Electronic Supporting Information

One-pot solution synthesis of carbon-coated silicon nanoparticles as anode material for lithium-ion batteries

Fei Wang^[a], Changsheng Song^[a], Baoxun Zhao^[a], Lin Sun^[b], Hongbin Du^{*[a]}

 ^[a]State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, 210023, PR China.
^[b]Jiangsu Collaborative Innovation Center for Ecological Building Materials and Environmental Protection Equipments, and School of Chemistry and Chemical Engineering, Yancheng Institute of Technology, Yancheng, 224051, PR China.
*Corresponding author: hbdu@nju.edu.cn.

1. Experimental Procedures

1.1 Materials and methods

In a typical process, 2.2 mL of HSiCl₃ (TCI) were mixed with 2.0 mL of Pr₃N (Alfa Aesar), and 30 mL of anhydrous hexane. The formed colorless solution was stirred at room temperature overnight. Afterwards, 0.56 g of magnesium powder (Sigma-Aldrich) were added to the above solution. The mixture was further stirred for three days at 80°C. The precipitates were collected by centrifugation, washed with anhydrous CH₂Cl₂ several times, and dried under vacuum at 60°C for 8 h. Then, the dried products were heated at 800°C for 4 h under Ar flowing with a heating rate of 15°C min⁻¹. After cooling down, the heat-treated products were successively washed with 1.0 M HCl solution and distilled water in sequence for several times to remove redundant magnesium powders and inorganic salts. The final products were dried in a vacuum oven for further use. The yield of the porous silicon (470 mg) was approximately 77% based on the HSiCl₃ content.

The synthesis could be carried out in a larger scale: 11.0 mL of HSiCl₃ were mixed with 10.0 mL of Pr_3N and 150 mL of anhydrous hexane. The forming colorless solution was stirred at room temperature overnight. Afterwards, 2.80 g of magnesium powder were added to the above solution and reacted for 3 d at 80°C under stirring. The precipitates were collected by centrifugation, washed with anhydrous CH_2Cl_2 several times, dried and then heated at 800°C for 4 h under Ar. The yield of the porous silicon (2.10 g) was approximately 67% based on the HSiCl₃ content.

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 K α radiation, λ = 1.5406 Å, 40 kV, 40 mA). The morphologies and element composition were characterized by a field-emission scanning electron microscopy (SEM, Hitachi, S-4800) equipped with energy-dispersive spectrometer (EDS) and transmission electron microscopy (TEM, JEM-2100). The surface area and porous property was determined by nitrogen adsorption-desorption isotherms (Micromeritics ASAP 2020 analyzer) at 77 K after degassing of the sample at 150°C for 10 h. The specific surface area and pore size distribution of the obtained samples were calculated based on the Brunauer-Emmett-Teller (BET) and Density-Functional-Theory (DFT) methods, respectively. The surficial chemical compositions of the obtained samples were investigated by Xray photoelectron spectroscopy (XPS, PHI 5000 VersaProbe). The samples were also characterized by Raman spectroscopy (LabRAM Aramis, Horiba, 633 nm laser). Fourier-transform infrared spectroscopy (FT-IR) were measured on a FT-IR spectrometer (Vector22) with the KBr pellet method. Thermogravimetric analysis (TGA) were carried out on a simultaneous Netzche STA449F3 thermal analyzer at a heating rate of 10°C/min from room temperature to 700°C under flowing air.

1.3 Electrochemical Characterizations

The electrochemical performance measurements were performed by using the 2032 coin cells. The 2032-type half cells consist of the active materials as the working

electrode, the Li foil as the reference electrode and counter electrode, a Celgard 2400 membrane as the separator, and 1 M LiPF₆ in a mixed solvent of 1:1 (v/v) ethylene carbonate (EC)/diethyl carbonate (DEC) with 2 wt % vinylene carbonate (VC, DoDoChem) as the electrolyte additive. The cells were assembled in an Ar-filled glove box (H₂O, $O_2 < 0.1$ ppm). The working electrodes were prepared by mixing 70 wt % active materials, 15 wt % carbon black (Shenzhen Kejingstar Technology Ltd., China) and 15 wt % sodium alginate (Sinopharm) in water. The homogeneous slurries were then pasted uniformly on a copper foil and dried at 80°C in vacuum for 10 h. The loading density of active materials on the electrodes was appropriately 0.5 mg cm⁻². The galvanostatic charge/discharge cycles were performed on a Neware battery testing device (Shenzhen, China) at a voltage window of 0.01-1.5 V vs. Li⁺/Li. Cyclic voltammetry (CV) curves were collected on an electrochemical station (CHI650d, Shanghai Chenhua Instruments Inc., China) at a potential range of 0.01-1.5 V with a scan rate of 0.1 mV s⁻¹. Electrochemical impedance spectra (EIS) were recorded over the frequency range from 0.01 Hz to 100 kHz on a CHI650d electrochemical workstation.



