Supplementary Materials for

Facile fabrication of cellulose-derived hard carbon for high-rate performance sodium-ion batteries by regulating degrees of polymerization

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Materials and genernal methods

Synthesis of hard carbons and electrodes

1. Chemicals

Bleached softwood pulp used as original fibers (FO) in this work was purchased from Canfor Corporation. Sodium Chlorite ($NaClO_2$) is purchased from Macklin. Acetic Acid (CH_3COOH) is purchased from Energy Chemical. $C_4H_{18}CuN_4O_2$ is purchased from Shanghai Taixuan Industrial Co., Ltd.

2. Materials synthesis

First, two parts of 10 g cellulose are mixed with 160 mL deionized water in a sealed bag and placed in a 75 ℃ water bath, and 6 g $NaClO_2$ and 3 mL CH_3COOH are added for reaction time of 3h and 4 h respectively . Cellulose with polymerization degrees of 600 and 300, respectively, and unreacted cellulose with polymerization degrees of 1200. When the cellulose is dried at 50 ℃ for 12h, the cellulose is named DP-x, where x indicates the degree of polymerization. Second, the obtained cellulose is pyrolyzed at 1400℃ for 120 mins under Ar with ramping rate of 3℃ min^{-1}. The acquired HC is named as C1200, C600 and C300.

Determination method of fiber polymerization: The viscosity average polymerization degree (DP_v) of bleached pulp is determined by copper ethylenediamine method. The appropriate amount of fiber raw material is completely dissolved in 0.5 mol/L copper ethylenediamine solution, and held in a constant temperature water bath at 25 ℃ for 30 min. After that, the outflow time of the solution is determined using the Nordic standard viscoseter, and the characteristic viscosity of the solution was calculated by Martin

formula [η], and substituted into the following formula: $DP_v^{0.905}=0.75[\eta]$.

3. Material characterization

The crystallinity of cellulose is calculated by reported articles[1, 2]. Thermogravimetric analysis (TGA) measurement is performed on a TA SDT Q600 analyzer from room temperature to 1400 °C at a rate of 10 °C min^{-1} in Ar atmosphere. The structure of samples is measured by X-ray diffraction (XRD) with Cu K_α radiation (λ = 1.5418 Å), voltage of 36 kV, current of 20 mA and a scan speed of 10° min^{-1}. L_a and L_c are calculated from Scherrer equation:

$$La\&Lc = \frac{\kappa\lambda}{\beta\cos\theta}$$

In this formula, κ is scherrer constant (κ is 0.9 for L_c and κ is 1.84 for L_a), λ is the radiation wavelength, β is the half-height width of the (002) peak, θ is the reflection angle of (002) or (100).

Raman spectra are conducted by HORIBA Scientific LabRAM HR Evolution with a laser wavelength of 532 nm. $L_{a,\,Raman}$ is calculated from the equation:

$$La, Raman = (2.4 \times 10^{-10})\lambda^{-4}(I_{D1}/I_G)$$

Where λ is the laser wavelength. Scanning electron microscope (SEM) is conducted by a Regulus8100 field-emission scanning electron microscopy. High resolution transmission electron microscope (HRTEM) is conducted by JEM 2100F. Fourier transformed infrared (FT-IR) is operated on a Nicolet IS50 - Nicolet Continuum infrared spectrometer (Thermo Fisher Scientific). X-ray photoelectron spectroscopy (XPS) analysis is measured by Thermo Kalpha. N_2 and CO_2 adsorption-desorption experiments are performed with Mike ASAP2460. Small angle X-ray scattering

(SAXS) is tested by Xeuss 2.0 (Xenocs, France), sample test distance: 150 mm and the data of SAXS is fitted according to previous work[3]. Ture density test is tested by an AccuPyc II 1345 analyzer using Helium. The volume of closed pores was calculated based on the work by Hu et al[4]. Electron paramagnetic resonance (EPR) is carried out by Bruker ELEXSYS-II E500 CW-EPR, operating at a frequency of 9.83 GHz.

