

## Electronic Supplementary Information

### Top-Down Approach Making Cellulose Carbonaceous Aerogel/MnO<sub>2</sub> Ultrathick Bulk Electrodes with High Mass Loading for Supercapacitors

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## Experimental Section

### Materials and Chemicals

Balsa wood (*Ochroma pyramidale*) was collected and cut into dimension of 20 × 20 × 2 mm (longitudinal × tangential × radial). The wood samples were rinsed with distilled water three times and dried at 60 °C for 10 h before use. Sodium hypochlorite solution (NaClO, 14%), sodium hydroxide (NaOH, 97%), and sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>, 99%) were purchased from Shanghai Macklin Biochemical Co., Ltd. (Shanghai, China). Ethanol (C<sub>2</sub>H<sub>5</sub>OH, 99.5%) and potassium permanganate (KMnO<sub>4</sub>, 99.3%) were supplied by Beijing Chemical Works (Beijing, China). All chemicals were used as received without further purification. Deionized (DI) water was used for sample preparation.

### Preparation of Cellulose Aerogel (CA)

Balsa wood samples were bleached in an aqueous solution containing 5% NaClO at room temperature until the color of the wood turned white. Then, the wood samples were further extracted with an 8% NaOH solution at 60 °C for 2 h to remove the residual hemicellulose. Next, the treated wood samples were washed using ethanol and water in turn. Finally, the wood samples were preserved in a freeze dryer at -62 °C for 36 h to acquire the CA.

### Preparation of Cellulose Carbonaceous Aerogel (CCA)

The CA was placed in a tubular furnace under the protection of nitrogen, and the heating rate was set as 5 °C·min<sup>-1</sup>. As in a typical process, it was heated to 500 °C and was kept at this temperature for 1 h. Then the sample was heated to 1000 °C and held for 2 h. Finally, the temperature was allowed to decrease to room temperature.

### Preparation of Cellulose Carbonaceous Aerogel/MnO<sub>2</sub> (CCA/MnO<sub>2</sub>) composites

The CCA/MnO<sub>2</sub> composite was prepared via the hydrothermal process. First, 30 mL of KMnO<sub>4</sub> (0.05, 0.1, 0.15, and 0.2 mol·L<sup>-1</sup>) solution and 10 mL of Na<sub>2</sub>SO<sub>4</sub> (0.1 mol·L<sup>-1</sup>) solution were mixed and stirred with a magnetic bar at room temperature for 6 h. A clean CA sample was

dipped in a mixed solution. Then, the mixed solution with the precursors was transferred into a 100 mL Teflon-lined autoclave and kept in an oven at 150 °C for 1.5 h. The obtained sample was washed with deionized water and dried at 60 °C for 24 h in a vacuum.

### Materials Characterization

A Thermo Nicolet IS 10 FT-IR was used to measure the FT-IR spectrum. Scanning electron microscopy (SEM, JEOL JSM-7610F) was performed for morphological and microstructural characterization of the samples. TEM images were obtained using a high-resolution transmission electron microscope (TEM, TF30 (200 KV)). Powder X-ray diffraction (XRD) patterns were determined using an X-ray diffractometer (D8 ADVANCE) with a Cu K $\alpha$  radiation source (0.154 nm). The N<sub>2</sub> adsorption-desorption isotherms were measured using Quantachrome Autosorb IQ at 77 K. The specific surface area was calculated using BET method. Pore size distribution was obtained using the non-local density functional theory (NLDFT) model. X-ray photoelectron spectroscopy (XPS) was performed using a Thermo Kalpha X-ray photoelectron spectrometer. Raman spectra were recorded at 633 nm excitation using a Raman spectrometer (LabRam HR Evolution).

### Electrochemical Measurements

An electrochemical workstation (CHI 760E) was used to perform electrochemical tests at room temperature in a three electrode setup. CCA/MnO<sub>2</sub> (or CCA) served as the working electrode, and had an effective area of 1.0 × 1.0 cm. A Pt wire served as the counter electrode and an Ag/AgCl electrode as the reference electrode. 1 M Na<sub>2</sub>SO<sub>4</sub> solution was used as the electrolyte. Cyclic voltammetry (CV) curves were measured over the potential window from 0-0.8 V, and galvanostatic charge-discharge (GCD) curves were measured in the potential range of 0-0.8 V. Electrochemical impedance spectroscopy (EIS) measurements were performed in the frequency range of 10<sup>5</sup>-0.01 Hz with an alternate current amplitude of 5 mV. For the WCA and WCA/MnO<sub>2</sub> electrodes, areal (C<sub>s</sub>, mF·cm<sup>-2</sup>) specific gravimetry (C<sub>m</sub>, F·g<sup>-1</sup>) and capacitances were calculated from the discharge curve according to the following equation:

$$C_s = I\Delta t/s\Delta V, C_m = I\Delta t/m\Delta V \text{ and } C_v = C_s/d$$

where I (A) is the discharge current,  $\Delta t$  (s) is the discharge time, s (cm<sup>2</sup>) is the specific area of the electrodes, m (g) is the total mass of the electrodes,  $\Delta V$  (V) is the operation discharge voltage window (excluding IR drop) and d (cm) as the efficient thickness of electrode.

