

**Electronic Supplementary Information**

**Mass production of uniform-sized nanoporous silicon nanowire anodes  
via block copolymer lithography**

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## Experimental Section

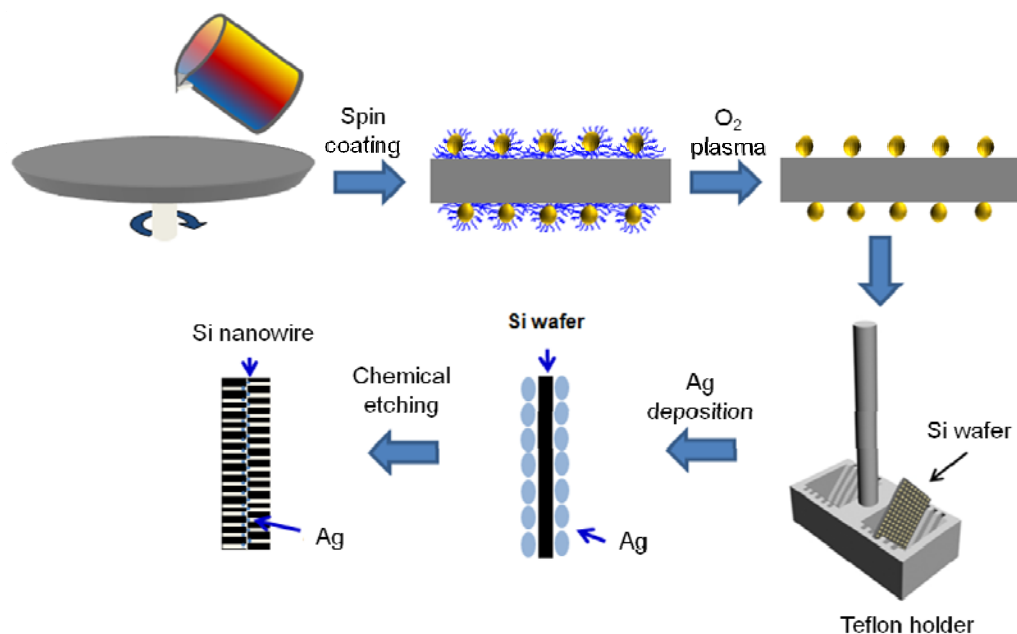
**Materials:** Highly boron-doped silicon (p-type, Si(100) plane, resistivity of 0.008  $\Omega\cdot\text{cm}$ ) and silicon wafer with low doping level (p-type, Si(100) plane, resistivity of 1  $\Omega\cdot\text{cm}$ ) were purchased from International Wafer Source, Inc. Prior to use, silicon pieces were cleaned in acetone and isopropyl alcohol and dried under nitrogen. Three polystyrene-*block*-poly(4-vinylpyridine) (PS-*b*-P4VP) samples were purchased from Polymer Source, and were used without further purification (High molecular weight:  $M_n, \text{PS} = 109 \text{ kg/mol}$ ,  $M_n, \text{P4VP} = 27.0 \text{ kg/mol}$ ,  $M_w/M_n = 1.12$ , middle molecular weight:  $M_n, \text{PS} = 35.0 \text{ kg/mol}$ ,  $M_n, \text{P4VP} = 21.0 \text{ kg/mol}$ ,  $M_w/M_n = 1.09$ , and low molecular weight:  $M_n, \text{PS} = 16.0 \text{ kg/mol}$ ,  $M_n, \text{P4VP} = 15.0 \text{ kg/mol}$ ,  $M_w/M_n = 1.08$ ). PS-*b*-P4VP copolymers were dissolved in toluene at 35°C for 6 hr and cooled to room temperature to yield a 0.5 wt% polymer solution. Subsequently, iron (III) chloride ( $\text{FeCl}_3$ , Sigma-Aldrich) was loaded to the polymer solutions with a molar ratio of metal to pyridine of 0.5 and stirred for 24 hr. The PS-*b*-P4VP solutions containing iron salts were spin-coated onto silicon wafer at 3000 rpm for 60 sec, and followed by oxygen plasma treatment (SPI Plasma Prep II, 50 watts) to obtain iron oxide ( $\text{Fe}_2\text{O}_3$ ) dotted arrays with the removal of polymers. This process was applied to the both sides of silicon wafers. For the electroless deposition (galvanic displacement reaction) of silver, silicon pieces were immersed in 10% hydrofluoric acid (HF) and 3 mM silver nitrate ( $\text{AgNO}_3$ ) to deposit silver particles, and subsequently rinsed with deionized water to remove extra silver ion for several times. Ag-deposited silicon wafer was immersed in an etchant composed of 10% HF and 1.2% hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) at 50 °C for a certain time to make silicon nanowires at both sides of silicon pieces. When the Ag-deposited silicon pieces having resistivity of 1  $\Omega\cdot\text{cm}$  were etched at 50 °C for 3 hrs, there was no supporting Si layer,

