Electronic Supporting Information

Restriction of silicon aggregation upon enhanced bond cleavage

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1. Experimental Procedures

1.1 Materials and methods

In a standard procedure, 10 g of melamine was heated to 550 °C under an argon atmosphere for 2 hours to synthesize g-C_3N_4. The resulting g-C_3N_4 was subsequently placed in a tube furnace with the inlet connected to a triethylsilane bubbler through an argon flow, the mass of g-C_3N_4 was 5 g and the volume of triethylsilane was 10 ml. The material underwent high-temperature calcination at 650 °C for 5 hours. Then, g-C_3N_4 was finally removed through self-decomposition at 800 °C for 2 hours. The final collected black powder was designated as SiNS-G. For comparison, the directly pyrolyzed triethylsilane (DP-Si) was prepared without atomic nitrogen inductive effect, while all other preparation steps remained identical to those described above. To test the carbon part, silicon was removed by alkali etching, in which SiNS-G was immersed in a 3 M NaOH solution, heated to 80°C, and stirred for 8 hours. The residual carbon material was washed and dried.

1.2 Materials Characterization

The structures and crystallinity of the obtained samples were investigated by power X-ray diffraction (XRD, Bruker D8 X-ray diffractometer, Cu Kα radiation, λ= 1.5418 Å, 40 kV, 40 mA). The morphologies and element composition were characterized by a field-emission scanning electron microscopy (JEOL JSM7500F) equipped with energy-dispersive spectrometer (EDS) and transmission electron microscopy (Tecnai-F20). The surface chemical compositions of the collected samples were analyzed using X-ray photoelectron spectroscopy (XPS, PHI 5000 VersaProbe). Additionally, the samples underwent characterization through Raman spectroscopy (LabRAM Aramis, Horiba, 633 nm laser).

1.3 Electrochemical Characterizations

First, the slurry, consisting of the active material (80%), Super P (10%), and polyvinylidene fluoride (PVDF) (10%) in N-methylpyrrolidone (NMP), was mixed and

coated onto an copper foil. The obtained slurry was cast onto a Cu foil with a wet film thickness of about 15 μm, and dried at 100 °C in vacuum for 12 h then compressed at 10 MPa pressure. Subsequently, CR 2032 coin-type cells were assembled in an argon-filled glove box using SiNS-G as the working electrode, Li discs as both the counter and reference electrode, microporous polypropylene film (Celgard 2325) as separator, and 1 M $LiPF_6$ dissolved in a 1:1 mixture of ethylene carbonate and diethyl carbonate as the electrolyte. Constant current charge/discharge curves were performed using a battery test system (Neware-BTS3000). Cyclic voltammetric curves (CV) were evaluated on CHI660D.

2. Description of theoretical calculations

The computations of all reagents were performed on Gaussian 16 Program on the basis of double-polarized Density Functional Theory (DFT). All molecules were optimized at B3LYP-D3(BJ)/6-311G* level. Subsequently, the single point energies of all structures are recalculated at B3LYP-D3(BJ)/def2-TZVP level to get accurate information about orbital energy and so on, and frontier molecular orbitals are evaluated and presented by Multiwfn.

