Supporting Information

π-π Stacking of Unsaturated Sulfonates on Natural Graphite Enables a Green and Cost-Effective Cathode for High-Voltage Dual-Ion Batteries

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Experimental Section

Preparation of sulfonate-modified NG: Natural graphite particles without any other carbon coatings (Qingdao Haida Graphite Co., Ltd., China) were used as the pristine electrode materials. The coating materials, sodium propyne sulfonate (PyS), sodium allyl sulfonate (AlS) and sodium propane sulfonate (PaS) were purchased from Adamasbeta Reagent Co., Ltd. and used as received. The different amounts of organic sulfonates (0.03, 0.05, and 0.07 g) were separately dissolved in 5 g of deionized water under stirring, and then 1 g of NG powder was added. Next, the mixed solutions were heated in a water-bath at 80 °C to evaporate the water and obtain an almost dry powder, which was further completely dried at 110 °C under vacuum.

Electrochemical measurements: To prepare the cathode slurry, the organic sulfonate-modified NG or bare NG, super P and polyvinylidene fluoride (PVDF) with a mass ratio of 8/1/1 were uniformly dispersed in N-methyl-2-pyrrolidone (NMP) with a high speed shearing machine. The slurry was coated onto Al foil current collector to obtain laminated cathodes, which were pre-dried at 60 °C for about 5 h and then cut into small discs. These discs were dried completely for 16 h at 120 °C in a vacuum oven and then moved into an argon-filled glovebox to assemble CR2032 coin-cells. The Li||NG cells were assembled with the organic sulfonate-modified NG or bare NG as cathode and lithium metal as counter electrode. The voltage of the cells was controlled in the region of 3.0-5.0 V or 3.0-5.4 V vs. Li/Li$^+$. 4.0 M LiPF$_6$ dissolved in ethyl methyl carbonate (EMC) and glass fiber filters were used as electrolyte and separator, respectively.

The Si||NG cells were assembled using prelithiated Si electrodes as anodes. The

Si anode slurry was prepared by mixing Si, polyvinyl alcohol (PVA) and super P (weight ratio: 7/2/1) in deionized water. The anode slurry was coated on Cu foil current collector. The Si anode and NG cathode laminates were cut into small discs and the diameters of the anode and cathode discs are 14 and 13 mm, respectively. The loading of NG cathodes was about 2.8 mg cm^{-2}, and that of Si anodes was about 0.7 mg cm^{-2}. The Si anodes were first prelithiated through electrochemical cycling of the Li||Si half cells at the current density of 210 mA g^{-1} for 8 cycles in the potential region of 1.5-0.01 V vs. Li/Li$^+$ and then discharging them at a current density of 200 mA g^{-1} for 10 h. The charge/discharge voltage region of Si||NG cells was controlled within 3.0-5.0 V.

Computational Methods: RDG simulation was used to investigate the available interactions between sulfonates and graphite layers through the Gaussian 16 program. Geometry optimization calculations were performed by using the 6-311g+(d, p) DFT method.[1] In order to hypothesize the interactions well, RDG plots were plotted using Multiwfn 3.8 and VMD 1.9.3 software.

The adsorption energies calculations were performed by using the Vienna Ab-initio Simulation Package (VASP).[2] The exchange-correlation interactions were described by generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) function.[3] Spin-polarization was included in all the calculations and a damped van der Waals correction was incorporated using Grimme's scheme to better describe the non-bonding interactions.[4] The cut-off energies for plane waves were set to be 500 eV, and the residual force and energy on each atom during structure relaxation were converged to 0.005 eV Å^{-1} and 10^{-5} eV, respectively. The adsorption energy (E_a) is

