Uniform Lithium Nucleation/Deposition Regulated by N/S Co-doped Carbon Nanospheres towards Ultra-stable Lithium Metal Anodes

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1. Materials and Methods

1.1 Preparation of NSMC

First, 0.12 g of phenol, 0.64 g of 4-hydroxythiophenol, and 0.8 g of melamine were dissolved in 15 mL of 0.1 M NaOH aqueous solution under magnetic stirring at 350 rpm for 30 min. This solution was heated at 50 °C in an oil bath and then 4.2 mL of aqueous formaldehyde solution (37 wt%) was added and stirred at 70 °C for 60 min. Subsequently, 0.96 g of triblock copolymer pluronic F127 (Mw = 12600) in 15 mL of deionized (DI) water was added and further stirred at 66 °C for 120 min. Then, the mixture was diluted with 50 mL of DI water and stirred at 70 °C for 16–18 h. The solution was rested until the precipitate settled and the supernatent became clear. Then, 112 mL of DI water and 36 mL of the supernatent were added to a 250-mL Teflon-lined autoclave and then heated at 130 °C for 24 h. After cooling to room temperature naturally, the obtained precipitate was washed with ethanol and water several times, and dried in a vacuum oven at 80 °C for 24 h to obtain a light-yellow powder. The following calcination process was performed in steps. First, the powder was calcinated at 380 °C for 6 h with a heating rate of 2 °C min^{-1}. Then, the temperature was increased to 600 °C at a rate of 1 $^{o}C\ min^{-1}$, and then to 800 °C at 5 °C min^{-1}, followed by a hold time of 3 h at this temperature. Finally, the N/S-co-doped ordered mesoporous carbon nanospheres (NSMC) was obtained after to room temperature. The control samples were synthesized via the same method with the following molar ratios of phenol, melamine, and 4-hydroxythiophenol: 10:0:0, 5: 5:0, 5:0:5, 2:4:4, 0:6:4, 2.5:5:2.5, and 0:5:5 giving samples MC, NMC, SMC, N_1SMC, N_2SMC, NS_1MC, and NS_2MC respectively.

2. Characterizations and Calculation

2.1 Material characterizations

Small-angle X-ray scattering (SAXS) datas were obtained on a Xeuss2.0 system (Xenocs, France), Nitrogen adsorption–desorption isotherms were measured at -196 ^{o}C using a TriStar II 3020 V1.03 analyzer. All samples were degassed at 120 °C for 6 h before measurement. Elemental analysis (EA) was performed using a Vario EL cube elemental analyzer from Elementar (Germany). X-ray photoelectron

spectrometry (XPS) was performed using a Perkin Elmer PHI5000 ESCT System with an Al Kα (1486.6 eV) excitation source. Transmission electron microscopy (TEM) was performed using a JEOL-2100 with a LaB_6 filament at an accelerating voltage of 200 kV. Field-emission scanning electron microscopy (FE-SEM) images were obtained using a Hitachi S-4800 system at 5.0 kV. Raman spectroscopy (LabRam 11, Dilor Company) was performed over a spectral scanning range of 50–1000 nm. Cyclic voltammetry (CV) tests were performed using a Bio-Logic-Science Instruments setup.

2.2 Electrochemical characterizations

The electrochemical performance tests were carried out using a battery test system (CT 2001A, LAND) at various current densities. CR2032-type coin cells (MTI Corporation) were assembled in an argon-filled glove box. The water and oxygen contents in the glove box were both less than 0.1 ppm. NSMC (80 wt%), Super-P (10 wt%), and polyvinylidene fluoride (10 wt%) were mixed in N-methylpyrrolidone (NMP) to form a uniform slurry. The slurry was coated on the copper foil with a doctor blade, and dried at 100 °C for 12 h under vacuum to prepare NSMC electrodes. The MC, NMC, SMC, N_1SMC, N_2SMC, NS_1MC, and NS_2MC electrodes were prepared using the same process. The loading of the active substance was approximately 1.0 mg cm^{-2} in all cases. The electrode sheet was punched into discs with a diameter of 12 or 14 mm. 1M lithium hexafluorophosphate ($LiPF_6$) in 1:1 (v/v) ethylene carbonate (EC)/dimethyl carbonate (DMC), and 10 vol% ethylene fluoride carbonate (FEC) was used as the electrolyte. To evaluate the cycling stability and Coulombic efficiency, asymmetric cells were assembled with NSMC as the working electrode and Li foil as the counter electrode. These cells were initially cycled for 10 cycles at a current density of 0.05 mA cm^{-2} over a voltage range of 0.01 to 1 V (vs. Li^+/Li). All electrodes were pre-deposited for 6 or 25 mAh cm^{-2} at 0.5 mA cm^{-2}.

