Supporting Information

Nano-Size Porous Carbon Spheres as a High-Capacity Anode with High Initial Coulombic Efficiency for Potassium-Ion Batteries

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Fig. S1. SEM images of (a, b) CS and (d, e) SCS, TEM images of (c) CS and (f) SCS.



Fig. S2. Morphologies and size distributions of SCS with different addition of SDS: (a, d) 0.1 g, (b, e) 0.2 g and (c, f) 0.3 g.



Fig. S3. (a) Morphology of $SiO_2@SPCS$ at low magnification. (b) Cage-like SiO_2 template after removing carbon.



Fig. S4. Pore size distribution of (a) CS, (b) SCS and (c) SPCS.



Fig. S5. (a) XPS survey spectra, (b) C 1s spectra and (c) N 1s spectra of CS. (d) XPS survey spectra, (e) C 1s spectra and (f) N 1s spectra of SCS.

Table S1. The atomic percentage of CS, SCS, and SPCS calculated from the results of XPS.

Materials	Atomic % (XPS)		
	С	Ν	Ο
CS	94.48	1.96	3.56
SCS	94.58	1.7	3.72
SPCS	93.08	2.38	4.54



Fig. S6. The cyclic voltammetry (CV) curves of (a) CS and (b) SCS at 0.1 mV s⁻¹.

The CV curves of the first second cycles of CS and SCS electrodes was shown in Fig. S6. Obviously, the open circuit potential (OCP) of CS and SCS are 2.53 and 2.49 V, respectively, which are higher than that of SPCS (1.65 V). Besides, the redox peaks become more broad from CS to SCS and SPCS, which demonstrates that the redox sites are distributed over a more wide range of potential for SPCS. For carbon electrodes, these increased redox sites might be contributed by the adsorption mechanism, which is associated with numerous active sites such as edges, defects, and functional groups. This phenomenon may demonstrate the increased surface-controlled process of SPCS from the side.



Fig. S7. (a) Cycle performance and (b) rate capability of SPCS, SPCS-800, and SPCS-900.



Fig. S8. (a) XPS survey spectra, (b) C 1s spectra and (c) N 1s spectra of SPCS-800. (d) XPS survey spectra, (e) C 1s spectra and (f) N 1s spectra of SPCS-900.

Materials	Atomic % (XPS)		
	С	Ν	О
SPCS	93.08	2.38	4.54
SPCS-800	93.87	1.92	4.21
SPCS-900	94.05	1.93	4.02

Table S2. The atomic percentage of SPCS, SPCS-800, and SPCS-900 calculated from the results of XPS.

Table S3. The atomic percentage of Pyridinic N, Pyrrolic N, and Graphitic N calculated from the total N 1s of SPCS.

Materials	Atomic % (XPS)		
	Pyridinic N	Pyrrolic N	Graphitic N
SPCS	35.2	28.3	36.5
SPCS-800	25.7	34.8	39.4
SPCS-900	24.4	32.5	43.1



Fig. S9. The first and second charge-discharge curves at 200 mA g⁻¹ of SPCS.

As shown in Fig. S8, obvious irreversibility occurs between 0.2 and 3 V from the first cycle to the second cycle. Taking into account the decomposition voltage of the ether-based electrolyte and the K⁺ insertion voltage are all below than 0.2 V, the capacity between 0.2 and 3 V should be contributed by the adsorption mechanism, which is associated with numerous active sites such as edges, defects, and functional groups. This capacity loss demonstrates that some irreversibility comes from the trapping of potassium ion in some sites as the reviewer mentioned.



Fig. S10. CV curves of (a) CS and (b) SCS at a scan rate range of 0.1-2 mV s⁻¹. Surfacecontrolled contribution at 1 mV s⁻¹ for (c) CS and (f) SCS.



Fig. S11. Nyquist plots of CS, SCS and SPCS before cycling.

