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Supporting information

Spatial Separation of Lithiophilic Surface and Superior Conductivity for Advanced Li Metal Anode: The Case of Acetylene Black and N-Doped Carbon Spheres

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Figures of Content:

Experimental Section

Preparation of N-doped carbon submicrospheres (NCS)

Typically, 0.6 mL of aqueous ammonia (NH_4OH, Sinopharm Chem., 28-30%), 90 mL of deionized water and 40 mL of ethanol (Sinopharm Chem., 99.7%), were mixed and stirred for 30 min at 30 ^oC. Then, 10 mL of 263.7 mM dopamine hydrochloride (Aladdin, 98%) was added into this solution. 30 h later, the dark brown precipitate was obtained by centrifugation and rinse three times by deionized water. Finally, the precipitate was dried at 60 ^oC overnight and calcined at 800 ^oC for 1 h in Ar.[1] The resultant powders were collected for structure characterization and Li anode protection.

Structure and Component Characterization of NCS

Powder XRD patterns were obtained on a Bruker D8 X-ray diffractometer with graphite-monochromatized Cu Kα line as a radiation source (λ=1.5418 Å). Scanning electron microscope (SEM) images were recorded on a field-emission scanning electron microscope (Zeiss Gemini 300, Germany) with an energy dispersive X-ray (EDX) spectrometer (Bruker Quantax 200, Germany). Transmission electron microscope (TEM) images and high-resolution transmission electron microscope (HRTEM) images were acquired from transmission electron microscopes (JEOL JEM 1011 and JEOL 2100F, Japan). Raman spectra were measured on a LABRAM-HR confocal laser MicroRaman spectrometer, using an excitation wavelength of 514.5 nm as an excitation. N_2 sorption isotherms were achieved on an ASAP 2020 HD88 surface area and porosity analyzer at 77 K. X-ray photoelectron spectra (XPS) was taken from ESCALAB 250 X-ray photoelectron spectrometer using monochromatic Al Kα radiation. Digital four probe SZ82 tester was used to test the electrical resistivity of NCS and AB respectively.

Electrochemical Performances

The electrochemical performances of Li anode modified by NCS and acetylene black (AB) were investigated with CR2032-type coin cells. In half cells, the working electrode was made of 80 wt% of NCS, 10 wt% of AB, and 10 wt% of SA (sodium alginate). These materials were milled in a trace of deionized water, until they lead to a viscous slurry. Then, the slurry was cast on a clean Cu foil and dried in vacuum at 60 ^{o}C for 24 h. The average mass loadings of NCS and AB on the Cu foil were approximately ~0.8 and ~ 0.1 mg cm^{-2}. Finally, this foil was roll pressed and pouched into small discs with a diameter about 12 mm as the working electrodes. These working electrodes were coupled with Celgard 2400 membrane as the separator, and Li foil as the counter electrode in an argon-filled glove box (Mikrouna, Super 1220/750/900). Meanwhile, the electrolyte, *i.e.* 1 M lithium bis(tri-fluoromethane-sulphonyl)imide (LiTFSI) in 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) (volume ratio 1:1) containing 2% of lithium nitrate, were added to wet the separator. Galvanostatic cycling was conducted on a battery cyclor (Land CT2001A, China) at room temperature. The controls, where only NCS or AB was involved in the recipe, were also examined to illustrate their synergistic effect. It was noted that the amount of NCS or AB in the controls was kept as the same as that of NCS+AB, indicating the same carbon content in the electrode. In full cells, the commercial cathode material, $LiFePO_4$, was used to further demonstrate the promising potential of NCS+AB for the stable cycling of Li anodes. $LiFePO_4$, AB, and PVDF (poly (vinylidene fluoride)) in a weight ratio 8: 1: 1, were milled, then casted on an Al foil. After dried in vacuum overnight, the cathode was assembled with different anodes, (NCS+AB, or NCS, AB only) that had been plated with Li metal in advance. The mass loading of $LiFePO_4$ is 4.2 mg cm^{-2} approximately.

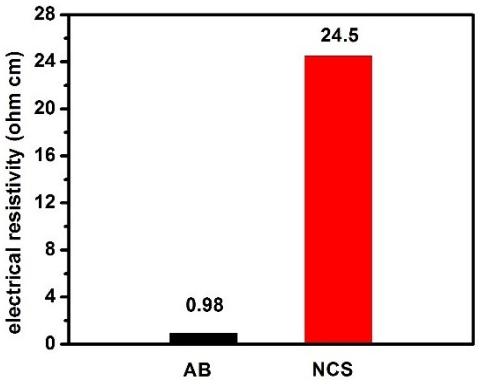

Fig. S1 The electrical resisitivity of AB, NCS.