$LiFePO_4$ (LFP) electrodes were prepared using commercial LFP (80 wt%), Super-P (10 wt%), and polyvinylidene fluoride (10 wt%) in NMP to form a uniform slurry. The slurry was coated on an aluminum film with a doctor blade and then dried at 100 °C for 12 h under vacuum. The electrode sheet was punched into a disc with a

diameter of 12 mm. The loadings of LFP were approximately 5 or 11 mg cm^{-2}.

2.3 Theoretical Calculation

All first-principles calculations were performed within the Vienna Ab Initio Simulation Package (VASP)[1] based on density functional theory (DFT). The projector augmented wave (PAW)[2] potentials were used to deal with the electronic exchange-correlation interaction along with the GGA functional in the parameterization of the Perdew Burke and Ernzerhof (PBE)[3] pseudopotential. A plane wave representation for the wave function with a cut-off energy of 450 eV was applied. Geometry optimizations were performed using conjugate gradient minimization until all forces acting on the ions were less than 0.02 eV $Å^{-1}$ per atom. A 15 Å vacuum in the *z* direction was used to separate the slabs. In the calculations, a k-point mesh with a spacing of around 0.03 $Å^{-1}$ was adopted. Spin polarization was included for the correct description of magnetic properties. The long-range interactions (DFT-DF3) were considered as a correction for all calculations.

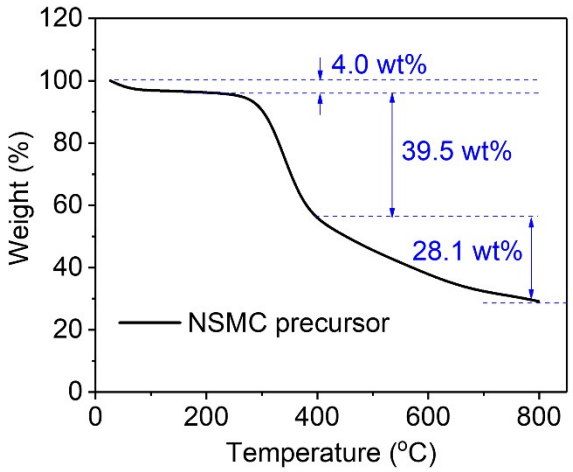


Fig. S1. TGA curve of NSMC precursor achieved under Ar atmosphere with heating rate of 5 °C min^{-1}.

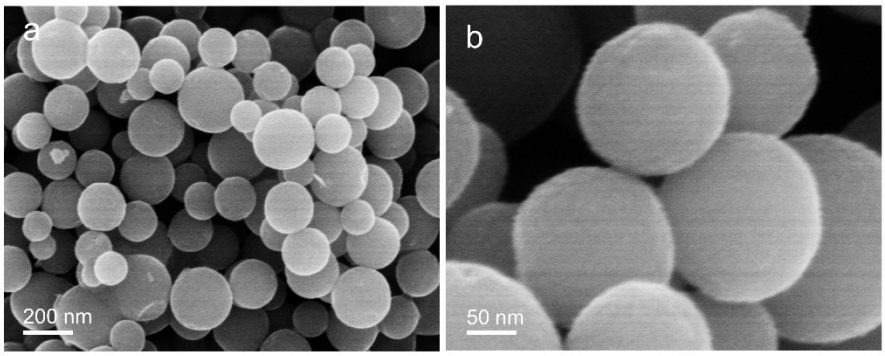


Fig. S2. SEM images of NSMC.

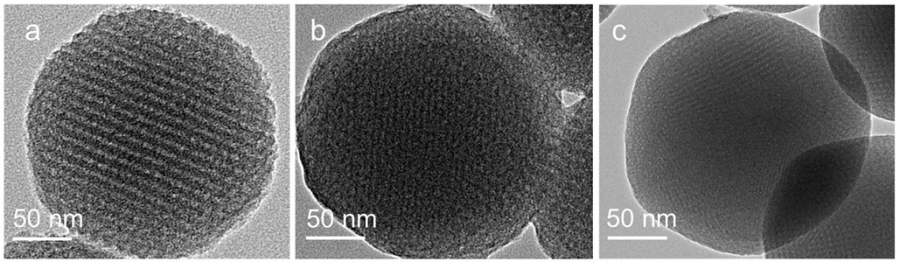


Fig. S3. High-resolution TEM images of (a) MC, (b) NMC and (c) SMC samples.

