Supporting Information

Soft-carbon-coated, Free-standing, Low-defect, Hard Carbon Anode to Achieve 94% Initial Coulombic Efficiency for Sodium-Ion Batteries

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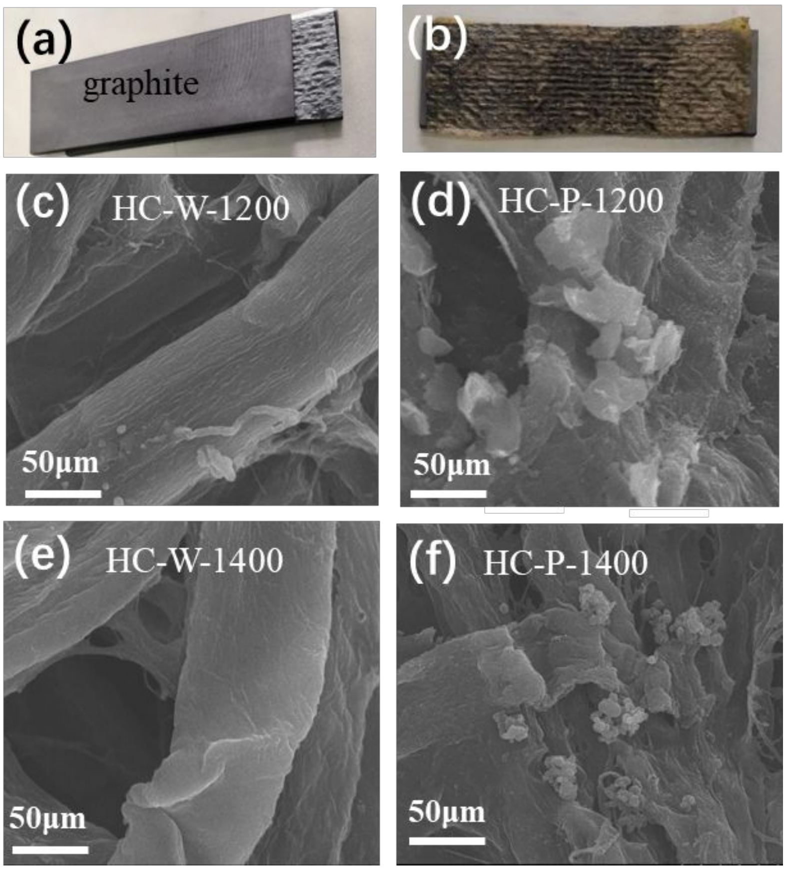

Figure S1. Digital photos of commercial paper towels impregnated with a) water and b) asphalt sandwiched on a graphite board. SEM image after heat treatment of c) HC-W-1200, d) HC-P-1200, e) HC-W-1400; f) HC-P-1400;

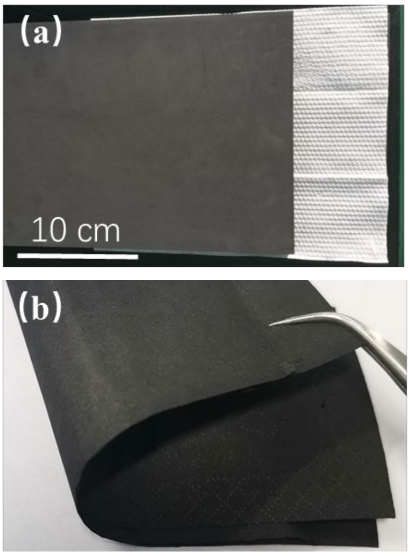

Figure S2. Digital photo of a) paper and b) bent carbon paper.

