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Electronic Supplementary Information

Highly Porous Carbon-Coated Silicon Nanoparticles with Canyon-Like Surfaces as a High-Performance Anode Material for Li-Ion Batteries

Bokyung Kim,[1‡] Jihoon Ahn,[1‡] Yunjung Oh,[1] Jeiwan Tan,[1] Daehee Lee,[1] Jin-Kyu Lee[2] and Jooho Moon[1,*]

[1] Department of Materials Science and Engineering, Yonsei University, 50 Yonsei-ro, Seodaemun-gu, Seoul, 120-749, Republic of Korea
[2] Department of Chemistry, Seoul National University, 1 Gwanak-ro, Gwanak-gu, Seoul, 151-742, Republic of Korea

**E-mail: jmoon@yonsei.ac.kr*

Calculation 1: Ratio of total pore volume to Si volume
Ratio of total pore volume to Si volume was calculated assuming 1 g of Si.
Total pore volume / Volume of Si
= [Total pore volume ($\text{cm}^3\ \text{g}_{\text{Si}}^{-1}$) × 1 g_{Si} / Specific volume of Si ($\text{cm}^3\ \text{g}_{\text{Si}}$) × 1 g_{Si}] × 100 (%)
= [Total pore volume ($\text{cm}^3\ \text{g}_{\text{Si}}^{-1}$) × 1 g_{Si} / 0.4294 ($\text{cm}^3\ \text{g}_{\text{Si}}$) × 1 g_{Si}] × 100 (%)
Based on this equation, the ratio of total pore volume to Si volume can be calculated for each sample.

(1) For npSi
When the measured total pore volume (0.03 $\text{cm}^3\ \text{g}_{\text{Si}}^{-1}$) was utilized for the calculation,
[0.03 ($\text{cm}^3\ \text{g}_{\text{Si}}^{-1}$) × 1 g_{Si} / 0.4294 ($\text{cm}^3\ \text{g}_{\text{Si}}$) × 1 g_{Si}] × 100 (%)
= 6.99%
(2) For pSi
When the measured total pore volume (0.716 $\text{cm}^3\ \text{g}_{\text{Si}}^{-1}$) was utilized for the calculation,
[0.716 ($\text{cm}^3\ \text{g}_{\text{Si}}^{-1}$) × 1 g_{Si} / 0.4294 ($\text{cm}^3\ \text{g}_{\text{Si}}$) × 1 g_{Si}] × 100 (%)
= **167%**
When the expected total pore volume (0.801 $\text{cm}^3\ \text{g}_{\text{Si}}^{-1}$) was utilized for the calculation (see Calculation 2 for the details of calculating expected total pore volume),
[0.801 ($\text{cm}^3\ \text{g}_{\text{Si}}^{-1}$) × 1 g_{Si} / 0.4294 ($\text{cm}^3\ \text{g}_{\text{Si}}$) × 1 g_{Si}] × 100 (%)
= **187%**
(3) For cpSi
The total pore volume of cpSi was calculated by adding the pore volume from MgO etching and the pore volume of the canyon-like structure because direct measurement of the pSi structure cannot be implemented owing to the collapse of the canyon-like structure after MgO etching without carbon coating. The pore volume from MgO etching (0.801 $\text{cm}^3\ \text{g}_{\text{Si}}^{-1}$) from Calculation 2 was adopted, and the pore volume of the canyon-like structure (1.01 $\text{cm}^3\ \text{g}_{\text{Si}}^{-1}$) is adopted from Calculation 3. Therefore, the ratio of the pore volume to Si volume can be calculated as follows:
[1.802 ($\text{cm}^3\ \text{g}_{\text{Si}}^{-1}$) × 1 g_{Si} 0.4294 ($\text{cm}^3\ \text{g}_{\text{Si}}$) × 1 g_{Si}] × 100 (%)
= **419%**

Calculation 2: Expected total pore volume of pSi

In this calculation, the total pore volume of pSi is assumed to be derived only from MgO etching. In our calculation, we assumed 1 mol of SiO_2 and 2 mol of Mg was used for magnesiothermic reduction ($SiO_2(s) + 2Mg(g) \rightarrow Si(s) + 2MgO(s)$). When the reaction completes, a composite of 1 mol of Si and 2 mol of MgO is obtained. As the MgO volume would become the pore volume, we can calculate the total pore volume by the following equation:
(Volume of MgO)/(mass of Si)
= [(mole of MgO) × (molecular weight of MgO) ÷ (density of MgO)] / [(mole of Si) × (molecular weight of Si)]
= (2 mol × 40.3044 g mol^{-1} ÷ 3.58 g cm^{-3}) / (1 mol × 28.0855 g mol^{-1})
= **0.801 cm^3 g_{Si}^{-1}.**