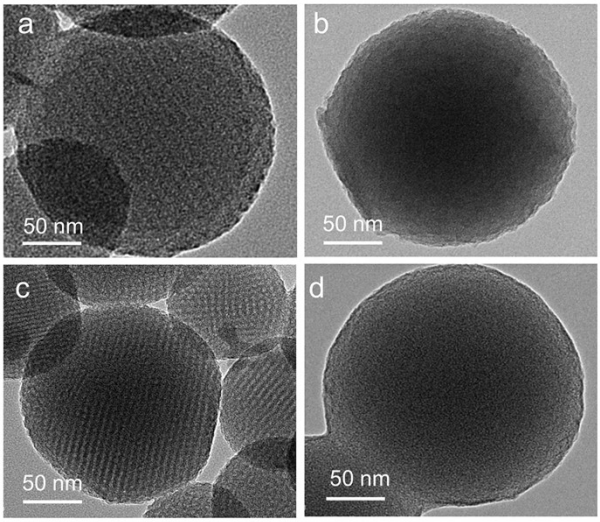


Fig. S4. High-resolution TEM images of (a) N_1SMC, b) N_2SMC, (c) NS_1MC and (d) NS_2MC.

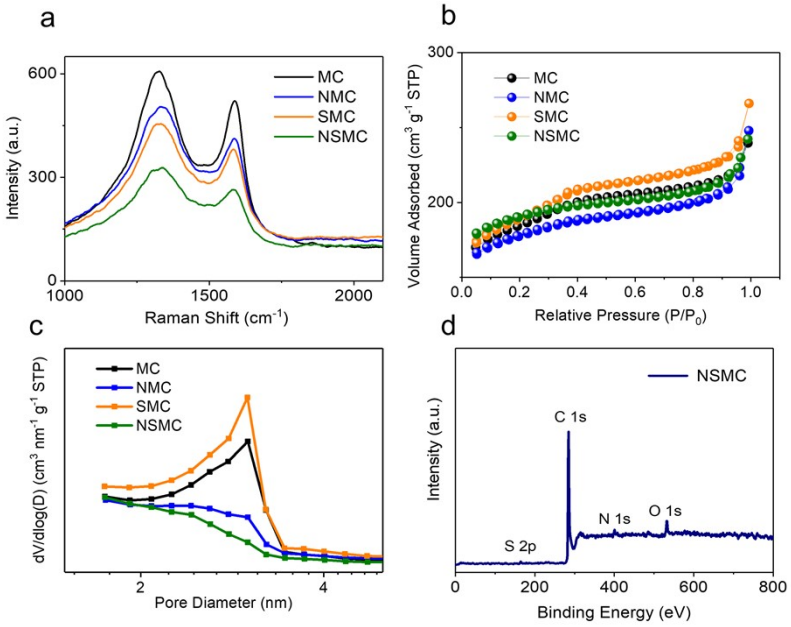


Fig. S5. (a) Raman spectra, (b) nitrogen absorption–desorption isotherms and (c) pore size distributions calculated using the Barrett–Joyner–Halenda method for MC, NMC, SMC, and NSMC. (d) XPS survey scan for NSMC.

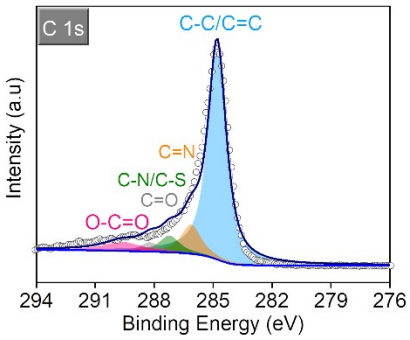


Fig. S6. XPS spectra of C 1s of NSMC.

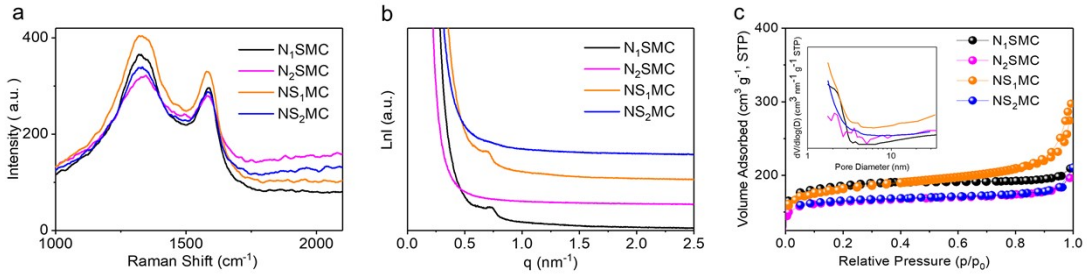


Fig. S7. (a) Raman spectra, (b) small-angle X-ray scattering patterns, and (c) nitrogen absorption–desorption isotherms (inset: pore size distribution calculated using the Barrett–Joyner–Halenda method for N_1SMC, N_2SMC, NS_1MC, and NS_2MC.

