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A Space-Confined Atom-Cluster Catalytic Strategy for Direct Superassembly of Silicon Nanodots in Carbon Frameworks for Lithium-ion Batteries

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Abstract

Incorporating nanoscaled Si into carbon matrix with high dispersity is desired for lithium-ion batteries (LIBs); however, it remains challenging. Herein, we propose a novel space-confined atom-cluster catalytic strategy for direct superassembly of Si nanodots-embedded carbon (Si NDs@C) framework via a copyrolysis of triphenyltin hydride (TPT) and diphenylsilane (DPS), where self-created Sn atom clusters from TPT pyrolysis serve as the catalyst for DPS pyrolysis and Si catalytic growth. The use of Sn atom cluster catalyst can alter the reaction pathway to avoid SiC generation and enable forming Si nanodots with reduced dimensions. The typical Si NDs@C framework demonstrates a remarkable comprehensive performance comparable to other Si-based high-performance half LIBs and higher energy densities than commercial full LIBs, due to the high dispersity of Si nanodots with low lithiation stress revealed by mechanic simulations. This study paves a new way to construct ideal Si/C composites for future energy applications.

Introduction

There is a strong demand to develop rechargeable lithium-ion batteries (LIBs) with higher energy capacity and longer cycle life for applications in portable electronic devices and electrical/hybrid vehicles.^[1-2] Si has been recognized as one of the most promising anode candidates due to its high theoretical lithium storage capacity (4200 mAh g^{-1} for

$\text{Li}_{22}\text{Si}_5$) and moderate Li-uptake potential (0.4 V vs Li/Li^+).^[3-6] However, the serious volume variation ($\sim 400\%$) of Si electrodes plus poor conductivity often caused electrode pulverization and active material loss, resulting in the overall performance deterioration of batteries.^[7-11] Incorporating Si into carbon matrix has been recognized an effective way to improve structural and electric integrity of Si-based electrodes for enhanced lithium-ion battery performance.^[12-14] However, the Si/C composites prepared by physical mixing of the two components,^[15-18] often caused weak interfacial interactions and uneven dispersion of the two components, adverse to electron transfer at interfaces and cycling stability of composite anodes.

It is noted that the metal catalyst-based chemical vapor deposition (CVD) strategy where catalyst nanoparticles dispersed on necessary substrates as catalytic sites for *in situ* growth of Si nanowires with a vapor-liquid-solid (VLS) mechanism^[8,10,19-22] provides a good possibility to uniformly anchor Si into carbon matrix in Si/C composites. However, the introduction of metal catalysts to carbon matrix were mainly through extra manipulations of physical sputtering or chemical deposition, suffered from complicated processes and poor distribution of metal catalysts. Moreover, the catalytic growth of Si was mostly conducted in unconfined space with uninterruptible Si source feeding, leading to the overgrowth of Si and the formation of Si nanowires with long length (hundreds of nanometer \sim micrometer). Besides, in most cases, the catalysts employed were in the form of nanoparticles with

relatively big diameters, which, according to the catalytic growth mechanism,^[23] results in the generation of large-diameter Si nanowires (over 50 nm). In principle, Si nanowires with long length and large diameter are not conducive to electron transfer from Si to current collector via Si-carbon interface and volume change suppression of Si. Therefore, the development of a simple and effective metal-catalytic strategy to construct Si/C composites with favorable structures for high-performance LIBs is highly desired.^[24,25]

In this article, we propose a novel Sn atom-cluster catalytic strategy for the superassembly of Si nanodots (Si NDs) embedded carbon (Si NDs@C) framework for high-performance lithium-ion batteries. The strategy was realized through an elaborate design of copyrolysis of triphenyltin hydride (TPT) and diphenylsilane (DPS), during which Sn atom clusters were produced firstly from TPT pyrolysis and served as the catalyst for the pyrolysis of DPS and the catalytic growth of Si. The employment of Sn atom cluster catalyst can not only break Si-C bonds of DPS and graphitize carbon framework at lower temperatures avoiding the generation of SiC, but also reduce the dimensions of Si product to form Si nanodots according to the reported size-dependent correlation between catalysts and Si product.^[26] The prepared Si@C composite made of silicon nanodots dispersed uniformly in hybrid amorphous/graphitized carbon framework with a hierarchical pore structure (micropore of ~ 1.6 nm, large mesopore of 12.0 ~ 50.0 nm and macropores over 50 nm) is beneficial for stable, fast and high-capacity lithium storage. Most significantly, the Si

NDsC framework shows low lithiation stress and an outstanding mechanical stability, revealed by Finite Element Calculations.^[27-30] As a result, the SiC framework anode exhibited high reversible capacity, long cycling stability as well as superior rate capability. Moreover, a series of full batteries assembled based on the SiC framework anodes and commercial cathode exhibited remarkable performance over the commercial full cells.

