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Harnessing the concurrent reaction dynamics in active Si and Ge to achieve high performance lithium-ion batteries†

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Advanced composite electrodes containing multiple active components are often used in lithium-ion batteries for practical applications. The performance of such heterogeneous composite electrodes can in principle be enhanced by tailoring the concurrent reaction dynamics in multiple active components for promoting their collective beneficial effects. However, the potential of this design principle has remained uncharted to date. Here we develop a composite anode of Cu/Si/Ge nanowire arrays, where each nanowire consists of a core of Cu segments and a Si/Ge bilayer shell. This unique electrode architecture exhibited a markedly improved electrochemical performance over the reference Cu/Si systems, demonstrating a stable capacity retention (81% after 3000 cycles at 2C) and doubled specific capacity at a rate of 16C (1C = 2 A g⁻¹). By using *in situ* transmission electron microscopy and electrochemical testing, we unravel a novel reaction mechanism of dynamic co-lithiation/co-delithiation in the active Si and Ge bilayer, which is shown to effectively alleviate the electrochemically induced mechanical degradation and thus greatly enhance the long-cycle stability of the electrode. Our findings offer insights into a rational design of high-performance lithium-ion batteries *via* exploiting the concurrent reaction dynamics in the multiple active components of composite electrodes.

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Broader context

Breakthroughs for the development of high-performance energy storage devices such as rechargeable batteries critically hinge on a fundamental understanding of the dynamic electrochemical reactions in active electrode components. By integrating electrochemical testing, *in situ* transmission electron microscopy and computational modeling, this work unravels a previously unknown reaction dynamics of co-lithiation/co-delithiation in the active Si and Ge shells of a Cu/Si/Ge nanowire anode for Li-ion batteries. Importantly, the synergistic co-lithiation/co-delithiation can unexpectedly alleviate the electrochemically induced mechanical degradation, thus greatly enhancing the long-cycle stability of the present composite anode. The findings are expected to have a profound impact on the development of advanced composite electrodes *via* harnessing the concurrent reaction dynamics in multiple active electrode components.

Introduction

The fast-growing market for portable electronics and electric vehicles has created a strong demand for lithium-ion batteries

(LIBs) with high energy density, fast charge/discharge rate, and long cycle life.^{1–3} Silicon is one of the most promising anode materials for next-generation LIBs,^{4–11} due to its high theoretical capacity of 3579 mA h g⁻¹ (Li₁₅Si₄) at room temperature.

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However, dramatic volume changes ($\sim 280\%$) occur during lithiation/delithiation of Si and thereby cause severe cracking of Si anodes.^{11–15} Such mechanical degradation often leads to loss of electrical contact between the active Si and current collector, as well as destruction and regeneration of solid electrolyte interphases (SEIs) on the fractured Si surfaces, thereby resulting in rapid capacity fade.

Tremendous efforts have been devoted to mitigate the electrochemically induced mechanical degradation of Si electrodes.¹⁴ In recent studies, several material and electrode design strategies have been demonstrated for alleviating Si degradation during cycling. For example, reducing the feature size of Si particles and wires to the nanoscale can avert cracking and fracture.^{11,16} Creating a hollow space in Si shells and tubes can reduce the outward expansion during lithiation, thereby alleviating the mechanical damage and regeneration of SEIs.^{17–20} Besides engineering the geometry of Si electrodes, coatings of carbonaceous materials,^{21–23} metals,^{24,25} oxides^{18,26–29} or conducting polymers³⁰ are often used. These coatings can enhance the transport of electrons and ions, thus improving both the rate performance and uniform utilization of active Si.

Meanwhile, coatings impose mechanical constraints, thus mitigating the chemomechanical degradation of Si. However, one drawback associated with these coatings is that the specific capacity of the resulting electrode is reduced, due to the low Li storage capacity of the coating material relative to Si. Nonetheless, these studies have pointed to a promising route of engineering the high-performance Si electrodes through an effective integration of small feature size, hollow space, conductive and high-capacity coatings.

Here we report the fabrication, testing and understanding of an anode of Cu/Si/Ge nanowire (NW) arrays for LIBs. Fig. 1a shows a schematic of this composite electrode consisting of Cu/Si/Ge NW arrays grown on a substrate of porous Ni foam, and each Cu/Si/Ge NW has a core of Cu segments and a Si/Ge bilayer shell (Fig. 1b). This architecture integrates several favorable design attributes for high performance. Specifically, the nanoscale geometry of the NWs enables facile strain relaxation;^{31,32} the sufficient free space between NWs facilitates volume accommodation; the metallic Cu segments in the core enhance electron transport; and the hollow space between Cu segments accommodates Si deformation during cycling. Moreover, the outer Ge shell serves

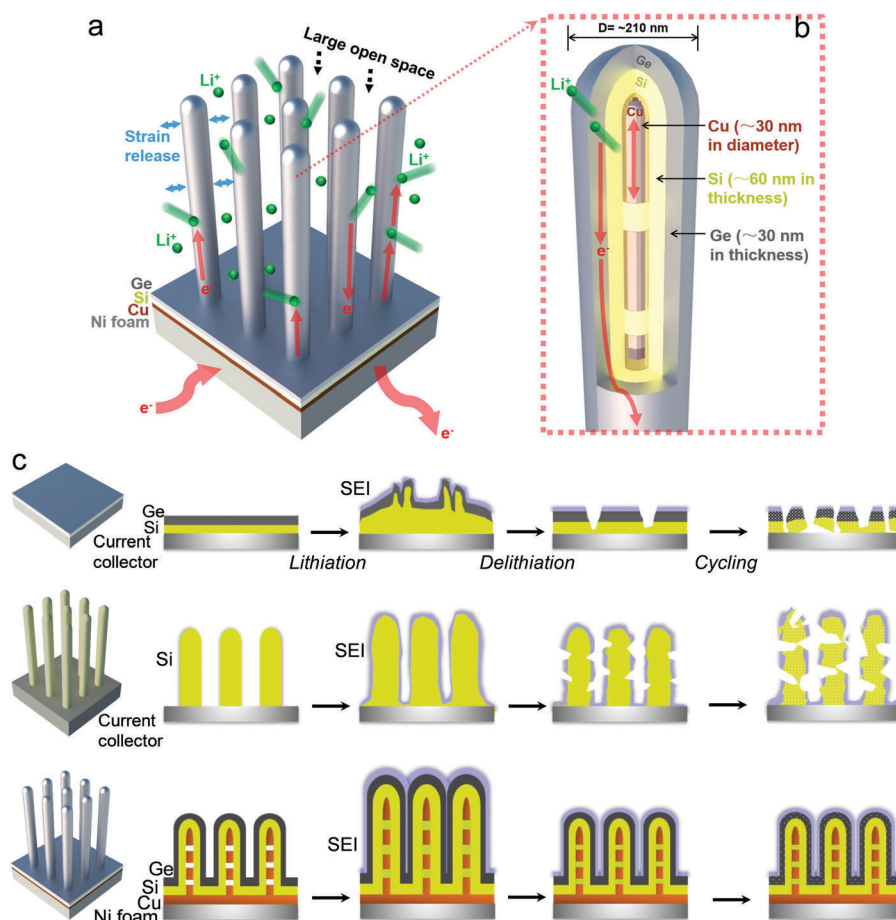


Fig. 1 Schematic illustration of a high-performance Cu/Si/Ge nanowire (NW) electrode. (a) The Cu/Si/Ge NW array was grown on a Ni foam substrate, and (b) each NW had a core of Cu segments and a Si/Ge bilayer shell. (c) The favorable design features, in conjunction with the concurrent reaction dynamics in active Si and Ge through co-lithiation/co-delithiation, enable a long-cycle stability in the Cu/Si/Ge NW electrode, while the Si/Ge thin-film electrode and Si NW (or NT) electrode are prone to mechanical degradation in both active components and SEIs during cycling.

as an active high-capacity coating.^{33,34} Compared with Si, Ge has both a higher electrical conductivity (two orders of magnitude higher than Si) and a higher Li-ion diffusivity (more than 400 times higher than Si).³⁵ Hence, the active Ge coating on Si can significantly enhance the rate capability relative to a pure Si electrode while maintaining a high specific capacity. While a combined use of Si/Ge has been previously reported,³⁴ the concurrent reaction dynamics in active Si and Ge is yet to be explored, and their impact on electrode performance remains largely unknown. Here we report our findings on the concurrent reaction dynamics using the Cu/Si/Ge NW array electrode as a model system. We show that the active Si and Ge exhibit a novel mechanism of co-lithiation/co-delithiation, which is unraveled by *in situ* transmission electron microscopy (TEM), electrochemical testing (e.g., cyclic voltammetry), and chemomechanical modeling. The unique co-lithiation/co-delithiation processes in active Si and Ge are shown to effectively accommodate large volume changes during cycling and thus enhance the damage tolerance of Cu/Si/Ge NWs. As a result, this composite electrode exhibits a superior performance and long-cycle stability relative to both the Si/Ge thin-film electrode and the Si NW (or NT) electrode (Fig. 1c). Our findings offer insights into a rational design of high-performance LIBs *via* exploiting the concurrent reaction dynamics in the multiple active components of composite electrodes.