indicating that SiNWs from both sides were fully developed. As-prepared SiNWs were dispersed in ethanol by ultrasonication for 10 min and dried in vacuum oven for 12 hrs to obtain nonporous SiNW anode materials. In the same manner, nano-porous SiNW anode materials were prepared. Nonporous SiNWs were synthesized with a yield of ~40%, while porous SiNWs were obtained with relatively low yield of ~15% due to a formation of mesopores within nanowires. To coat the carbon layer on the surface of silicon nanowires, thermal decomposition process of acetylene gas was performed at 700 °C for 30 min in quartz furnace.

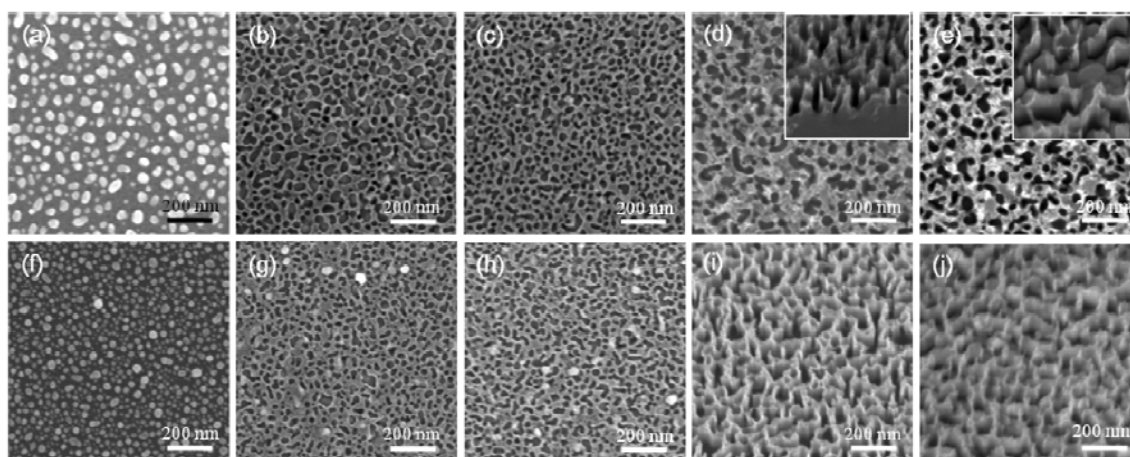
**Characterization of block copolymer films and Silicon nanowires:** Iron-incorporated PS-*b*-P4VP thin films and iron oxide patterns on a silicon wafer were imaged by atomic force microscope (AFM, Digital Instruments, Nanoscope III) in the tapping mode. For high resolution transmission electron microscopy (HR-TEM) measurements, vertically aligned silicon nanowires were dispersed in ethanol by ultra-sonication, and transferred onto Formvar-coated copper grids. TEM images were taken in the bright-field mode using JEM 2100 (JEOL) operated at 200 kV accelerating voltages. Silicon nanowires prepared from various etching time were characterized by scanning electron microscope (SEM, NanoSEM 230, FEI) operating at 10 kV without any metal coating. The crystal structures of the silicon nanowires were measured by high power X-ray diffractometer (XRD) on a Rigaku D/MAX at 2500 V using Ni-filtered Cu K $\alpha$  radiation with a graphite diffracted beam monochromator. Raman spectra were obtained, and the dimensional ratio of disordered (D) band to the graphene (G) band ( $I_D/I_G$ ) was fitted after baseline correction (WITEC, Alpha-300M). A He-Ne laser operating at  $\lambda = 632.8$  nm was used as the excitation source.