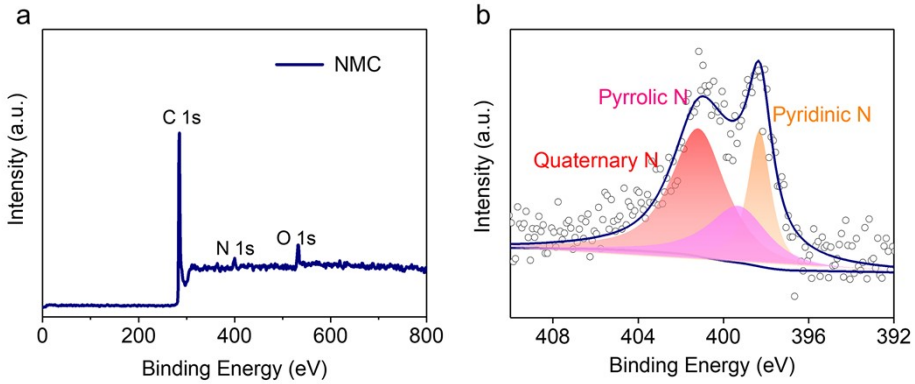


Fig. S8. XPS spectra of (a) survey scan and (b) N 1s of NMC.

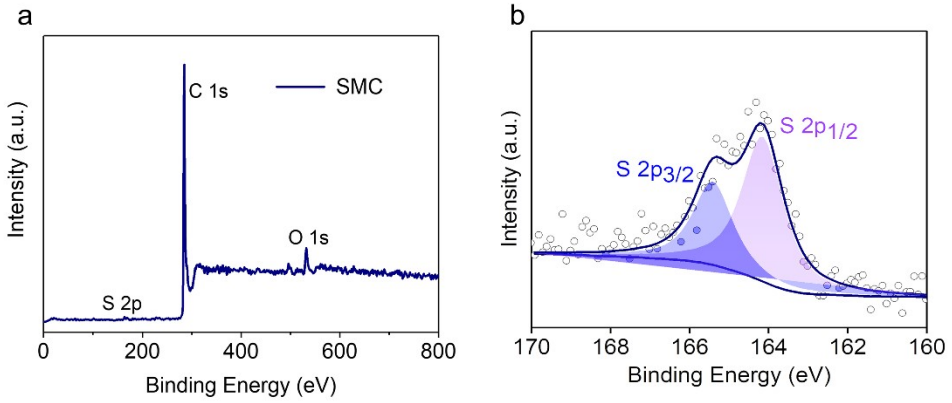


Fig. S9. XPS spectra of (a) survey scan and (b) S 2p of SMC.

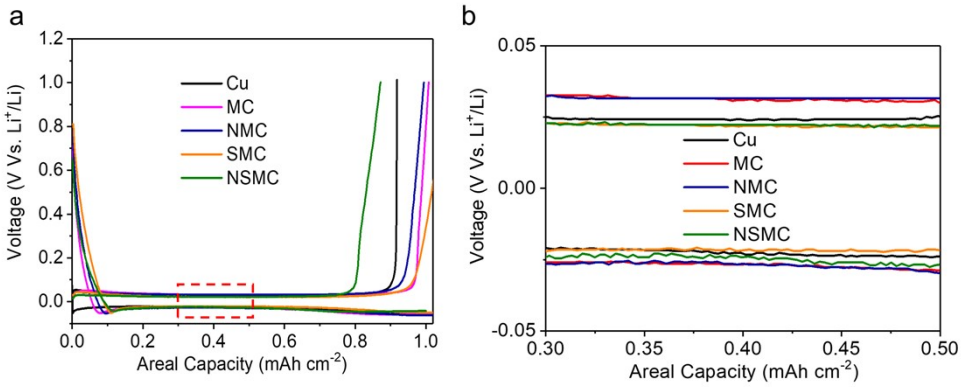


Fig. S10. (a) Voltage–capacity profiles of Cu, MC, NMC, SMC, and NSMC electrodes and (b) the corresponding enlarged view indicated by the box in (a).

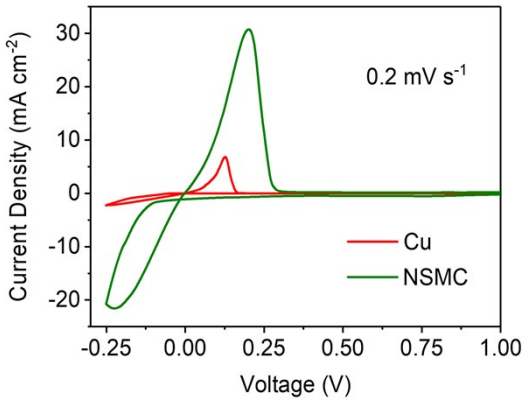


Fig. S11. (a) CV curves of bare Cu and NSMC electrodes with a cutoff voltage of -0.25–1 V at a scanning rate of 0.2 mV s^{-1}.