Results and discussion

Fig. S1 (ESI†) shows the schematic of the fabrication of Cu/Si/Ge NW arrays on a porous Ni foam (see Methods). A pre-cleaned

porous Ni foam (0.5 mm thick) was used as an electrically conducting substrate. A thin Cu layer (of 2 μm thick) was deposited onto the Ni foam by e-beam evaporation. CuO NWs (about 30 nm in diameter) were grown on the surface of the Cu layer by thermal oxidation in air (Fig. S2, ESI†). An inner shell of Si (60 nm thick) and an outer shell of Ge (30 nm thick) were sequentially sputter-coated on the surface of CuO NWs (Fig. S3, ESI†). The as-fabricated CuO/Si/Ge NWs were annealed in H_2/Ar to reduce the CuO cores, resulting in Cu core segments enclosed by a bilayer Si/Ge shell. Individual Cu/Si/Ge NWs had an average diameter of about 220 nm.

Fig. 2a–c show the scanning electron microscopy (SEM) images of a CuO/Si/Ge NW array on a porous Ni foam. These NWs have uniform geometry. The free space between NWs facilitates both electrolyte penetration and volume accommodation during lithiation/delithiation cycling. Fig. 2d and e show the TEM images of an individual Cu/Si/Ge NW with a Si/Ge bilayer shell enclosing a core of Cu segments. The high resolution TEM (HRTEM) image in Fig. 2f indicates that the Si/Ge bilayer is amorphous, which is verified by selected area electron diffraction (SAED, inset of Fig. 2f) and further confirmed by X-ray diffraction (XRD) measurement (Fig. S4, ESI†). Fig. 2g presents the scanning TEM (STEM) image of a Cu/Si/Ge NW along with energy dispersive spectroscopy line scanning profiles, confirming the bilayer structure with the outer Ge and inner Si shells enclosing Cu core segments. The elemental distribution of the Cu/Si/Ge NW was further analyzed by energy dispersive X-ray (EDX) spectroscopy mapping (Fig. 2h). Evidently, Cu is locally confined in the core region, while the inner shells consist of Si and the outer shells have Ge and O. The O content may be introduced during sample transfer as the substrates have been

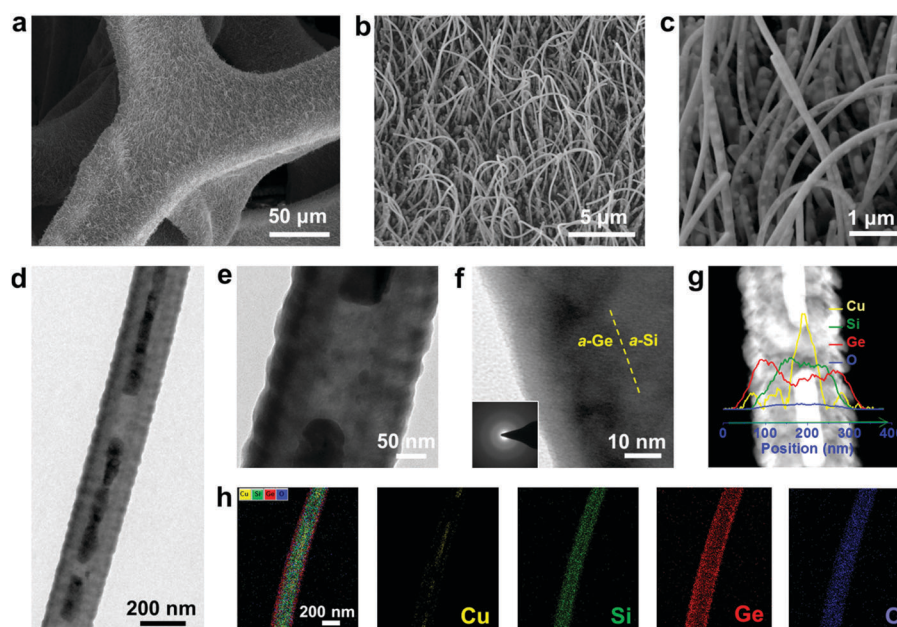


Fig. 2 Characterization of the Cu/Si/Ge NW electrode. (a–c) SEM images of Cu/Si/Ge NW arrays grown on a Ni foam. (d and e) TEM image of a single Cu/Si/Ge NW, (f) HRTEM image of the Si/Ge bilayer with the corresponding SAED pattern (inset). (g) STEM image of a Cu/Si/Ge NW, with corresponding EDX spectra and (h) STEM image and corresponding Cu, Si, O and Ge EDX maps.

exposed to air during different steps in the transfer process, which could induce spontaneous oxidation of amorphous Ge. Similar results have also been observed for Cu/Ge NWs,³⁶ amorphous Ge/C composites,³⁷ and alloyed $\text{Si}_{1-x}\text{Ge}_x$ NWs³⁸ in previous studies by other groups. To compare with the Cu/Si/Ge NW electrode, we also fabricated a Cu/Si NW electrode without

the Ge coating (Fig. S5, ESI†) and a Si/Ge bilayer thin-film electrode without Cu (Fig. S6, ESI†). These two reference electrodes were grown directly on a porous Ni foam under similar conditions to the Cu/Si/Ge NW electrode.

The Cu/Si/Ge NW electrode exhibited a superior performance with large capacity, high rate capability, and long cycle stability,