**Electrochemical performance:** Coin-type half cells (2016R type) were assembled in

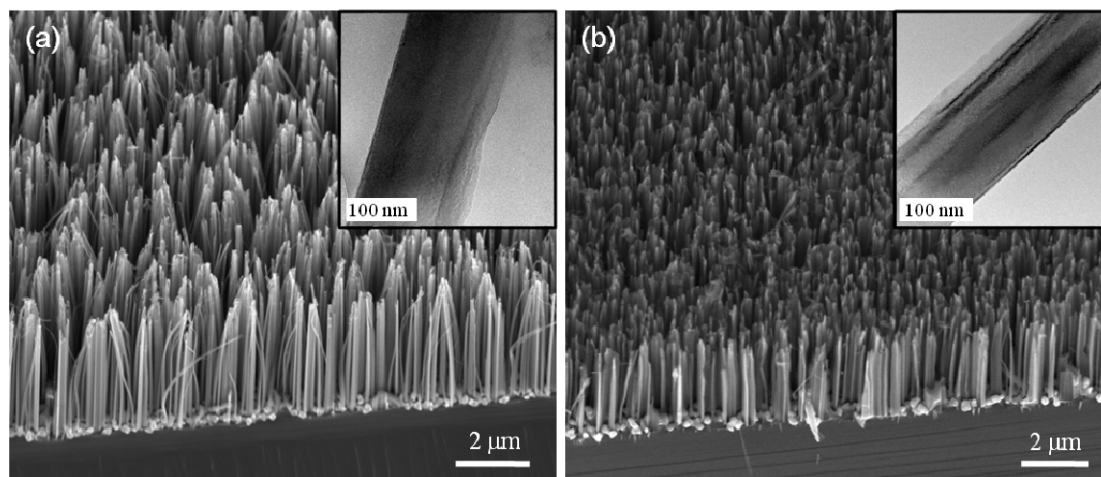
an argon-filled glove box. As-prepared silicon nanowires obtained by Ag-assisted chemical etching process were dispersed in ethanol by ultrasonication, and completely removed the solvent in vacuum oven. Prior to carbon coating, the SiNWs were etched in 5% HF for 10 min to remove silicon oxide layer that may form during the dispersion in ethanol, and subsequently dried in vacuum oven for 12 hr. Carbon-coated silicon nanowires were used as the working electrodes and lithium metal foils as the counter electrodes. The electrolyte was  $\text{LiPF}_6$  (1.0 M) with ethylene carbonate/dimethyl carbonate/diethylene carbonate (EC/DMC/DEC, 30:40:30 vol%, Cheil Industries, Korea). The coin-type half cells were cycled at a rate of 0.1 C between 0 and 1.5 V. The electrode was composed of carbon coated silicon nanowires (60 wt%), Super P carbon black (20 wt%), and poly(vinylidene fluoride) (20 wt%).



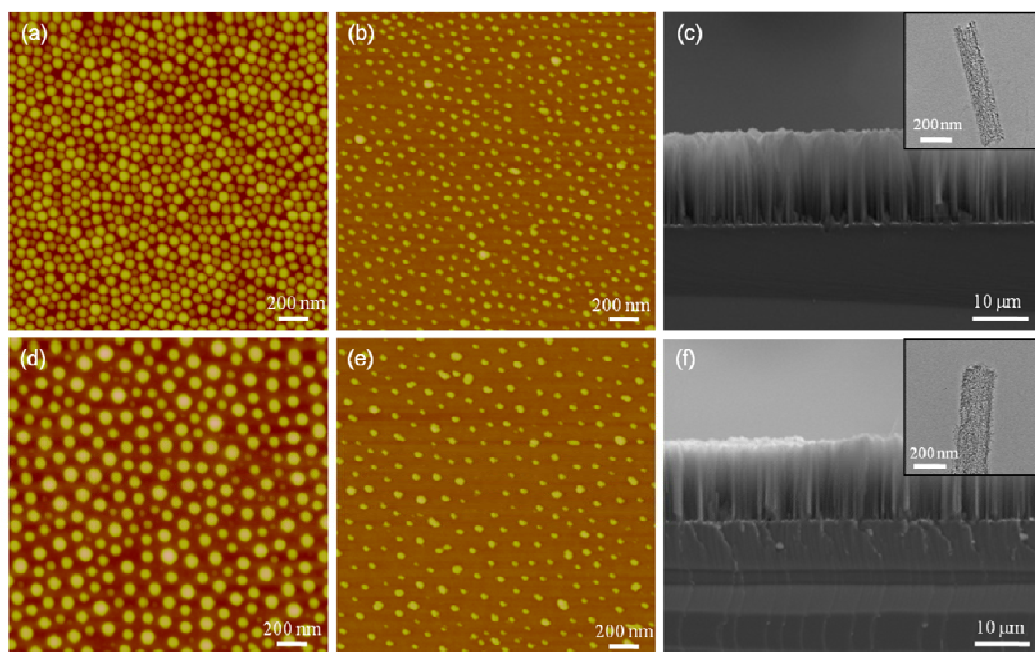
**Fig. S1** Schematic illustration of the fabrication of nonporous and porous SiNW arrays by combining block copolymer templates and silver catalytic etching process. Block copolymer containing iron salts were spin-coated onto both sides of silicon surfaces and treated with oxygen plasma to make iron oxide dotted arrays. Subsequently, Ag was deposited onto silicon surface and followed by immersing in an etchant to obtain vertical aligned SiNWs with mass production.