Results and discussion

The atom-cluster catalytic strategy for the Si NDsC framework is simple and straightforward, governed by stepwise elevating system temperature from 25 to 800 °C, as shown in Figure 1a,b. Firstly, the reactants of DPS and TPT powder were mixed up in a vacuumed quartz capsule at room temperature and vaporized to form a gas mixture at elevated temperature of 200 °C. When the temperature was increased to 600 °C, part of TPT molecules was preferentially decomposed to generate Sn metal due to the lower bond energy of Sn-C bonds in TPT than Si-C bonds in DPS (Figure S1). The evidence of TPT decomposition at 600 °C is shown in Figure S2. It is noted that a low molar ratio (1: 15) of TPT to DPS with a very low Sn atom concentration ($\text{Sn atom\%} = \text{number of Sn atoms} / \text{total number of Sn, Si and C} = 1:214 = 0.47\%$) enables the formation of Sn atom clusters dispersed uniformly on the synchronously formed amorphous carbon framework. Subsequently, with further elevating temperature to 800 °C, the formed Sn atom clusters

served as the catalyst to break the Si-C bonds of DPS and catalyze the growth of Si. It is noted that due to the insulation of carbon framework, the catalytic growth of Si was proceeded in a confined space, which results in the formation of Si NDs other than nanowires that were usually formed in conventional catalytic systems.^[31,32] With the catalytic pyrolysis going on, the superassembly of Si NDs and carbon components was occurred, promoted by the continuous generation of Si and carbon. Finally, the sphere-like Si \subset C composite made of Si NDs uniformly dispersed in partially graphitized carbon framework was produced after carbonization for another 5 h at 800 °C.

Figure 2 shows characterizations on morphology, structure and composition of the as-prepared Si NDs \subset C framework. The scanning electron microscopy (SEM) images shown in Figure 2a,b indicate that the Si \subset C composite holds a sphere-like shape with diameters of 1.0-1.5 μ m. The surface of those composite microspheres is covered by vertically arrayed carbon nanosheets (Figure 2b). The samples undergone different carbonization time at 800 °C imply that the carbon nanosheets in surface layer were formed during carbonization process (Figure S3 a,b). After sonication treatment, the nanosheets arrayed on the surface are peeled off and a relatively dense core of the microsphere appears (Figure S4a,b). From a much damaged microsphere, it can be seen that the inner core is made of layer-by-layer stacked carbon nanosheets surrounding the core (Figure S4c,d), exactly as that illustrated in Figure 1b. A low-magnification transmission electron microscopy (TEM) image (Figure 2c)

reveals that Si NDs with an average diameter of ~5 nm are dispersed uniformly in the carbon matrix. A Si nanodot that was arbitrarily selected shows clear crystal lattices with a spacing of 0.315 nm, corresponding to the (111) plane of Si crystal (Figure 2c, inset). The high-resolution TEM image in Figure 2d reveals that the carbon component in the composite is partially graphitized, which is divided into two different microdomains of few-layer graphitized carbon (g-carbon) nanosheets and amorphous carbon, while Si NDs are uniformly distributed in the interspaces of g-carbon nanosheets. The formation of g-carbon nanosheets on the surface or surrounding Si NDs in the interior of the composite microspheres is due to the catalytic effect of the Sn catalyst,^[33] by comparing with the product obtained under the same conditions except for the carbonization process in the absence of Sn removed by 1M HCl (Figure S5). The elemental mappings of a composite microsphere (Figure 2e) show that the elements of C, Si and Sn are homogeneously distributed throughout the microsphere. The corresponding line scanning illustrates the element distribution with relative content ratios of the three elements (Figure 2e). The energy-dispersive spectroscopy (EDS) measurement (Figure S6) and X-ray photoelectron spectroscopy (XPS) analysis (Figure S7) confirm the coexistence of C, Si and Sn elements.

The X-ray diffraction (XRD) pattern of the Si NDs/C framework is shown in Figure 2f, which displays a set of diffraction peaks assigned to rhombohedral silicon (JCPDS 27-1402) and two broad peaks corresponding to graphite carbon.^[34] It is noted that no signal for

crystalline Sn is detected. Considering the very low atomic concentration (0.47%) of Sn in the composite, Sn species is speculated to exist as single atom clusters dispersed uniformly in the carbon framework, taking EDS, XPS and XRD results into account. Raman spectra of the Si NDs/C frameworks with different carbonization times (Figure 2g, Figures S8) show sharp peaks at 517.3 cm^{-1} corresponding to F_{2g} mode of Si^[35] and two intense peaks at 1347 and 1580 cm^{-1} , corresponding to D and G bands of graphitic carbon^[36]. The content of Si and C in the Si NDs/C framework is measured to be ~ 16.4 and $83.6\text{ wt}\%$, respectively, by thermogravimetric (TG) method (Figure S9). Brunauer–Emmett–Teller (BET) measurement and pore analysis indicate that the Si/C framework holds a specific surface area (S_{BET}) of $\sim 158.5\text{ m}^2\text{ g}^{-1}$ and a hierarchical pore structure with pore size distribution ranging from 1.0 to 60 nm (in set, Figure 2h, Table S1) implying the coexistence of micropores, mesopores and macropores in the composite framework.