Table S1 The mass of NW, CA, CCA

	NW	CA	CCA
Weight	0.1063	0.0319	0.0032

Table S2 The MnO<sub>2</sub> content of the CCA/MnO<sub>2</sub> composites

Sample	MnO <sub>2</sub> content measured by TGA method (wt%)
CCA	-
CCA/MnO <sub>2-0.05</sub>	84.6
CCA/MnO <sub>2-0.1</sub>	89.1
CCA/MnO <sub>2-0.15</sub>	91.0
CCA/MnO <sub>2-0.2</sub>	91.7

Table S3 Electrochemical performance of this work compared with existing porous carbon/MnO<sub>2</sub> composites

Materials	Scan rates	Mass special capacitance (F·g <sup>-1</sup> )	Areal special capacitance (mF·cm <sup>-2</sup> )	Thickness of electrodes (μm)	Referenes
MnO <sub>2</sub> /WDB	0.05 A·g <sup>-1</sup> <sub>1</sub>	101	-	~1000	[48]
MnO <sub>2</sub> /WC	1 mA·cm <sup>-2</sup>	55	4155	800	[9]
MnO <sub>2</sub> /porous biocarbon	1 mV·s <sup>-1</sup>	592	-	~1000	[56]
MnO <sub>2</sub> /3D-PC	1 mV·s <sup>-1</sup>	416	2770	-	[49]
PWC/MnO <sub>2</sub> /GQDs	1 mA·cm <sup>-2</sup>	188.4	2712	900	[33]
CCA/MnO <sub>2-0.15</sub>	1 mA·cm <sup>-2</sup>	663.7	3982	1500	This work

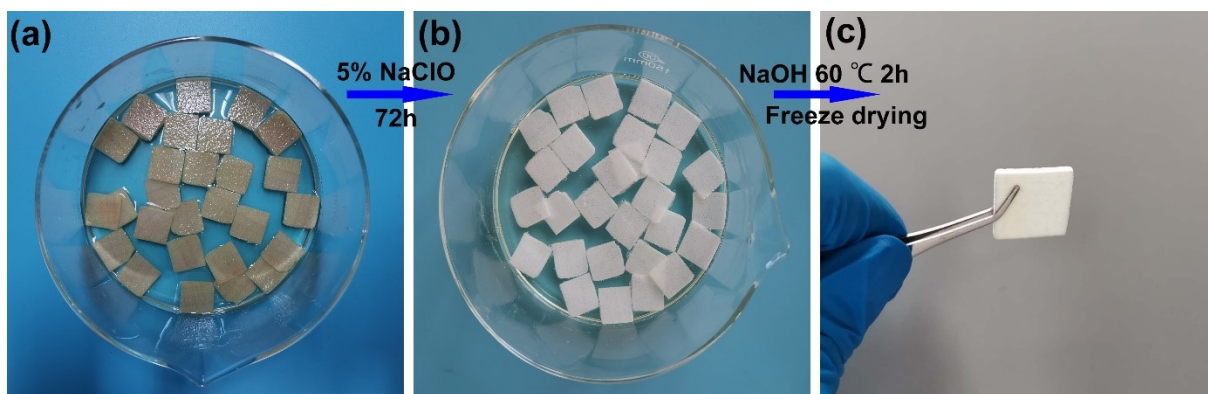


Fig. S1 Photo images of wood with different chemical treatments. (a) Before and (b) after treated 72 h with 5% NaClO solution. (c) Photo images of CA.

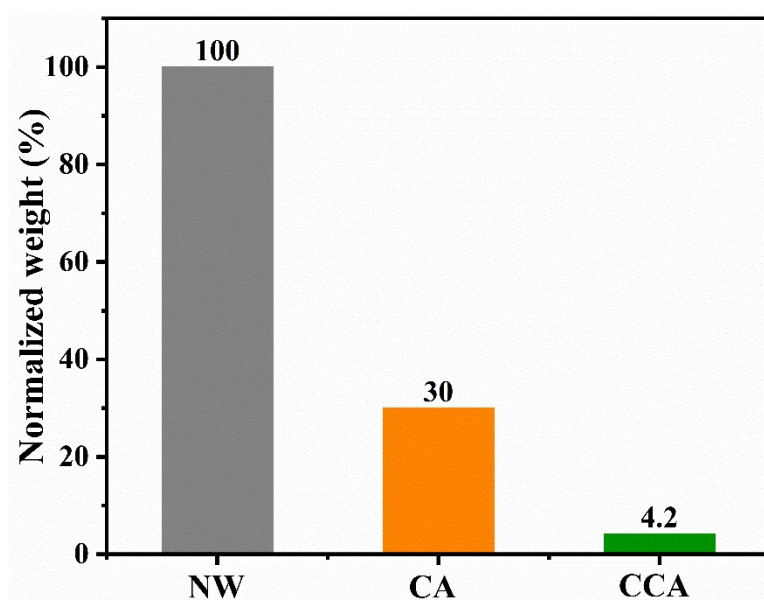


Fig. S2 Weight loss of NW, to CA, and CCA.

