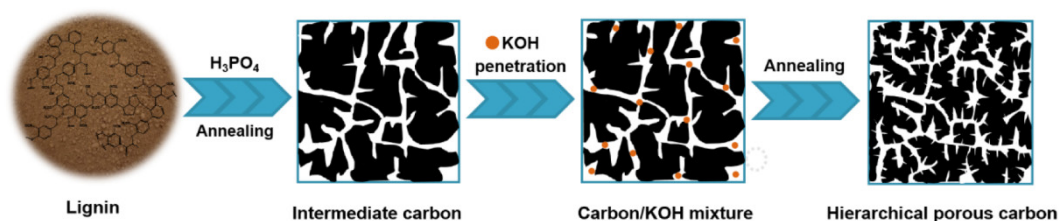
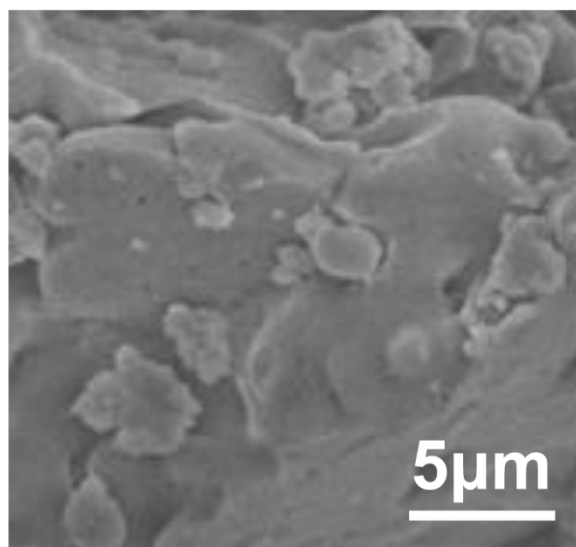


## Supporting data

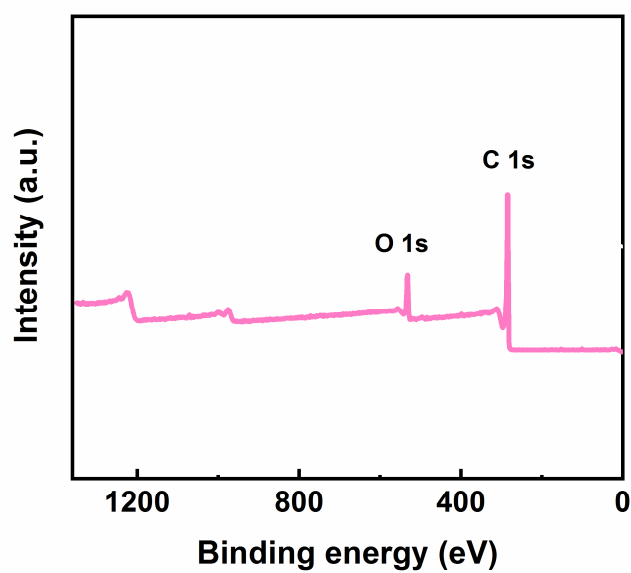


**Figure S1.** Schematic representation of the synthetic strategy of lignin-derived OHPC.

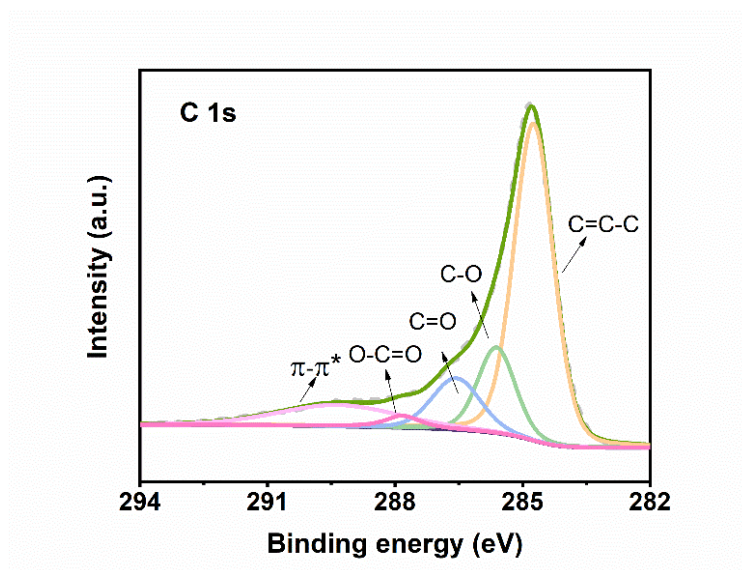
Figure S1 illustrated the detailed synthetic strategy of lignin-derived OHPCs. Firstly, lignin as carbon source was thoroughly immersed into H<sub>3</sub>PO<sub>4</sub> aqueous solution. After dried, the mixture was annealed at 400 °C for 1 h to obtain IC. Subsequently, the IC was homogeneously mixed with KOH solution, followed by heat treatment under a N<sub>2</sub> atmosphere to form lignin-derived OHPCs. Actually, the initial H<sub>3</sub>PO<sub>4</sub> pre-treatment played positive advantage in subsequent KOH activation process and effectively led to the formation of OHPCs. Concretely, the H<sub>3</sub>PO<sub>4</sub> assistants cross-linked with lignin sources and generated phosphate (and/or polyphosphate) esters groups throughout the lignin structure, which endowed the pre-activated IC with hierarchical porous structure. In addition, the IC also inherited rich oxygen-containing groups as shown in Figure S4. During subsequent KOH activation, such multi-scale porous structure and abundant oxygen species of IC collectively improved the wettability between IC and KOH solution and facilitated the evolution of pore morphologies, eventually forming the lignin-derived OHPCs. The formation of phosphate groups and the role of pre-treatment in subsequent KOH activation was systemically discussed in supplemental materials.