Calculation 3: Pore volume of canyon-like structure
The pore volume of the canyon-like structure can be obtained from the pore volume of cpSi+MgO (0.26 cm^3 g_{Si+MgO}^{-1}) as measured by N_2 sorption. Conversion of the unit into the pore volume per mass of Si was necessary, so the following calculation was conducted:
Assuming a complete magnesiothermic reduction with 1 mol of SiO_2 and 2 mol of Mg, we can obtain 1 mol of Si and 2 mol of MgO. As 1 mol of Si is 28.0855 g and 2 mol of MgO is 80.6088 g, the total mass of Si+MgO would be 108.6943 g. When the Si+MgO composite was converted to Si, the weight of MgO was lost. Therefore, the pore volume of the canyon-like structure in the final structure should be:
0.26 cm^3 g_{Si+MgO}^{-1} × 108.6943 g_{Si+MgO} ÷ 28.0855 g_{Si} = **1.01 cm^3 g_{Si}^{-1}**

Calculation 4: Calculation of carbon wt% per contour surface area of Si nanoparticles
In order to calculate the carbon wt% per surface area, we measured the BET surface area of cpSi+MgO, pSi+MgO, and npSi. The BET surface areas of cpSi+MgO and pSi+MgO were utilized for this calculation because the carbon coating was performed before MgO etching, so the carbon only coated the contour surface region of the nanoparticle and not the surface of pores made by MgO etching. However, as the BET surface areas of cpSi+MgO and pSi+MgO are given in units of m^2 g_{Si+MgO}^{-1}, they should be converted to m^2 g_{Si}^{-1} for the calculation and comparison with npSi. A similar conversion process as that used for Calculation 3 was performed, so the contour surface area of the Si nanoparticle on which carbon was coated can be calculated likewise:
(Contour surface area of Si (m^2 g_{Si}^{-1})) = (measured surface area of Si+MgO (m^2 g_{Si+MgO}^{-1})) × (108.6943 g_{Si+MgO} ÷ 28.0855 g_{Si}.)
The results of this calculation are listed in Table S1.
Subsequently, carbon per surface area can be calculated using the carbon weight ratio to Si (g_C/g_{Si}) obtained from the carbon wt% (g_C/g_{Si+C} × 100) obtained by the TGA analysis in Figure S8.
(Carbon amount per contour Si surface area, g_C m^{-2})
= (carbon weight ratio to Si weight, g_C/g_{Si}) / (modified Si surface area, m^2 g_{Si}^{-1}).
By this equation, we can obtain the values as follows:
1) For cpSi@C:
20.2 wt%C ÷ 175.58 m^2 g_{Si}^{-1}
= (20.2 g_C/100 g_{Si+C}) ÷ 175.58 m^2 g_{Si}^{-1} = (20.2 g_C/79.8 g_{Si}) ÷ 175.58 m^2 g_{Si}^{-1}
= **0.00144 g_C m^{-2}**
2) For pSi@C: 7.98 wt%C / 63.04 m^2 g_{Si}^{-1} = **0.00137 g_C m^{-2}**
3) For npSi@C: 1.52 wt% C / 13.22 m^2 g_{Si}^{-1} = **0.00117 g_C m^{-2}**
From these calculations, all the samples have virtually the same values, i.e. 0.00144 g_C m^{-2} for cpSi@C, 0.00137 g_C m^{-2} for pSi@C, and 0.00117 g_C m^{-2} for npSi@C. As the carbon weight per contour surface area is associated with the thickness of the carbon layer on the nanoparticle, it can be concluded that we prepared Si-based materials with different pore morphologies but similar carbon thicknesses.

Calculation 5: Pore volume of pSi irrelevant with the MgO etching

Pore volume of pSi which does not originate from MgO etching can be calculated from the pore volume of pSi+MgO similarly as Calculation 3.
0.03 cm^3 g_{Si+MgO}^{-1} × 108.6943 g_{Si+MgO} ÷ 28.0855 g_{Si} = **0.12 cm^3 g_{Si}^{-1}**