defined as $E_a = E_{A+B} - (E_A + E_B)$, where E_{A+B} is the total energy of combined A and B, $E_A + E_B$ is the sum of the total energies of A and B before combination. A and B refer to the sulfonates and (002) planes of graphite, respectively.
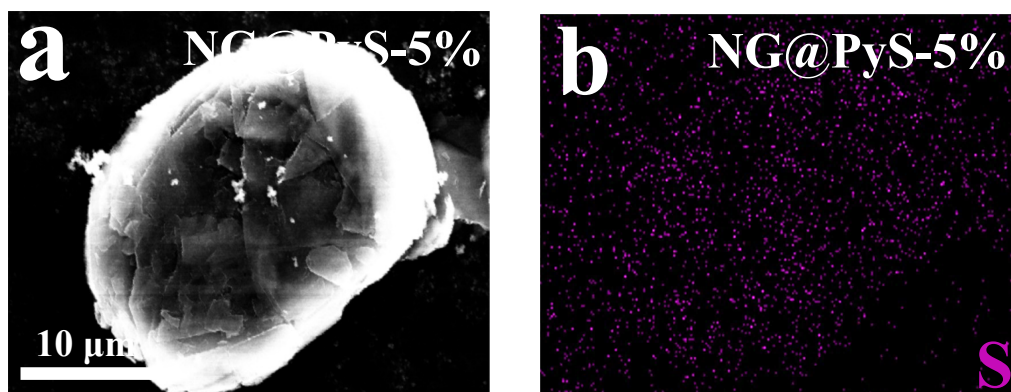
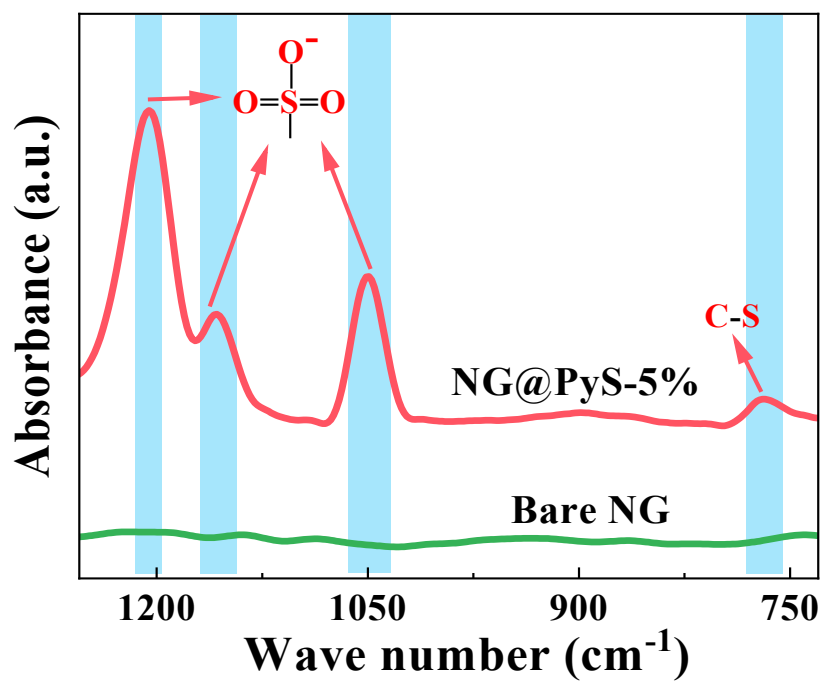**Figure S1.** The SEM image and EDX element map of NG@PyS-5% sample.