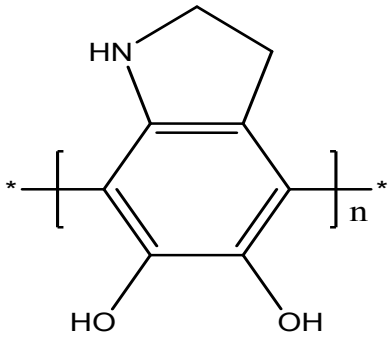

Fig. S2 The chemical structure of polydopamine.

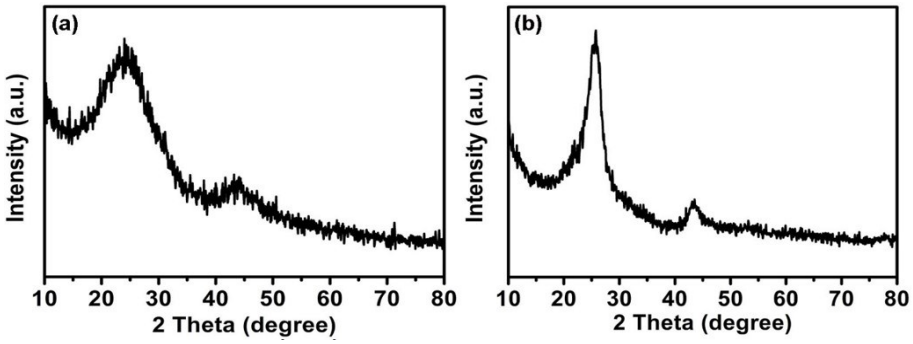

Fig. S3 XRD patterns (a) NCS, (b) AB respectively.

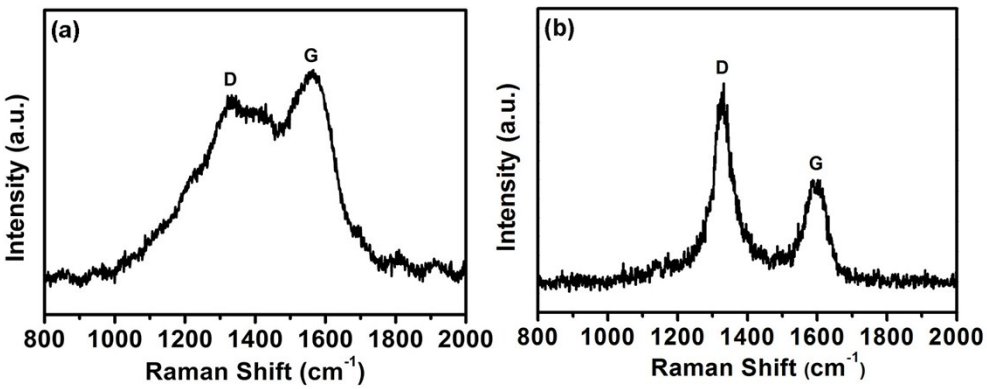

Fig. S4 Raman spectrums of (a) NCS, (b) AB respectively.

