

**Supporting Information for:**

**Facile synthesis of free-standing silicon membranes with three-dimensional nanoarchitecture for anodes of lithium ion batteries**

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**This PDF file includes:**

Methods

Supplementary Figures S1-S5

Supplementary references

## Methods

### *Synthesis of 3D-Shaped Si membranes.*

3D-shaped Si membranes were synthesized by conformal coating of ~50-nm-thick Si layers on a template of ZnO hexagonal rod array, as schematically illustrated in Figure S1a. First, the Langmuir-Blodgett assembly method was used to deposit a hexagonally close-packed monolayer of colloidal silica spheres (600 nm diameters) on a 300-nm-thick ZnO epilayer coated with a 200 nm PMMA layer.<sup>s1</sup> The sample was then heated at 180 °C to soften the PMMA and naturally push silica spheres down into the PMMA layer (a-I). In some cases, the size of silica spheres could be reduced by chemical etching in a buffer oxide etchant (BOE) solution, and then the sample was heated again at 180 °C (Figure S1b,c). Second, embedded silica spheres were removed via chemical etching with HF acid ( $\text{H}_2\text{O} : \text{HF} = 50:1$ ) (a-II). The resulting topographical pattern in the PMMA layer consists of a hexagonal array of circular depressions corresponding to spaces that were occupied by silica spheres before etching. Mild oxygen plasma treatment at 30 W eroded the PMMA layer to expose the underlying ZnO layer (a-III). This process was controlled by etching time in the range of 15–20 sec. The patterned substrate was then immersed in an aqueous solution containing equimolar zinc nitrate hexahydrate ( $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , Sigma-Aldrich) and hexamethylenetetramine ( $\text{C}_6\text{H}_{12}\text{N}_4$ , Sigma-Aldrich) to undergo hydrothermal growth of ZnO rods at 70 °C for 12 h (a-IV). ZnO growth occurred selectively on the exposed ZnO layer to create well ordered, vertically aligned ZnO hexagonal pillars. Third, the remaining PMMA pattern was removed by acetone and cleaned with deionized (DI) water. A thin layer of Si (typically 50 nm thick) was conformally coated conformally on ZnO nanostructure templates by CVD with  $\text{SiH}_4$  gas. Typically, 10 standard cubic centimeters per minute (sccm) of  $\text{SiH}_4$  (10% diluted in  $\text{H}_2$ ) and 50 sccm of  $\text{H}_2$  were mixed at 540 °C for 10-15 min. Finally, the sample was coated with a thin protecting layer of PMMA. By submerging the sample in HF

solution (50 wt% diluted 1:20 v/v in DI water), the ZnO layer and pillars were selectively etched, and the PMMA/Si membrane was separated from the substrate and rinsed with DI water. The freestanding form of PMMA/Si membrane floated on water due to its hydrophobic nature. Notably, the original GaN substrate was cleaned to repeat this experiment. The separated PMMA/Si membrane was then transferred to the designated substrate, followed by removal of the PMMA with acetone. van der Waals force is expected to make it adhere firmly to the substrate as similar to case in graphene after transfer. A short period of thermal annealing at 300 °C was then applied to improve the adhesion of the Si membrane to the substrate.