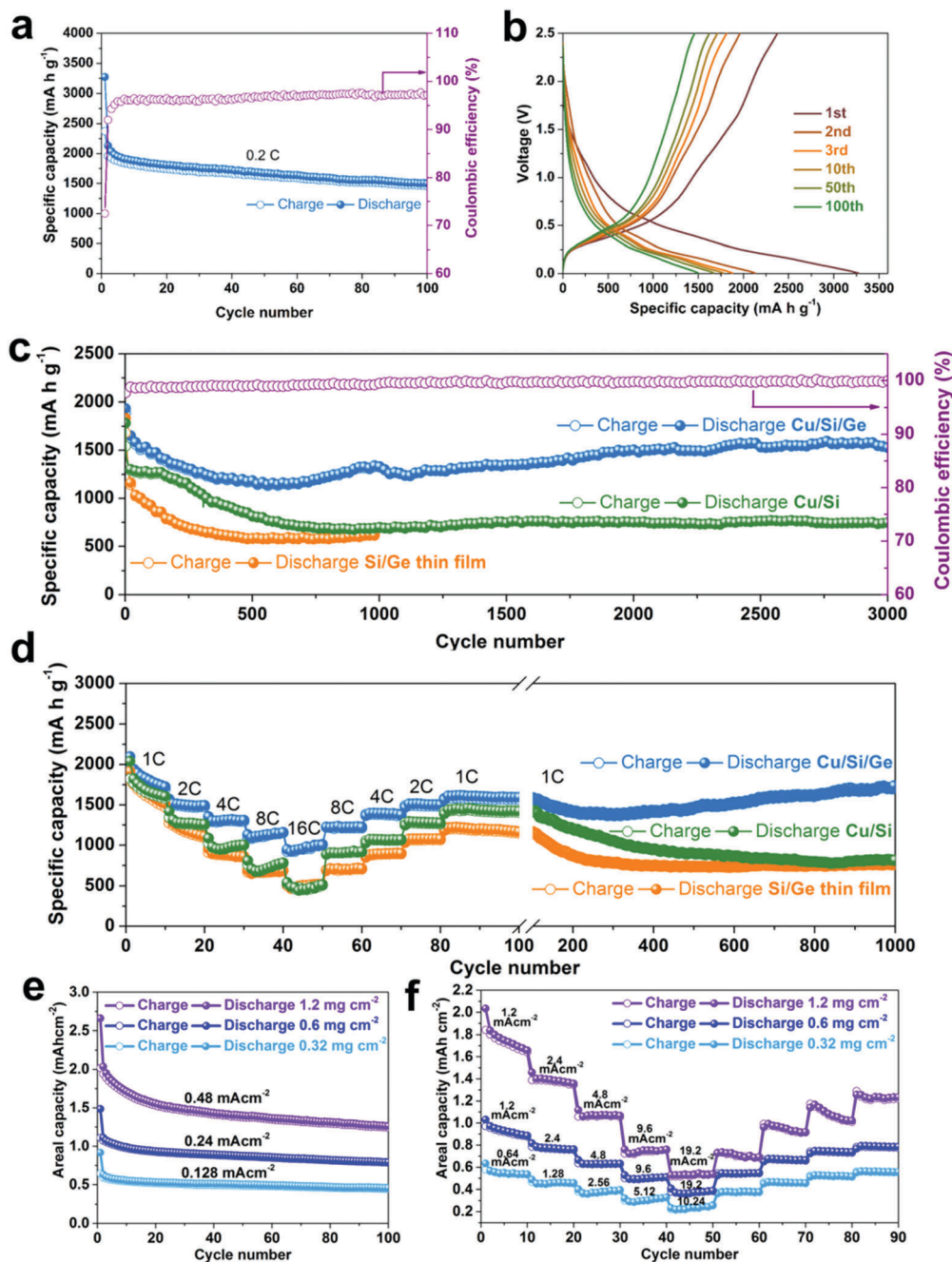


Fig. 3 Electrochemical performance of the Cu/Si/Ge NW electrode. (a) Capacity performance at a low rate of 0.2C. (b) Corresponding galvanostatic charge–discharge profiles at different cycles. (c) Long-cycle performance for Cu/Si/Ge NW, Cu/Si NW and Si/Ge thin-film electrodes at 2C; all the electrodes were first tested at 0.2C for two cycles and then subjected to long-term cycling. (d) Comparison of specific capacity of Cu/Si/Ge NW, Cu/Si NW and Si/Ge thin-film electrodes at various C rates (from 1C to 16C) for 100 cycles and then at 1C for another 900 cycles; all the electrodes were first tested at 0.2C for two cycles (not shown in (c) and (d)) and then subjected to rate tests. (e) Capacities at a slow rate of 0.2C with mass loadings of 0.32 mg cm⁻², 0.60 mg cm⁻² and 1.2 mg cm⁻². (f) Corresponding rate performance at various areal current densities. The electrodes were first tested at 0.2C for two cycles (not shown in Fig. 3f) and then subjected to rate tests.

which outperformed the reported results of Si/Ge and Si-based core/shell anodes (in gravimetric capacities) as shown in Table S1 (ESI[†]). It is noteworthy that the capacity contribution from the heat treated Ni foam after being annealed in H₂/Ar at 300 °C for 8 h is negligible, as can be seen from Fig. S7 and S8 (ESI[†]). The initial discharge and charge capacities were 3273 and 2373 mA h g⁻¹ (as calculated with the mass ratio of Si and Ge in the Si/Ge bilayer shell being 1.75:1) at a low rate of 0.2C (1C = 2 A g⁻¹, corresponding to a current density of 0.36 mA cm⁻²), respectively (Fig. 3a). The corresponding first-cycle Coulombic efficiency was 72.5% (Fig. 3b), which was higher than 51.8% (with the initial discharge and charge capacities being 4265 and 2209 mA h g⁻¹) from the Cu/Si NW electrode (Fig. S9b, ESI[†]). The large irreversible capacity loss at the first cycle is related to the formation of SEIs consuming active Li, and can be compensated by prelithiation through either chemical or electrochemical methods or by using stabilized Li metal powder.^{12,17} At this rate, a capacity of 1500 mA h g⁻¹ was maintained for the Cu/Si/Ge NW electrode after 100 cycles (with ~70% capacity retention from the 2nd to the 100th cycle). It was comparable to 1615 mA h g⁻¹ from the Cu/Si NW electrode (Fig. S9, ESI[†]), indicating a high specific capacity. In contrast, the capacity of the Si/Ge thin-film electrode faded rapidly, retaining only 857 mA h g⁻¹ after 100 cycles (~40% capacity retention from the 2nd to the 100th cycle, see Fig. S10, ESI[†]). Moreover, the Cu/Si/Ge NW electrode exhibited an outstanding long-cycle performance, retaining a specific capacity of 1523 mA h g⁻¹ (0.274 mA h cm⁻²; ~81% capacity retention) after 3000 cycles at a high cycling rate of 2C (Fig. 3c). The long-cycle performance of three electrodes was first activated at 0.2C for two cycles (not shown in Fig. 3c) and the galvanostatic charge–discharge profiles for Cu/Si/Ge and Cu/Si at 0.2C are provided in Fig. S11 (ESI[†]). In contrast, the Cu/Si NW electrode had a marked capacity decay, retaining only 745 mA h g⁻¹ of the initial 1542 mA h g⁻¹ (~48% capacity retention) after 3000 cycles. The capacity of the Si/Ge thin-film electrode decayed even faster, retaining only 628 mA h g⁻¹ of the initial 1683 mA h g⁻¹ after 1000 cycles (only ~37% capacity retention). The Coulombic efficiencies for the Cu/Si/Ge, Cu/Si, and Si/Ge thin-film electrodes at a 2C rate are shown in Fig. S12 (ESI[†]). It should be noted that the Cu/Si electrode has the lowest Coulombic efficiency in the initial several cycles. A similar phenomenon has also been reported by Kim *et al.*,³⁹ due primarily to the inherently larger interfacial contact area between the electrolyte and Si surface, large outward expansion during charge/discharge, as well as a relatively thick native oxide layer formed on the Si surface, which facilitates the extensive formation of SEIs.³⁹ Importantly, after a few cycles the Coulombic efficiencies of all the electrodes approaching or exceeding 99% are measured (especially for Si anodes). This indicates that a stable SEI layer forms during the initial cycles and renders the active surface substantially inert to further electrolyte decomposition, despite the extreme volume changes experienced by the underlying material during discharge/charge.^{24,39} Interestingly, the Cu/Ge NW electrode exhibited a stable cycling performance, retaining a specific capacity of 782 mA h g⁻¹ (~85% capacity retention) after 3000 cycles at 2C, which clearly

demonstrates the benefit of Ge for the cycling stability of Si/Ge electrodes (see Fig. S13, ESI[†]).

The Cu/Si/Ge NW electrode also exhibited an excellent rate performance with long-cycle stability (Fig. 3d). A high charge capacity of 1010 mA h g⁻¹ (0.182 mA h cm⁻²) was measured at a high rate of 16C after 10 cycles, almost twice higher than that of the Cu/Si NW electrode (506 mA h g⁻¹ at 16C), which can be attributed to both fast electronic conductivity and high Li ion diffusivity of Ge. As shown in Fig. S14 (ESI[†]), the Cu/Si/Ge electrode shows much lower impedance than the Cu/Si electrode, indicative of faster charge transfer and higher electrode conductivity, consistent with the rate capability measurements of the Cu/Si/Ge and the Cu/Si electrodes. The capacity retention (~60%) of the Cu/Si/Ge NW electrode was also better than those of the Cu/Si NW electrode (~33%) and the Si/Ge thin-film electrode (~35%) from 1C to 16C. More interestingly, even at a rate of up to 16C, the lithiation potential of the Cu/Si/Ge NW electrode still showed a sloping profile between 0.5 and 0.005 V (Fig. S15, ESI[†]), consistent with a previous report of lithiation-induced formation of amorphous Li_xSi (a-Li_xSi) and Li_xGe (a-Li_xGe).^{40,41} Furthermore, the Cu/Si/Ge NW electrode exhibited superior cycle stability, retaining a capacity of 1728 mA h g⁻¹ (0.311 mA h cm⁻²; ~89% capacity retention) after initial 100 cycles at rates ranging from 1C to 16C and additional 900 cycles at 1C. This result demonstrates that the Cu/Si/Ge NW electrode possesses an exceptional ability to retain a high capacity after charge/discharge at high rates. In comparison, the capacities of the Cu/Si NW and Si/Ge thin-film electrodes fade rapidly, retaining only 816 mA h g⁻¹ (~45% capacity retention) and 761 mA h g⁻¹ (~42% capacity retention) after 1000 cycles, respectively.