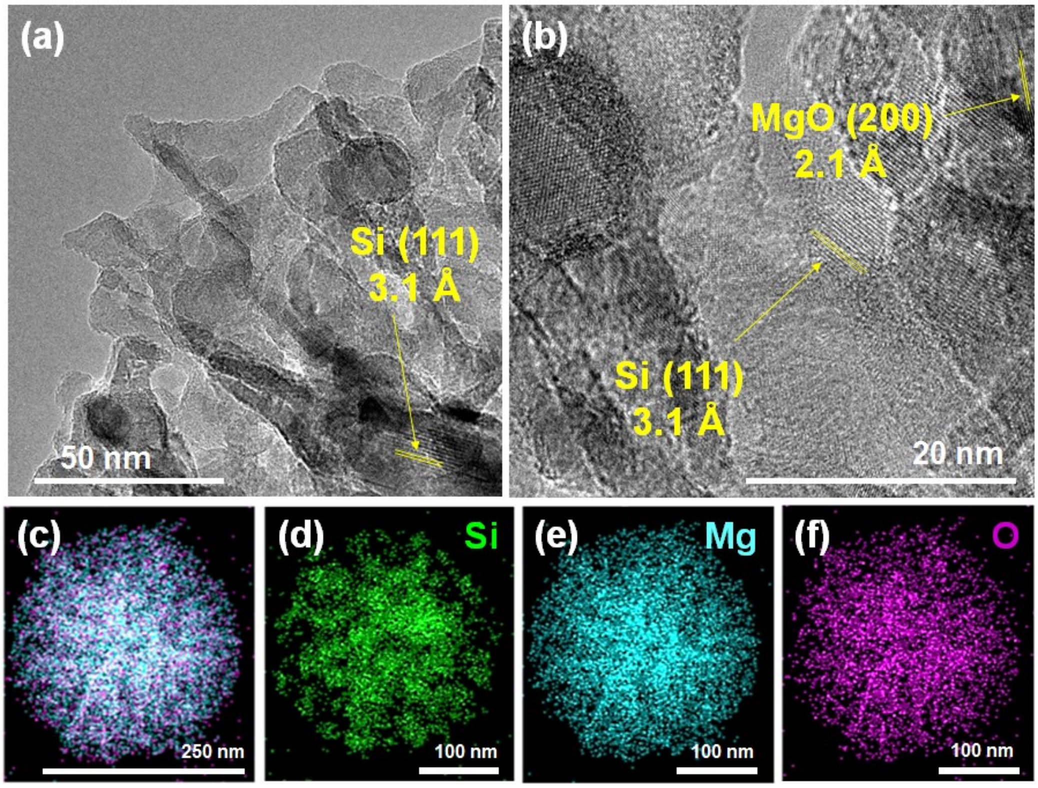

Fig. S1 Microstructure of cpSi+MgO composite particles. Cs-corrected HR-TEM image of the (a) edge and (b) core of cpSi+MgO. EDX elemental mapping images of the cpSi+MgO nanoparticle are shown for (c) all elements, (d) elemental Si, (e) elemental Mg, and (f) elemental O.

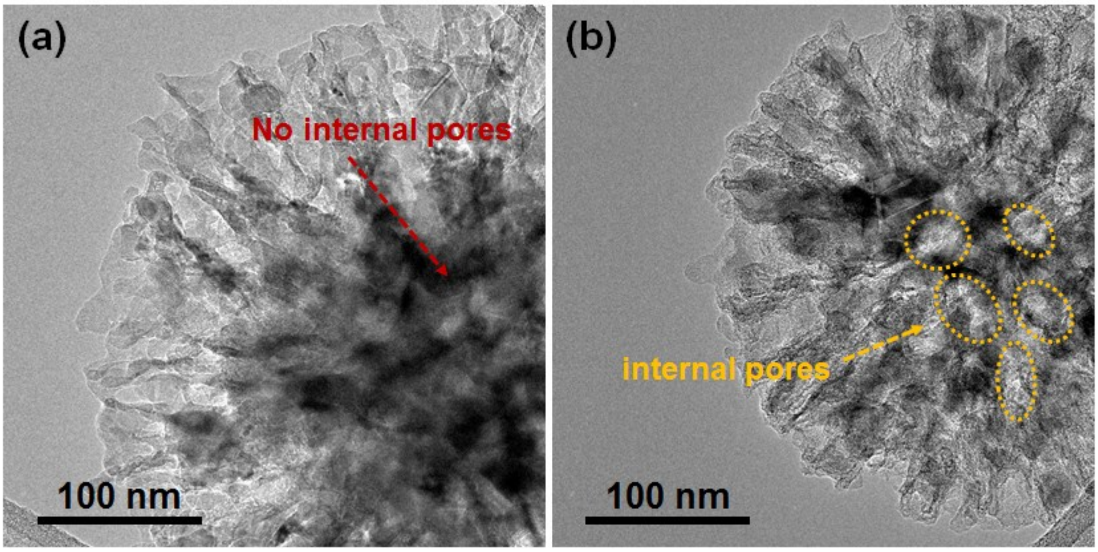

Fig. S2 Microstructure of nanoparticles presenting morphological differences of internal pore originatedfrom MgO etching. C_s-corrected HR-TEM image of (a) before MgO etching (cpSi+MgO) and (b) after MgO etching and carbon coating (cpSi@C).

