

Coaxial CNT@Si/SiO_x Nanowires Enable High-Capacity and Stable Lithium Storage

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Cite This: *ACS Appl. Mater. Interfaces* 2026, 18, 21945–21953



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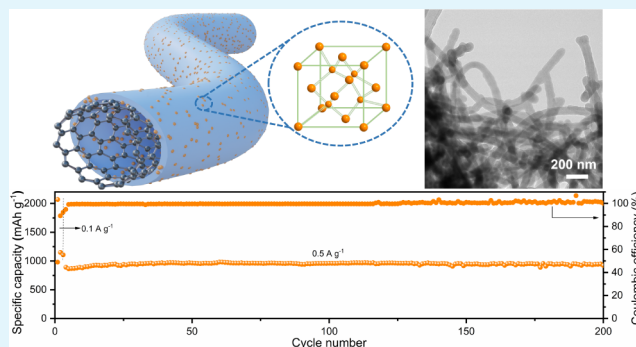
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Supporting Information

ABSTRACT: Si represents a promising anode material to complement graphite in commercial lithium-ion batteries (LIBs). Whereas, its practical implementation is still hampered by unsatisfactory cyclability, primarily caused by the lithiation/delithiation-induced large volume variation. One-dimensional (1D) Si-based nanostructures offer effective volumetric change accommodation, yet their facile fabrication remains challenging. Herein, we develop a facile sol–gel method to synthesize 1D coaxial core@shell structured CNT@Si/SiO_x nanowires. The material features a CNT core and a Si/SiO_x composite shell, in which sub-5 nm Si grains (3–5 nm) are uniformly embedded in an SiO_x matrix. The design achieves a high reversible capacity (1078 mAh g^{−1} at 0.1 A g^{−1}), high-rate capability (540 mAh g^{−1} at 10 A g^{−1}), and decent cyclability (867 mAh g^{−1} after 200 cycles at 2 A g^{−1}). This contribution provides a scalable strategy for designing stable, high-capacity Si anodes.

KEYWORDS: nanowires, SiO_x, Si-based anode, core@shell structure, CNT



INTRODUCTION

The surging market for electric vehicles and the accelerating adoption of portable electronic devices have created an urgent need for lithium-ion batteries (LIBs) that deliver superior energy density, longer service life, and lower manufacturing costs.¹ Since conventional graphite anodes are currently nearing their theoretical capacity ceiling, the exploration of alternative high-capacity anode materials has become imperative. Among these, silicon-based anodes—encompassing both elemental Si and silicon suboxides (SiO_x)—stand out as premier candidates, offering a compelling combination of ultrahigh theoretical capacity, natural abundance, environmental sustainability, and cost-effectiveness.^{2–6} Nevertheless, the repeated volume fluctuations during lithiation/delithiation often result in continuous thickening of the solid-electrolyte interphase (SEI), particle cracking, and detachment of active mass from the current collector.^{7–11} To address these obstacles, efforts have been dedicated to rational microstructure design,^{12–15} crystallinity control,^{16–18} and Si oxidation state modulation.^{17,19–21}

One-dimensional (1D) nanostructures with continuous electron transport paths and short ion diffusion paths demonstrate great potential in energy storage.^{22–25} Various 1D nanostructured materials, including oxides,^{26,27} sulfides,^{28,29} and nitrides,^{30,31} have been constructed and applied in energy storage. For silicon-based anodes that suffer from

undesirable volume expansion and unsatisfactory conductivity, the 1D nanostructure could provide unique merits such as free space for volume fluctuation accommodation and strain relaxation, as well as short lengths for Li⁺ transmission.^{32–34} Despite these benefits, the synthesis of 1D silicon-based nanostructures usually requires special synthesis equipment, harsh conditions, high production costs, or cumbersome processes, making large-scale production challenging.^{35–37}

Herein, we construct 1D coaxial CNT@Si/SiO_x core@shell nanowires (NWs) via a facile, scalable, and cost-effective sol–gel process using triethoxysilane ((C₂H₅O)₃SiH) as the precursor and highly conductive carbon nanotubes (CNTs) as the backbone. In the obtained CNT@Si/SiO_x NWs, sub-5 nm Si grains are uniformly embedded in the SiO_x matrix within the Si/SiO_x composite shell with a thickness of ~20 nm. The sub-5 nm Si grains and SiO_x possess high reactivity toward Li; the highly conductive CNT backbone wires the whole composite; the thin Si/SiO_x composite shell shortens the Li⁺ transport distance; and the rich internanowire porosity enables

Received: December 27, 2025

Revised: February 27, 2026

Accepted: March 30, 2026

Published: April 10, 2026



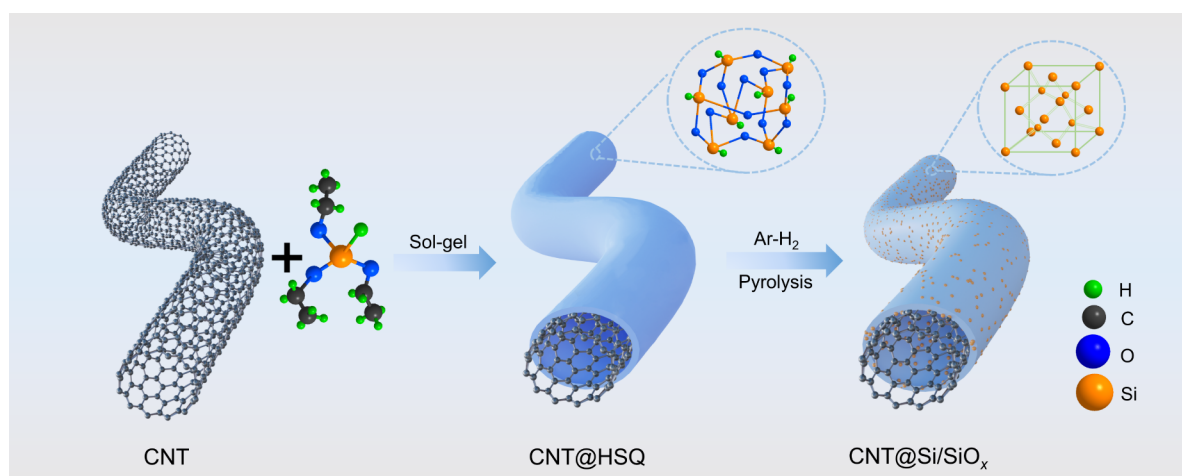


Figure 1. Schematic synthetic process of CNT@Si/SiO_x NWs.

efficient electrolyte accessibility and volume fluctuation accommodation. With such rational structure design, the obtained CNT@Si/SiO_x NWs demonstrate high capacity and stable cycling, as well as decent rate capability.

EXPERIMENTAL SECTION

Material Synthesis

One milliliter portion of CNT dispersion (3 wt %) was first dispersed into 100 mL of H₂O. Subsequently, 0.1 mL of concentrated HCl and 1 mL of triethoxysilane ((C₂H₅O)₃SiH, 99.8% were sequentially introduced into the mixture under vigorous stirring. Following a 5-h reaction period at ambient temperature, the resulting hydrogen silsesquioxane (HSiO_{1.5}, HSQ)-coated CNT nanowires (CNT@HSQ NWs) were harvested via centrifugation and vacuum-dried at 60 °C. Lastly, the dried precursor underwent annealing at 1000 °C under Ar/H₂ flow for 1 h (ramp rate: 20 °C min^{−1}).

For comparison, the Si/SiO_x nanoparticles were obtained by a similar procedure without the addition of a CNT suspension.