To further study the effect of the mass loading of NW electrodes on the cyclability of half cells, we fabricated the NW electrodes with higher mass-loadings of 0.32 mg cm⁻² (in this case, NWs had a thicker Si/Ge bilayer shell and were grown only on the front face of a Ni foam as shown in Fig. S16b–g, ESI[†]), 0.6 mg cm⁻² (*i.e.*, NWs had a thicker Si/Ge bilayer shell and were grown on both front and back faces of a Ni foam as shown in Fig. S16, ESI[†]), and 1.2 mg cm⁻² (*i.e.*, NWs had double layers of the Si/Ge bilayer shell and were grown on both front and back faces of a Ni foam as given in Fig. S17, ESI[†]) and compared their performance with the mass-loading of 0.15–0.18 mg cm⁻². At a low rate of 0.2C, the respective areal capacity for electrodes with mass-loadings of 0.32 and 0.6 mg cm⁻² was 0.45 mA h cm⁻² (1432 mA h g⁻¹) and 0.79 mA h cm⁻² (1324 mA h g⁻¹) after 100 cycles; and their corresponding capacity retention was 76% and 74% from the 2nd to the 100th cycle. More interestingly, at this rate, the NW electrodes with a high mass-loading of 1.2 mg cm⁻² could deliver an initial areal capacity of 2.01 mA h cm⁻² (corresponding to a gravimetric capacity of 1681 mA h g⁻¹) and a relative large areal capacity of 1.26 mA h cm⁻² (1052 mA h g⁻¹) with a capacity retention of 64% from the 2nd to the 100th cycle after 100 cycles, which outperformed the majority of reported results of Si/Ge and Si-based core/shell anodes (in areal capacities) as shown in Table S1 (ESI[†]). These results imply that the Si/Ge active materials are utilized effectively at low rate due to the high conductivity and structural stability of the Cu/Si/Ge NW electrode

and the electrode with high mass-loading can also operate stably while supplying high capacity. The rate performance under various current densities was also tested after activation at 0.2C for two cycles (the capacities of electrodes after activation at 0.2C are not shown in Fig. 3f). It can be seen that the areal capacity retention ($\sim 43\%$) of the electrode with a low areal mass loading of 0.32 mg cm^{-2} was better than that of the electrode ($\sim 40\%$) with a high areal mass loading of 0.60 mg cm^{-2} and was also better than that of the electrode ($\sim 30\%$) with an even high areal mass loading of 1.2 mg cm^{-2} . This is likely due to the increased series resistance of the NW-electrolyte interface as well as the electrode-level disintegration when the mass loading of Si/Ge is increased.⁴² A future challenge is to balance the high mass loading with the capacity retention and high rate capability over extended cycling. The long-term cycling stability of the electrode with a high areal mass loading of 1.2 mg cm^{-2} at a high current density of 4.8 mA cm^{-2} is presented in Fig. S18 (ESI†). It has an areal capacity of $0.64 \text{ mA h cm}^{-2}$ and 52% capacity retention over 500 cycles. It should be noted that the much increased mass loading of 1.2 mg cm^{-2} is still insufficient for practical applications; increasing the areal mass loading of the anodes based on Si/Ge NWs without sacrificing the capacity retention and high rate capability over extended cycling is still a challenge and warrants further effort in the future.⁴³

Overall, the superior performance of the Cu/Si/Ge NW electrode can be attributed to the beneficial effects of small feature size, hollow space, a conductive metallic core, and a high-capacity coating, as discussed in the Introduction. We stress that while Ge is more expensive than Si in practical applications, the Ge/Si bilayer shell can serve as a model system for studying the effect of concurrent reaction dynamics in multiple active components (*i.e.*, Si and Ge in this work) on the long-cycle stability of composite electrodes.

To understand the reaction dynamics in active Si and Ge, we performed *in situ* TEM (Fig. S19, ESI†) and cyclic voltammetry experiments. Fig. 4a shows the TEM snapshots taken during lithiation of a single Cu/Si/Ge NW (Video S1, ESI†). During lithiation, the Cu/Si/Ge NW expanded in both the axial and radial directions. This contrasted with the dominant radial expansion with negligible axial elongation in Si NWs revealed by previous *in situ* TEM studies.^{44,45} The axial elongation of the Cu/Si/Ge NW arises because the Ge outer layer tends to elongate in the axial direction.³³ At 240 s, the axial elongation and radial expansion were respectively 118% and 124–133% (measured for different radial cross-sections), resulting in a total volume expansion of 180–207% in the Si/Ge bilayer. Interestingly, the lithiated NW became bent. The distance between adjacent Cu segments increased with the overall elongation of the lithiated

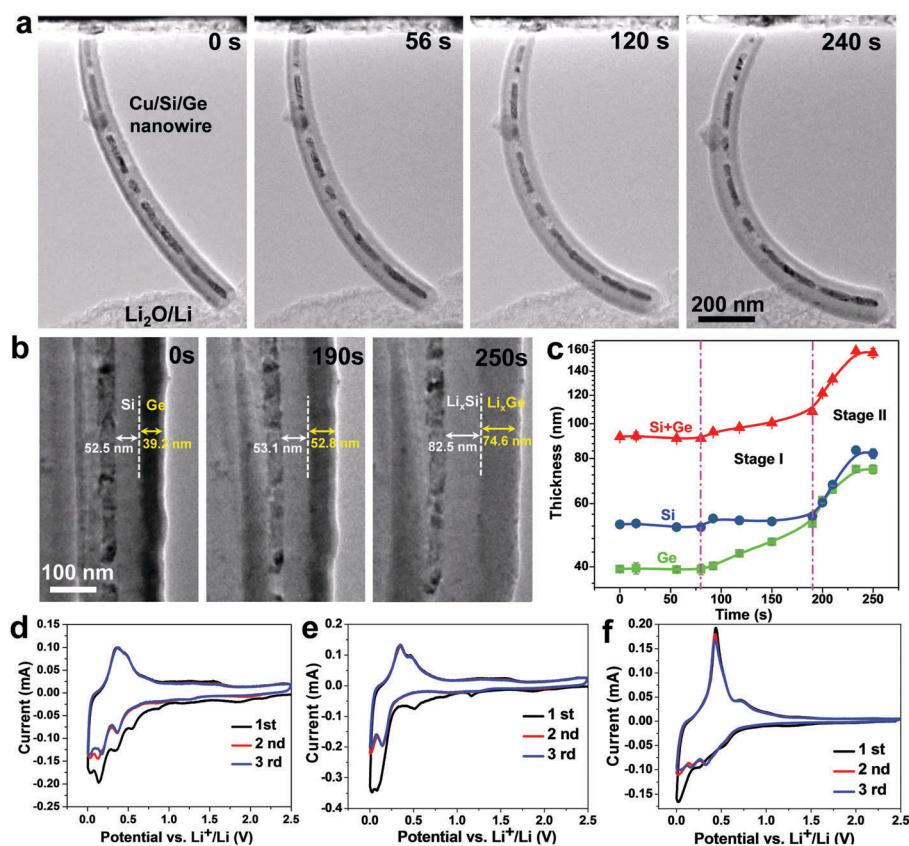


Fig. 4 *In situ* TEM and cyclic voltammetry (CV) experiments. (a) Time-lapse TEM images of lithiation of a single Cu/Si/Ge NW. (b) Magnified TEM images showing the thicknesses of the Si/Ge bilayer shell as a function of time during lithiation, and (c) corresponding quantitative measurements showing the thickness changes of the Si/Ge bilayer shell as a function of lithiation time. (d–f) CV curves for the Cu/Si/Ge NW, Cu/Si NW, and Cu/Ge NW electrodes during the first three discharge/charge cycles, respectively.

