Supporting Information

Flexible Freestanding *Cladophora* Nanocellulose Paper based Si Anodes for Lithium-ion Batteries

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Experimental Section

Preparation of compact SiNP/CNT/CNC composite paper electrodes: 20 mg *Cladophora* nanocellulose and 20 mg carboxylic acid functionalized multi-walled CNTs were dispersed in 60 mL water by sonication using a high-energy ultrasonic equipment (Sonics and Materials Inc., USA, Vibra-Cell 750) with a total pulse time of 10 min under water cooling. The as-obtained dispersion was vacuum filtered through a nylon membrane filter (0.45 μ m). When the filtration had proceeded so that no water was visible on the filter cake surface, another 50 mL dispersion consisting of 30 mg SiNPs (with a diameter of ~ 50 nm), 20 mg CNC and 30 mg CNT was poured onto the CNT/CNC cake surface. Under vacuum filtration a SiNP/CNT/CNC filter cake was then formed and this cake, which was subsequently dried. The Si, CNC and CNT concentrations in the electrodes were 25%, 33% and 42%, respectively. The mass loading of Si is 0.78 mg cm⁻².

For comparison, traditional Si electrodes with a weight ratio of 80:12:8 of SiNPs:carbon black:binder (CMC) prepared by casting the components onto copper foil were also tested in charge/discharge experiments as described above.

Material Characterizations: SEM images for all samples were obtained employing a Leo Gemini 1550 FEG SEM instrument (Zeiss, Germany) operated at 1 kV employing an in-lens secondary electron detector. The samples were mounted on aluminium stubs with double-sided adhesive carbon tape and no sputtering was used prior to imaging. The Fourier transform infrared spectrometry (FTIR) experiments were performed with a Spectrum One FTIR spectrometer equipped with a Diamond/ZnSe crystal (PerkinElmer, U.S.) while the Raman analysis was performed using a Renishaw Ramascope equipped with a Lieca LM optical microscope, a CCD camera, and an argon ion laser ($\lambda = 514.5$ nm) source.

Electrochemical Characterizations: The flexible Si-based paper material was cut into pieces which were used as freestanding anodes in lithium-ion batteries. Electrochemical tests were carried out with polymer coated aluminium pouch (i.e. "coffee-bag") cells, which were assembled to contain Li metal discs as counter electrodes and fiberglass separators. The electrolyte was LP40 (i.e. 1.0 M LiPF6, ethylene carbonate (EC): diethyl carbonate (DEC) = 1:1, Merck) with 10 wt.% fluoroethylene carbonate (FEC, 99%, Aldrich). The electrodes were dried under vacuum at 120 °C for 12 hours prior to use. The cells were assembled in an argon-filled glove box (O2 < 2 ppm, H2O < 1 ppm) and the charge/discharge tests were performed between 1.0 and 0.01 V using a Digatron BTS-600 system at room

temperature. The charge capacity of the cells was calculated with respect to the weight of the silicon in the anode, unless stated otherwise. Cyclic voltammetry was performed with an electrochemistry workstation (PARSTAT 2273) between 0.01 and 1.0 V at a scan rate of 0.1 mV s-1.



Figure S1. Stress-strain curve for flexible Si anodes.



Figure S2. SEM image (a) and a photograph (b) of CNC paper.



Figure S3. Current-potential response of the CNT/CNC paper. The potential was scanned between -0.1 V and + 0.1 V at a scan rate of 20 mV/s while recording the current. The conductivity of CNT/CNC composites was calculated according to the equations $\sigma = 1/\rho$, $R = \rho \times L/A$ and $R = \Delta U/\Delta I$ (where σ denotes the conductivity, ρ the resistance, L the length and A the area of CNT/CNC composites paper) ΔU represents the potential change within the applied current range ΔI .



Figure S4. SEM image (a) and a photograph (b) of a CNT film.



Figure S5. SEM images of SiNPs containing layer without CNT (a, b) and photograph of a corresponding layer without CNC (c). A region containing SiNPs/CNT aggregates is highlighted by a red ellipse in panel b.



Figure S6. Electrochemical performance of the CNT/CNC paper: The 1st, 2nd and 5th charge/discharge cycles recorded at 1 A g^{-1} (a) and the corresponding specific capacity vs. cycle number (b).



Figure S7. Specific capacity as a function of the cycle number for a conventional SiNP electrode recorded between 0.01 and 1.0 V using a current density of 1 A g⁻¹.



Figure S8 (a) A flexible Li-Si battery comprised of a Si/CNT/CNC electrode and a lithium strip counter electrode under flat and bent battery conditions. (b) Charge/discharge profiles for the flexible battery under flat and bending conditions for an applied current of ± 1.18 mA within a working window of 1 to 0.1V. Note that the battery was pre-cycled for 3 cycles at 1.18 mA prior to these experiments.

Sample	Technology	Time	Flexiblility	Ref.
Si/CNT/cellulose	plasma-enhanced CVD	days	yes	1
4-layed Si/CNT	CVD, high temperature	hours	yes	2
Soft Si anode	Electrospinning, sputtering	days	Yes	3
Si-PEDOT:PSS-CNT	Solution- process	hours	Yes	4
Si/MWCNT paper	filtration, high-temperature carbonization	days	No	5
CNT-Si film	CVD, high-temperature	days	Yes	6
Si@C/RGO	high-temperature treatment	hours	No	7
Si-NP@G	high-temperature treatment	hours	No	8
Si@C-CNTs	high-temperature treatment	hours	No	9
SG paper	high-temperature treatment	hours	No	10
3D Si/C Fiber Paper	Electrospinning, high- temperature carbonization	days	Yes	11
Si/RGO film	high-temperature treatment	hours	No	12
Si/CNT/CNC	Paper-making process	minutes	Yes	Our work

Table S1: Preparation details for recently reported Si-carbon anode materials.

