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Solid-liquid-solid growth of doped silicon nanowires for high-performance lithium-ion battery anode

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ABSTRACT

Silicon nanowires (SiNWs) have great potential in electronic devices, sensors, energy storage and conversion devices. Despite various ways to synthesize SiNWs, however, the growth of SiNWs directly from stable, abundant, sustainable silica sources has yet to be achieved. Herein, we report a modified alumino-reduction process of the silica to produce tin (Sn)-doped SiNWs that can be initiated at low temperature (250 °C) based on a solid-liquid-solid growth mechanism in analogy to the well-known vapor-liquid-solid (VLS). In this growth process, the reduced silicon atoms migrate freely in the molten salt and alloy with pre-reduced Sn. The supersaturation of silicon in the Sn-Si alloy leads to the precipitation of single-crystal SiNWs. The prepared SiNWs are of excellent crystallinity and doped with high non-equilibrium concentration (\sim 3.0 at%) of Sn. This process with the solid-liquid-solid mechanism can also be extended to produce other group IV elements-based nanowires such as germanium. In addition, the prepared Sn-doped SiNWs as the anode material in lithium-ion batteries exhibit excellent performance with a high initial Coulombic efficiency of 85.4 %, and a substantial reversible capacity of 1133 mAh g⁻¹ even after 500 cycles at 4 A g⁻¹. By utilizing the solid-liquid-solid mechanism, this modified alumino-reduction process offers a novel route for synthesizing doped SiNWs, holding promise for diverse applications.

1. Introduction

Silicon nanowires (SiNWs) have great potential for application in microelectronics, sensors, photovoltaic devices, and lithium-ion batteries (LIBs) [1–7]. Wagner and Ellis were the first to report the pyrolysis of a mixture of H_2 and silicon chloride, resulting in the formation of SiNWs using gold (Au) as the catalyst [8]. The pyrolyzed silicon dissolved into Au and formed the Si-Au liquid alloy. With an increased concentration of silicon to supersaturate, silicon precipitated and grew into nanowires. This is the vapor-liquid-solid (VLS) growth mechanism of SiNWs based on the chemical vapor deposition (CVD) process.

Thereafter, many precursors (e.g., silane and disilane) and catalysts (e.g., Au and Sn) have been used to synthesize SiNWs [9–12]. Although CVD processes without catalysts for SiNWs have also been reported, they are complicated and require air-sensitive or flammable precursors [13–15]. The above-mentioned CVD processes follow a typical 'bottom-top' strategy, while metal-assisted catalytic etching (MACE) follows a 'top-down' one [16–18]. In MACE, the HF solution etched the wafer using the deposited metal as a catalyst. With the catalytic effect of the metal, silicon dissolved, and SiNWs were obtained. This method utilizes a large amount of toxic HF, and a large portion of silicon ingot (\sim 80 %) is wasted during sawing and etching [19]. This disadvantage makes it

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impractical for the large-scale production of SiNWs. In addition to these methods, SiNWs can be grown from precursors in a liquid state like diphenylsilane under high-pressure or supercritical conditions [20,21]. However, the yield per time was less than 1.0 g due to the limitations of closed pressurized reaction conditions. Yu et al. developed an in-plane solid-liquid-solid (IPSLS) method to fabricate super-long SiNWs with solid silicon thin films as the precursor and Sn or indium (In) as the catalyst [22–25]. However, the fabrication process is very complicated, and the yield is still limited. To date, cheap, highly stable, and sustainable SiO₂ has not been successfully used as a precursor to synthesize SiNWs.

In this study, Sn-doped SiNWs were successfully synthesized through the modified alumino-reduction of low-cost SiO₂ as the starting material with Sn as the catalyst in the molten salt at 250–300 °C. SiNWs are highly crystalline and doped with high concentration (\sim 3.0 at%) of Sn. The growth of SiNWs is proposed to be based on a solid-liquid-solid mechanism, which can be extended to synthesize the nanowires with tailored compositions. As an anode material of lithium-ion batteries, the synthesized SiNWs deliver a high initial Coulombic efficiency of 85.4 %. In addition, it exhibits a reversible capacity of 1133 mAh g⁻¹ after 500 cycles at 4 A g⁻¹. The synthesis process under ambient pressure based solid-liquid-solid with low-cost, abundant silica as precursors can enable the potential large-scale application of SiNWs.