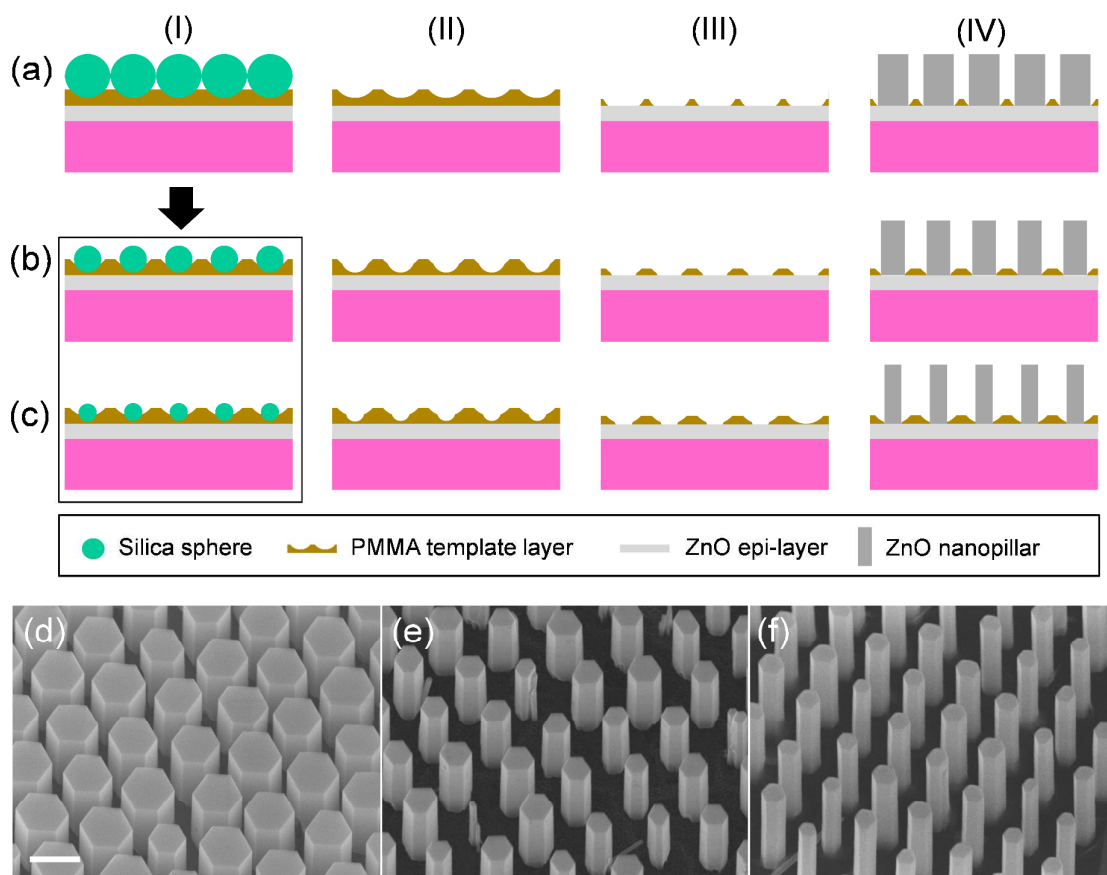
#### ***Half cell fabrication and battery test.***

To test the battery performance of the anode material, the Si membrane was transferred to stainless steel. Coin-type half cells (2032R type) were prepared in an argon-filled glove box. The mass of Si membrane materials was accurately measured using a microbalance. By comparing the total mass before and after Si membrane transfer to SUS foil, the final mass loading of Si membranes was estimated to be the range of  $\sim 0.015\text{--}0.02\text{ mg/cm}^2$ . Pure lithium metal foil was used as the counter electrode. The electrolyte was 1.0 M LiPF<sub>6</sub> with ethylene carbonate/diethylene carbonate (1:1 vol.%, Cheil Industries, Korea). The coin-type half cells were cycled between 0.01 V and 1.5 V.