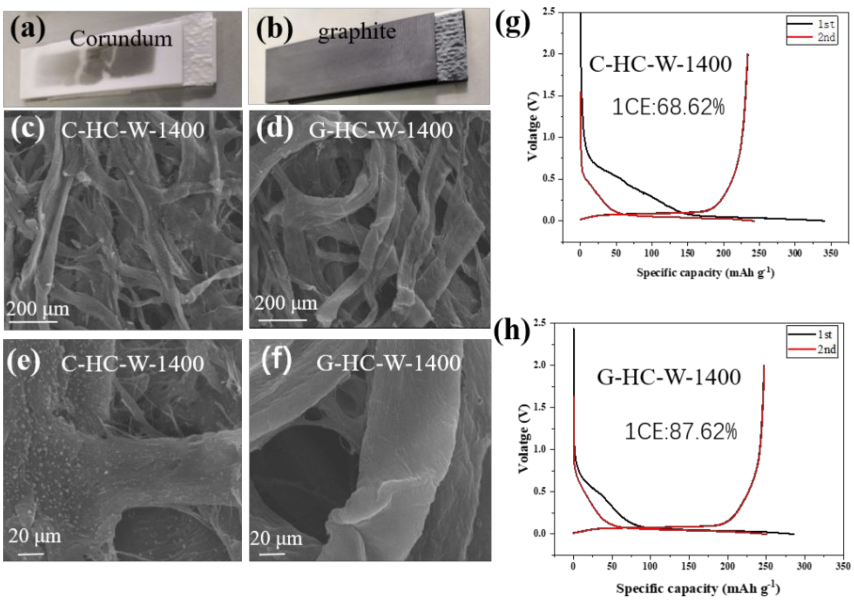

Figure S3. Digital photo of impregnation before carbonization a) C-HC-W-1400, b) G-HC-W-1400. SEM image after heat treatment of c, e) C-HC-W-1400, d, f) G-HC-W-1400; g, h)Comparison of charging and discharging performance of carbon paper under pressure between graphite board and corundum board.

For Figure S3b , the graphite plate has two functions, and the first of which has a fixed paper prevents the paper from being blown out during the carbonization process in the tubular furnace. The ingredients of the second graphite plate are also carbon, and they are used to sandwiched carbon paper without introducing other pollution. In addition, we have found that the self-supporting carbon paper synthesized by paper towels sandwiched by two corundum plates has a low initial coulombic efficiency, which can be seen from the supporting material Figure S3.

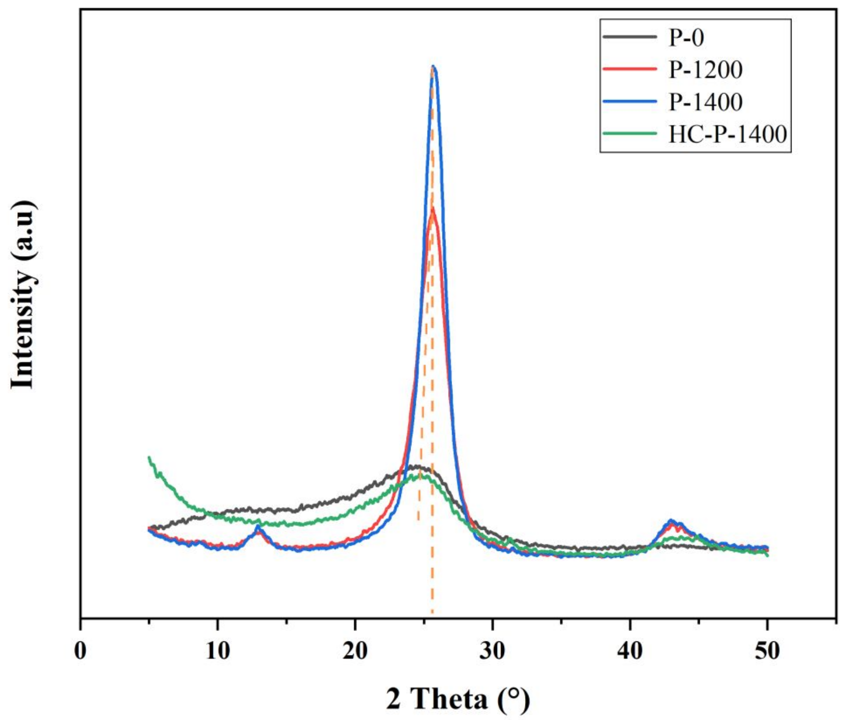

Figure S4. XRD patterns of coal pitch and its derivative soft carbon. P-0, P-1200, P-1400 respectively represent untreated pitch, soft carbon obtained by carbonizing pitch at 1200 ℃ and 1400 ℃. HC-P-1400 is a coated hard carbon obtained by pitch impregnation treatment.