Battery Fabrication

CR2016-type coin half-cells were constructed in a glovebox maintained under an argon atmosphere. The synthesized samples were utilized as the working electrode, and lithium foils functioned as the reference electrode, separated by Whatman glass fiber membranes (GF/A). To prepare the working electrodes, a homogeneous slurry was obtained by dispersing the active material, acetylene black, and sodium alginate binder (weight ratio = 70:20:10) in deionized water. This paste was subsequently applied onto a copper foil substrate and dried under vacuum at 60 °C overnight. The mass loading of the active material was maintained at approximately 1.0–1.5 mg cm^{−2}. The electrolyte employed in this study consisted of 1.0 M LiPF₆ dissolved in a binary solvent of ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1 by volume), supplemented with 5 vol % fluoroethylene carbonate (FEC). To assemble the full cells, the as-prepared CNT@Si/SiO_x anode was coupled with a LiFePO₄ cathode. The cathode fabrication involved casting a mixture of LiFePO₄ (70 wt %), acetylene black (20 wt %), and polyvinylidene fluoride (PVDF, 10 wt %) in *N*-methyl-2-pyrrolidone (NMP) onto an aluminum foil current collector, followed by vacuum drying at 60 °C. The fabrication of CNT@Si/SiO_x||LiFePO₄ full cells was conducted in an argon-filled glovebox. A Celgard-2400 membrane was used as the separator, while the electrolyte was prepared by dissolving 1.0 M LiPF₆ in EC/DEC/DMC (1:1:1 by volume).

Electrochemical Measurements

Galvanostatic charge–discharge (GCD) measurements were performed on a Neware CT4008 battery test system. For half-cell measurements, the voltage window was set between 0.01–2.0 V.

Electrochemical impedance spectroscopy (EIS) measurements spanned a frequency range of 100 kHz to 10 mHz. Cyclic voltammetry (CV) data were collected by using an Autolab PGSTAT 302N workstation. Prior to full-cell integration, the CNT@Si/SiO_x anodes underwent a prelithiation process in half-cells for 3 cycles at 0.1 A g^{−1}. The anode-to-cathode capacity ratio (N/P ratio) was maintained at approximately 1.1. Full-cell cycling was performed at 1 C (1 C = 170 mA g^{−1}) within a 2.2–4.0 V range, with specific capacities normalized to the cathode mass.

Sample Characterizations

To determine the crystallographic phases via X-ray diffraction (XRD), a Bruker D8 Discover diffractometer (Cu K α radiation source) was utilized. Microstructural and morphological investigations were carried out by employing a JEOL-7100F scanning electron microscope (SEM). Further detailed structural and elemental analyses were acquired via transmission electron microscopy (TEM)—including high-resolution (HRTEM) and high-angle annular dark-field scanning (HAADF-STEM) modes—coupled with energy-dispersive X-ray spectroscopy (EDS). The surface chemical compositions and elemental oxidation states were probed by using a PerkinElmer PHI-5000C ESCA X-ray photoelectron spectrometer (XPS). Carbon content was quantified using an SDT-Q600 instrument via thermogravimetric analysis (TGA) from ambient temperature to 1200 °C in an air atmosphere. The specific surface area was evaluated by the Brunauer–Emmett–Teller (BET) method using nitrogen adsorption–desorption isotherms measured on a Micromeritics 3Flex system.

RESULTS AND DISCUSSION

The construction of core@shell structured CNT@Si/SiO_x NWs involves the sol–gel reaction of triethoxysilane and subsequent pyrolysis (Figure 1). Hydrophilic CNT is employed as the backbone material. The hydrolysis and condensation of triethoxysilane lead to the growth of HSQ on CNT, yielding coaxial CNT@HSQ NWs. With subsequent high-temperature treatment in H₂/Ar, HSQ undergoes a disproportionation reaction to form Si/SiO_x, in which sub-5 nm Si nanocrystals are uniformly embedded within an amorphous SiO_x matrix. Importantly, the rigid Si–O network of HSQ spatially confines Si nucleation and suppresses grain growth during the annealing process, thereby enabling the formation and homogeneous dispersion of ultrasmall Si nanocrystals.^{38,39} Eventually, CNT@Si/SiO_x NWs are achieved. Structurally, the coaxial core@shell geometry offers distinct advantages over noncoaxial or randomly mixed architectures: (I) the CNT core serves as a continuous

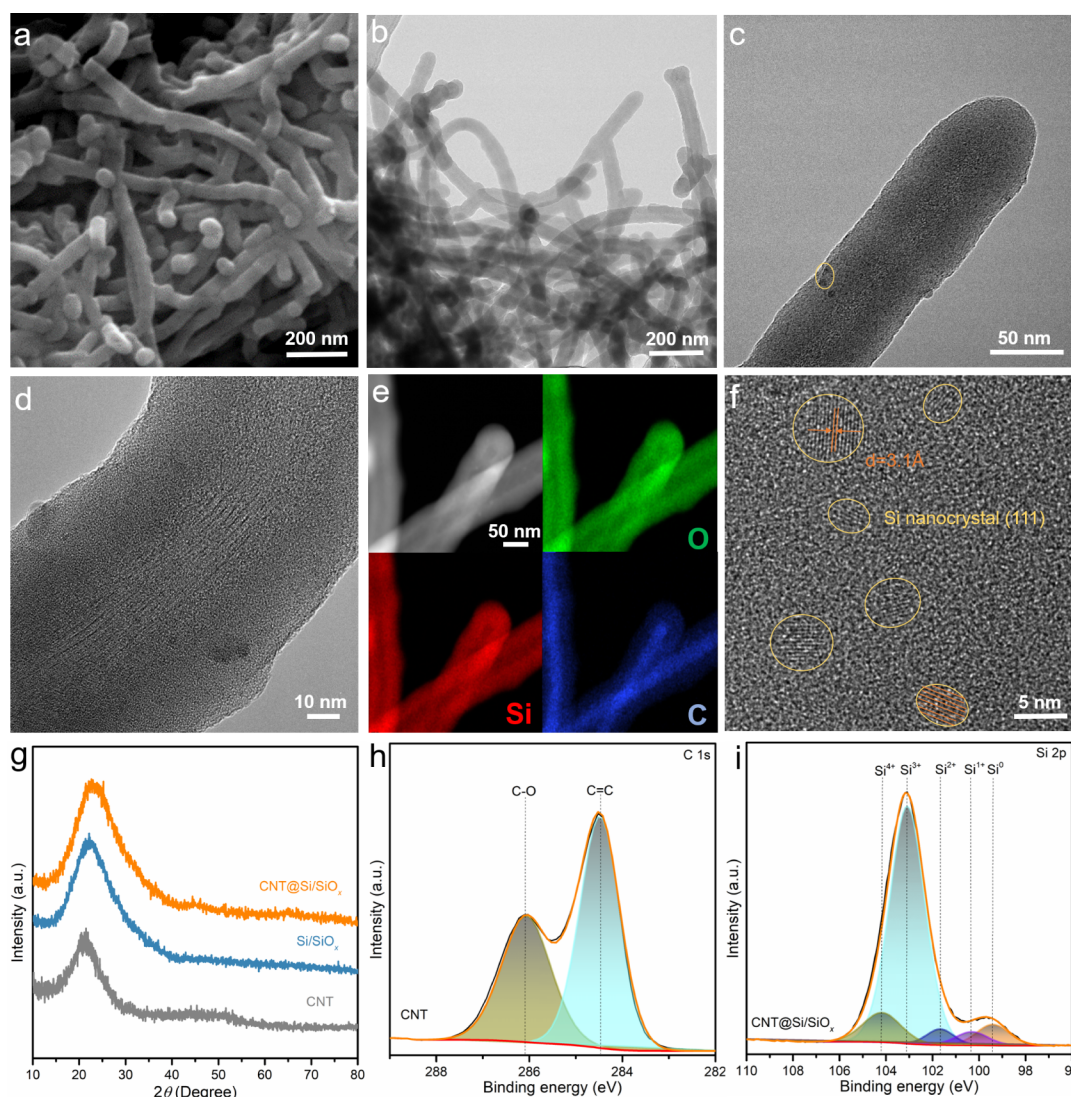


Figure 2. a) SEM and b–d) TEM images of CNT@Si/SiO_x NWs; e) HAADF-STEM image and corresponding EDS elemental mappings of CNT@Si/SiO_x NWs; f) HRTEM image of CNT@Si/SiO_x NWs; g) XRD patterns of CNT, Si/SiO_x, and CNT@Si/SiO_x NWs; h) C 1s XPS spectrum of CNTs; and i) Si 2p XPS spectrum of CNT@Si/SiO_x NWs.

electron-transport highway that wires the entire active shell; (II) the conformal Si/SiO_x shell with uniform thickness promotes homogeneous stress distribution during lithiation/delithiation; and (III) the intimate core–shell contact mitigates shell delamination and particle isolation, thereby preserving electrical percolation upon cycling.

