Adina Rubella-Like Microsized SiO@N-Doped Carbon Grafted with N-Doped Carbon Nanotubes as Anodes for High-Performance Lithium Storage

Weilan Xu, Cheng Tang, Na Huang, Aijun Du, Minghong Wu, Jiujun Zhang,* and Haijiao Zhang*

1. Introduction

With the extensive exploration of clean and sustainable energy sources such as solar, wind, waterfall, geothermal, etc., the rapid development of electrochemical energy storage and conversion technologies for the electricity generated from such intermittent sources has been seen in most recent years. Among different electrochemical energy storage and conversion technologies, lithium-ion batteries (LIBs) have become one type of the most reliable, efficient, and practical devices for many applications such as electric vehicles, portable powers, and stationary power plants due to their high energy/power densities, relatively long cycle life, and friendly environmental compatibility.\(^{[1,2]}\) In the effort to further increase the energy density to prolong the recharge mileage of the devices, besides increasing the capacity and voltage of cathode materials, developing high-capacity anode materials has been identified as an effective way.\(^{[3]}\) However, the current commercial graphite anodes are difficult to meet the demand of high energy density of the batteries because of their low theoretical specific capacities.\(^{[4]}\) Therefore, it is necessary to develop ideal anode materials for practical LIBs with low cost, high capacity, and good durability.

Silicon (Si)-based materials have long been considered to be one type of the most potential anodes for next-generation high-energy LIBs owing to their high theoretical capacity (4200 mA h g\(^{-1}\)), low delithiation potential (<0.5 V), rich reserves, and low cost.\(^{[5−7]}\) However, Si-based anodes suffer from
drawbacks including huge volume change (≈400%) during charge/discharge and poor internal conductivity. Although Si-based nanomaterials with small particle sizes can improve the transmission dynamics of electrons and Li ions, their high cost seriously hinders the large-scale commercial applications. Alternatively, microsized Si-based materials have attracted attention because of their high tap densities and low preparation cost. For example, silicon monoxide (SiO) with much less volume expansion has emerged as a promising substitute for Si recently.[10] However, its poor ionic/electronic conductivities are not conductive to the transport of Li ions and electrons, and its volume change in long-term cycles is still seen as an issue. Especially, the microsized SiO also has polarization of particle size.[8] It is 35 nm. Particularly, NCNTs show a distinct bamboo-like structure, as seen from the magnified TEM image in Figure 1e, which should be in favor of improving the electronic conductivity.[20] The controlled experiments indicate that the SiO@NCNT sample has also a similar morphology to natural adina rubella. Transmission electron microscopy (TEM) images further confirm that NCNTs are firmly connected over the whole SiO@NC-NCNTs sample (Figure 1h), suggesting the good combination of the middle NC layer and pristine SiO@NCNTs with SiO particles.

Figure 1a describes the fabrication procedures for microsized SiO@NC-NCNTs, where a lot of vertical CNTs are homogeneously grown on the surface of SiO@NC, showing a well-defined morphology. Interestingly, SiO@NC-NCNTs show a similar morphology to natural adina rubella. Transmission electron microscopy (TEM) images further confirm that NCNTs are firmly connected over the whole SiO@NC-NCNTs sample (Figure 1h), suggesting the good combination of the middle NC layer and pristine SiO@NCNTs with SiO particles.

### 2. Results and Discussion
#### 2.1. Material Synthesis and Characterizations

In the effort to develop high-performance anode materials for LIBs, we have achieved a facile and scalable catalytic pyrolysis process for synthesizing core–shell particles with microsized SiO core and N-doped carbon shell (SiO@NC) on which N-doped CNTs (NCNTs) are in situ grown to form a composite (SiO@NC-NCNTs). The in situ growth of NCNTs onto the core–shell SiO@NC can form a highly stable 3D conductive network, further enhancing the mechanical strength. More importantly, the flexible NC shell layer derived from polydopamine (PDA)-tightly grafted NCNTs can effectively alleviate the large volume expansions during the cycling process, as verified by the cross-sectional scanning electron microscopy (SEM) images. Meanwhile, the double N doping can also improve the wettability and conductivity of the anode material and provide more additional lithium storage sites. Accordingly, when this SiO@NC-NCNT is used as the anode for LIBs, both higher reversible capacity and better cycle durability in comparison with SiO@NCNTs and pristine SiO electrodes are achieved. The enhancement mechanism for the electrochemical performance is also investigated by the theoretical calculations for fundamental understanding.