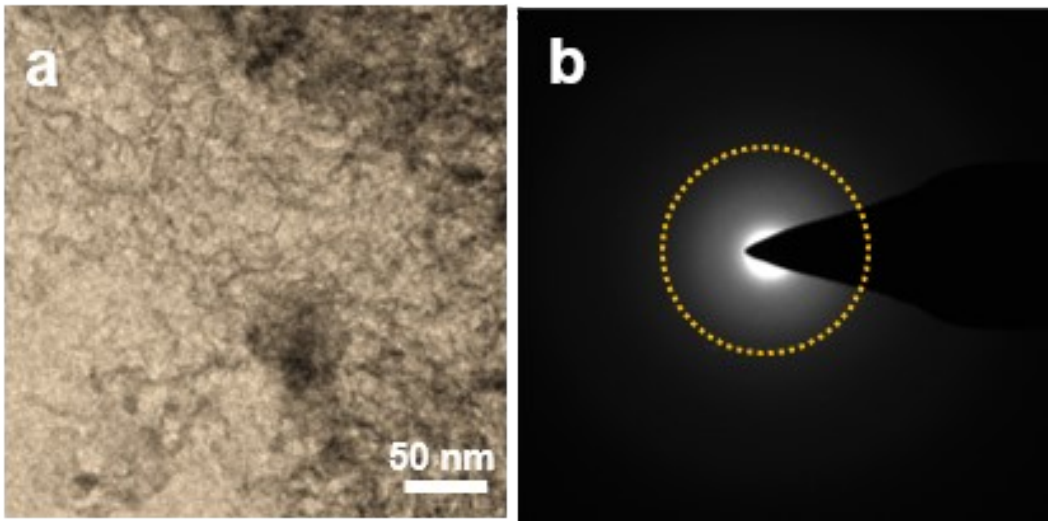

Figure S1 (a) SEM images of the SiNS-G viewed under high magnification. (b) Selected area diffraction pattern of the SiNS-G

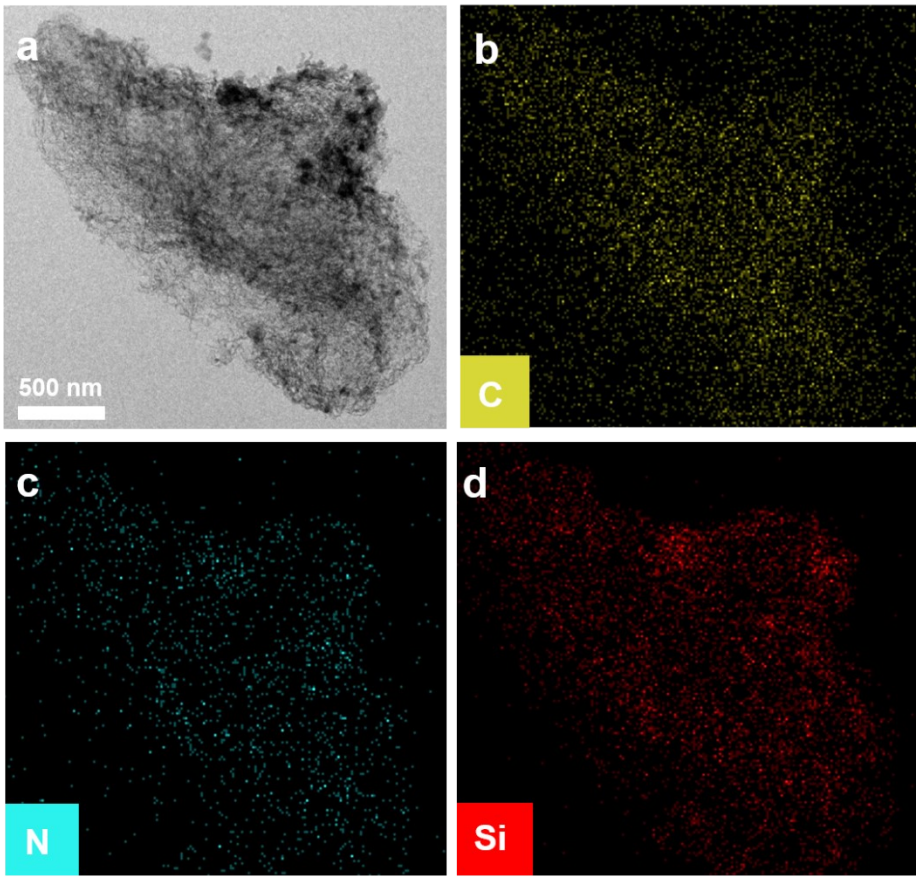

Figure S2 (a) TEM images of the SiNS-G under high magnification. (b-d) Corresponding elemental mapping results of the SiNS-G.