The CNT@HSQ precursor (Figure S1) presents a coaxial core@shell nanowire structure with lengths up to micrometers, in which the HSQ layer is uniformly and conformally coated on the CNT backbone. After high-temperature pyrolysis, the obtained CNT@Si/SiO_x presents a similar coaxial nanowire structure with a uniform diameter of ~60 nm (Figure 2a,b). The CNT is completely covered by Si/SiO_x, and there is no exposure of bare CNT. Under higher magnifications, a bundle of CNTs can be observed in the TEM image of CNT@Si/SiO_x NWs (Figure 2d). The diameter of the CNT bundle is ~10 nm (Figure S2) and the thickness of the Si/SiO_x shell is measured to be ~20 nm. A number of tiny black particles are present in the shell of CNT@Si/SiO_x NWs (Figure 2c,d), which can be ascribed to the Si nanocrystals.³⁸ A statistical analysis based on the TEM image indicates that these Si nanocrystals exhibit a

narrow size distribution mainly in the range of ~3–5 nm (Figure S3), suggesting their uniform embedding within the SiO_x matrix. HAADF-STEM and EDS elemental maps (Figure 2e) distinctly localize the Si and O signals within the exterior shell, whereas the C signal is predominantly confined to the core, corroborating the coaxial configuration. HRTEM clearly shows that the crystalline Si nanodots with sizes of 3–5 nm are embedded in an amorphous SiO_x matrix (Figure 2f). The Si nanodots show *d* spacings of ~3.1 Å, corresponding to the (111) planes of elemental Si.^{40,41} Without the CNT backbone, the Si/SiO_x particles show a size of 50–200 nm (Figure S4). Such uniformly confined ultrasmall Si nanocrystals within a conformal thin shell are expected to homogenize stress distribution and shorten Li⁺ transport distance, which underpins the enhanced mechanical integrity and charge-transport kinetics discussed below.

XRD patterns (Figure 2g) of Si/SiO_x and CNT@Si/SiO_x NWs show a broad peak at 21.8°, a hallmark feature of amorphous SiO_x.^{42,43} The absence of diffraction peaks from crystalline Si is due to the low crystallinity, small particle size, relatively low content of Si nanodots, and the dominant

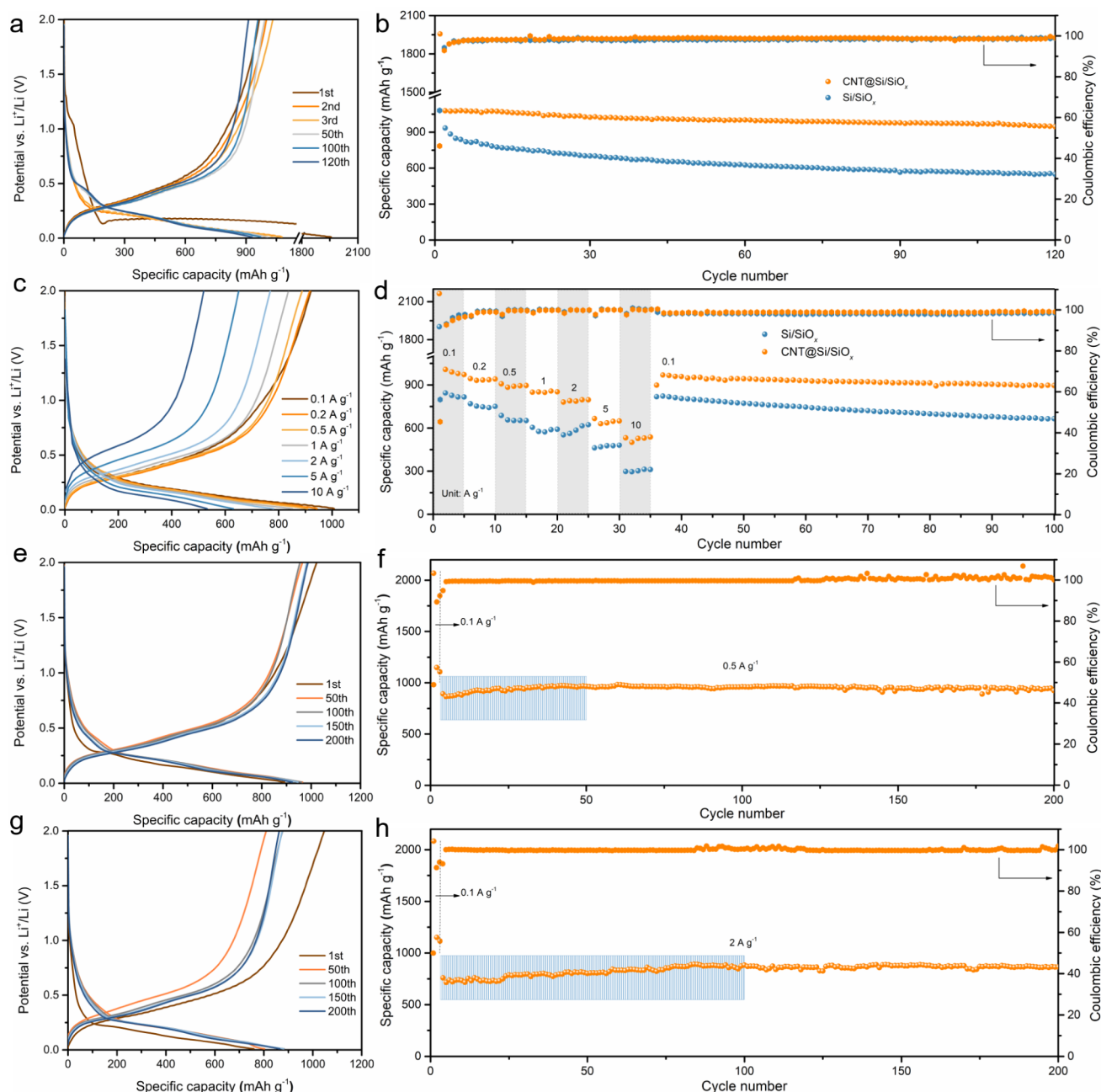


Figure 3. Lithium storage capabilities of Si/SiO_x and CNT@Si/SiO_x NWs. a) GCD profiles of CNT@Si/SiO_x NWs at 0.1 A g⁻¹; b) cycling performance of Si/SiO_x and CNT@Si/SiO_x NWs at 0.1 A g⁻¹; c) GCD profiles of CNT@Si/SiO_x NWs at different current densities; d) rate capability of Si/SiO_x and CNT@Si/SiO_x NWs; e) GCD profiles of CNT@Si/SiO_x NWs at 0.5 A g⁻¹ and f) corresponding cycling performance; and g) GCD profiles of CNT@Si/SiO_x NWs at 2 A g⁻¹ and h) corresponding cycling performance. For f and h, the electrodes are activated at 0.1 A g⁻¹ for 5 cycles.