4. Electrochemical Measurements

A slurry of 80wt% HC, 10wt% Super-P, and 10wt% PVDF is coated onto a carbon coated Cu foil current collector followed by drying in a vacuum oven at 110°C for 10 h to remove water totally. The average mass of active materials coated on the carbon coated Cu foil is about 1.2-1.5 mg cm^{-2}. The CR2032-type coin cells are assembled in glove box (H_2O, O_2 < 0.1 ppm) using 1 M $NaPF_6$ in diglyme (DME), GF/C glass microfiber filter (Whatman) and metallic Na counter electrode. Galvanostatic charge-discharge (GCD) tests and Galvanostatic intermittent titration technique (GITT) are conducted by LAND 2001A battery test system in the voltage range of 0.001–3 V (vs Na^+/Na) at approximately 25°C. The GITT is tested using a pulse current of 50 mA g^{-1} for 10 mins accompanied with a rest interval of 2.0 h. The apparent diffusion coefficients of Na^+ ions are calculated based on the Fick's second law[5]. Cyclic voltammetry (CV) tests are conducted via Bio-Logic VSP electrochemical workstation with the potential range from 0.001 to 3 V (vs Na^+/Na) and the scanning rate from 0.1 to 1 mV s^{-1}. Electrochemical impedance spectroscopy (EIS, frequency ranges: 100 kHz−0.01 Hz, amplitude: 5 mV) are performed by Bio-Logic VSP. The full cell consists of C600 as the anode and $Na_3V_2(PO_4)_3$ as the cathode, and the N/P is 1.1.