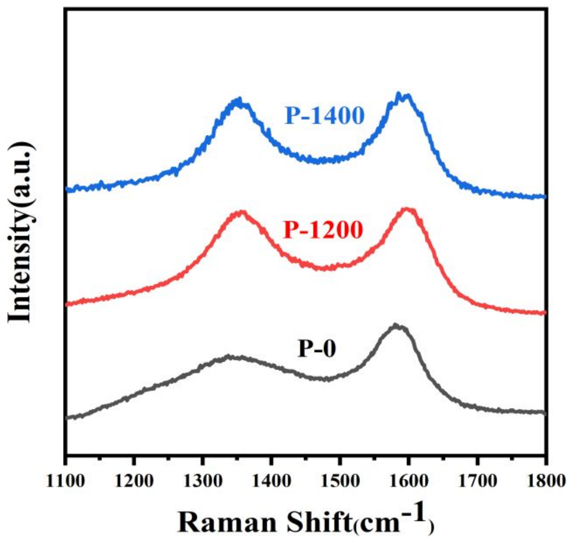

Figure S5. Raman spectra of coal pitch and its derivative soft carbon. P-0, P-1200, P-1400 respectively represent untreated pitch, soft carbon obtained by carbonizing pitch at 1200 ℃ and 1400 ℃.

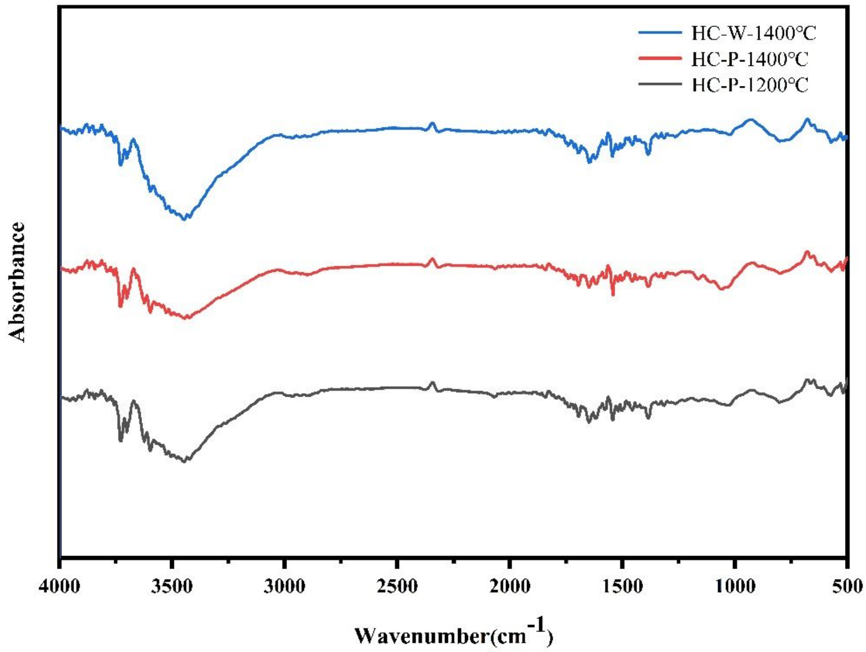

Figure S6. FTIR spectra of the HC-P-1200, HC-P-1400, and HC-W-1400.

By comparing the FTIR spectra of HC-P-1200, HC-P-1400, and HC-W-1400, in the wavelength range of 3000-3600 cm^{-1}, the peak of carbon paper with coal tar pitch is wider than that without coal tar pitch, which is caused by the association of - OH function group, unsaturated hydrocarbon bond and functional groups on carbon paper. It also shows that coal pitch as soft carbon has been coated on hard carbon, which supports our view in the article. In addition, this law also exists at -C=O function group with a wavelength of about 1600 cm^{-1}. After adding asphalt, its strength decreases and the number of irreversible functional groups on the surface of carbon paper is reduced.

