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Supporting Information

A novel strategy for the synthesis of highly stable ternary SiO_x composites for

Li-ion-battery anodes

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References

Experimental Section

1.1 Materials and reagents.

All chemicals were purchased from Shanghai Sinopharm Chemical Reagent, co. ltd., and used without further treatment or purification. All aqueous solutions were prepared with high-purity de-ionized water. (DI-water, resistance $18 \text{ M}\Omega \text{ cm}^{-1}$).

1.2 Synthesis

1.2.1 Synthesis of SiO_x/Nitrogen-Doped Carbon (SiO_x/NC, SC)

Dried bamboo leaves were collected from the campus of Yangzhou University and washed for several times with water to remove the surface dirt and dried in an oven at 60 °C for 12 h. Then, the dried bamboo leaves were calcined in N₂ atmosphere at 600 °C for 2 h with a heating rate of 5 °C min⁻¹ then cooled naturally to room temperature. Finally, the obtained products were cleaned with HCl solution to remove the metal species inside the products. The acidtreated products were washed with DI water for several times until pH reaches \approx 7, then centrifugated and dried at 60 °C for 12 h.

1.2.2 Synthesis of Ni₃Si₂O₅(OH)₄/Nitrogen-Doped Carbon (Ni₃Si₂O₅(OH)₄/NC)

Typically, 0.04 g SC was mixed with 0.281 g nickel(II) acetate tetrahydrate (Ni(OAc)₂·4H₂O) and 20 mL of H₂O before transferring into a steel autoclave for hydrothermal treatment at 180 °C for 24 h. The resultant products were centrifuged, washed with ethanol and deionized water repeatedly for three times, and then dried under 60 °C for 12 h.

1.2.3 Synthesis of Ni/SiO_x/Nitrogen-Doped Carbon (NSC)

Typically, 0.2 g Ni₃Si₂O₅(OH)₄/nitrogen-doped carbon powers were calcined in N₂ atmosphere at temperatures of 700 °C, 800 °C, 900 °C and 1000 °C for 2 h with a heating rate of 2 °C min⁻

¹, respectively.

1.2.4 Synthesis of Co₃Si₂O₅(OH)₄/Nitrogen-Doped Carbon (Co₃Si₂O₅(OH)₄/NC) and Co/SiO_x/Nitrogen-Doped Carbon (CSC)

The Synthesis of $Co_3Si_2O_5(OH)_4/NC$ and CSC samples are similar to those of $Ni_3Si_2O_5(OH)_4/NC$ and NSC samples, respectively, with all of the synthetic conditions being the same except Nickel(II) acetate tetrahydrate (Ni(OAc)_2·4H_2O) is replaced by cobalt(II) acetate tetrahydrate (Co(OAc)_2·4H_2O).

1.3 Characterization of as-synthesized materials

The products were tested by X-ray diffraction (XRD) on a Bruker D8 Advanced X-ray Diffractometer (Cu-K α radiation: λ =0.15406 nm) for the phase analysis. Scanning electron microscope (SEM, Zeiss_Supra55) was used for observing the morphology of the samples at an acceleration voltage of 5.0 kV. High-resolution transmission electron microscopy (HRTEM) images, SAED images, and energy dispersive X-ray spectroscopy mapping were captured on a Tecnai G2 F30 transmission electron microscopy at an acceleration voltage of 300 kV. The electron tomography (ET) was conducted using the same TEM Instrument that was employed to perform the TEM-analysis of samples. The electron beam as well as conditions were kept the same as the one used during the aforementioned TEM analysis. Samples were tilted from -68° to +68° with two-degree intervals during the acquisition of tilt-series. It is to be noted that Explore3D software package from Thermo-Fisher Scientific was used during the acquisition of tilt-series. The series were then aligned and reconstructed by using Inspect3D also from Thermo-Fisher Scientific to generate the volume-series of tomograms of samples.

rendering of Ni Nanoparticles present on within the composite material. X-ray photoelectron spectroscopy (XPS) was carried out on a Thermo Scientific ESCALAB 250 apparatus. In addition, TENSOR27 Fourier Transform Infrared Spectrometer (FTIR) was used, and Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) were tested on Autosorb IQ3.