NW, thus providing additional internal space to accommodate the inward expansion of lithiated Ge/Si; the diameters of Cu segments remained nearly constant. Hence the unique segmental structure of Cu cores is beneficial to reducing the outward swelling, thereby mitigating the mechanical degradation of lithiated Si/Ge and SEIs. During delithiation, the Cu/Si/Ge NW shrunk in both the axial and radial directions (Fig. S20 and Video S2, ESI†). As lithiation and delithiation were repeated for several cycles, there was no observable mechanical damage such as cracking or fracture. Occasionally, the Cu/Si/Ge NW experienced a sudden change in contact with $\text{Li/Li}_2\text{O}$, leading to an abrupt variation in the expansion/contraction rate for a few seconds (Video S3, ESI†). Nonetheless, the structural evolution of Cu/Si/Ge NWs was sufficiently robust and largely reversible without observable mechanical degradation in multiple lithiation/delithiation cycles.

To gain a deep understanding of lithiation/delithiation dynamics, we performed an in-depth analysis of *in situ* TEM images. The results revealed a novel mechanism of dynamic co-lithiation/co-delithiation in the Si/Ge bilayer shell. As shown in Fig. 4b and Video S4 (ESI†), the initial lithiation, referred to as stage I, occurred primarily in the outer Ge layer, while the inner Si layer remained nearly unlithiated. For example, the left image in Fig. 4b displays a segment of the Cu/Si/Ge NW before lithiation, where the thicknesses of the outer Ge and inner Si layers were 39.2 nm and 52.5 nm, respectively. At the end of stage I (the middle image in Fig. 4b), the thickness of the outer Ge layer was increased to 52.8 nm, indicating the ongoing lithiation therein. In contrast, the thickness of the inner Si layer remained nearly unchanged, implying that Si lithiation had not started yet. Following stage I, both Ge and Si layers were co-lithiated simultaneously, referred to as stage II. Co-lithiation was evident from a concurrent thickness increase in both the Ge and Si layers. For example, the right image in Fig. 4b shows an intermediate state of stage II, where the thicknesses of the Ge and Si layers were increased to 74.6 nm and 82.5 nm, respectively. Fig. 4c shows the measured thicknesses of Ge, Si and Si/Ge layers as a function of time. It is seen that the incubation period without lithiation initially lasted for about 80 s; stage I of lithiation of Ge spanned between 80–190 s; and stage II of co-lithiation of Ge and Si between 190–250 s. Similarly, delithiation also experienced a two-stage process, *i.e.*, the initial delithiation of the outer Ge layer was followed by the subsequent co-delithiation of both the Si and Ge layers (Fig. S20, ESI†).

To understand the *in situ* TEM results of two-stage lithiation/delithiation, we performed cyclic voltammetry (CV) and galvanostatic charge–discharge measurements with a standard coin cell configuration. Fig. 4d shows the CV curves of the Cu/Si/Ge NW electrode measured at a scan rate of 0.1 mV s^{-1} over the potential window of 0.005–2.5 V *versus* Li/Li^+ . It is seen that a peak occurs at 0.55 V during the first discharge process, but disappears in subsequent cycles, suggesting that this peak can be attributed to the formation of SEIs.⁴⁶ In Fig. 4d, a peak occurs at 0.35 V in the first discharge process. There is no corresponding peak in the CV curves of both the Cu/Si NW electrode (Fig. 4e) and the Si thin-film electrode,⁴⁰ while a

similar peak occurs in the CV curves of the Cu/Ge NW electrode (Fig. 4f) measured in this work and the Ge thin-film electrode in a previous study.⁴¹ Such a peak should correspond to the conversion of a-Ge to a- Li_xGe , suggesting that Ge first reacts with Li without Si being involved. This is consistent with our *in situ* TEM observation of stage I of lithiation of only Ge. Previous *in situ* TEM experiments^{47,48} showed that the lithiation of a-Si occurred in a two-phase process through migration of a sharp phase boundary, resulting in a- Li_xSi ($x \sim 2.5$). The peak at 0.35 V in the CV curve also indicates that the initial lithiation of a-Ge occurs at a characteristic voltage, suggesting a possible two-phase lithiation in the outer layer of Ge and the resulting formation of a- Li_xGe .

In Fig. 4d, the following two peaks arise at 0.14 V and 0.03 V, respectively. These two peaks are also observed in the CV curves of both the Cu/Si NW electrode (Fig. 4e) and the Cu/Ge NW electrode (Fig. 4f). Hence, they should correspond to co-lithiation of Li_xGe and Si, as observed in our *in situ* TEM experiments. It should be emphasized that these characteristic peaks are also observed during the second and third cycles, suggesting that a similar reaction pathway of two-stage lithiation persists beyond the first cycle. Moreover, during the first charge of the Cu/Si/Ge NW electrode (Fig. 4d), two anodic peaks at 0.38 V and 0.47 V are observed. However, these two peaks are not sharp and also somewhat overlap. Based on *in situ* TEM observations, they should correspond to stage I of delithiation of a- Li_xGe and stage II of co-delithiation of a- Li_xSi and a- Li_xGe , respectively. During subsequent charging processes, all peaks were reproducible, indicating the operation of the same reaction mechanisms. In addition, recall that Fig. 3b presents the galvanostatic charge–discharge profiles of the Cu/Si/Ge NW electrode tested at 0.4 A g^{-1} between 2.5 V and 0.005 V. The observed plateaus in the first discharge curve are in accordance with the CV results and associated reaction steps.

To understand the above *in situ* TEM results, we performed the chemomechanical modeling of lithiation in a bilayer Si/Ge nanotube (NT) (see Methods). Our model was focused on elucidating the origin of bending deformation in the lithiated Si/Ge NT. From *in situ* TEM images (Fig. 4a), we observed that the cross-sectional thicknesses of both the Si and Ge layers were non-uniform. This implies that the centers of both the Si and Ge shells did not coincide, and also deviated from the nominal center of the whole Si/Ge NT. Fig. 5a–e show the simulated snapshots of two-stage lithiation in a bilayer Si/Ge NT with an eccentricity of 0.125 (see Methods), which was assigned based on the TEM image (Fig. 4a). In our simulations, the bending deformation arose during stage I of lithiation of Ge and continued to increase during stage II of co-lithiation of Ge and Si. Hence, a key insight from our chemomechanical modeling is that the observed bending deformation during *in situ* TEM was caused by the eccentricity of Cu/Si/Ge NWs, leading to a non-uniform lithiation in the NW cross section. As a result, the axial elongation became non-uniform within the cross section, causing the bending deformation in the lithiated Si/Ge NW.

The dynamic co-lithiation/co-delithiation in active Si and Ge has important beneficial effects on mitigating the lithiation-induced

degradation in large-volume-change electrode materials. First of all, it should be stressed that a common mode of electrochemically-induced mechanical degradation in high-capacity Si particles/wires is surface cracking/damage, which is caused by large hoop tensile deformation in the surface layer that increases with increasing expansion of Si particles/wires during progressive lithiation.^{47,48} For Si particles/wires, the large hoop tensile deformation in the surface layer mostly occurs by pure mechanical stretching⁴⁹ (as illustrated in Fig. 5e). As a result, the surface layer is prone to damage. In contrast, during co-lithiation of the Si/Ge bilayer shell, the hoop tensile deformation in the surface Ge layer, which is driven by lithiation-induced volume expansions in both Si and Ge layers, can be partially accommodated by the electrochemical lithiation in the outer Ge layer. In other words, the large hoop tensile deformation in the surface Ge layer occurs by the combined actions of electrochemical insertion of Li and mechanical stretching (as illustrated in Fig. 5f). As a result, the surface Ge layer is less prone to damage compared to the case of lithiation in Si particles/wires. The above beneficial effects of dynamic co-lithiation in the Si/Ge bilayer should similarly hold during co-delithiation and hence during lithiation/delithiation cycling. In addition to the benefits of dynamic co-lithiation/co-delithiation, both the metallic Cu core and the Ge outer layer (as opposed to the Si NW) can enhance electronic/ionic transport in the Cu/Si/Ge NW electrode. As a result, lithiation/delithiation would be more uniform in the Cu/Si/Ge NW electrode than the pure Si NW one. The above factors can collectively contribute to mitigating the electrochemically induced mechanical degradation, thereby enhancing the long-cycle structural stability of the Cu/Si/Ge NW electrode during cycling.

To demonstrate the enhanced long-cycle stability in the Cu/Si/Ge NW electrode, we examined the electrode structures after 3000 charge/discharge cycles with *ex situ* SEM and TEM imaging.