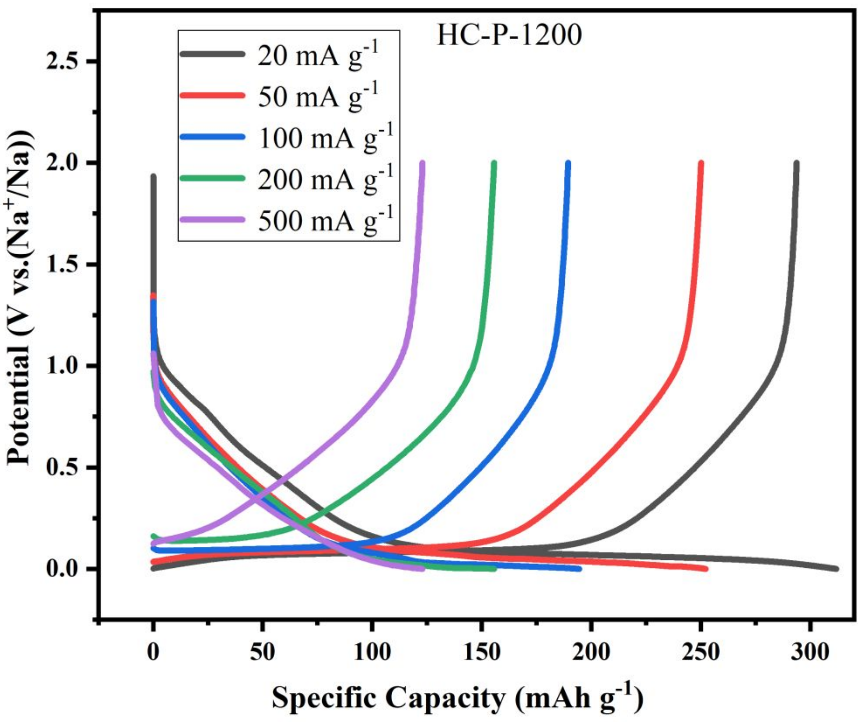

Figure S7. Charge and discharge curves of HC-P-1200 at different current densities

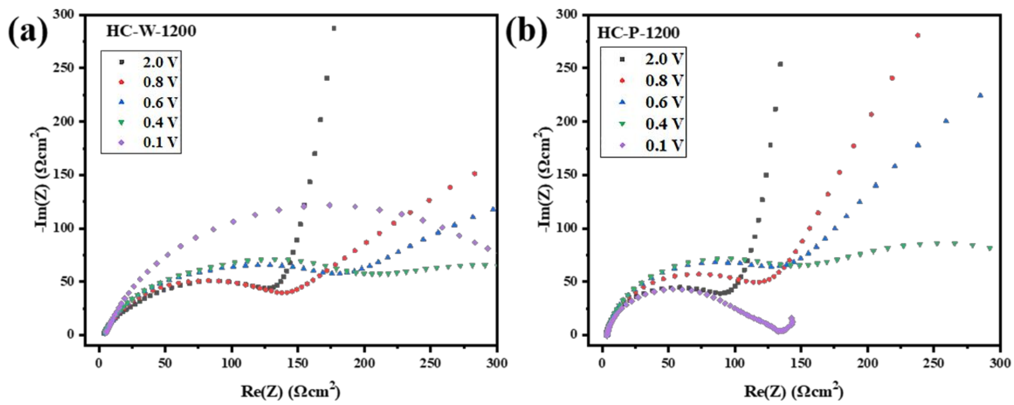

Figure S8. Electrochemical impedance spectroscopy of different potentials during the first cycle discharge of a) HC-P-1200 and b) HC-W-1200.

