A Beaded-String Silicon Anode

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ABSTRACT Interfacial instability is a fundamental issue in heterostructures ranging from biomaterials to joint replacement and electronic packaging. This challenge is particularly intriguing for lithium ion battery anodes comprising silicon as the ion storage material, where ultrahigh capacity is accompanied by vast mechanical stress that threatens delamination of silicon from the current collectors at the other side of the interface. Here, we describe Si-beaded carbon nanotube (CNT) strings whose interface is controlled by chemical functionalization,



producing separated amorphous Si beads threaded along mechanically robust and electrically conductive CNT. *In situ* transmission electron microscopy combined with atomic and continuum modeling reveal that the chemically tailored Si—C interface plays important roles in constraining the Si beads, such that they exhibit a symmetric "radial breathing" around the CNT string, remaining crack-free and electrically connected throughout lithiation—delithiation cycling. These findings provide fundamental insights in controlling nanostructured interfaces to effectively respond to demanding environments such as lithium batteries.

KEYWORDS: lithium ion battery · carbon nanotube · nanofabrication · interface · in situ TEM · propagation · modeling

nterfacial instability is a fundamental issue in maintaining structural integrality and functionality in heterogeneous materials, especially when different materials respond differently to the thermal, chemical, or electrochemical environmental changes.¹⁻³ Depending on the balance between adhesive forces and functional driving forces (e.g., differential thermal expansion) that change stress gradients or reactions that modify the materials chemically (e.g., metal silicide formation) or electrochemically (e.g., battery electrode charge/discharge), the interface can become deteriorating and unstable. These issues are particularly challenging for lithium ion battery anodes comprising silicon as the ion storage material. Silicon is a very attractive anode material for lithium ion batteries because it has the highest theoretical capacity, nearly 10 times in excess of conventional graphite electrodes.4-6 However, the vast mechanical stress that arises from nearly 300% volume changes between lithium insertion and extraction not only causes Si to fracture,⁴⁻⁶ but also leads to Si delamination from the conductive carbon or copper phases, resulting in quick capacity loss.

Nanostructured Si materials may enable strain relaxation to prevent fracture-induced capacity loss. Spurred by the pioneering

work of Chan et al.,⁷ intensive effort has been recently focused on silicon nanomaterial as a potential anode material for high capacity lithium ion batteries.^{8–12} In a onedimensional silicon nanowire, the mechanical stress that arises during lithiation/ delithiation cycles can be effectively relaxed along the radial directions. This reduceddimension benefit could potentially be maximized in quasi-zero-dimensional nanoparticles, where stress relaxation can occur in all three dimensions. In situ TEM studies of the detailed lithiation processes of single Si particles provide direct evidence that silicon nanoparticles below a critical size are indeed immune from cracking.¹⁰

However, retaining electrical connectivity for silicon nanoparticles in an electrochemically demanding environment remains an even greater challenge to electrode design. Even if nanoparticles do not crack, they easily detach from the current collector or other conducting phases, resulting in undesirable capacity loss.^{13,14} To maintain electrical connectivity in Si electrodes, there is substantial interest in incorporating low dimensional carbon nanomaterials such as CNTs and graphene in the design and synthesis of heterostructured Si anodes,^{9,15,16} in part because such nanostructures provide

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Figure 1. Functional bands control α -Si nucleation on *f*-CNTs. (A) Schematic and (B) TEM images showing symmetrical relation of α -Si beads on the end and sidewall of a *f*-CNT. (C) HRTEM images show the bare CNT between two Si beads and the interface of CNT-core/ α -Si-shell. (D) Raman spectra of *f*-CNT@ α -Si beaded-string structures in comparison with the pristine CNTs and alkylcarboxylated CNTs. The peaks marked by the asterisk (*) arise from the crystalline silicon substrate. The excitation line was 632.8 nm.

complementary properties including excellent electrical conductivity and mechanical durability. However, the native adhesion between Si and sp² carbon layers has proven to be inherently weak,^{15,17} and interfacial delamination remains a significant challenge in such nanocomposite materials. With the potential to alleviate this problem, it has already been shown that binders containing carboxyl groups can enhance stability, thus reducing irreversible capacity loss;^{11,18–21} however, the detailed mechanisms are largely unknown.

Here, we demonstrate the synthesis of electrically connected silicon beads on covalently functionalized CNT (f-CNT) strings to create a beaded-string structure that does not crack during lithiation-delithiation cycling. Carboxylic functional groups are covalently attached to the sp² carbon lattice in a unique "banding" fashion, allowing the growth of discrete amorphous silicon beads symmetrically threaded along the CNT at regular intervals with strong interfacial bonding due to the high density functional groups. This beaded-string structure affords advantageous features unattainable in a conventional continuous coaxial morphology, where Si is uniformly coated on CNTs over the entire surface. Both theoretical modeling and comparative in situ TEM studies reveal remarkably improved structural durability of this novel beaded-string structure during lithiation and delithiation.

RESULTS AND DISCUSSION

Controlled Synthesis and Characterization of Beaded-String and Core–Shell Structures. Arc-discharge multiwall carbon nanotubes are chosen for this study because their high crystallinity and low defect-density are ideal for synthesis of well-defined model heterostructures. Functional bands of $-(CH_2)_5COOH$ groups are covalently attached to the outermost walls through C–C bonds using a propagation chemistry developed previously by some of us.²² Unlike oxidative chemistries, this propagation chemistry does not remove carbon atoms from the sp² lattice of a CNT. Each functional group is instead amplified into a band consisting of hundreds of $-(CH_2)_5$ COOH groups. Amorphous Si (α -Si) is grown on both the *f*-CNTs and on pristine CNTs at 460 °C by low pressure chemical vapor deposition using silane as the silicon source.