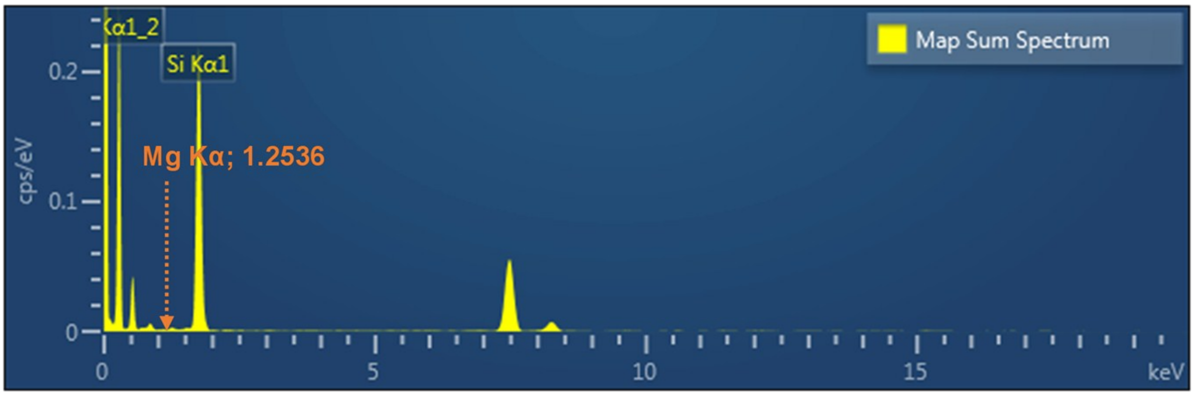

Fig. S3 EDX spectrum of cpSi@C; note that signal of Mg (Kα= 1.2536) which can be from MgO residue does not exist.

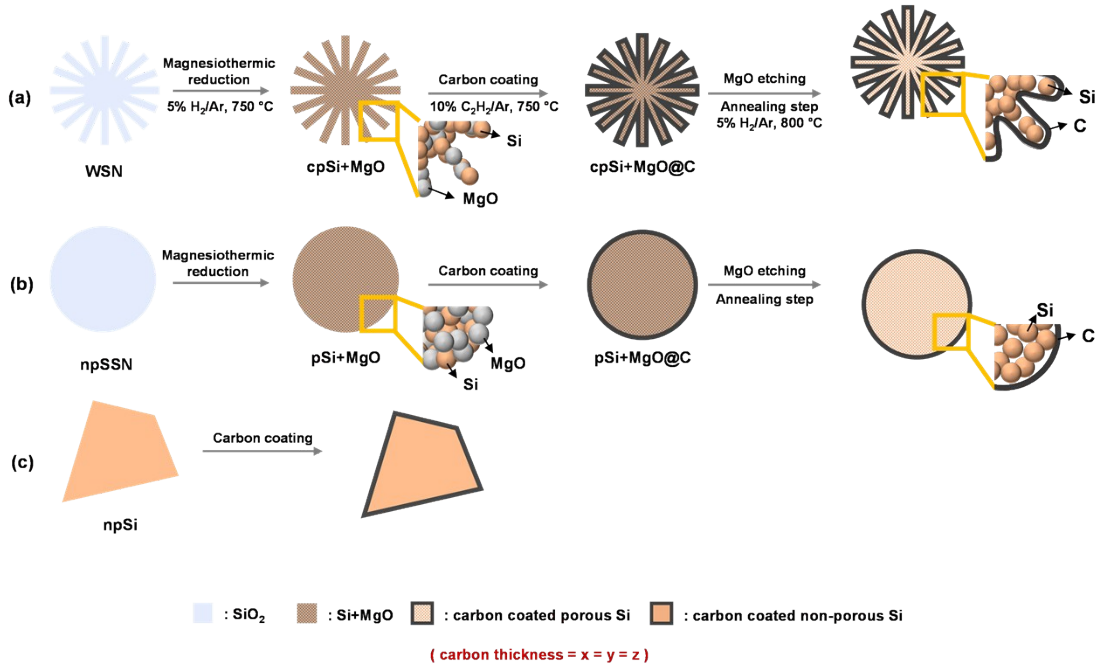

Fig. S4 Schematic illustration of the preparation of samples; (a) cpSi@C was synthesized from magnesiothermic reduction of WSNs, carbon coating, MgO etching, and annealing step; (b) pSi@C was prepared by magnesiothermic reduction of non-porous spherical SiO_2 nanoparticles (npSSN), carbon coating, MgO etching, and annealing step; (c) npSi@C was fabricated from commercial non-porous nanoparticles (npSi) with carbon coating. It should be noted that carbon was only coated on the contour surface region of the particles before MgO etching. Also, the MgO etching formed porosity inside the carbon layer for cpSi@C and pSi@C.

