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# **Supporting Information**

# Ultrafast preparation of saccharide-derived carbon microspheres with excellent dispersibility via ammonium persulfate-assisted hydrothermal carbonization

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# **Experimental Section S1: Preparation of HTCS**

Cx-APS (x represents a sugar) was prepared by APS-assisted hydrothermal carbonization. In a typical process, the mixed solution (the third column in Table S1) was transferred into a 100 mL Teflon-lined autoclave, sealed and placed in an oven. The autoclave was incubated at 70 °C (or 120 °C), and then heated to 180 °C (or 230 °C) and maintained for a certain time (the 4th column in Table S1) at a heating rate of 3 °C min<sup>-1</sup>. To determine the yield of HTCS, after reaching the specified time, the autoclave was rapidly cooled to room temperature in a water bath, and the reaction liquid was filtered. The obtained carbonaceous materials were washed several times with water and ethanol, and then dried in the air at 80 °C for 8 h.

The yield of HTCS  $(q_t)$  was calculated as follows:

$$q_{t} = \frac{W_{t}}{W_{0}} * 100\%$$
(1)

where  $W_0$  is the initial weight of sugar,  $W_t$  is the weight of the HTCS obtained by hydrothermal carbonization, and t is the time of hydrothermal carbonization.

#### S2: Carbonization and potassium oxalate (K<sub>2</sub>C<sub>2</sub>O<sub>4</sub>·H<sub>2</sub>O) activation

In a typical experiment, first 1 g of HTCS and 3 g of  $K_2C_2O_4$ ·H<sub>2</sub>O (Sinopharm Chemical Reagent Co., Ltd. AR  $\geq$  99.8 %) were ground homogeneously using a grinding mill. Secondly, the resulting mixture was placed in a horizontal quartz pipe reactor, and activated at 700 °C for 2 h with a heating rate of 5 °C min<sup>-1</sup> in a N<sub>2</sub> stream of 50 mL min<sup>-1</sup> before cooling to the ambient temperature. The activated sample was rinsed with 1 M HCl solution and deionized water until the pH value of the postwashing water became neutral. Finally, the resulting sample was dried at 110 °C for 12 h.

#### S3: Boehm titration procedure

Boehm titration procedure was summarized as follows [1]:

(1) 0.5 g of HTCS was added into the 0.05 M base solutions (100 mL each) as stated below in different beakers. a. NaHCO<sub>3</sub> (neutralizes the carboxylic groups on the carbon surface); b. Na<sub>2</sub>CO<sub>3</sub> (neutralizes carboxylic and lactone groups on the carbon surface); c. NaOH (neutralizes carboxyl, lactone and phenol groups on the carbon surface).

(2) The slurries with carbons were placed in a shaking incubator at 25 °C for 24 h.

(3) The HTCS sample was filtered. The amount of acidic functional groups on the samples studied was estimated after titrating the obtained filtrate using 0.05 M HCl solution. The end point of each titration was estimated by observing the color change of methyl orange (the indicator) in the filtrate.

# S4: Material characterization

XRD measurements to identify the structure and composition of the samples were performed using a Rigaku D/MAX-RB diffractometer with Cu K $\alpha$  radiation (1.5406 Å) at 10.0°<20<80.0°. FT-IR spectra were characterized by a Nicolet 6700 spectrometer to analyze the surface chemical characteristics of HTCS. The spectra were collected between 4000 cm<sup>-1</sup> and 400 cm<sup>-1</sup>. Morphology analysis was performed on a JSM-IT300 scanning electron microscope (JEOL, Japan). Electrospray ionization mass spectrometry (ESI-MS) was measured with a Thermos TSQ quantum ultra. Elemental analysis was conducted using a PerkinElmer model PE2400 CHNS/O elemental analyzer. Nitrogen adsorption isotherms were performed at –196 °C using BELSORP-max surface area and porosity manufactured by MicrotracBEL (Japan). The samples were degassed for 7 h at 200 °C in a vacuum environment before measurement. The specific surface area ( $S_{BET}$ ) was obtained by the multipoint Brunauer–Emmett–Teller (BET) method in the P/P<sub>0</sub> range between 0.01 and 0.1. The pore size distribution (PSD) of the samples was determined by using a nonlocal density functional theory (NLDFT) method. The total pore volume ( $V_0$ ) was estimated from the N<sub>2</sub> adsorption amount at a relative pressure of 0.99, and the total micropore volume ( $V_t$ ) was obtained by the t-plot analysis of N<sub>2</sub> adsorption data. The isotherms of CO<sub>2</sub> adsorption were measured at 25 °C, using a Micromeritics ASAP 3020 analyzer (Micromeritics Instrument Corporation, U.S.A.). All samples were degassed for 4 h at 150 °C before testing to remove guest molecules in the pores. Particle size of HTCS was measured by the Microtrac S3500 laser diffraction particle size analyzer in distilled water.