We found that the surface chemistry of CNTs plays a vital role in controlling the growth of α -Si on the CNTs. For f-CNTs, the functional bands serve as nucleation centers, from which the growth of α -Si starts and extends axially away in both directions, leading to a beaded-string structure with discrete ellipsoidal α -Si beads threaded on the nanotube (Figure 1 and Supporting Information, Figure S1). All α -Si beads have similar axial length, except those at the end of CNTs, which are half-beads. This difference can be explained by assuming that Si can grow in only one direction at the end of a CNT but in both directions from functional bands on the CNT sidewall. All Si beads in an *f*-CNT@ α -Si structure have a similar shape and diameter. High resolution transmission electron microscopy (HRTEM) images (Figure 1C and Supporting Information, Figure S3c) clearly show a well-defined f-CNT/Si interface, with the segment between two adjacent Si beads being a bare CNT with little Si coating. SEM and TEM images collected at different rotation angles confirm that Si grows with nearly perfect rotational symmetry along the nanotube (Supporting Information, Figure S4). Micro-Raman spectroscopy confirms the characteristic G and G' peaks of CNT at 1580 and 2660 cm⁻¹, respectively, as well as the peak of α -Si around 480 cm⁻¹ (Figure 1D). Covalent attachment of alkylcarboxylic functional groups to the nanotube sidewall introduces sp³ defect centers,

VOL.7 • NO.3 • 2717-2724 • 2013



Figure 2. Microstructural evolution of beaded-string heterostructures upon lithiation propagation. (A,E) Schematic drawings show two different nucleation models with the free sliding and fixed interfaces. (B–D) Microstructural evolution of CNT@ α -Si core–shell structure upon lithiation. (F,G) Microstructural evolution of *f*-CNT@ α -Si beaded-string structure upon lithiation. (H) Microstructural evolution of *f*-CNT@ α -Si upon lithiation (0 V, *t* = 15 s) shows that Li⁺ propagated in two pathways: along both the α -Si surface and CNT/Si interface in the radial direction. (I) Schematic drawing indicates two reaction fronts for the formation of Li₁₅Si₄ in *f*-CNT@ α -Si beaded-string structure.

which activate the disorder mode around 1325 cm⁻¹. This disorder peak persists in the beaded-string structures, suggesting a CNT surface chemistry-dictated CNT/Si interface. In contrast, for pristine, unfunctionalized CNTs, a uniform, continuous α -Si coating is typically formed (Figure 2A,B). This is attributed to uniform nucleation on the nearly defect-free and atomically smooth surface of a pristine CNT.

Electrochemical Evolution of Beaded-String and Core-Shell Si Electrodes. To follow the structural evolution of these heterostructured electrodes, a prototype nanoscale electrochemical cell is built inside the TEM (Supporting Information, Figure S5) using lithium metal as a counter electrode and its native surface Li₂O layer as an electrolyte.^{12,23} As the Li₂O electrolyte is brought into contact with the CNT@ α -Si/f-CNT@ α -Si heterostructure using an in situ nanomanipulator, a constant bias with respect to Li metal (-2 V unless otherwise specified) is applied to the nanowire. Upon application of the electrochemical bias, lithium rapidly propagates axially toward the opposite end of the structure (Supporting Information, movies S1 and S2). The propagation front is evident as a two-phase structure consisting of unreacted silicon (dark) and fully lithiated silicon (light), both being amorphous (Figure 2). Electron diffraction patterns of lithiated beads clearly indicate the formation of the crystalline Li₁₅Si₄ (c-Li₁₅Si₄) phase, Li₂O, and an amorphous Li_xSi (α -Li_xSi) alloy at room temperature (Supporting Information, Figure S6),

SUN *ET AL*.

consistent with previous studies.^{12,16} Therefore the dark/light interface in TEM observations represents the *c*-Li₁₅Si₄/ α -Si interface. The rotational symmetry of the beads is retained in the lithiated structure (Supporting Information, Figure S7), which results from the isotropic propagation of lithiation reaction front in the α -Si beads. Note this lithiation mode of α -Si is in stark contrast with that of crystalline Si, in which anisotropic reaction rate in crystalline Si can lead to faceted or asymmetric nanostructures after lithiation.^{12,24}

We found that lithium quickly diffuses along the surface of the α -Si in the axial direction, followed by a lithiation reaction front propagating from the outer surface of α -Si radially inward toward the CNT at the center (Figure 2 and Supporting Information, Figure S8). As a result, a tapered lithiation front is formed in the α -Si during the lithiation process. In the core-shell structures, Li⁺ propagates along the axial direction at a high rate of 140 \pm 10 nm/s, in agreement with previous literature.¹⁶ The propagation along the radial direction is much slower than the lithium diffusion along the axial direction. In contrast, the beaded-string structure has a markedly different morphology change upon lithiation (Figure 2G). Besides the surface reaction, radially inward from the outer surface of each bead, there is also a second lithiation front propagating outward from the CNT/Si interface toward the outer surface (Figure 2H,I). This new reaction pathway is not observed with the