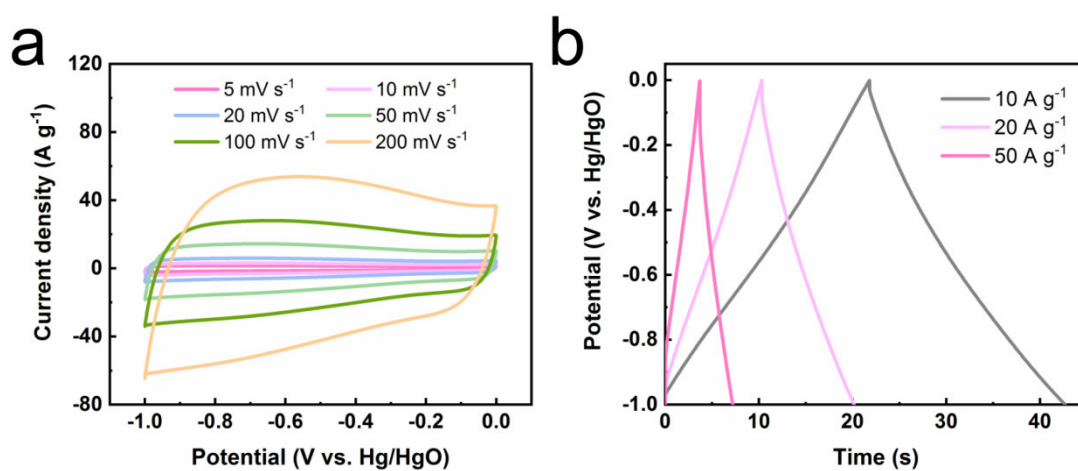
**Figure S2.** SEM image of the raw lignin particles.



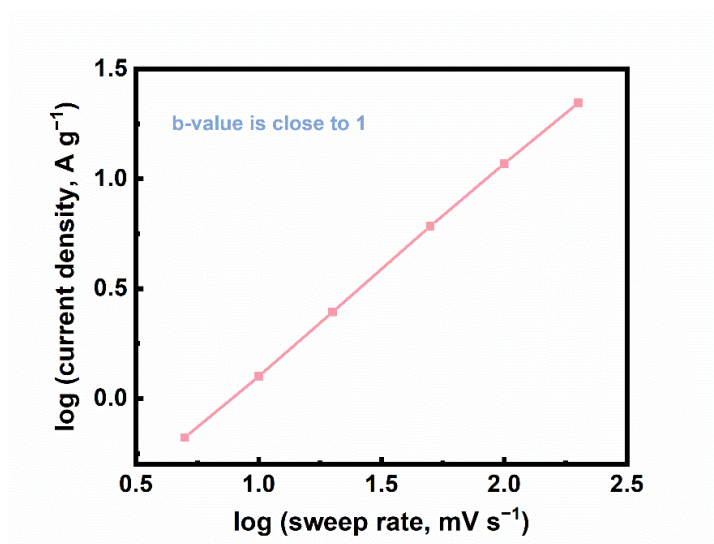
**Figure S3.** XPS survey spectrum of OHPC.