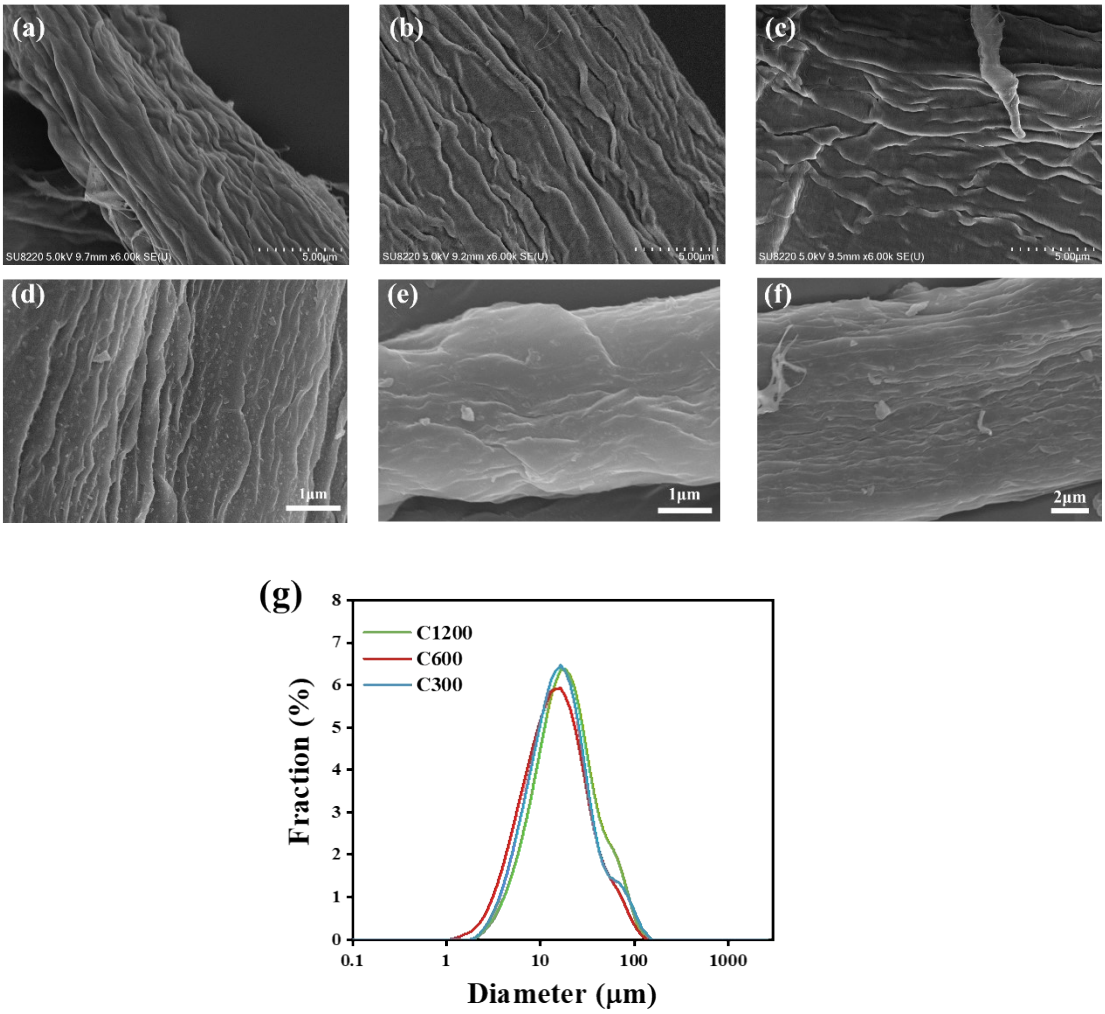

Figure S1. SEM images of the (a)DP-1200, (b) DP-600, (c)DP-300, (d) C1200, (e) C600, (f) C300 samples and (g) particle size distribution.

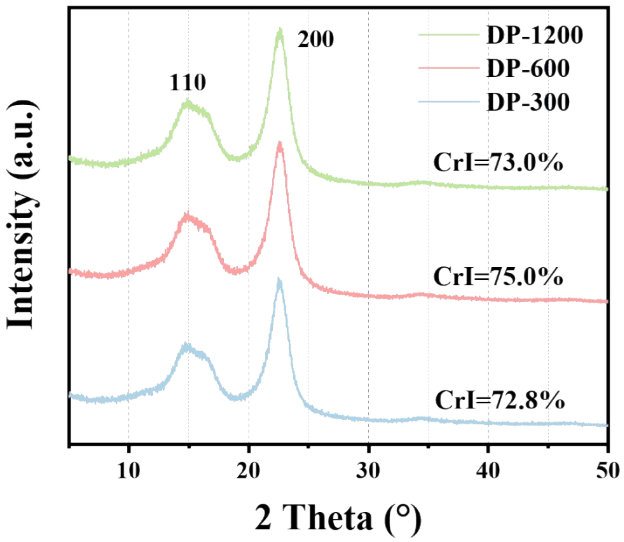

Figure S2. XRD pattern of the cellulose.

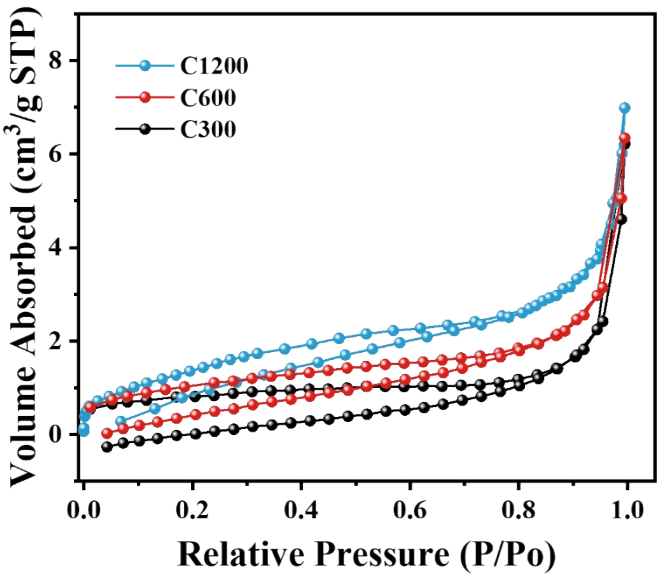

Figure S3. N_2 adsorption−desorption isotherms of as-prepared hard carbon materials.