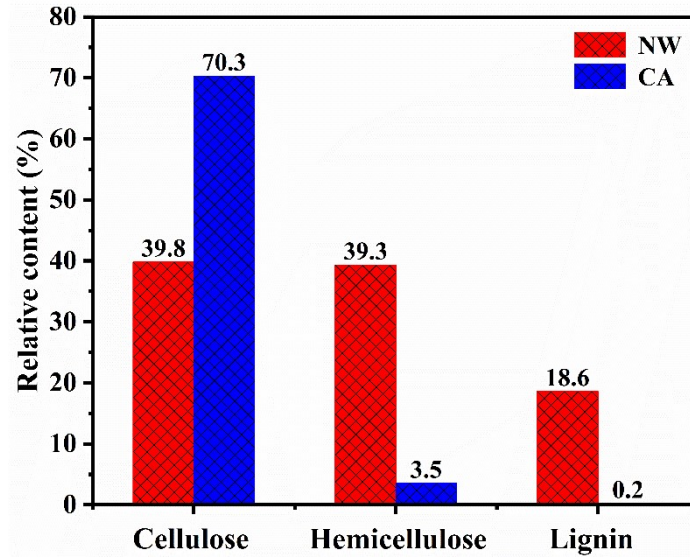


Fig. S3 Cellulose, hemicellulose, and lignin content in the NW and CA.

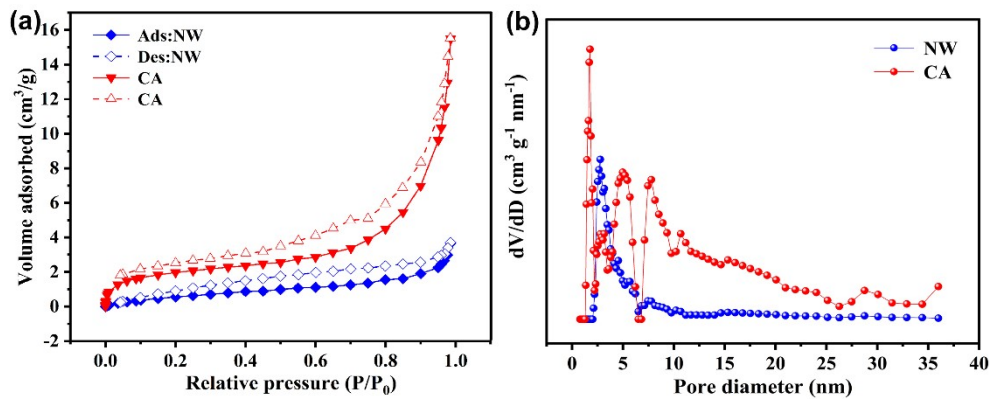


Fig. S4 NW and CA: (a) Nitrogen adsorption-desorption isotherms and (b) the corresponding pore size distributions.

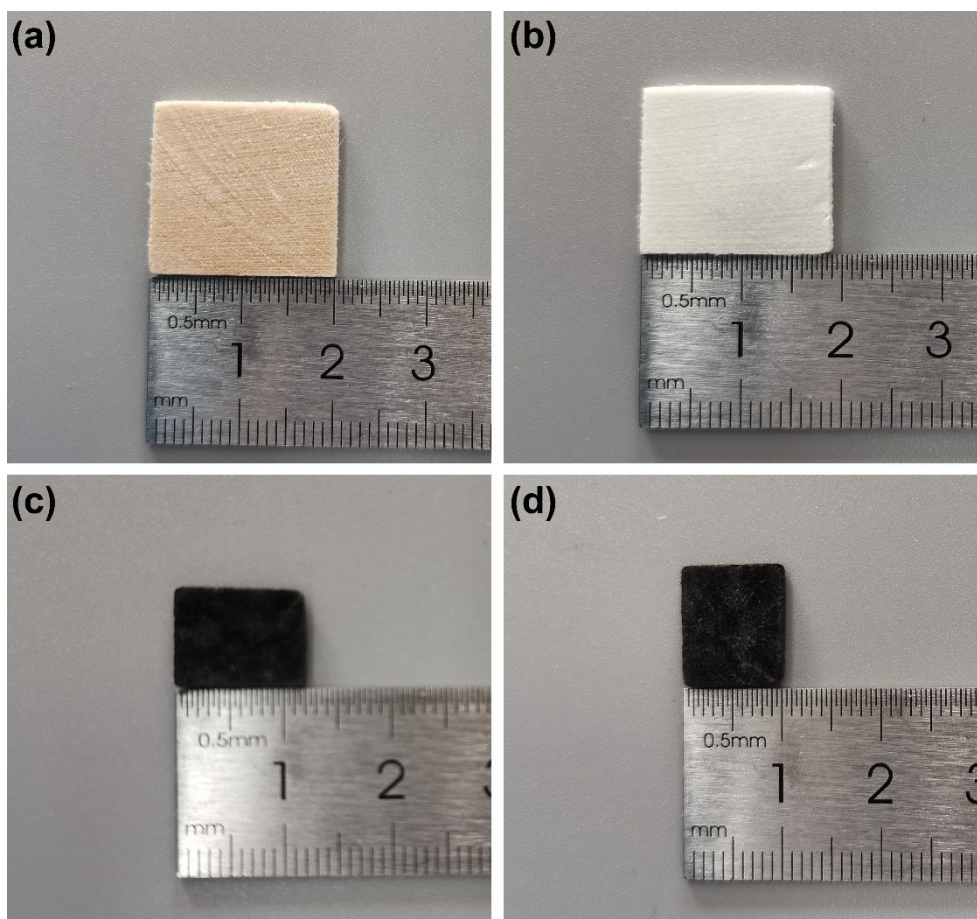


Fig. S5 Size information image of samples: (a) NW (b) CA and (c-d) CCA.