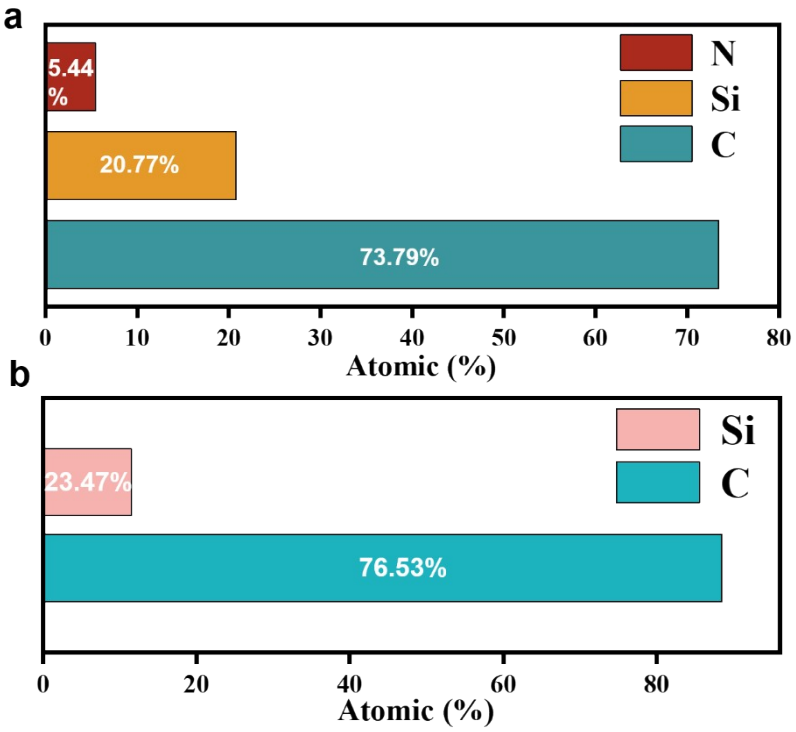

Figure S3 (a) Content of C, N and Si elements in SiNS-G materials prepared in EDS testing. (b) Content of C and Si elements in the prepared DP-Si materials in EDS testing.

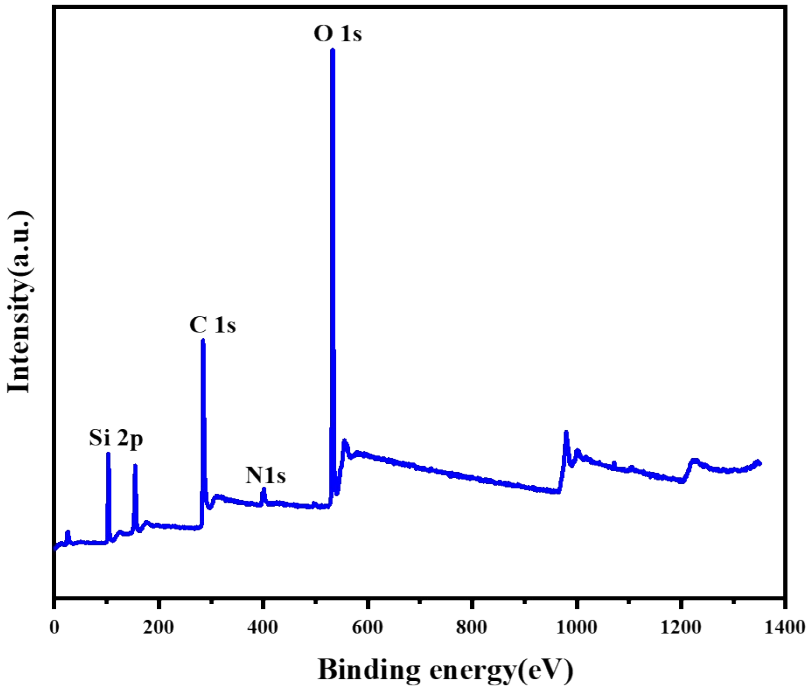

Figure S4 Survey XPS spectra of the SiNS-G sample.

