



Progress in the preparation of silicon/carbon composites for use as anodes in lithium-ion batteries

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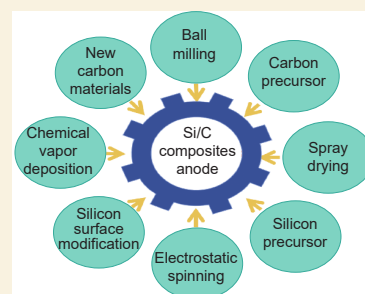
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Abstract: Silicon/carbon (Si/C) composites are promising anodes for high-energy-density lithium-ion batteries (LIBs), because they solve the typical problems of a huge volume expansion and poor conductivity of pure Si anodes. Methods for their production are summarized, including ball milling, spray drying, electrostatic spinning, and chemical vapor deposition (CVD), and methods for improving their structure in order to improve electrical conductivity, mitigate expansion, and improve electrochemical performance are outlined, including carbon precursor coating, Si-precursor-based wet chemistry, and Si surface modification.

Key words: Silicon; Carbon; Silicon/Carbon composites; Anode; Lithium-ion batteries



1 Introduction

With the increasingly diverse usage scenarios of lithium-ion batteries (LIBs), like 3C electronic products, electric vehicles, industrial and household energy storage applications, the demands on the electrochemical performance of LIBs are becoming stringent^[1-3]. Among the various parameters for the electrochemical performance of LIBs, energy density has always been people's top concern because it is directly related to the user comfort^[4-6]. Generally, the energy density (E) of a LIB could be calculated by the formula: $E = \left(\frac{U_a \times K}{C_c + C_a} \right) \div m_{\text{LIB}}$, in which C_c , C_a , U_a , m_{LIB} and K represent the capacity of cathode and anode, the average voltage of a LIB, the whole mass of a LIB and the actual efficiency, respectively. According to the formula, both increasing the capacity of cathode or anode and decreasing the weight of other components like electrolyte or current collectors can elevate the energy density of the LIBs^[7]. In terms of the efficacy to improve the energy density based on proven industrial technology of the LIBs, the most suitable methods mentioned above are increasing the

capacity of anode, because the iteration difficulty of anode is minimal^[8]. In the case of factual industry, Silicon (Si)-based anode also partially and gradually replace the already commercialized graphite anode mainly on account of the large theoretical capacity and abundance in the earth^[9-11]. For example, Si and SiO as the Si-based anode possess the theoretical capacities of 4200 mAh g⁻¹ and 1200–2000 mAh g⁻¹, much higher than that of 372 mAh g⁻¹ of graphite anode^[12-14].

However, many issues arise when the Si-based anode is employed as anode in the LIBs, which is discussed later. The most fatal shortage of the Si-based anodes is the low electrical conductivity and their big volume expansion during Li⁺ storage^[15]. The effective amelioration of the shortage of the Si-based anodes is introducing carbon materials (C) to form Si/C com-

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posites due to the utilization of high electrical conductivity and flexibility of graphite^[3,10,16–17]. In this case, Si/C composites as anodes in LIBs are a hot topic in the field of LIBs and many studies have summarized the progress of Si/C composites as an anode in LIBs^[18–20], including the development of Si/C composites^[21–23], Si-based anode with different size and structure^[4,24], binder for Si/C composites anode^[25–27].

However, few studies have systematically summarized the preparation progress of the Si/C composites as anode in LIBs although it is known to be of significance^[9]. In this work, we focus on the preparation process of the Si/C composites as an anode in LIBs, since Si/C composites with good electrochemical performance are derived from the suitable material characteristics originating from its preparation. As shown in Fig. 1, the synthesis routes of Si/C composites could be categorized into 2 major categories, and each major category has 4 sections. For instance, the featured technologies are included in a major category, including ball milling, spray drying, electrostatic spinning, chemical vapor deposition. And featured materials systems are included in another major category, including new carbon materials, carbon precursor, silicon precursor, and silicon surface modification. In this case, this mini-review's key highlight lies in its systematic categorization of Si/C composite synthesis (7 methods in 2 groups), clear performance-comparison

table, and focus on bridging lab-industry gaps (scalability, cost, sustainability) in the regard. It also links preparation methods directly to solving Si's core issues (volume expansion, poor conductivity) with detailed mechanisms and data. Furthermore, we believe that this review can help the reader quickly grasp several key points about the preparation of Si/C composites, thus laying the foundation for the development of high energy density LIBs.

2 Utilization shortage of pure Si anode

In the process of utilizing Si to replace the graphite anode for obtaining high-energy-density LIBs, some issues appear, which originate from the different mechanisms of Li^+ storage in Si and graphite anodes^[7,28]. For the mechanism of Li^+ storage in graphite, a Li^+ -graphite intercalation compounds (Li-GICs) is formed after Li^+ intercalates into graphite interlayers from the bulk electrolyte. During this reversible intercalation process, the thickness of graphite anode increases by only 12% so that the solid electrolyte interphase (SEI) on the edge plane of graphite anode can bear this change^[29]. However, when Si is employed as an anode, the situation is quite different. Due to the lower electric conductivity of Si than that of graphite, Si powder materials with smaller particle sizes are needed when utilized as anode in LIBs.

Fig. 2a shows the classic charge-discharge curves of Si anode with nano size (nano-Si)^[30]. It is seen that a slope contributes the most part of capacity in the charge-discharge curves of nano-Si anode, different from the main contribution of plateaus in the charge-discharge curves of graphite anode, which originates from the differences between stage-wise Li-GICs formation^[31] and Li-Si alloy formation^[32]. For the case of the Li-Si alloy formation to store Li^+ in Si anode, much effort was devoted to exploring the two-phase lithiation mechanism of crystal Si (c-Si) and amorphous Si (a-Si). As shown in Fig. 2b, both c-Si and a-Si can store Li^+ to generate amorphous Li_xSi (a- Li_xSi), which is proved by the sharp phase boundary between the reactant of c-Si or a-Si and the product of a- Li_xSi

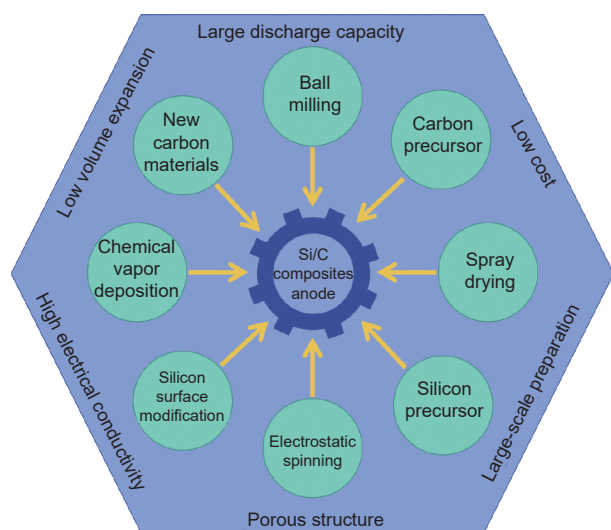


Fig. 1 Schematic diagram of Si/C composites anode obtained through different synthesis routes

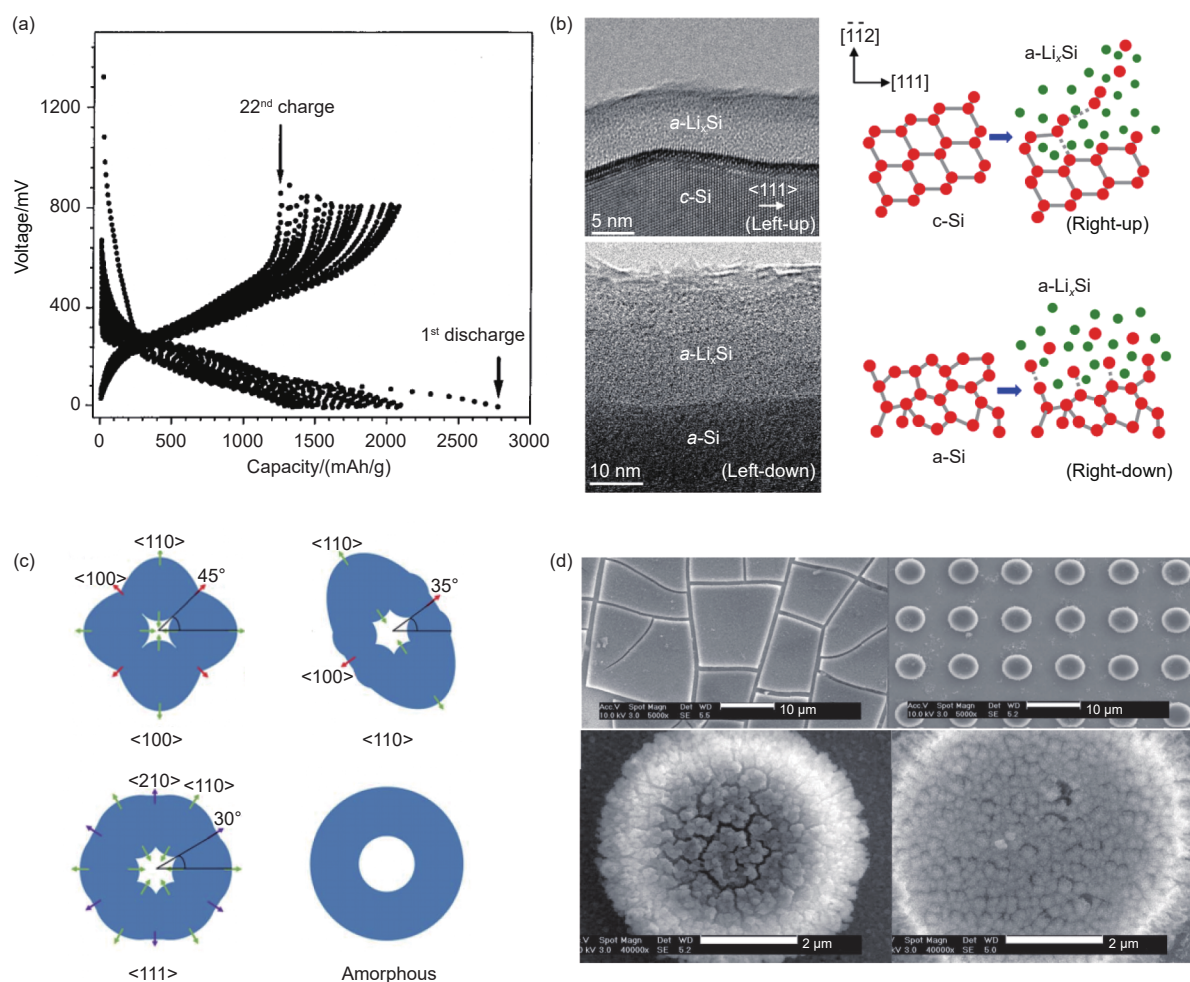


Fig. 2 (a) The discharge and charge curves of the cell using nano-Si as anode active materials. Reproduced with permission^[30]. Copyright 1999. The Electrochemical Society. (b) Comparison of the two-phase lithiation mechanism in c-Si and a-Si. (b, left-up) high-resolution TEM image showing a sharp phase boundary between the reactant of c-Si and the product of a-Li_xSi; (b, right-up) The Li concentration is locally high near the surface of c-Si (red) and a group of Li atoms (green) collectively weakens the strong Si-Si covalent bonding, thereby facilitating the dissolution of Si atom from c-Si surface; (b, left-down) A high resolution TEM image showing a sharp phase boundary between a-Si and a-Li_xSi ($x=2.5$); (b, right-down) Schematics showing the proposed mechanism of dissolution of Si atoms from the a-Si surface into a-Li_xSi alloy. Reproduced with permission^[33]. Copyright 2013. American Chemical Society. (c) Schematics of the cross-sectional shape and fracture angles of nanotubes based on the statistical analysis of the expansion and fracture behavior of the <100>, <110>, <111> and amorphous silicon nanotubes after full lithiation. Reproduced with permission^[34]. Copyright 2019. Royal Society of Chemistry. (d) SEM images of Si based electrode at different conditions. (d, left-up) unetched silicon thin film electrode after the first charge to 2 V; (d, right-up) patterned silicon electrode after the first charge to 2 V. (d, left-down) Si electrode and (d, right-down) Al₂O₃ coated-Si electrode in their fully charged state after 40 charge-discharge cycles in the voltage range of 0.005–2 V. Reproduced with permission^[35]. Copyright 2011. Wiley Ltd.