2. Results and discussion

2.1. Synthesis and characterization

The modified alumino-reduction of silica in molten salt has been

demonstrated to produce nano-crystalline silicon and hollow silicon spheres [26,27]. In the reaction, silicon is reduced from silica by Al in the molten salts of $AlCl_3$ and NaCl, following the reaction below [27]:

$$4A1 + 3SiO_2 + 3A1C1_3 + NaC1 \rightarrow 3Si + 6A1OC1 + NaA1C1_4$$
(1)

Here, silica nanopowder (~ 40 nm, Fig. S1a) was used as the reactant, adding 10 wt% SnO₂ (~ 50 nm, Fig. S1b). After it reacted with Al for 8 h in the molten salts at 300 °C, the product was washed with deionized water (H2O) and subsequently etched with hydrochloric acid (HCl). The X-ray diffraction (XRD) patterns (Fig. 1a) of the products after H₂O rinsing exhibit five typical peaks located at 28.4°, 47.3°, 56.1°, 69.1° , and 76.4° , which match well with the silicon phase (JCPDS no. 27-1402). The other peaks are related to unreacted Al and reduced Sn, which disappear after further etching with HCl. XRD analyses were performed on silicon samples to determine the crystal structure and parameters of silicon samples. As shown in Fig. S2, both silicon and Sndoped silicon samples exhibit a cubic crystal structure of space group Fd-3m. Notably, as the reactant SnO₂ content increased from 0 to 5 wt% and 10 wt%, the (111) XRD peak of the Sn-doped silicon samples is observed to shift slightly to a lower diffraction angle. The corresponding lattice parameters of the three samples, as listed in Table S1, are 5.44131 Å, 5.45339 Å, and 5.50946 Å, respectively. The above results are consistent with the lattice expansion caused by the incorporation of Sn [28]. Scanning electron microscopy (SEM) image (Fig. 1b) and transmission electron microscopy (TEM) image (Fig. 1c) of the product morphology after water washing. It can be observed that the addition of SnO₂ to the reactants led to the formation of SiNWs, whereas the reactants without SnO₂ resulted in the formation of silicon nanoparticles (Fig. S3). Additionally, TEM energy dispersive X-ray spectroscopy (EDX) elemental



Fig. 1. (a) XRD patterns of the silicon products. (b) SEM, (c) TEM images and corresponding EDX element maps (inset) of Sn (blue), Si (green) images after H₂O rinsing. (d) SEM and (e) TEM images after HCl etching. (f) Raman spectra. (scale bar for insets = 25 nm).

maps provided in the inset of Fig. 1c distinctly show the presence of both Sn and Si signals at the tips of the nanowires with H₂O rinsing, with a relative composition of 71 % Sn and 29 % Si. This confirms that the Sn signal at the tip is primarily from catalyst residue material [25,29]. Fig. 1d and Fig. 1e display the SEM and TEM images of the product after HCl etching, respectively. The diameter distribution of SiNWs is shown in Fig. S4. The results reveal that the final product is kinked nanowires with a diameter of 34 ± 5 nm. Moreover, Fig. S5 shows the SEM image of the Si product prepared at 250 °C, where the generation of nanowires is observed, indicating that this temperature is sufficient to induce the modified alumino-reduction of silica process and successfully produce SiNWs. Fig. 1f shows a comparison of Raman spectra of the silicon nanoparticles (SiNPs) and SiNWs. An obvious Raman peak is observed around 501 cm⁻¹, corresponding to the first-order transverse optical phonon mode (TO) of SiNPs [30,31]. However, compared with SiNPs, the Raman peak corresponding to SiNWs shifts from 501 cm^{-1} to 494 cm⁻¹. The second-order optical phonon mode (2TO, shifting from $924\,\mathrm{cm}^{-1}$ to $910\,\mathrm{cm}^{-1}$) and the second-order transverse acoustic phonon mode (2TA, shifting from 288 cm^{-1} to 282 cm^{-1}) are observed in SiNWs. The shift of the Raman peak to lower wavenumbers is mainly attributed to phonon confinement effects [32–35]. When phonons are confined to nanoscale dimensions, the translational symmetry of the crystal is destroyed, and phonons not in the center of the Brillouin zone can also participate in phonon scattering, consequently leading to a shift of the Raman peaks [35].

High-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) was used to further analyze the phase, crystallinity and components of the resulting HCl-etched SiNWs. Fig. 2a shows a HAADF-STEM image of typical SiNWs. It exhibits twisted nanowire morphology. The Fourier transforms of atomic resolution HAADF-STEM images acquired from regions 1–3 (Fig. 2a) are shown in Fig. 2b–d. It is evident that the nanowire possesses a near single crystal