Figure S1. Digital images of (a) pSi@C obtained after pre-heat treatment (a1: after heat-treated; a2: after washing; a3: after exposed in air for 3d, respectively), and (b) pSi obtained by directly acid pickling (b1: after directly acid pickling; b2: after exposed in air for 3d, respectively).



Figure S2. (a) SEM image; (b) EDS spectra; (c) elemental mapping of the raw product obtained by drying directly.



Figure S3. (a) SEM image; (b) TEM image; (c) HRTEM image; (d) EDS spectra; (e) elemental mapping; (f) Si 2p XPS spectra of the sample obtained after acid pickling directly and without pre-heated treatment.



Figure S4. (a) N_2 adsorption isotherms and (b) corresponding DFT pore size distribution curves of the heat-treated raw product and pSi@C. (c) N_2 adsorption isotherms and (d) corresponding DFT pore size distribution curves of the sample obtained after acid pickling and without pre-heated treatment.



Figure S5. (a) SEM image, (b) TEM image; (c) HRTEM image, (d) EDS spectra, (e) elemental mapping of the pre-heated raw product.



Figure S6. (a) Fourier Transform Infrared Spectroscopy (FT-IR): green-outlined area were peaks of absorbed water and purple-outlined area were peaks of contaminated CO_2 . (b) TGA curve of the pSi@C.



Figure S7. Raman spectra of the pSi@C anodes: the uncycled and after 200 cycles at a current density of 2.0 A g^{-1} .



Figure S8. (a) Voltage profiles of the pSi electrode. (b) Cycling performance of pSi at a current density of 0.5 A g^{-1} .



Figure S9. The discharge-charge curves of the pSi@C anodes at different current densities



Figure S10. EIS spectra of the pSi@C anodes after 0th, 5th and 200th cycles at a current density of 2.0 A g^{-1} .

Samples (Pafaranaas)	Cycling performance			Synthetic method		
(References)	Current	Capacity	Initial	Raw material	Advantage/	
	density	$(mAh g^{-1})$	CE (%)	Synthesis conditions	Disadvantage	
	(A g ⁻¹)					
Si-C composite	1.0	1459 mA h g-1	77%	SiO powder	multi-step	
[S1]		after 200 cycles		The disproportionation of SiO	synthesis	
				followed thermal decomposition		
				of acetylene		
Nanosilicon	1.4	1060 mA h g ⁻¹		SiH_4	harsh and	
coated		after 150 cycles		uniform Si and C coatings	difficult to	
grapheme [S2]				deposited on graphene via	control	
				vapor decomposition		
Si/C Hybrids ^[S3]	0.5	904 mA h g ⁻¹	85.4%	pyrolysis-cumelectrolysis (PCE)	high	
		after 100 cycles		of SiO ₂ @polydopamine in	temperature	
				molten NaCl–CaCl ₂ at 800 °C		
Si@ZIF-8-	0.2	1050 mA h g ⁻¹		in situ MOF layers coated on Si	multi-step	
700N ^[S4]		after 500 cycles		particles followed pyrolysis	synthesis	
Core-Shell Si/C	1.0	1018 mA h g ⁻¹	72%	in-situ magnesium reduction	high	
[85]		after 200 cycles		and glucose carbonization	temperature	
				method with the assistance of		
				the NaCl template		
Si/C/G	0.1	938 mA h g ⁻¹	56%	diatomite mineral	tedious and	
composite [S6]		after 300 cycles		magnesiothermic reduction and	time-	
				glucose carbonization and	consuming	
				mixed graphite		

Table S	51. Comparison	of the latest	various ro	utes of syr	nthesizing	nanostructure	d Si
and por	ous Si-based as	anodes for L	IBs.				