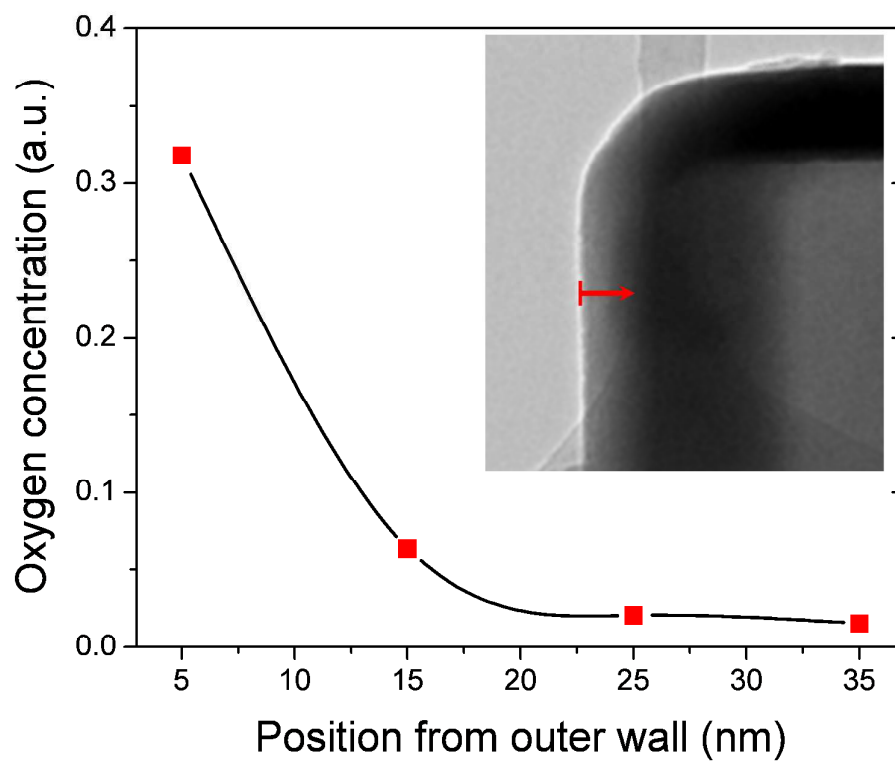
#### ***Finite element model for calculating diffusion-induced strains***

The favorable mechanics behavior of outer silicon oxide layer is understood by the finite element analysis. Energy dispersive X-ray spectroscopy in Figure S2 confirms the formation of SiO<sub>x</sub> layer near the outer surface of the walls. Although the oxygen concentration near the outer surface is not uniform and decreases rapidly in the range of 5-15 nm, we simplified the modeling by assuming that the membrane is double layer heterostructure consisting of outer

SiO<sub>2</sub> (10 nm) and inner Si (40 nm) layers with abrupt interface. In this structure, the thin SiO<sub>2</sub> layer would prevent the membrane from outward expansion upon lithiation since the yield strength of lithiated silicon oxides Li<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> (yield strength of 2.52 GPa, Poisson's ratios of 0.17 and Young's modulus of 90 GPa) is ~42 times of that of lithiated silicon Li<sub>22</sub>Si<sub>5</sub> (yield strength of 60 MPa, Poisson's ratios of 0.33 and Young's modulus of 15 GPa).<sup>S2</sup> Assuming that Li ions react with SiO<sub>2</sub> layer to form lithium silicate prior to diffusing into inner layers, we describe that lithiation of the Si nanotubes happens after the SiO<sub>2</sub> layer is fully lithiated. As reported by Wu et al,<sup>S2</sup> the SiO<sub>2</sub> layer of 10 nm is sufficiently thin to be flaw-tolerant such that fracture of the oxide layer would not occur during subsequent lithiation of the Si nanotubes. In the finite element analysis, an axisymmetric model was used where the hexagonal walls were simplified to cylindrical shapes and the diffusion of lithium ions is modeled by the analogy between heat transfer and diffusion. The finite element analysis shows that, due to the mechanical constraining effect from the outer SiO<sub>x</sub> layer, the outward expansion of the membrane is significantly reduced whereas the inward expansion dominates. The reduced outward expansion suppresses the formation of additional surfaces for excess SEI growth, thereby facilitating excellent cycling performance and superior rate capability.