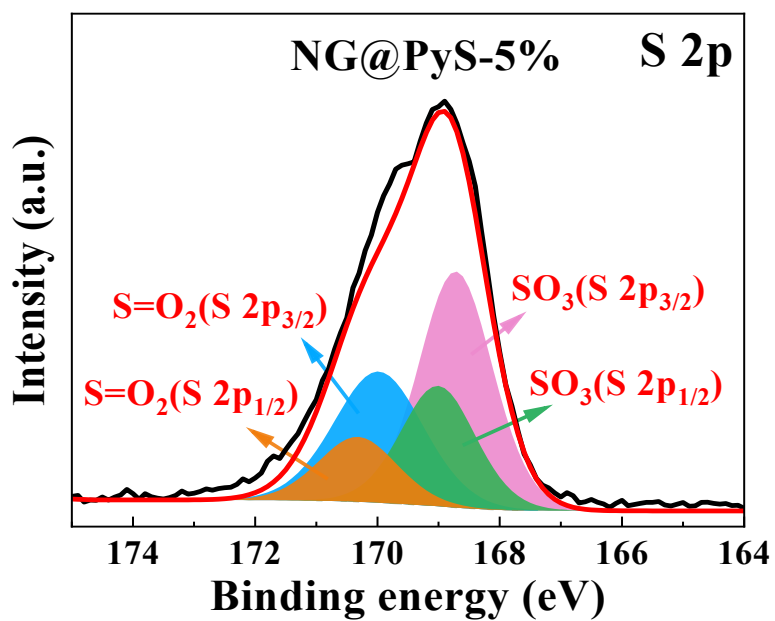**Figure S2.** FTIR spectra of bare NG and a NG@PyS-5% sample.

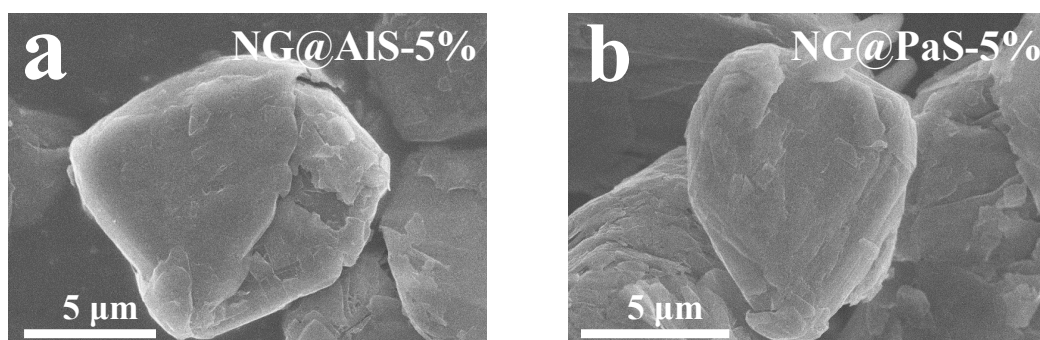**Figure S3.** XPS spectra of NG@PyS-5% sample in the core-level region of S 2p.

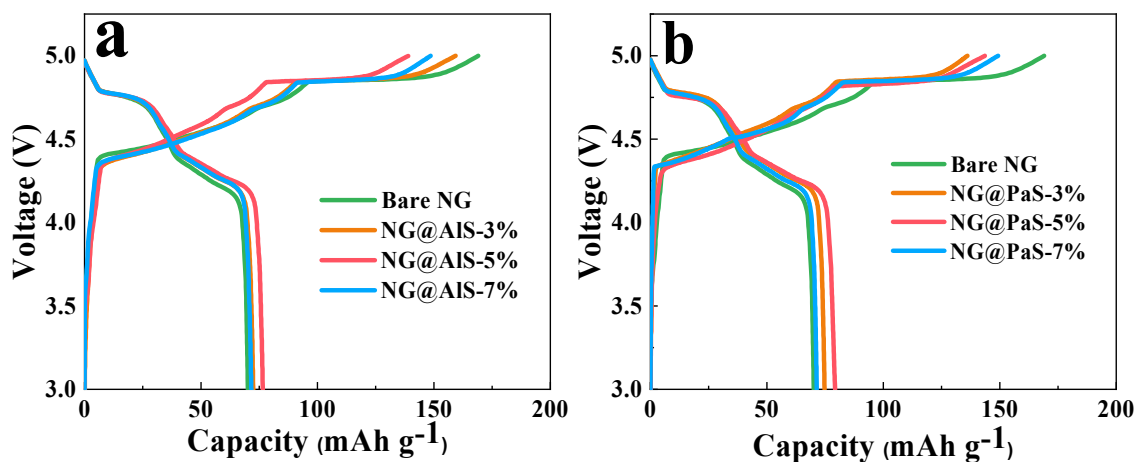**Figure S4.** SEM images of uncycled (a) NG@AlS-5% and (b) NG@PaS-5% cathodes.