**Fig. S2** SEM images showing silver catalytic etching process in the silicon wafer without (a-e) and with (f-j) iron oxide patterns as a function of etching time. When bare (a) and patterned (b) silicon pieces were immersed in HF/AgNO<sub>3</sub> mixture for 3 min, small nanoparticles were deposited onto the patterned one, while nanoparticles with broader size distribution deposited onto unpatterned one. As sample (a) and (f) were immersed in a HF/H<sub>2</sub>O<sub>2</sub> etchant for 5 s (b, g), 10 s (c, h), 30 s (d, i), and 60 s (e, j), silver catalytic chemical etching was carried out. With the increase of etching time, areas of nanopits were significantly increased due to the strong interconnection of silver particles. The density of SiNWs prepared from iron oxide patterned silicon wafer is higher than unpatterned silicon wafer. SEM was measured with top-view (panel (a) & (f)) and tilt-view at tilting angle of 30° (the other panels).

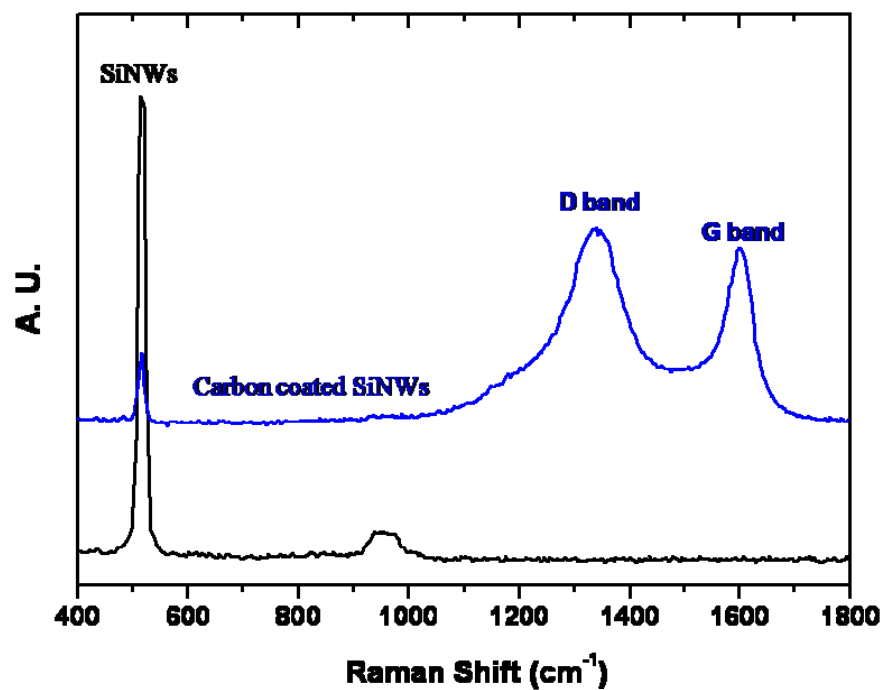


**Fig. S3** SEM images of vertical aligned SiNWs prepared from unpatterned (a) and iron oxide patterns silicon wafer (b). Ag-deposited samples were immersed in an etchant at 50 °C for 90 min to make isolated long silicon nanowires. The SiNWs having diameter of 20-300 nm were synthesized from unpatterned silicon wafer, while uniform-sized SiNWs with 80-100 nm were formed in the patterned wafer. Moreover, the population of SiNWs prepared from patterned silicon was much higher than unpatterned one, as shown in both SEM images.