structure and maintains an identical crystal orientation at positions 1–3, even though the morphology shows a kinked structure. The elemental mapping of the nanowires using STEM energy dispersive X-ray spectroscopy (STEM-EDX) is shown in Fig. 2e-h. Sn is uniformly distributed inside silicon, forming Sn-doped Si alloys. In contrast, oxygen (O) is only distributed around the outer regions of the nanowires, indicating the oxidation of silicon at the surface (Fig. 2g). To determine the relative composition of the nanowire, the STEM-EDX spectral background is removed, and the Schreiber-Wims ionization cross-section model is used to quantify the edge spectra of Si, Sn, and O. The EDX relative composition line profiles of the three elements are shown in Fig. S6, further confirming the homogeneous distribution of Sn in SiNWs. We have also performed quantitative EDX analysis at 10 positions along the top-left nanowire. The statistical result (Fig. 2h and Fig. 2i) reveals an average Sn atomic fraction of 2.49 % \pm 0.5 % in the alloy, which is 1–2 magnitude order higher than the equilibrium concentration (~ 0.01 at %) [36]. This value is consistent with the Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) result of 3.74 at% Sn. Such non-equilibrium doping, where Sn atoms are kinetically trapped in the silicon lattice at concentrations far exceeding equilibrium solubility due to rapid growth processes, is also found in Al and Sn doped SiNWs grown at high heating rates with CVD deposition [23,37,38]. This phenomenon can be explained using a model of solute trapping at step edges [38]. The starting ratio of SnO₂:SiO₂ varies from 5:95 to 10:90, and the doping concentration in the resulting SiNWs changes from 3.30 at% to 3.74 at %, as the ICP-OES result indicated in Table S2. The slight variation in doping concentration can be attributed to the reaction conditions used for the silicon samples. The concentration can be further adjusted by regulating the final synthesis temperature and the control of the catalyst chemistry [38]. Fig. 2J and Fig. S7 show the atomic-resolution HAADF-STEM image of the top right nanowire and selected area electron diffraction (SAED), revealing that the nanowire is imaged along the



Fig. 2. Morphology and chemical distributions of Sn-doped Si nanowires. (a) STEM-HAADF image. (b–d) Fourier transform of high-resolution STEM-HAADF images taken from the selected regions indicated by the numbers of 1–3 in Fig. 2a. (e–g) STEM-EDX elemental mapping of Si, Sn, and O in the nanowires. (h) Color-mixed image of three elements: O(red), Si (green), and Sn (blue). (i) Sn concentration of ten white rectangular-labeled is determined by STEM-EDX surface-scanning mapping results. (j) Atomic resolution HAADF-STEM image of the nanowires.

silicon $[\overline{1}11]$ zone axis. These results indicate that the sample consisted of Sn-doped SiNWs with high crystallinity.

2.2. Density functional theory calculations and molecular dynamic simulation

Density functional theory (DFT) calculations were utilized to further explore the growth mechanism of Sn-doped SiNWs. Fig. 3a shows the formation energies for different doping amounts of Sn. As the Sn/Si ratio changes from 56/8 to 1/1, the formation energy also shows a positive correlation. This indicates that the energy required to form a stable alloy system gradually increases with increasing Sn doping. However, there is an upper limit of Sn doping. Similar to VLS growth of SiNWs, Sn catalyzes the growth of Si, and after reaching the upper limit, Si supersaturates, precipitates, and crystallizes, resulting in crystal growth. According to the Gibbs-Curie-Wulff theorem [39], crystal faces with low surface energy grow faster and will become the main exposed crystal faces. DFT results (Fig. 3b) revealed that the (220) crystal face has the lowest surface energy (0.27 eV), which suggests that it is more easily exposed during the growth of nanowires. This makes the (220) facet the main part of the shell that occupies the maximum surface area of the nanowire, thus enabling the axial growth of nanowires in a directional manner. The density of states (DOS) of the Si and Si₆₀Sn₄ was calculated, and the results are shown in Fig. 3c. The DOS results indicate that the presence of Sn reduces the band gap of the nanowires, thereby increasing the electrical conductivity. Based on molecular dynamics calculations incorporating deeply learned potential functions, it is demonstrated that the Si-Sn alloy particles tend to form nanowire-like structures with increasing reaction time at a temperature of 600 K, as shown in Fig. 3d. Overall, the underlying growth mechanism of SiNWs is illustrated in Fig. 3e. SnO₂ is firstly reduced into metallic Sn. Since the reaction is above the melting point (231.9 °C) of Sn, liquid droplets are formed. After that, the reduced silicon atoms enter the Sn droplets and form the Sn-Si alloy liquid. As more and more silicon atoms dissolve in the liquid, the silicon atoms supersaturate and precipitate in the form of nanowires (Fig. 3e, right). As a comparison, silicon atoms nucleate homogeneously and grow into SiNPs without the participation of the Sn catalyst (Fig. 3e, left).