from the high-resolution TEM characterization^[33]. Meanwhile, the formation of the a-Li_xSi leads to the volume increase of Si, up to over 300%. Moreover, the a-Li_xSi formation preferentially occurs at <110> orientation of Si materials, leading to the stress accumulation inside the Si materials^[34] (Fig. 2c). After the stress accumulation exceeds the endurance limit of Si materials, both the pulverization and detachment of Si materials from the current collector occur, simultaneously resulting in the repeated growth of SEI on Si surface and the continuous consumption of electro-

lyte. In this case, several strategies are designed to suppress the stress accumulation inside the pure Si materials, like etching to form patterned Si and coating Al₂O₃ on Si surface. As shown in the SEM images of the cycled Si anodes in Fig. 2d, the gill-shape cracks are witnessed both on the unetched Si surface and on the uncoated Si surface^[35]. As a comparison, intact structures are maintained on the patterned Si surface and Al₂O₃-coated Si surface. However, up to now, the drawbacks of pure Si anodes (such as stress accumulation and volume expansion) have not been

completely resolved yet. Instead, Si/C composites as anode materials have been attracting much attention in the future field of high-energy LIBs.

3 Synthesis methods of Si/C composites

In order to replace the commercial graphite anode, Si/C composites as anode materials are gradually becoming the new favorite in the field of LIBs. However, compared to the layer-structured graphite with the single C element, the structure of Si/C composites, the selection of carbon materials in Si/C composites and the element adjustment of Si or C in Si/C composites have a significant effect on the electrochemical performance of Si/C composites anode^[15,36]. Moreover, the materials' properties (e.g. structure, carbon type, element composition) of Si/C composites are directly related to its preparation process. In this case, the synthesis methods of Si/C composites are focused and discussed, which are divided into two categories based on featured technologies and materials.

3.1 Synthesizing Si/C composites by featured technologies

3.1.1 Ball milling

Mechanical ball milling is the most common synthesis method to prepare Si/C composites because of its low cost, high efficiency, simple process, and suitability for industrial production^[36–38]. Meanwhile, the Si/C composites prepared by mechanical ball milling possess small particle sizes and uniform size distribution^[39]. However, by mechanical ball milling method, the Si/C composites with small size face the issue of particle agglomeration^[40]. Meanwhile, post-treatments (e.g. drying and high-temperature annealing) are needed to obtain the final Si/C composites products^[41–45]. Fig. 3 displays several classic mechanical ball milling methods for obtaining Si/C or SiO₂/C composites. As shown in Fig. 3a, the primitive Si/graphite (Si/G) composites can be synthesized by mechanical ball milling, using Si powder and graphite as raw materials^[46]. To increase the electrical conductivity and structural stability of the obtained Si/G

composites, pitch as a carbon organic precursor can be introduced to coat the surface of the obtained Si/G composites, meanwhile NaCl as a pore-forming agent can be added into this coating process. After the post-treatments of high-temperature annealing under an inert atmosphere and removing NaCl, one with a dense carbon layer (C@Si/G) and the other with a perforated carbon layer (C@void@Si/G) could be gained. Moreover, the obtained Si/G, C@Si/G and C@void@Si/G can be characterized by XRD. The decrease of the peak intensity and the broadening of the peak width at half-height at 26.5° corresponding to graphite (002) demonstrates a formation of the perforated amorphous carbon layer on Si/G (Fig. 3b). When comparing the electrochemical performance of a LIB with the obtained C@Si/G or C@void@Si/G as anode materials, C@void@Si/G exhibits a better high-rate performance, delivering a capacity over 500 mAh g⁻¹ at a current density of 1 C (Fig. 3c). Meanwhile, as shown in Fig. 3d, similar to the mechanical ball milling route to obtain Si/G in Fig. 3a, the utilization of less SiO_x to replace Si powder in the ball milling process can make SiO_x rivete on graphite surface (SiO_x@G)^[47]. After being coated by pitch and subjected to high-temperature annealing under an inert atmosphere, the amorphous carbon coated SiO_x@G (C@SiO_x@G) can be further obtained, and the amplified local contact diagram of SiO_x and G or C are shown in Fig. 3e and 3f, respectively. On the other hand, replacing Si powder with SiO₂ and graphite with carbon sources in the ball milling process (Fig. 3a) can yield carbon-coated SiO₂ (C@SiO₂) (Fig. 3g). In order to transform SiO₂ into Si and obtain C@Si, the magnesiothermic reaction is usually employed: SiO₂(s) + 2Mg(s) → Si(s) + 2MgO(s). Meanwhile, the etching reaction between MgO and acid is also applied to remove undesired products^[48]. The final obtained C@Si possesses a void space inside the carbon shell due to the volume reduction from SiO₂ to Si (Fig. 3h). Moreover, the obtained C@Si as anode exhibits a far better high-rate performance than that of Si, in which a capacity over 1000 mAh g⁻¹ is delivered at a current density of 1 C. This is explained

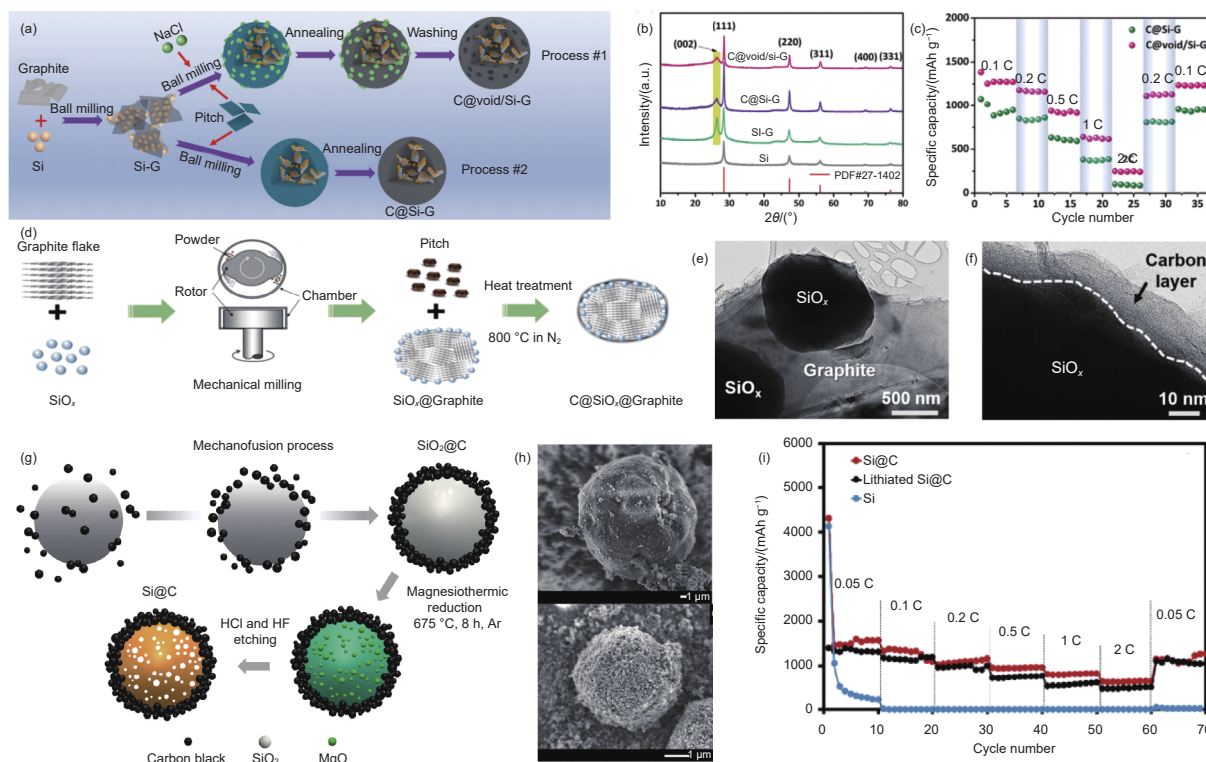


Fig. 3 (a) Schematic diagram shows formation procedures for C@Si-G and C@void/Si-G composites. (b) XRD patterns of the Si, Si-G, C@Si-G, and C@void/Si-G. (c) Rate performance of C@Si-G and C@void/Si-G at different current densities. Reproduced with permission^[46]. Copyright 2023. Elsevier Ltd. (d) Schematic illustrations of a mechano-fusion process for fabricating the C@SiO_x@G. (e-f) TEM images of the C@SiO_x@G. Reproduced with permission^[47]. Copyright 2025. Elsevier Ltd. (g) Schematic of Si@C synthesis employing SiO₂ as raw materials. (h) SEM images of SiO₂ and Si@C core-shell. (i) Rate capability tested at 0.05-2 C of Si@C, lithiated Si@C, and Si anodes. Reproduced with permission^[48]. Copyright 2020. Elsevier Ltd.

by the accommodation of the volume expansion of Si particles during cycling because of the void space inside the carbon shell of C@Si.

In order to elevate the electrical conductivity of Si/C composites as anodes in LIBs, some new kinds of carbon materials are introduced into the ball milling procedure, in which graphene oxide (GO) and carbon nanotubes (CNTs) are the representative new carbon materials^[49–51]. Huang et al. developed a scalable high energy bead milling approach to obtain Si/C composites by minimizing the size of Si granules and the thickness of graphene oxide (GO) simultaneously^[52], as shown in the upper half in Fig. 4a. In the high energy bead milling process, the milling energy can intensify Si/GO interaction to form BM-μSi(TA)/GO. Meanwhile, after a co-reduction process at 800 °C in Ar gas atmosphere, r(BM-μSi/GO) powder consisting of submicron Si particles enveloped by reduced GO (rGO), can be further produced. In the whole preparation process with two important steps of bead milling

and co-reduction, surface defects like oxidation and atomic disordered arrays induced by bead milling can be restored by thermoreduction to maintain a normal crystalline structure, as shown in the bottom half in Fig. 4a. Moreover, the products BM-μSi(TA)/GO and r(BM-μSi/GO) formed during the respective bead milling and co-reduction processes can be characterized by Raman spectra, in which the characteristic peaks of both Si and graphene Raman peaks can be witnessed^[52] (Fig. 4b). For the effect of rGO coated on μSi surface, the rGO encapsulation improved the Li⁺ transport efficiency and electron transport rate by reducing the volume expansion and direct exposure of Si particles, resulting in promoting of the stable SEI-films formation and reduction of the irreversible Li⁺ consumption. In this case, the specific capacity of 1508.3 mAh g⁻¹ at 1 A g⁻¹ and 960.4 mAh g⁻¹ at 5 A g⁻¹ is delivered by r(BM-μSi/GO) (Fig. 4c). This good rate performance is explained by the rGO layer attached intimately on Si to construct a network with