amorphous SiO_x matrix, which produces a strong background signal.³⁸ The C 1s XPS spectrum of hydrophilic CNTs (Figure 2h) presents a strong peak for the C–O component (286.34 eV), indicating the existence of rich hydroxyl groups on CNTs.⁴⁴ After organosilica coating and pyrolysis, the intensity of the C–O component weakens significantly (Figure S5). Deconvolution of the Si 2p spectra for CNT@Si/SiO_x NWs (Figure 2i) and Si/SiO_x (Figure S6) reveals five distinct oxidation states: Si⁰ (99.31 eV), Si¹⁺ (100.36 eV), Si²⁺ (101.65 eV), Si³⁺ (103.11 eV), and Si⁴⁺ (104.09 eV).^{38,45} For both samples, Si³⁺ represents the dominant component. The emergence of Si⁰ species confirms the formation of the Si

nanodots. TGA (Figure S7) reveals a CNT content of 5.21 wt % for the CNT@Si/SiO_x NWs. The observed mass gain at temperatures exceeding 600 °C is attributed to the oxidation of Si/SiO_x. N₂ sorption measurements reveal relatively (Figure S8) low specific surface areas: 34.87 m² g⁻¹ for CNT@Si/SiO_x NWs and 11.48 m² g⁻¹ for Si/SiO_x. Despite the moderate BET value, the internanowire porous network enables efficient electrolyte access and short Li⁺ diffusion paths, while the relatively low surface area mitigates excessive SEI growth.

The electrochemical properties of the CNT@Si/SiO_x NWs were systematically evaluated and compared with Si/SiO_x. As depicted in Figures 3a and S9, the GCD profiles are at 0.1 A

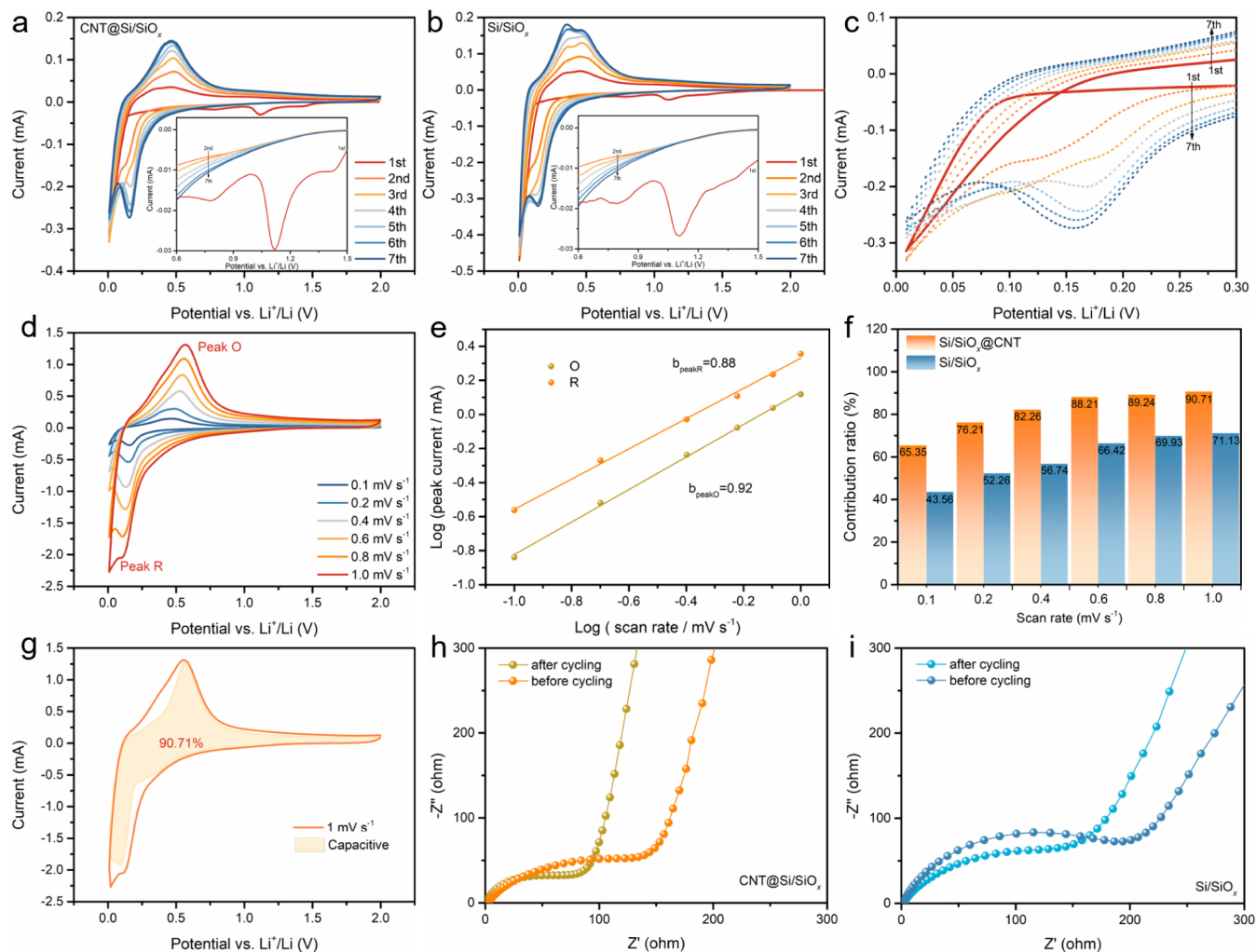


Figure 4. CV curves of: a) CNT@Si/SiO_x NWs and b) Si/SiO_x at 0.1 mV s⁻¹; c) enlarged CV curves of the CNT@Si/SiO_x NWs at 0.1 mV s⁻¹; d) CV curves of CNT@Si/SiO_x NWs at various scan rates; e) log(*i*) versus log(*v*) plots and the corresponding linear fits of CNT@Si/SiO_x; f) capacitive contribution ratios at various scan rates; g) CV curve at 1 mV s⁻¹ and the calculated capacitive contribution; and EIS plots of h) CNT@Si/SiO_x NWs and i) Si/SiO_x before and after cycling.

g^{-1} for both materials. A distinct discharge plateau is evident near 0.2 V, followed by a charge plateau at approximately 0.4 V. Notably, CNT@Si/SiO_x NWs demonstrate an initial discharge capacity of 1957 mAh g⁻¹, corresponding to an initial Coulombic efficiency (CE) of 46.1%. Despite its larger specific surface area leading to a lower initial CE (46.1% vs 57.4% for Si/SiO_x), the CNT@Si/SiO_x NWs exhibit superior cyclability. Specifically, the reversible capacity remains at 1006 mAh g⁻¹ after 50 cycles and at 946 mAh g⁻¹ after 120 cycles. From the second to the 120th cycle, the capacity undergoes only a minor decay from 1078 to 946 mAh g⁻¹ (Figure 3b), equating to a retention of 87.8%. Conversely, the Si/SiO_x counterpart suffers from rapid degradation, retaining only 549 mAh g⁻¹ by the 120th cycle (58.7% retention). At elevated current densities of 2, 5, and 10 A g⁻¹, reversible capacities of 774, 660, and 540 mAh g⁻¹ are achieved (Figure 3c,d), much higher than those of Si/SiO_x (547, 471, and 299 mAh g⁻¹) (Figure S10). Notably, the characteristic voltage plateaus of Si still exist, even under high-rate cycling conditions. Upon returning to 0.1 A g⁻¹ (Figure 3d), the capacity of CNT@Si/SiO_x NWs is recovered to 975 mAh g⁻¹.