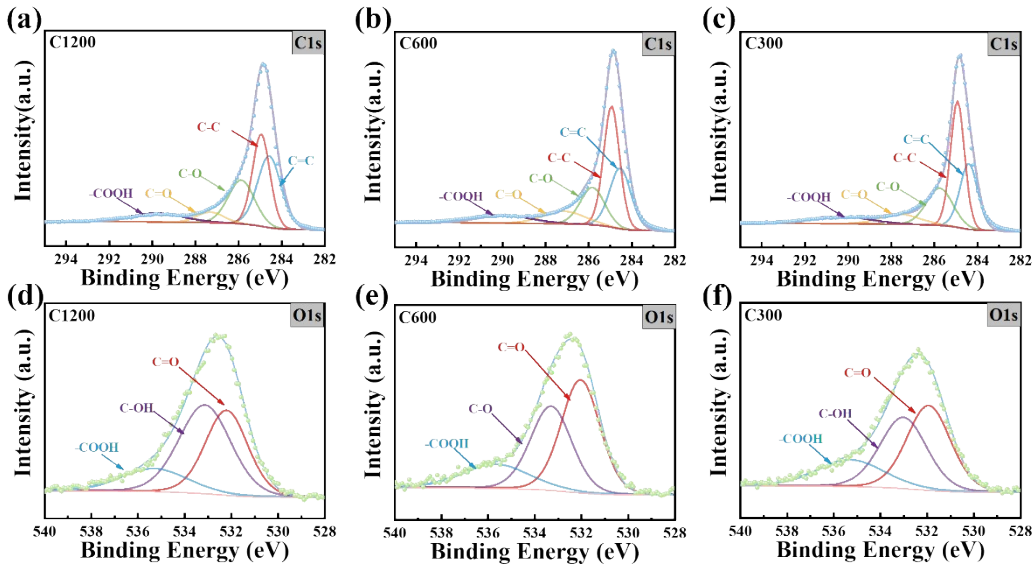

Figure S4. (a-c) XPS C1s and (d-f) O1s spectra and fitted curves of C1200,C600 and C300 samples.

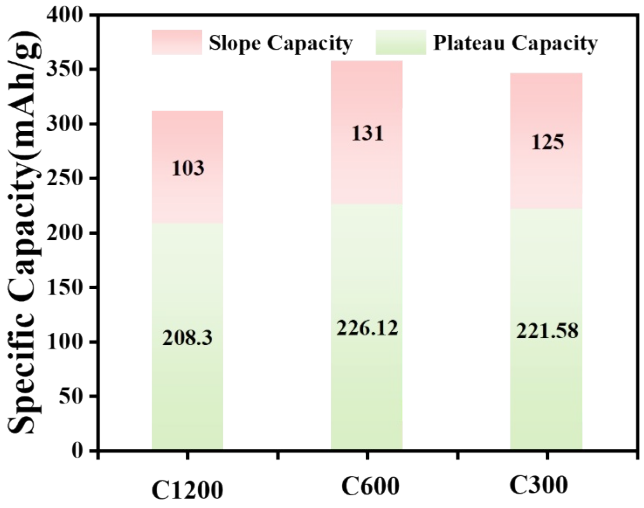

Figure S5. Capacity ratios of the slope region and plateau region in the second cycle discharge curve.

