. The structure was studied using Raman scattering spectra (Renishaw, InVia-Reflex) using a 532 nm laser.

1.4 Electrochemical measurements

The working electrode was fabricated by painting slurry containing porous carbon, carbon black and polytetrafluorethylene with weight ratio of 75:15:10 on a nickel foam with a 1 cm×1 cm square area. Then the electrode was pressed under a pressure of 2 MPa after dried at 120 °C for 12 h. A three-electrode system were carried out in 6.0 M KOH aqueous solution with electrode active material mass of 2 mg. The Hg/HgO and Pt wire was used a reference electrode and counter electrode, respectively. The electrochemical performance was determined by cyclic voltammetry (CV), electrochemical impendence spectroscopy (EIS), and galvanostatic charge/discharge cycling (GC) tests with a potential window ranging from -1 to 0 V (vs. Hg/ HgO). CV and EIS tests were conducted in VSP-300 electrochemical interface. CV curves were obtained at various scan rates from 5.0-100 mV s^{-1} and EIS tests were performed by sweeping with an AC-amplitude of 10 mV at the frequency from 50 mHz to 40 kHz. The galvanostatic charge-discharge capacitance measurements was conducted on an Arbin-BT2000 test station with different current densities from 0.1 to 100 A g^{-1}. Gravimetric capacitance (C_g) of the device was calculated by the following equation:

$$C_g = I*\Delta t/(\Delta V*m) \quad (1)$$

where I, Δt, ΔV and m are the constant current (A), discharge time(s), total potential deviation (V),

and mass (g) of the active materials. Volumetric capacitance (C_v) was calculated by the following equation:

$$C_v = \rho\, C_g \quad (2)$$

$$\rho = 1/(V_{total}+1/\rho_{carbon}) \quad (3)$$

where ρ and V_{total} are the mass density (g cm^{-3}) and the total pore volume (cm^3 g^{-1}) of the material, and ρ_{carbon} is the true mass density of carbon (2 g cm^{-3}).

Symmetric two electrode aqueous supercapacitor was also fabricated using a 2032 stainless steel coin cell. Each working electrode was fabricated by painting slurry containing porous carbon, carbon black and polytetrafluorethylene with weight ratio of 75:15:10 on a nickel foam with a 1 cm×1 cm square area. Two electrode contains approximately equivalent mass of active materials of about 5 mg. Volumetric energy density (E_v) was calculated by numerically integrating the t-V curve area through the equation:

$$E_v = \int (\rho * V * I * dt)\ /M \quad (4)$$

Where V and I are potential (V) and current (A), M is the total mass of active material in two electrodes (g). Volumetric power density (P_v) was calculated by the following equation:

$$P_v = E_v\ /\Delta t \quad (5)$$

2. Supplementary Figures and Tables

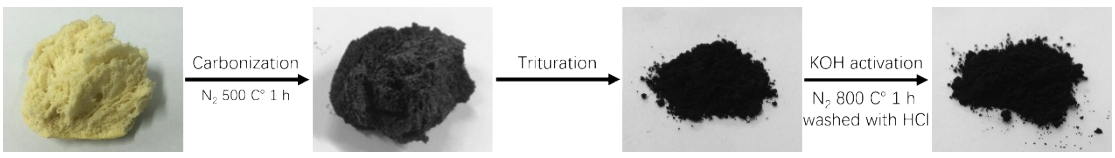

Fig. S1 Schematic diagram representing synthesis of flour-based porous carbon

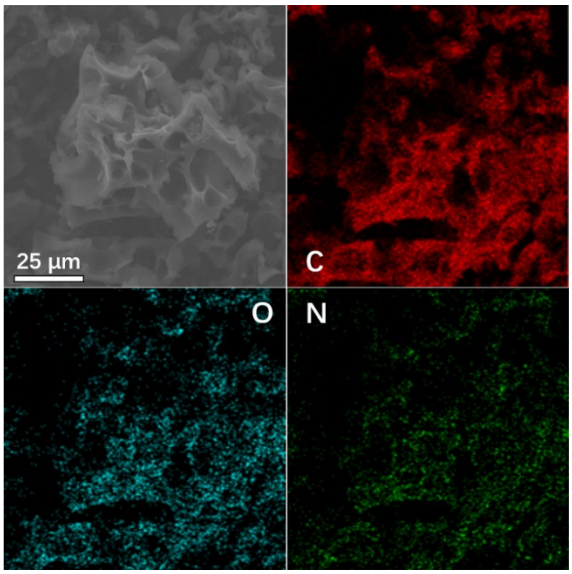

Fig. S2 SEM image and the corresponding elemental mapping images of FBC, showing the homogeneous distribution of elements: of C, O, and N.