2.3. Electrochemical performance

Fig. 4a illustrates the cyclic voltammogram (CV) of Sn-doped SiNWs electrode for the first three cycles, depicting the typical lithiation/delithiation potentials of silicon-based electrodes. The obvious peak at 0.01 V observed during the initial cathodic scan (lithiation) corresponds to lithium alloying with silicon to form $\text{Li}_{15}\text{Si}_4$ [40,41]. The peaks located near 0.35 V and 0.57 V in the first anodic scan (delithiation) correlate to the dealloying process. During the lithiation scan of the Sn-doped SiNWs electrode, no obvious electrolyte reduction/decomposition peaks are observed. During the subsequent cycles, the peak at 0.18 V corresponds to the formation of amorphous Li_xSi . The peak intensity in the CV curve gradually increases with the number of cycles, indicating that the electrode material is progressively activated during cycling [42,43]. The Sn-doped SiNWs anode rate performance at various current densities is shown in Fig. 4b. At a current density of 0.1 A g⁻¹, a capacity of 3121 mAh g⁻¹ was obtained (Fig. S8).



Fig. 3. (a) Formation energy of different amounts of Sn-doped Si. (b) Surface energy of different surfaces of Sn-doped Si. (c) DOS of Si and Si₆₀Sn₄. (d) Evolution snapshots of doped SiNWs. (e) Proposed growth mechanism of Sn-doped SiNWs (right) and SiNPs (left).



Fig. 4. Electrochemical performance of Sn-doped SiNWs as LIBs anode. (a) CV curves at a scan rate of 0.1 mV s^{-1} . (b) Rate performance (unit: A g⁻¹). (c) Dischargecharge curves at different current densities. (d) Cycling performance. (e) Specific capacities at different current densities. (f)Full-cell charge at 0.3 C (1 C = 170 mA g^{-1}) with prelithiated Sn-doped SiNWs anode and a LiNi_{0.5}Mn_{0.3}Co_{0.2}O₂ (NMC532) cathode. (g) Rate performance of the full cell.

Additionally, it exhibits a high initial Coulombic efficiency (ICE) of 85.4 %. At current densities of 0.2, 0.5, 1, 2, 4, 6, and 8 A $g^{-1},$ the corresponding capacities preserved are 2725, 2499, 2194, 1766, 1398, 1012, and 778 mAh g^{-1} , respectively. When the current density returned to 0.2 Ag^{-1} , the capacity of the electrode slightly dropped to 2389 mAh g^{-1} . The observed decrease in capacity during this process is primarily attributed to irreversible lithiation [44]. Fig. 4c shows discharge/charge curves at various current densities, demonstrating that even under a high current density of 8 Ag^{-1} , the Sn-doped SiNWs electrode maintains distinct plateaus. The above results indicate that the Sn-doped SiNWs electrode exhibits small polarization, thus highlighting its exceptional rate performance. Fig. 4d demonstrates the cycling performance of Sn-doped SiNWs electrode at a higher current density of 4 A g⁻¹. It underwent an activation at different current densities, such as 0.1 Å g^{-1} (1 cycle), 1 Å g^{-1} (5 cycles), and 2 Å g^{-1} (5 cycles). Within the first 15 cycles, the capacity rapidly decreases to 1502 mAh $g^{-1},$ with subsequently diminished decaying rate. This phenomenon may be attributed to the requirement of more cycles for the formation of a stable solid electrolyte interface (SEI) at higher current densities. It can be observed that the discharge capacity increases from 1502 mAh g^{-1} to 1666 mAh g^{-1} for 100 cycles. This increase in capacity reflects the typical activation process of Si-based electrodes at high current densities [45]. The Sn-doped SiNWs anode provides a reversible capacity of 1133 mAh g^{-1} after 500 cycles at 4 A g^{-1} . Furthermore, Fig. S9 shows the electrochemical performance of SiNWs electrodes at higher mass loadings (~ 1.0 mg cm^{-2} and 2.0 mg cm^{-2}). Compared to lower mass loadings, the specific capacity shows a slight decrease at higher mass