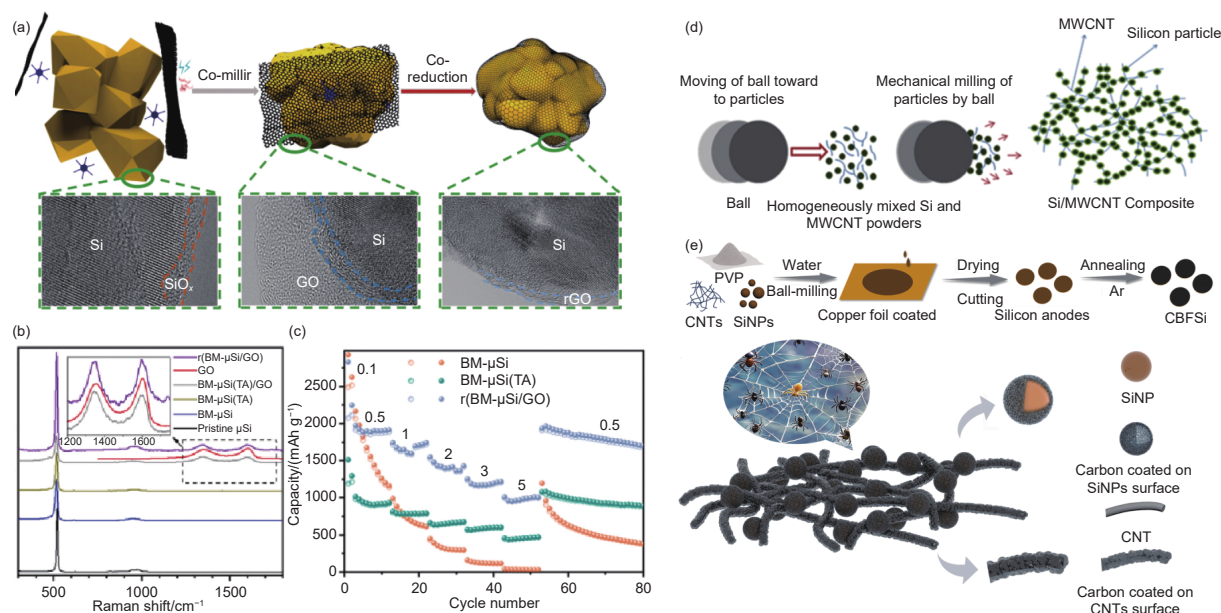


Fig. 4 (a) Schematic illustration of bead milling assisted synchronized size reduction of μ Si particles and GO flakes, the strengthened Si/C interaction and the simultaneously restored crystal structure, and corresponding TEM images. (b) Laser Raman spectroscopy (LRS) of bead-milled and reduced μ Si powders. (c) Rate performance of BM- μ Si, BM- μ Si(TA) and r(BM- μ Si/GO). Reproduced with permission^[53]. Copyright 2023. Elsevier Ltd. (d) Schematic illustration of the projected nanocomposite structure. Reproduced with permission^[52]. Copyright 2013. Elsevier Ltd. (e) Schematic of process flow for CBFSi and Schematic of CBFSi local structure simulation. Reproduced with permission^[54]. Copyright 2025. Elsevier Ltd.

enhanced conductivity^[52]. Similar to the method of constructing conductive network by adding GO in the ball mill process, another new carbon material of multi-walled carbon nanotubes (MWCNTs) is also usually introduced into the ball mill process to obtain Si/MWCNTs composites^[53] (Fig. 4d). However, unlike the role of rGO as encapsulation in r(BM- μ Si/GO), MWCNTs seems to act as twigs and the Si particles act as fruit on the twig, resulting in a fast electrical conductivity in the MWCNTs network and excellent electrochemical performance of Si/MWCNTs. In addition, the carbon precursor like vinyl pyrrolidone (PVP) can be added into the ball mill process, together with CNTs and Si nanoparticles. After carbonization, the carbonized PVP not only tightly bonded the electrode materials to the copper foil but also provided ample space for CNT skeleton to accommodate the volume expansion resulting from the lithiation reaction of Si nanoparticles. Moreover, the carbonized PVP was uniformly dispersed across the surfaces of Si nanoparticles and CNTs, forming a layer of carbon coating. This carbon layer harnesses the superior conductivity of CNTs to guarantee a reliable electrical interface with Si nanoparticles^[54]. The cor-

responding structural simulation schematic is depicted in Fig. 4e. It simulated the spider web structure in the inset. Even though a binder was not present, the as-prepared carbon coated Si/CNTs anode (CBFSi) exhibited remarkable structural stability. After more than ten times of forward and reverse bending and folding, CBFSi did not crack or pulverize, indicating its excellent mechanical properties.

3.1.2 Spray drying

Spray drying is a common method to dry the solid-liquid mixtures, thus producing the solid particles with a microscale sizes. When spray drying is employed to prepare Si/C composites, it possesses the advantages of uniform particle size, rapid drying, and suitability for large-scale production^[55]. Meanwhile, spray drying also offers the disadvantages of high equipment costs, large energy consumption, and complex process parameters^[56–58]. Moreover, in the practical applications, the process conditions need to be finely adjusted to meet the specific indices of Si/C composites, thus guaranteeing the electrochemical performance of Si/C anode. In order to better illustrate how to utilize spray drying to prepare Si/C composites, two representative preparation routes that in-

clude a spray drying step are introduced below.

For the first classic route involving a spray drying step to produce Si/C composites, the solid-liquid mixtures consisting of carbon precursor, Si particles and solvents are first prepared^[59], like the droplet shown in Fig. 5a. Then spray drying can be employed to remove the solvent and pyrolysis is subsequently used to transform the precursors into carbon, thus fabricating the Si/C composites, as shown in the preparation of Si/AC-700 composite corresponding to the route-④. Moreover, other steps like doping and etching can be integrated into aforementioned preparation process to modify the structure of the Si/C composites, as shown in the preparation of Si/AC@GC-700 composite in corresponding to the routes-①–③. It

should be noted that Fe doping into the Si/carbon precursors could transform the precursors into graphitic carbon (GC) at relatively low temperature of 700 °C because of the catalytic effect, as shown in the process corresponding to the route-②. In addition, the existence of graphitic carbon in Si/carbon composites can be characterized by the thermogravimetric analysis (TGA) (Fig. 5b). A two-step decline curve at approximately 450 and 570 °C can be witnessed in the TGA results of the Si/AC@GC-700 composite, which is attributed to the combustion of amorphous carbon and graphitic carbon, respectively, because graphitic carbon has a higher thermal resistance than amorphous carbon. Moreover, the existence of graphitic carbon in Si/carbon composites is beneficial for

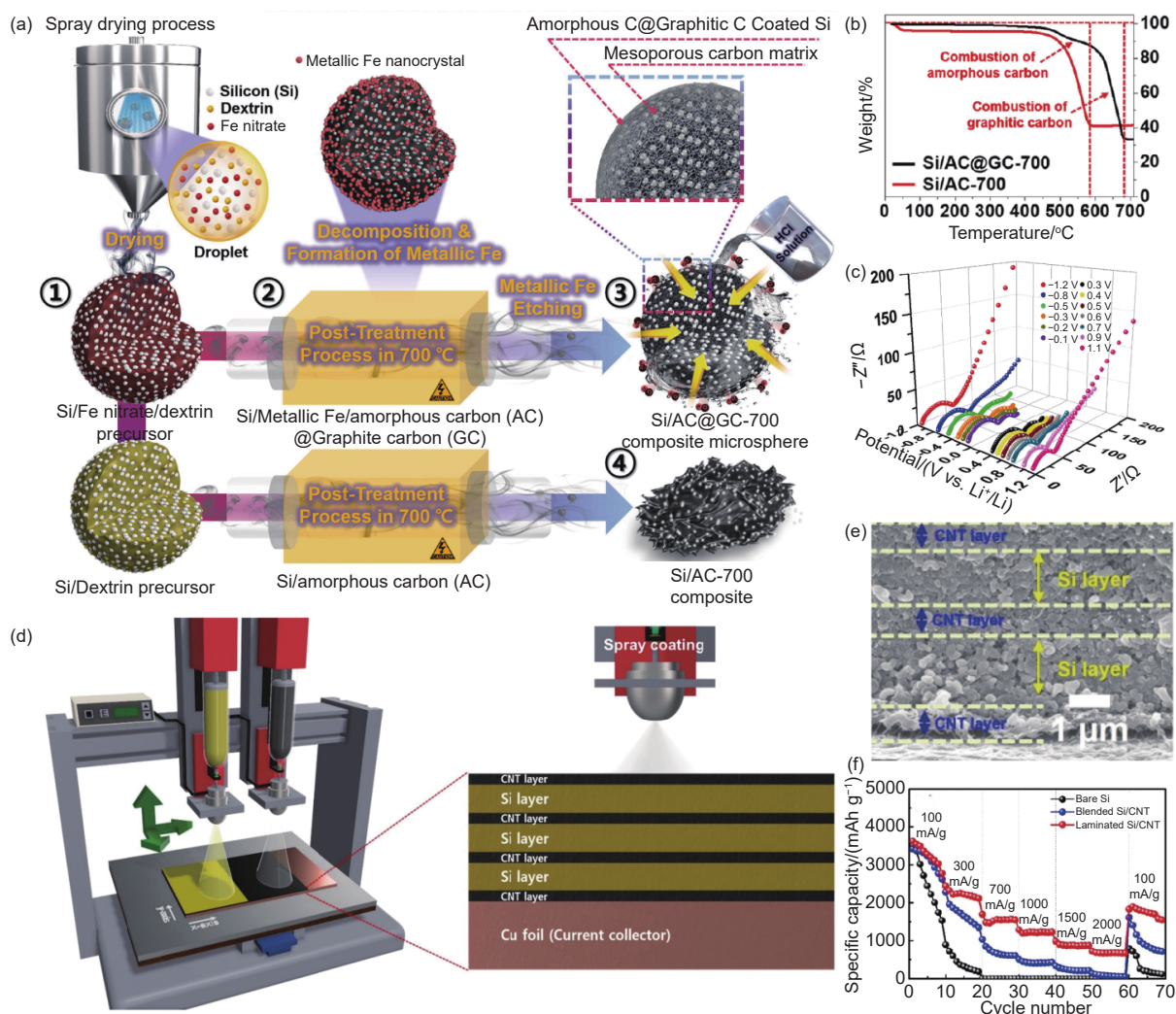


Fig. 5 (a) The formation mechanism of Si/AC@GC-700 and Si/AC-700 composites by spray drying process. (b) TG data of Si/AC@GC-700 and Si/AC-700 composites. (c) In-situ EIS of Si/AC@GC-700 electrode. Reproduced with permission^[59]. Copyright 2022. Elsevier Ltd. (d) Schematic illustration of laminated structure of Si layers and CNT layers. (e) High-magnification FE-SEM cross-sectional view images of laminated-Si/CNT electrode. (f) Rate performance of bare Si, blended Si/CNTs, laminated-Si/CNTs electrode. Reproduced with permission^[60]. Copyright 2024. Springer US Ltd.

Si/AC@GC-700 to accommodate the volume expansion during lithiation. Fig. 5c shows the in-situ electrochemical impedance spectroscopy (EIS) data of the Si/AC@GC-700 electrode obtained during the initial cycle. Meanwhile, the value of the total resistance (R_{tot} = sum of R_e , R_{sei} , and R_{ct}) slightly increased at approximately -0.3 V of the initial discharge process (discharging to 0.3 V vs. Li/Li^+), demonstrating the formation of an SEI-film with resistive characteristics. The small change in the R_{tot} values indicates the improved structural stability of Si/AC@GC-700, because the alloying reaction of Li_xSi and Li_{15}S_4 induces significant structural stress.