VOL.7 • NO.3 • 2717-2724 • 2013

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Figure 3. Lithium ions propagate along a string of merging silicon beads. Upon lithiation, the average diameter of the silicon beads increased from 198 nm in the pristine structure (A) to 352 nm in (J). Note the purely radial expansion, which prevents the beads from coalescing, even though they are nearly touching at the beginning.

core—shell structures grown on relatively defect-free CNTs. The two radial reaction front propagating rates, inward and outward, are ~1.7 and ~1 nm/s, respectively (Supporting Information, Figure S9). Both propagation rates are faster than the radial propagation rate in the core—shell structure, which is 0.24–0.9 nm/s. This fast, interfacial propagation pathway, similar to that reported by Wang *et al.*,²⁵ can be attributed to the finite length of the beads and the fast diffusion of Li⁺ on both Si and CNT surfaces. This results in the beaded-string structure reaching full lithiation faster than the core—shell structure, leading to improved rate capability.

Notably, the beaded-string exhibits remarkable flexibility in accommodating the volume expansion during lithiation. Upon lithiation, the unlithiated portion of the α -Si shell of the continuous core-shell heterostructure tends to crack across the axial direction (Figure 2D, Supporting Information, Figures S8 and S17). Even by slow and gentle lithiation of comparable structures at a minimum bias (0 V) with respect to lithium metal, the α -Si shell failed to avert the formation of these cracks (Supporting Information, Figure S11a). Such fragmentation of the unlithiated Si shell can severely degrade the cycle stability of CNT@α-Si electrodes. By contrast, all f-CNT@a-Si beaded-string electrodes sustained significant lithiation-induced deformation without appreciable fracture, suggesting a highly robust noncracking nanostructure design of anodes for lithium ion batteries.

To further evaluate the stability of beaded-string structures, we followed the lithiation and delithiation of these structures for many cycles with *in situ* TEM (Supporting Information, Figure S12). Constant biases

SUN *ET AL*.

of -0.1 V and +3 V with respect to lithium metal are applied to the beaded-string structures during lithiation and delithiation, respectively. The complete state of lithiation and delithiation is assessed by the observable morphological changes in the structures, which stabilize toward the lithiated and delithiated states. During the initial eight cycles, the volume expansion of the lithiated beads nearly reached the theoretical limit. We note that the delithiated silicon did not recover its original size, probably due to the incomplete removal of Li during delithiation or the generation of pores and/or voids, as previously observed in Ge nanowires.²⁶ However, analysis of the changes in diameter and length of Si beads over 18 cycles reveals a consistent and reliable "radial breathing mode" of expansion and contraction as Li⁺ inserts and extracts from the silicon beads (see also Supporting Information, movies S2 and S3). The axial length of the beads barely changes over all cycles, while the main volume expansion is reflected only in the changing radius of the beads. This radial breathing mode further suggests highly reversible mechanical durability of the beaded-string structures.

One major concern with nanoparticle-based electrode materials is their low volumetric storage capacity due to the large inaccessible interparticle space. We found that with beaded-string structures, the silicon beads can be grown during synthesis to the point where adjacent beads just begin to touch and even merge slightly. Since the Si beads do not elongate axially upon lithiation, the spacing between beads can be designed to be very small. An example is shown in Figure 3 where Si beads with diameters approaching 200 nm were grown on a CNT of merely ~20 nm in

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Figure 4. DFT and FEM simulations of the Si–C interface and lithiation-induced stress in Si. (A–D) $CNT@\alpha$ -Si core-shell structure and (F–I), *f*-CNT@\alpha-Si beaded-string structure; (A,F) schematics of the FEM models. Taking advantage of rotational symmetry, only the part demarcated by red solid lines is modeled. (B,G) DFT-minimized atomic structures of the α -Si (gold color) on unmodified graphene surface and $-(CH_2)_5COOH$ -modified graphene surface (C, gray; O, red; H, white), respectively. The *g*(*r*) for the atomic pairs across the interface is shown in part E. The bond distance of Si–O, Si–C bonds are in the range of 1.6–2.3 Å. Snapshots of the distribution of normalized Li⁺ concentration (C) and stress component along axial direction (D) in CNT@\alpha-Si core-shell structure at five sequential lithiation stages, respectively: *t* denotes normalized simulation time (=1 for full lithiation). Note the sharp reaction front separating the fully lithiated Si phase and unlithiated Si phase, and the crack initiation and propagation in the unlithiated Si phase due to high axial tensile stress. Parts H and I plot the corresponding snapshots in *f*-CNT@\alpha-Si beaded-string structure at five sequential lithiation stages. Simulations capture the morphology and Li⁺ concentration profile as observed in the experiment. Note that the Si bead can sustain full lithiation without fracture and the overall stress level after full lithiation becomes negligible.

diameter. *In situ* TEM studies confirm noncracking behaviors in all such beaded-string structures investigated. The diameter of these Si beads is ~33% larger than the critical size (~150 nm) for nonfracture silicon nanoparticles.¹⁰ Therefore, these beaded-strings can have a volumetric capacity comparable to that of silicon nanowires, but with better cycle life due to their enhanced mechanical durability. We note that in these larger beads, the second interfacial lithiation pathway is lost, probably because all the CNT surfaces are covered by silicon making it behave virtually like a core—shell structure with respect to lithium diffusion. However, the noncracking behavior is again clearly evident.