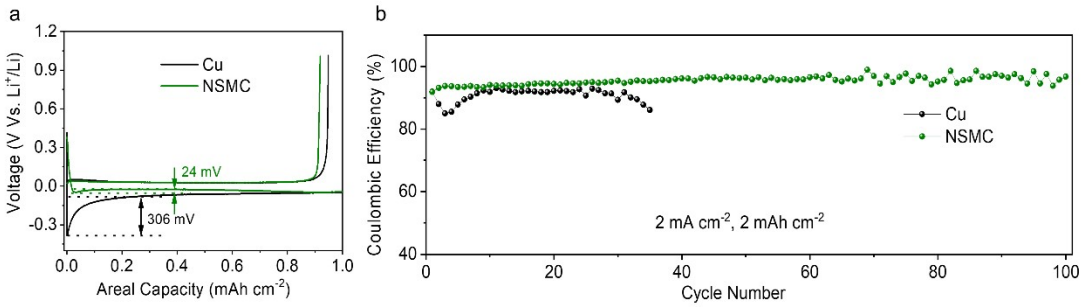


Fig. S12. (a) Initial voltage-capacity profiles and (b) Coulombic efficiencies of Cu and NSMC electrodes at 2 mA cm^{-2} and 2 mAh cm^{-2}.

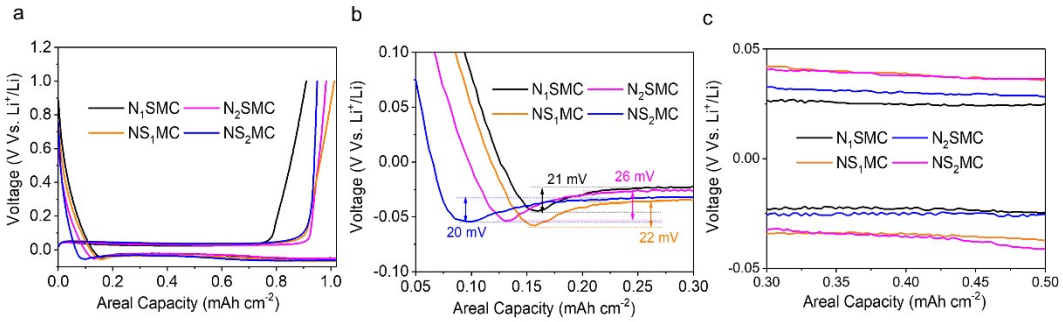


Fig. S13. (a) Initial voltage-capacity profiles and (b and c) corresponding enlarged views of N_1SMC, N_2SMC, NS_1MC, and NS_2MC electrodes at 1 mA cm^{-2} and 1 mAh cm^{-2}.

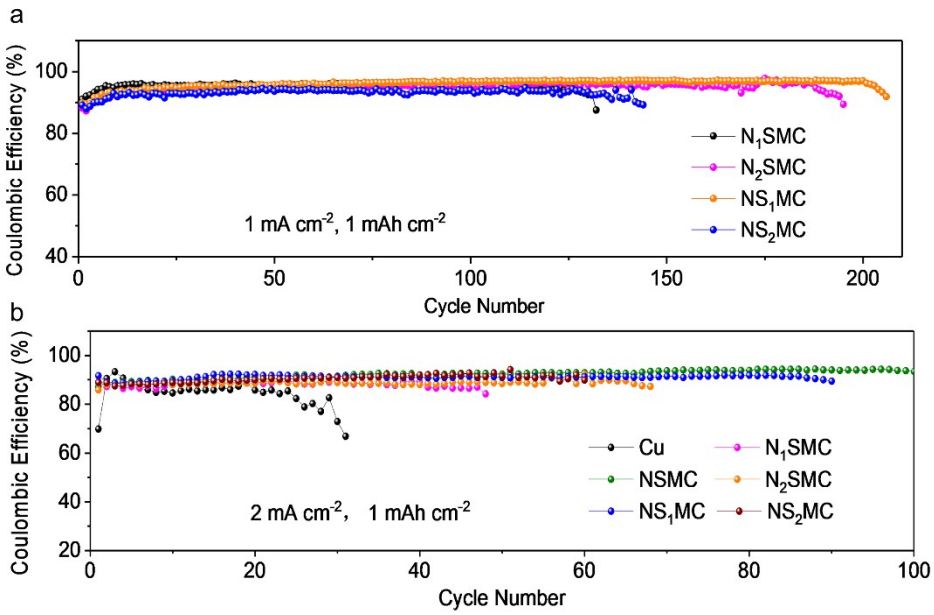


Fig. S14. (a) Coulombic efficiencies of N_1SMC, N_2SMC, NS_1MC, and NS_2MC electrodes at 1 mA cm^{-2} and 1 mAh cm^{-2}. (b) Coulombic efficiencies of Cu, NSMC, N_1SMC, N_2SMC, NS_1MC, and NS_2MC electrodes at 2 mA cm^{-2} and 1 mAh cm^{-2}.