loadings, mainly due to the increased electrode thickness, which leads to longer ion and electron transport paths and the lower intrinsic conductivity of silicon materials [46,47]. Nonetheless, even under higher load conditions, the SiNWs electrode can still maintain excellent electrochemical performance, indicating that it has stable electrochemical behavior under different load conditions. Additionally, Fig. S10a and b show the SEM images of the cross-section of the silicon nanowire electrode before and after 100 cycles at 1 Ag^{-1} , respectively. After 100 cycles at a current density of 1 A g^{-1} , the electrode thickness increased from 21.4 µm to 26.8 µm, corresponding to an electrode expansion of 25.2 %. This value is smaller than that of most Si-based anodes previously reported (Table S3). The small electrode thickness expansion indicates that SiNWs have good application prospects in high-energy lithium-ion batteries. Fig. S11 demonstrates that SiNWs, SiNPs, and commercial Si nanoparticles (100-200 nm) exhibit significant differences in cycling performance at a current density of 1 A g⁻¹. Specifically, SiNWs retained 73.8 % of their initial capacity after 200 cycles at 1 A g^{-1} , whereas the capacity of SiNPs dropped significantly, preserving only 45.4 % of their initial capacity. The capacity degradation of commercial Si nanoparticles (100-200 nm) under the same conditions is markedly more severe, resulting in a capacity of only 10 mAh g^{-1} after 200 cycles. The Sn-doped SiNWs-based electrode exhibited an enhanced electrochemical performance, as demonstrated in Fig. 4e and Table S3, in comparison to the SiNWs fabricated using alternative methods [42, 48-571

To further evaluate the application potential of Sn-doped SiNWs in lithium-ion batteries, the full cell with commercial $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$

(NMC532) as the positive electrode and prelithiated Sn-doped SiNWs as the negative electrode was assembled. The operating voltage range of the full cell is 2.5–4.1 V. Fig. S12 shows the typical charge-discharge curves of the Sn-doped SiNWs//NCM532 full cell at 0.3 C rate, and Fig. 4f shows its cycling performance. At 0.3 C, the full cell exhibits a high reversible capacity of 125 mAh g⁻¹ (1 C = 170 mA g⁻¹, based on the cathode active material), with a capacity retention rate of 91.6 % after 150 cycles. Additionally, the full cell exhibits a good rate performance of 86 mAh g⁻¹ at a high rate of 1.2 C (Fig. 4g). These results illustrate the promising of Sn-doped SiNWs as anode materials for practical applications.

The storage mechanism of Li⁺ was further explored through CV curves at different scan rates (0.2–1.0 mV s⁻¹), as shown in Fig. 5a. As the scan rate increases, the cathodic peak moves to a lower potential, while anodic peaks gradually merge into one peak and move to a higher potential. Given that battery capacity encompasses both diffusion and capacitance reactions, the relationship between the peak current (*i*) and the scan rate (*v*) of the CV curve of lithiation and delithiation processes can be expressed as [58]:

$$i = a v^b \tag{2}$$

The parameter b is determined from the slope of the linear fit of log (*i*)-log (ν), as shown in Fig. S13. When b = 0.5, it indicates diffusioncontrolled behavior, while it suggests capacitive-controlled behavior when b = 1. Here, the value of b is 0.52, indicating the involvement of both diffusion and capacitive-controlled behaviors. However, the proximity of this value to 0.5 emphasizes the predominant diffusioncontrolled nature of the charge transfer process, highlighting the battery behavior characteristics of Sn-doped SiNWs electrode [50,59]. To further quantify the contribution of diffusion and capacitance-controlled mechanism, the following equation was used [60]:

$$i = k_1 v + k_2 v^{1/2} \tag{3}$$

Where $k_1 v$ represents the dominance of the capacitive effect, and $k_2 v^{1/2}$ is the dominance of the diffusion effect. Fig. 5b displays the CV curve of the Sn-doped SiNWs electrode at a scan rate of 1.0 mV s⁻¹, separated into capacitance-controlled (red region) and diffusion-

controlled (green region) contributions. At 1.0 mV s^{-1} , the capacitance-controlled component contributes 83.6 % of overall performance. Fig. 5c illustrates that as the scan rate increases, the diffusion contribution of the Sn-doped SiNWs electrode reduces while the capacitance contribution increases. Furthermore, the charge transfer kinetics and diffusion coefficient of Li^+ (D_{Li^+}) at the interface of the Sndoped SiNWs electrode were investigated through electrochemical impedance spectroscopy (EIS) testing. Fig. 5d shows the Nyquist plots of the Sn-doped SiNWs electrode in the open circuit voltage (OCV) state and after cycling. For comparison, the Nyquist plots of SiNPs are shown in Fig. S14. The corresponding fitted equivalent circuit for the EIS results is illustrated in Fig. S15, and the fitting results are shown in Fig. 5e and Table S4. Where equivalent series resistance (Rs) represents the intercept on the Z' axis at high frequencies, indicating the resistance of separator and electrolyte, Ret represents charge transfer resistance, and R_{SEI} represents resistance concerning SEI film [61,62]. The diffusion coefficient of Li^+ (D_{Li^+}) can be determined using $D_{Li^+}=$ $R^{2}T^{2}/(2A^{2}n^{4}F^{4}C^{2}\sigma^{2})$, where R, T, n, A, F, and C represent gas constant, absolute temperature, charge transfer number, electrode surface area, Faraday constant, and Li⁺ concentration, respectively [63]. σ is the Warburg coefficient, which is determined by fitting the line obtained from Z' and $\omega^{-1/2}$ (Fig. S16). According to the simulation results (Fig. 5f and Table S4), the Li⁺ diffusion coefficient after ten cycles is $2.14 \times$ 10^{-11} cm² s⁻¹, significantly higher than the Li⁺ diffusion coefficient at OCV. It indicates that the formation of the SEI film reduces impedance, enhancing the ion diffusion and electron transfer of the Sn-doped SiNWs electrode. Compared with the SiNPs, the diffusion coefficients are 1-2 magnitude order higher. It can be attributed to the doping effect, which lowers the energy barrier for the diffusion of Li⁺. The higher diffusion coefficients can account for the better rate capability in Sn-doped SiNWs than in SiNPs (Fig. S17). It can be inferred that Sn doping in SiNWs aid to reduce the transport pathways for Li⁺ and electrons, consequently enhancing the overall electrode conductivity.