#### **S5: Electrochemical measurements**

Prior to the electrochemical tests, the nickel foam was ultrasonically cleaned in acetone, ethanol, and deionized water, successively. Electrochemical measurements were performed on a CHI 760D electrochemical workstation with a three-electrode configuration. The working electrodes were prepared by mixing 80 wt% of ACsuc-APS, 10 wt% of polytetrafluoroethylene, and 10 wt% of carbon black. The mass loading of the active material was approximately 3–4 mg cm<sup>-2</sup>. A 6.0 M KOH solution was used as the electrolyte. Platinum wire and a saturated calomel electrode were used as the counter and reference electrodes, respectively.

All the electrochemical measurements were conducted using a two electrodes system under  $H_2SO_4$ -PVA electrolyte. Both the CV tests and GCD tests were delivered at the potential window from 0 to 1 V, and the EIS tests were achieved at the frequency from 0.01 to 500000 Hz. The specific areal capacitance was calculated from the GCD curves, according to the following equation:

$$C = \frac{I\Delta a}{\Lambda V}$$

where I(A) is the total current,  $\Delta t$  (s) refers to the discharge time, A (cm<sup>-2</sup>) represents the foot print

area of the interdigital patterns,  $\Delta V$  (V) is the potential window.



**Fig. S1** SEM image of HTCS: (a-c) Cglu obtained at 180 °C for 2 h, 4 h and 6 h, respectively; (d-f) Cglu-APS obtained at 180 °C for 5 min, 30 min and 2 h, respectively; (g-h) Csta obtained at 190 °C for 2 h and 4 h, respectively; (i-j) Csta-APS obtained at 180 °C for 30 min and 1 h, respectively. A comparison of these images shows that the growth of HTCS obtained by APS-assisted hydrothermal carbonization is fast.



**Fig. S2** The XRD patterns (a) and the FT-IR spectra (b) of HTCS prepared using different saccharides with or without addition of APS.



**Fig. S3** Color change of glucose solution in hydrothermal carbonization at 180 °C (a), APS-assisted glucose solution in hydrothermal carbonization at 180 °C (b), starch solution in hydrothermal carbonization at 190 °C (c), and APS-assisted starch solution in hydrothermal carbonization at 190 °C (d).



**Fig. S4** Effects of addition amount of APS on the yield of HTCS (a) and the preparation rate of HTCS (b) obtained from sucrose.



Fig. S5  $N_2$  adsorption-desorption isotherms (a) and the pore size distribution curves (b) of Csuc, Csuc-APS and Csuc-APS (Fe<sup>2+</sup>).



**Fig. S6** ESI-MS spectra of the reaction solution without APS (a) and with APS (b) before carbonization at 180 °C using sucrose as a carbon source. The compounds showing intensive signals are identified in this figure.



**Fig. S7**  $N_2$  adsorption–desorption isotherms and pore size distribution curves of activated carbon microspheres: (a) and (b), and the comparisons of ACsuc, ACsuc-APS and ACsuc-APS (Fe<sup>2+</sup>); (c) and (d), ACglu and ACglu-APS; (e) and (f), ACsta and ACsta-APS; (g) and (h), and ACsss and ACsss-APS. Filled and empty symbols represent adsorption and desorption branches, respectively. The micropore pore size distribution was calculated by NLDFT model, and the mesoporous pore size distribution was obtained by BJH model calculation (insets).