**Small Sci. 2022, 2, 2100105**
The peak at 26.3° corresponds to the (002) crystal plane of graphite carbon (JCPDS No. 41-1487), confirming the CNT formation. The peaks of metal Co (JCPDS No. 15-0806) at 44.2°, 51.4°, and 75.8° mainly result from the residual Co particles after etching.

The chemical states and surface composition of SiO@NC-NCNTs were investigated using X-ray photoelectron spectra (XPS). The XPS full survey spectrum in Figure 2b reveals the presence of Si, C, N, and O in the sample, while the Co 2p peak is almost invisible, further indicating that most Co nanoparticles have been removed. Figure 2c shows the high-resolution Si 2p spectrum, and two peaks at 99.8 and 103.5 eV are ascribed to Si0 and Si4+, in line with the XPS results of pristine SiO (Figure S7, Supporting Information). Meanwhile, the O 1s high-resolution spectrum (Figure 2d) shows the peak of Si–O (532.4 eV).[20] In Figure 2e, the C 1s XPS spectrum can be divided into five peaks at 284.27, 284.8, 287.4, 290.1, and 292.6 eV, which correspond to C=C, C=C, C=N, C=O, and CO–O, respectively.[21] Particularly, the generation of C–N bond means that N atoms have been in situ doped into the carbon matrix.[22] The N 1s peak from Figure 2f then affirms this fact, which consists of pyridinic N, pyrrolic N, and graphite N. The existence of C–N bond and nitrogen doping can provide more active sites for Li+ adsorption and regulate the surface energy barrier of the carbon substrate, resulting in the increased electrochemical performances.[23]

Figure 2g shows Raman spectra of two samples. The characteristic peaks at around 1343, 1571, and 2690 cm−1 are generally ascribed to the D, G, and 2D bands of CNTs, respectively.[22] The relative intensity ratio of the peaks (I_D/I_G) is used to discern the graphitization degree of carbon materials.[24] The I_D/I_G ratio of SiO@NC-NCNTs and SiO@NCNTs is calculated to be 0.90 and 0.84, indicating good crystallinity of NCNTs. The I_D/I_G value of the sample synthesized without Co catalyst is about 0.95 (Figure S8, Supporting Information), further confirming the catalytic role of Co. TG analysis was conducted to determine the carbon contents in the composite (Figure 2h and S9, Supporting Information). The significant weight loss between 300 and 650 °C is mainly ascribed to the combustion of carbon. In addition, the curve shows the increased weight profile after 650 °C, which is due to the oxidation of SiO. By further analysis, the carbon content in SiO@NC-NCNTs and SiO@NCNTs was estimated to be 37.9 and 29.6 wt%, respectively.

Figure 1. a) Schematic illustration of the formation process of microsized SiO@NC-NCNTs composite. b) SEM image, c–e) TEM images, f) HRTEM image, g) EDS spectrum, h) STEM image of SiO@NC-NCNTs, and i–l) the corresponding elemental mapping of Si, O, C, and N.
The specific surface area and pore structure were also analyzed according to N\textsubscript{2} sorption isotherms (Figure 2i and S10, Supporting Information). As shown in Figure 2i, SiO@NC-NCNTs exhibit a type-IV isotherm with sharp capillary condensation at high relative pressure. The result indicates the existence of mesopores, which is further confirmed by the pore size distribution curve (inset in Figure 2i) with a narrow pore distribution centered on 2.3 nm. The SiO@NC-NCNT product has a large surface area of 143.2 m\textsuperscript{2} g\textsuperscript{-1}, much higher than 56.2 m\textsuperscript{2} g\textsuperscript{-1} of SiO@NCNTs. The large surface area and narrow mesoporous structure are conducive to the sufficient contact between electrolyte and electrode material and fast electrochemical reaction dynamics during the Li storage process.\textsuperscript{[28,29]}