The electrochemical properties of the typical Si NDs/C framework were evaluated as a LIB anode material cycled between 0.05 V and 2 V vs Li^+/Li . Figure 3a shows cyclic voltammetry (CV) curves of the first three cycles at a scan rate of 0.025 mV s^{-1} . During the initial cathodic scan, a sloping cathodic peak in the range of 0.75~ 0.25 V is observed, caused by the irreversible formation of the SEI layer on the carbon surface.^[37] In the anodic sweeps, two weak peaks located at 0.35 V and 0.51 V are assigned to the delithiation from the electrode. In the subsequent cycles, a cathodic peak at $\sim 0.18\text{ V}$ appears, related to

lithiation of Si to Li_xSi ($0 \leq x \leq 4.4$).^[38] The voltage profiles for the first three cycles are shown in Figure 3b, all of which exhibit a discharge plateau between 0.2 and 0.05 V and a charge plateau between 0.3 and 0.5V, in accordance with the CV analysis in Figure 3a. All the specific capacities are calculated based on the total mass of the Si NDs/C framework. The theoretical capacity of the Si NDs/C framework electrode is calculated to be 1000 mAh g^{-1} according to the weight percent of the composites ($C_{\text{composite theoretical}} = C_{\text{carbon}} \times \text{Mass percentage of carbon} + C_{\text{Si}} \times \text{Mass percentage of Si} = 372 \times 83.6\% + 4200 \times 16.4\% = 1000 \text{ mAh g}^{-1}$). Figure 3c presents the cycling performance of the Si NDs/C framework electrode at a current density of 0.1 A g^{-1} for 1500 cycles. It is found that the Si NDs/C framework electrode delivers a discharge capacity of 1203 mAh g^{-1} and a charge capacity of 777 mAh g^{-1} in the first cycle. The coulombic efficiency in the second cycle reaches 93.4% and then remains stable at 99% during later long-term cycling. After 1500 cycles, a high reversible capacity of 837 mAh g^{-1} is still remained, giving a capacity retention of nearly 100%. The capacity increase in the initial 150 cycles is possibly ascribed to a combined activation mechanism induced by carbon activation and Si amorphization.^[39-42] The amorphization of Si NDs upon cycling is observed by the corresponding *in situ* XRD measurement (Figure S10). In contrast, the Si NDs/C framework electrode displays much better cycling performance than those based on the carbon framework anode obtained after removing Si by HF and composites anodes with short carbonization times of 1 and 3 h

(Figures S11 and S12). Long-term cycling tests of the composite electrode at the higher current density of 1 A g^{-1} and 2 A g^{-1} were also conducted, showing the reversible capacities of 647 and 527 mAh g^{-1} after 1500 cycles (Figure 3c and Figure S13), respectively. The Si NDs@C framework still remains the spherical morphology after 1000 cycles at 2 A g^{-1} (Figure S14), and exhibits a much smaller electrode thickness change ratio (4%) than the electrode based on commercial Si nanoparticles (61.6%) with significantly enhanced battery performance (Figure S15). The Si NDs@C framework electrode also displays remarkable rate capability, thanks to its facilitated reaction kinetics and efficient charge transfer interface (Figure S16 and Table S2). High reversible capacities of ~ 784 , 682 , 622 , 568 , 505 , 448 mAh g^{-1} are achieved at current densities of 0.1 , 0.2 , 0.5 , 1 , 2 and 3 A g^{-1} (Figures 3d), respectively. When the current returns to 0.1 A g^{-1} after 100 cycles, a reversible capacity of 829 mAh g^{-1} is still achieved, with a high capacity retention of 105.7% . The comprehensive battery performance based on the typical Si NDs@C framework electrode with a low Si content surpasses that of the reported lithium-ion batteries based on Si anodes (Figure S17). In addition, the effect of different carbonization temperatures, different Si pyrolysis precursors, and especially, Sn catalyst on the composition and battery performance of composite products were also conducted (Figures S18-23, Table S3 and S4). The results suggest that the existence of Sn catalyst can avoid SiC generation, and is essential for Si formation as well as the Si NDs@C framework.

To further understand the Sn atom-cluster catalytic mechanism of DPS pyrolysis for the formation of Si other than SiC, the most energy-favorable pathways for DPS pyrolysis with and without Sn atom cluster catalyst were simulated by the density functional theory (DFT) calculations, as shown in Figure 4. The calculation details with all possible pathways were shown in Figure S24, which was according to different bond breaking order/manner of Si-C and Si-H bonds in DPS molecules. Apparently, Figure 4 illustrates that the pathway with catalyst shows much lower reaction energy and energy barrier at each step than that of the pathway without catalyst, indicating that the presence of Sn catalyst can significantly reduce energy barrier and promote the pyrolysis of DPS. Accordingly, pyrolysis of DPS could occur to form Si at the lower temperature of 800 °C catalyzed by Sn atom clusters, but could not in the absence of Sn catalyst at the same temperature, leading to SiC formation at the higher temperature.^[43]

