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Carbon Nanomaterials in Silicon Anodes of Lithium-Ion Batteries: Structural Design from Zero to Three Dimensions

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Abstract. Silicon is the most promising anode candidate for next-generation lithium-ion batteries owing to its theoretical capacity of 4200 mAh/g, which is approximately ten times that of commercial graphite. Its practical application, however, is severely hindered by a large volume expansion of about 300% during lithiation, which causes particle pulverization, an unstable solid electrolyte interphase, and poor electronic conductivity. Carbon nanomaterials have proven to be the most effective components for addressing these challenges. Based on the structural dimensionality of the carbon component, this review classifies carbon nanomaterials in silicon anodes into five categories: zero-dimensional carbon coatings, one-dimensional carbon nanotubes and nanofibers, two-dimensional graphene-based sheets, three-dimensional porous carbon matrices, and hierarchical architectures that integrate components across these dimensions. For each category, the structural features, working mechanisms, representative performance, and remaining limitations are analyzed, and the failure mechanism–structural function–carbon architecture relationship is emphasized throughout. Zero-dimensional coatings provide interfacial protection, one- and two-dimensional carbons construct conductive networks, three-dimensional porous matrices reserve expansion space, and hierarchical structures integrate these functions synergistically. Current challenges and future directions, including initial Coulombic efficiency, cost, and scalable production, are also discussed.

Keywords: silicon anode, carbon nanomaterials, lithium-ion battery, hierarchical architecture, volume expansion

1. Introduction

Commercial graphite anodes in lithium-ion batteries have approached their theoretical capacity of approximately 372 mAh/g and can no longer meet the rapidly growing demand for higher energy density in electric vehicles and portable electronics [1]. Silicon has emerged as the most attractive alternative because it delivers a theoretical capacity of 4200 mAh/g (Li22Si5), roughly ten times that of graphite, while also offering a low discharge potential, natural abundance, and environmental compatibility [2]. Despite this promise, silicon anodes suffer from three critical failure modes that have prevented widespread adoption [2]. First, silicon expands by approximately 300–400% in volume upon full lithiation, generating enormous mechanical stress that fractures particles and destroys electrical contact [2]. Second, the repeated volume change ruptures the solid electrolyte

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interphase (SEI), exposing fresh silicon to the electrolyte and causing continuous side reactions that consume lithium and electrolyte [2]. Third, silicon possesses intrinsically low electronic conductivity (~10−3 S/cm) and therefore suffers from severe polarization at high current densities [2].

Nanostructuring has been the first-line strategy to suppress fracture. According to Griffith fracture mechanics, the strain energy released during cracking scales with the particle radius cubed (R3), whereas the surface energy required to create new surfaces scales with the radius squared (R2) [3]. Consequently, reducing silicon particles below a critical size of approximately 150 nm makes fracture physically unfavorable [2, 3]. Nanosizing alone, however, introduces new problems: the high specific surface area increases parasitic SEI formation, lowers the initial Coulombic efficiency (ICE), and reduces the tap density, all of which compromise the practical energy density [4].

Among the many hybridization strategies that have been explored, carbon nanomaterials have demonstrated the most consistent and significant success [5], because carbon can simultaneously serve as a pathway for electron transport, a cushion against mechanical stress, and a chemically stable surface that confines SEI formation to the carbon side. The remainder of this review is organized as follows. Section 2 classifies carbon nanomaterials according to the dimensionality of the carbon component and discusses the four dimensionality-based categories; Section 3 addresses hierarchical architectures that integrate components across dimensions; Section 4 summarizes the challenges and future directions.

2. Carbon nanostructures in silicon anodes

The three failure modes identified above define the functions that the carbon component must provide: pulverization calls for mechanical buffering and electrical wiring, SEI instability calls for a chemically stable surface that excludes the electrolyte, and poor conductivity calls for a continuous electron network [5]. A convenient way to organize the numerous carbon strategies is the structural dimensionality of the carbon unit [5]. Zero-dimensional coated particles mainly isolate and protect the interface; one-dimensional nanotubes and nanofibers act as long-range wiring; two-dimensional graphene sheets provide flexible, face-to-face contact; and three-dimensional porous frameworks reserve internal expansion volume while maintaining continuous conduction. It should be noted that the fifth category, hierarchical architectures, is not an additional dimension: it combines components of different dimensionalities within a single particle or assembly, and it is therefore treated separately in Section 3. The five categories are schematically illustrated in Figure 1, and their structural features, primary functions, and key limitations are summarized in Table 1.