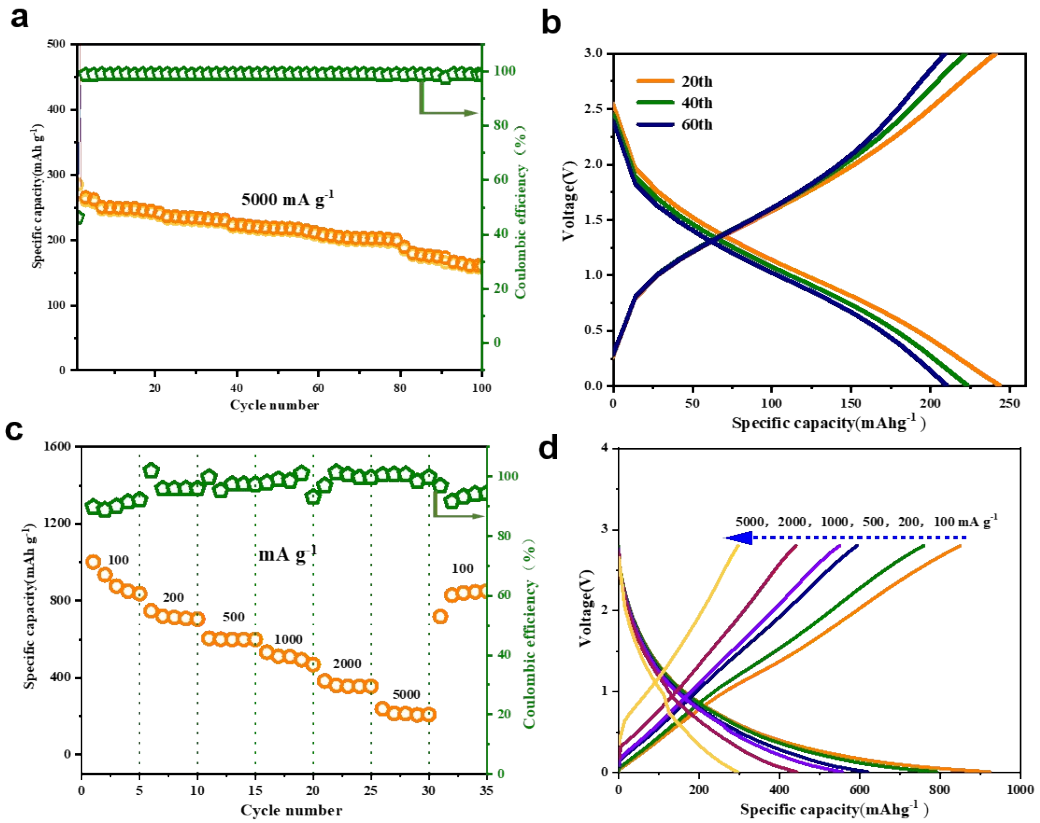

Figure S5 (a) Long-term cycling stability of the DP-Si at 5000 mA g^{-1}. (b) Corresponding charge/discharge profiles at current density of 5000 mA g^{-1}. (c) Rate performance and (d) corresponding galvanostatic charge/ discharge profiles of the DP-Si.

The DP-Si demonstrates a low lithium storage capacity of 157.64 mAh g^{-1} at 5000 mA g^{-1} with a suboptimal capacity retention of 55.34% retained after 100 cycles (Fig. S4a). The poor overlap of the charging/discharging curves at the 20th, 40th and 60th cycles further indicates the poor stability of DP-Si (Fig. S4b). The unsatisfactory rate capability of DP-Si was unveiled at different current densities. As shown in Fig. S4c and d, the reversible specific capacities of DP-Si are 837.6, 705.58, 599.97, 469.17,

356.52, and 209.29 mAh g^{-1} at 100, 200, 500, 1000, 2000 and 5000 mA g^{-1}, respectively, much lower than those of SiNS-G.