1.4 Electrochemical measurements

Electrochemical measurements were conducted using 2032 coin-type cells. The working electrodes were prepared by mixing 80 wt% active materials, 10 wt% super P and 10 wt% sodiuolyvinylidene fluoride (PVDF) in N-methylpyrrolidone (NMP) and milling for more than 30 min to form a slurry, and then the slurry was coated on Cu foil, the mass loading of active material was about 0.53 mg cm⁻². The working electrodes were then used along with pure lithium foil to assemble the Li-ion half-cell. The electrolyte was a mixture of 1 M LiPF₆ in ethylene carbonate (EC), dimethyl carbonate (DMC) and diethyl carbonate (DEC) (volume ratio of 1:1:1) and the separator was Celgard 2250 film. The cells were left still for 12 h before measurements. Galvanostatic cycling test of the assembled cells were carried out on a Land CT2001A system within the potential range of 0.01-3.0 V. The cyclic voltammetry (CV) curves and the electrochemical impedance spectra (EIS) were carried out on a CHI 660E instrument.



Figure S1. Si 2p spectrum of SC precursor.



Figure S2. The thermogravimetric analysis of $Ni_3Si_2O_5(OH)_4/NC$ in N_2 atmosphere at a rate of 5 °C min⁻¹.



Figure S3. a-c) SEM images of NSC600; d) optical photograph of NSC600 placed in a glass bottle showing magnetic property; e) XRD pattern of NSC600; f) optical photograph of NSC500 placed in a glass bottle without magnetic property.



Figure S4. a-c) SEM images of SC; d) EDS-mapping results of SC.



Figure S5. a-f) SEM images of Ni₃Si₂O₅(OH)₄/NC; g) TEM image, h) SAED pattern, and i)

HRTEM image of Ni₃Si₂O₅(OH)₄/NC.



Figure S6. XRD patterns of the Ni₃Si₂O₅(OH)₄/NC composites.



Figure S7. EDS-mapping results of NSC900



Figure S8. a,b) SEM images, c,d) TEM images, e) HRTEM image, f) SAED pattern, and g) elemental mapping results of NSC700.



Figure S9. a,b) SEM images, c,d) TEM images, e) HRTEM image, f) SAED pattern, and g) elemental mapping results of NSC800.



Figure S10. a,b) SEM images, c,d) TEM images, e) HRTEM image, f, g) elemental mapping

results of NSC1000.



Figure S11. XPS survey spectrum of NSC700, NSC800, NSC900 and NSC1000.



Figure S12. O1s and C1s spectrum of NSC900.



Figure S13. Ni2p spectrum of NSC700, NSC800 and NSC1000.



Figure S14. Si2p spectrum of NNSC700, NNSC800 and NNSC1000.



Figure S15. N1s spectrum of NSC700, NSC800 and NSC1000.



Figure S16. O1s spectrum of NSC700, NSC800 and NSC1000.



Figure S17. C1s spectrum of NSC700, NSC800 and NSC1000.

Sample	Ni(0)/%	Ni(II)/%	Pyridinic	Pyrrolic	Graphitic	Oxidized	Si(II)/%	Si(III)/%	Si(IV)/%
			N/%	N/%	N/%	N/%			
NSC700	31.56	68.44	11.86	18.04	52.55	18.55	23.2	49.29	27.51
NSC800	35.06	64.94	21.81	5.32	53.19	19.68	30.78	37.58	31.64
NSC900	51.78	48.22	19.42	10.52	54.61	15.44	27.69	43.62	28.69
NSC1000	44.80	55.20	17.14	6.29	57.14	19.43	41.03	45.47	13.50

Table S1. XPS peak results of percentages of Ni(0), Ni(II), graphitic N, Si(II), Si(III) and Si(IV) species calculated from Ni2p, N1s and Si2p, respectively.



Figure S18. N₂ adsorption desorption isotherm of SC, NSC700, NSC800 and NSC1000.



Figure S19. The pore size distribution curve of NSC900 sample.



Figure S20. CV curves of NSC700 electrode in a potential window of 0.01-3 V at a scan rate of

0.5 mV s⁻¹.



Figure S21. CV curves of NSC800 electrode in a potential window of 0.01-3 V at a scan rate of

0.5 mV s⁻¹.



Figure S22. CV curves of NSC900 electrode in a potential window of 0.01-3 V at a scan rate of

0.5 mV s⁻¹.



Figure S23. CV curves of NSC1000 electrode in a potential window of 0.01-3 V at a scan rate

of 0.5 mV s⁻¹.



Figure S24. Rate performance comparison between NSC900 and SC electrodes.



Figure S25. a,b) SEM images of SC-HCl (treated by 6 M hydrochloric acid of NSC900) and NC-NaOH (treated by 6M NaOH of SC-HCl), respectively; c) EDX result of SC-HCl; d) XRD pattern of SC-HCl and NC-NaOH; e) Cycling performances of NSC900, SC-HCl and NC-NaOH samples at 500 mA g⁻¹.