The cycling performances of the CNT@Si/SiO_x NWs at 0.5 and 2 A g⁻¹ are also evaluated (Figure 3e–h). Interestingly, the

discharge capacity gradually increases at the early cycling stage, which is referred to “activation” process in the literature.^{38,46,47}

This activation behavior can be mainly attributed to (I) the gradual electrochemical activation of Si nanocrystals/domains generated from the SiO_x matrix during the initial conversion/alloying processes; (II) progressive stabilization/optimization of the SEI layer; and (III) improved electrode wetting and interfacial contact upon cycling. As a result, the reaction kinetics become more favorable, and a higher reversible capacity is progressively released in the early cycles. In general, as the current density increases, a greater number of cycles are required to achieve complete capacity release from the active materials. Following 200 cycles, the electrode delivers substantial reversible capacities of 932 mAh g⁻¹ at 0.5 A g⁻¹ (Figure 3e,f) and 867 mAh g⁻¹ at 2.0 A g⁻¹ (Figure 3g,h). Moreover, the CNT@Si/SiO_x NWs sustain average CEs of 99.57% and 99.82% at these respective current densities. A comprehensive comparison with reported SiO_x-based anodes (Table S1) confirms that the CNT@Si/SiO_x NWs offer competitive metrics in terms of capacity, rate response, and long-term cyclability.

To understand the electrochemical reactions, CV measurements are performed for the CNT@Si/SiO_x and Si/SiO_x NWs

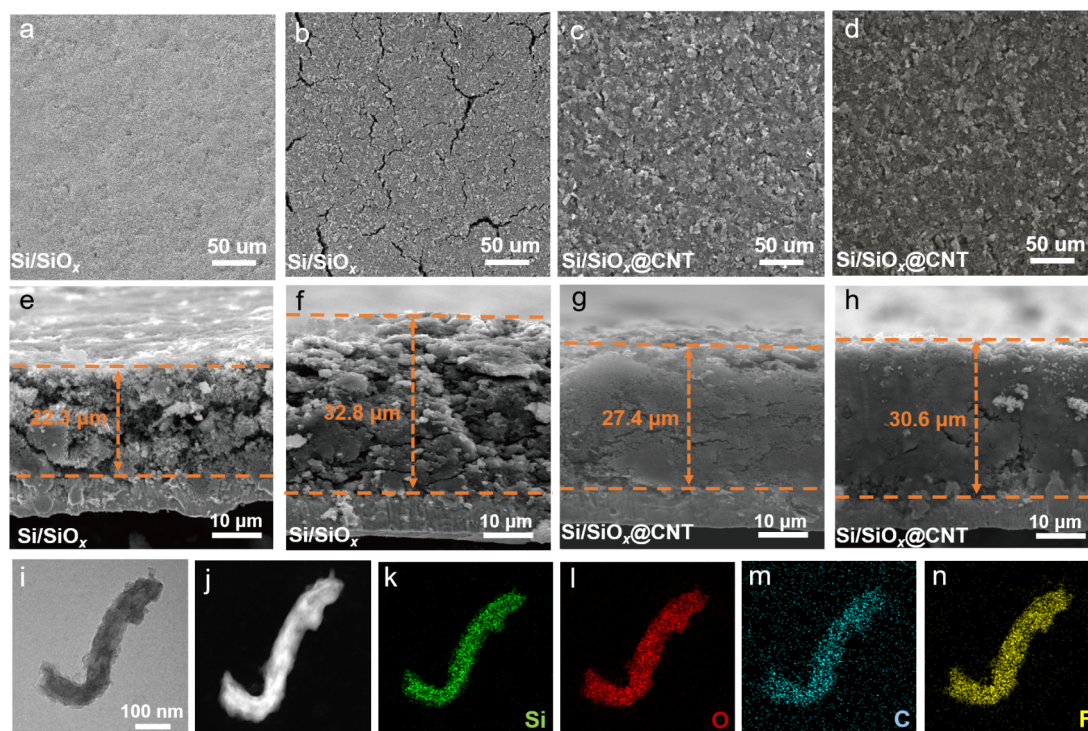


Figure 5. Top-view SEM images of a) Si/SiO_x electrode before and b) after cycling; c) CNT@Si/SiO_x electrode before and d) after cycling; cross-sectional SEM images of e) Si/SiO_x electrode before and f) after cycling; g) CNT@Si/SiO_x electrode before and h) after cycling; (i) TEM image; j) HAADF-STEM image of CNT@Si/SiO_x NWs after cycling; and k–n) the corresponding elemental mappings.

(Figure 4a,b). In the first lithiation process, the broad reduction peak around 1.18 V is attributed to the irreversible decomposition of the fluoroethylene carbonate (FEC) additive.⁴⁸ The pronounced reduction signal detected at 0.81 V corresponds to two key electrochemical processes (Figure 4a,b): primarily the growth of the SEI and the lithiation of the SiO_x matrix.^{48,49} The latter process generates elemental Si, Li₂O, and various lithium silicates.^{50,51} Both cathodic peaks diminish in subsequent cycles, indicating their irreversibility. With further lithiation, a classic crossover of curves occurs in both CNT@Si/SiO_x NWs and Si/SiO_x (Figure 4c and S11). This characteristic phenomenon indicates the lithium intercalation behavior of crystalline Si, which is consistent with previous literatures.^{52,53} From the second cycle onward, a cathodic peak appears at around 0.16 V and strengthens. This peak is associated with the lithiation of Si, which generates amorphous Li_xSi. During the initial delithiation, two broad peaks are observed at 0.36 and 0.47 V, mainly attributed to the delithiation from Li_xSi to amorphous Si.

To study the electrochemical kinetics of CNT@Si/SiO_x NWs and Si/SiO_x, CVs are collected at different scan rates (Figures 4d and S12). The relationship between peak current (*i*) and scan rate (*v*) is quantitatively analyzed using the power-law equation:

$$\log(i) = \log(a) + b\log(v)$$

The fitted *b* values (0.92 for Peak O and 0.88 for Peak R) of CNT@Si/SiO_x NWs are higher than those of Si/SiO_x (0.83 for Peak O and 0.81 for Peak R) (Figure 4e and S13). The high *b* values (close to 1) suggest that the charge storage mechanism of CNT@Si/SiO_x NWs mainly involves a capacitive process with fast kinetics.

To quantitatively determine the charge storage mechanisms at a specific scan rate, the current (*i*) is analyzed according to the equation:

$$i = k_1v + k_2v^{1/2}$$

Herein, the former term (*k*₁*v*) represents the surface-controlled capacitance, and the latter (*k*₂*v*^{1/2}) represents diffusion-controlled behavior (Figure 4f).^{45,54} At each scan rate, CNT@Si/SiO_x demonstrates a higher capacitive contribution than Si/SiO_x. At 0.1 mV s^{−1}, the capacitive contributions are 43.56% and 65.35% for Si/SiO_x and CNT@Si/SiO_x, respectively. With the increase of the scan rate to 1.0 mV s^{−1}, the capacitive contribution reaches 90.71% for CNT@Si/SiO_x NWs (Figure 4g), while that of Si/SiO_x is only 71.13% (Figure S14).

EIS spectra of CNT@Si/SiO_x NWs and Si/SiO_x (Figure 4h,i) have been collected in their pristine state and after 3 cycles at 0.1 A g^{−1} (fully discharged). After cycling, the charge transfer resistance (semicircles at high frequency) of both electrodes decreases. Meanwhile, the low-frequency slope increases owing to electrochemical activation and SEI formation. The CNT@Si/SiO_x demonstrates a lower charge transfer resistance and greater slope than the Si/SiO_x before and after cycling, proving that the 1D core@shell structure with a CNT backbone could promote charge transfer and ionic diffusion. The reduced charge transfer resistance after the initial cycling is consistent with the activation process observed in Figure 3e–h. The EIS results experimentally corroborate the role of the coaxial CNT core in providing a continuous conductive pathway and the conformal shell in facilitating fast interfacial charge transfer and Li⁺ diffusion.