In order to elucidate the exceptional cycling performance of Sndoped SiNWs electrodes, *in-situ* TEM experiments were further conducted to observe their electrochemical lithiation/delithiation cycling. The schematic of the *in-situ* TEM experimental configuration is shown in



Fig. 5. Electrochemical kinetic analysis of Sn-doped SiNWs. (a) CV curves at different scan rates. (b) Total charge storage through capacitance and diffusion contribution at a scan rate of 1.0 mV s⁻¹. (c) Contribution of capacitance and diffusion at different scan rates. (e) Nyquist plots before and after cycling. (f) Fitted values of R_{ct} , R_{SEI} , and D_{Li^+} for SiNWs and SiNPs.

Fig. S18. In the experiment, the working electrode, comprising Sn-doped SiNWs, and the counter electrode, consisting of lithium metal, are individually affixed onto the tungsten tip. The lithium oxide layer on the surface of the lithium metal is used as a solid electrolyte. Upon lithiation, the migration of lithium is observed, leading to the expansion of nanowires as shown in the in-situ TEM images (Fig. 6a). A silicon-rich core and a lithium-rich shell can be observed during lithiation. The silicon core always maintains the structure of the nanowire, indicating rapid and uniform diffusion of Li across all surfaces [64]. Li predominantly concentrates on the surface of lithiated Sn-doped SiNWs. The lithiation process is completed within 60 s, after which the volume change nearly ceases (Fig. S19). As shown in Fig. 6b, after the delithiation process, lithium almost disappears, indicating that Li⁺ is extracted from the interior of the Sn-doped SiNWs. Electron energy-loss spectroscopy (EELS, Fig. S20) confirms the intercalation of lithium, as evidenced by a pronounced Li-K edge ($\sim 60 \text{ eV}$) [64,65]. Furthermore, the intensity of the Si-L_{2,3} edge increases after delithiation, which confirms the extraction of lithium. Fig. 6c-h shows the morphological change of the Sn-doped SiNWs after the first three lithiation/delithiation cycles. Sn-doped SiNWs can maintain reversible volume expansion and contraction with lithiation and delithiation after multiple cycles. The phase transition process of doped SiNWs during lithiation/delithiation exhibits remarkable reversibility (Fig. S21), which is the fundamental reason for their excellent cycling stability.

The synthesis conditions of SiNWs from the various processes, including the synthesis temperature, precursors, and pressure, are listed in Table S5. The modified alumino-reduction process-based solid-liquid-solid mechanism exhibits enormous advantages, such as the mild synthesis temperature (300 °C) and the cheapest and the most abundant precursors (SiO₂ and Al). A 10 g SiNWs sample (optical image; Fig. S22) was prepared in a single batch to demonstrate its scalability. The process can also be successfully extended to the synthesis of Sn-doped Ge nanowires (Fig. S23 and Table S6) and Sn-doped Ge/Si nanowires (Fig. S24 and Table S7), while the reactant of SnO₂/SiO₂ replaced with



Fig. 6. In-situ TEM observation of lithiation/delithiation process of Sn-doped SiNWs. HAADF-STEM image and corresponding EELS elemental map after (a) lithiation and (b) delithiation. (c–h) Microstructural evolution of Sn-doped SiNWs during the first three cycles of electrochemical lithiation/delithiation.

SnO₂/GeO₂ and SnO₂/GeO₂/SiO₂, respectively. These materials also exhibit good electrochemical performance as lithium-ion anode materials, as shown in Fig. S25 and Fig. S26. Based on the solid-liquid-solid mechanism, metals with low melting points, such as Bi (271.5 °C), can also be used in the alumino-reduction process to form Bi-doped Si or Ge nanowires. Furthermore, these elements can be mixed to form the nanowires with multi-dopants. Therefore, nanowires with varied components can be synthesized and optimized for various applications.