For the second new route involving spray drying to prepare Si/C composites, the ultrasonic spray-coating system is employed to produce the laminated-Si/CNT electrode with a layer-by-layer structure^[60] (Fig. 5(d-e)). In the fabrication process, silicon (Si) was loaded into one syringe, while carbon nanotubes (CNTs) were placed in the other. Ultrasonic vibrations from the spray nozzle generated fine droplets, which deposited uniform CNT and Si layers onto the copper (Cu) foil. Each CNT layer formed a fibrous network that facilitated excellent ionic and electronic conductivities, as well as decent cycling performance. Furthermore, the top CNT layer prevented direct contact between the electrolyte and the Si layer, thereby enhancing cycling stability by mitigating side reactions—including the pulverization of the Si layer. Ultimately, the laminated Si/CNT electrode structure improved cycling stability by suppressing the volume expansion of the Si layer active material through the buffering effect of the CNT layers. As a result, the laminated-Si/CNT anode delivered a specific capacity as high as $1546.32 \text{ mAh g}^{-1}$, compared to 716.46 and $117.27 \text{ mAh g}^{-1}$ for the blended-Si/CNT and bare Si electrodes, respectively, when the current density was increased from 0.1 to 2 A g^{-1} (Fig. 5f). This exceptional performance arises from the synergistic effects of CNT layer stacking, which effectively mitigate the inherent limitations of Si-based electrodes.

3.1.3 Electrostatic spinning

Electrostatic spinning is a frequently utilized

method to synthesize nanowires in the laboratory^[61–63]. For the Si/C composites as anode in LIBs, the nanowire structure possesses the unique advantages as follows. First, the skeleton of carbon nanowire can provide high conductivity, thus ensuring an excellent rate performance of Si/C composites; second, the carbon nanowire embedded with Si nanoparticles can provide a more compact buffer space to accommodate the expansion of Si during lithiation process, thus improving the cycling performance of Si/C composites.

As shown in Fig. 6a, Si/PMMA@PPy fibers are fabricated by directly collecting intermediate Si/PVP/PMMA fibers into a pyrrole reaction solution bath^[64]. This process efficiently removes the hydrophilic PVP component, forming porous Si/PMMA fibers, while simultaneously initiating in-situ growth of PPy on their surface. Under low Si loading (Si/PMMA-1 and Si/PMMA-2), the composite fibers exhibit no obvious aggregate of Si nanoparticles on their surface. Conversely, Si/PMMA-3 displays large Si nanoparticle agglomerations, indicating that excessive Si loading impedes uniform dispersion. After in-situ PPy deposition, the surfaces of Si/PMMA@PPy fibers become rougher than those of Si/PMMA fibers due to the random nucleation and granular growth of the PPy coating^[64]. Fig. 6b shows that the diameters of Si/PMMA-3@PPy fibers are approximately $1.53 \mu\text{m}$. The PPy coating thickness exceeds 300 nm , while the internal porous structure of the composite fibers is fully preserved, ensuring the subsequent formation of a Si-based composite electrode with abundant porous architectures. During high-temperature treatment process, the PMMA template decomposes completely, transforming the PPy coatings into nitrogen-doped porous carbon nanofibers. Electron microscopy confirms that Si nanoparticles are uniformly distributed on the surfaces and within the interiors of the nitrogen-doped porous carbon fiber framework (NPCNF), avoiding redundant repetition of the term “framework”. This morphology facilitates rapid electron/electrolyte transport and accommodates severe volume expansions of Si nanoparticles during

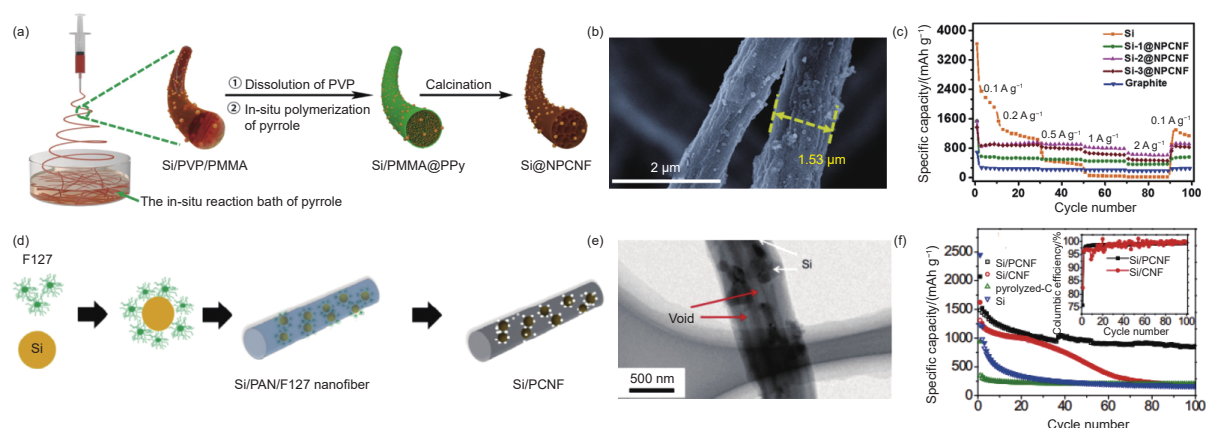


Fig. 6 Preparation of Si/C by electrostatic spinning. (a) Schematic showing the preparation of Si@NPCNF composites through an in-situ reaction collection bath. (b) SEM image of Si/PMMA-1@PPy. (c) Rate performance of Si, Si-1@NPCNF, Si-2@NPCNF, Si-3@NPCNF. Reproduced with permission^[64]. Copyright 2019. Elsevier Ltd. (d) Schematic fabrication of Si/PCNF. (e) HRTEM image of Si/PCNF. (f) Cycling performance of Si, pyrolyzed-C, Si/CNF and Si/PCNF. Inset of Fig. (f) The coulombic efficiency of Si/CNF and Si/PCNF. Reproduced with permission^[65]. Copyright 2015. Elsevier Ltd.

lithiation. Moreover, Fig. 6c shows the corresponding rate performances of Si nanoparticles, Si-1@NPCNF, Si-2@NPCNF, Si-3@NPCNF and graphite^[64]. For the pure Si nanoparticle, although it delivers a rather high discharge capacity of 3637 mAh g⁻¹ at 0.1 A g⁻¹, there is only an ultra-low retention (0.1%) of the initial capacity at 2 A g⁻¹ due to the large volume changes upon working. Moreover, compared with graphite, the Si-2@NPCNF anode delivers higher reversible capacities of 1521, 921, 910, 822 and 647 mAh g⁻¹ at the current densities of 0.1, 0.2, 0.5, 1.0 and 2.0 A g⁻¹, respectively. In addition, when the current density drops back to 0.1 A g⁻¹, the capacity of Si-2@NPCNF returns to 923 mAh g⁻¹, a value much higher than that of graphite (237 mAh g⁻¹). In this case, Si-2@NPCNF demonstrates a better rate performance than Si nanoparticles and graphite. Meanwhile, similar favorable performance of Si/C nanowires can be achieved with other formulations consisting of different carbon precursors and surfactant. As shown in Fig. 6d, F123 as the surfactant and polyaniline (PANI) as the carbon precursors are employed to produce silicon nanoparticle/porous carbon nanofiber (Si/PCNF) hybrids with high Si loading (52%), in which a void space can be witnessed in the SEM image because of the pyrolysis of F123 at high temperature as shown in Fig. 6e. As a result, this Si/PCNF composites exhibits a stable cycling performance (ca. 870 mAh g⁻¹ at 0.1 A g⁻¹ after 100 cycles) in the absence of binders and con-

ductive agent^[65], displaying a promising potential as a free-standing anode for LIBs (Fig. 6f).

3.1.4 Chemical vapor deposition

Among the multiple strategies for synthesizing Si/C composites as anode materials in LIBs, those prepared by chemical vapor deposition (CVD) have attracted great attention^[66–70], due to their advantages including high coulombic efficiency, excellent cycle stability, low equipment cost, and compatibility with large-scale production. As is well known, CVD is a materials synthesis technique in which gaseous reactants undergo chemical reactions on a solid surface to deposit thin films or coatings^[71–73]. For the Si/C composites produced by CVD, they can be roughly categorized by the types of gaseous reactant sources, including carbon precursors^[74–76] and Si precursors^[77–79].

For the Si/C composites prepared by CVD using carbon precursors, the process involves the pyrolysis of carbon precursors (e.g., CH₂=CH₂) on the surface of Si particles^[74]. As shown in Fig. 7a, Si and Si@C nanoparticles were synthesized using a two-stage reactor system under atmospheric Ar^[80]. In Stage 1, a focused laser beam dissociates SiH₄ to generate Si nanoparticles, which is carried by Ar into Stage 2. Here, CH₂=CH₂ is coaxially introduced, and the laser beam, redirected by mirrors and defocused to extend interaction time, induces decomposition of CH₂=CH₂, depositing a carbon shell around Si nanoparticle agglomerates, as shown in the bright-field

HRTEM images and STEM-EELS mapping of silicon and carbon elements of Si/C nanoparticles in Fig. 7b. Meanwhile, the controlled experiments (with/without $\text{CH}_2=\text{CH}_2$ in Stage 2, identical otherwise) were conducted to isolate the effects of carbon coating on Si properties, in which carbon coating on Si surface promotes better cycling performance^[80]. As shown in Fig. 7c, the capacities of Si or Si/C anode at first cycle are 3500 and 1750 mAh g^{-1} and the capacity retention rates of Si and Si/C anode at 30th cycle are nearly 30% and over 100%, respectively. It demonstrates that the thin carbon coating on Si nanoparticles can decrease the discharge capacity but increase the retention rates, which is attributed to the excellent electronic conductivity and extra space to suppress irreversible expansion of Si during lithiation process^[80]. In addition, in the carbon precursor-based

CVD process to produce Si/C composites, many related preparation conditions have been explored to optimize the properties of the Si/C composites, such as carbon precursor types^[66] (e.g. CH_4 , $\text{CH}_2=\text{CH}_2$), CVD treatment time^[70], carbon structure^[71] and Si morphology^[71,73].

On the other hand, the Si/C composites produced by CVD utilizing Si precursor, in which Si precursors (e.g., SiH_4) are pyrolyzed on the surface of porous carbon, are in the stage of large-scale commercialization. The best advantage of this Si precursor-based CVD method to prepare Si/C composites is the control of Si size to nanometer level, which mitigates the volume expansion issue, thus providing Si/C composites with excellent electrochemical performances^[79]. Moreover, an interfacial SiC chemical bonding strengthens the interaction between Si nan-