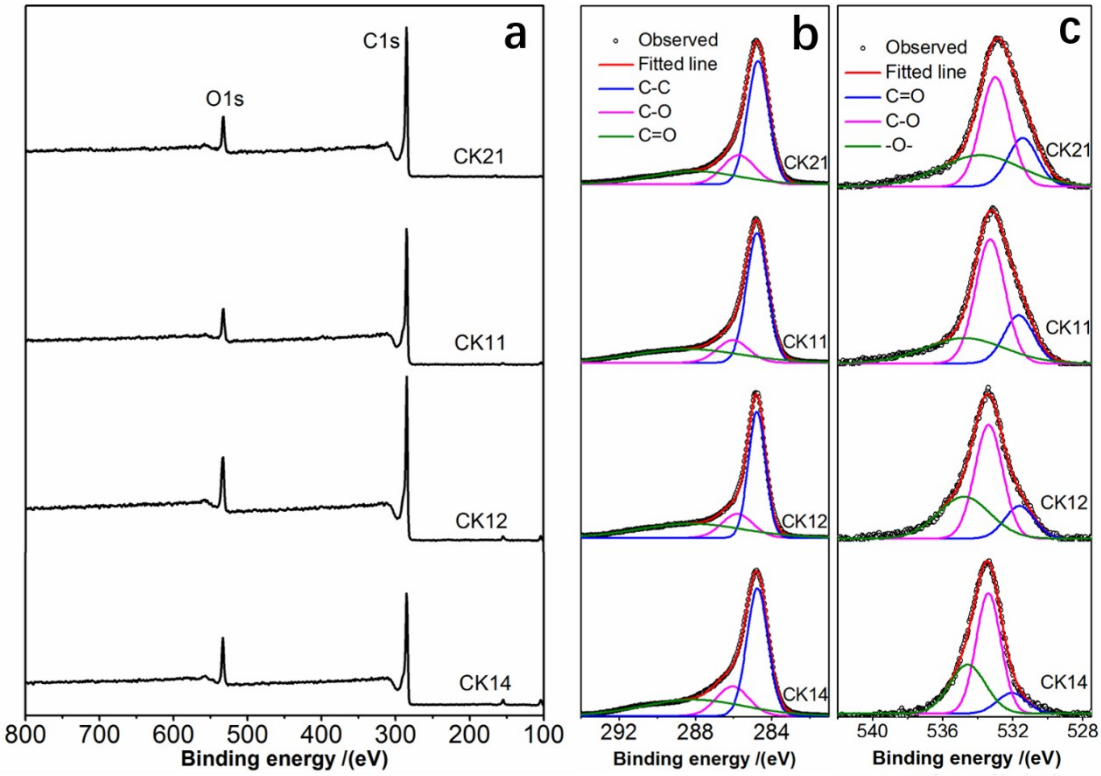

Fig. S3.The survey XPS spectra (a) and the high-resolution C1s (b) and O1s (c) XPS spectra for samples.

