Supporting Information

Rational Design of Robust Si/C Microspheres for High Tap Density Anode Materials

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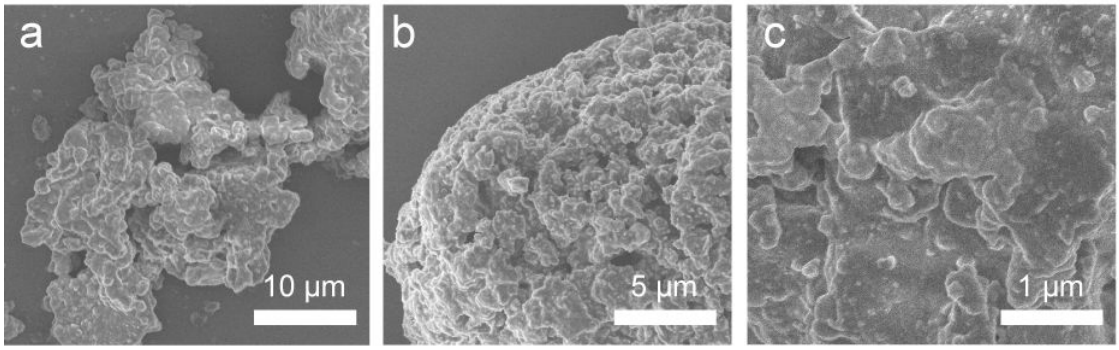

Figure S1. (a) Typical SEM image of Si NPs anchored on the graphite with pitch, (b) high-resolution (HR-) SEM image of composites after 1.5 h reaction, (c) HR-SEM image of surface of Si/C microsphere.

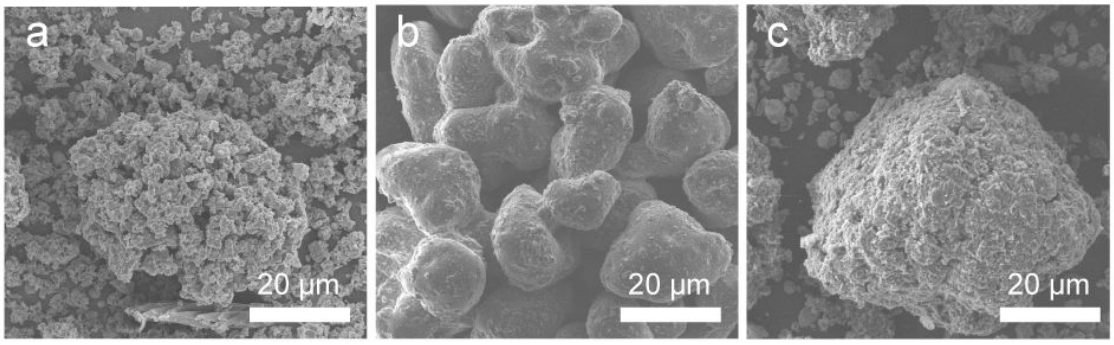

Figure S2. (a) SEM image of composites after reacting at 350 °C under 2 MPa, (b) SEM image of composites after reacting at 480 °C under 4 MPa, (c) SEM image of composites after reacting at 430 °C under 2 MPa.

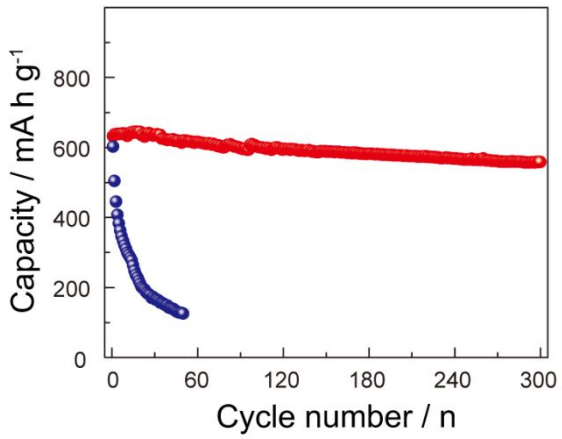

Figure S3. Cycling performance of Si/C microspheres (red) and mixture (blue) at 0.2 C.

Table S1. Values of resistance components estimated by curve fitting

Resistance components	1st cycle	5th cycle	20th cycle	50th cycle
Rs /Ω	2.5	2.4	2.2	2.2
Rsei /Ω	31.1	47.8	84.8	88.1
Rct /Ω	208	217	241	249

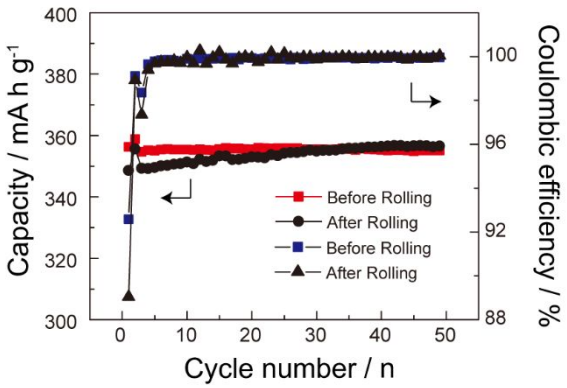

Figure S4. Electrochemical performance of commercial graphite before and after rolling process.