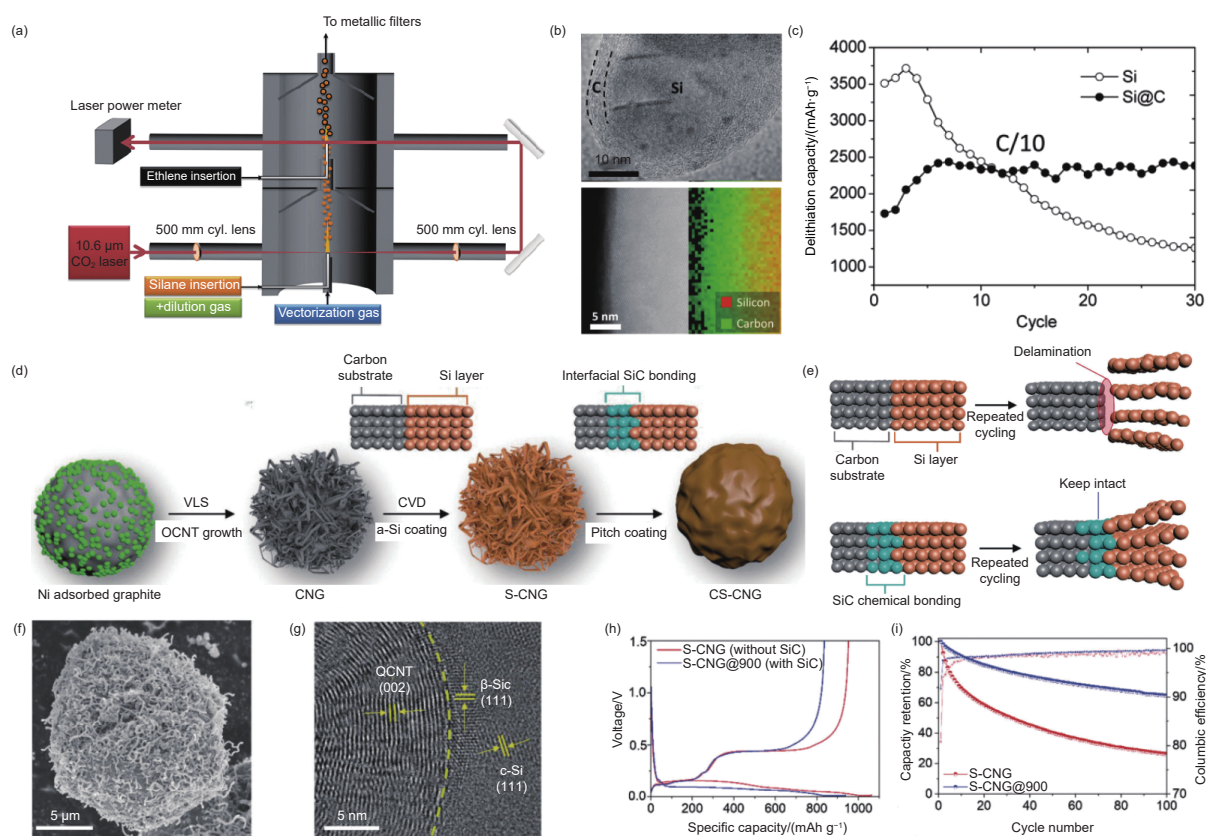


Fig. 7 Preparation of Si/C by chemical vapor deposition. (a) Schematic diagram of the laser pyrolysis reactor in the two stages configuration with $\text{CH}_2=\text{CH}_2$ as gas resource. (b) Relative bright-field HRTEM images of one Si@C nanoparticles and STEM-EELS mapping of silicon and carbon elements on the surface of one Si@C nanoparticle. (c) Cycling performance of Si and Si/C. Reproduced with permission^[80]. Copyright 2015. American Chemical Society. (d) Schematic illustrating the synthesis of CS-CNG particles with SiH_4 as gas resource. (e) Schematic illustration of Si delamination from a conventional carbon substrate (top) and carbon substrate with interfacial SiC bonding (bottom) before and after cycling. (f) SEM image of CS-CNG particles. (g) Cross-sectional high-resolution TEM image of S-CNG@900. (h) The voltage profiles of S-CNG and S-CNG@900 half-cell within a voltage window of 0.01–1.5 V at 0.1 C. (i) Half-cell discharge capacity retention of S-CNG and S-CNG @900 at 0.5C. Reproduced with permission^[81]. Copyright 2023. Wiley Ltd.

oparticles and the carbon substrate, which in turn suppresses the evolution of nano-sized voids and prevents Si delamination^[81] (Fig. 7d). The open-edge structure of carbon nanotubes (OCNTs) enables the formation of interfacial SiC specifically at the junction without overgrowth into the bulk (Fig. 7e–f). High-resolution TEM (Fig. 7(g)) confirms the presence of three distinct lattice distances corresponding to Si, SiC and carbon, respectively. Electrochemical tests of Si/C composites with and without SiC bonding (Fig. 7(h,i)) reveal that SiC-bonded composites (e.g., S-CNG@900) exhibit lower initial capacity (836 mAh g⁻¹ vs. 953 mAh g⁻¹ for S-CNG) but superior cycling stability. Both materials show comparable initial Coulombic efficiencies (89.1% for S-CNG@900 vs. 89.6% for S-CNG). During the first charge, S-CNG displays a high lithiation peak at 0.15 V (attributed to amorphous Si, a-Si), while S-CNG@900 exhibits a lower peak at 0.09 V (characteristic of crystalline Si, c-Si)^[81]. The improved cycling performance of S-CNG@900 is attributed to the more stable electrochemical properties of a-Si compared to c-Si.

In summary, we present a comparison of the synthesis method of Si/C composites by the discussed featured technologies in Table 1, including the key advantages and disadvantages of each technology, to help readers choose the appropriate preparation

scheme.

3.2 Synthesizing Si/C composites by featured material systems

3.2.1 Carbon precursor coating

The method of carbon precursor coating to produce Si/C composites is usually witnessed in the published literature, which is mainly due to the various sources containing the element of carbon, the low equipment cost and the peculiar properties of the generated carbon^[82–84]. In this case, this section of Si/C composites preparation can be categorized by the source types of carbon precursor into 3 parts, including biomass^[85–87], pitch^[88–90] and resin^[91–93].

First, in the case of employing biomass to produce Si/C composites, biomass-derived carbon materials often originate from renewable organic sources such as crop residues^[94–96] and agricultural waste^[82,86,97], and embody a range of distinct characteristics rooted in their natural precursor and thermal conversion process. They feature a hierarchically porous structure with abundant micropores and mesopores that contribute to its notable surface area and strong adsorption capacity, which is formed through the decomposition of cellulose, hemicellulose, and lignin during pyrolysis. The typical preparation process from biomass (e.g. grape stem) to Si/C composites is shown in Fig. 8a. The waste grape stem bio-

Table 1 Comparison of the synthesis method of Si/C composites by featured technologies

Synthesis method	Key advantages	Key disadvantages	Relative performance & comparisons
Ball milling	Low cost, high efficiency, and simple process.	Prone to particle agglomeration (due to mechanical force-induced mixing).	Electrochemical performance is limited by agglomeration (vs. CVD or electrospinning).
	Suitable for industrial scale production.	Requires post-treatments (e.g., drying, high-temperature annealing).	Lower equipment cost but higher post-processing complexity (vs. spray drying).
	Produces composites with small, uniformly distributed particles.		
Spray drying	Uniform particle size and rapid solvent removal.	High equipment cost and energy consumption.	Superior structural uniformity (vs. ball milling) but higher cost.
	Scalable for large-scale production.	Complex process parameters (require fine adjustment for desired performance).	Better rate performance than ball milling (due to uniform carbon coating) but lower cycling stability than CVD.
Electrospinning	Fabricates carbon nanofiber (CNF) skeletons with high conductivity (enhances rate performance).	Primarily a laboratory-scale method (challenges in large-scale production).	Best cycling and rate performance among all methods (e.g., 870 mAh g ⁻¹ after 100 cycles for Si/PCNF).
	CNFs provide compact buffer space to suppress Si volume expansion (improves cycling stability).	Limited Si loading capacity (excessive Si causes agglomeration).	Outperforms spray drying/CVD in mechanical flexibility but is less scalable.
CVD	High Coulombic efficiency and excellent cycling stability.	Carbon-precursor-based CVD reduces initial discharge capacity.	Superior cycling stability (vs. all methods; e.g., Si@C retains >100% capacity after 30 cycles).
	Precise control of Si size (~ nm scale, avoids expansion issues).	Requires strict control of gaseous reactant flow (risk of uneven coating).	Lower initial capacity than electrospinning but better long-term durability.
	Low equipment cost and scalable.		

mass underwent pre-carbonization at 400 °C for 2 h to yield pre-carbonized grape stem (PGC)^[98]. The PGC was then processed with a K_2FeO_4 solution to create pores and introduce functional groups, forming a porous carbon framework (PCF). Tetraethyl orthosilicate (TEOS) was hydrolyzed within the hierarchical pores of the PCF to generate a PCF/SiO₂ precursor. Finally, magnesiothermic reduction of this precursor produced the PCF/Si composites. The morphology of PCF/SiO₂ precursor and PCF/Si composites is shown

in Fig. 8b. Moreover, the PCF content in PCF/Si composites was systematically varied to prepare samples with high, medium, and low PCF loadings (denoted as H-PCF/Si, PCF/Si, and L-PCF/Si, respectively). X-ray photoelectron spectroscopy (XPS) and thermogravimetric analysis (TGA) were employed to characterize compositional differences among the 3 PCF/Si composites^[99]. As shown in Fig. 8c, XPS spectra confirm that Si, C and O are the primary elements, with the relative Si content increasing progressively from H-

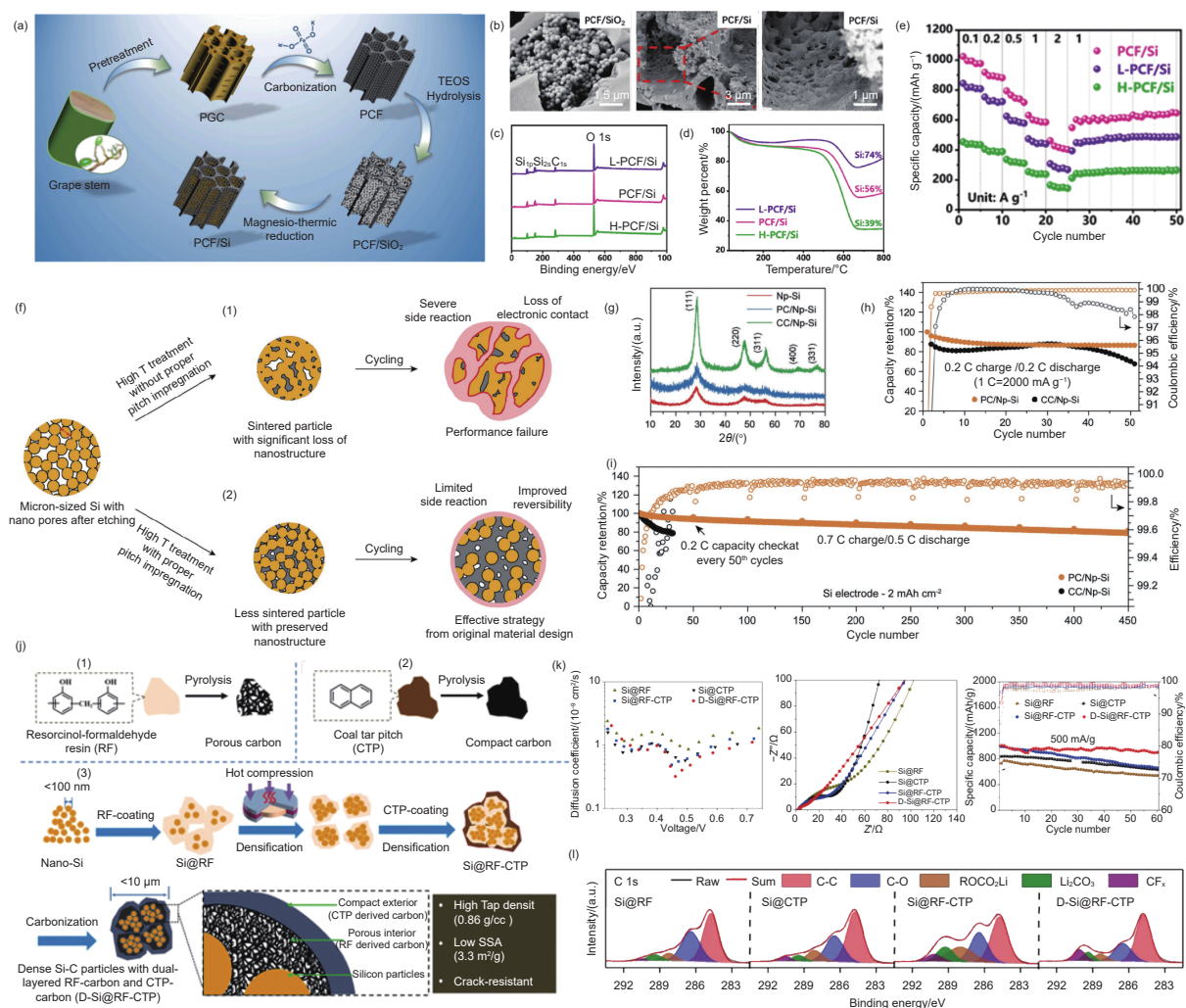


Fig. 8 (a) Schematic illustration of the synthesis of the PCF/Si composites from grape stem. (b) SEM images of PCF/SiO₂, PCF/Si. (c) XPS wide survey profiles. (d) TGA curves. (e) Rate performance of the L-PCF/Si, PCF/Si, and H-PCF/Si composites. Reproduced with permission^[98]. Copyright 2022. Elsevier Ltd. (f) Importance of preserving designed nanostructure during high-temperature treatment. (g) XRD patterns of Np-Si, PC/Np-Si, and conventional CC/Np-Si. (h) Cycling performance of PC/Np-Si and CC/Np-Si for 50 cycles in the half cell. (i) Cycling performance of PC/Np-Si and CC/Np-Si in the full cell paired with a NMC532 cathode. Areal capacity is controlled at 2 mAh cm⁻². Reproduced with permission^[99]. Copyright 2021. Wiley Ltd. (j) Schematic illustration of Si/C particle design with high tap density, low specific surface area, and crack resistant characteristics. (k) Electrochemical performance of Si@RF, Si@CTP, Si@RF-CTP, and D-Si@RF-CTP. Li⁺ Diffusion coefficients with respect to work potential; Electrochemical impedance spectroscopy (EIS) Nyquist plots of the post-cycled electrodes; Reversible capacities and cycling CEs at 500 mA g⁻¹. (l) XPS 1 C s spectra of the post-cycled electrodes. Reproduced with permission^[100]. Copyright 2023. Elsevier Ltd.