2.2. Lithium Storage Performances

To evaluate the electrochemical performances of SiO@NC-NCNTs, SiO@NCNTs, and pristine SiO anodes, the half cells were assembled with metal Li wafer as the counter electrode. Figure 2a shows cyclic voltammetry (CV) curves of the SiO@NC-NCNTs electrode between 0.001 and 2.0 V at the scan rate of 0.1 mV s\textsuperscript{-1} for the initial four cycles, the cathodic peak centered at 0.14 V represents the formation of Li\textsubscript{x}Si alloys,\textsuperscript{[30]} and a broad cathodic peak at about 0.6 V in the first cycle generally corresponds to the formation of the solid electrolyte interfacial layer and the irreversible conversion of SiO\textsubscript{x} to active Si.\textsuperscript{[31]} In addition, the anodic peaks at 0.35 and 0.54 V can be ascribed to the delithiation of Li\textsubscript{x}Si phase.\textsuperscript{[32]} Based on the charge–discharge curves in Figure 3b and S11, Supporting Information, the initial discharge and charge specific capacity of SiO@NC-NCNTs, SiO@NCNTs, and SiO are 1809.6 and 953.6 mA h g\textsuperscript{-1}, 1714.4 and 1211 mA h g\textsuperscript{-1}, and 1380.1 and 1000.2 mA h g\textsuperscript{-1}, respectively. The initial Coulomb efficiencies (ICE) of SiO@NC-NCNTs, SiO@NCNTs, and SiO are 53%, 63%, and 51%, and the lower ICE is mainly attributed to the relatively high surface area of SiO@NC-NCNT, which consumes a lot of electrolytes in the early stage, and the generation of the SEI film.\textsuperscript{[33,34]}
SiO@NC-NCNTs increases rapidly to 91.7%, and from the fifth cycle, the coulomb efficiency is stable at above 96.7%, showing good reversibility.

The cycling durability of three electrodes was further investigated. As seen from Figure 3c, the SiO@NC-NCNT electrode shows the best cycling stability. At the current density of 200 mA g\(^{-1}\), it delivers a high reversible capacity of 1103.7 mA h g\(^{-1}\) with a capacity retention of 99.6% (compared with the fourth cycle) after 200 cycles, much larger than those of SiO@NCNTs (851.1 mA h g\(^{-1}\)) and SiO (136.9 mA h g\(^{-1}\)). Even at a high current density of 1 A g\(^{-1}\) (Figure 3d), SiO@NC-NCNTs can still give a specific reversible capacity of 700.2 mA h g\(^{-1}\) after 300 cycles, indicating durable cycling stability for fast lithium storage.

Figure 3e presents the rate capabilities of three electrodes under different current densities. At the current densities of 200, 500, 1000, 2000, and 5000 mA g\(^{-1}\), the specific discharge capacities of SiO@NC-NCNTs are 1138.4, 1081.8, 937.6, 763, and 569.2 mA h g\(^{-1}\), corresponding to 100%, 95%, 82%, 67%, and 50% capacity retention rates, respectively. By comparison, other two electrodes have relatively lower specific capacity at each current density. When the current density returns to 500 mA g\(^{-1}\), SiO@NC-NCNTs still have a high specific capacity of 1109 mA h g\(^{-1}\) with a 102.5% of capacity retention (compared with the capacity at 500 mA g\(^{-1}\)), exhibiting an excellent electrochemical reversibility at high current density. The superior rate performance is due to the smart design of such a unique ternary heterostructure, in which NCNTs tightly grafted onto the surface of SiO@NC can withstand the large stress changes at the high current density, thus maintaining good mechanical stability for the electrode material. In addition, the cycling performance of the SiO@NC-NCNTs electrode is also compared with those reported Si-based anode materials, as presented in Figure 3f and Table S1, Supporting Information. Briefly, the increased lithium storage performance of SiO@NC-NCNTs is mainly assigned to the enhanced conductivity and double protection effect of NC and NCNTs, which enable the full utilization of the energy storage capability of SiO.

2.3. Dynamic Analysis and Theoretical Simulations

Electrochemical impedance spectroscopy (EIS) was applied to probe the conductivity and ion diffusion behavior of the electrode. Figure 4a displays the Nyquist plots of the freshly assembled batteries. It has been acknowledged that a semicircle in the high-frequency region is attributed to the charge transfer resistance (\(R_\text{ct}\)), while the sloping line in the low-frequency region is related to Warburg impedance (\(Z_\text{W}\)).\(^{[15]}\) The \(R_\text{ct}\) of SiO@NC-NCNTs electrode is 42.3 Ω, which is apparently lower than those of SiO@NCNT (65.9 Ω) and SiO (228.3 Ω) electrodes. This result further indicates that the full combination of NCNTs and NC layer can significantly increase the conductivity and interfacial stability.