Figure S26. a) Impedance equivalent circuit diagram of SC and NSC samples before cycling; b)

Nyquist plots of SC and NSC anodes before cycling.



Figure S27. a,b) TEM and HRTEM image of NSC900 anode at 1^{st} discharge state at 5 A g⁻¹; c,d) TEM and HRTEM image of NSC900 anode at 1^{st} charge state at 5 A g⁻¹; e,f) TEM images of NSC900 anode at 200th discharge and charge states at 5 A g⁻¹; g,h) TEM images and elemental mapping results of NSC900 anode after 1000 cycles at 5 A g⁻¹.



Figure S28. a) Ni 2p and b) Si 2p XPS spectra of NSC900 at different charge and discharge states.



Figure S29. a,b) SEM images of SC before cycling and after cycling 1000 cycles, respectively; c,d) SEM images of NSC900 sample before cycling and after cycling for 1000 cycles, respectively; e) XRD results of NSC900 sample after 1000 cycles; f,g) Ni 2p and Si 2p spectrum of NSC900 before (down) and after (up) 1000 cycles.



Figure S30. a,b) SEM images of Co₃Si₂O₅(OH)₄/NC; c) XRD pattern of Co₃Si₂O₅(OH)₄/NC; d,e)

SEM images of CSC900; f) XRD pattern of CSC900; g-i) TEM images of CSC900.

Table 52. The electrochemical performances of the as synthesized samples.								
	1st DC/CC/mA h g ⁻¹		Rate capability/mA h g ⁻¹	Rate capability/mA h g-1				
Sample	(500 mA g ⁻¹)	1st CE/%	(100, 200, 500, 1000, 2000 mA g ⁻¹)	Cycle stability/mA h g ⁻¹				
NSC700	782.1/476.0	60.86	569.5, 467.1, 425.8, 366.4, 306.7	392.7/150th/500 mA g ⁻¹				
NSC800	1031.6/684.9	66.39	702.8, 641.2, 565.4, 512.7, 417.9	528.8/150th/500 mA g ⁻¹				
NSC900	1215.3/842.7	69.34	844.2, 774.5, 738.6, 631.9, 540.6	719.4/150th/500 mA g ⁻¹				
NSC1000	548.1/290.7	53.04	366.2, 291.7, 251.3, 194.2, 156.1	252.1/150th/500 mA g ⁻¹				
SC	_	_	380.4, 339.8, 289.3, 214.7, 134.2	305.2/70th/200 mA g ⁻¹				

 Table S2. The electrochemical performances of the as-synthesized samples.

	Content of SiO ₂	1st DC/CC			Current density
Materials	or SiO _x (wt%)	(mA h g ⁻¹)/ICE(%)	Capacity	Cycles	(mA g ⁻¹)
			(mA h g ⁻¹)		
Carbon coated SiO ₂ NPs ¹	50.1	536/-/-	> 500	50	50
Dual-porosity SiO ₂ /C spheres ²	_	_	635.7	200	100
SiO _x /C microspheres ³	60.25	1460/965/66.1	689	400	500
SiO _x /graphene ⁴	63.5	> 1000/-/69	> 900	100	500
SiO _x @C nanorods ⁵	65.4	1324/906/-	~720	350	100
SiO _x -C ⁶	_	_	485	100	500
Ni/SiO ₂ hierarchical hollow Spheres ⁷	40.65	1195/676/56.6	672	50	100
SiO _x -C from rice husks ⁸	_	998.5/466/46.67	582.1	100	100
SiO ₂ -carbon ⁹	~23	586.2/-/-	294.7	190	200
SiO _x @C nanosheets ¹⁰	_	1750/1087/62.1	760	400	500
Carbon coated SiO _x nanowires ¹¹	~90.67	2215/-/-	623	150	500
SiO _x /C ¹²	~68.6	2223.6/-/47.3	800	50	100
SiO _x @C spheres ¹³	_	1160/-/-	563	400	100
Si@SiO _x /C ¹⁴	~75	_	760	_	600
NSC900 (This work)	~28.7	1215.3/842.7/69.34	719.4	150	500
NSC900 (This work)	~28.7	_	427.6	1000	5000

Table S3. Comparison of the lithium-storage performance between the NNSC900 and similarmaterials reported recently.

ICE: Initial Coulombic efficiency

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