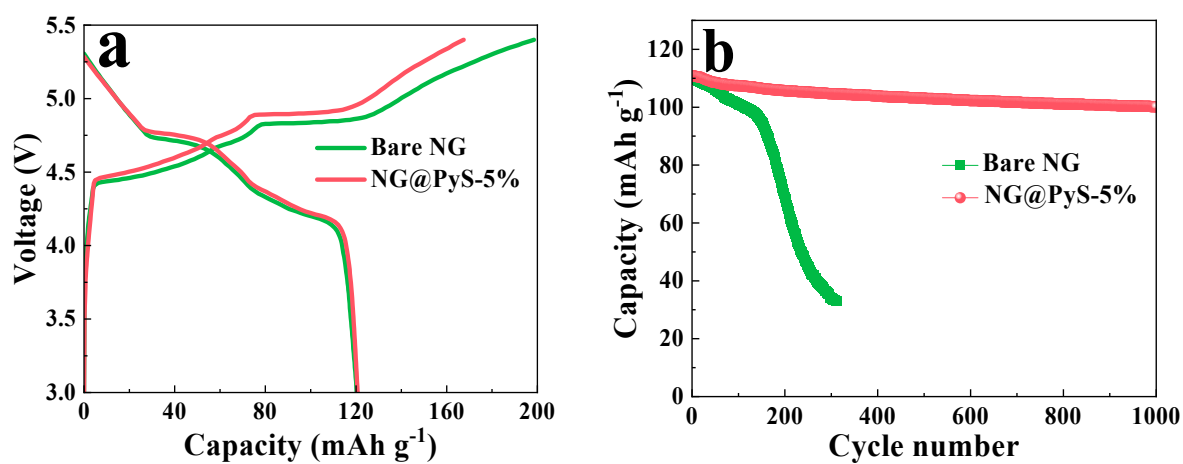**Figure S5** The charge/discharge profiles of different NG cathodes during the first cycle at 0.1 C.

Figure S6. (a) The charge/discharge curves of different NG cathodes during the first

cycle at 0.1 C between 3.0 and 5.4 V, (b) the long-term cycle performance of different

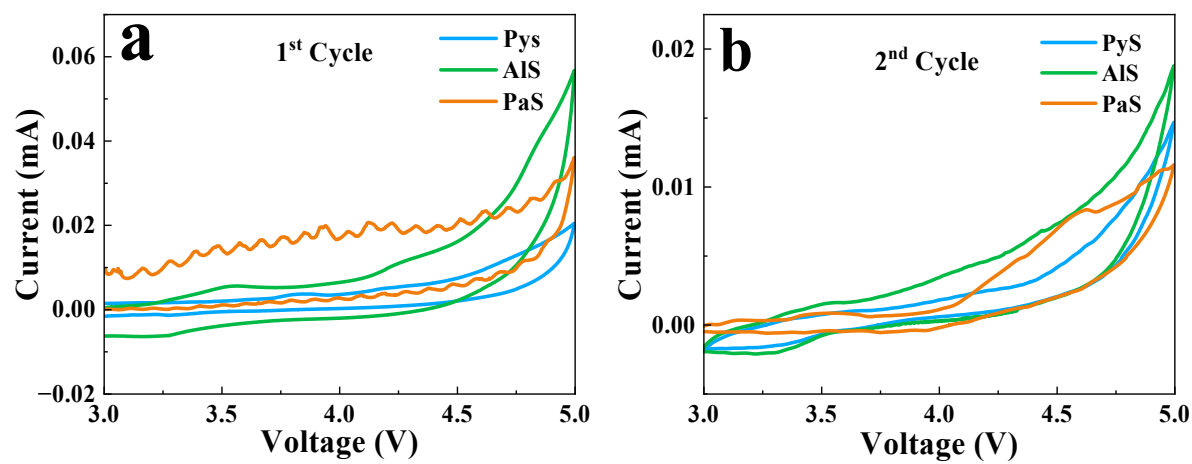NG cathodes at the current rate of 1 C.