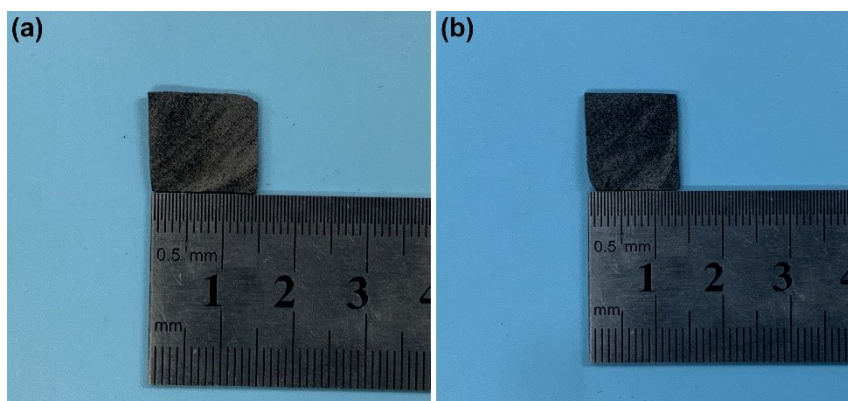


Fig. S6 Size information image of carbonized natural balsa wood



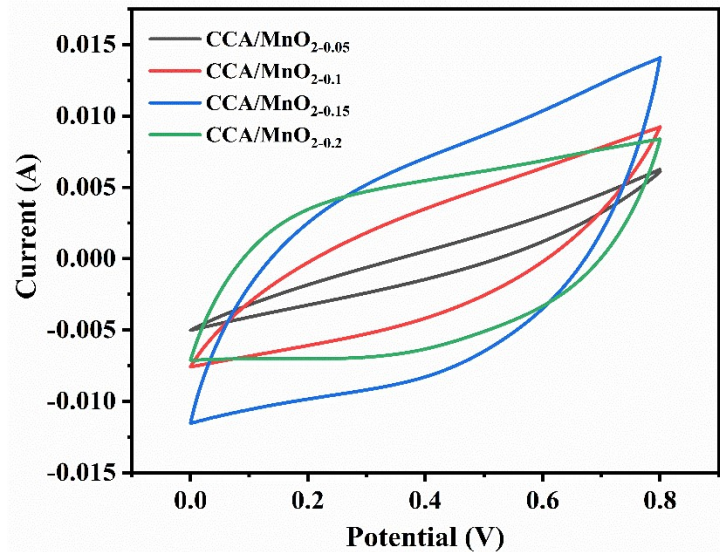


Fig. S7 CV curves for different concentration of  $\text{KMnO}_4$  at 5 mV/s.

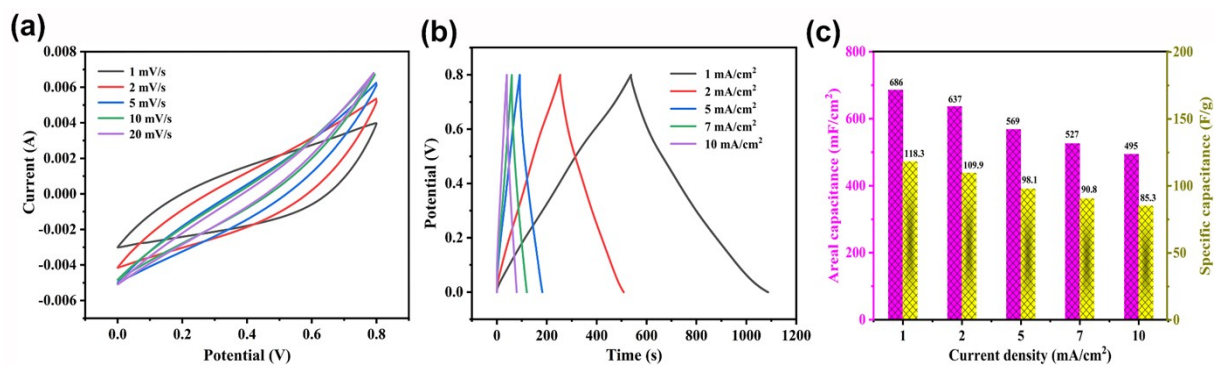


Fig. S8 Electrochemical performances of  $\text{CCA/MnO}_{2-0.05}$  electrode. (a) CV curves at various scan rates (b) GCD profiles at different current densities and (c) rate performances.