Fig. S8 Effects of recycle times on  $CO_2$  uptake of ACsuc-APS(5 g) and ACsuc at 25 °C.



**Fig. S9** CV curves for ACsuc, ACsuc-APS and ACsuc-APS(Fe<sup>2+</sup>) at the scan rate of 5 mv s<sup>-1</sup> (a), 10 mv s<sup>-1</sup> (b), 20 mv s<sup>-1</sup> (c), 50 mv s<sup>-1</sup> (d), 100 mv s<sup>-1</sup> (e), 200 mv s<sup>-1</sup> (f); specific areal capacitances of ACsuc, ACsuc-APS and ACsuc-APS(Fe<sup>2+</sup>) at different scan rates (g); cycling performance of ACsuc, ACsuc-APS and ACsuc-APS(Fe<sup>2+</sup>) at the scan rate of 0.5 V s<sup>-1</sup> after 10000 cycles (h); GCD curves of ACsuc, ACsuc-APS and ACsuc-APS(Fe<sup>2+</sup>) at the current densities of 0.5 A g<sup>-1</sup> (i), 1 A g<sup>-1</sup> (j), 2 A g<sup>-1</sup> (k), 5 A g<sup>-1</sup> (l), 10 A g<sup>-1</sup> (m), 20 A g<sup>-1</sup> (n); specific capacitances of ACsuc and ACsuc-APS calculated from GCD tests at different current densities (o).



**Fig. S10** SEM comparison of HTC prepared from sunflower seed shell powder (SFSSP) with different additives: hydrothermal carbonization without APS (a, b), with APS (c, d), and  $H_2SO_4$ -assisted hydrothermal carbonization with APS (e, f).



**Fig. S11** SEM images of the monodisperse HTCS obtained by adding traces of sodium polyacrylate to the APS-assisted hydrothermal carbonization system of sucrose.

Number	Hydrochar	Reactant	Hydrothermal conditions	
1	Csuc	6 g sucrose + 40 mL water	70 °C for 2 h and 180 °C for 1-12 h	
2	Csuc-APS	6 g sucrose + 40 mL water + 1 g APS	70 °C for 2 h and 180 °C for 1-12 h	
2	Csuc-APS(Fe <sup>2+</sup> )	6 g sucrose + 40 mL water + 1 g APS	70 % for 2 h and 190 % for 1 12 h	
3		+ 0.5 mL, 0.1M FeSO <sub>4</sub>	70 C 101 2 h and 180 C 101 1-12 h	
4	Cglu	6 g glucose + 40 mL water	70 °C for 2 h and 180 °C for 1-12 h	
5	Cglu-APS	6 g glucose + 40 mL water + 1 g APS	70 °C for 2 h and 180 °C for 1-12 h	
6	Csta	6 g starch + 40 mL water	70 °C for 2 h and 190 °C for 1-12 h $$	
7	Csta-APS	6 g starch + 40 mL water + 1 g APS	70 °C for 2 h and 190 °C for 1-12 h	
8	Csss	1 g Sunflower seed shell powder (SSS, 100 mesh) + 40 mL water	120 °C for 12 h and 230 °C for 24 h	
9	Csss-APS	1 g SSS + 40 mL water + 1 g APS	120 °C for 12 h and 230 °C for 24 h $$	
10	Csss-APS(H <sub>2</sub> SO <sub>4</sub> )	1 g SSS + 40 mL water + 1 g APS + 0.5 mL H <sub>2</sub> SO <sub>4</sub> (98 %)	120 °C for 12 h and 230 °C for 24 h $$	
11	Csuc-APS	6 g sucrose + 40 mL water + 1 g APS	$70 ^{\circ}\text{C}$ for 2 h and 190 $^{\circ}\text{C}$ for 1 12 h	
	(monodisperse)	+ 0.02 g sodium polyacrylate	70 C 101 2 II and 180 C 101 1-12 II	