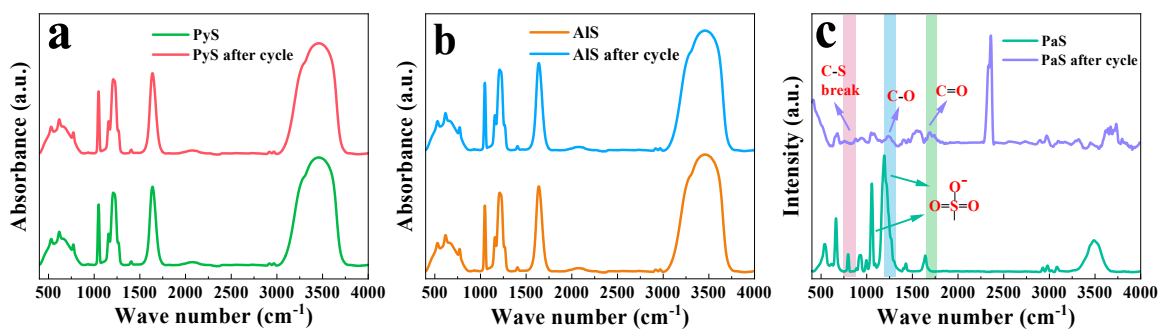**Figure S7.** CV curves of pure PyS, AlS and PaS electrodes.

Figure S8. FTIR spectra of pure (a) PyS, (b) AlS and (c) PaS electrodes before and after electrochemical cycling.
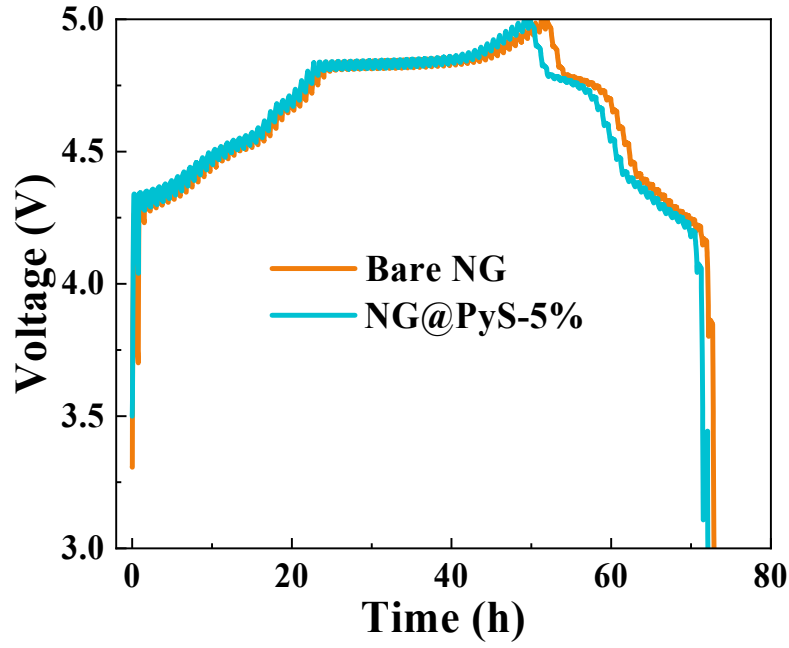
Figure S9. The GITT tests of different NG cathodes.