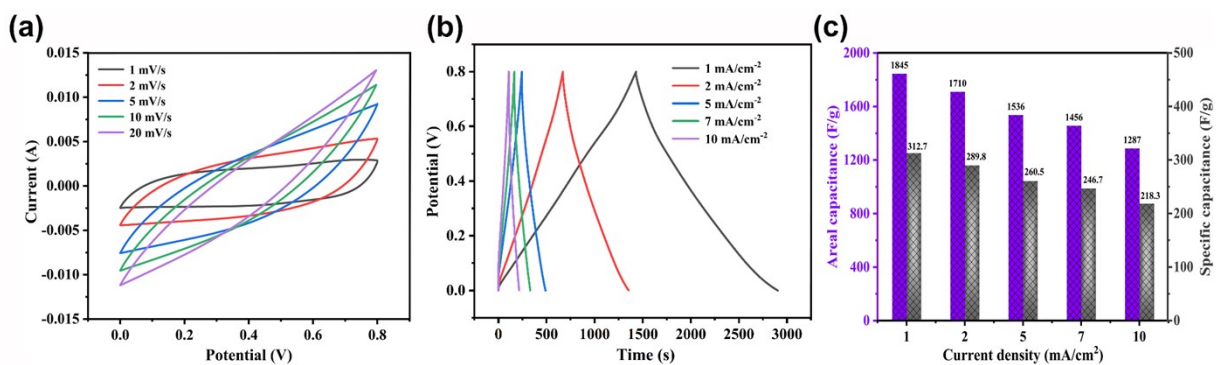


Fig. S9 Electrochemical performances of  $\text{CCA/MnO}_{2-0.1}$  electrode. (a) CV curves at various scan rates (b) GCD profiles at different current densities and (c) rate performances.

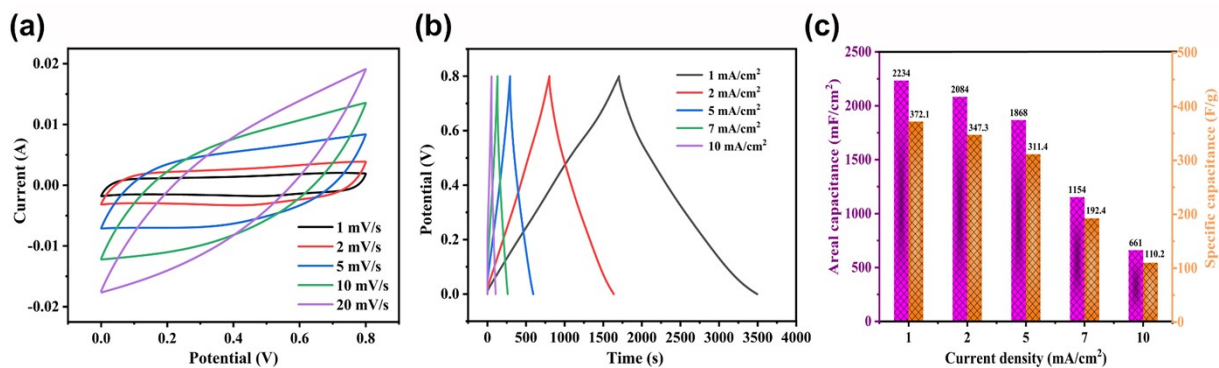


Fig. S10 Electrochemical performances of CCA/MnO<sub>2-0.2</sub> electrode. (a) CV curves at various scan rates (b) GCD profiles at different current densities and (c) rate performances.

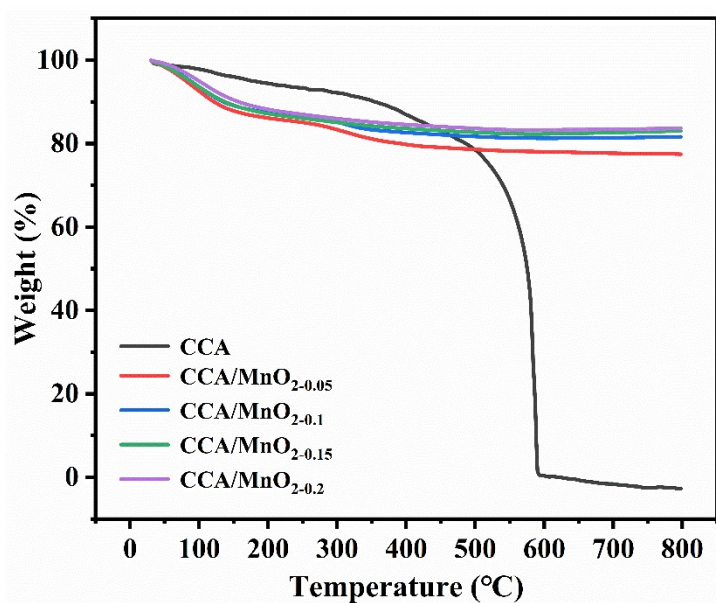


Fig. S11 The TGA curves of the CCA and CCA/MnO<sub>2</sub> with different concentration of KMnO<sub>4</sub>.