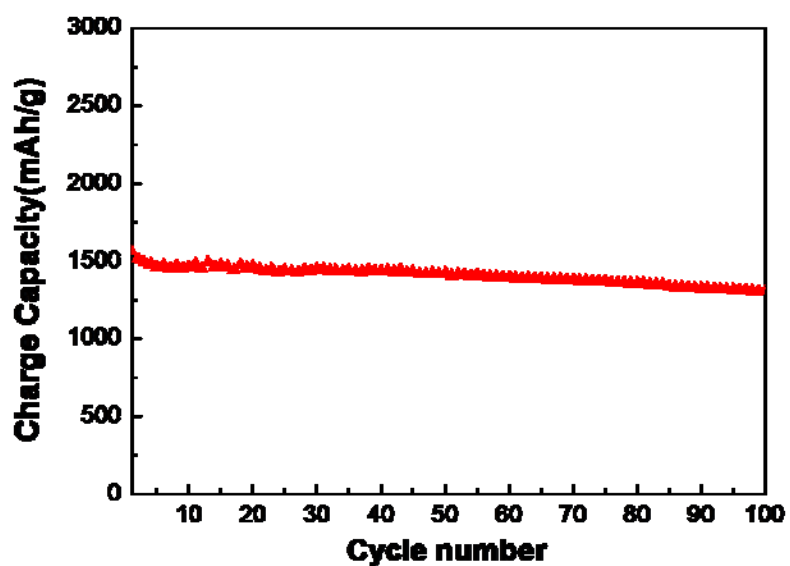


**Fig. S4** Preparation of diameter-controlled SiNWs with high molecular weight PS-*b*-P4VP copolymer templates. Iron oxide dotted arrays from two different molecular weight ( $M_n = 59$  kg/mol: panel a-c) and 136 kg/mol: panel d-f) were fabricated by using the same procedure as mentioned in the low molecular weight system. When silver was deposited onto the patterned silicon wafer having an average separation distance of 70 and 100 nm, immersed in an etchant at 50 °C for 1 hr, porous silicon nanowires with diameter of 190 and 240 nm were synthesized, respectively.

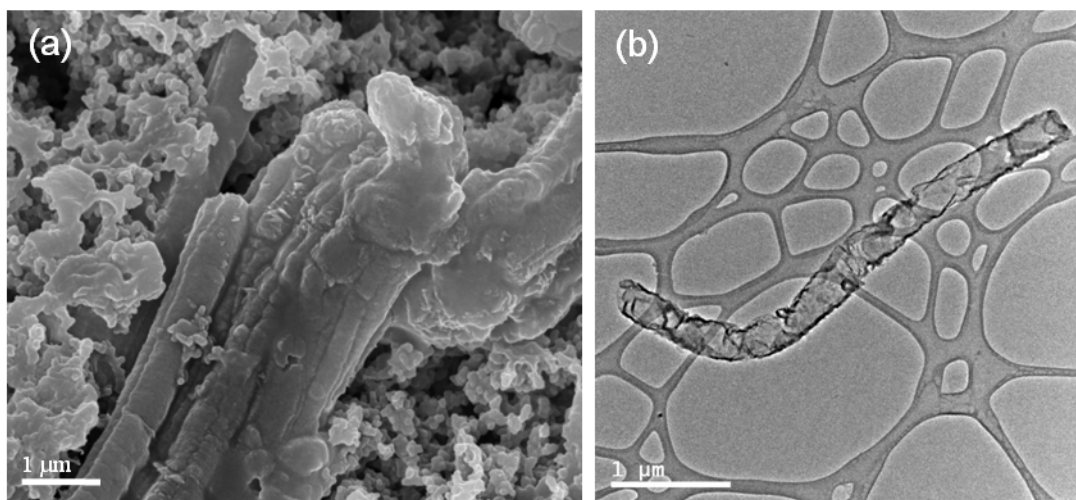




**Fig. S5** Raman spectra of SiNWs with carbon layer prepared from thermal decomposition of acetylene gas at 700 °C. The large ratio of the D band to the G band ( $I_D/I_G = 2.5$ ) indicates low graphitic degree of carbon layer.



**Fig. S6** Cycling retention of nanoporous SiNW anodes at a rate of 0.2 C between 1.5 and 0.01 V in coin-type half cells.



**Fig. S7** SEM (a) and TEM (b) images of nonporous silicon nanowires after 50 cycles at 0.1 C rate. The diameter of nonporous SiNWs increased from ~100 nm to ~200 nm after cycling and the morphology was also transformed to nanosheet-like structure.