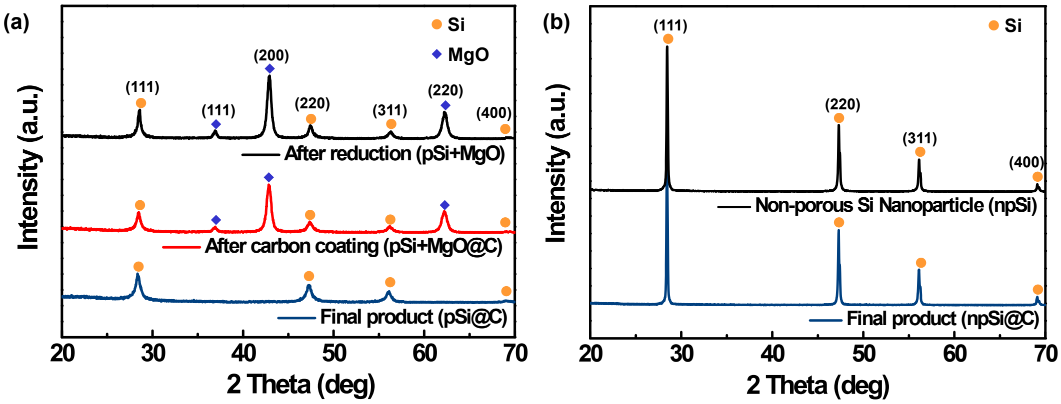

Fig. S5 XRD patterns of samples in the course of synthesizing (a) pSi@C and (b) npSi@C.

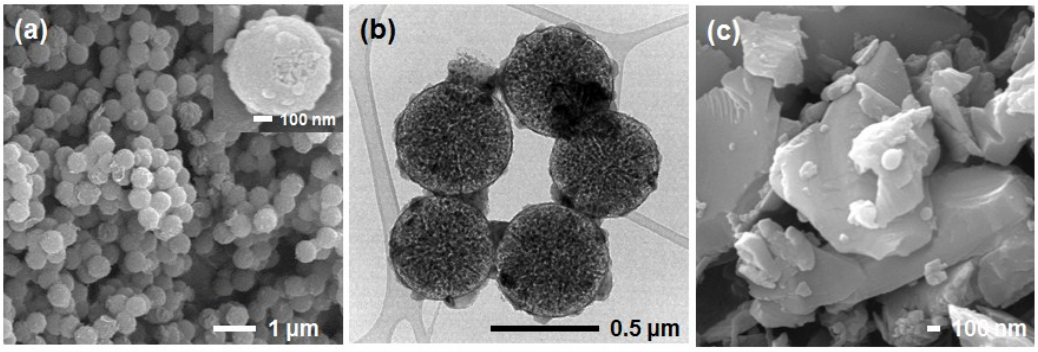

Fig. S6 FE-SEM and TEM images of two control samples. (a, b) pSi@C has spherical morphology formed of porous Si with a conformally coated carbon shell. (c) npSi@C has an irregular shape with a carbon layer because it was obtained from commercial non-porous Si, which had irregular particle morphology.