Table 1. Structural features, functions, and limitations of the five carbon nanostructure categories

Category	Structural feature	Primary function	Key limitation
0D carbon coating	Amorphous/pitch carbon shell on Si core	SEI stabilization; mechanical constraint; conductivity	Shell cracks without void; low ICE
1D CNT/CNF	High-aspect-ratio conductive wires	Long-range percolation network; mechanical wiring	SWCNT cost; dispersion difficulty
2D graphene	Single-atom-thick flexible sheets	Face-to-face electron contact; flexible buffering	Restacking; medium scalability
3D porous carbon	Mesoporous/CVD/MOF/biomass carbon scaffold	Void reservation; continuous conduction; fast Li+ diffusion	Low tap density; complex synthesis
Hierarchical	Multi-carbon combination (shell + void + CNT + graphene)	Synergistic integration of all functions	Multi-step synthesis; high cost; ICE gap

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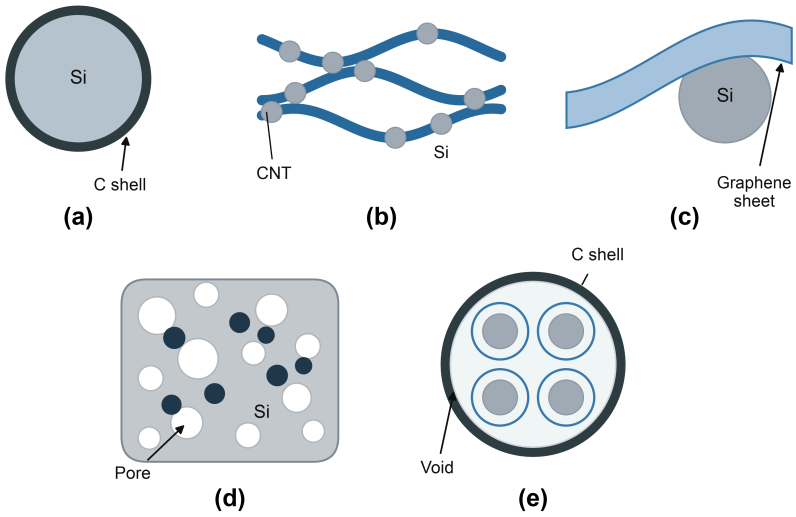

Figure 1. Schematic illustration of five categories of carbon nanostructures in silicon anodes: (a) core–shell Si@C; (b) CNT network; (c) graphene wrapping; (d) porous carbon matrix; (e) yolk–shell/pomegranate structure

2.1. Zero-dimensional carbon coatings

Strictly speaking, a carbon coating is a conformal ultrathin film rather than a zero-dimensional object; in this classification the term refers to the coated silicon nanoparticle acting as a discrete building block with no extended dimension, in contrast to the one-, two-, and three-dimensional carbon units discussed below. With this clarification, zero-dimensional carbon coatings, most commonly realized as core–shell Si@C structures, represent the most straightforward and industrially accessible carbon strategy [2]. In this design, a conformal layer of amorphous carbon, pitch-derived carbon, or soft/hard carbon is deposited directly onto silicon nanoparticles [5]. The carbon shell performs three essential functions: it physically separates silicon from the electrolyte so that the SEI forms once on the stable carbon surface rather than repeatedly breaking and reforming on silicon [5]; it provides mechanical constraint that partially absorbs the expansion stress; and it improves electronic transport across the electrode and suppresses particle agglomeration during cycling [5].

Representative original studies demonstrate the effectiveness of this approach. A micrometer-sized porous silicon/carbon composite (M-pSi@C) synthesized by scalable spray drying retained 95% of its capacity (1002 mAh/g) after 500 cycles at 2 A/g [6]. An ant-nest-like porous silicon derived from a magnesium–silicon alloy, after carbon coating, retained 90% of its capacity after 1000 cycles together with a low electrode swelling of 17.8% [7]. A rigid–flexible double carbon shell design (B-PSi@doubleC), in which an inner flexible carbon layer buffers the volume change while an outer rigid carbon layer stabilizes the SEI, maintained 1105.8 mAh/g after 300 cycles at 0.5 A/g [8]. Common coating routes include chemical vapor deposition (CVD) and pitch pyrolysis; pitch-derived carbon is particularly attractive because of its low cost and tunable graphitization degree [9].

Nevertheless, core–shell coatings without internal void remain vulnerable. When silicon expands by roughly 300%, the carbon shell eventually cracks and re-exposes silicon to the electrolyte [5]. In addition, the carbon content dilutes the overall specific capacity, and the ICE of many Si@C

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composites remains below 90%, which is still inferior to graphite [5]. These limitations motivated the development of structures that deliberately reserve internal space for expansion, as discussed in Sections 2.4 and 3.