To study the benefits of the 1D nanostructure in buffering volume expansion, top-view and cross-sectional SEM (Figure

5a–h) are used to monitor the Si/SiO_x and CNT@Si/SiO_x electrodes before and after 120 cycles (at the lithiated state). Both electrodes present a uniform, crack-free surface before cycling (Figure 5a and c). Following the cycling process, the Si/SiO_x electrode exhibits severe surface fracturing (Figure 5b), accompanied by a substantial thickness increase of 47.1% (Figure 5e and f). The results illustrate that the Si/SiO_x electrode shows a large volume expansion and poor integrity during cycling. In contrast, the CNT@Si/SiO_x electrode presents a relatively compact, crack-free surface after cycling (Figure 5d). The thickness of the CNT@Si/SiO_x electrode increases from 27.4 to 30.6 μm, showing a thickness expansion rate of only 11.7% (Figure 5g and h). The markedly reduced electrode swelling and crack-free morphology further verify that the conformal core@shell geometry homogenizes stress and prevents shell delamination/particle isolation during cycling, thereby maintaining electrical integrity. The relatively low expansion ratio originates from the interconnected 1D nanowire network with rich internanowire porosity for volume variation accommodation. Notably, after long-term cycling, distinct crystalline Si domains are not clearly observed in the postcycling TEM analysis (Figure 5i), which is commonly attributed to the conversion of Si/SiO_x into amorphous Li_xSi and lithium silicates during repeated lithiation/delithiation. Meanwhile, the coaxial CNT@Si/SiO_x nanowire framework remains well-preserved without noticeable aggregation or pulverization, indicating robust structural integrity upon prolonged cycling. The F element, which comes from the electrolyte and participates in SEI formation, distributes homogeneously on the cycled CNT@Si/SiO_x core@shell NWs, as shown in the EDS mappings (Figure 5j–n).

Full cells are constructed by employing the CNT@Si/SiO_x anode and LiFePO₄ (LFP) cathode (Figure S15). At 1.0 C, the LFP cathode displays a discharge platform at ~3.4 V, corresponding to a capacity of 119.5 mAh g⁻¹ (Figure S16). The CNT@Si/SiO_x||LFP full cell demonstrates a mean working voltage of ~3.2 V and delivers 112.4 mAh g⁻¹ (Figure S17). Furthermore, 80.1% of the initial capacity is retained after 100 cycles.

Overall, the decent electrochemical properties of CNT@Si/SiO_x NWs originate from the following factors: (I) Both the sub-5 nm Si grains and the SiO_x phase provide high electrochemical activity. (II) The highly conductive CNT backbone wires the whole composite material. (III) The thin Si/SiO_x shell shortens the solid-state Li⁺ transfer distances. (IV) The 1D CNT@Si/SiO_x NWs provide rich internanowire porosity, buffering the volume variation of Si and SiO_x as well as enabling electrolyte accessibility.

CONCLUSIONS

In summary, we demonstrate a facile, efficient approach to construct 1D core@shell-structured CNT@Si/SiO_x nanowires. The CNT backbone is encapsulated by an ~20 nm thick Si/SiO_x layer, in which Si nanocrystals (sub-5 nm) are homogeneously distributed throughout the oxide matrix. The 1D core@shell structure possesses multiple structural merits for lithium storage, such as high electrochemical activity, high electrical conductivity, short Li⁺ diffusion lengths, and rich porosity. Consequently, the rationally designed 1D core@shell CNT@Si/SiO_x NWs demonstrate a comprehensively high electrochemical performance. The contribution would provide insights into the rational design of high-performance Si anodes.

ASSOCIATED CONTENT

Data Availability Statement

Data will be made available on request.

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsami.5c26120>.

Supplementary data for this article can be found online. Figure S1: SEM and TEM images of CNT@HSQ; Figure S2: TEM images of CNTs; Figure S3: HRTEM image and size distribution histogram of Si nanocrystals in CNT@Si/SiO_x; Figure S4: SEM and TEM images of Si/SiO_x nanoparticles; Figure S5: The C 1s XPS spectrum of CNT@Si/SiO_x; Figure S6: The Si 2p XPS spectrum of Si/SiO_x; Figure S7: TGA curves of Si/SiO_x and CNT@Si/SiO_x; Figure S8: Nitrogen sorption isotherms of Si/SiO_x and CNT@Si/SiO_x; Figure S9: GCD curves of Si/SiO_x at 0.1 A g⁻¹; Figure S10: GCD curves of Si/SiO_x at different current densities; Table S1: Comparison of the electrochemical performances of CNT@Si/SiO_x with previously reported SiO_x-based anode materials; Figure S11: Enlarged CV curves of Si/SiO_x at 0.1 mV s⁻¹; Figure S12: CV curves of Si/SiO_x at various scan rates; Figure S13: Log(*i*) versus log(*v*) plots and the corresponding linear fits of Si/SiO_x; Figure S14: CV curve and the calculated capacitive contribution of Si/SiO_x at 1 mV s⁻¹; Figure S15: The schematic diagram of the CNT@Si/SiO_x||LFP full cell; Figure S16: GCD profiles of the LFP cathode and cycling performance at 1.0 C in Li half cells; and Figure S17: GCD profiles of CNT@Si/SiO_x||LFP full cell and cycling performance at 1.0 C (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the National Key Research and Development Program of China (2022YFB3803501).