Theoretical Modeling. We attribute the unique deformation behaviors of beaded-string electrodes to the significantly improved bond strength of the CNT–Si interfaces. To elucidate the atomistic details of this interface, we numerically model a graphene plane consisting of 64 C-atoms, two of which are covalently bonded with $-(CH_2)_5COOH$ functional groups, and Si atoms randomly packed onto the functionalized

graphene surface to approximate an amorphous structure. Density functional theory (DFT) calculations (see Supporting Information for details) reveal that, in the optimized structure, the C=O bond in the $-(CH_2)_5COOH$ group is broken, bonding instead with two Si atoms as -Si-C-O-Si-, covalently connecting the functional group to the amorphous Si. The work of separation, W_{sep} , of the native CNT/Si interface (Figure 4B) in the CNT@α-Si core-shell nanostructure is rather weak, with $W_{sep} \approx 0.10$ J/m² (similar to that computed from DFT for Si on graphite basal plane¹⁷). We found that covalently attached -(CH₂)₅COOH functional groups, at a 12.5% surface coverage as experimentally estimated,²² leads to $W_{\rm sep} \approx 0.40 \text{ J/m}^2$, four times higher than Si on pristine CNTs. A plot of the radial distribution function g(r) of atomic pairs shows that various chemical bonds, including Si–O and C–Si bonds, are developed at the f-CNT/ α -CNT interface (the solid line in Figure 4E). Owing to these covalent bonds between the functional group and Si, the interfacial strength in the beaded-string nanostructure is substantially enhanced.

VOL.7 • NO.3 • 2717-2724 • 2013

www.acsnano.org

Finite element modeling (FEM) further shows that the difference in interfacial bonding strength leads to the fracture mechanisms of core-shell structures and the crack-avoiding properties of the beaded-string structures (Figure 4). The simulations clearly capture the lithiation process of both structures, as observed in TEM. The lithiation-induced volume expansion leads to compressive stress in the axial direction in the Li⁺-rich phase of the α -Si shell, which is balanced by the axial tensile stress in the unlithiated α -Si shell. In the continuous core-shell structure, as the lithiation front sweeps from the outer surface into the α -Si shell, the axial tensile stress in the unlithiated α -Si shell increases monotonically. Because of poor bonding between the Si and the CNT core, there is effectively no load transfer to the high strength sp² carbon, leaving a free inner surface for the Si shell.¹⁵ Once the axial tensile stress exceeds the cohesion strength of α -Si, cracks initiate from the free inner surface of the α -Si shell and propagate along the radial direction outward (Figure 4D). This radial crack propagation is arrested near the reaction front due to the compressive stress in the fully lithiated phase, agreeing well with experimental observations. For the f-CNT@a-Si beadedstring structure, even though the unlithiated phase of the α -Si bead is under tension, the magnitude of the tensile stress is effectively mitigated due to the strong mechanical constraint of the chemically tailored Si-C interface (Figure 4I). As a result, the axial tensile stress in the α -Si bead is never high enough to initiate cracks in the unlithiated Si. Without the strong mechanical

METHODS

Controlled Synthesis of CNT@a-Si/f-CNT@a-Si Heterostructures. Crystalline arc-discharge multiwall CNTs, with few surface defects and a diameter range of 2-50 nm, were covalently functionalized with $-(CH_2)_5$ COOH groups using a propagation chemistry as described previously.²² The functionalized CNTs were dispersed in aqueous sodium hydroxide solution (pH = 10) and then extracted with hexane to separate the less functionalized CNTs into a hexane layer, leaving the f-CNTs in water. The large and small graphitic particles that typically contaminate arc discharge CNTs were removed by centrifugation at 3000 and 16000 rpm, respectively. Then, the purified *f*-CNTs solution was drop-cast onto a clean Si(100) thin-wafer substrate (250 μ m). After drying in air and rinsing with ultrapure deionized water three times to remove salts, the Si substrate was cleaved, leaving a controllable number of cantilevered f-CNTs protruding over the cleaved edge. Nonfunctionalized arc-discharge CNTs were used as control. Amorphous Si was grown on the f-CNTs and CNTs at 460 °C in a low pressure chemical vapor deposition (LPCVD) system (Atomate Nanowire Growth System) using 2 Torr of silane as the silicon source and 1 Torr of argon as the protective gas. The thickness of the amorphous Si shell was controlled by the growth time.

Structural Characterization and in Situ TEM Studies. Raman scattering spectra were collected on a Horiba Yvon LabRam ARAMIS Raman spectroscope with a helium neon laser excitation source (632.8 nm). Scanning electron microscopy (SEM) images were collected using a SU-70 SEM (Hitachi) at 3 or 10 kV with an emission current of 33 µA. In situ characterization was employed using a JEOL JEM-2100 LaB₆ TEM operating at 200 kV. We use a specialized piezoactuated Nanofactory holder which simultaneously allows manipulation and imaging with three degrees of freedom in

constraint of the *f*-CNT, Li⁺ diffusion along the α -Si bead inner surface can only help mitigate the axial tensile stress in the unlithiated phase but cannot sufficiently avert its cracking (Supporting Information, Figures S13 and S14). By contrast, if the *f*-CNT/ α -Si interface is strong enough, the α -Si bead can survive full lithiation without cracking, even if Li⁺ diffusion only occurs from the bead outer surface (Supporting Information, Figure S15), as experimentally observed in

CONCLUSIONS

merging beads.