2.2. One-dimensional carbon conductive networks

One-dimensional carbon nanotubes (CNTs) and carbon nanofibers (CNFs) possess exceptionally high aspect ratios and sp2-bonded conductive backbones. Because of their long-range geometry, they establish percolated electron pathways throughout the electrode at remarkably low loadings and simultaneously act as mechanical wiring that binds silicon particles together, so that even pulverized fragments remain electrically connected during cycling [5].

He et al. fabricated binder-free dry electrodes combining a single-walled carbon nanotube (SWCNT) network with SiOx@C particles and elucidated the difference between SWCNTs and multi-walled CNTs (MWCNTs) by in situ Raman spectroscopy [10]. The SiOx@C|SWCNT electrode delivered an initial discharge capacity of 1785 mAh/g with an ICE of 81.52%, and its lithium-ion diffusion coefficient was 3–4 orders of magnitude higher than that of the MWCNT counterpart. Mechanistically, the flexible SWCNTs maintained electrical contact with the active material even under tensile stresses of up to 6.2 GPa, whereas the stiffer MWCNTs lost contact under the alternating compressive (up to 8.9 GPa) and tensile (2.5 GPa) stresses that arise during long-term cycling [10].

Lee et al. further described an "acupuncture effect" whereby short, thick CNTs pierce through the SEI under gigapascal-level compressive stress during expansion, whereas long, thin CNTs wrap around particles and preserve contact; after 200 cycles the capacities followed the order long SWCNT > long MWCNT > short SWCNT > short MWCNT [11]. A near-commercial formulation of pitch-coated silicon microparticles with only 0.1 wt% SWCNT reduced the first-cycle electrode swelling from 170% to 27% and retained 94.6% of its capacity after 100 cycles [11]. The principal barriers are economic and technical: SWCNTs still cost 1500–2000 $/kg, the global production capacity remains at only 100–200 tons per year, and achieving a uniform CNT dispersion in electrode slurries is difficult at scale [11].

2.3. Two-dimensional graphene-based sheets

Two-dimensional graphene and its derivatives, including graphene oxide (GO) and reduced graphene oxide (rGO), offer single-atom-thick flexible sheets with outstanding in-plane electronic conductivity [9]. In silicon anodes, graphene wraps around particles like a flexible blanket, providing face-to-face contact that maximizes the electron-transfer area while accommodating volume changes through sheet deformation [2, 9]. Oxygen-containing functional groups on GO can further form chemical bonds with the silicon surface, strengthening the interface adhesion [9].

Representative examples compiled in recent studies include a Si/rGO composite that retained 1433 mAh/g after 100 cycles [9], spray-dried silicon@graphene microspheres that delivered 2882.3 mAh/g with an ICE of 86.9% [4], and a covalently bonded graphite shell prepared by copper-catalyzed CVD that used only 3.8 wt% carbon while achieving an areal capacity of 5.6 mAh/cm2 and a volumetric capacity of 2564 mAh/cm3 [11]. A pronounced size effect was also identified: small-lateral-size rGO limited the electrode swelling to +82%, whereas large sheets allowed +117% [11].

Despite these merits, graphene faces practical barriers. The sheets tend to restack during electrode processing, which reduces the accessible surface area and the ion transport channels [4]. Large-scale

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production of high-quality graphene remains limited, and its commercial scalability has been rated as "medium" [4]. Depending on quality, costs range from 50 to 500 $/kg [11].

2.4. Three-dimensional porous carbon matrices

Three-dimensional porous carbon matrices, including mesoporous carbon, CVD-derived carbon frameworks, metal–organic framework (MOF)-derived carbon, and biomass-derived carbon, provide a continuous scaffold whose internal voids accommodate the large volume expansion of silicon [9]. These structures perform three simultaneous roles: the pores reserve space for expansion, the carbon walls maintain continuous electron conduction, and the interconnected channels shorten the lithium-ion diffusion pathways [4, 9].

Magasinski et al. demonstrated an early hierarchical bottom-up approach in which porous carbon was grown by CVD around silicon nanoparticles, creating a robust three-dimensional conductive matrix [12]. More recent results include carbon-coated n-Si/C microspheres that delivered 3320 mAh/g with 90% capacity retention after 100 cycles [4]. Biomass-derived porous carbon offers a sustainable route: phosphorus-doped carbonized cotton fibers loaded with silicon achieved 3408.2 mAh/g initially and 1777 mAh/g after 150 cycles [9]. MOF-derived carbon inherits regular pore structures from the parent framework; a PDA@CoZn-NC@Si composite delivered 2252 mAh/g, retained 814 mAh/g after 400 cycles, and reached a full-cell energy density of 419.8 Wh/kg [9].