PCF/Si to L-PCF/Si. As shown in Fig. 8d, TGA curves reveal three distinct thermal events: below 200 °C: minor weight loss (< 5%) due to desorption of surface-adsorbed water; 400–700 °C: sharp weight reduction attributed to combustion of carbon components; above 750 °C: slight weight gain from oxidation of Si to SiO₂. The quantitative analysis of TGA data yields Si contents of 39%, 56% and 74% for H-PCF/Si, PCF/Si and L-PCF/Si, respectively. These results demonstrate precise control over composite composition through adjustment of precursor ratios. Comparing the electrochemical performance of three materials, the rate performances of L-PCF/Si, PCF/Si, and H-PCF/Si composites are presented in Fig. 8e. The PCF/Si composites exhibited reversible capacities of 1024, 895, 795, 632 and 462 mAh g⁻¹ at current densities of 0.1, 0.2, 0.5, 1 and 2 A g⁻¹, respectively. Upon returning to 0.1 A g⁻¹, PCF/Si recovered a capacity of 1058 mAh g⁻¹, significantly outperforming L-PCF/Si and H-PCF/Si. These results underscore the superior rate capability of the PCF/Si composites, which is attributed to the efficient electron and ion transport capabilities provided by the carbon skeleton based on an appropriate carbon-to-Si ratio.

Second, in the case of employing pitch to produce Si/C composites, pitch carbon, derived from pitch through processes like carbonization and graphitization, exhibits a range of distinctive characteristics^[89,101–102]. The typical preparation process for producing Si/C composites using pitch is illustrated in Fig. 8f. To form highly conductive Si/C nanocomposites, pitch often requires high-temperature carbonization (> 600 °C). It should be noted, however, that the nanosized primary Si particles within micrometer-sized Si particles are prone to activation at high temperatures due to surface lattice vibrations, leading to their fusion into larger particles. Consequently, the nanopores in micrometer-sized porous Si particles (Fig. 8(f-1)) shrink, causing these micrometer-sized particles to lose their porous structure—undermining the intended design goal of forming Si nanostructures. To address this, a pitch impregnation method has been developed to protect the

nanostructure from damage during the fabrication of micrometer-sized Si particles with the desired nanostructural features^[99]. As depicted in the panel b of Fig. 8(f-2), the resulting product enables the full realization of the advantages of Si as a high-capacity anode for LIBs. To underscore the advantage of pitch-derived carbon (PC) in relation to nanoporous Si (Np-Si), conventional chemical vapor deposition-derived carbon (CC) is introduced for comparison. As shown in Fig. 8g, the XRD patterns of PC/Np-Si and pristine Np-Si are similar. Using the Scherrer equation, the crystallite size is estimated to be 1.4 nm, indicating that the nanoscale size of the primary Si particles is preserved. In contrast, conventional CC/Np-Si exhibits sharp peaks corresponding to a crystallite size exceeding 3.3 nm. Preserving the original size of the primary particles not only helps mitigate stress intensification caused by large volume changes but also reserves sufficient space within the structure for the protective PC^[99]. Moreover, when comparing the electrochemical performance of PC/Np-Si and CC/Np-Si as anodes in LIBs, notable differences emerge. In Fig. 8h, CC/Np-Si undergoes drastic capacity fading after 30 cycles, whereas PC/Np-Si maintains 90% capacity retention after 50 cycles in half-cell tests, with negligible capacity loss observed from the 10th cycle onward. For the full cell configured as PC/Np-Si||NMC532 as shown in Fig. 8i, cycling tests were conducted using a standard protocol (0.7 C charge, 0.5 C discharge) with capacity checks every 50 cycles (0.2 C charge/discharge). Remarkably, this cell achieved stable cycling with 80% capacity retention after 450 cycles, even without pretreatment steps such as prelithiation. In contrast, conventional CC/Np-Si failed to maintain long-term cycling stability, retaining only 80.2% of its capacity after a mere 26 cycles.

Finally, in the case of utilizing resin or polymer to fabricate Si/C composites as anode in LIBs, the resin-derived carbon typically formed through processes like carbonization and subsequent graphitization of polymeric resins, exhibits a set of distinct characteristics that make it versatile in various applications^[103]. It generally features a high degree of structural uniform-

ity and controlled porosity, which can be tailored by adjusting the type of resin precursor, crosslinking density, and heat treatment conditions, allowing for precise customization of pore size distribution and surface area^[100]. It should be noted that a low specific surface area of the carbon layer in Si/C anodes effectively reduces the irreversible consumption of Li^+ during the formation of the SEI and mitigates side reactions with electrolyte, enhancing the initial Coulombic efficiency and long-term cycling stability of the Si/C anode. Meanwhile, the structural uniformity and controlled porosity of resin-derived carbon are beneficial to improve the electrical conductivity and suppress the volume expansion of Si/C composites^[104]. However, the abundant porosity of the resin-derived carbon will lead to the decrease of tap density of Si/C composites, especially for the nano-size Si. In this case, two structurally differing carbon precursors are employed to serve as agglomerating agents in hosting and densifying Si nanoparticles. As shown in Fig. 8(j-1) and Fig. 8(j-2), resorcinol-formaldehyde resin (RF) and coal tar pitch (CTP) were employed as precursors for the inner and outer carbon layers, respectively. As a polycondensation product of resorcinol and formaldehyde, the RF resin contains abundant oxygen-containing groups and releases substantial gaseous species (such as methane, CO_2 , and H_2O) during pyrolysis, leading to the formation of RF-derived carbon rich in mesopores. In contrast, CTP, primarily composed of aromatic hydrocarbons, releases very little gas during carbonization, resulting in a compact, nearly pore-free carbon structure. Meanwhile, Fig. 8j-3 illustrates the synthesis procedure of dense Si/C particles with dual-layered RF-carbon and CTP-carbon (termed D-Si@RF-CTP). And the average particle size of the resulting secondary particles (D-Si@RF-CTP) was $9.66\ \mu\text{m}$. As shown in Fig. 8k, regarding electrochemical performance, Si@RF exhibits the highest average Li^+ diffusivity of $1.4 \times 10^{-9}\ \text{cm}^2\ \text{s}^{-1}$, while Si@CTP has the lowest at $9.5 \times 10^{-10}\ \text{cm}^2\ \text{s}^{-1}$, which is attributed to the porous nature and high specific surface area (SSA) of the former. Despite its highly densified structure and low SSA, D-Si@RF-

CTP still achieves a Li^+ diffusivity of $8.9 \times 10^{-10}\ \text{cm}^2\ \text{s}^{-1}$. Meanwhile, electrochemical impedance spectroscopy (EIS) results reveal that D-Si@RF-CTP exhibits the smallest charge transfer resistance (R_{ct}) of $6.5\ \Omega$, in contrast to $65.8\ \Omega$ for Si@RF, $30.6\ \Omega$ for Si@CTP, and $22.3\ \Omega$ for Si@RF-CTP. This indicates that the densification step not only enhances intra-particle electron transport but also facilitates Li^+ migration through the carbon matrix to reach the active Si surface, benefiting from the more intimate interfacial contact. Furthermore, the low-frequency Warburg slope of the straight line for D-Si@RF-CTP reflects the highest bulk-phase Li^+ diffusion rate among the materials, which is consistent with the GITT-derived Li-diffusivity results: Li^+ diffusion in D-Si@RF-CTP is not hindered by the densification process but remains at a relatively high level throughout cycling, thanks to its superior crack resistance. For the cycling performance of Si@RF, Si@CTP, Si@RF-CTP, and D-Si@RF-CTP samples tested at an elevated current density of $500\ \text{mA}\ \text{g}^{-1}$, D-Si@RF-CTP delivers an initial specific capacity of $1007.5\ \text{mAh}\ \text{g}^{-1}$ and retains a reversible capacity of $900.8\ \text{mAh}\ \text{g}^{-1}$ after 60 cycles at $500\ \text{mA}\ \text{g}^{-1}$, corresponding to a capacity retention of $\sim 89.4\%$. In comparison, Si@RF, Si@CTP and Si@RF-CTP only retain 540.5 , 633.5 and $659.7\ \text{mAh}\ \text{g}^{-1}$ after 60 cycles, with retentions of 73.9% , 75.5% and 66.5% , respectively. The excellent cycling performance of D-Si@RF-CTP is attributed to the formation of an SEI-film with F-rich components, which is directly verified by the stronger peak of $-\text{CF}_x$ around $688.2\ \text{eV}$ in the F 1s XPS spectrum of cycled D-Si@RF-CTP than the other 3 control groups of Si@RF, Si@CTP and Si@RF-CTP, as shown in the XPS spectra of the post-cycled electrodes in Fig. 8l.

3.2.2 Wet chemistry based on silicon precursors

The majority of the previous content is about controlling the type of carbon source, the hybridization method of Si and carbon based on Si nanoparticles to produce Si/C composites. In fact, the strategies of obtaining Si/C composites by wet chemistry based on Si precursors have attracted growing attention due to the controllable Si size and Si morpho-

logy. The Si precursors in wet chemistry to produce Si/C composites can be roughly categorized into 2 kinds: Si-based micromolecules and Si-based polymer.

The most commonly utilized Si-based micromolecule to obtain Si/C composites is orthosilicate due to its good solubility in H_2O , such as tetraethyl orthosilicate (TEOS)^[105–108], tetrapropyl orthosilicate (TPOS)^[109]. Taking the production of SiO_2 from TEOS aqueous solution as an example, TEOS forms SiO_2 by hydrolysis and condensation in aqueous solution^[110]. Hydrolysis, catalyzed by acid or base, replaces the ethoxy groups in TEOS with hydroxyls, producing silicic acid and ethanol^[110]. Silicic acid then undergoes condensation, forming Si-O-Si bonds through dehydration or dealcoholization, building a network. Drying and calcining the resulting gel removes organics, yielding solid SiO_2 . Moreover, the reaction process from TEOS aqueous solutions to SiO_2 can be further upgraded together with other reactions, such as precipitation reaction, etching reaction^[107], the self-assembling process of metal-organic frameworks (MOFs)^[105,111]. As shown in Fig. 9a, the introduced surfactants like cetyltrimethylammonium bromide (CTAB) and polyvinylpyrrolidone (PVP) help to form spherical SiO_2 . Meanwhile, the LiF can be simultaneously prepared together with SiO_2 by the reaction of CH_3COOLi and NH_4F under hydrothermal conditions^[112]. After carbothermal modification, $SiO_2/LiF@C$ can be further obtained, in which the TEM image of $SiO_2/LiF@C$ is shown in Fig. 9b. Furthermore, other Si-based micromolecules like 3-aminopropyltriethoxysilane (APTES)^[113], silicone oil^[114], sodium silicate ($Na_2O \cdot nSiO_2$)^[115], $SiCl_4$ ^[116], can be also employed to produce Si/C composites.