Fig. 6a shows that the NW arrays were retained without drastic morphological changes. They also remained in close contact with the current collector. At the individual NW level, Fig. 6c–e shows that the hollow space between Cu segments in the core was filled with extruded Si. While the outer Ge layer experienced volume expansion during lithiation, there was no obvious cracking therein. Moreover, the outer Ge layer appeared as a highly porous sponge composed of interconnected ligaments of a-Ge. Such spongy Ge has been shown with beneficial effects on accommodating the volume changes,³⁴ so as to mitigate the mechanical degradation under lithiation/delithiation cycling. More importantly, the inner Si layers remained coherent and did not turn into a fluffy structure. This can be reasonably attributed to the protection of the outer Ge layer, which was retained due to their capability to effectively accommodate volume changes during Si lithiation/delithiation through the unique dynamic co-lithiation/co-delithiation mechanism of Ge and Si layers. The elemental distribution of NW was analyzed by energy dispersive X-ray (EDX) spectroscopy mapping (Fig. 6f). Evidently, Cu is locally confined in the core region, while Ge and Si are distributed over the outer and inner shells, respectively, confirming the retained bilayer structure with the outer Ge and inner Si shells enclosing the Cu core segments. The O and F elements are from the SEI layer. No major intermixing and element redistribution in NWs was observed over repeated cycling. Similar results of well-maintained electrode structures after repeated cycling have also been reported for amorphous Si/Cu nanopillar anodes by Kim *et al.*⁵⁰ and for amorphous Si coated on Sn-containing Si NW anodes by Lu *et al.*⁵¹ This is likely due to the fact that the volume expansion of amorphous Si and Ge upon Li insertion is more homogeneous and causes less pulverization than crystalline Ge and Si.^{24,52} Thus, the susceptibility to lithium-assisted welding and pore formation in amorphous Si/Ge could be less than that of

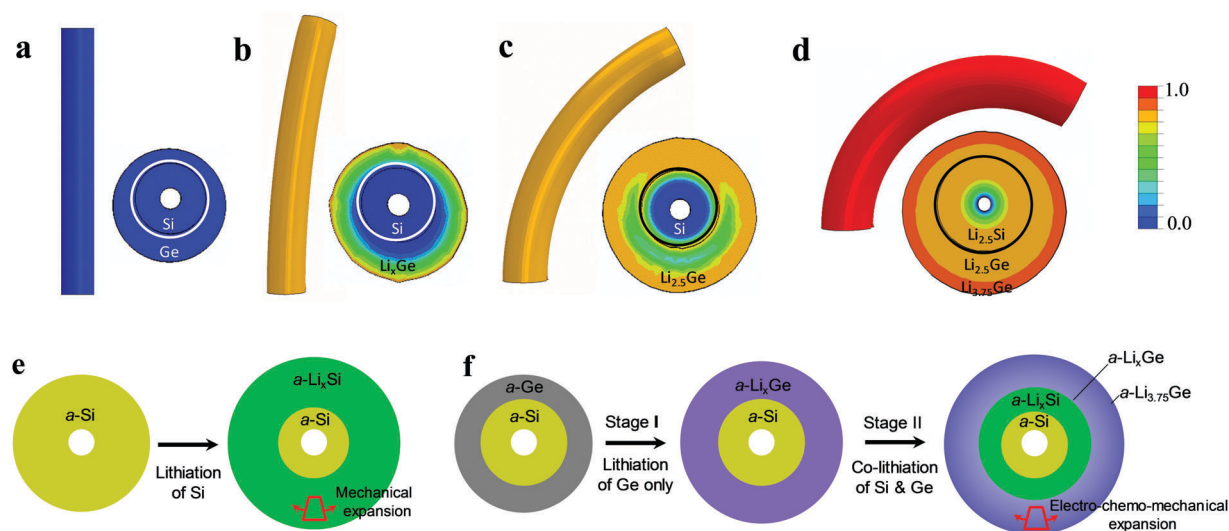


Fig. 5 Chemomechanical effects of lithiation of a Si/Ge NT. (a–d) Chemomechanical simulation snapshots showing progressive bending (left) and the cross-sectional distribution of the normalized Li/Ge concentration (right) in a Si/Ge NT during stage I of lithiation of only Ge and stage II of co-lithiation of Si and Ge. (e) Illustration of dominant mechanical expansion near the surface during lithiation of a Si NT. (f) Illustration of electrochemical-mechanical expansion associated with insertion of active Li near the surface during co-lithiation of a Si/Ge NT.

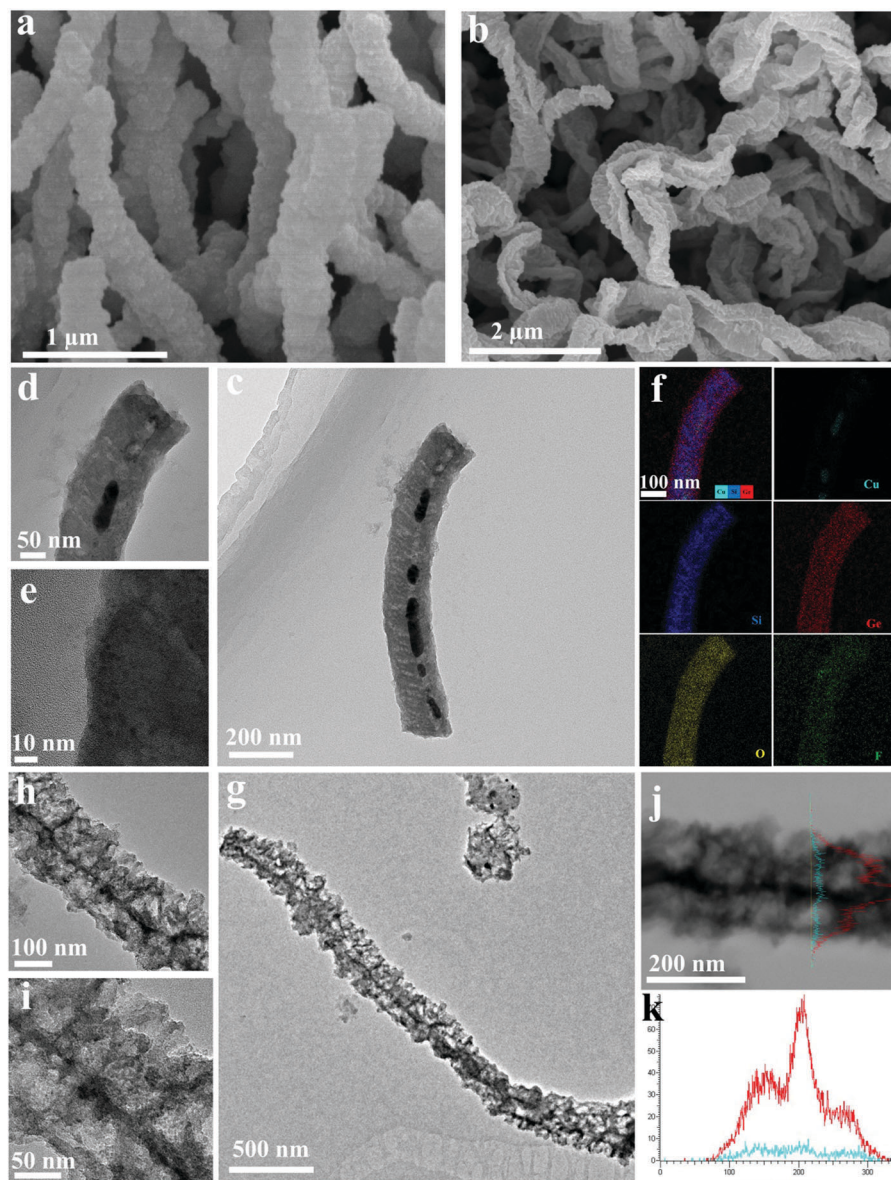


Fig. 6 Comparison of microstructural changes in the Cu/Si NW and Cu/Si/Ge NW electrodes after 3000 cycles at 2C. (a) SEM image of a Cu/Si/Ge NW array. (b) SEM image of a Cu/Si NW array. (c–e) TEM image of a single Cu/Si/Ge NW. (f) STEM image of a single Cu/Si/Ge NW and corresponding Cu, Si, Ge, F and O X-ray maps. (g–i) TEM image of a single Cu/Si NW. (j) STEM image of a single Cu/Si NW, with corresponding EDX spectra and (k) corresponding enlarged EDX spectra.

crystalline Ge/Si under repeated cycling. These results suggest that the amorphous Si/Ge NWs possess the advantages of more uniform volume changes and could better maintain structural stability than the crystalline Si/Ge nanostructures during cycling. In contrast, the Cu/Si NW exhibited drastic structural changes, resulting in a highly fluffy morphology (Fig. 6b). Compared to the Cu/Si/Ge NW (Fig. 6c–e), Fig. 6g–i shows that the surface of the Cu/Si NW became rougher, the structure became more fluffy with pores between grains on edges, and the diameters of Cu/Si NW arrays appeared to be larger, which indicates more irreversible changes. Additionally, the core of Cu segments disappeared (Fig. 6g–i), which was confirmed by EDX line scanning results (Fig. 6j and k), suggesting the

dissolution of Cu possibly by electrolytes due to the poor structural integrity of Cu/Si NWs.