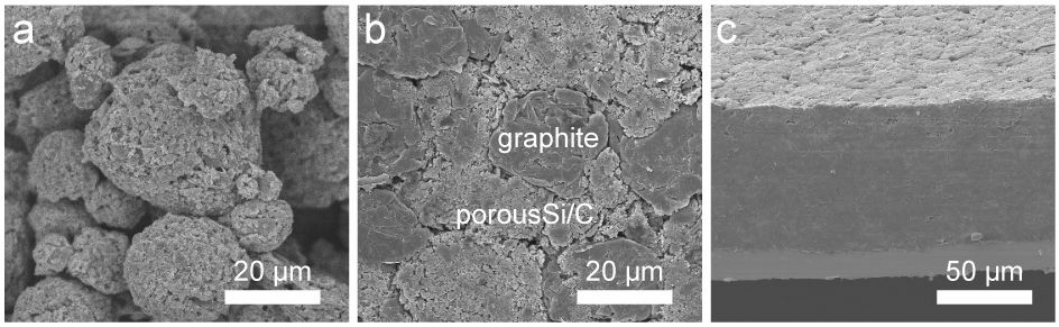

Figure S5. SEM image of (a) Si/C microspheres with porous structure fabricated by spray-drying, (b) top view of electrode prepared with Si/C microspheres and graphite, (c) cross-section view of electrode prepared with Si/C microspheres and graphite.

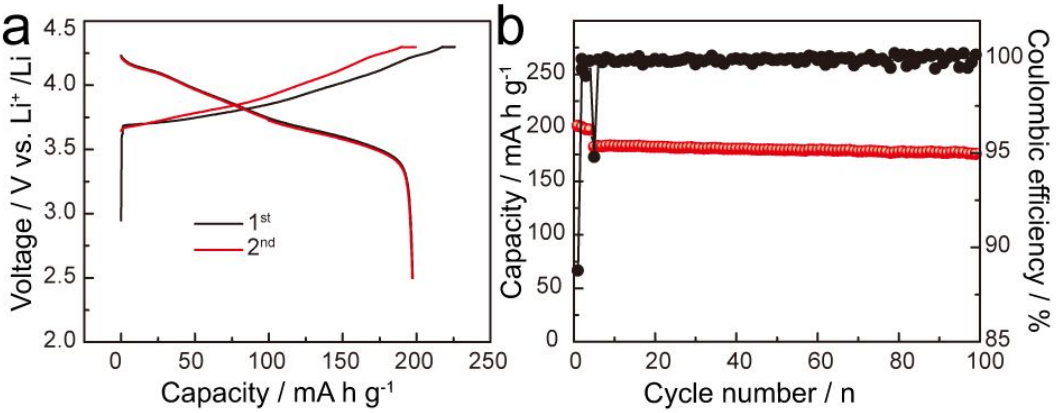

Figure S6. (a) charge and discharge curves of $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ in half cell, (b) cycling stability and CE of $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ in half cell.

Table S2. The electrochemical performance of various Si/C anodes

Ref. No.	Initial Coulombic efficiency / %	Specific capacity / mAh g^{-1}	Capacity retention in half cell / %	Capacity retention in Full cell / %
1	80.5	712	80% (100 cycles)	-
2	92	510	96% (100 cycles)	92% (100 cycles)
3	88.1	694	91% (100 cycles)	-
4	81.4	3154	89.8% (70 cycles)	-
Our work	90.5	640	85% (300 cycles)	84% (100 cycles)

References

(1) Kim, S. Y.; Lee, J.; Kim, B. H.; Kim, Y. J.; Yang, K. S.; Park, M. S. Facile Synthesis of Carbon-Coated Silicon/Graphite Spherical Composites for High-Performance Lithium-Ion Batteries. *ACS Appl. Mater. Interfaces* **2016,** *8*, 12109-17.

(2) Ko, M.; Chae, S.; Ma, J.; Kim, N.; Lee, H.-W.; Cui, Y.; Cho, J., Scalable Synthesis of Silicon-Nanolayer-Embedded Graphite for High-Energy Lithium-Ion Batteries. *Nat. Energy* **2016,** *1*, 16113.

(3) Lin, Y.; Chen, Y.; Zhang, Y.; Jiang, J.; He, Y.; Lei, Y.; Du, N.; Yang, D., Wet-Chemical Synthesized MCMB@Si@C Microspheres for High-Performance Lithium-Ion Battery Anodes. *Chem. Commun.* **2018**, 54, 9466-9469.

(4) Lee, P.-K.; Tan, T.; Wang, S.; Kang, W.; Lee, C.-S.; Yu, D. Y. W., Robust Micron-Sized Silicon Secondary Particles Anchored by Polyimide as High-Capacity, High-Stability Li-Ion Battery Anode. *ACS Appl. Mater. Interfaces* **2018,** *10*, 34132-34139.