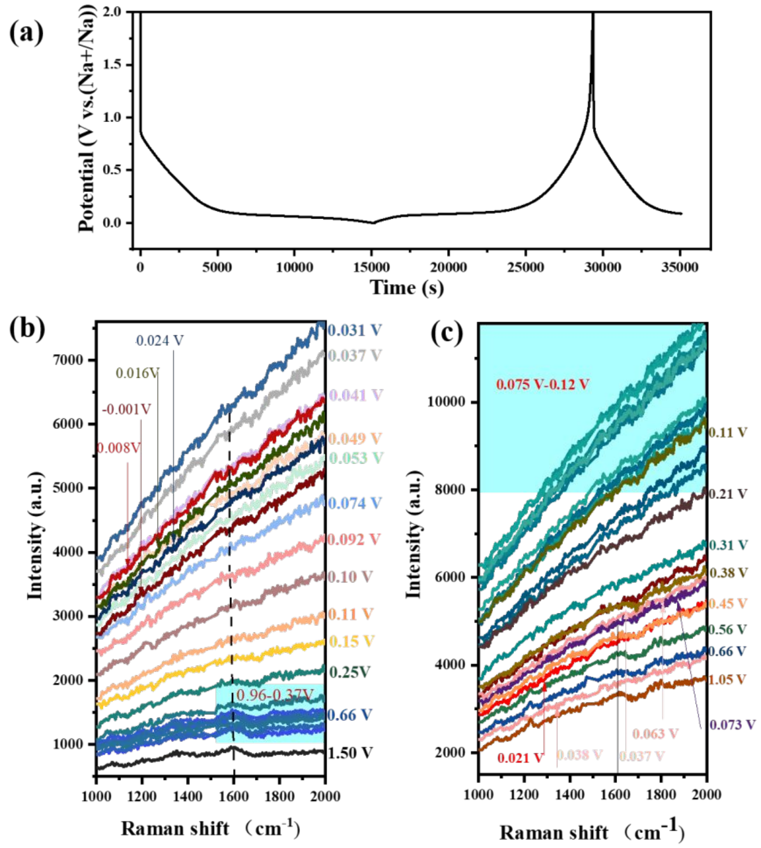

Figure S9. a) Charge and discharge vs. time of the first cycle and the slope section of the second cycle. *operando* Raman spectra of b) the discharge part of the first cycle and (c) the charge part of the first cycle. (The first discharge time was 15210 s with the calculated specific capacity ~ 253.6 mAh g^{-1}, the charging time was 14100 s with the calculated specific capacity ~ 235.10 mAh g^{-1}, and the ICE of the original cell was 92.7%)

Figure S9a shows the actual test curves of *operando* Raman spectroscopy. The reversible change of the G peak in the process of charge and discharge can be observed. We have plotted some of the data in Figure S9b. During discharging from 1.5 V to 0.1 V the position of the G peak will slowly move to lower wavenumbers, and the shape of peak and its width will change gradually, until the G peak almost disappears in the plateau region after 0.1 V. The gradual (reversible) decrease of the G peak position can be understood as due to the electron doping caused by the gradual addition and uniform diffusion of sodium in each layer. In addition, the intensity and background of the Raman curve increased continuously during the discharge from 0.25 V to 0.031 V, but the overall intensity of the Raman curve from 0.031 V to -0.001 V decreased suddenly. In the charging process, the peak intensity from 0.021 V to 0.063 V is low, but it increases sharply after 0.075 V and then decreases continuously after 0.11 V to 1.0 V during charging.