All considered, the proposed space-confined atom-cluster catalytic strategy is unique and effective for preparing the novel Si NDs@C framework for high-performance LIBs, avoiding the formation of SiC (without catalyst, Figure S25a,) and Si nanowires in conventional catalytic growth systems (Figure S25b). Notably, finite element calculations (Figure S26-S28) reveal that the Si NDs@C carbon framework comprising of hybrid a/g-carbon show both lower radial and hoop stress during lithiation compared to that of amorphous or graphite carbons, endowing the electrode with an outstanding mechanical

stability for stable lithium storage. Moreover, a series of full batteries based on the Si₂C framework anodes and commercial cathodes including LiCoO₂ (LCO), LiFePO₄ (LFP) and LiNi_{0.8}Co_{0.15}Al_{0.05}O₂ (NCA) were assembled and exhibited higher capacities and energy densities than commercial full batteries (Figure S29 and Tables S5-S7).

Conclusion

In summary, the novel space-confined atom-cluster catalytic strategy for constructing the Si NDs₂C framework has been proposed, through the elaborate design of controlled copyrolysis of TPT and DPS. The self-created Sn atom cluster catalyst is able to not only catalyze the pyrolysis of DPS and growth of Si at the low temperature, changing reaction pathway to avoid the generation of electrochemical inert SiC, but also to reduce the dimensions of Si leading to Si ND formation. The prepared Si NDs₂C framework with hierarchical pore structure, well-dispersed Si NDs, and hybrid phase carbon framework is favorable for high-capacity lithium storage, fast Li ion diffusion and effective suppression of lithiation stress. As a result, the Si NDs₂C framework based half and full Li-ion batteries exhibited superior comprehensive battery performance which are comparable to the state-of-the-art half LIBs or even far surpass the commercial full LIBs. This study provides a new and effective strategy for design and preparation of advanced Si/C composite anodes towards practical energy applications.

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Conflict of Interest

The authors declare no competing financial interest.

Keywords

silicon, carbon, atom-cluster catalysis, structural stability, lithium ion batteries

References

- [1] B. Dunn, H. Kamath, J. M. Tarascon, *Science* **2011**, 334, 928.
- [2] K. Kang, Y. S. Meng, J. Bréger, C. P. Grey, G. Ceder, *Science* **2006**, 311, 977.
- [3] S. Chae, M. Ko, K. Kim, K. Ahn, J. Cho, *Joule* **2017**, 1, 47.
- [4] M. T. McDowell, S. W. Lee, W. D. Nix, Y. Cui, *Adv. Mater.* **2013**, 25, 4966.
- [5] W. Luo, X. Chen, Y. Xia, M. Chen, L. Wang, Q. Wang, W. Li, J. Yang, *Adv. Energy Mater.* **2017**, 7, 1701083.
- [6] X. Zhang, D. Kong, X. Li, L. Zhi, *Adv. Funct. Mater.* **2019**, 29, 1806061.
- [7] J. Wang, L. Liao, Y. Li, J. Zhao, F. Shi, K. Yan, A. Pei, G. Chen, G. Li, Z. Lu, Y. Cui, *Nano Lett.* **2018**, 18, 7060.
- [8] C. K. Chan, H. Peng, G. Liu, K. McIlwrath, X. F. Zhang, R. A. Huggins, Y. Cui, *Nat. Nanotechnol.* **2008**, 3, 31.
- [9] S. Choi, T. W. Kwon, A. Coskun, J. W. Choi, *Science* **2017**, 357, 279.
- [10] C. Peng, H. Chen, Q. Li, W. Cai, Q. Yao, Q. Wu, J. Yang, Y. Yang, *J. Mater. Chem. A* **2014**, 2, 13859.
- [11] W. Luo, Y. Wang, L. Wang, W. Jiang, S. L. Chou, S. X. Dou, H. K. Liu, J. Yang, *ACS Nano* **2016**, 10, 10524.
- [12] Q. Xu, J. Li, J. Sun, Y. Yin, L. Wan, Y. Guo, *Adv. Energy Mater.* **2017**, 7, 1601481.
- [13] M. Jeong, H. Du, M. Islam, J. Lee, Y. Sun, H. Jung, *Nano Lett.* **2017**, 17, 5600.