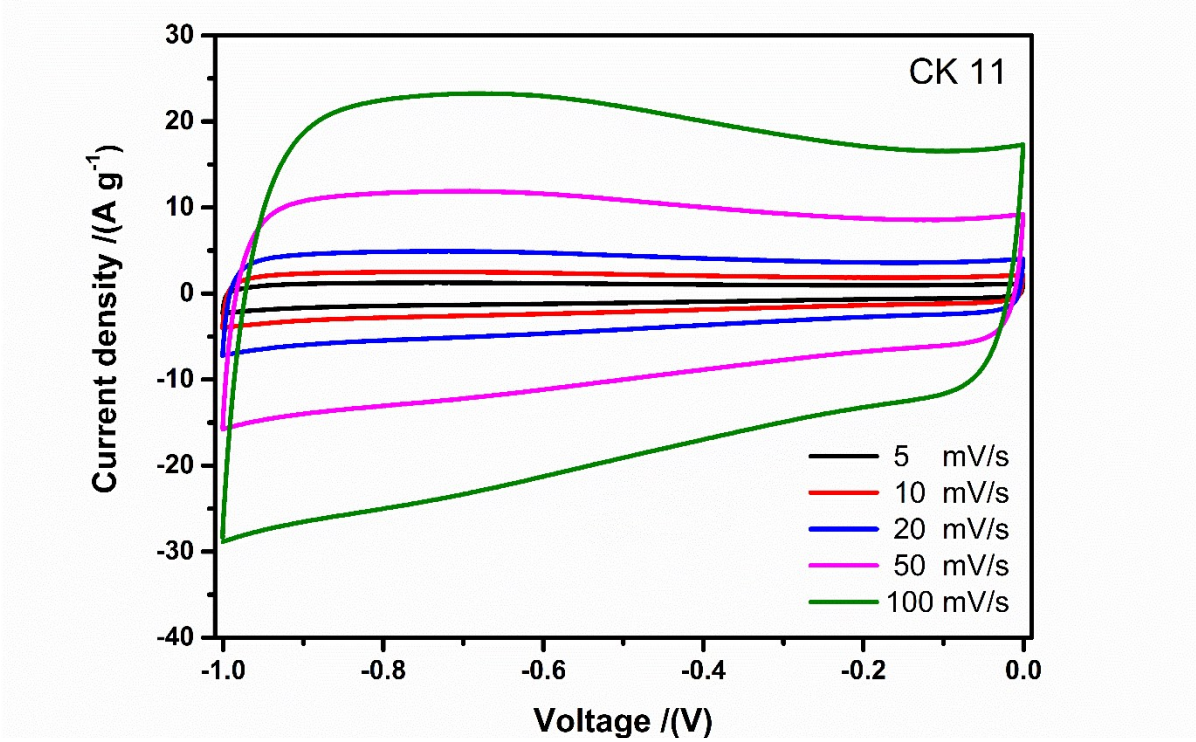

Fig. S4 CV curves of CK11 at different scan rates from 5 to 100 mV/s

Table S1

Physicochemical properties of the samples.

Samples	Elemental analysis		
	C%	O%	N%
Residue	76.16	21.73	1.96
FBC	81.92	13.59	4.5
FBC800	87.97	7.06	4.97
DN-Residue	78.22	21.78	-
DN-FBC	84.16	15.84	-

Table S2 Electrochemical properties of literature reported porous carbons from biomass precursors.

Precursor	S_{BET} (m^2 g^{-1})	Electrolyte	C_g (F g^{-1})	C_v (F cm^{-3})	C_g at high rate	Reference
Starch	1510	6 M KOH	194	-	93% at 7.4A g^{-1}	*Solid State Ionics*, 2008, **179**, 269.
Cherry stones	1273	1 M HS_2O_4	232	87	-	*Mater. Chem. Phys.*, 2009, **114**, 323.
Cassava peel	1352	0.5 M HS_2O_4	264	-	-	*Bioresour. Technol.*, 2010, **101**, 3534.
Sugar cane	1788	1 M HS_2O_4	300	134	67% at 50A g^{-1}	*J. Power Sources*, 2010, **195**, 912.
Fish scale	2237	6 M KOH	168	52	77% at 40A g^{-1}	*J. Mater. Chem.*, 2010, **20**, 4773.
Seed shell	2509	30 wt% KOH	311	169	46% at 10 A g^{-1}	*Bioresour. Technol.*, 2011, **102**, 1118.
Pig bone	2157	6 M KOH	185	67	70% at 100A g^{-1}	*Carbon*, 2011, **49**, 838.
Human hair	2100	6 M KOH	264	235	56% at 6 A g^{-1}	*Electrochim. Acta*, 2013, **107**, 397.
Potato	1052	2 M KOH	255	227	75% at 10A g^{-1}	*Bioresour. Technol.*, 2015, **197**, 137.
Pomelo peel	2725	6 M KOH	342	171	62% at 20 A g^{-1}	*Nanoscale,* 2014, **6**, 13831.
Flour food waste residue	**1516**	**6 M KOH**	**278**	**241**	**68% at 20 A g^{-1}; 51% at 100 A g^{-1}**	**This work**