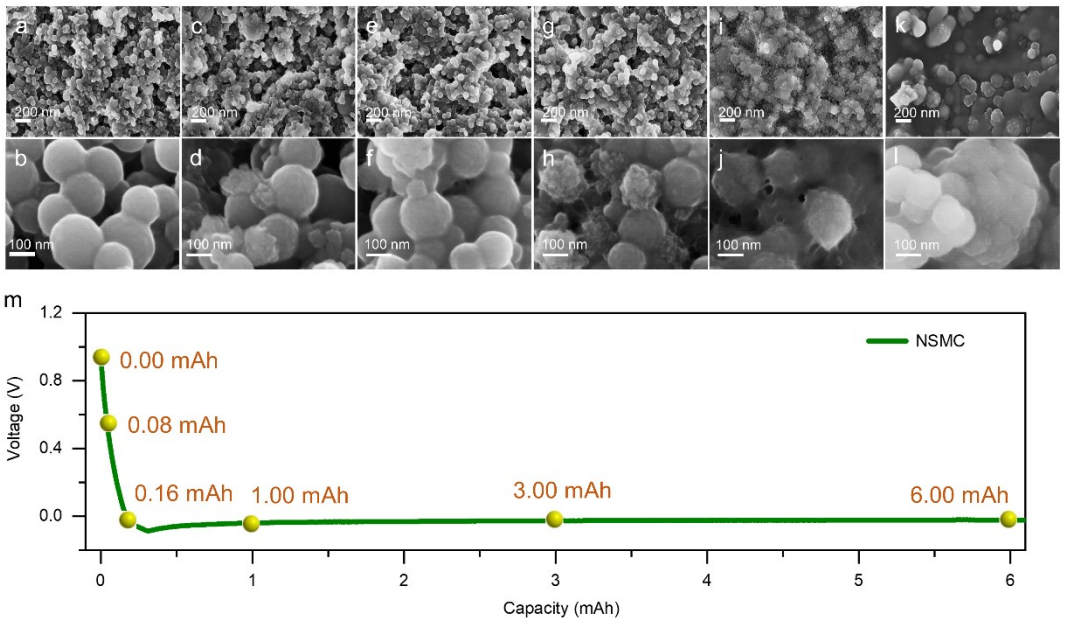


Fig. S15. SEM images of NSMC electrode at lithium depostion capacity of (a, b) 0.00 mAh, (c, d) 0.08 mAh, (e, f) 0.16 mAh, (g, h) 1 mAh, (i, j) 3 mAh, (k, l) 6 mAh. (m) Corresponding votage-capacity curve of NSMC electrode.

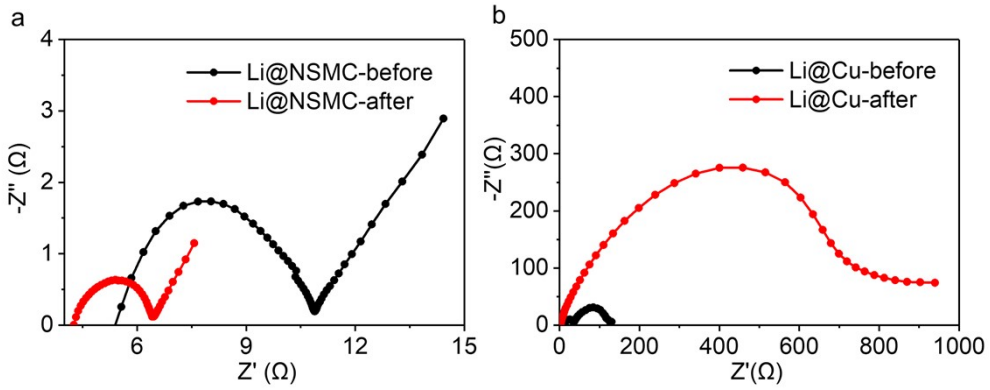


Fig. S16. Nyquist plots of (a) Li@NSMC and (b) Li@Cu electrodes in symmetric cells before and after 10 cycles at 1 mA cm^{-2} and 4 mAh cm^{-2}.