- [14] H. Su, A. Barragan, L. Geng, D. Long, L. Ling, K. Bozhilov, L. Mangolini, J. Guo, *Angew. Chem., Int. Ed.* **2017**, *129*, 10920.
- [15] W. Sun, R. Hu, M. Zhang, J. Liu, M. Zhu, *J. Power Sources* **2016**, *318*, 113.
- [16] S. Guo, X. Hu, Y. Hou, Z. Wen, *ACS Appl. Mater. Interfaces* **2017**, *9*, 42084.
- [17] G. Liang, X. Qin, J. Zou, L. Luo, Y. Wang, M. Wu, H. Zhu, G. Chen, F. Kang, B. Li, *Carbon* **2018**, *127*, 424.
- [18] S. Kim, A. Manthiram, *J. Mater. Chem. A* **2015**, *3*, 2399.
- [19] A. Morales, C. Lieber, *Science* **1998**, *279*, 208.
- [20] J. Hannon, S. Kodambaka, F. Ross, R. Tromp, *Nature* **2006**, *440*, 69.
- [21] Y. Wang, V. Schmidt, S. Senz, U. Gösele, *Nat. Nanotechnol* **2006**, *1*, 186.
- [22] Y. Civale, L. Nanver, P. Hadley, E. J. G. Goudena, *Catalyst* **2014**, *4*, 2.
- [23] Y. Cui, L. Lauhon, M. Gudiksen, J. Wang, C. Lieber, *Appl. Phys. Lett.* **2001**, *78*, 2214.
- [24] J. Wu, Y. Cao, H. Zhao, J. Mao, Z. Guo, *Carbon Energy* **2019**, *1*, 57.
- [25] Y. Liu, Z. Tai, T. Zhou, V. Sencadas, J. Zhang, L. Zhang, K. Konstantinov, Z. Guo, H. K. Liu, *Adv. Mater.* **2017**, *29*, 1703028.
- [26] H. Al-Taay, M. Mahdi, D. Parlevliet, P. Jennings, *Mater. Sci. Semicond. Process.* **2013**, *16*, 15.
- [27] X. Liu, L. Zhong, S. Huang, S. Mao, T. Zhu, J. Huang, *ACS Nano* **2012**, *6*, 1522.
- [28] L. Zu, Q. Su, F. Zhu, B. Chen, H. Lu, C. Peng, T. He, G. Du, P. He, K. Chen, S. Yang, J.

- Yang, H. Peng, *Adv. Mater.* **2017**, 29, 1701494.
- [29] W. Zhang, L. Zu, B. Kong, B. Chen, H. He, K. Lan, Y. Liu, J. Yang, D. Zhao, *iScience* **2018**, 3, 149.
- [30] G. Zheng, Y. Xiang, L. Xu, H. Luo, B. Wang, Y. Liu, X. Han, W. Zhao, S. Chen, H. Chen, Q. Zhang, T. Zhu, Y. Yang, *Adv. Energy Mater.* **2018**, 8, 1801718.
- [31] T. Kennedy, M. Bezuidenhout, K. Palaniappan, K. Stokes, M. Brandon, K. Ryan, *ACS Nano* **2015**, 9, 7456.
- [32] K. Stokes, G. Flynn, H. Geaney, G. Bree, K. Ryan, *Nano Lett.* **2018**, 18, 5569.
- [33] D. Chao, B. Ouyang, P. Liang, T. Huong, G. Jia, H. Huang, H. Fan, *Adv. Mater.* **2018**, 30, 1804833.
- [34] Q. Xu, J. Sun, Z. Yu, Y. Yin, S. Xin, S. Yu, Y. Guo, *Adv. Mater.* **2018**, 30, 1707430.
- [35] R. Wang, G. Zhou, Y. Liu, S. Pan, H. Zhang, D. Yu, Z. Zhang, *Phys. Rev. B* **2000**, 61, 16827.
- [36] D. Vrankovic, M. Graczyk-Zajac, C. Kalcher, J. Rohrer, M. Becker, C. Stabler, G. Trykowski, K. Albe, R. Riedel, *ACS Nano* **2017**, 11, 11409.
- [37] S. Chen, L. Shen, P. van Aken, J. Maier, Y. Yu, *Adv. Mater.* **2017**, 29, 1605650.
- [38] F. Du, Y. Ni, Y. Wang, D. Wang, Q. Ge, S. Chen, H. Yang, *ACS Nano* **2017**, 11, 8628.
- [39] L. Cui, R. Ruffo, C. Chan, H. Peng, Y. Cui, *Nano Lett.* **2008**, 9, 491.
- [40] C. Peng, B. Chen, Y. Qin, S. Yang, C. Li, Y. Zuo, S. Liu, J. Yang, *ACS Nano* **2012**, 6,

1074.

[41] R. Meng, J. Huang, Y. Feng, L. Zu, C. Peng, L. Zheng, Z. Chen, G. Liu, B. Chen, Y. Mi, J. Yang, *Adv. Energy Mater.* **2018**, 8, 1801514.

[42] L. Qie, W. Chen, Z. Wang, Q. Shao, X. Li, L. Yuan, X. Hu, W. Zhang, Y. Huang, *Adv. Mater.* **2012**, 24, 2047.

[43] S. Choi, J. Kim, D. Y. Hwang, H. Park, J. Ryu, S. K. Kwak, S. Park, *Nano Lett.* **2016**, 16, 1179.