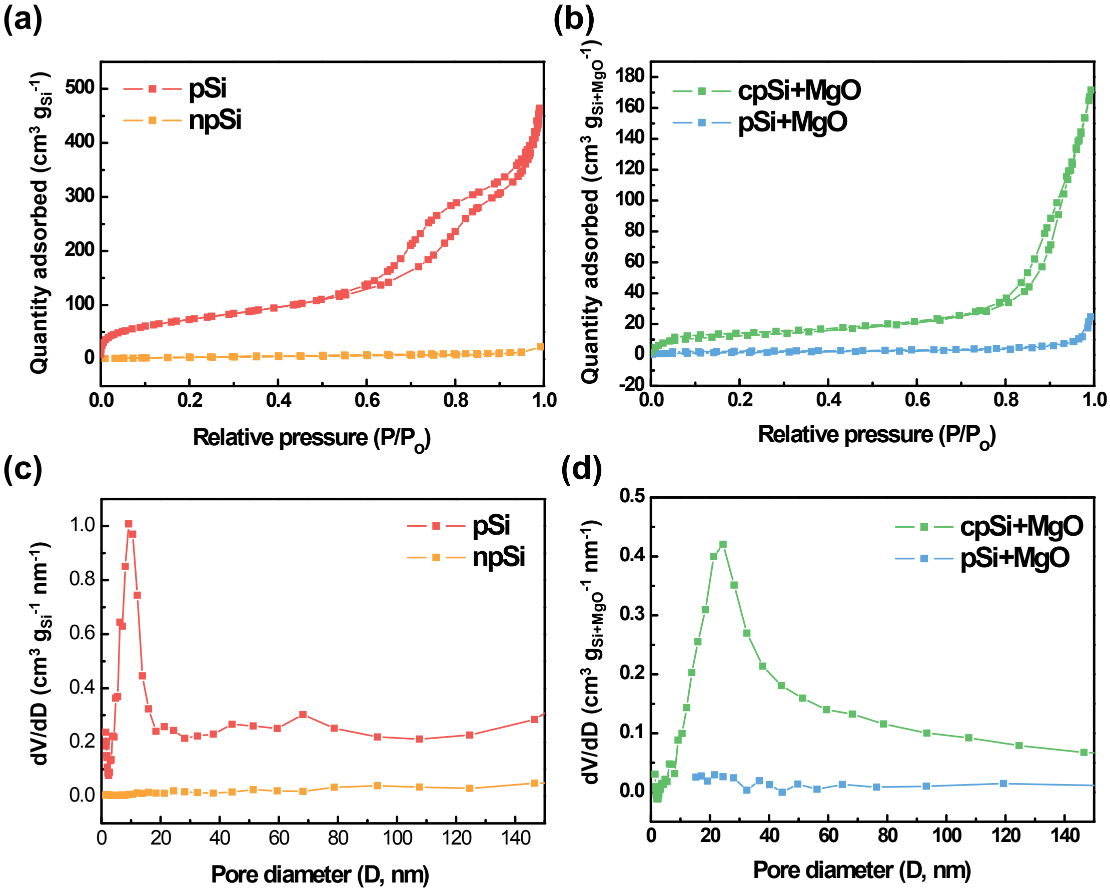

Fig. S7 N_2 sorption isotherms of (a) npSi, pSi, and (b) cpSi+MgO, pSi+MgO; BJH pore diameter distributions of (c) npSi, pSi, and (d) cpSi+MgO, pSi+MgO extracted from the adsorption branches of the isotherms. (pSi denotes the npSSN sample magnesiothermically reduced after MgO etching without carbon coating, V and D stand for pore volume and pore diameter, respectively.)

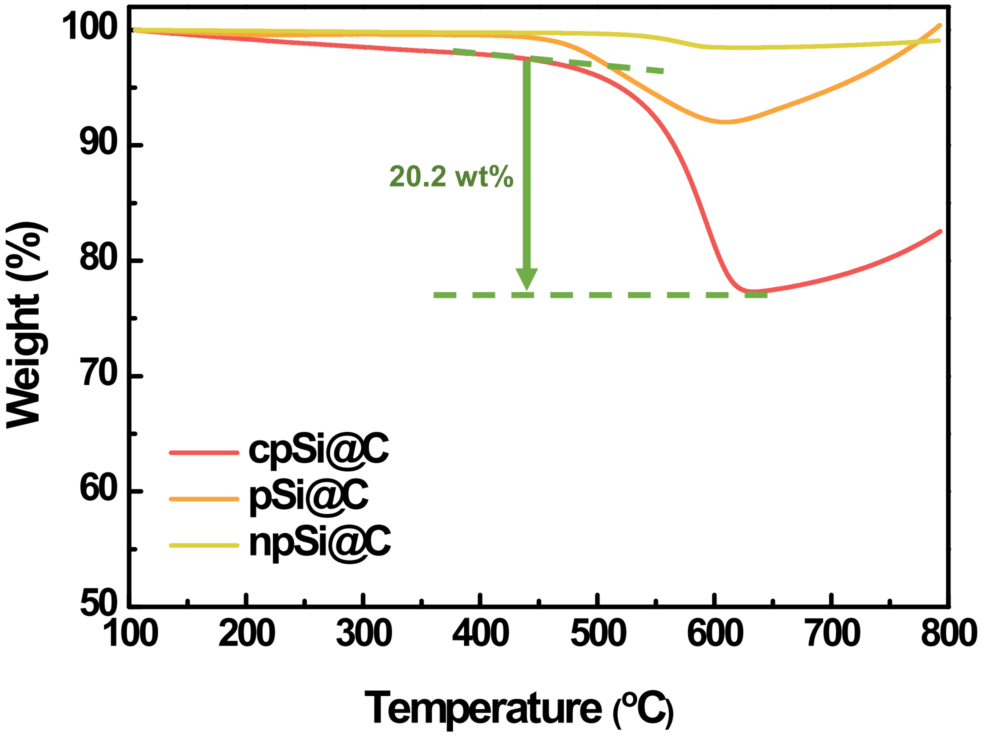

Fig. S8 TGA profile of cpSi@C, pSi@C, and npSi@C, demonstrating the pyrolytic decomposition of carbon around 600 °C under an atmosphere of artificial air (O_2 21% and N_2 79%). The gradual weight gains above 600 °C can be attributed to oxidation of Si. This indicates that the carbon contents are 20.2, 7.98, and 1.52 wt%, respectively.

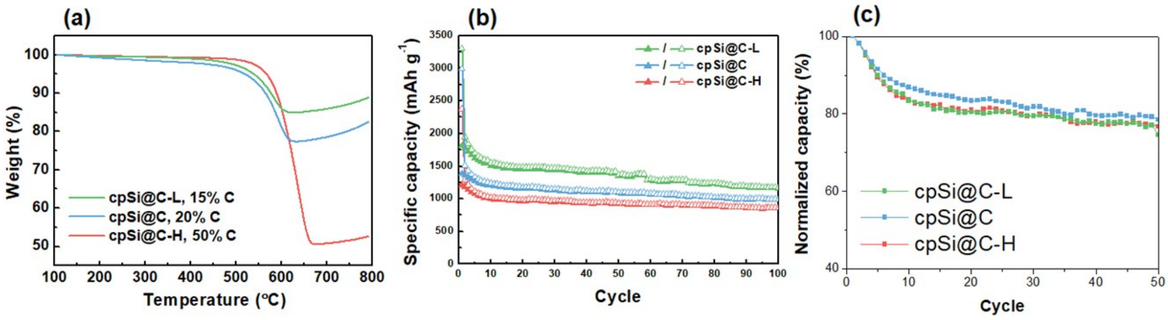

Fig. S9 (a) TGA plots, (b) cycling performances, and (c) normalized charging capacities of cpSi@C series samples with the varying carbon contents.