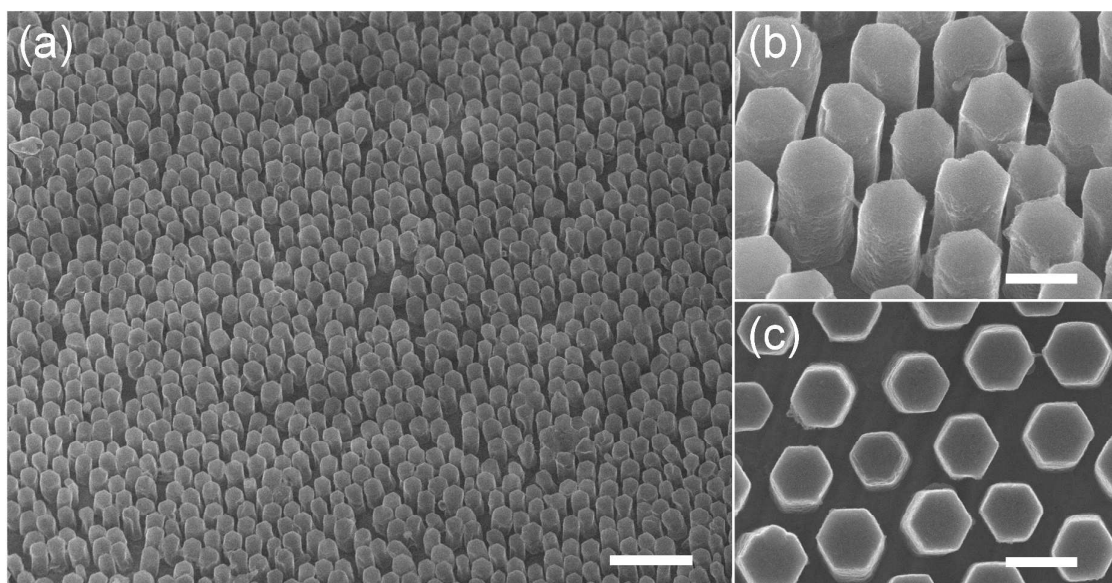
**Figure S1.** Schematic diagrams and related SEM images showing variation of ZnO nanopillar diameter depending on the silica sphere etching time: (a) 0 s; (b) 15 s; (c) 30 s. The resulting ZnO nanopillar arrays are shown in (d), (e), and (f), respectively. Scale bars: 1  $\mu\text{m}$ .



**Figure S2.** Variation of oxygen concentration along radial direction from outer surface. Inset is a TEM image of fraction of Si membrane, and the red arrow indicates the measurement direction.

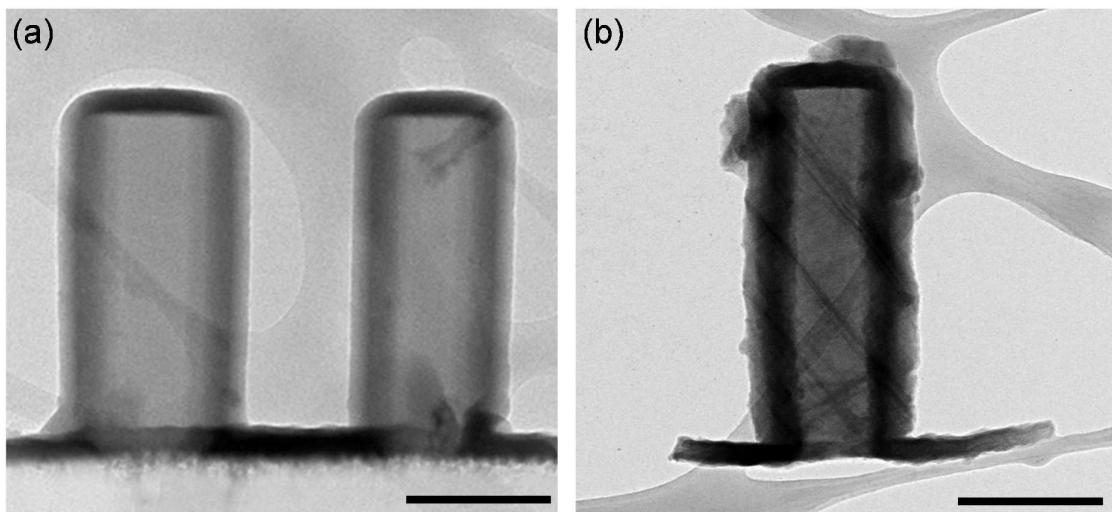
**Table S1.** Densities and theoretical capacities for Si, SiO<sub>x</sub> (x = 1 or 2), and Si/SiO<sub>x</sub> heterostructure membranes.