Figures and Captions

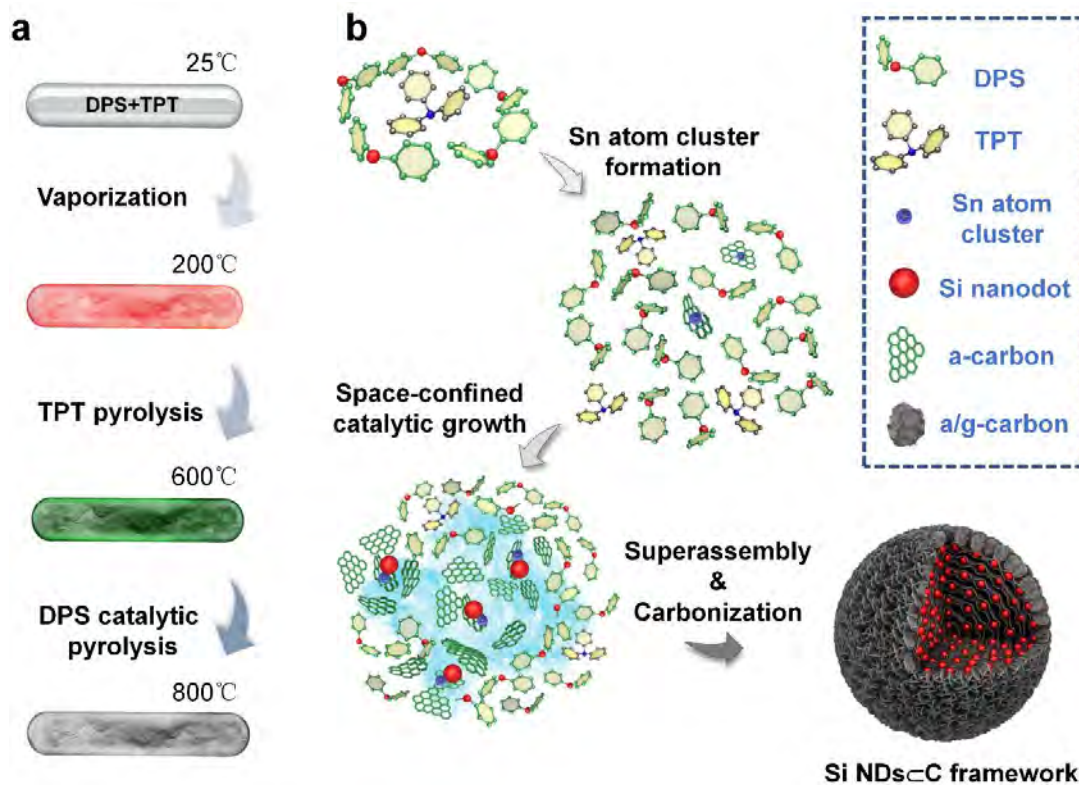


Figure 1. a) Schematic illustration for the synthetic procedure. b) Schematic illustration for the fabrication of the Si NDs⊂C framework.