f-CNT@a-Si beaded-string heterostructures with chemically tailored carbon-silicon interfaces were designed and synthesized based on a fundamental understanding of carbon surface chemistry and Si nucleation on covalently modified CNT surfaces. In situ TEM studies of lithiation propagation reveal that these novel heterostructures can accommodate huge volume changes during lithiation and delithiation without appreciable mechanical failure. By contrast, CNT@α-Si continuous core-shell nanostructures fracture upon lithiation. DFT and continuum FEM studies consistently suggest that the strong Si-C interface made possible by the carboxylic functional bands on CNTs plays key roles in enabling noncracking f-CNT@α-Si beadedstring heterostructures. These findings thus provide important new insights in the synthesis of high performance Si electrodes, laying a foundation for nextgeneration lithium ion batteries.

real-time. Lithiation and delithiation were controlled by applying constant voltages ranging from -3 to 0 V and +1 to +3 V, respectively. The manipulation tip carries a piece of lithium metal, which acts as a Li source and a counter electrode. The thin native Li₂O layer, which is formed on the surface of pristine Li metal inside the TEM due to residual O2 and H2O gas in the TEM column, serves as a solid-state electrolyte, allowing the diffusion of Li⁺ between the electrodes under potential bias.^{23,2}

DFT Calculations. All first-principles calculations were conducted with the Vienna ab Initio Simulation Package (VASP), a plane wave density functional code.²⁸ Potentials constructed by the projector-augmented wave (PAW) method²⁹ were used for the elements. The exchange-correlation part of the density functional was treated within the local density approximation (LDA) of Ceperley-Alder³⁰ as parametrized by Perdew and Zunger.³¹ From convergence studies, we determined the kinetic energy cutoff in the plane wave expansion to be 400 eV and a 3 \times 3 \times 1 Monkhorst-Pack k-mesh^{32} for the slab modeled. The amorphous Si was generated via ab intio molecular dynamics simulation and used in previous elastic properties calculations for lithiated silicon.³³ All the relaxed structures achieved a Hellman-Feynman force convergence of 0.05 eV/Å. To determine the energy required to break the interfacial bonds on a unit area, W_{sep} , we constructed a flat single sheet of graphene with and without surface modifications. This is reasonable considering the diameter of the CNT used in the experiment is larger than 10 nm. Thus the $W_{\rm sep}$ for the slab interface model is defined as

$$W_{\rm sep} = \frac{1}{A} [E_{\rm Si} + E_{\rm sub} - E_{\rm interface}]$$



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where E_{Sir} , E_{subr} , and $E_{interface}$ are the total energies of the relaxed atomic structures of amorphous Si, substrate (graphene or modified graphene), and the interface of the two phases, respectively. The radial distribution g(r) is computed only for atomic pairs between the Si phase and the substrate in the interface structure.

Finite Element Modeling. To model the evolving lithiatiated/ pristine Si interface, we adopt an isotropic diffusivity of Li⁺ in Si with a nonlinear dependence on Li⁺ concentration in our model. The diffusion-induced stress is simultaneously calculated through a coupled chemomechanical model as the distribution of Li⁺ concentration evolves. We implement cohesive zone elements at locations that are most susceptible to cracking (see Supporting Information for details of FEM simulations). For the CNT@ α -Si core—shell nanostructure, the inner surface of the α -Si shell is set to be free, as suggested by the rather weak interface with the CNT. Li⁺ can diffuse into the α -Si shell only from its outer surface, as shown in the experiments. For the f-CNT@ α -Si beaded-string nanostructure, the inner surface of the α -Si shell is covalently bonded to a CNT, giving the strong interface.

Conflict of Interest: The authors declare no competing financial interest.

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Supporting Information Available: Movies of in situ TEM showing electrochemical evolution of Si–C heterostructures, detailed finite element modeling, Figures S1–S17 and additional references. This material is available free of charge via the Internet at http://pubs.acs.org.

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Supporting Information

A Beaded-String Silicon Anode

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1. Detailed Finite Element Modeling.

To understand the fracture of CNT@ α -Si core-shell nanostructure and the crack-averting feature of the *f*-CNT@ α -Si beaded-string nanostructure observed in experiments from a mechanics point of view, we model the lithiation process and the associated mechanics deformation/stress in these two nanostructures. We describe Li⁺ diffusion in Si by classic diffusion equation and set Li⁺ diffusivity to be concentration dependent: $D = D_0(1/(1-c) - 4c)$, where *c* is the normalized Li⁺ concentration (*e.g.*, c = 1 denotes fully lithiated stage and c=0 denotes pristine stage),¹ and D_0 is a diffusivity constant and chosen to be $10^{-18} m^2/s$ in order to give a realistic velocity of the lithiation reaction front.² Such a concentration dependent diffusivity can capture the lithiation reaction boundary separating a fully lithiated Si phase (c = 1) and a pristine α -Si phase (c = 0). Lithiation process involves deformation of Si due to lithium insertion. The abovementioned nonlinear diffusion model and the lithiation-induced deformation and stress are solved by the finite element codes ABAQUS through a fully-coupled