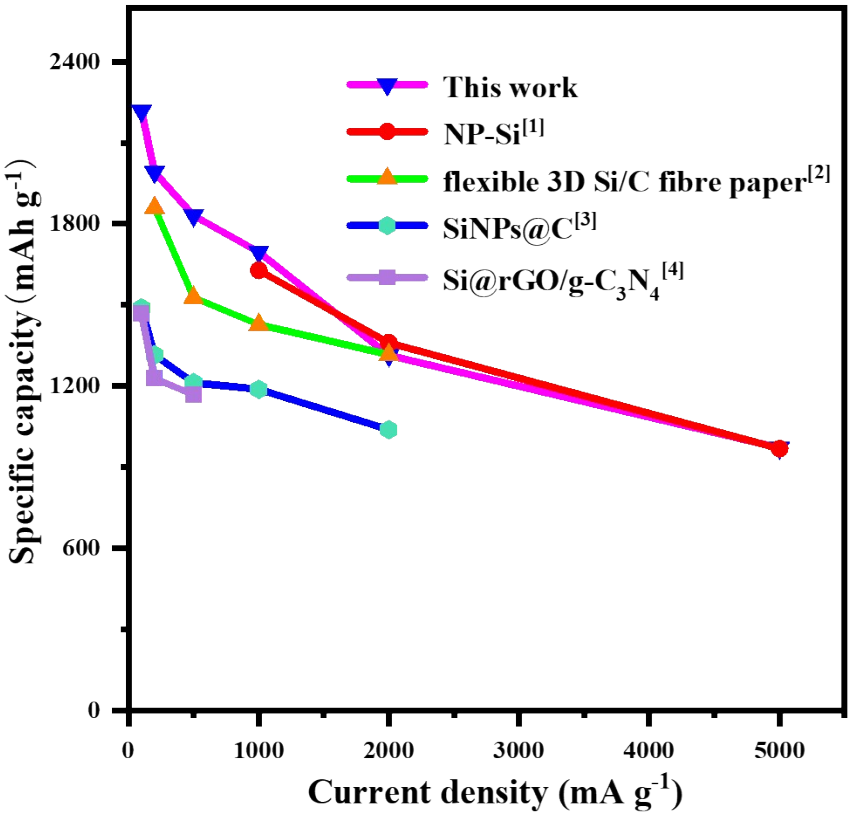

Figure S6 Comparison of rate performance with previous works.

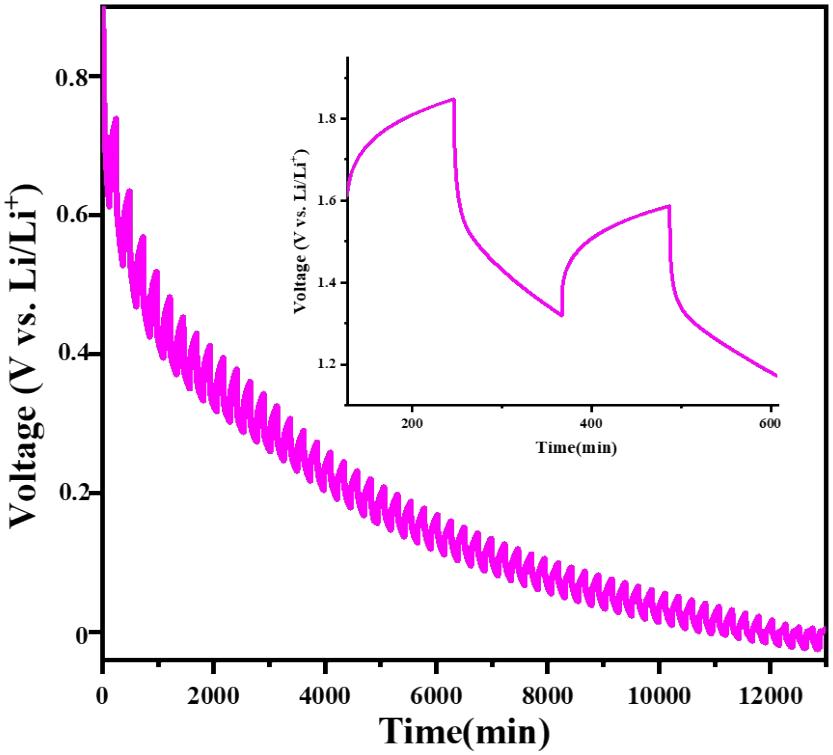

Figure S7 Galvanostatic intermittent titration technique test of the SiNS-G sample.