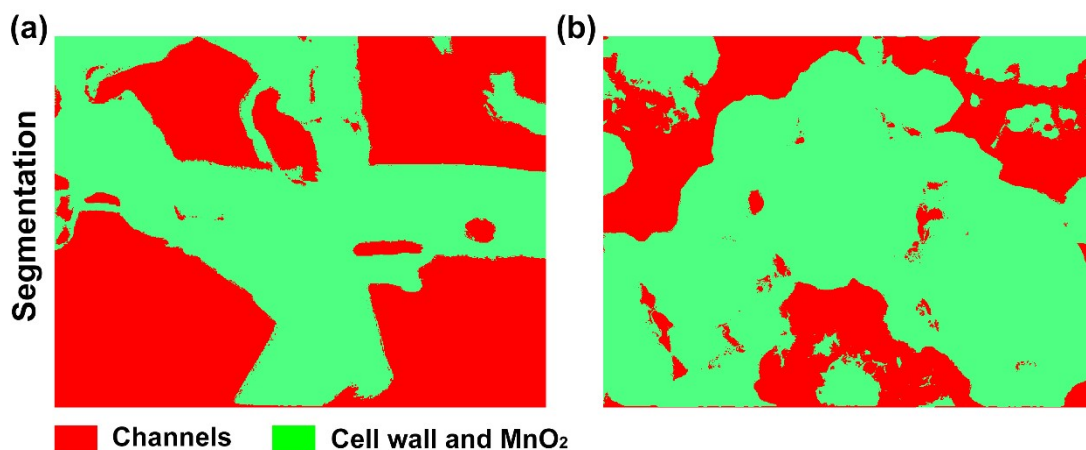


Fig. S12 The segmentation recognition of different electrodes: (a) CCA (corresponding to Fig. 2h) and (b)



CCA/MnO<sub>2-0,15</sub> (corresponding to Fig. 3g)

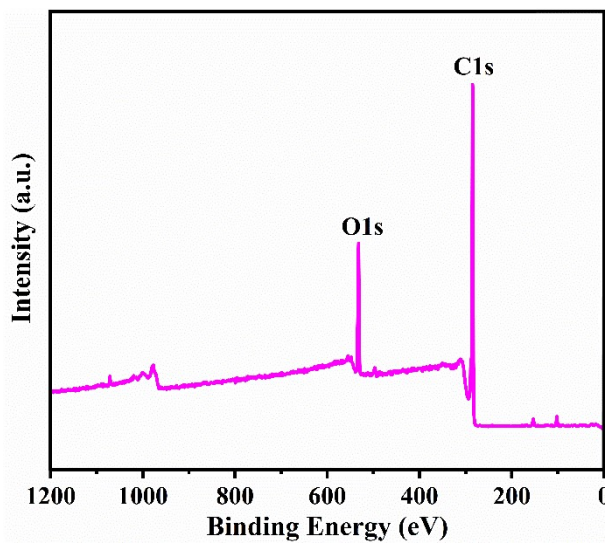


Fig. S13 XPS spectrum of the CCA composite.

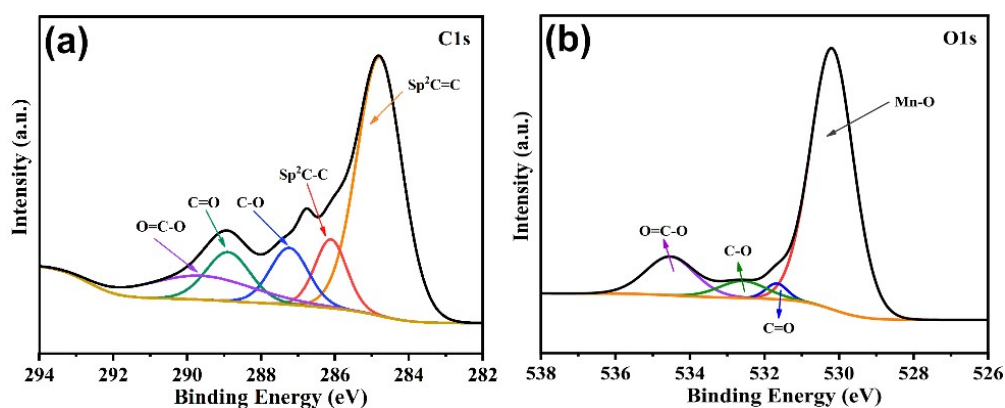


Fig. S14 (a) XPS C 1s and (b) O 1s core-level spectra of the CCA/MnO<sub>2-0.15</sub>.

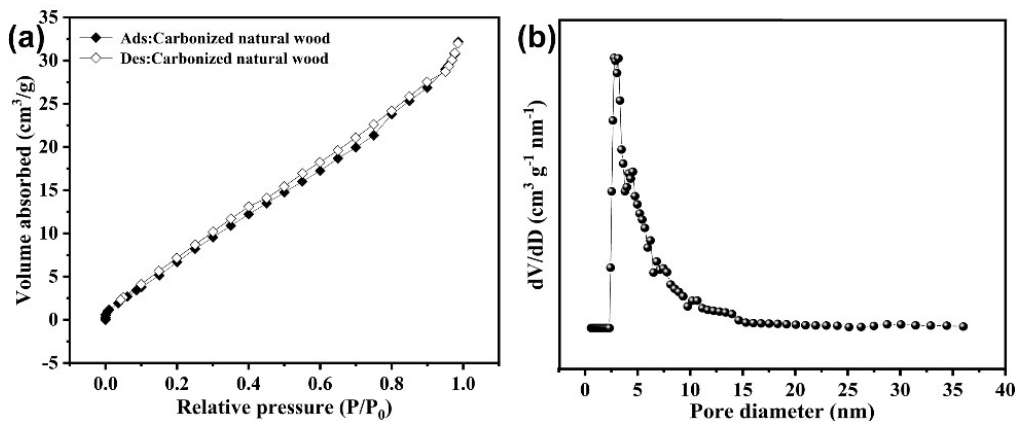


Fig. S15 Carbonized natural wood: (a) Nitrogen adsorption-desorption isotherms and (b) the corresponding

pore size distributions.