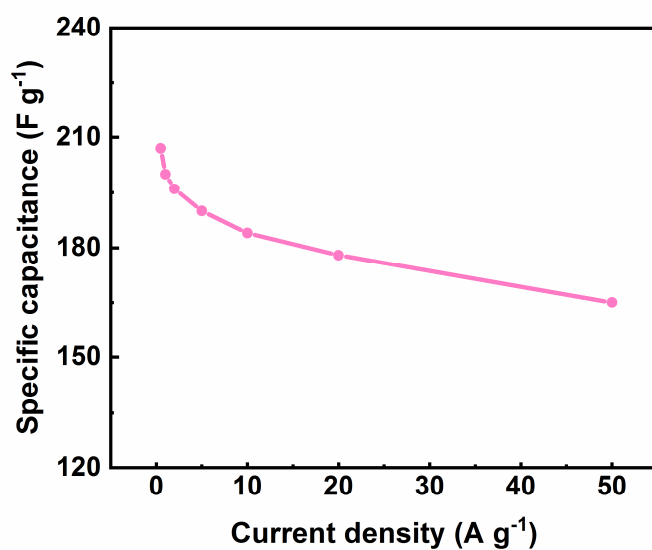
**Figure S4.** High-resolution C1s XPS spectrum of OHPC material.



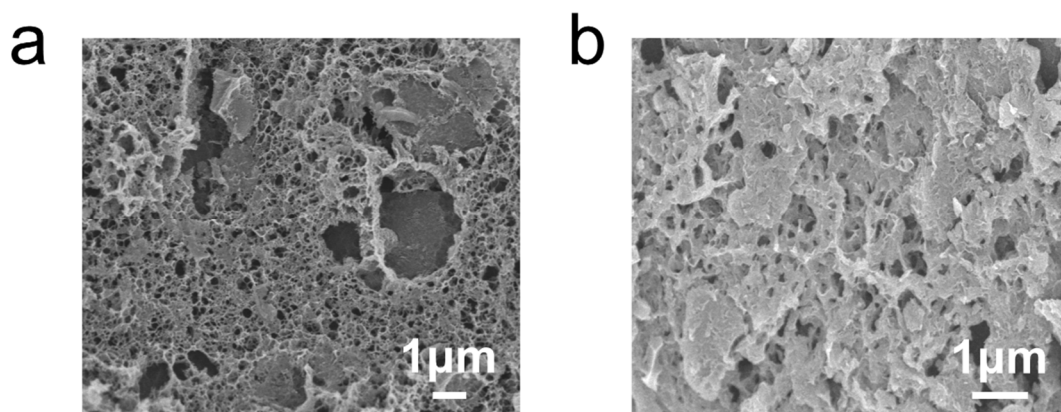
**Figure S5.** (a) The rate-dependent CV curves of OHPC at scan rates varied from 5 to 200 mV s<sup>-1</sup>. (b) The GCD profiles of OHPC at different rate from 10 A g<sup>-1</sup> to 50 A g<sup>-1</sup>.



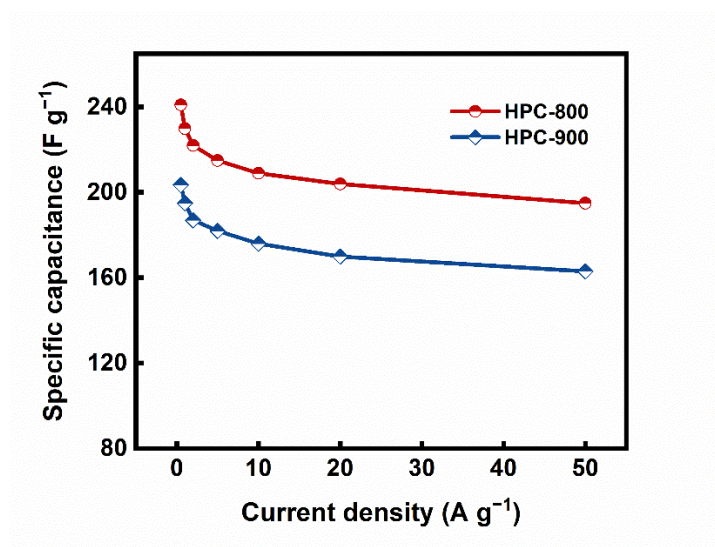
**Figure S6.** b-value determination of the anodic peak current density shows that this value is approximately 1.



**Figure S7.** The capacitance performance of the porous carbon electrode by direct KOH activation of lignin at 700 °C.



**Figure S8.** The SEM images of lignin-derived hierarchical porous carbon calcinated at different temperatures (a) 800 °C and (b) 900 °C.



**Figure S9.** The gravimetric rate performance of lignin-derived hierarchical porous carbon calcinated at 800 °C and 900 °C from 0.5 to 50  $\text{A g}^{-1}$ .