Galvanostatic intermittent titration technique (GITT) was performed to further study the dynamic process of electrodes (Figure 4b,c).\(^{[16]}\) The chemical diffusion coefficient of Li\(^+\) (\(D_{\text{Li}^+}\)) can be evaluated according to the known formula.
where \( n_m \) and \( V_m \) is the molar mass and molar volume of electron material, \( \tau \) is the duration of the pulse, \( S \) is the contact area of electrode/electrolyte, and \( \Delta E_S \) and \( \Delta E_{\tau} \) are the voltage changes caused by pulse and constant current charge discharge, respectively. From the results, it can be obtained that the \( D_{Li} \) value of SiO@NC-NCNTs (3.22 \( \times 10^{-14} \text{ cm}^2 \text{ s}^{-1} \)) is higher than those of SiO@NCNT (1.84 \( \times 10^{-14} \text{ cm}^2 \text{ s}^{-1} \)) and SiO (1.88 \( \times 10^{-16} \text{ cm}^2 \text{ s}^{-1} \)), further confirming the fast transport dynamics of the SiO@NC-NCNTs electrode.

To better understand the lithium storage mechanism of the SiO@NC-NCNTs electrode, a series of CV curves were collected at different scanning rates ranging from 0.2 to 1 mV s\(^{-1}\) (Figure 4d). Clearly, all curves exhibit similar shapes with a small shift along with cycling. The degree of capacitive contribution can be analyzed by the relationship between the current \( i \) and the scan rate \( \nu \).

\[
i = av^b
\]  

where \( a \) and \( b \) are fitting parameters. The results of Figure 4e show that the \( b \) values of anodic (peak A) and cathodic peak (peak B) of SiO@NC-NCNTs are 0.78 and 0.70, respectively, suggesting the capacitive-guided mechanism for SiO@NC-NCNTs. The capacitive contribution can be further determined via the relationship between current value \( i(\nu) \) at fixed voltage \( (V) \), capacity contribution \( (k_1\nu) \), and diffusion contribution \( (k_2\nu^{1/2}) \).

\[
i(V) = k_1\nu + k_2\nu^{1/2}
\]

As observed from Figure 4f, the capacitive contribution is 63.04\% of the total capacity at 1.0 mV s\(^{-1}\), and the proportion of capacitive contribution increases with increasing scanning rate. The results illustrate that the capacitive-dominated behavior can store Li\(^+\) more effectively at a higher scan rate, which is in agreement with the superior rate capability of SiO@NC-NCNTs.

Figure 5g describes the possible morphological evolution of SiO, SiO@NCNTs, and SiO@NC-NCNTs upon cycling. For pristine SiO, the low conductivity and large volume expansion lead to slow ion–electron transport and serious polarization of the electrode material.\(^{[37]}\) Although the introduction of NCNTs can shorten the ion diffusion path and improve the conductivity, falling off from the SiO surface due to weak bonding can happen. Fortunately, the problem can be solved through a
smart design of the flexible middle NC layer. The strong combination of the middle NC layer and NCNTs can provide short transfer channels for Li ions and electrons and realize fast charge transfer kinetics. Accordingly, the buffering capability and cycling stability of SiO@NC-NCNTs have been greatly improved.

On the basis of the experimental results, the first-principle calculation was adopted to further reveal the underlying reason for the enhanced lithium storage performance of the ternary SiO@NC-NCNT composite anode. In this case, the Si- or O-saturated Si surfaces with and without CNTs are considered as the references. As displayed in Figure 6, electrons are mainly depleted around Li and accumulate around the surface Si or O or CNTs, indicating the strong electron transfer between Li and heterostructures. For Si or O exposed surface, Li atom is strongly bonded with surface atoms, leading to an extremely high adsorption energy (−5.35 and −5.16 eV for Si and O surface, respectively). Such high energy will hardly move Li atoms or release them from the surface, which may show an impact on the battery charging/discharging process. When loading CNTs onto the exposed Si or O surface, the adsorption energy will shift to a moderate range, reaching −1.87 and −1.10 eV for Si@CNTs and SiO@CNTs, respectively. By further adding the carbon layer, it will screen the interaction between CNTs and Si or O surface and slightly enhance the Li adsorption performance with the energy reaching up to −2.85 eV. Bader charge analysis shows that 0.78 and 0.77 electron transfer from Li to CNTs in Si@C-CNTs and SiO@C-CNTs, respectively, which are much larger than those in other cases. Therefore, the formation of crystal Si in the heterostructure will improve the Li adsorption performance. Then, the density of states for each substrate under Li adsorbed situations was examined. Due to the surface atomic distortion of Si, the Li adsorbed heterostructures possess the metallicity with the large electronic states of Si or O surface existing near the Fermi level. In addition, the electrons’ states of