To demonstrate the applicability of our electrode to practical applications, we assembled a full cell with a Cu/Si/Ge NW anode and a LiCoO₂ cathode (Fig. 7a). To prepare full cells, we first prelithiated the Cu/Si/Ge NW anodes using half cells at 0.2C for one cycle, considering the low initial Coulombic efficiency of about 72.5%. After prelithiation the half cells were disassembled, and then the Cu/Si/Ge and LCO electrodes were combined into full cells. When tested with this full-cell configuration, the Cu/Si/Ge NW electrode exhibited a reversible capacity of 937 mA h g^{−1} (based on the weight of active materials in the anode) after 100 cycles (with 72% capacity retention)

at a current density of 0.5 A g^{-1} (Fig. 7c and e), as well as a high rate performance of 709 mA h g^{-1} after 10 cycles at 10 A g^{-1} with a capacity retention of 51% from 0.2 A g^{-1} to 10 A g^{-1} . (Fig. 7d and f). Furthermore, the full cell exhibited a capacity of 756 mA h g^{-1} after the initial 100 cycles at 0.2 A g^{-1} to 10 A g^{-1} and additional 100 cycles at 0.5 A g^{-1} (Fig. 7f). The full cell exhibited a lower reversible capacity than its half-cell

counterpart, which could be attributed to the cut-off voltage of 3.9 V for Cu/Si/Ge anodes with controlled lithiation states in the half-cell, thus resulting in the lower capacity of the Cu/Si/Ge NW anode in the full cell. Moreover, the as-assembled full cell can power red light-emitting diodes (LEDs) with a working voltage of 2 V (Fig. 7b), indicating that the Cu/Si/Ge NW electrode could be potentially used in practical devices. It should be noted

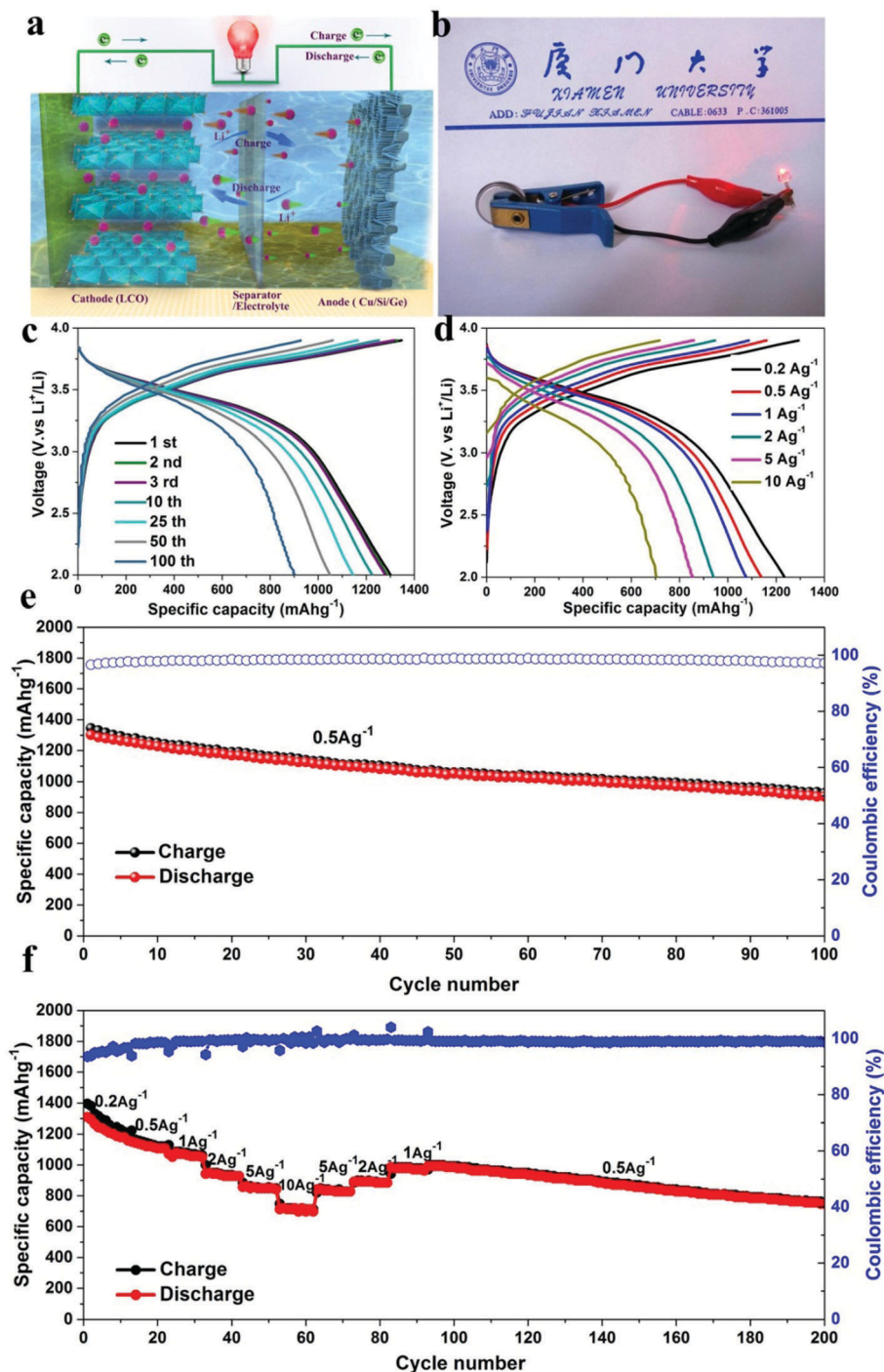


Fig. 7 Electrochemical data of a full cell. (a) Schematic illustration of the full cell. (b) Operation of a full cell lighting up a LED indicator. (c) Charge-discharge curves at 0.5 A g^{-1} . (d) Charge-discharge curves at various rates. (e) Cycling performance at a current density of 0.5 A g^{-1} . (f) Rate performance at various rates.

that an improvement of cell performance is expected by optimizing the Cu/Si/Ge NW anode, balancing the anode and cathode, as well as improving the cell design and electrolyte performance. Further studies on full cells are underway and the results will be reported in the future.

To further verify the feasibility of Cu/Si/Ge NW electrodes in practical devices, the Cu/Si/Ge NWs were grown on both front and back faces of a Ni foam, giving a high mass loading of about 0.6 mg cm^{-2} ; this NW anode was prelithiated and coupled with a commercial LiCoO_2 cathode and preliminarily tested in full cells (as shown in Fig. S21, ESI†). This full cell exhibited a decent rate capability (552 mA h g^{-1} after 10 cycles at 10 A g^{-1}) and suitable stability, attaining a reversible capacity of 513 mA h g^{-1} with a capacity retention of 54% even after 300 cycles at a relatively high current density of 2 A g^{-1} . The gradual increase of capacity from the 25th to 75th cycle may be due to a gradual activation process.⁵³ Additionally, we assembled an LED array with a XMU (Xiamen University) logo consisting of 31 red LEDs in parallel powered by our Cu/Si/Ge NW anode-based full cells (Fig. S21b, ESI†). It is seen that the full cells could light up the whole LED array. All the bulbs exhibited favorable brightness, demonstrating the viability and potential of Cu/Si/Ge NW anodes in practical applications.