implicit analysis. In the finite element model, we adopt an isotropic linear elastic model to describe pristine α -Si and lithiated Si, with both Young's modulus and Poisson's ratio varying linearly with Li^+ concentration from 80 GPa and 0.24 (for prinstine Si, c = 0) to 12 GPa and 0.22 (for fully lithiated Si, c = 1), respectively.²⁻⁴ The linear elasticity assumption of lithiated Si could lead to overestimated stress level in Si, as in reality the lithiated phase behind the reaction front often undergoes the structural relaxation by plastic deformation. We found that even at an overestimated stress level, the f-CNT@ α -Si beaded-string nanostructure still can sustain the huge lithiation-induced volume change without fracture (Figure 4 and also further demonstrated later in Figures S13-S15). In this sense, the linear elasticity assumption for Si only results in quantitative difference in stress prediction, but the underlying mechanistic understanding of the different deformation and failure behaviors of the two nanostructures under lithiation remains valid. To capture the possible cracking in Si during lithiation, cohesive zone elements are implemented locations that are most susceptible to cracking (along the center line in radial direction in both FEM models as described in Figures 4A and 4F, respectively). In these cohesive zone elements, the cohesion strength and the toughness of Si are set to be 3 GPa and 12.5 I/m^2 , respectively.^{5,6} Viscosity stabilization of the deformation of cohesive zone elements is employed to improve FEM numerical convergence. For the CNT@ α -Si core-shell nanostructure, the inner surface of the α -Si shell is set to be free. To satisfy the deformation compatibility, kinematic constraints are applied at the two ends of the α -Si shell to ensure the same axial displacement during lithiation. For the *f*-CNT@ α -Si beaded-string nanostructure, the f-CNT is modeled as a thin layer of linearly elastic elements with a Young's Modulus of 300 GPa and the *f*-CNT/ α -Si interface is assumed to be perfectly bonded.

2. Key underpinning mechanism of non-cracking f-CNT@ α -Si beaded-string nanostructures under lithiation

To decipher the key underpinning mechanism that f-CNT@ α -Si beaded-string nanostructures can sustain huge volume increase during lithiation without fracture, we perform the following further simulations.

First, using the same FEM model as depicted in Figure 4d and similar simulation strategy described above, we set the inner surface of the α -Si bead to be free and allow the diffusion of Li⁺ only from the outer surface of the α -Si bead. In other words, these boundary conditions correspond to the case that the deformation of α -Si bead is not constrained by the CNT and there is no fast Li⁺ diffusion path along the CNT surface. Figure S13 plots the sequential snapshots (as counterparts of Figures 4E and 4F) of the lithiation process of the *f*-CNT@ α -Si beaded-string nanostructure under the above boundary conditions. Without Li⁺ diffusion along the bead inner surface, the Li⁺ concentration in the α -Si bead assumes a profile similar with that in the α -Si shell as shown in Figure 4B, with a sharp reaction front moving radially toward the bead inner surface. The stress in the lithiated phase is compressive and that in the pristine phase is tensile. Without the mechanical constraint from the CNT, the tensile stress in the pristine Si phase increases significantly until it reaches the cohesion strength of Si. Cracking then initiates and propagates in the unlithiated Si, which eventually is arrested near the reaction front, similar with the cracking process shown in Figures 4B and 4C.

Next, we set the inner surface of the α -Si bead to be free but allow the diffusion of Li⁺ from both the inner and outer surfaces of the α -Si bead. As shown in Figure S14, such a boundary condition leads to a Li⁺ concentration profile and stress distribution similar with those in Figures 4E and 4F, respectively. Without the strong interfacial bonding of the *f*-CNT, however,

the tensile stress in the unlithiated phase of Si can become high enough in later stages of lithiation to initiate cracking inside the Si bead.

Finally, we let the inner surface of the α -Si shell perfectly bonded to a CNT of high stiffness but only allow the diffusion of Li⁺ from the outer surface of the α -Si bead. In other words, these boundary conditions correspond to the case that the deformation of α -Si bead is constrained by the CNT but there is no fast Li⁺ diffusion path along the CNT surface. As shown in Figure S15, even though the resulting Li⁺ concentration profile and stress distribution are similar with those in Figures S13a and S13b, respectively, the strong mechanical constraint from the *f*-CNT can avert crack initiation in the Si bead. Upon full lithiation, the stress in the Si bead decreases to a negligible level, comparable to that as shown in the last panel of Figure 4F.

The above further simulations clearly reveal that the strong mechanical constraint from the *f*-CNT is the key underpinning mechanism of non-cracking *f*-CNT@ α -Si beaded-string nanostructure under lithiation, while the fast lithiation from the inner surface of the Si bead helps mitigate lithiation-induced stress but cannot sufficiently avert cracking occurrence.

3. Predicting saturated crack spacing in CNT@α-Si core-shell nanostructure

As shown in Figure 4C, the crack opening effectively releases the lithiation-induced stress ahead of the crack tip. However, as the lithiated phase remains nearly intact, axial tensile stress in the unlithiated α -Si shell away from the crack can still be high enough to cause more cracks, as shown in Figures 2D, S8, S10 and S11a. As more radial cracks form, the lithiation-induced stress is further released. Eventually, radial crack formation saturates with certain spacing between neighboring cracks. To estimate the saturated crack spacing and the radius of the unlithiated α -Si shell, we consider a theoretical mechanics model based on the force

equilibrium in the unlithiated phase and that in the fully lithiated phase of an α -Si segment between two neighboring radial cracks, respectively.