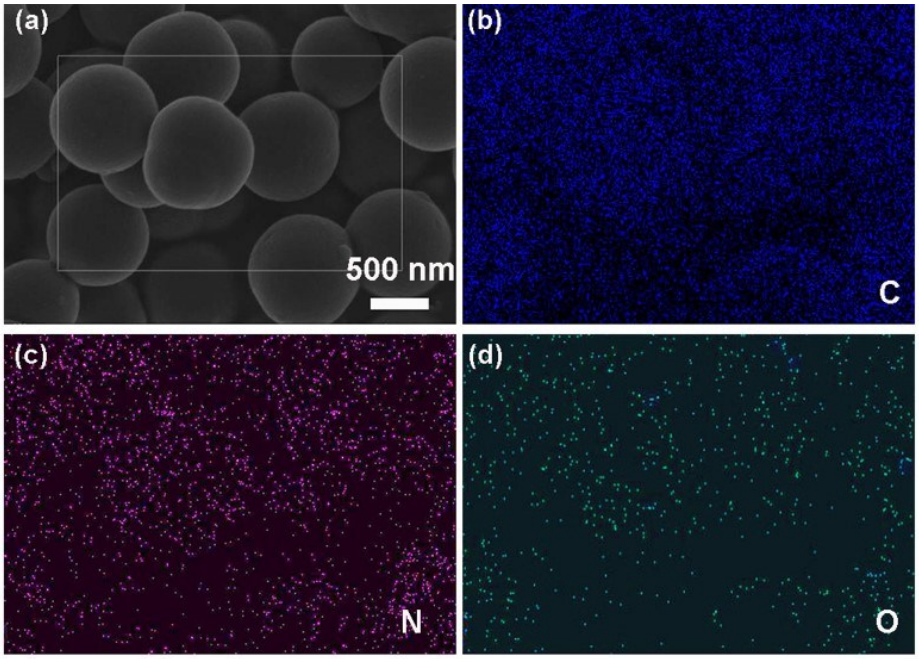

Fig. S5 Element maps of C, N and O of NCS.

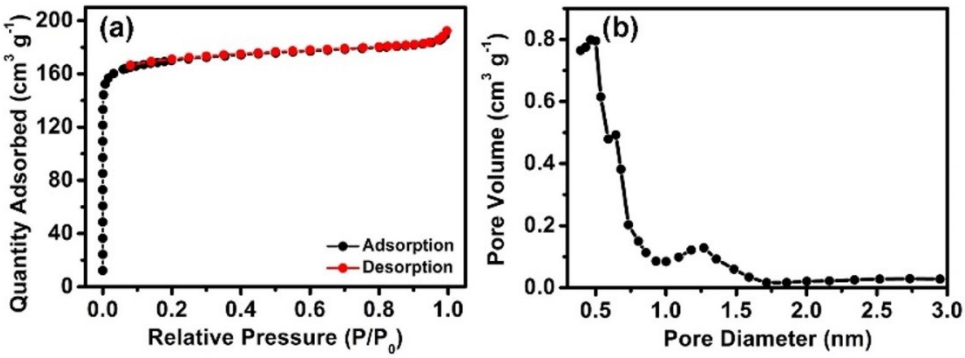

Fig. S6 (a) Nitrogen sorption isotherms, (b) pore-size distribution of NCS.

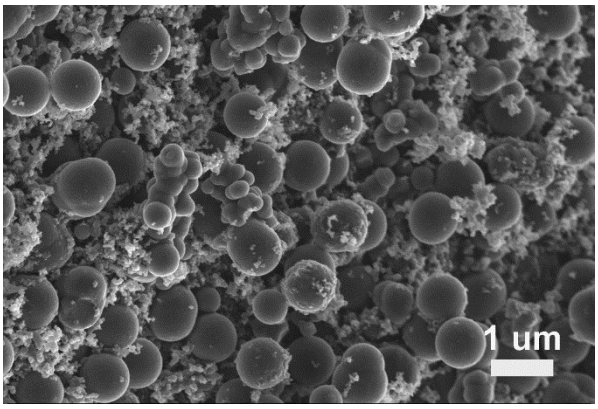

Fig. S7 SEM image of NCS+AB.