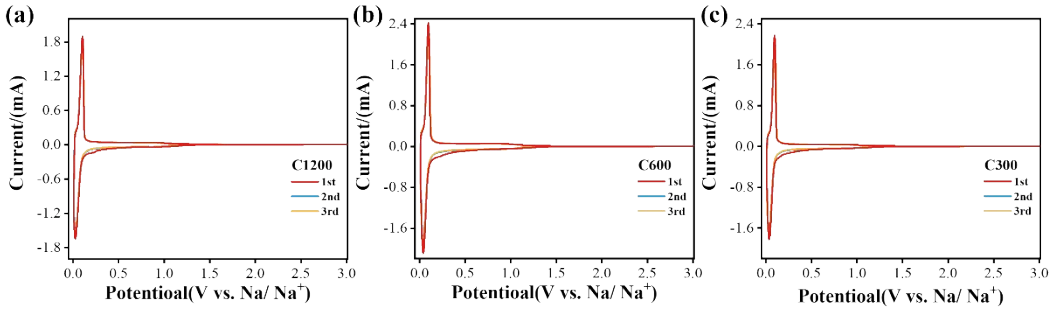

Figure S6. CV curves under 0.1 mV s^{-1} for (a) C1200, (b) C600 and (c) C300 anodes.

Table S1. Physical parameters of different hard carbons from the XRD spectra and Raman spectra.

		C1200			C600			C300		
Area (%)	High disordered	29.49			36.28			30.29		
	Pseudo-graphitic	41.77			46.54			45.42		
	Graphite-like	28.74			17.18			24.29		
	2Θ(°)	20.29	23.28	26.46	20.62	23.45	26.31	20.12	23.52	26.55
	d_{002} (nm)	0.372			0.384			0.377		
	L_c (nm)	0.998			1.271			1.022		
	AD1/AG	1.406			1.608			1.431		
	AD3/AG	0.574			1.452			1.401		
	La	13.68			11.96			13.43		

Table S2. Pore structure parameters of hard carbon materials.

Samples	Specific surface area(m^2/g)	Specific surface area(m^2/g)(CO_2)	V_{Total}(cm^3/g)	V_{Total}(cm^3/g))(CO_2)	R_{micro}(%)	R_{Meso}(%)	Average pore radius(Å)	Close pore Volume(cm^3/g)
C1200	5.61	36.45	0.0066	0.00086	8.60	91.40	10.91	0.004
C600	3.83	21.48	0.0026	0.00059	19.12	80.88	8.44	0.046
C300	2.97	15.21	0.0033	0.00019	19.95	80.05	8.76	0.012

Table S3. Percentage of the component after peak splitting fitting from XPS spectrum.

Samples	C	O	Percentage of the component after peak splitting fitting (at%)				
			C1s		O1s		
			sp^2-C	sp^3-C	C=O	C-O	-COOH
C1200	92.94	7.06	32.46	30.84	37.29	47.39	15.32
C600	93.15	6.85	25.28	38.08	46.57	36.64	16.80
C300	90.83	9.17	24.63	37.36	42.26	37.73	20.01

Reference

1. S. Park, J. O. Baker, M. E. Himmel, P. A. Parilla and D. K. Johnson, *Biotechnology for Biofuels*, 2010, **3**, 10.
2. J. Zhang, Y. Wang, L. Zhang, R. Zhang, G. Liu and G. Cheng, *Bioresource Technology*, 2014, **151**, 402-405.
3. D. Saurel, J. Segalini, M. Jauregui, A. Pendashteh, B. Daffos, P. Simon and M. Casas-Cabanas, *Energy Storage Materials*, 2019, **21**, 162-173.
4. Y. Li, Y. Lu, Q. Meng, A. C. S. Jensen, Q. Zhang, Q. Zhang, Y. Tong, Y. Qi, L. Gu, M.-M. Titirici and Y.-S. Hu, *Advanced Energy Materials*, 2019, **9**, 1902852.
5. Y. Li, Y.-S. Hu, M.-M. Titirici, L. Chen and X. Huang, *Advanced Energy Materials*, 2016, **6**, 1600659.