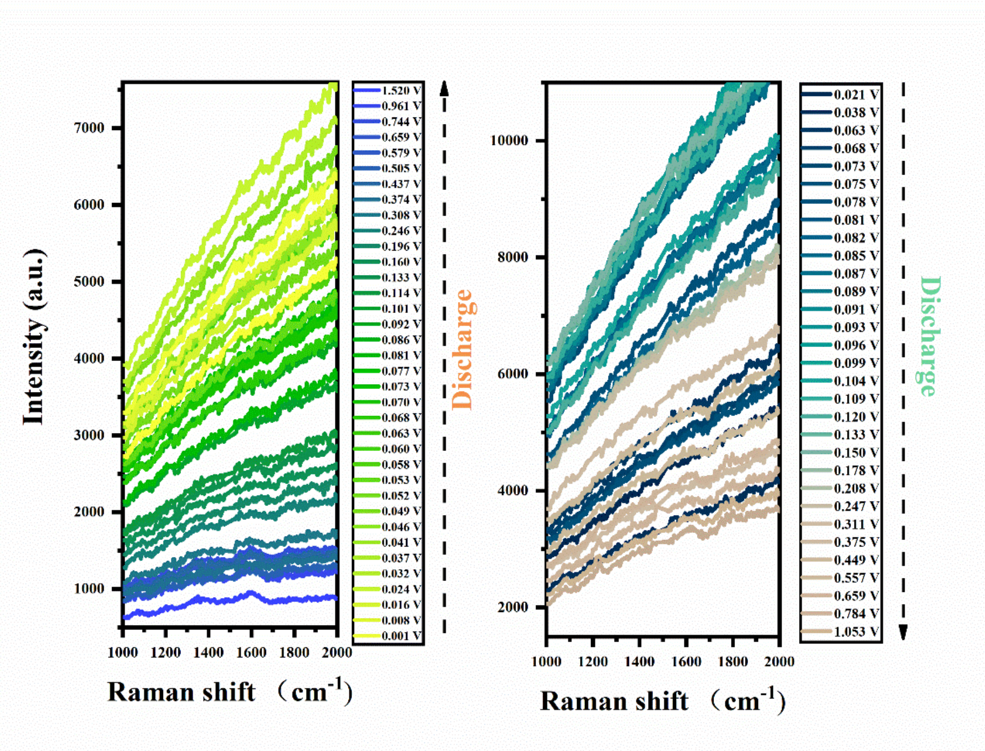

Figure S10. Full information of Operando Raman spectra of charge-discharge process.

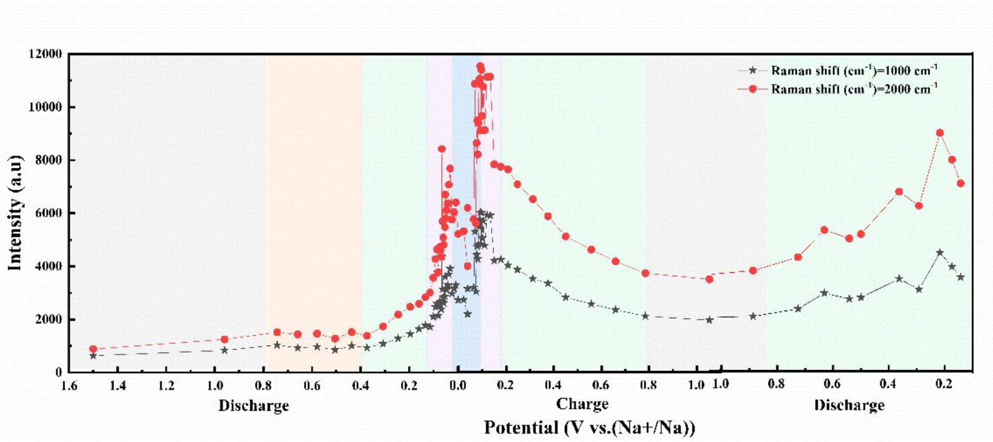

Figure S11. The periodic variation of the intensity of the charge-discharge of the first cycle and the slope of the second cycle at 1000 and 2000 cm^{-1} Raman shift

Table S1. Proportion of hard carbon and soft carbon before carbonization

Serial number	Quality of paper towel impregnated with DMF after solvent removal（mg）	Quality of paper towel impregnated with asphalt solution after removing DMF(mg)	Remarks
1	113.8	115.7	In this experiment, the weight of paper towels was all controlled to be the same, which was 111.9 mg
2	113.6	115.3	
3	114.2	115.8	
Average value	113.867	115.600	
Proportion of soft carbon before carbonization		1.52%	

Table S2. Proportion of hard carbon and soft carbon after carbonization

	Mass before carbonization(mg)		Mass after carbonization(mg)		Productivity
Number of experiments	1	2	1	2	
Quality of paper(mg)	329.2	337.3	42.3	43.2	12.83%
Total weight of asphalt and graphite boat (mg)	44890.0	45705.2	44398.2	45293.0	51.82%
graphite boat (mg)	43863.5 (Graphite boat for Experiment 1)	44854.2 (Graphite boat for Experiment 2)			
Proportion of soft carbon after carbonization			5.88%		