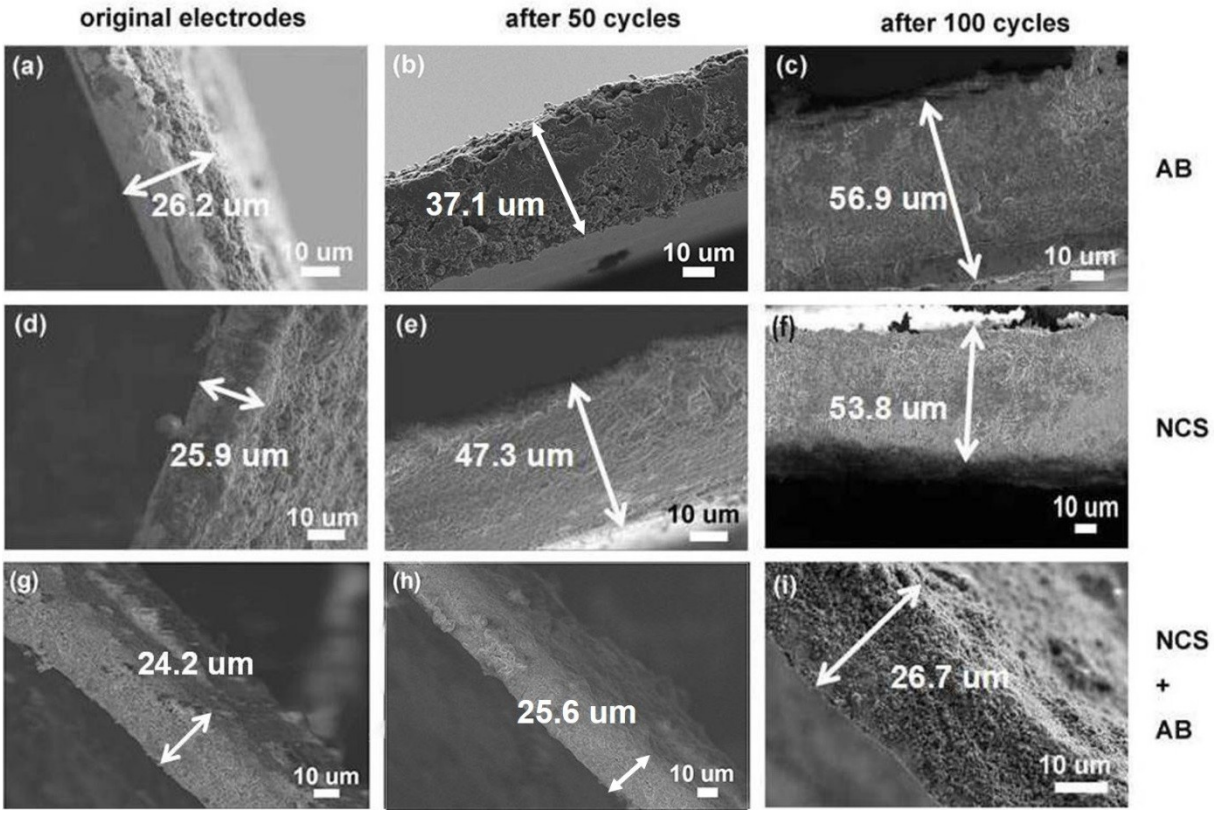

Fig. S8 Cross-sectional SEM images of (a, b, c) AB control electrodes, (d, e, f) NCS control electrodes, (g, h, i) NCS+AB electrodes. (a, d, g) original electrodes; (b, e, h) after 50 cycles; (c, f, i) after 100 cycles.

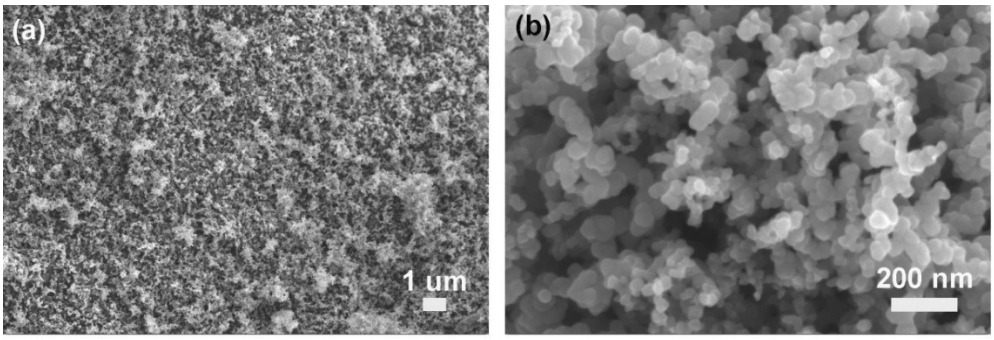

Fig. S9 SEM images of super P in different magnifications.

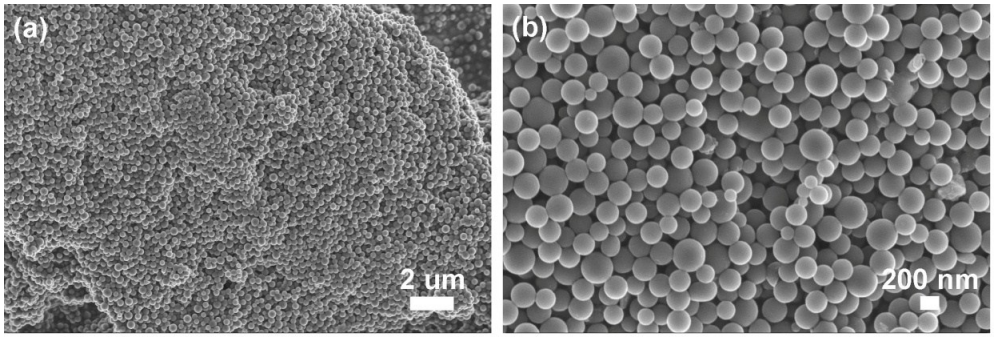

Fig. S10 SEM images of OCS.

Notes and references

1 Ai, K.; Liu, Y.; Ruan, C.; Lu, L.; Lu, G. M. *Adv. Mater.*, 2013, **25**, 998-1003.