D_{app} was calculated through GITT using equation (1).

$$\frac{4}{\pi\tau}\left(\frac{m_B V_M}{M_B S}\right)^2\left(\frac{\Delta E_s}{\Delta E_t}\right)^2 \quad \left(\tau \ll \frac{L^2}{D}\right) \tag{1}$$

where τ is the constant current titration time; V_M represents the molar volume of active materials; m_B refers to the weight of active materials; M_B means molecular weight of active materials; S is the electrode surface area; ΔE_s indicates the steady-state voltage change after a current disturbance; ΔE_t is the voltage change during the constant current titration.[5]
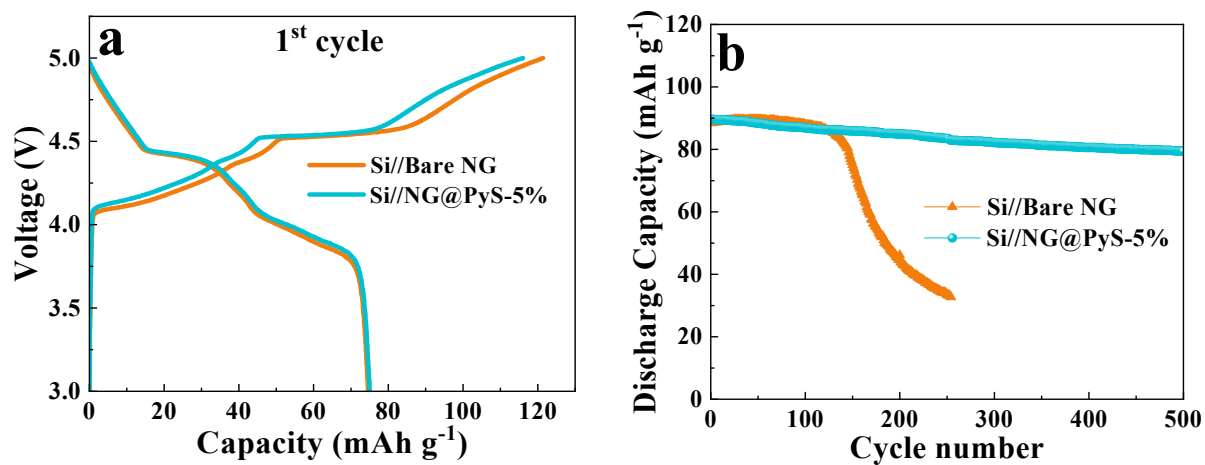
Figure S10. The electrochemical performance of Si‖bare NG and Si‖NG@PyS-5% cells: (a) the first galvanostatic charge/discharge profiles at 0.1 C and (b) long-term cycle performance at 1 C rate.
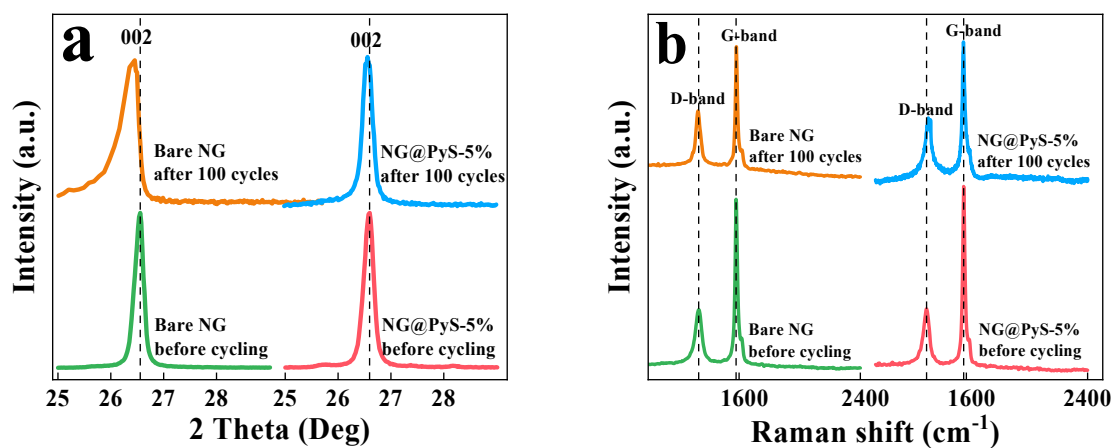
Figure S11. (a) XRD patterns and (b) Raman spectra of bare NG and NG@PyS-5% cathodes before and after long-term cycling.