The used Si-based polymers to produce Si/C composites are diverse because Si can form bonds like $-Si-C-$, $-Si-O-$ and $-Si-H$ with C, O and H in organic monomer^[117]. After polymerization like self-polymerization^[118], copolymerization^[119], and crosslinking polymerization^[120], the mentioned organic monomer can become the polymer comprising the elements of Si, C, O, as shown in Fig. 9 (c–e).

Moreover, the elements of Si, C, O in the Si-based polymer can transform into corresponding components in Si/C composites by pyrolysis in an inert atmosphere. The elements of Si and O can form SiO_2 and the element of C in the organic carbon chain can form C networks. By this strategy, the structure of SiO_2 particles anchored in C network is tended to form, which is beneficial for the electrochemical performance of Si/C composites due to the high electrical conductivity and suppression of volume expansion of C network. It should be noted that the temperature of pyrolysis in inert atmosphere is not the higher the better, because a higher content of inactive SiC will form when the temperature is about $1200\text{ }^\circ\text{C}$ ^[120], as the Fourier-transform infrared (FT-IR) spectroscopy shown in Fig. 9f. By the way, the Si/C anode derived from the pyrolysis of poly(dimethylsilylene)diacetylenes (PDSDA) at $1200\text{ }^\circ\text{C}$ delivers a capacity of about 200 mAh g^{-1} at a current density of 400 mA g^{-1} , which is much lower than that of over 900 mAh g^{-1} delivered by the Si/C anode derived from the pyrolysis of PDSDA at $800\text{ }^\circ\text{C}$.

3.2.3 Wet chemistry based on modification on silicon surface

For the method of wet chemistry to obtain Si/C composites, the modification on Si surface is also usually involved, of which importance is equivalent to the utilization of Si precursors^[93,121–123]. The modification on Si surface originates from the intrinsic shortcomings of Si nanoparticles in aqueous solution, such as aggregation and inactivity. In this case, the modification on Si surface mainly involves improving the dispersivity and the reactivity of Si nanoparticles. As is well known, improving the dispersivity and the reactivity is achieved mainly by using surfactants and charging the Si surface, respectively. Moreover, charging the Si surface can lay the groundwork for the preparation of Si/C composites. In this case, we focus on how to charge Si surface by the wet chemistry in this section. As shown in Fig. 10a, after the dispersion of Si nanoparticles in ethanol through ultrasonication, 3% HF solution is introduced into the aforementioned solution, which can remove the oxide layer and form Si-H bonds on the surface^[124]. HF-etched Si can react

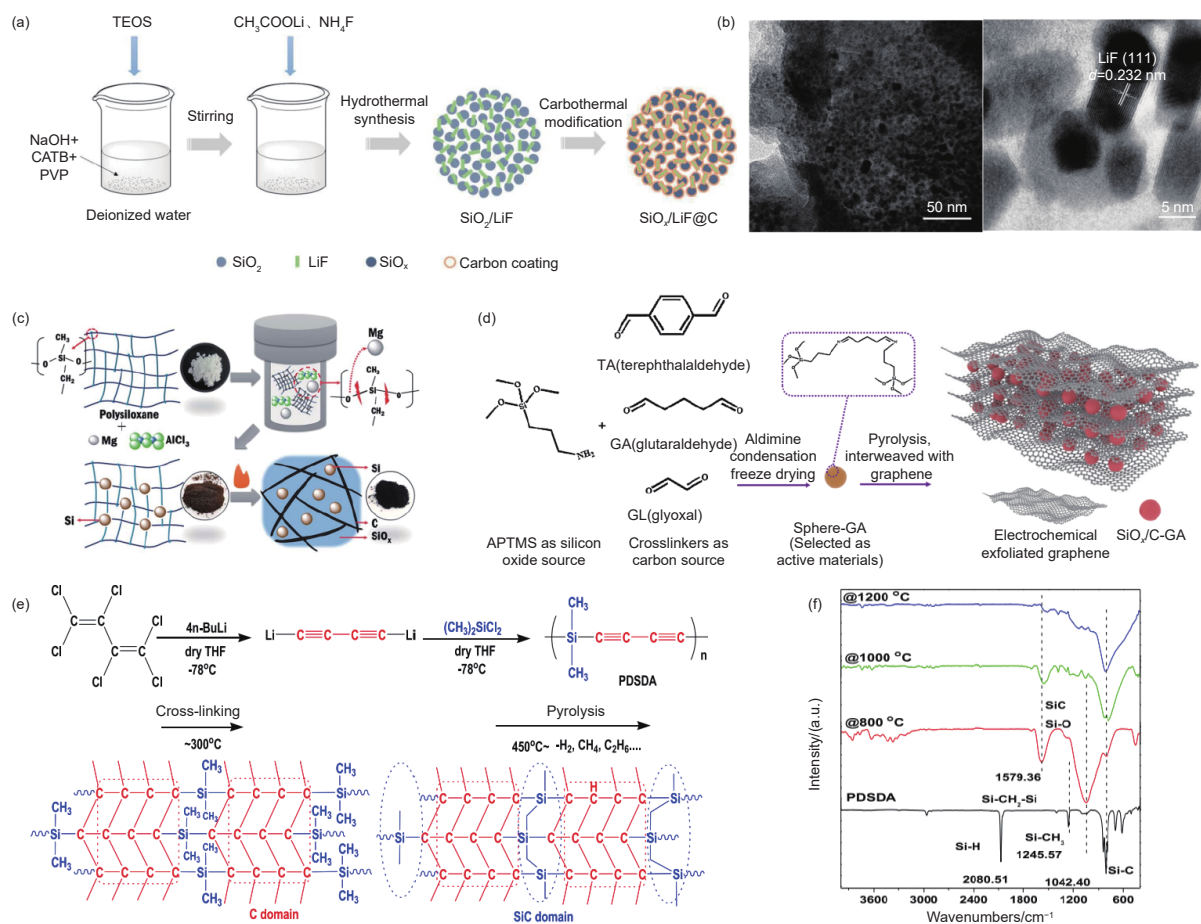


Fig. 9 Preparation of Si/C from the soluble silicon source. (a) Schematic illustration of synthetic route for $\text{SiO}_2/\text{LiF}@C$ from TEOS. (b) TEM images of $\text{SiO}_2/\text{LiF}@C$. Reproduced with permission^[112]. Copyright 2023. Springer US Ltd. (c) Synthesis of the $\text{Si}/\text{SiO}_2@C$ in situ nanocomposite from a single polysiloxane precursor. Reproduced with permission^[118]. Copyright 2017. Royal Chemical society. (d) Schematic synthesis route of SiO_2/C -Graphene from (3-aminopropyl) trimethoxysilane. Reproduced with permission^[119]. Copyright 2023. Elsevier Ltd. (e) Progressive conversion of poly(dimethylsilylene diacetylenes) (PDSDA) into crosslinking networks and consolidated Si/C linkage and amorphous carbon (ceramic product) after cross-linking and pyrolysis at high temperature. (f) FT-IR spectra of: PDSDA, $\text{Si}/\text{C}@800^\circ\text{C}$, $\text{Si}/\text{C}@1000^\circ\text{C}$, $\text{Si}/\text{C}@1200^\circ\text{C}$. Reproduced with permission^[120].

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with acrylic acid (AA) to form AA-coated Si. Subsequently, the $-\text{COOH}$ in AA-coated Si can undergo other reactions with different reactants, like condensation reaction with aniline. After carbonization of the organic components around Si nanoparticles, the Si/C composites can be produced, whose cycling performance is better than that of bare Si nanoparticles and polyaniline directly coated Si nanoparticles (Si -PANI) (Fig. 10b). It was ascribed to the tight integration of Si and carbon layer originating from the formation of Si-H bond, thus improving the electrical conductivity of Si/C composites, as shown in the surface morphology of Si/C composites in Fig. 10c. Similarly, the treatment of tannic acid (TA) on Si nanoparticles can make the Si surface possess hydroxyl groups ($-\text{OH}$).

In the anode fabrication, combined with the conductive agent of carboxylated carbon nanotubes (CNTs- COOH), binder of carboxymethyl cellulose (CMC), the $-\text{OH}$ on the surface of Si nanoparticles can form hydrogen bond with $-\text{OH}$ in both CMC and CNT- COOH ^[125] (Fig. 10d-e). The internal hydrogen bond in the anode can stabilize the structure of Si/C composites under the operation under high current density of 2, 4 or 10 A g^{-1} (Fig. 10f). Moreover, polydimethyl diallyl ammonium chloride (PDMA) is a classic and widely used reagent to make Si nanoparticle positively charged^[121, 126-127] (Fig. 10g), a charge-driven strategy for dispersing Si nanoparticles and stepwise self-assembly is proposed. Polydimethyl diallyl ammonium chloride (PDMA) functionalizes Si nano-

particles, with acetic acid and chitosan inducing step-wise self-assembly, forming porous Si-C composites (PDDA@Si/C) with open/closed pores, mainly by the electrostatic interaction between the positive charges in PDDA and negative charges in acid^[121] (Fig. 10h).

N-doped graphene-coated Si nanoparticles disperse uniformly in closed pores (Fig. 10(i-j)). Their features are as follows: high Si dispersion enabling rapid ion transport and reduced lithiation stress; graphene coating maintaining integrity, suppressing side reac-