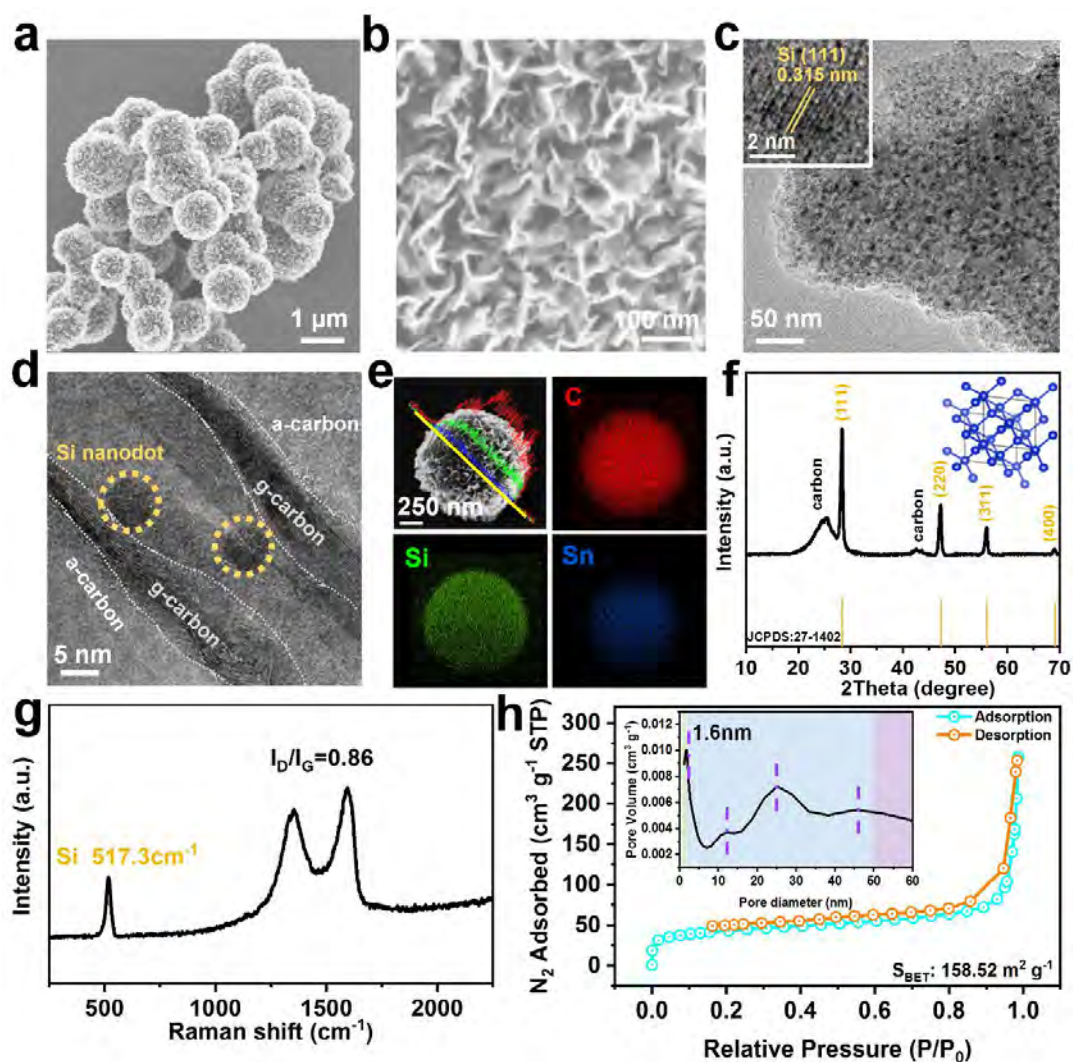


Figure 2. a, b) SEM images, c) TEM image, d) high-resolution TEM image, e) line scanning profiles and elemental mappings, f) XRD pattern, g) Raman spectrum and h) BET and the pore-size distribution curve of the Si NDs@C framework. Inset in c) is the high-resolution TEM image of a Si ND selected arbitrarily.