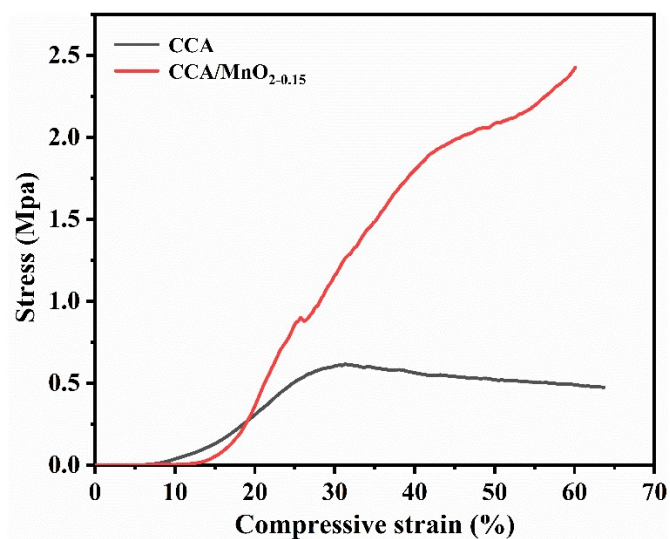


Fig. S16 The compressive stress-strain curves of the CCA and CCA/MnO<sub>2-0.15</sub>.

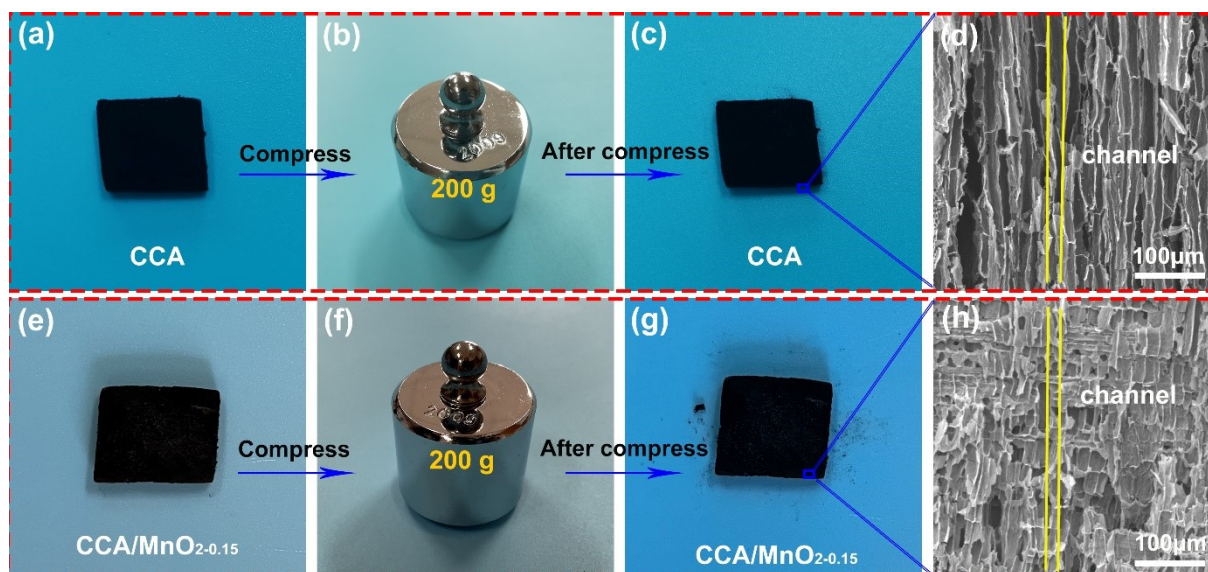


Fig. S17 (a) Photo images of the CCA before compressing. (b) image of CCA (0.0032g) supporting 200g weights. (c) photo images of the CCA after compressing. (d) SEM images of CCA after supporting 200g weights. (e) photo images of the CCA/MnO<sub>2-0.15</sub> before compressing. (f) image of CCA/MnO<sub>2-0.15</sub> (0.0047g) supporting 200g weights. (g) photo images of the CCA/MnO<sub>2-0.15</sub> after compressing. (h) SEM images of CCA/MnO<sub>2-0.15</sub> after supporting 200g weights.

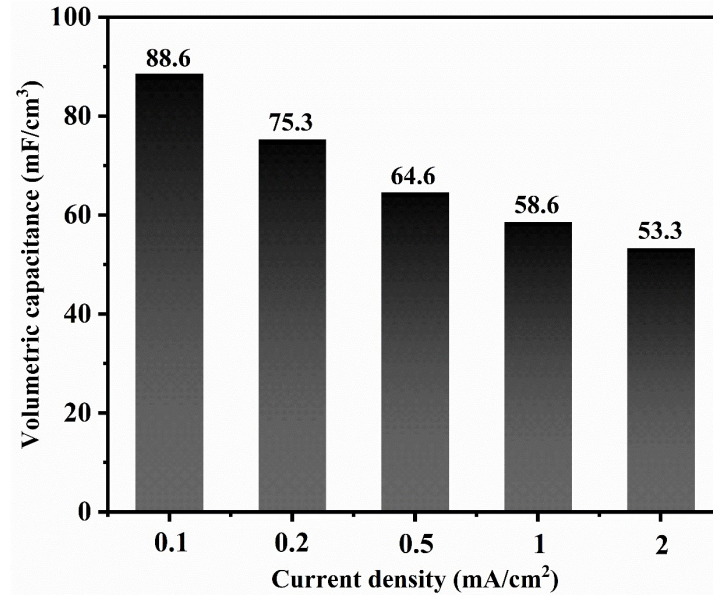


Fig. S18 The volumetric capacitance of CCA electrode.