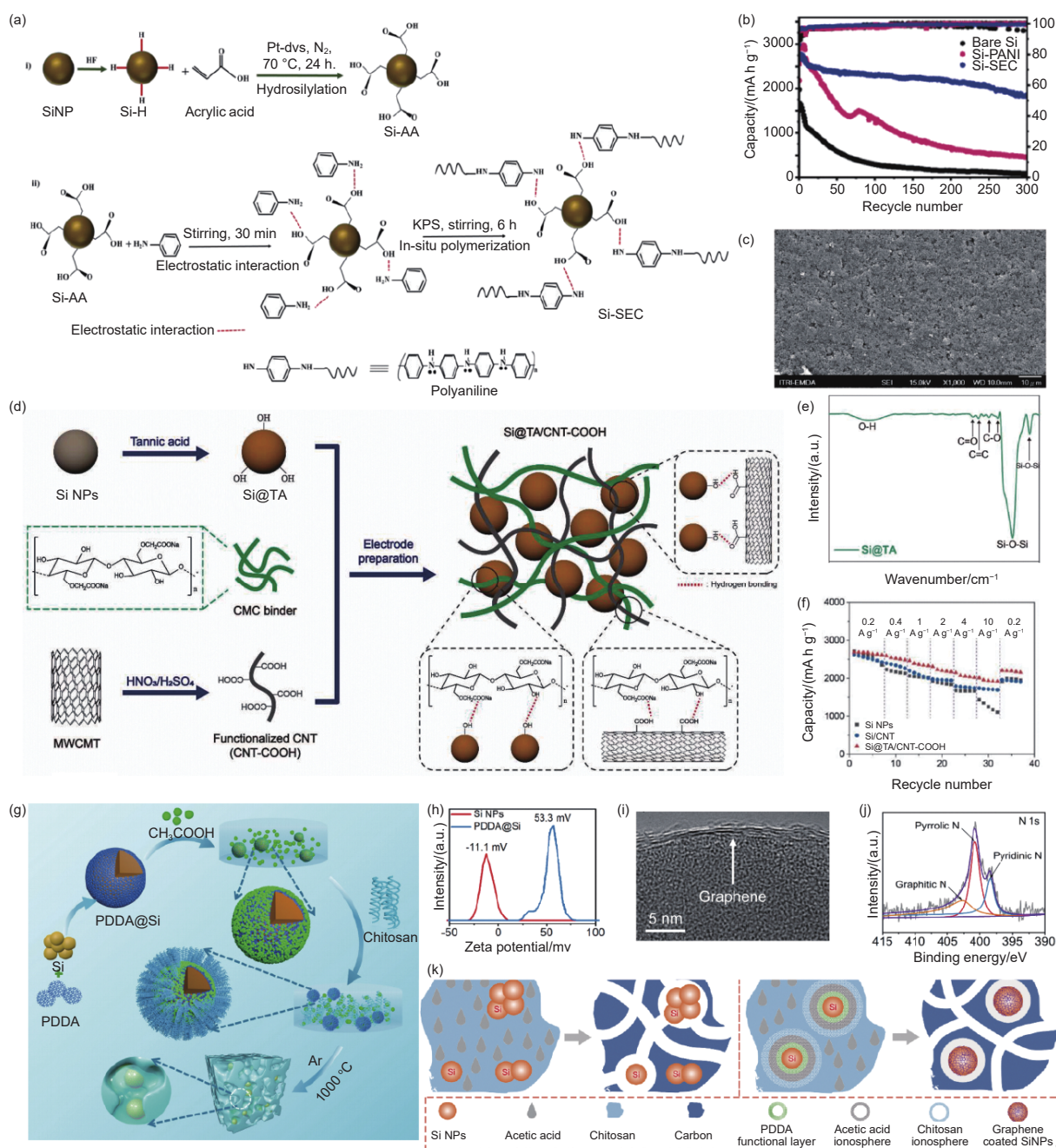


Fig. 10 Preparation of Si/C from the modification on Si surface. (a) The reaction mechanism of the formation of Super-Electrical-Conductive-Si material with emeraldine and polymer brush acid. (b) Cycle performance of bare Si, Si-PANI, Si-SEC electrode. (c) SEM images of Si-SEC electrode after 300 cycles. Reproduced with permission^[124]. Copyright 2022. Elsevier Ltd. (d) Schematic illustration for synthetic procedure of the Si/CNT and Si@TA/CNT-COOH electrodes. (e) FTIR spectra of Si NPs and Si@TA. (f) Rate performance of Si NPs, Si/CNTs and Si@TA/CNT-COOH. Reproduced with permission^[125]. Copyright 2024. Elsevier Ltd. (g) Schematic of the synthesis process of the PDDA@Si/C. (h) Zeta potentials of Si nanoparticles and PDDA@Si. (i) HRTEM image of PDDA@Si after carbonization. (j) High-resolution N 1s spectrum of PDDA@Si after carbonization. (k) Schematic of Si/C and PDDA@Si/C fabrication mechanism. Reproduced with permission^[126]. Copyright 2024. American Chemical Society

tions, and enhancing electron transport; open pores facilitating electrolyte access (Fig. 10k). These features promote excellent electrochemical performance of PDDA@Si/C composites.

In summary, we present a comparison of the syn-

thesis method of Si/C composites by the discussed featured material systems in Table 2, including the key advantages and disadvantages of each technologies, to help readers choose the appropriate preparation scheme.

Table 2 Comparison of the synthesis method of Si/C composites by featured material systems

Synthesis method	Key advantages	Key disadvantages	Relative performance & comparisons
Carbon precursor coating	Diverse carbon sources (biomass, pitch, resin) with low equipment cost.	Resin-derived carbon reduce tap density (due to high porosity).	Cost-competitive (vs. CVD/spray drying) but lower tap density than ball milling.
	Biomass-derived carbon materials: hierarchical porosity (high surface area). Pitch-derived carbon materials: preserves Si nanostructure (by impregnation).	Biomass carbon require pre-carbonization (adds materials process steps).	Pitch-based composites show better cycling stability (90% retention after 50 cycles) than resin-based ones.
Wet chemistry (Si precursors)	Precise control of Si size/morphology (by precursor selection).	Complex reaction steps (e.g., hydrolysis, condensation, pyrolysis).	Better Si size control than ball milling but higher process complexity.
	Enables in-situ formation of SiO ₂ /C networks (enhances conductivity).	High-temperature pyrolysis (>1200 °C) forms inactive SiC (reduces capacity).	Lower capacity than electrospinning (due to SiC formation) but more scalable than electrospinning.
Wet chemistry (Si surface modification)	Improves Si dispersion/reactivity (via surfactants or charge functionalization).	Requires expensive modifiers (e.g., PDDA, tannic acid).	Superior dispersion (vs. unmodified wet chemistry) but higher cost.
	Enhances Si-carbon interface bonding (e.g., Si-H bonds, hydrogen bonds).	Surface modification adds process steps (increases cost).	Better rate performance than Si-precursor wet chemistry (due to improved conductivity) but lower scalability than CVD.

4 Conclusion

Silicon-based materials have emerged as promising alternatives to commercial graphite, thanks to their ultrahigh theoretical capacity—with silicon itself boasting a capacity of 4200 mAh g⁻¹. However, they suffer from 2 critical drawbacks: poor electrical conductivity and massive volume expansion (exceeding 300%) during lithiation. Combining silicon with carbon materials effectively mitigates these issues, making Si/C composites a key research focus. The review categorizes synthesis methods for these composites into several major types. Ball milling, for instance, stands out for its low cost and scalability, with examples including the production of Si/graphite or Si/reduced rGO composites. Spray drying, on the other hand, yields uniformly sized particles, making it suitable for large-scale manufacturing—such as the creation of layered Si/CNTs structures. Electrospinning forms conductive carbon nanofibers that provide buffer space for Si expansion, while CVD enables controlled carbon coating or silicon deposition, significantly enhancing cycling stability. Other important preparation methods include carbon precursor coating, which uses biomass, pitch, or resins to tailor porosity

and conductivity; wet chemistry with silicon precursors like TEOS or silicones, allowing precise control over silicon's size and morphology; and silicon surface modification, which improves dispersion and reactivity through surfactants or charge functionalization—such as self-assembly induced by PDDA. All these methods aim to enhance silicon dispersion, material conductivity, and structural stability, thereby alleviating volume expansion and reducing side reactions. By systematically organizing various preparation strategies, the review provides a clear reference for developing high-energy-density LIBs. In addition, some performance parameters of commercial products of Si/C composites from different companies are listed in Table 3. Moreover, for the Si/C composites as anode materials utilized for the advanced all solid-state batteries, their fabrication relies on two optimized electrode configurations to leverage its ultrahigh volumetric capacity^[128–129]. For composite electrodes, homogeneous mixing with solid electrolytes and size ratio tuning, plus high aspect ratio electrolytes, build continuous ionic pathways to mitigate expansion-induced impedance. For diffusion-dependent electrodes, seamless interparticle contact, shortened Li⁺ diffusion

Table 3 Some performance parameters of commercial products of Si/C composites from different companies

Company	Grade	Specific capacity / mAh g ⁻¹	Initial coulombic efficiency / %	Volume expansion / %	Cycle life / cycles
BTR	6th Gen Si/C	2000–2300	>90	<20	>1000
Shanshan	AS6BP Series	1800–2200	>88	<8	>800
Group14 (US)	SCC55	1800–2500	>92	<15	>1500
Putailai	CVD Si/C	1800–2000	>92	≤3	>1200
Xiangfenghua	VS-2	2000	>75	10–15	>500
Sila nanotech	Titan Silicon	2000–2800	>90	<12	>1000

length, and thin electrode design enable fast charge-discharge property.

5 Perspective

The development of Si/C composite anodes for LIBs will prioritize bridging the critical gaps between laboratory-scale preparation and industrialization, with a focus on resolving 3 core challenges: (1) performance inconsistencies between lab prototypes and industrial products; (2) high production costs; and (3) unsustainable fabrication processes. To address the fundamental discrepancies between lab-scale and industrial-scale manufacturing, a comprehensive analysis is presented from the perspectives of cost control, mass transfer efficiency, heat transfer optimization, and reactor design.

Firstly, multi-scale structural engineering will enhance electrochemical performance while tackling industrial mass and heat transfer bottlenecks. Hierarchical porous carbon frameworks (2–5 nm pores for rapid Li⁺ diffusion, 50–100 nm pores for volume expansion buffering) constructed by PDDA self-assembly will reduce Si volume expansion to < 60% and boost electron conductivity—this is critical for eliminating mass transfer resistance in thick industrial electrodes, where ion transport is far more constrained than in thin lab-scale samples. In-situ N/P doping (1%–3%, atom fraction) or uniform 5–10 nm carbon layers will cut interfacial resistance by 20%–35% and prevent Si particle delamination, a prevalent issue in large-scale reactors caused by uneven stress distribution during batch processing.

Secondly, hybrid fabrication processes will enable scalable production through optimized reactor design, cost reduction, and heat transfer management. For ball milling, integrating high-efficiency bead

milling (1000–1500 r/min) with in-situ phenolic resin coating (10%–15%) in large batch reactors (5–10 kg/batch) will yield electrodes with 1800–2000 mAh g⁻¹ specific capacity and 85% capacity retention over 600 cycles, while lowering unit operation costs by 30% compared to gram-level lab synthesis. Ultrasonic spray drying coupled with low-temperature carbonization (400–600 °C) in continuous flow reactors will reduce energy consumption by 40%–50% through uniform heat distribution, avoiding local overheating that frequently degrades lab-scale samples prepared in muffle furnaces.

Thirdly, synergistic material design will balance performance metrics and industrial mass transfer requirements. Incorporating multi-walled carbon nanotubes (MWCNTs) into porous carbon matrices (porosity >60%) will construct continuous electron/ion transport networks, ensuring >80% capacity retention over 1000 cycles even in high-loading industrial electrodes (≥ 3 mAh cm⁻²)—a scenario where mass transfer limitations are significantly amplified relative to low-mass-loading lab electrodes.

Fourthly, in-situ characterization combined with artificial intelligence will accelerate lab-to-industry translation by optimizing reactor parameters. In-situ TEM and EIS will monitor SEI-film formation dynamics in real time, optimizing electrolyte consumption, which is a key cost-saving parameter for industrial production lines. Machine learning models trained on over 500 experiments (covering both lab and pilot-scale data) will predict electrode performance with >90% accuracy, slashing trial-and-error time by 60% and guiding the design of large-scale reactors with tailored mass and heat transfer coefficients.

Finally, sustainability will be embedded into

every stage of Si/C composite fabrication to reduce industrial costs and environmental footprint. Using biomass-derived carbon precursors (achieving 70%–80% carbon conversion yield) will cut raw material costs by 25% and reduce cradle-to-gate emissions by 35%–45%. Replacing toxic HF with 0.1 mol L⁻¹ H₂O₂ for Si surface modification will eliminate costly wastewater treatment steps in industrial plants. Adopting microwave-assisted carbonization (200–300 °C) will reduce energy consumption by 60%–70% compared to traditional high-temperature processes, enabled by uniform volumetric heating in industrial microwave reactors that outperforms the uneven heat transfer of lab-scale setups. Collectively, these measures will lower the carbon footprint of Si/C composites to < 5 kg CO₂ per kilogram of composite.

In summary, the commercialization of high-performance Si/C composite anodes will depend on performance-oriented structural design, cost-effective and scalable processes, and sustainability-driven fabrication. These advances will further facilitate the realization of high-energy-density LIBs (350–400 Wh/kg) by 2028–2030.

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