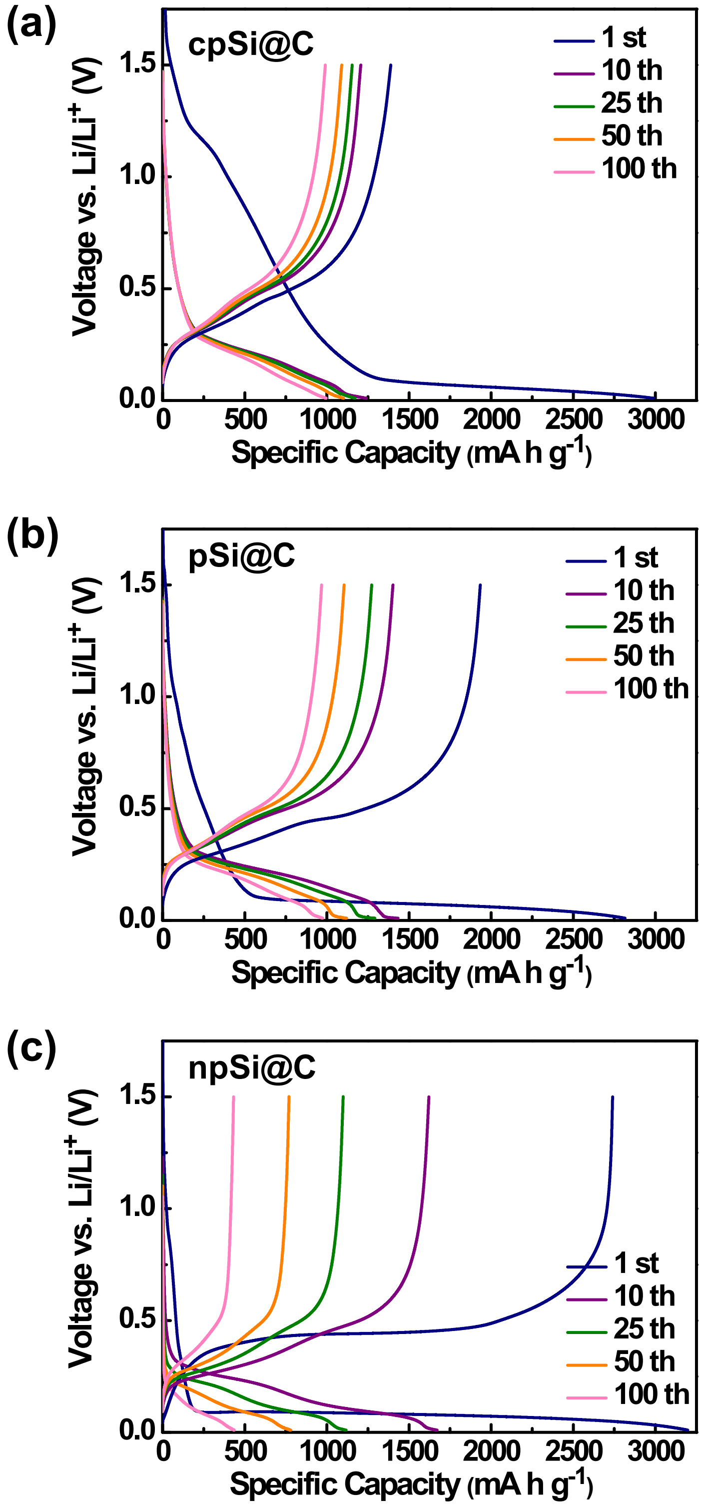

Fig. S10 Discharge-charge potential profiles of (a) cpSi@C, (b) pSi@C, and (c) npSi@C for the 1st, 10th, 25th, 50th, and 100th cycles at 0.5 A g^{-1}.

