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REVIEW

The critical role of carbon in marrying silicon and graphite anodes for high-energy lithium-ion batteries

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Abstract

Increasing the energy density of conventional lithium-ion batteries (LIBs) is important for satisfying the demands of electric vehicles and advanced electronics. Silicon is considered as one of the most-promising anodes to replace the traditional graphite anode for the realization of high-energy LIBs due to its extremely high theoretical capacity, although its severe volume changes during lithiation/delithiation have led to a big challenge for practical application. In contrast, the co-utilization of Si and graphite has been well recognized as one of the preferred strategies for commercialization in the near future. In this review, we focus on different carbonaceous additives, such as carbon nanotubes, reduced graphene oxide, and pyrolyzed carbon derived from precursors such as pitch, sugars, heteroatom polymers, and so forth, which play an important role in constructing micrometer-sized hierarchical structures of silicon/graphite/carbon (Si/G/C) composites and tailoring the morphology and surface with good structural stability, good adhesion, high electrical conductivity, high tap density, and good interface chemistry to achieve high capacity and long cycling stability simultaneously. We first discuss the importance and challenge of the co-utilization of Si and graphite. Then, we carefully review and compare the improved effects of various types of carbonaceous materials and their associated structures on the electrochemical performance of Si/G/C composites. We also review the diverse synthesis techniques and treatment methods, which are also significant factors for optimizing Si/G/C composites. Finally, we provide a pertinent evaluation of these forms of carbon according to their suitability for commercialization. We also make far-ranging suggestions with regard to the selection of proper carbonaceous materials and the design of Si/G/C composites for further development.

KEYWORDS

carbonaceous additives, graphite, high energy, lithium-ion batteries, silicon

1 | INTRODUCTION

Lithium-ion batteries (LIBs) have been dominant in the market for powering the portable electronic devices since they were first commercialized, due to their desirable energy and power densities. To meet the market demand for lighter batteries with longer service life, the energy densities of LIBs have to be continually increased. The recent development of electrical vehicles and their widespread use also call for LIBs with high energy. Therefore, there is always constant pressure on the relevant academic and industry communities to improve the energy density of LIBs.[1-3] Nevertheless, the conventional LIBs using carbonaceous anode and lithium transition-metal oxide cathode are approaching their theoretical energy density.

The energy density of LIBs is closely related to the electrode materials and their specific capacity. Compared to the cathode materials, there is more room in anode materials to increase the capacity. For example, the gravimetric capacity of conventional $LiCoO_2$ cathode is around 165 mAh/g, which is 0.2 to 1 times lower than that of Ni-rich or Li-rich cathodes,[4-6] while the gravimetric capacity of Si anode is 10 times higher than that of conventional graphite anode (372 mAh/g). With the same cathode material, replacing graphite with Si can significantly improve the energy density of LIBs. Therefore, Si has been considered as one of the most-promising next-generation anodes towards high-energy LIBs because of its high theoretical capacity (3572 mAh/g), low working voltage (~0.2 V vs Li/Li^+), and abundance in the earth's crust.[7] However, unlike the intercalation-type anodes (eg, graphite), the alloying/dealloying reaction of Si with Li induces huge volume changes (>300%). Such huge volume changes during electrochemical cycling will lead to repeated cracking and pulverization of Si, and hence the disintegration and fracturing of the Si electrode, accompanied by electrical isolation. The repeated cracking and pulverization will also lead to the continual breaking up of the solid electrolyte interphase (SEI) layer and the explosion of new surface, which will quickly consume the electrolyte and Li ions. Therefore, the use of sole Si anode suffers from extremely fast capacity decay and low coulombic efficiency (CE) as a result of the severe volume changes and unstable SEI films. Design strategies for advanced materials, such as employing unique nanostructures (nanowire, nanotube, core/shell, yolk shell, nanoporous materials, etc) and forming composites with electrochemically inactive/less active materials, such as carbon, conductive polymer, and so forth, have been applied as academic approaches to significantly improve the cycle life.[8-10] Nevertheless, the volumetric energy density of these materials and the areal mass loading on electrodes are generally too low for industrial implementation. The commercial goal of achieving high-performance anodes to replace the existing commercial graphite materials in the near future, involves reaching a specific capacity of 500 mAh/g or higher with a capacity retention of 80% after 500 cycles, while the initial CE and average CE should exceed 90% and 99.8%, respectively (Figure 1). Accordingly, the pressing density should reach ~1.65 g/cm^3, and electrode swelling should be restricted to ~10%.[11]

Recently, the co-utilization of Si and graphite has emerged as the most practical anode for high-energy LIBs. Graphite is a commercial anode with low cost, high CE, excellent cycle life, good mechanical flexibility, only small volume change, and high electrical conductivity. The addition of graphite into Si can buffer the volume change, increase the electric conductivity, and achieve high specific, areal and volumetric capacities at the same time. Moreover, the co-utilization of Si and graphite can use the same commercial production lines, translating into high manufacturability and minimal investment. Therefore, the co-utilization hybridizes two distinct anodes on the materials level into a single composite, retaining the advantages while circumventing the disadvantages of both, and can secure its success in the anode market. However, it is still a challenge to integrate the Si and graphite into a single system or composite to