<b>Material</b>	<b>Density [unit: g/cm<sup>3</sup>]</b>	<b>Theoretical capacity [unit: mAh/g]</b>
Si	2.1	4200
SiO	2.1	3082
SiO <sub>2</sub>	2.5	1965
Si/SiO (40 nm/10 nm)	2.1	3951
SiO <sub>2</sub> (40 nm/10 nm)	2.18	3631

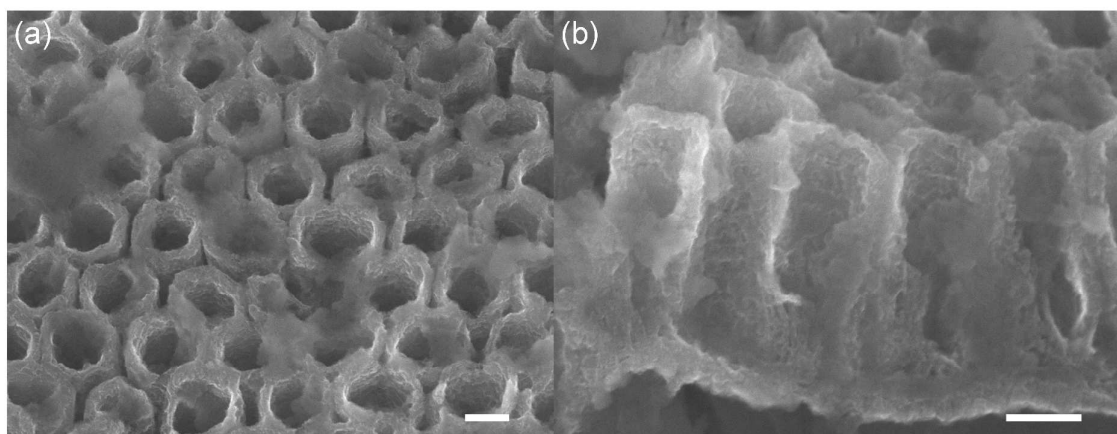


**Figure S3.** (a) Low-magnification SEM image of the Si membrane electrode after 100 cycles with a rate of 0.1 C (current density of 300 mA/g). Scale bar: 3  $\mu\text{m}$ . (b, c) Enlarged tilted (b) and top-view (c) images of the Si membrane in (a). Scale bars: 500 nm. The electrode was washed with ethanol to remove residual electrolyte and etched with acetonitrile solution to remove SEI layer.<sup>S2</sup>





**Figure S4.** TEM images of Si membrane before (a) and after (b) the first cycle (lithiation and delithiation). Scale bars: 500 nm.



**Figure S5.** 30° tilted (a) and cross sectional (b) SEM images of Si membrane electrode after 100 cycles with a rate of 8 C (current density of 24 A/g). The electrode was cleaned with ethanol to remove residual electrolyte, but etching of SEI layer by acetonitrile was not performed in this case. Scale bars: 300 nm.

## Supplementary References

S1. Kim, S. B.; Lee, W. W.; Yi, J.; Park, W. I.; Kim, J. S.; Nichols, W. T. *Acs Appl. Mater. Inter.* **2012**, *4*, 3910–3915.

S2. Wu, H.; Chan, G.; Choi, J. W.; Ryu, I.; Yao, Y.; McDowell, M. T.; Lee, S. W.; Jackson, A.; Yang, Y.; Hu, L. B.; Cui, Y. *Nat. Nanotechnol.* **2012**, *7*, 309–314.

## Supporting Movies Captions:

**Movie S1.** Strain distribution during lithiation in Si membrane at a rate of 0.1 C.