3. Conclusion

In this study, a modified alumino-reduction process of SiO₂/SnO₂ in the molten salt at 250–300 °C under ambient pressure is demonstrated to synthesize the Sn-doped SiNWs with high crystallinity for the first time. A novel solid-liquid-solid mechanism is suggested to explain the growth of SiNWs. The synthesized SiNWs exhibit excellent electrochemical performance with an ICE of 85.4 %, an initial capacity of 3121 mAh g⁻¹. This method is sustainable and scalable due to its stable chemical feature, low price, and ample sources of silica as a reactant. This study will open ways to low-temperature synthesis of many other metal-doped nanowires under ambient pressure to meet the needs of large-scale applications (*e.g.*, electrode materials for energy storage devices) through an inexpensive method.

4. Materials and methods

4.1. Synthesis of SnO₂

Firstly, 0.1 mol SnCl₂·2H₂O was dissolved in 0.7 M HCl, followed by heating to 75 °C and stirring for 10 min. After the solution was cooled to room temperature, dilute ammonia water was slowly added to adjust the pH of the solution to 9 and stirred for another 10 min. Subsequently, the precipitate was washed with deionized water and ethanol until the pH was close to neutral. The precipitate was dried at 70 °C overnight. Finally, the dried precipitate was placed in a muffle furnace and annealed at 500 °C for 1 h.

4.2. Preparation of Sn-doped Si nanowires

 SnO_2/SiO_2 with a mass ratio of 1:9, AlCl₃/NaCl with a molar ratio of 3:2, and excess Al powder were mixed in an argon-protected glove box. The mixture was then transferred into a round-bottomed flask reactor and sealed. Next, the reactor was removed and heated to 300 °C under ambient pressure for 8 h. After cooling to room temperature, the product was washed with deionized water and dilute HCl. Finally, Sn-doped SiNWs were obtained by centrifugation and vacuum drying. For comparison, the SiNPs are obtained without adding SnO₂.

4.3. Materials characterization

Crystallographic phase structure was analyzed using XRD (D8 advance, Bruker) in the 2θ range 10–80°. SEM characterized the morphology of Sn-doped SiNWs with a Zeiss-Sigma 300 instrument. TEM analyses were performed using a JEOL JEM-2100F microscope operated at 200 kV, equipped with an EDS spectrometer and a Gatan Enfina electron spectrometer. Raman spectra (Thermo Scientific DXR3) were acquired using a 532 nm laser. The HAADF-STEM and elemental mapping of the nanowires were performed using a field-emission S/TEM (Themis Z, Thermo Fisher Scientific) equipped with a probe and an image aberration corrector (SCORR and CETCOR, CEOS GmbH). For the HAADF-STEM image, the probe forming lens semi-angle is 21.4 mrad, and the semi-collection angle of the detector is set from 76 to 200 mrad. Energy-dispersive spectroscopy (EDS) spectra were obtained using a Super-X detector with a beam current of 400 pA. Doping elements were quantified using ICP-OES (Agilent 7700 ICP-OES).

4.4. Preparation of electrode

The active material, sodium alginate, and carbon black were mixed in deionized water according to the mass ratio 6:2:2 to form a homogeneous slurry. After the slurry was coated on the copper foil, it was dried in a vacuum oven at 80 °C for 12 h. The active material loading in the electrode was controlled at approximately 0.5 mg cm⁻².

4.5. Electrochemical measurement

The electrochemical performance of the samples was tested using CR2016 coin cells, with a metallic lithium foil as the counter electrode. The electrolyte was a 1 M LiPF₆ solution of ethylene carbonate and diethylene carbonate (1:1 by volume) containing 10 wt% fluoroethylene carbonates. The galvanostatic charge and discharge tests were performed in the 0.01–1.5 V (vs. Li/Li⁺) using the LAND-CT2001A battery test instrument. CV and EIS measurements were performed using an electrochemical workstation (Autolab 302N). The full battery was assembled with prelithiated Sn-doped SiNWs as the anode and commercial LiNi_{0.5}Mn_{0.3}Co_{0.2}O₂ (NMC532) as the cathode. The capacity ratio between the anode and cathode was controlled at about 1.3:1. The electrochemical performance was evaluated at 0.3 C (1 C = 170 mA g^{-1} . based on the cathode active material) in the voltage range of 2.5 V to 4.1 V. Sn-doped SiNWs were used as the working electrode in a half-cell configuration with lithium foil, where electrochemical prelithiation was performed on the anode. Prelithiation was achieved by lithiating the Sndoped SiNWs anode to 0.01 V at a current density of 0.1 A g^{-1} during the first discharge. After prelithiation, the Sn-doped SiNWs//Li half-cell was disassembled in an argon-filled glove box, and the prelithiation Sndoped SiNWs electrode was quickly taken out and assembled with the NMC532 cathode to form the full cell.