**Table S1.** The element concentration of OHPC sample.

Elements	Concentration (%)
C	89.22
O	10.78

**Table S2.** Comparison of electrochemical performances for the lignin-based carbon materials.

Electrode	precursor	Specific surface area (m <sup>2</sup> g <sup>-1</sup> )	Mass loading	Voltage window (V)	Electrolyte	Specific capacitance (F g <sup>-1</sup> )	Rate capability	E (W h kg <sup>-1</sup> ) (P (KW kg <sup>-1</sup> ))	References
PGBC <sup>a</sup>	Bamboo char	1732	4.8 mg	3.0	KOH/PVA	222.0 at 0.5 A g <sup>-1</sup>	51.8% at 20 A g <sup>-1</sup>	6.68 (0.1)	[60]
HOMC <sup>b</sup>	Walnut shell lignin	2033	2.4 mg	0–1.0	6 M KOH	286 at 0.2 A g <sup>-1</sup>	72.1% at 20 A g <sup>-1</sup>	13.5 (44.3)	[58]
Porous carbons	Lignin	3065	3 mg	0–1.0	6 M KOH	325 at 0.5 A g <sup>-1</sup>	80.8% at 50 A g <sup>-1</sup>	8.1 (0.1)	[37]
Porous carbon	Oxidized lignin	3094	-	0–1.0	6 M KOH	352.9 at 0.5 A g <sup>-1</sup>	82.7% at 10 A g <sup>-1</sup>	9.5 (0.025)	[52]
PCS <sup>c</sup>	Sodium lignosulphonate	1372.87	5 mg	0–1.0	3 M KOH	340 at 0.5 A g <sup>-1</sup>	72% at 10 A g <sup>-1</sup>	9.7 (0.25)	[62]
CAs <sup>d</sup>	lignin	1681.6	-	0–1.0	1 M H <sub>2</sub> SO <sub>4</sub>	260.3 at 1.0 A g <sup>-1</sup>	60.7% at 20 A g <sup>-1</sup>	26.25 (1.0)	[63]
N, S-HPC <sup>e</sup>	Sodium lignosulfonate	1454.7	-	0–1.0	6 M KOH	269 at 0.5 A g <sup>-1</sup>	62% at 50 A g <sup>-1</sup>	37.4 (0.062)	[54]
lignin/PAN nanofiber	Alkali lignin	1176.0	-	0–1.0	lignin hydrogel in 3.3 M KOH	-	-	4.49 (0.252)	[61]
Porous carbon	Alkali lignin	1831	2.5 mg cm <sup>-2</sup>	0-1.0	6 M KOH	□428 at 1.0 A g <sup>-1</sup>	82.9% at 30 A g <sup>-1</sup>	66.18 (0.312) in EMIM TFSI	[36]
LCNFs <sup>f</sup>	Melon seed shells and peanut shells	1254.5	-	-1.6-0	1 M Na <sub>2</sub> SO <sub>4</sub>	533.7 at 0.25 A g <sup>-1</sup>	90.6% at 10 A g <sup>-1</sup>	69.7 (0.78)	[56]

CNFs <sup>g</sup>	Softwood Kraft lignin	1124	2.212 mg cm <sup>-2</sup>	0-0.8	6 M KOH	103.6 at 0.25 A g <sup>-1</sup>	58.2 at 4 A g <sup>-1</sup>	-	[57]
Carbon aerogels	Softwood kraft lignin	1,609	-	0-1.0	1.0 H <sub>2</sub> SO <sub>4</sub>	122 at 1.0 A g <sup>-1</sup>	46.4% at 1A g <sup>-1</sup>	3.2 (0.209)	[53]
Carbon nanofibers	Lignin/PVA blend (80:20)	2170	-	3.5	Pyr <sub>14</sub> TFSI	87 at 1.0 A g <sup>-1</sup>	-	38 (1.67)	[59]
LCNFs-PRL <sup>h</sup>	Poplar	1062.5	-	0-1.0	6 M KOH	349.2 at 1.0 A g <sup>-1</sup>	85.4% at 5A g <sup>-1</sup>	56.9 (0.4) in 1 M Na <sub>2</sub> SO <sub>4</sub>	[55]
OHCP	Industrial lignin	1289.7	1.5-2.0 mg cm <sup>-2</sup>	0-1.0	6 M KOH	258 F g <sup>-1</sup> at 0.5 A g <sup>-1</sup>	80% at 50 A g <sup>-1</sup>	9.27 (0.025)	This work

<sup>a</sup> Three-dimensional porous graphitic biomass carbon

<sup>b</sup> Ordered mesoporous carbons (OMCs) with hierarchical pore structure

<sup>c</sup> Porous carbon spheres

<sup>d</sup> Carbon aerogels (CAs) with hierarchically porous morphologies

<sup>e</sup> Three-dimensional interconnected nitrogen and sulfur codoped porous carbon materials

<sup>f</sup> Light-weight lignin-based carbon nanofibers

<sup>g</sup> Freestanding nonwoven carbon fiber

<sup>h</sup> Poplar lignin (PRL) based lignin-based carbon nanofibers