Sample	Capacity retention after cycles	Mass loadings (mg cm ⁻²)	Applied current (A g ⁻¹)	Ref.
Si/CNT/cellulose	77% (100)	0.046	0.80	1
4-layed Si/CNT	82.5% (100)	0.28	0.84	2
Si-PEDOT:PSS-CNT	75% (100)	1.14	0.42	4
Si/MWCNT film	49% (30)	0.79	0.10	5
Si/CNT/CNC	67% (100)	0.78	1.00	Our work

 Table S2: Comparison of cycling performance for freestanding Si electrodes.

 Table S3: Lithium storage properties for recently reported Si-carbon anode materials.

Sample	Areal capacity $(m \Delta h \ cm^{-2})$	Capacity (mAh/g)	Capacity retention	Ref.	
		2100 41/ 4			
Si/CNT/cellulose	~ 0.1 at	2100 mAh/g at	//%, 100th,	1	
	0.8A/g*	0.8 A/g	0.8A/g		
4-layed Si/CNT	~1.4 at	3210 mAh/g at	82.5%, 1000th,	2	
	0.84A/g*	0.84 A/g*	0.84A/g		
Soft Si anode	~ 1.0 at	3210 mAh/g at	56.9%, 1000th,	3	
Soft SI dilode	0.42A/g*	0.84 A/g	0.84A/g		
S. DEDOTIDES CNT	~ 2.2 at	2180 mAh/g at	75% (100),	4	
SI-PEDOT:PSS-CNI	0.42A/g*	0.42 A/g	0.42A/g	т	
Si/MWCNT paper	~ 1.0 at	1301 mAh/g at	82%, 30th,	5	
	0.05A/g*	0.05 A/g	0.05A/g	5	
	unknown	2000 mAh/g at	~80%, 50th,	6	
CNT-Si film		0.36 A/g	0.36A/g	0	
Si/RGO film	unknown	1560 mAh/g at	94%, 30th.		
		0.05 A/g*	0.05 A/g	12	
Si@C/RGO	~ 1 15 at	1226 mAh/g at		_	
	0.5A/g*	0.5 A/g	unknown	7	
Si-NP@G	0.0119	1720 mAh/g at	~70% 150th		
	unknown	0.1 A/g	0.1 A/g	8	
		600 mAh/g at 0.1	$\sim 70\%$ 40 th		
Si@C-CNTs	unknown	$\sqrt{\alpha}$	0.1 A/c	9	
		A/g	0.1 A/g		
SG paper	unknown	$\sim 2800 \text{ mAn/g at}$	~34%, 20011,	10	
		0.1 A/g	0.1A/g		
3D Si/C Fibre Paper	1.28 at	1589 mAh/g at	75%, 100th,	11	
	0.5A/g*	0.5 A/g	0.5A/g		

Si/CNT/CNC	2.5 of 1 A/a	3200 mAh/g at	67%, 100th,	Our
	2.5 at 1A/g	1.0 A/g	1.0A/g	work

*calculated from data reported in the reference.

References:

- L. Hu, N. Liu, M. Eskilsson, G. Zheng, J. McDonough, L. Wågberg and Y. Cui, *Nano Energy*, 2013, 2, 138-145.
- 2. Q. Xiao, Y. Fan, X. Wang, R. A. Susantyoko and Q. Zhang, *Energy & Environmental Science*, 2014, 7, 655.
- 3. Q. Xiao, Q. Zhang, Y. Fan, X. Wang and R. A. Susantyoko, *Energy & Environmental Science*, 2014, 7, 2261-2268.
- Z. Chen, J. W. F. To, C. Wang, Z. Lu, N. Liu, A. Chortos, L. Pan, F. Wei, Y. Cui and Z. Bao, *Advanced Energy Materials*, 2014, 4, DOI: 10.1002/aenm.201400207..
- 5. L. Yue, H. Zhong and L. Zhang, *Electrochimica Acta*, 2012, **76**, 326-332.
- 6. L.-F. Cui, L. Hu, J. W. Choi and Y. Cui, *ACS Nano*, 2010, 4, 3671-3678.
- 7. N. Lin, J. Zhou, L. Wang, Y. Zhu and Y. Qian, ACS Applied Materials & Interfaces, 2014, 7, 409–414.
- X. Zhou, Y.-X. Yin, L.-J. Wan and Y.-G. Guo, *Advanced Energy Materials*, 2012, 2, 1086-1090.
- L. Xue, G. Xu, Y. Li, K. Fu, S. Li, Q. Shi and X. Zhang, ACS Appl Mater Interfaces, 2012, 2013, 5, 21–25.
- 10. J. K. Lee, K. B. Smith, C. M. Hayner and H. H. Kung, *Chemical Communications*, 2010, **46**, 2025-2027.
- Y. Xu, Y. Zhu, F. Han, C. Luo and C. Wang, *Advanced Energy Materials*, 2014, DOI: 10.1002/aenm.201400753..
- H.-C. Tao, L.-Z. Fan, Y. Mei and X. Qu, *Electrochemistry Communications*, 2011, 13, 1332-1335.