From an industrial perspective, CVD-based silicon–carbon composites are considered the most promising route for large-scale production because of the short processing cycles, simple operation, and low expected cost [9]. The trade-off, however, lies between the pore volume and the packing density: excessive porosity lowers the tap density and hence the volumetric energy density of the electrode [5]. Template removal and carbon deposition steps also add process complexity, and the high surface area of porous carbons can promote parasitic reactions with the electrolyte [9].

3. Hierarchical carbon architectures

Hierarchical architectures integrate multiple carbon forms into a single structure so that each component addresses a specific weakness of silicon anodes: a carbon shell stabilizes the SEI, internal voids accommodate the expansion, CNTs provide long-range electron transport, and graphene offers face-to-face contact [2, 5]. When these elements are combined, the overall performance exceeds what any single carbon form can achieve alone.

The yolk–shell Si@void@C structure is a representative example. A rigid carbon shell encloses a silicon core with a deliberately engineered gap between them; during lithiation, silicon expands into the internal void while the outer shell and its SEI remain geometrically unchanged, enabling stable long-term cycling [2]. The pomegranate structure advanced this concept by assembling multiple yolk–shell units into a micro-sized secondary particle, which lowers the specific surface area, raises the tap density, and retains the benefits of nanosizing [2, 13]. The pomegranate anode reported by Liu et al. retained 97% of its capacity after 1000 cycles, exhibited a Coulombic efficiency of 99.87%, and delivered a volumetric capacity of 1270 mAh/cm3 [13].

A further generation of CNT-reinforced yolk–shell structures grows a CNT network inside the cavity to bridge the silicon yolk and the carbon shell, solving the point-contact problem that limits electron transfer in simple yolk–shell designs [2]. Multi-component composites have also shown strong results: a Si@C@CNT dual-carbon structure delivered 1607 mAh/g and retained 610 mAh/g after 1000 cycles [9], while a Si@C@SWCNT double-layer electrode achieved 2337/2072 mAh/g with an ICE of 88.7% and 1267.3 mAh/g after 500 cycles [11].

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Jang and Kwon concluded that among all hybridization strategies, carbonaceous materials have demonstrated the most significant and consistent success, with yolk–shell Si@void@C and three-dimensional graphene frameworks identified as the most promising directions [5]. The remaining hurdles for hierarchical designs are the multi-step synthesis complexity, the elevated cost, and ICE values that still lag behind graphite.

4. Challenges and future directions

Although carbon nanomaterials have substantially improved silicon anode performance, several challenges must be resolved before commercialization becomes widespread. Initial Coulombic efficiency remains a critical bottleneck: most nanostructured silicon–carbon composites exhibit ICE values of 80–87%, whereas graphite exceeds 90% [4]. Prelithiation offers a promising remedy; stabilized lithium metal powder (SLMP), for instance, has been shown to raise the first-cycle efficiency substantially, and chemical prelithiation can push ICE values above 94% [4].

Cost and scalability represent equally pressing barriers. SWCNTs remain prohibitively expensive for mass production, and the scalable synthesis of high-quality graphene is still limited [4, 11]. In contrast, pitch-derived carbon and CVD carbon frameworks benefit from mature supply chains and are already entering pilot production [9, 11]. The research community is therefore shifting from maximizing the specific capacity alone toward optimizing the tap density, areal loading, full-cell energy density, manufacturing cost, and safety simultaneously [4, 9].

A clear trend is the move toward multi-scale synergistic architectures that combine inexpensive pitch carbon coatings with small amounts of high-performance CNTs or graphene, achieving near-commercial performance at an acceptable cost [11]. In operando characterization techniques, such as real-time transmission electron microscopy, are also expected to provide deeper mechanistic understanding that will guide the next generation of structural designs [2].

5. Conclusion

Silicon anodes offer a transformative increase in lithium-ion battery energy density, yet their practical use is blocked by severe volume expansion, unstable SEI formation, and poor electronic conductivity. Carbon nanomaterials have emerged as the most versatile and effective strategy for mitigating these problems, and each structural dimensionality addresses a distinct part of the failure chain. Zero-dimensional carbon coatings provide essential interfacial protection and mechanical constraint. One-dimensional CNTs and CNFs build long-range conductive networks and mechanical wiring at ultralow loadings. Two-dimensional graphene sheets deliver face-to-face electron contact and flexible buffering. Three-dimensional porous carbon matrices reserve internal expansion space while maintaining continuous conduction. Hierarchical architectures that integrate these carbon forms synergistically achieve the best overall performance, with representative designs demonstrating capacity retention above 97% after 1000 cycles.

Moving forward, the field must focus on raising the initial Coulombic efficiency through prelithiation, reducing the material and processing costs, and transitioning from laboratory-scale demonstrations to scalable manufacturing. Carbon nanomaterials will remain central to every stage of this evolution.

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