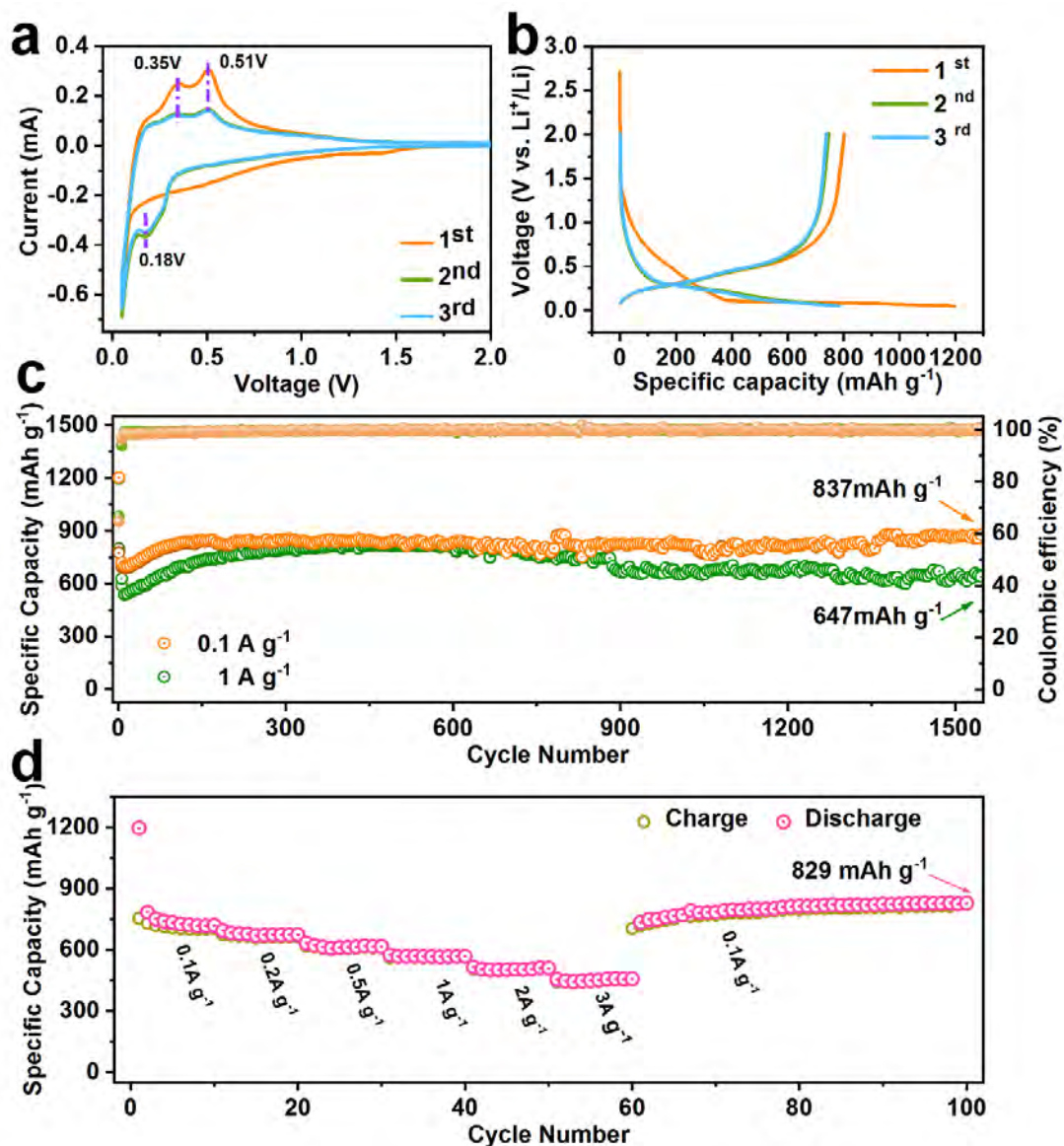


Figure 3. a) Cyclic voltammetry (CV) curves and b) Voltage profiles of the typical Si NDs@C framework electrode at 0.1 A g⁻¹. c) Cycling performance comparisons of the typical Si NDs@C framework electrode at 0.1 A g⁻¹ and 1 A g⁻¹. d) Rate capability of the typical Si NDs@C framework electrode.

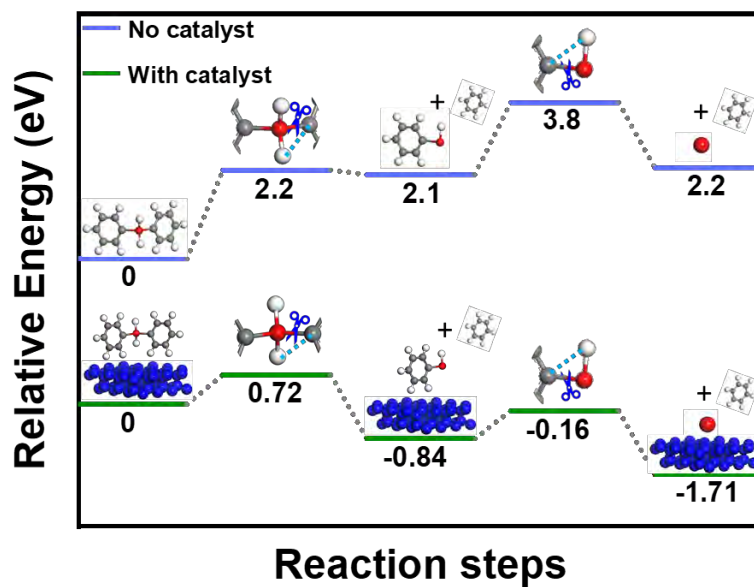
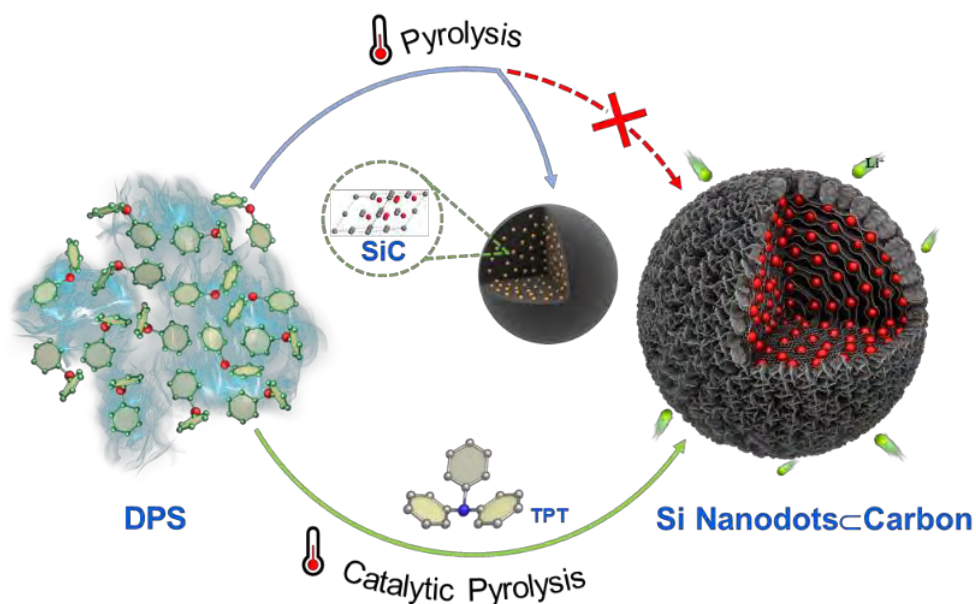


Figure 4. Schematic of most energy-favorable pathways for DPS pyrolysis in the absence and in the presence of Sn atom cluster catalyst from DFT simulation.

Table of contents



A unique space-confined atom-cluster catalytic strategy for direct superassembly of Si nanodots-embedded carbon framework has been developed via a designed copyrolysis of phenides, which proceeds the reaction in a different pathway to avoid SiC generation and enables forming Si nanodots with reduced dimensions, beneficial for stable and high-capacity lithium storage.

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