Figure 5. Cross-sectional SEM images of the pristine SiO electrode a) before and b) after 100 cycles at 1.0 A g⁻¹. Cross-sectional SEM images of the SiO@NCNTs electrode c) before and d) after 100 cycles at 1.0 A g⁻¹. Cross-sectional SEM images of the SiO@NC-NCNT electrode e) before and f) after 100 cycles at 1.0 A g⁻¹. g) Schematic illustration of the structural changes of SiO, SiO@NCNT, and SiO@NC-NCNT electrodes for LIBs after many cycles.
CNTs and carbon layer also demonstrate strong coupling with those of Si and SiO near the Fermi level, leading to the improved electronic conductivity. Therefore, the SiO@C-CNTs heterostructure with balanced Li adsorption energies and improved electronic conductivity can be used as the promising material platform for LIB applications.

3. Conclusion

In conclusion, N-doped CNTs are in situ grown onto PDA-coated microsized SiO particles based on a facile metal catalytic pyrolysis approach. The strong coupling of 1D NCNTs with the flexible middle NC layer endows the SiO anode with excellent properties including a large surface area of 143.2 m² g⁻¹ and a highly stable 3D conductive network. With these structural and compositional advantages, the as-obtained SiO@NC-NCNTs electrode demonstrates a high reversible specific capacity of 1103.7 mA h g⁻¹ at 0.2 A g⁻¹ and a superior rate performance of 569 mA h g⁻¹ at 5000 mA g⁻¹. Compared with SiO@NCNTs and pristine SiO electrodes, the SiO@NC-NCNTs electrode has only about 20% particle level expansion, as confirmed by the cross-sectional SEM images. Importantly, the DFT theoretical analysis further confirms that the ternary SiO@NC-NCNTs heterostructure can balance the adsorption and release of Li and improve conductivity. These results indicate that the flexible middle NC layer can alleviate large volume changes and enhance electrical contact of SiO@NC-NCNTs, thus boosting the Li-storage capability.

Figure 6. Charge density difference and the corresponding density of states for Li-adsorbed a) Si, Si@CNTs, Si@C-CNTs and b) SiO, SiO@CNTs, and SiO@C-CNTs, respectively. The yellow and blue areas represent the electron accumulation and depletion, respectively. Fermi levels (dashed lines) are set to be zero.
current study is expected to promote the commercialization of microsized SiO-based anodes in high-energy-density LIB applications.

4. Experimental Section

Materials: All chemical reagents were used as received without further purification. The microsized SiO powder (2–3 μm), dopamine hydrochloride, FeCl₃·6H₂O, CoCl₂·6H₂O, melamine, ethanol, and nitric acid solution (HNO₃) were all purchased from Sinopharm Chemical Reagent Co., Ltd. Distilled water was used in all the experiments.

Preparation of SiO@polydopamine Particles: The core–shell SiO@polydopamine particles (SiO@PDA) were first prepared as follows. Typically, 100 mg of commercial SiO powder with a diameter of 2–3 μm was dispersed in 200 mL of tri-buffer solution (pH = 8.5) under ultrasonication for 20 min, and then 20 mg of dopamine hydrochloride and 18.4 mg of FeCl₃·6H₂O were added to the above solution and ultrasonically treated for 10 min to form a homogeneous suspension. After reacting at room temperature for 24 h under continuous stirring, the resulting precipitates were harvested by centrifugation and washed with deionized water and ethanol several times and dried at 60 °C in a vacuum oven overnight to get the core–shell-structured Si@PDA particles.

Preparation of Microsized SiO@NC-NCNTs Composite: The microsized SiO@NC-NCNTs composite was synthesized via a facile catalytic pyrolysis technique, where melamine and CoCl₂·6H₂O were used as the carbon precursor and the catalyst, respectively. In an optimized synthesis, 200 mg of CoCl₂·6H₂O, 800 mg of melamine, 80 mg of Si@PDA synthesized earlier, and 8 mL of ethanol were homogeneously mixed. Then, the resulting powder was heated in a tube furnace at 800 °C for 3 h with a heating rate of 4 °C min⁻¹ under N₂ atmosphere to convert the PDA into N-doped carbon layer (NC), which then in situ catalyzed the growth of N-doped CNTs (NCNTs) onto SiO@PDA particles. After that, the obtained product was dispersed in 30 mL of HNO₃ solution (6.5M) and reacted at 60 °C for 12 h under stirring to remove the Co nanoparticles. After being cooled naturally, the microsized SiO@NC-NCNT composite was collected by centrifugation and washed thoroughly by deionized water and dried at 60 °C overnight under vacuum. As the comparison, the SiO@NCNTs product without the middle NC layer was also prepared following the same procedure without PDA coating.