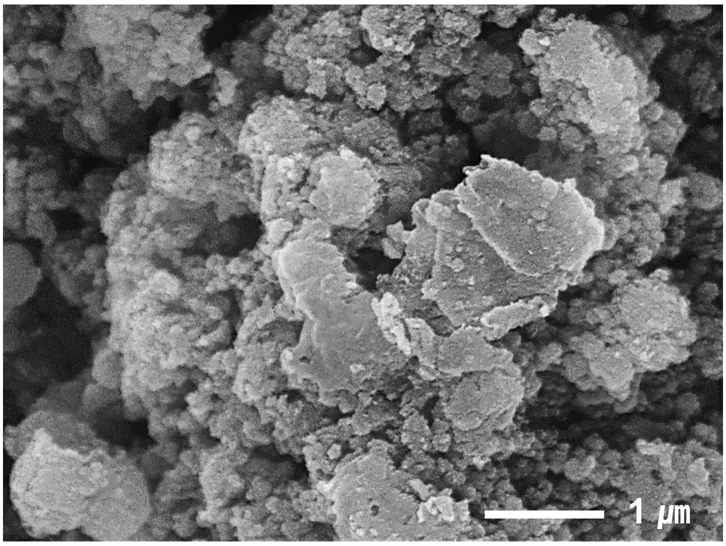

Fig. S11 SEM images of the pSi@C electrode after 50th cycles.

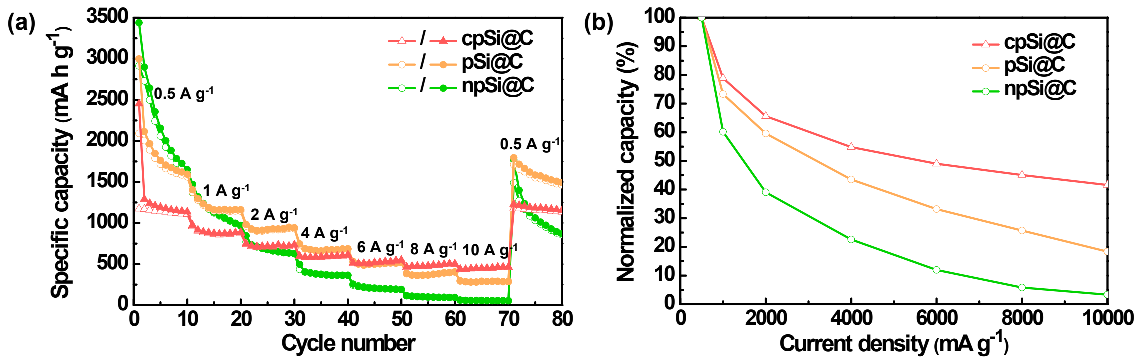

Fig. S12 (a) Rate capabilities for cpSi@C, pSi@C, and npSi@C; and (b) Normalized charge capacities for cpSi@C, pSi@C, and npSi@C at different current densities ranging from 0.5 to 10 A g^{-1}.

Table S1. Total pore volumes, ratios of total pore volume to Si volume, and carbon-coated contour surface areas for cpSi, pSi, and npSi

	Total pore volume [$cm^3\ g_{Si}^{-1}$]	Ratio of total pore volume to Si volume[a] [%]	Carbon coated contour surface area[b] [$m^2\ g_{Si}^{-1}$]
Canyon-like porous structure (cpSi)	1.802[c]	419	175.58
Porous structure (pSi)	0.716 (0.801)[d]	167 (187)[d]	63.04
Non-porous structure (npSi)	0.03	6.99	13.22

a) See Calculation 1 in ESI† for details. b) Contour surface area on which carbon layer was coated (see Calculation 4 in ESI† for details). c) Theoretically calculated value; total pore volume of cpSi was calculated by adding the pore volume of the canyon-like structure and the pore volume from MgO etching (see Calculation 3 in ESI†), whereas the total pore volume of pSi and npSi were obtained from N_2 sorption experiments. d) Theoretically calculated value on the basis of only MgO etching contributing to the total pore volume. See Calculation 1 and 2.

Table S2. Performance comparison between cpSi@C and magnesiothermically prepared Si-C composites in literature.

Description of structure	maximum capacity[a] [mAh/g]	Retained capacity at specific cycles[a] [mAh/g]	Retention [%]	Rate [mA/g or C-rate]	Ref.
cpSi@C	1389	1090 (50th) 990 (100th) 822 (200th)	78.5 71.6 59.1	500	This work
Porous Si from sand @reduced graphene oxide	~2625	~1400 (50th)	53.3	200	S1
Porous Si from SiO_2 nanoparticle+CNT	~2980[a]	2200 (50th)	73.8	0.05C	S2
Porous Si from sand @C	~2300	~1500 (100th)	65.	1000	S3
Porous Si@C from reed plant	~2435	~1050 (200th)	43.1	0.5C	S4

a) Discharging capacity at second cycle was adopted, if charging capacity is not available.

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S3 J.-K. Yoo, J. Kim, M.-J. Choi, Y.-U. Park, J. Hong, K. M. Baek, K. Kang and Y. S. Jung, *Adv. Energy Mater.*, 2014, **4**, 1400622.
S4 J. Liu, P. Kopold, P. A. van Aken, J. Maier and Y. Yu, *Angew. Chem. Int. Ed.*, 2015, **54**, 9632-9636.