REFERENCES

- (1) Kim, J.-H.; Kim, N.-Y.; Ju, Z.; Hong, Y.-K.; Kang, K.-D.; Pang, J.-H.; Lee, S.-J.; Chae, S.-S.; Park, M.-S.; Kim, J.-Y. Upscaling high-area-capacity battery electrodes. *Nat. Energy* **2025**, *10*, 295–307.
- (2) Xiao, Z.; Wu, H.; Quan, L.; Zeng, F.; Guo, R.; Ma, Z.; Chen, X.; Zhan, J.; Xu, K.; Xing, L.; Li, W. Micro-sized CVD-derived Si-C anodes: challenges, strategies, and prospects for next-generation high-energy lithium-ion batteries. *Energy Environ. Sci.* **2025**, *18* (9), 4037–4052.
- (3) Kim, N.; Kim, Y.; Sung, J.; Cho, J. Issues impeding the commercialization of laboratory innovations for energy-dense Si-containing lithium-ion batteries. *Nat. Energy* **2023**, *8* (9), 921–933.
- (4) Ge, M.; Cao, C.; Biesold, G. M.; Sewell, C. D.; Hao, S.-M.; Huang, J.; Zhang, W.; Lai, Y.; Lin, Z. Recent advances in silicon-based electrodes: from fundamental research toward practical applications. *Adv. Mater.* **2021**, *33* (16), 2004577.
- (5) Wang, Y.; Xu, C.; Fu, J.; Che, S.; Ma, G.; Chen, K.; Yang, J.; Liu, S.; Cheng, G.; Zhang, D.; et al. Preparation of high-performance SiO_x anode materials via dual interfacial reinforcement strategy. *Chem. Eng. J.* **2025**, *510*, 161895.
- (6) Tao, J.; Yan, Z.; Yang, J.; Li, J.; Lin, Y.; Huang, Z. Boosting the cell performance of the SiO_x@C anode material via rational design of a Si-valence gradient. *Carbon Energy* **2022**, *4* (2), 129–141.
- (7) He, W.; Xu, W.; Li, Z.; Hu, Z.; Yang, J.; Qin, G.; Teng, W.; Zhang, T.; Zhang, W.; Sun, Z.; et al. Structural design and challenges of micron-scale silicon-based lithium-ion batteries. *Adv. Sci.* **2025**, *12* (6), 2407540.
- (8) Cheng, Z.; Jiang, H.; Zhang, X.; Cheng, F.; Wu, M.; Zhang, H. Fundamental understanding and facing challenges in structural design of porous Si-based anodes for lithium-ion batteries. *Adv. Funct. Mater.* **2023**, *33* (26), 2301109.
- (9) Huang, Z.; Yu, R.; Liu, J.; Zhong, Y.; Zhang, L.; Zhou, L. Surface nitridation of Si enabled gradient artificial solid electrolyte interface and self-optimized structural evolution. *Sci. Bull.* **2025**, *70*, 3580–3588.
- (10) Sun, Z.; Yin, Q.; Chen, H.; Li, M.; Zhou, S.; Wen, S.; Pan, J.; Zhang, Q.; Jiang, B.; Liu, H.; Kim, K.; Li, J.; Han, X.; He, Y. B.; Zhang, L.; Li, M.; Zhang, Q. Building better solid-state batteries with silicon-based anodes. *Interdiscip. Mater.* **2023**, *2* (4), 635–663.
- (11) Li, Z.; Tang, W.; Yang, Y.; Lai, G.; Lin, Z.; Xiao, H.; Qiu, J.; Wei, X.; Wu, S.; Lin, Z. Engineering prelithiation of polyacrylic acid binder: a universal strategy to boost initial coulombic efficiency for high-area-capacity Si-based anodes. *Adv. Funct. Mater.* **2022**, *32* (40), 2206615.
- (12) Yu, P.; Li, Z.; Zhang, D.; Xiong, Q.; Yu, J.; Zhi, C. Hierarchical yolk-shell silicon/carbon anode materials enhanced by vertical graphene sheets for commercial lithium-ion battery applications. *Adv. Funct. Mater.* **2025**, *35* (2), 2413081.
- (13) Du, H.; Yu, R.; Tan, X.; Wu, J.; Zhao, D.; Mai, L.; Zhou, L. Encapsulating Si nanoparticles in multi-shell hollow spheres: An effective approach to boost the cyclability. *Sci. China Mater.* **2023**, *66* (6), 2199–2206.
- (14) Ma, J.; Zhang, H.; Liu, R.; Zhang, W.; Han, S.; Han, J.; Xu, G.; Li, L.; He, Y.-S.; Ma, Z.-F. In-situ processing nano-porous silicon into 3D conductive structure as high-capacity anode for lithium-ion batteries. *Sci. China Mater.* **2023**, *66* (2), 493–504.
- (15) Zhou, J.; Lu, Y.; Yang, L.; Zhu, W.; Liu, W.; Yang, Y.; Liu, K. Sustainable silicon anodes facilitated via a double-layer interface engineering: inner SiO_x combined with outer nitrogen and boron co-doped carbon. *Carbon Energy* **2022**, *4* (3), 399–410.
- (16) Li, Z.; Han, M.; Yu, P.; Lin, J.; Yu, J. Macroporous directed and interconnected carbon architectures endow amorphous silicon nanodots as low-strain and fast-charging anode for lithium-ion batteries. *Nano Micro Lett.* **2024**, *16* (1), 98.
- (17) Zhang, Y.; Tang, W.; Gao, H.; Li, M.; Wan, H.; Kong, X.; Liu, X.; Chen, G.; Chen, Z. Monolithic layered silicon composed of a crystalline-amorphous network for sustainable lithium-ion battery anodes. *ACS Nano* **2024**, *18* (24), 15671–15680.
- (18) Shen, L.; Sun, K.; Xi, F.; Jiang, Z.; Li, S.; Wang, Y.; Tong, Z.; Lu, J.; Ma, W.; Green, M.A.; et al. Conversion of photovoltaic waste silicon into amorphous silicon nanowire anodes. *Energy Environ. Sci.* **2025**, *18* (9), 4348–4361.
- (19) Liu, B.; Liu, J.; Zhong, C.; Hu, W. Mg-doped, carbon-coated, and prelithiated SiO_x as anode materials with improved initial coulombic efficiency for lithium-ion batteries. *Carbon Energy* **2023**, *6* (3), No. e421.
- (20) Gong, S.; Lee, Y.; Choi, J.; Lee, M.; Chung, K. Y.; Jung, H.-G.; Jeong, S.; Kim, H.-S. In Situ mesopore formation in SiO_x nanoparticles by chemically reinforced heterointerface and use of chemical prelithiation for highly reversible lithium-ion battery anode. *Small* **2023**, *19* (16), 2206238.
- (21) Hernandha, R. F. H.; Rath, P. C.; Umesh, B.; Patra, J.; Huang, C. -Y.; Wu, W. -W.; Dong, Q. -F.; Li, J.; Chang, J. -K. Supercritical CO₂-assisted SiO_x/carbon multi-layer coating on Si anode for lithium-ion batteries. *Adv. Funct. Mater.* **2021**, *31* (40), 2104135.
- (22) Cheong, J. Y.; Cho, S.-H.; Lee, J.; Jung, J.-W.; Kim, C.; Kim, I.-D. Multifunctional 1D nanostructures toward future batteries: a comprehensive review. *Adv. Funct. Mater.* **2022**, *32* (49), 2208374.
- (23) Sun, H.; Zhang, Y.; Zhang, J.; Sun, X.; Peng, H. Energy harvesting and storage in 1D devices. *Nat. Rev. Mater.* **2017**, *2* (6), 17023.
- (24) Tian, Y.; Pei, Z.; Luan, D.; Lou, X. W. Anchoring Sn nanoparticles in necklace-like B, N, F-doped carbon fibers enables anode-less 5V-class Li-metal batteries. *Angew. Chem., Int. Ed.* **2025**, *64* (13), No. e202423454.
- (25) An, Y.; Pei, Z.; Luan, D.; Lou, X. W. Foldable anode-free sodium batteries enabled by N, P-codoped carbon macroporous fibers incorporated with CoP nanoparticles. *Sci. Adv.* **2025**, *11* (19), No. eadv2007.
- (26) Wang, H.; Guo, R.; Ma, Y.; Zhou, F. Cross-doped Mn/Mo oxides with core-shell structures designed by a self-template strategy for durable aqueous zinc-ion batteries. *Adv. Funct. Mater.* **2023**, *33* (38), 2301351.
- (27) Lai, Q.; Yin, B.; Dou, Y.; Zhang, Q.; Zhu, Y.; Yang, Y. Electrospun carbon nanofiber-supported V₂O₃ with enriched oxygen vacancies as a free-standing high-rate anode for an all-vanadium-based full battery. *Carbon Energy* **2024**, *6* (9), No. e517.
- (28) Saddam, Z. I.; Muthukumar, K.; Rajendran, S.; Sekar, A.; Liu, B.; Nepal, A.; Li, J. Improving Li-S battery performance by tuning the active sites of MoS_x/rGO electrocatalysts in the S/C cathode. *Chem. Eng. J.* **2025**, *519*, 164963.
- (29) Yang, M.; Yao, Y.; Chang, M.; Tian, F.; Xie, W.; Zhao, X.; Yu, Y.; Yao, X. High energy density sulfur-rich MoS₂-based nano-composite for room temperature all-solid-state lithium metal batteries. *Adv. Energy Mater.* **2023**, *13* (28), 2300962.
- (30) Cheong, J. L.; Hu, C.; Liu, W.; Ng, M.-F.; Sullivan, M. B.; Ying, J. Y. 3D carbonaceous nanostructured transition metal nitride,

carbonitride and carbide as polysulfide regulators for lithium-sulfur batteries. *Nano Energy* **2022**, *102*, 107659.

(31) Ryu, J.; Park, J.; Park, J.; Kim, M. G.; Park, M. Molecular engineering of atomically dispersed Fe-N₄ and Cu-N₄ dual-sites in carbon nitride nanotubes for rechargeable zinc-air batteries. *Energy Storage Mater.* **2023**, *55*, 397–405.

(32) Ahad, S. A.; Kennedy, T.; Geaney, H. Si nanowires: from model system to practical Li-ion anode material and beyond. *ACS Energy Lett.* **2024**, *9* (4), 1548–1561.