Material Characterizations: The powder XRD measurements were recorded on a Japan Rigaku D/max-2550 instrument using Cu Kα radiation (λ = 0.154 nm). The morphology and composition of the samples were examined using SEM (ZEISS Gemini 300 and HITACHI SU-1500), TEM (JEOL 200CX), and HRTEM (JEOL-2000), accompanied by energy-dispersive X-ray spectroscopy (EDX, OXFORD Xplore). Raman spectra were obtained on the InVia confocal Raman microspectrometer. X-ray photoelectron spectra (XPS) were recorded on the Thermo Scientific K-Alpha XPS device with monochromatized Al Kα radiation. Thermogravimetric analysis (TGA) was conducted via the TA TGA Q50 instrument under flowing air atmosphere. The nitrogen adsorption/desorption isotherms were measured using a micromeritics ASAP 2010 analyzer.

Electrochemical Measurements: The electrochemical performances of the samples were evaluated by assembling CR2032-type half cells in an argon-filled glove box. Lithium metal was used as the counter electrode, and 1 M LiPF₆ dissolved in ethylene carbonate/diethyl carbonate (1:1 by volume) with 5% fluoroethylene carbonate was employed as the electrolyte. The working electrodes were prepared by a doctor-blade process, where the electrode slurry consisted of 80 wt% active materials, 10 wt% super-P, and 10 wt% sodium alginate were cast onto the copper foil and dried at 70 °C for 12 h in a vacuum oven. The mass loading of the active materials was 0.8–1.0 mg cm⁻². A LAND-CT2001A system was employed for the galvanostatic charge–discharge tests at different current densities at the voltages between 0.005 and 2.00 V, and the GITT analysis was also used. The CV and EIS were recorded with a CHI 660D electrochemical work station.

Computational Details: The first-principles calculations were based on density functional theory (DFT) as implemented in the Vienna ab initio simulation package (VASP). Functional for exchange correlation was described by the Perdew–Burke–Ernzerhof (PBE) functional within generalized gradient approximation (GGA). A more than 15 Å vacuum layer along the z-direction was adopted to screen the interactions caused by structural periodicity. The first Brillouin zone was sampled by the 7 × 9 × 1 and the kinetic cutoff energy was set to be 400 eV. To simulate the slab structure and reduce the cost of calculations, the bottom two-layer silicon atoms during the structural optimization were fixed. The force and energy for each atom were relaxed to be less than 0.001 eV Å⁻¹ and 10⁻⁶ eV, respectively. DFT-D3 correction was adopted to correct the van der Waals interactions. In the calculation, a surface of silicon crystal to model the amorphous silicon oxide and silicon was used due to the difficulties on DFT calculations. Then, to illustrate the influence of the existence of oxygen atoms, the surface silicon atoms with the oxygen ones (SiO) were replaced and their Li adsorption behaviors were investigated. In addition, the adsorption energy (E_ads) was obtained by

$$E_{\text{ads}} = E_{\text{Li-sub}} - E_{\text{Sub}} - E_{\text{Li}}$$

where $E_{\text{Li-sub}}$ and $E_{\text{Sub}}$ are the energies of the Si-based substrates with and without Li adsorption, respectively, while $E_{\text{Li}}$ represents the energy of the single Li atom.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements
The authors appreciate support from the Shuguang Program supported by Shanghai Education Development Foundation and Shanghai Municipal Education Commission (18SG035), The Development Research Center of Shanghai Municipal People’s Government (2021-GP-16), and Shanghai Engineering Research Center of Advanced Thermal Functional Materials (Shanghai Polytechnic University).

Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
Research data are not shared.

Keywords
carbon nanotubes, in situ catalytic growth, lithium-ion batteries, micrometer-sized SiO, nitrogen doping

Received: September 24, 2021
Revised: October 31, 2021
Published online: January 12, 2022

[1] Y. Ding, Z. P. Cano, A. Yu, J. Lu, Z. Chen, Electrochem. Energy Rev. 2019, 2, 1.
[2] C. Wu, G. Zhu, Q. Wang, M. Wu, H. Zhang, Energy Storage Mater. 2021, 43, 430.