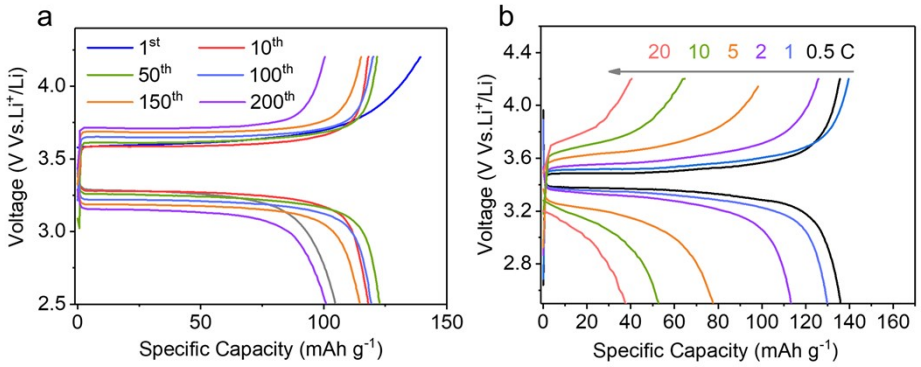


Fig. S17. Charge–discharge curves of LFP|Li@Cu full cells at (a) 2 C (for selected cycles) and (b) various rates.

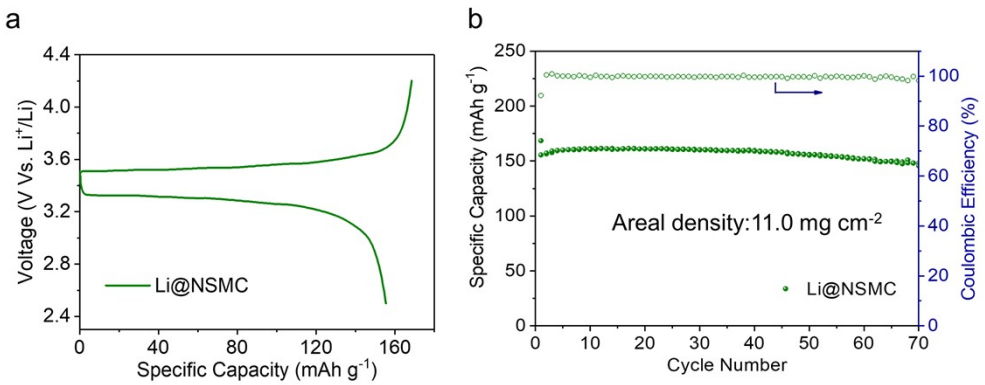


Fig. S18. (a) Charge–discharge curves and (b) cycling performance of LFP|Li@NSMC full cells at 0.5 C.

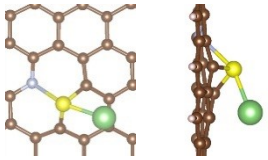
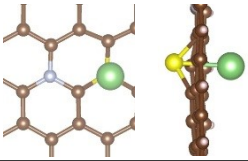
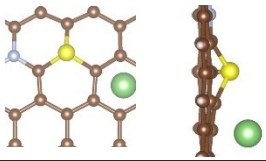
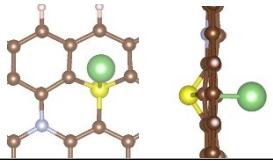
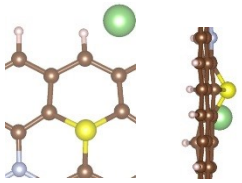
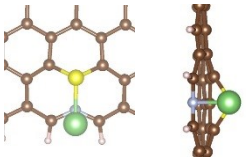
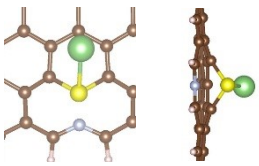
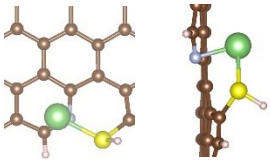
Table S1. N and S content, surface area, pore size, and pore volume of MC, NMC, SMC, and NSMC materials.