Figure S16 conceptually depicts the theoretical model. The inner and outer radii of the pristine Si shell are *r* and *R*, respectively. Figure S16b shows a segment of the Si shell of length *L* between two neighboring radial cracks after lithiation. Note that the lithiated phase of the Si shell is not fractured, as observed in the experiments. Due to large volume expansion induced by Li⁺ insertion, the outer radius of the lithiated outer shell of Si becomes R_c (greater than *R*). The radius of the unlithiated phase of the Si shell is R_I . Based on *in situ* TEM observation (*e.g.* Figure S8e), the radial expansion of the Si shell after lithiation is about 70%. That is, $R_c = R_I + 1.7(R - R_I)$. Due to stress relaxation near the crack surface, further cracking of the unlithiated Si segment, exceeds the cohesion strength of prinstine *a*-Si, σ_{SI} . Otherwise, the cracking of the unlithiated phases of the right half of the Si segment, as illustrated by the two free body diagrams shown in Figure 15c, respectively. Assuming a maximum tensile stress in the unlithiated Si core of σ_{SI} , we have

$$\sigma_{Si}\pi(R_I^2 - r^2) = \tau_Y(2\pi R_I \frac{L}{2})$$
(1)

for the unlithiated phase, and

$$(\sigma_Y - \sigma_r)\pi(R_c^2 - R_I^2) = \tau_Y(2\pi R_I \frac{L}{2})$$
⁽²⁾

for the lithiated phase. Here, τ_Y is the interfacial shear stress at the sharp phase boundary. Consider the yielding of the lithiated phase and assume von-Mises yield criterion, we have $\tau_Y = \frac{\sigma_Y}{\sqrt{3}}$, where σ_Y denotes the yielding stress of lithiated Si. σ_r represents the average residual stress level at the cross-section of the lithiated Si near an existing radial crack of the unlithiated Si. The stress relaxation due to crack opening dictates $0 < \sigma_r < \sigma_Y$. Solving Eqs. (1) and (2) yields a saturated crack spacing L_s and the corresponding radius of unlithiated Si core R_I . That is, any segment of unlithiated Si of length smaller than L_s and of radius greater than R_I is immune from further cracking. Use experimental values of r = 3 nm, R = 53 nm and take $\sigma_Y = 1.5 \ GPa$ and $\sigma_{Si} = 3 \ GPa$.^{7,8} The above model predicts that L_s ranges from 77 nm to 128 nm, and R_I ranges from 23 nm to 37 nm, when σ_r is assumed to be from 0 GPa (stress fully released ahead of a radial crack) to 1.2 GPa (stress partially released ahead of a radial crack). These predicted saturated crack spacing and radii of unlithiated α -Si agree well with experimental measurement within statistical scattering, (*e.g.*, Figures 2D, S8, S10 and S11a).

4. Crack-void model of CNT@α-Si structure

We present the cracks occurring in the continuous (non-bead) core-shell structures as arising due to stress-induced fracture of the unreacted silicon. Another possible model for explanation might be a heterogeneous reaction rate, producing discrete regions which lithiate more readily, giving only the appearance of mechanical cracks. To qualitatively better understand the nature of these transverse cracks, a superposition of line intensity profiles is obtained by using Digital Micrograph along the cross-section of cracks in a defocused high-magnification image as shown in Figure S17. The intensities depicted in the upper dashed yellow lines of Figure S17c represent the vacuum intensity level. The two large intensity spikes are due to the bright Fresnel edge contrast of the CNT@ α -Si structure. Ideally, if the cracks observed are filled with amorphous Li_xSi alloy, the dip in the intensity profiles should appear as negative-going curve representing the mass-thickness contrast in an amorphous-solid model. However, the higher intensity observed in the crack-region (positive curve) indicates the existence of voids in the cracks formed predominantly due to lithiation-induced stress in the unreacted silicon (crack-void

model). A small dip in the intensity seen in the center of the crack-region (deviating from the crack-void model) is due to the mass-thickness contrast of the CNT at the core, which is not fractured by the stress.

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I. Supporting Figures



Figure S1. *f*-CNT@ α -Si beaded-string nanostructures. (a-c) Schematic drawing and corresponding TEM images of *f*-CNT@ α -Si beaded-string structures with controlled morphologies. (d) Pitch distribution of Si beads on *f*-CNTs.



Figure S2. Scanning electron microscopy images of CNTs (a) *f*-CNTs (b) CNT@ α -Si core-shell structures (c), and *f*-CNT@ α -Si beaded-string structures (d).



Figure S3. TEM images of Si-C interfaces. (a, b) Mechanical fracture of a bead dimer in a *f*-CNT@ α -Si beaded-string structure reveals an abrupt interface between the two overlapped Si beads, suggesting a symmetrical overgrowth of the Si beads. (c) HRTEM image of a Si bead show the CNT-core, α -Si-shell and CNT/Si interface.



Figure S4. Rotational symmetry of silicon beads along a CNT string. SEM (a-e) and TEM (f-h) images of a *f*-CNT@ α -Si beaded-string at different rotation angles confirm that the Si-shell was uniformly deposited on *f*-CNTs in radial direction. All the SEM images have the same scale bar.



Figure S5. *In situ* TEM set up. The schematic depicts the half-cell configuration of the *in situ* electrochemical lithiation-delithiation experimental setup inside a TEM.



Figure S6. Electron diffraction (ED) patterns of Si beads (a,e, before lithiation; b,f, after lithiation (-3V)) and the segment between two Si-beads (c,g, before lithiation; d,h, after lithiation (-3V)). The pristine Si-shell is amorphous and corresponding ED of the lithiated state shows the formation of crystalline $Li_{15}Si_4$ (*c*- $Li_{15}Si_4$), Li_2O , and an amorphous Li_xSi (α - Li_xSi) alloy. The segment between two Si beads is bare CNT without amorphous Si, and the ED pattern is characteristic diffraction pattern of a CNT.