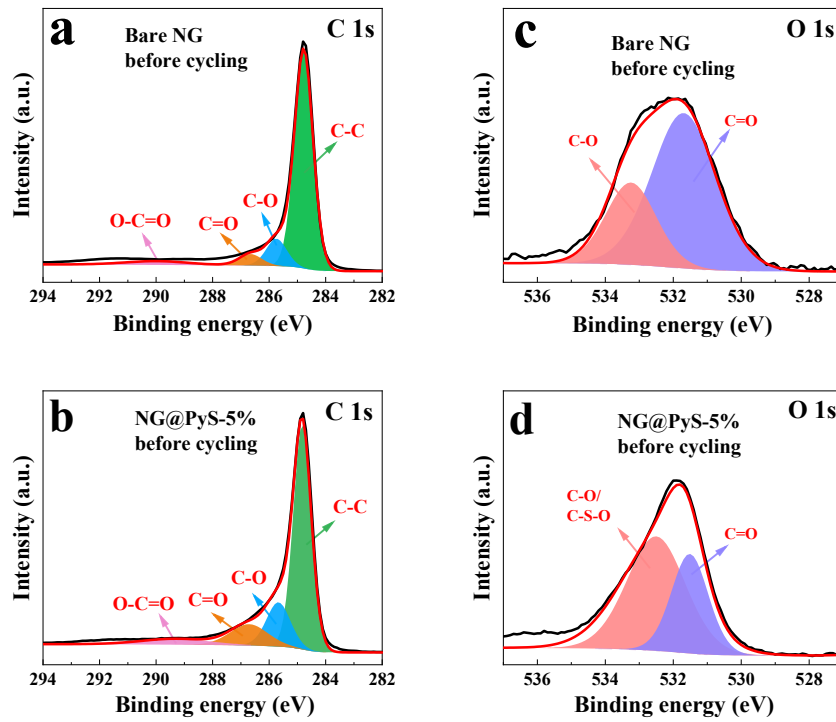
Figure S12. XPS spectra of bare NG and NG@PyS-5% before cycling in the core-level regions of C 1s and O 1s.

Table S1. The resistance data of the Li‖NG cells with bare NG and NG@PyS-5% cathodes.

Samples	Bare NG		NG@PyS-5%	
Cycles	3th	100th	3th	100th
R_{CEI} (Ω)	36.2	338.3	21.2	27.6
R_{ct} (Ω)	148.5	272.3	76.4	80.5

References

[1] Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.* **2008**, *120*, 215.

[2] a) G. Kresse, J. Furthmuller, *Comput. Mater. Sci.* **1996**, *6*, 15; b) G. Kresse, J. Furthmuller, *Phys. Rev. B* **1996**, *54*, 11169.

[3] a) J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865; b) J. P. Perdew, M. Ernzerhof, K. Burke, *J. Chem. Phys.* **1996**, *105*, 9982.

[4] S. Grimme, *J. Comput. Chem.* **2006**, *27*, 1787.

[5] W. H. Li, Q. L. Ning, X. T. Xi, B. H. Hou, J. Z. Guo, Y. Yang, B. Chen, X. L. Wu, *Adv. Mater.* **2019**, *31*, 1804766.