(33) Khan, M.; Yan, S.; Ali, M.; Mahmood, F.; Zheng, Y.; Li, G.; Liu, J.; Song, X.; Wang, Y. Innovative solutions for high-performance silicon anodes in lithium-ion batteries: overcoming challenges and real-world applications. *Nano Micro Lett.* **2024**, *16* (1), 179.

(34) Du, H.; Ma, G.; Yin, Z.; Rao, S.; Lin, S.; Zhang, T.; Ren, J.; Wu, Y.; Zhang, W.; Yu, R.; Zhao, D.; Li, W.; Zhou, L. Rambutan-inspired tri-layer architecture with regulated strain and lithium transport for high-capacity and stable lithium storage. *Sci. Bull.* **2026**, *71*, 1103–1112.

(35) Je, M.; Han, D.-Y.; Ryu, J.; Park, S. Constructing pure Si anodes for advanced lithium batteries. *Acc. Chem. Res.* **2023**, *56* (16), 2213–2224.

(36) Li, H.; Li, H.; Lai, Y.; Yang, Z.; Yang, Q.; Liu, Y.; Zheng, Z.; Liu, Y.; Sun, Y.; Zhong, B.; et al. Revisiting the preparation progress of nano-structured Si anodes toward industrial application from the perspective of cost and scalability. *Adv. Energy Mater.* **2022**, *12* (7), 2102181.

(37) Su, P.; Zhang, Z.; Luo, L.; Zhang, Z.; Lan, C.; Li, Y.; Xu, S.; Han, X.; Lin, G.; Li, C.; et al. Silicon nanowire array weaved by carbon chains for stretchable lithium-ion battery anode. *Small* **2024**, *20* (18), 2307716.

(38) Yoo, H.; Park, E.; Bae, J.; Lee, J.; Chung, D. J.; Jo, Y. N.; Park, M.-S.; Kim, J. H.; Dou, S. X.; Kim, Y.-J.; et al. Si nanocrystal-embedded SiO_x nanofolds: two-dimensional nanotechnology-enabled high performance Li storage materials. *Sci. Rep.* **2018**, *8* (1), 6904.

(39) Park, B. K.; Nam, D.-W.; Ma, D.; Yoo, J. H.; Kim, Y. M.; Kim, H.; Kim, K. J. Strategic design of a functional separator with dual-acting Si/SiO_x nanocomposite for dendrite-free Li-Metal batteries. *ACS Nano* **2025**, *19* (29), 26659–26672.

(40) Ou, S.; Liu, C.; Yang, R.; Fan, W.; Xie, Z.; Li, B.; Meng, T.; Zou, C.; Shu, D.; Tong, Y. Supramolecular-driven construction of multilayered structure by modified hummers method for robust silicon anode. *Energy Storage Mater.* **2024**, *73*, 103814.

(41) Wang, L.; Lu, J.-J.; Li, S.-Y.; Xi, F.-S.; Tong, Z.-Q.; Chen, X.-H.; Wei, K.-X.; Ma, W.-H. Controllable interface engineering for the preparation of high rate silicon anode. *Adv. Funct. Mater.* **2024**, *34* (40), 2403574.

(42) Shen, B.; Fu, N.; Chen, Y.; Shao, W.; Yan, Y.; Huang, J.; Yang, Z. Micron SiO_x encapsulated into amorphous B, N Co-doped carbon nanotube network for high-capacity and long-durable Li-ion half/full batteries. *Chem. Eng. J.* **2023**, *455*, 140820.

(43) Xu, S.; Zhou, J.; Wang, J.; Pathirana, S.; Oncel, N.; Robert Ilango, P.; Zhang, X.; Mann, M.; Hou, X. In situ synthesis of graphene-coated silicon monoxide anodes from coal-derived humic acid for high-performance lithium-ion batteries. *Adv. Funct. Mater.* **2021**, *31* (32), 2101645.

(44) Yin, Y.; Dong, X. Electrolyte engineering and material modification for graphite-based lithium-ion batteries operated at low temperature. *Interdiscip. Mater.* **2023**, *2* (4), 569–588.

(45) Luan, J.; Yuan, H.; Liu, J.; Zhao, N.; Hu, W.; Zhong, C. Amorphous AlPO₄ Layer coating vacuum thermal reduced SiO_x with fine silicon grains to enhance the anode stability. *Adv. Sci.* **2024**, *11* (36), 2405116.

(46) Sang, Z.; Su, D.; Wang, J.; Liu, Y.; Ji, H. Bi-continuous nanoporous carbon sphere derived from SiOC as high-performance anodes for PIBs. *Chem. Eng. J.* **2020**, *381*, 122677.

(47) Zhu, R.; Wang, Z.; Hu, X.; Liu, X.; Wang, H. Silicon in hollow carbon nanospheres assembled microspheres cross-linked with N-doped carbon fibers toward a binder free, high performance, and

flexible anode for lithium-ion batteries. *Adv. Funct. Mater.* **2021**, *31* (33), 2101487.

(48) Liu, Y.; Sun, M.; Yuan, Y.; Wu, Q.; Wang, H.; He, Y.; Lin, Z.; Zhou, F.; Ling, M.; Qian, C.; et al. Accommodation of silicon in an interconnected copper network for robust Li-ion storage. *Adv. Funct. Mater.* **2020**, *30* (14), 1910249.

(49) Ge, K.; Wang, Z.; Liu, J.; Mu, Y.; Wang, R.; Xu, X.; Wang, Y.; Zou, Z.; Zhang, Q.; Han, M.; et al. Constructing LiF-enriched solid electrolyte interface on graphene arrays with abundant edges on microscale Si-C anodes toward high-energy lithium-ion batteries. *Adv. Funct. Mater.* **2024**, *35* (5), 2414384.

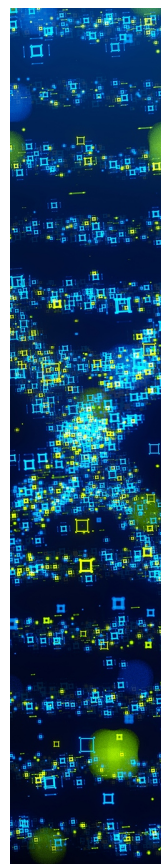
(50) Xie, G.; Tan, X.; Shi, Z.; Peng, Y.; Ma, Y.; Zhong, Y.; Wang, F.; He, J.; Zhu, Z.; Cheng, X.-B.; et al. SiO_x based anodes for advanced Li-ion batteries: recent progress and perspectives. *Adv. Funct. Mater.* **2024**, *35* (6), 2414714.

(51) Li, Z.; Du, M.; Guo, X.; Zhang, D.; Wang, Q.; Sun, H.; Wang, B.; Wu, Y. A. Research progress of SiO_x-based anode materials for lithium-ion batteries. *Chem. Eng. J.* **2023**, *473*, 145294.

(52) Zhou, Y.; Guo, H.; Yan, G.; Wang, Z.; Li, X.; Yang, Z.; Zheng, A.; Wang, J. Fluidized bed reaction towards crystalline embedded amorphous Si anode with much enhanced cycling stability. *Chem. Commun.* **2018**, *54* (30), 3755–3758.

(53) Hu, T.; Zhou, H.; Tang, J.; Chen, S.; Li, Z.; Yu, X.; Zhang, Y.; Yang, J.; Zhou, X. Stable lithium storage with strong-grain sustained pinning-reinforced nanocrystalline silicon. *Energy Environ. Sci.* **2024**, *17* (17), 6377–6392.

(54) Zhang, Y.; Yang, W.; Liu, X.; Ma, G.; Hu, G.; Liu, Z.; Yu, R.; Zhuang, D.; Xu, J.; Zhao, D.; et al. Necklace-structured silicon suboxide-based anode materials with multiple carbon networks for stable lithium storage. *Adv. Funct. Mater.* **2024**, *34* (25), 2315680.



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