Figure S7. TEM images of *f*-CNT@ α -Si beaded-string structure. (a) before lithiation, (b)-(f) after lithiation (-3V) with different rotation angles: (b) + 30°, (c) + 20°, (d) 0°, (e) - 20°, (f) - 30°. All images have the same scale bar.



Figure S8. Microstructural evolution of CNT@ α -Si core-shell structure upon lithiation at -2 V. (a-e) The Li⁺ surface diffusion pathway. The arrows indicate the radial and axial components, respectively. (d-f) Formation and propagation of cracks on partially lithiated α -Si shell. The black arrows in f indicate the occurrence and two-way propagation of cracks. Figures a-e have the same scale bar. Li⁺ propagates along the radial direction was fast in the primary stage with an average rate of 0.9 nm/s in the first 36 seconds but dropped to merely 0.24 nm/s after 188 s. (t = 36 seconds, Li⁺ radial propagation rate: 31 nm/36 s = 0.9 nm/s; t = 94 seconds, 42 nm/94 s = 0.45 nm/s; t = 188 seconds, 45 nm/188 s = 0.24 nm/s).



Figure S9. Two pathways of Li⁺ propagation on a beaded-string structure. Microstructural evolution of *f*-CNT@ α -Si shows that Li⁺ propagated in two pathways upon lithiation at 0 V: along both the α -Si surface and CNT/Si interface in the radial direction. Li⁺ radial propagation rates along the surface-towards-interface and interface-towards-surface in the first 15 seconds are 26 nm/15 s = 1.7 nm/s and 16 nm/15 s = 1 nm/s, respectively, with a ratio of 1.7.



Figure S10. Microstructural evolution of a CNT@ α -Si core-shell structure shows both radial and axial expansion. (a) before and (b) after being partially lithiated. The axial expansion of lithiated Si was calculated to be 377%. The elongation of core-shell structure was calculated to be 5.8%.



Figure S11. Mechanical response and cracking due to morphology change. (a) Formation of cracks on partially lithiated α -Si shell of CNT@ α -Si core-shell structure (0 V, t = 720s). (b) A fully lithiated *f*-CNT@ α -Si beaded-string structure without cracks (at -3 V, t = 540s).



Figure S12. Radial breathing mode of Si beads during lithiation and deliathiation cycling. (a) Microstructural evolution of f-CNT@ α -Si during 18 cycles of lithiation (at -0.1 V) and delithiation (at +3 V) (n-lithiation cycle, n'-delithiation cycle) (all the images have the same scale bar). (b) Plot of Si-bead dimensions, which change as a function of cycle, showing a "radial breathing mode" of Si beads during lithiation and delithiation cycles. The numbered upper and lower labels, except 0 (pristine) depict the number of lithiated and delithiated cycles respectively. The cross-sectional area of individual beads is calculated by estimating the maximum transverse radial change during lithiation and delithiation.



Figure S13. Snapshots of *f*-CNT@ α -Si bead under lithiation. Here the inner surface of Si bead is free (no mechanical constraint from CNT). Li⁺ can only diffuse from the outer surface of the Si bead. Note that the Si bead fractures under lithiation.



Figure S14. Snapshots of *f*-CNT@ α -Si bead under lithiation. Here the inner surface of Si bead is free (no mechanical constraint from CNT). Li⁺ can diffuse from both the inner and outer surfaces of the Si bead. Note that the Si bead fractures under lithiation.



Figure S15. Snapshots of *f*-CNT@ α -Si bead under lithiation. Here the inner surface of Si bead is perfectly bonded to the *f*-CNT. Li⁺ can only diffuse from the outer surface of the Si bead. Note that the strong mechanical constraint from the *f*-CNT can avert the fracture of Si bead under lithiation.



Figure S16. Theoretical model of saturated cracking spacing. (a) Schematic of pristine CNT@ α -Si core-shell nanostructure. r and R are the inner radius and initial outer radius of the Si shell, respectively. (b) Schematic of partial lithiated nanostructure. Blue denote unlithiated Si shell and red represent lithiated phase. R_I is the radius of unlithiated Si shell and R_c is the current outer radius of the Si shell after lithiation. (c) Free body diagrams at equilibrium of two representative elements (blue: unlithiated Si; red: lithiated Si), demarcated by the dashed lines in (b).



Figure S17. (a, b) High-magnification TEM images showing transverse cracks during lithiation of CNT@ α -Si core-shell nanostructure. (c) Intensity profile which is the sum of three cross-sections through this micrograph as depicted in (b), obtained using Digital Micrograph. The excess intensity shown in the center in (c) clearly supports the existence of large voids in the cracked regions of the core-shell structures.

II. Supporting Movies.

Movie S1: Low-magnification CNT@ α -Si continuous core-shell structure upon lithiation.

Movie S2: Low-magnification beaded-string heterostructures showing lithium propagation and simultaneous microstructural evolution during lithiation and delithiation. The first 11 and last 6 seconds of the video show lithiation and delithiation of the structure respectively.

Movie S3: Higher-magnification close-up of a similar structure showing both lithiation and delithiation of the Si beads. In the first 17 seconds of the video, the structure is lithiated, showing the expansion of the beads during lithiation and the two-pathway lithiation process. In the last 4 seconds of the video, the structure is delithiated, showing a contraction of the beads in the radial direction. A slight contraction of the beads along the axial direction during delithiation results in the straightening of the free (uncoated) nanotube segment, making it appear to lengthen in the projected view presented in these images.