4.6. In-situ TEM lithiation/delithiation of Si nanowires

The Sn-doped SiNWs were affixed to an electrochemically etched micro-sized tungsten tip using conductive silver epoxy. Subsequently, another tungsten tip featuring a submicron-sized end was employed to scratch the freshly exposed Li metal surface within an argon-filled glovebox. This latter tip was connected to a piezo-driven biasing probe integrated into the Nanofactory TEM scanning tunneling microscope (STM) holder. To maintain the integrity of the experimental setup, prior to transitioning from the glovebox to ambient air, the holder tip was securely sealed with a plastic cap and further protected with Para film tape. The sealed holder was promptly transferred to the TEM column for *in-situ* lithiation studies. Notably, the Li₂O layer on the Li metal surface acted as a solid electrolyte, facilitating the electrochemical reactions. A 5 V and -5 V voltage was applied to the Li/Li₂O to realize lithiation and delithiation.

4.7. Calculation method

The Vienna Ab initio Simulation Package (VASP) was utilized for doing first-principles calculations using density functional theory (DFT) [66]. The Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional, which was based on the generalized gradient approximation (GGA), was used to analyze the exchange-correlation energy [67,68]. The projector-augmented-wave (PAW) method was adopted for the pseudopotentials. An energy cutoff of 520 eV was designated for the expansion of the plane wave basis. The force acting on each atom was constrained to 0.01 eV/Å to meet the convergence criterion. Additionally, a convergence energy threshold of 10^{-6} eV was adopted for the self-consistent calculations. Furthermore, the DFT-D4 technique with corrections was employed to study van der Waals forces, and spin polarizability was considered to elucidate magnetic characteristics.

The formation energy is calculated based on the following equation [69]:

$$E_f = E_{SiSn} - E_{Single} + \Sigma n_j u_j$$

Where " E_f " is the energy of formation; " E_{SISR} " is the total energy of the alloy system; " E_{Single} " is the total energy of the monomer system; " n_j " is the number of atoms of the element dissolved in it; and " u_j " is the corresponding chemical potential of the element.

The calculation of surface energy is based on the following equation [70]:

$$E_{Surface} = \frac{E_{Slab} - \sum n_i u_i}{2A} \tag{5}$$

Where " $E_{Slurface}$ " is the surface energy, " E_{Slab} " is the total energy of the surface model, " n_i " is the number of atoms of the model's constituent elements, " u_i " is the chemical potential corresponding to the element, and "A" is the area of the crystalline surface cut out by the model.

We carried out isothermal ab initio molecular dynamics calculations for different ratios of Sn-Si alloy models (consisting of 64 atoms in a unit cell) for a duration of 10 ps to obtain a training dataset at 600 K, using periodic boundary conditions and a Nosé-Hoover thermostat. Further deep learning potential generation was accomplished using the DeePMD-kit software package, where the size of the embedding nets was set from left to right to 25, 50, and 100. To study the morphological changes of the Si-Sn alloy particles during melting at a temperature of 600 K, we implemented molecular dynamics simulations for 300 ps using the Lammps software in conjunction with the deep learning potential function. The model consists of 10,000 atoms in a 100 \times 100 \times 100 Å³ box with periodic boundary conditions in all three dimensions.

CRediT authorship contribution statement

Guohua Gao: Supervision, Software, Conceptualization. Jiawen Li: Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. Changlin Zheng: Writing – review & editing, Supervision, Resources, Funding acquisition. Tongde Wang: Software, Formal analysis. Ye Zhu: Writing – review & editing, Supervision, Resources, Formal analysis. Yajie Wang: Writing – original draft, Methodology, Formal analysis. Zengfeng Di: Supervision, Formal analysis, Conceptualization. Zhihang Xu: Methodology, Formal analysis. Yongfeng Mei: Supervision, Formal analysis, Conceptualization. Abdul Mateen: Writing – review & editing, Formal analysis. Zhihao Bao: Writing – review & editing, Supervision, Project administration, Funding acquisition, Formal analysis, Conceptualization. Wei Yan: Investigation, Formal analysis. Haojie Li: Visualization. Altaf Mujear: Formal analysis. Jing Chen: Formal analysis. Shengyuan Deng: Formal analysis.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.nanoen.2024.110455.

Data availability

Data will be made available on request.

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