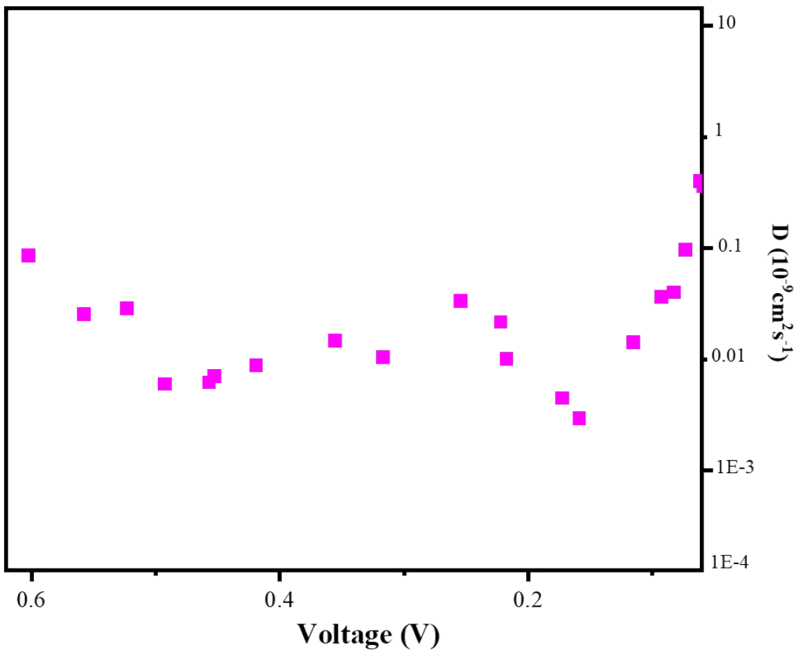

Figure S8 Diffusion coefficient plots of the SiNS-G sample.

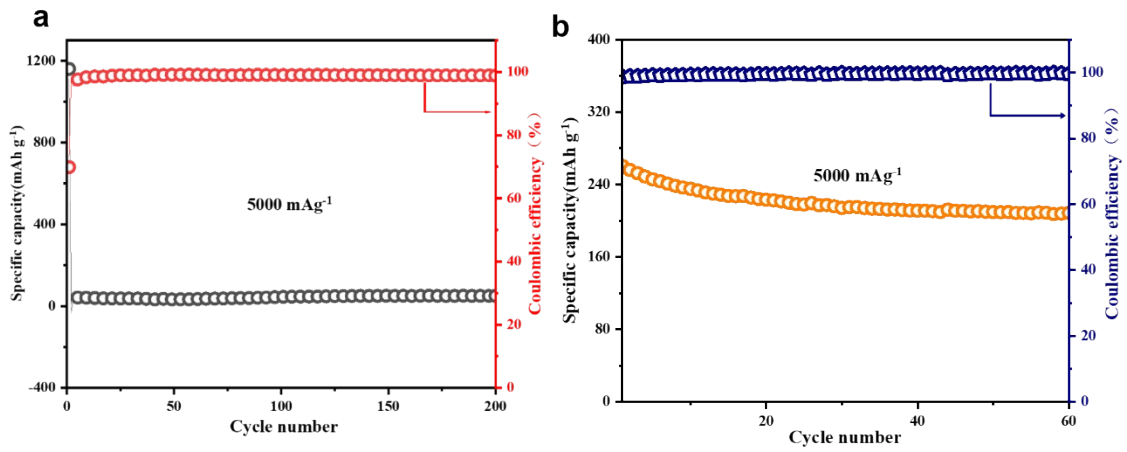

Figure S9 (a) Charge/discharge performance of the carbon-only electrode in DP-Si at 5000 mA g^{-1}. (b) Charge/discharge performance of Si-removed SiNS-G at 5000 mA g^{-1}.

References

[1] Y. L. An, H. F. Fei, G. F. Zeng, L. J. Ci, S. L. Xiong, J. K. Feng and Y. T. Qian,*ACS Nano*, 2018, **12**, 4993-5002.

[2] G. Q. Wang, Z. S. Wen, Y. E. Yang, J. P. Yin, W. Q. Kong, S. Li, J. C. Sun and S. J. Ji, *J. Mater. Chem. A*, 2018, **6**, 7557-7565.

[3] T. H. Hwang, Y. M. Lee, B.-S. Kong, J.-S. Seo and J. W. Choi, *Nano Letters*, 2012, **12**, 802-807.

[4] Y. H. Xu, Y. J. Zhu, F. D. Han, C. Luo and C. S. Wang, *Adv. Energy Mater.*, 2015,**5**,7.