PPy@PHSi [S7]	1.0	88% capacity retention after	68%	the magnesiothermic reduction followed the polymerization of	multi-step synthesis
		250 cycles		РРу	
Si-SiC/C-2	0.5	937 mA g ⁻¹	72.9%	hydrothermal treatment and	multi-step
[S8]		after 80 cycles		glucose carbonization	synthesis
				magnesiothermic reduction	-
Silicon-	0.5	1344 mA h g ⁻¹	70.1%	PEO-assisted electrospinning	high
graphene		after 200 cycles		method	voltage
composite [S9]					
Nanoscale	0.2	500 mA h g ⁻¹	75.7%	SiCl ₄	solvothermal
silicon		after 100 cycles		Zn powder reduction	reaction
[S10]				-	(500°C)
Crystalline	2.1	1600 mA h g ⁻¹	73.9%	SiCl ₄	active Na
nano-Si [S11]		after 500 cycles		Na metal	metal
				mechanical milling	
Nanoporous	1.0	1180 mA h g ⁻¹	76%	Mg ₂ Si	higher
silicon [S12]		after 400 cycles		vacuum dealloying	temperature
Mesoporous	1.0	923.5 mA h g ⁻¹	61.4%	SiO	higher
silicon [S13]		after 160 cycles		magnesiothermic reduction	temperature
p-SiNPs@HC-	1.0	600 mA g ⁻¹	55%	magnesiothermic reduction	high
1 [S14]		after 600 cycles		and glucose carbonization	temperature
Mesoporous	0.5	1018 mA g ⁻¹	54%	preparation of precursor	multi-step
C/Si composite		after 100 cycles		solution and dispersion of Si	synthesis
[S15]				nanoparticle, in situ	
				polymerization and	
				carbonization	
pSi@NC [S16]	1.0	1310 mA g ⁻¹	71.4%	HSiCl ₃	multi-step
		after 200 cycles		magnesium reduction of HSiCl ₃	synthesis
	2.0	750 mA g ⁻¹		and subsequent carbon coating	
		after 200 cycles			
in this work	2.0	1120 mA g ⁻¹	67.5%	HSiCl ₃	high yield
		after 500 cycles		magnesium reduction of HSiCl ₃	in situ carbon
		_		and in situ conformal coating of	coating
				carbon layers	

References

- S1 R. Yi, F. Dai, M. L. Gordin, S. Chen, D. Wang, *Adv. Energy Mater.*, 2013, *3*, 295-300.
- S2 K. Evanoff, A. Magasinski, J. Yang, G. Yushin, *Adv. Energy Mater.*, 2011, 1, 495-498.
- S3 C. Z. Wei Weng, and Wei Xiao, ACS Appl. Mater. Interfaces, 2019, 11, 9156-9163.
- S4 Y. Han, P. Qi, X. Feng, S. Li, X. Fu, H. Li, Y. Chen, J. Zhou, X. Li, B. Wang, ACS Appl. Mater. Interfaces, 2015, 7, 2178-2182.
- S5 W. Li, Y. Tang, W. Kang, Z. Zhang, X. Yang, Y. Zhu, W. Zhang, C. S. Lee, *Small*, 2015, 11, 1345-1351.
- S6 J. Wang, D. H. Liu, Y. Y. Wang, B. H. Hou, J. P. Zhang, R.-S. Wang, X. L. Wu, J. Power Sources, 2016, 307, 738-745.
- S7 F. H. Du, B. Li, W. Fu, Y. J. Xiong, K. X. Wang, J. S. Chen, Adv. Mater., 2014,

26, 6145-6150.

- S8 Z. Wen, G. Lu, S. Cui, H. Kim, S. Ci, J. Jiang, P. T. Hurley, J. Chen, *Nanoscale*, 2014, 6, 342-351.
- S9 X. Zhou, Y.-G. Guo, J. Mater. Chem. A, 2013, 1, 9019-9023.
- S10 K. Liang, H. Yang, W. Guo, J. Du, L. Tian, X. Wen, J. Alloys Compd., 2018, 735, 441-444.
- S11 Z. Liu, X. Chang, B. Sun, S. Yang, J. Zheng, X. Li, Chem. Comm., 2017, 53, 6223-6226.
- S12 Y. An, H. Fei, G. Zeng, L. Ci, S. Xiong, J. Feng, Y. Qian, ACS Nano, 2018, 12, 4993-5002.
- S13 A. Xing, J. Zhang, Z. Bao, Y. Mei, A. S. Gordin, K. H. Sandhage, Chem. Commun., 2013, 49, 6743-6745.
- S14 S. Guo, X. Hu, Y. Hou, Z. Wen, ACS Appl. Mater. Interfaces, 2017, 9, 42084-42092.
- S15 Y. Xu, Y. Zhu, C. Wang, J Mater. Chem.A, 2014, 2, 9751.
- S16 F. Wang, L. Sun, W. Zi, B. Zhao, H. Du, Chem. Eur. J., 2019, 25, 9071-9077.