Table S	1 Typical	conditions f	or APS-assisted	l hydrothermal	carbonization	of different	saccharides.
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Sampla	Hydrothermal reaction time	Carboxyl	Lactone	Phenol
Sample	(h)	(mmol g <sup>-1</sup> )	(mmol g <sup>-1</sup> )	(mmol g <sup>-1</sup> )
Csuc	12	0.22	1.53	0.69
Csuc-APS	1	1.42	0.95	Not measured
Csuc-APS	12	1.28	0.90	0.67
Csuc-APS(Fe <sup>2+</sup> )	1	1.50	0.91	Not measured
Csuc-APS(Fe <sup>2+</sup> )	12	1.34	0.82	0.79

 Table S2. Oxygen-containing groups on the surface of HTCS.

## **Table S3**. Particle sizes of HTCS.

Sample	D10 (µm)	D50 (µm)	D90 (µm)
Csuc	5.29	15.62	31.48
Csuc-APS	25.97	56.62	94.00
Csuc-APS(Fe <sup>2+</sup> )	30.38	67.94	114.82

Particle size distribution was determined by using D10, D50 and D90, which are the equivalent volume diameters at 10 %, 50 % and 90 % of the cumulative volume, respectively. Table S3 indicates that the average particle diameter of Csuc is much smaller than that of Csuc-APS.

Table S4. Elemental analysis of sucrose-derived HTCS.
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Sampla	wt%				Defenence		
Sample	С	Н	Ν	0	S	Kelelelice	
Csuc	65.47	4.84	0.19	28.90	0.61	This study	
Csuc-APS	61.12	5.00	1.64	31.54	0.70	This study	
Csuc-APS(Fe <sup>2+</sup> )	59.08	4.76	1.91	33.64	0.61	This study	
HW	65.72	4.80	< 0.05	28.89	0.58	[2]	
HWN	62.49	6.08	6.70	24.65	1.07	[2]	
ACsuc	77.50	1.84	0.05	20.46	0.15	This study	
ACsuc-APS	81.74	1.79	0.45	15.65	0.37	This study	
ACsuc-APS(Fe <sup>2+</sup> )	78.90	2.02	0.52	18.22	0.34	This study	

Sample	$S_{BET}{}^{a}(m^2 g^{-1})$	$V_0{}^b$ (cm <sup>3</sup> g <sup>-1</sup> )	$V_t^c$ (cm <sup>3</sup> g <sup>-1</sup> )	CO <sub>2</sub> adsorption (mmol g <sup>-1</sup> )
Csuc	5.4	0.007	_ d	-
Csuc-APS	7.1	0.010	-	-
Csuc-APS(Fe <sup>2+</sup> )	9	0.015	-	-
ACsuc	879	0.40	0.36	2.53
ACsuc-APS	1055	0.51	0.40	3.43
ACsuc-APS (Fe <sup>2+</sup> )	975	0.47	0.36	3.40
ACsuc-APS (5g)	-	-	-	3.74
ACglu	1115	0.53	0.39	2.85
ACglu-APS	1430	0.70	0.54	3.61
ACsta	696	0.39	0.27	2.95
ACsta-APS	1184	0.52	0.45	3.45
ACsss	1206	0.52	0.46	3.53
ACsss-APS	1473	0.78	0.56	3.43

**Table S5** Porosity data of activated carbon spheres (ACx) after thermal treatment of HTCS with potassium oxalate and their  $CO_2$  adsorption data obtained at 25 °C.

<sup>a</sup>Surface area was calculated using the t plot method using adsorption data at  $P/P_0 = 0.01-0.1$ . <sup>b</sup>Single-point total pore volume at  $P/P_0 = 0.990$ . <sup>c</sup>Micropore volume was evaluated by the t-plot method. <sup>d</sup> Not detected.

# Reference

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[2] K. G. Latham, G. Jambu, S. D. Joseph and S. W. Donne, ACS Sustain. Chem. Eng., 2014, 2, 755-764.