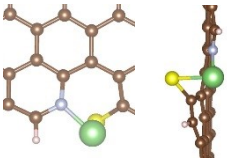
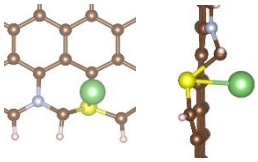
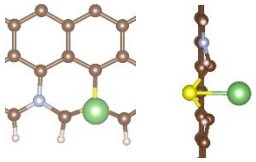
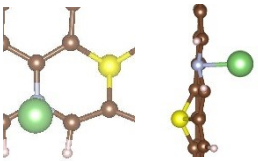
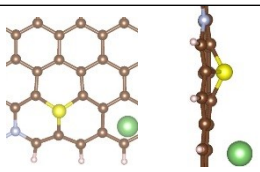
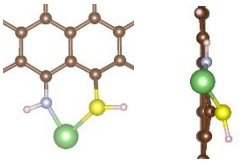
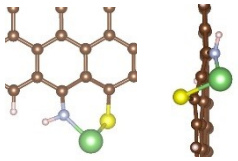
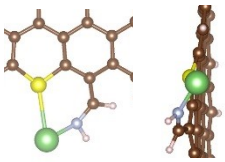
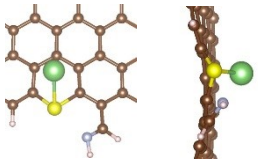
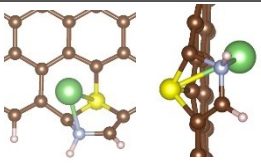
Sample	Molar ratio (phenol: melamine: 4-hydroxythiophenol)	N content (wt%)	S content (wt%)	BET Surface Area ($m^2 g^{-1}$)	Pore Size (nm)	Pore Volume ($cm^3 g^{-1}$)
MC	10:0:0	0	0	589	2.55	0.37
NMC	5:5:0	5.89	0	569	4.82	0.12
SMC	6:0:4	0	0.78	584	4.22	0.62
NSMC	1:5:4	6.05	0.92	541	2.52	0.34

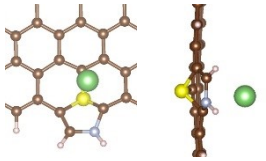
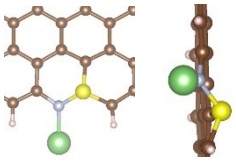
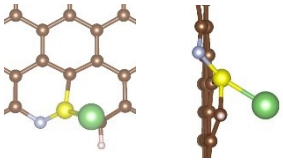
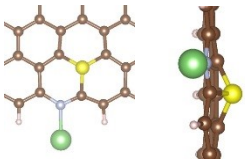
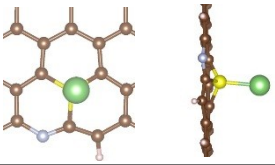
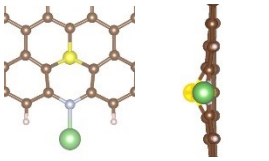
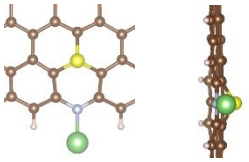
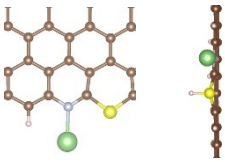
Table S2. N/S content, surface area, pore size. and pore volume of N_1SMC, N_2SMC, NS_1MC, and NS_2MC materials.

Sample	Molar ratio (phenol: melamine: 4-hydroxythiophenol)	N content (wt%)	S content (wt%)	BET Surface Area ($m^2 g^{-1}$)	Pore Size (nm)	Pore Volume ($cm^3 g^{-1}$)
N_1SMC	2:4:4	4.93	0.88	569	2.72	0.32
N_2SMC	0:6:4	7.92	0.86	483	3.11	0.23
NS_1MC	2.5:5:2.5	6.10	0.61	556	2.72	0.37
NS_2MC	0:5:5	5.96	1.14	457	2.85	0.33

Table S3. Possible N/S co-doping models and their corresponding adsorption Energy, bond lengths, and geometrical configuration.

Models		Adsorption Energy (eV)	Li-N Bond Length (Å)	Li-S Bond Length (Å)	Geometrical Configuration
bqN	1-1	-4.16	2.04	2.35	
	1-2	-4.06	4.77	2.37	
	2-1	-2.66	3.10	2.56	
	2-2	-2.35	5.82	3.35	
	3-1	-2.75	4.19	2.90	
	3-2	-2.40	6.92	4.41	
eqN	1-1	-3.71	1.97	2.38	
	1-2	-3.68	4.78	2.39	
	2-1	-1.83	2.08	2.38	

	2-2	-2.37	1.98	2.39	
	3-1	-2.30	3.03	2.64	
	3-2	-2.56	3.26	2.58	
	4-1	-1.50	2.04	4.26	
	4-2	-2.18	6.80	4.16	
pN	1-1	-1.74	1.98	2.36	
	1-2	-1.43	1.97	2.49	
	2-1	-3.24	1.96	2.84	
	2-2	-1.97	4.27	2.41	
	3-1	-3.08	2.09	2.93	

	3-2	-1.73	3.58	3.70	
rN	1-1	-2.18	1.98	3.20	
	1-2	-0.71	3.85	2.35	
	2-1	-2.98	2.07	4.58	
	2-2	-0.41	4.27	2.38	
	3-1	-3.11	1.99	4.89	
	3-2	-2.70	1.98	4.72	
	4-1	-2.48	2.17	3.22	
	4-2	-0.94	3.53	2.92