The diffusion coefficient (D) of CS and SPCS electrodes can be calculated from the GITT potential profiles using Fick's second law with the following equation:

$$D = \frac{4}{\pi \tau} \left(\frac{m_B V_M}{M_B S} \right)^2 \left(\frac{\Delta E_S}{\Delta E_\tau} \right)^2 \tag{S1}$$

where τ represents the duration of the current pulse; $m_{\rm B}$ represents the mass loading of the electrode material; *S* represents the geometric area of the electrode; ΔE_S is the quasi-thermodynamic equilibrium potential difference between before and after the current pulse; ΔE_{τ} is the potential difference during the current pulse; $V_{\rm M}$ is the molar volume of the materials; and $M_{\rm B}$ is the molar mass of carbon. The value of $M_{\rm B}/V_{\rm M}$ can be obtained from the density of the materials according to the following equation:

$$\rho = \frac{1}{V_{total} + \frac{1}{\rho_{carbon}}} \tag{S2}$$

where ρ (g cm⁻³) represents the density of PNHC, V_{total} (cm³ g⁻¹) is the total pore volume measured from the N₂ isotherm, and ρ_{carbon} is the true density of carbon (2 g cm⁻³).

Materials	High rate capacity	Cycling performance	Initial CE	Ref.
Graphite	$263 \text{ mAh g}^{-1} \text{ at } 27.9 \text{ mA g}^{-1}$	140 mA g ⁻¹ after 50	56.4%	1
	80 mAh g ⁻¹ at 279 mA g ⁻¹	cycles at 100 mAh g ⁻¹	(670 mA g ⁻¹)	
N- and O-rich	230 mAh g ⁻¹ at 140 mA g ⁻¹	170 mAh g ⁻¹ after 1900	41%	2
carbon nanofiber	110 mAh g ⁻¹ at 2800 mA g ⁻¹	cycles at 280 mA g ⁻¹	(27.9 mA g ⁻¹)	
N/O dual-doped	315 mAh g ⁻¹ at 50 mA g ⁻¹	130 mAh g ⁻¹ after 1100	25%	3

Table S4. Potassium storage performance of SPCS compared with previously reported materials.

carbon	118 mAh g ⁻¹ at 3000 mA g ⁻¹	cycles at 1050 mA g ⁻¹	(100 mA g ⁻¹)	
Ultra-high	388 mAh g ⁻¹ at 50 mA g ⁻¹	152 mAh g ⁻¹ after 3000	20%	4
pyridinic N	178 mAh g ⁻¹ at 5000 mA g ⁻¹	cycles at 1000 mA g ⁻¹	(1000 mA g ⁻¹)	
doped hard				
carbon				
N-doped	287.5 mAh g ⁻¹ at 50 mA g ⁻¹	121 mAh g ⁻¹ after 1000	30.28%	5
hierarchically	193.1 mAh g ⁻¹ at 500 mA g ⁻¹	cycles at 500 mA g ⁻¹	(50 mA g ⁻¹)	
porous carbon				
S/O co-doped	230 mAh g ⁻¹ at 50 mA g ⁻¹	108.4 mAh g ⁻¹ after 2000	61.7%	6
porous hard	158 mAh g ⁻¹ at 1000 mA g ⁻¹	cycles at 1000 mA g ⁻¹	(50 mA g ⁻¹)	
carbon				
microspheres				
S/N dual-doped	276 mAh g ⁻¹ at 100 mA g ⁻¹	144.9 mAh g ⁻¹ after 1200	35.2%	7
hard carbon	174 mAh g ⁻¹ at 3000 mA g ⁻¹	cycles at 3000 mA g ⁻¹	(100 mA g ⁻¹)	
P-doped N-rich	466.9 mAh g^{-1} at 50 mA g^{-1}	270.4 mAh g ⁻¹ after 1000	56.9%	8
honeycomb-like	268.1 mAh g^{-1} at 1 A g^{-1}	cycles at 1 A g ⁻¹	(200 mA g ⁻¹)	
carbon				
S/N co-doped	356 mAh g ⁻¹ at 100 mA g ⁻¹	168 mAh g ⁻¹ after 1000	53%	9
carbon nanofiber	112 mAh g ⁻¹ at 5000 mA g ⁻¹	cycles at 2000 mA g ⁻¹	(100 mA g ⁻¹)	
aerogels				
N/O dual-doped	382 mAh g ⁻¹ at 50 mA g ⁻¹	160 mAh g ⁻¹ after 4000	47.1%	10
carbon network	205 mAh g^{-1} at 1000 mA g^{-1}	cycles at 1000 mA g ⁻¹	(50 mA g ⁻¹)	
SPCS (This	345 mAh g ⁻¹ at 50 mA g ⁻¹	165.2 mAh g ⁻¹ after	68.2%	
work)	171.3 mAh g ⁻¹ at 1000 mA g ⁻¹	1500 cycles at 1000 mA	(200 mA g ⁻¹)	
		g^{-1}		

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