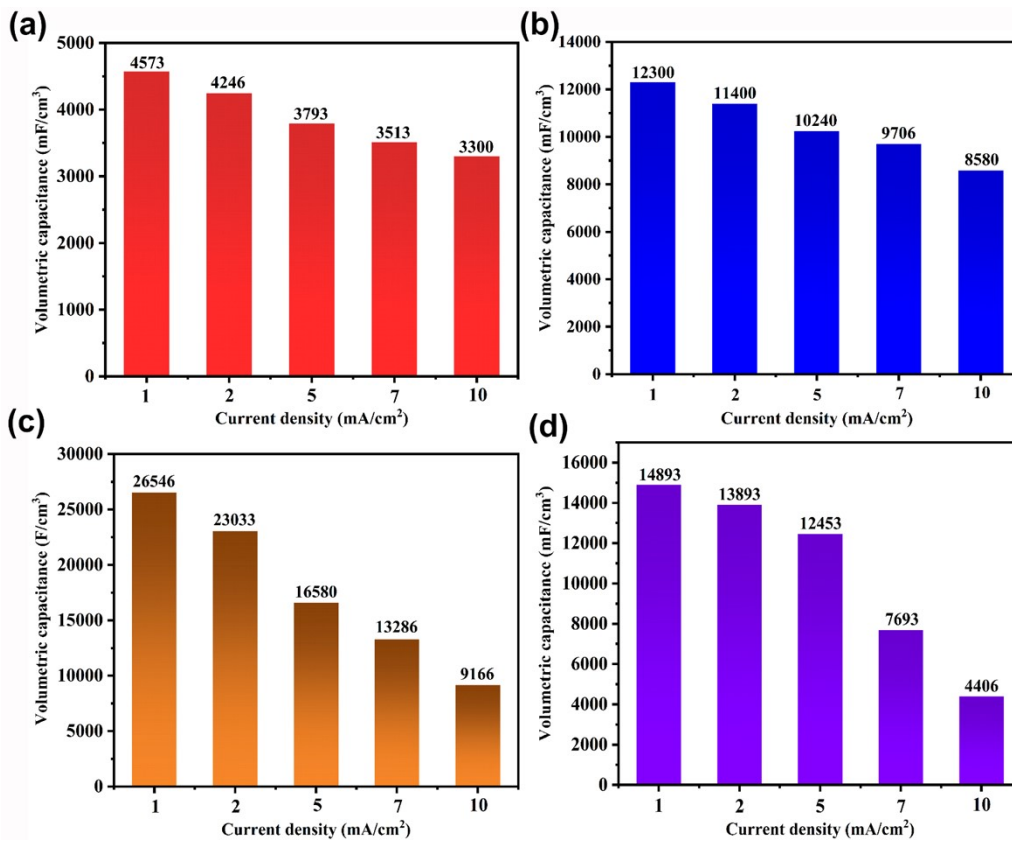


Fig. S19 The volumetric capacitance of CCA/MnO<sub>2-0.05</sub>, CCA/MnO<sub>2-0.1</sub>, CCA/MnO<sub>2-0.15</sub> and CCA/MnO<sub>2-0.2</sub> electrodes.

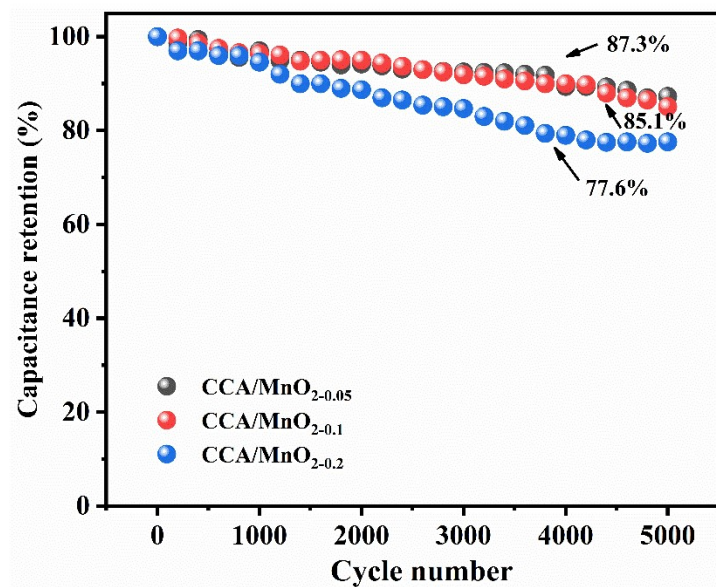


Fig. S20 Cycling performance of CCA/MnO<sub>2-0.05</sub>, CCA/MnO<sub>2-0.1</sub>, CCA/MnO<sub>2-0.2</sub> electrodes.