To summarize, our Cu/Si/Ge NW electrode architecture has integrated several favorable attributes for high performance: small feature size, interior hollow space, a conductive core, and a high-capacity and high-conductivity outer coating. Moreover, the concurrent reaction dynamics in active Si and Ge contributes to the outstanding capacity, rate capability and long-cycle stability of this composite electrode. Namely, we find that the Si/Ge bilayer shell exhibits a novel reaction dynamics of co-lithiation/co-delithiation in Si and Ge, which effectively accommodates the large volume changes of Cu/Si/Ge NWs during cycling. This reaction mechanism is vital to improving the tolerance to electrochemically induced mechanical damage, thus enhancing the long-cycle structural stability and performance of the electrode. More broadly, this work demonstrates a promising pathway of harnessing the concurrent reaction dynamics of multiple active components to improve the performance of heterogeneous composite electrodes for next-generation Li-ion batteries.

Materials and methods

Fabrication of CuO nanowires on Ni foam

A Ni foam (0.5 mm thick, surface density of about 420 g m^{-2} , 40–50 pores per centimeter, purity > 99.99%, Changsha Lyrin New Materials Co. Ltd) was used as the conducting substrate. This foam was cleaned in alcohol by ultrasonication for 10 min, adequately rinsed with alcohol and distilled (DI) water, and blow-dried by compressed air. Then it was placed inside a conventional electron beam evaporation system (JunSun EBS-500). After the vacuum level in the chamber reached 1.6×10^{-6} Torr, a Cu layer was deposited onto the Ni foam by e-beam evaporation. This sample was furnace-heated for 12 hours at 400°C in static

air for growing CuO NWs. After heating, the furnace was cooled down naturally to room temperature.

Synthesis of CuO/Si/Ge nanowire arrays on Ni foam

Si and Ge were deposited on the surface of CuO NWs grown directly on a Ni foam (circular disk with a diameter of 14 mm) by sputtering of a 99.999% pure Si target and a 99.999% pure Ge target at a working pressure of 3 Pa. Firstly, sputtering of Si was performed with Ar working gas of 70 sccm and power of 300 W for 300 seconds. Then the power of the Si target was turned off and the power of the Ge target of 300 W was turned on. Ge sputtering with Ar working gas of 70 sccm lasted for 295 seconds, while the sample was rotated at a speed of 20 rpm. The mass loading of Si/Ge was about $0.15\text{--}0.18 \text{ mg cm}^{-2}$, which was determined by measuring the CuO NW arrays on a Ni foam substrate on a microbalance (Mettler Toledo XS3DU with an accuracy of $1 \mu\text{g}$) before and after sputtering. The compositions of the CuO/Si/Ge film with different ratios of Si and Ge can be readily adjusted by changing the sputtering time of Si and Ge. The substrates were kept at room temperature. The electrodes with mass loadings of 0.32 mg cm^{-2} and 0.6 mg cm^{-2} were prepared through depositing a thick Si/Ge bilayer shell on the surface of CuO NWs by doubling the sputtering time for Si and then Ge, respectively, as well as by controlling the deposition to the front side only or to both the front and back sides of a Ni foam. The CuO NWs were fabricated by thermal oxidation of the Cu thin film ($3 \mu\text{m}$ thick) on a Ni foam. In addition, the electrodes with a mass loading of 1.2 mg cm^{-2} were prepared by depositing double layers of the thick Si/Ge bilayer shell on the surface of CuO NWs by repeated sputtering of Si and then Ge twice for both the front and back faces of a Ni foam. Once deposition on the front face of the Ni foam was finished, the Ni foam was reversed and deposition on the back face was performed.

Synthesis of Cu/Si/Ge NW arrays on Ni foam

The as-fabricated CuO/Si/Ge NW samples were annealed at 300°C in H_2/Ar (95% Ar and 5% H_2) for 8 hours to reduce the CuO cores with a flow rate of 60 sccm, so as to transform CuO/Si/Ge NW arrays into Cu/Si/Ge NW arrays, which were then naturally cooled to room temperature.

Material characterization

Cu/Si/Ge NW arrays were characterized by field emission SEM (Hitachi S4800 FESEM), TEM (FEI Tecnai G2 20 TEM) and X-ray diffraction (Rigaku Ultima IV). To observe the electrode surface morphology after cycling, the cell was disassembled and the electrodes were rinsed with dimethyl carbonate in an argon-filled glove box so as to remove the electrolyte. Then, they were dried at 80°C in a vacuum oven. For *ex situ* TEM studies, the electrode material was scraped off from the Ni foam substrate and the powder was recovered in a glove box and dispersed in ethanol. A drop of suspension was deposited on a Cu grid.

Electrochemical testing

Coin-type half cells (CR2025), assembled in an argon-filled glove box (MBRAUN, LABmaster 100, Germany), were used to

evaluate the electrochemical performance of the as-synthesized Cu/Si/Ge NW arrays grown on a Ni foam as a working electrode without the use of any binder or conductive agent. The counter and reference electrodes were Li metal foil (15 mm in diameter), and the electrolyte solution was 1 M LiPF₆ (EC:DMC:EMC = 1:1:1, in volume). The cells were charged and discharged over a voltage range of 0.005–2.5 V (*versus* Li⁺/Li) at room temperature by using a Land CT2001A system (Wuhan, China). Cyclic voltammetry (CV) was performed on a four-channel multifunctional electrochemical work station (VersaSTAT MC, America), and scanning was conducted from 2.5 V to 0.005 V *versus* Li/Li⁺ at a rate of 0.1 mV s^{−1}. The full cell was designed with a N/P ratio of 1:1.3; electrochemical analysis of the full cell was carried out in the voltage window between 2.0 V and 3.9 V. The cathode and anode areal capacities were 0.26 mA h cm^{−2} and 0.2 mA h cm^{−2}, respectively. For the anode with a mass loading of 0.6 mg cm^{−2}, the cathode and anode areal capacities were 0.91 mA h cm^{−2} and 0.70 mA h cm^{−2}, respectively. Prior to the full cell assembly, the Cu/Si/Ge NW anode was pre-lithiated galvanostatically to alleviate the effect of initially low Coulombic efficiency on the cycle life of the full cell. The cathode electrode was fabricated by mixing an 80 wt% commercialized LiCoO₂ cathode with 10 wt% carbon black as a conducting agent and 10 wt% polyvinylidene fluoride dissolved in *N*-methyl-2-pyrrolidone (NMP) as a binder to form a slurry, which was then spread onto an Al foil current collector and dried under vacuum at 80 °C for 24 hours. CR-2025 coin-type cells were assembled in a glove box filled with argon gas. The electrolytes and separator in the full cell were the same as those in the half-cell described above. All electrochemical tests were performed using a Land CT2001A system (Wuhan, China).

In situ TEM

Fig. S11 (ESI[†]) shows the schematic of *in situ* nano-battery testing *via* TEM.³⁴ Cu/Si/Ge NWs were loaded on a Pt tip and then connected to Li/Li₂O on a W tip. The native Li₂O on the Li surface served as a solid electrolyte. Lithiation of an individual Cu/Si/Ge NW started when a negative voltage was applied to the Pt end, while delithiation was initiated upon reversing the sign of the voltage bias.

Chemomechanical modeling

We simplified the Cu/Si/Ge NW system as a nanotube (NT) with a Si/Ge bilayer shell and without Cu segments in the core. Despite this simplification, the simulated inward displacement was reasonably small at the inner radius of the lithiated Si shell, consistent with *in situ* TEM observations. The center of the Si shell deviates from that of the Ge shell. The extent of deviation is quantified with eccentricity, which is defined as the ratio of the distance between the centers of Si and Ge shells over the radius of the Ge shell. In our simulations, the eccentricity was taken as 0.125, and the radius ratio of Si and Ge shells was 1.2 over 2. In addition, the length of the Si/Ge NT was 16 times the diameter of the Ge shell, consistent with geometries in the TEM images. Our chemomechanical model incorporated the key features of two-stage lithiation from *in situ*

TEM, *i.e.*, stage I of lithiation of only Ge and stage II of co-lithiation of both Ge and Si. To simulate lithiation within the Si/Ge bilayer, we adopted an earlier model of two-phase lithiation of a-Si.⁴⁷ The detailed model setup and material parameters are described in the ESI.[†]

Conflicts of interest

There are no conflicts to declare.

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