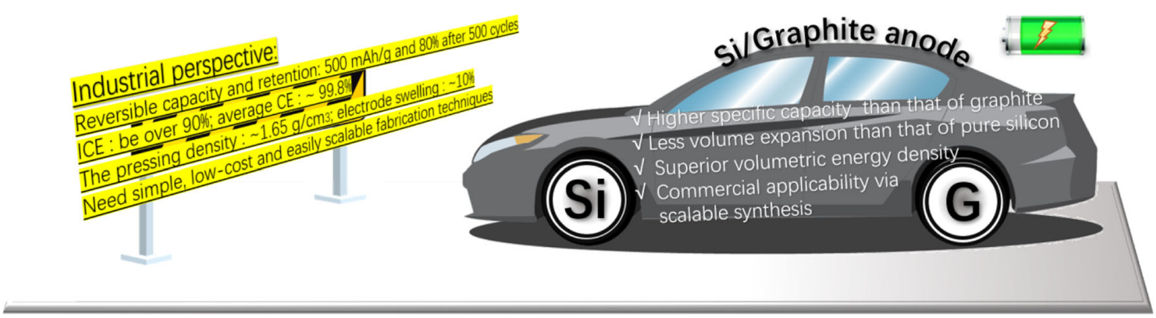

FIGURE 1 Schematic illustration of "dual-core" (Si and graphite)-powered vehicle, showing many advantages and also obstacles from the industrial perspective that need to be addressed in the near future. CE, coulombic efficiency; Si, silicon

obtain the desired performance, since both of these materials are significantly different in terms of their physical and chemical properties. Growing research efforts have been devoted to improving and achieving high electrochemical performance with the design and development of Si/G/C composite. The carbon additives play important roles in integrating the Si and graphite from many aspects, such as increasing the interface bonding between the graphite and Si, alleviating the volume variations of Si, and improving the interfacial chemistry, conductivity, and mechanical integration. This review attempts to highlight the critical role of carbon additives, as well as the associated synthesis methods and structures for achieving high-performance Si/G/C composites for developing high energy-density LIBs, and aims to provide possible insights for the future development of practical Si/G/C anodes.

2 | CHALLENGE OF THE INTEGRATION OF SILICON AND GRAPHITE ANODES FOR HIGH-ENERGY LITHIUM-ION BATTERIES

The co-utilization of graphite and Si is challenging because the issues for Si are still present in the Si/graphite (Si/G) composites. Due to its high specific capacity, Si has a major influence on the electrode performance of Si/G composites, even with small contents. For example, the cycle life of Si/G composites can be gradually improved as the content of graphite is increased, but this reduces the specific capacity.[12] Increasing the ratio of Si to graphite can increase the specific capacity, but has the risk of introducing severe volume change and limited cycling performance.

As discussed above, Si anodes suffer from significant volume change, leading to the degradation of the electrode structure, loss of contact between the active material and the conductive network, and unstable SEI formation. The severe volume changes of Si are also responsible for the major failure mechanism of the Si/G composite. Compared to Si, graphite has low volume expansion upon lithiation (~10%); so the addition of graphite can partly alleviate the huge volume changes of Si, since graphite can be a good mechanical buffer matrix, but it is hard to completely control the volume changes due to the poor interface adhesion between graphite and Si. Meanwhile, the huge difference in the volume changes of graphite and Si during cycling would result in electrical contact loss for graphite, leading to additional deterioration. A recent investigation on Si/G composite revealed that graphite loses its intrinsic capacity after cycling, because the graphite particles become isolated from the electrical network due to the deterioration of the microstructure of the electrodes caused by volume expansion of the Si particles, cracks, and excessive SEI formation at the interface.[13]

The repeated volume changes of Si during cycling process can seriously change the morphology of Si/G composite. It has been reported that the Si nanoparticles turn into nanoporous structure with very large surface area as a result of repeated cycling, which leads to electrode swelling with rearrangement of the electrode components, and thus disrupts the electrode.[14] The huge increase in the surface area due to the change into the nanoporous structure provides abundant sites for the electrolyte decomposition. Meanwhile, the strong mechanical stress derived from the volume expansion can break the SEI layer and will consume electrolyte to generate new SEI. The repeated breaking and repair of the SEI will not only lead to the accumulation of SEI layers but also the drying out of the electrolyte, leading to consistent capacity fading.

To mitigate the stress and strain from the volume change, nanosized Si has been mainly used to prepare the Si/G composites, but the cost of nanosized Si needs to be clarified. Although nanosized Si can be more strongly bonded to the graphite matrix, the Si/G composites still suffer from the critical incompatibility between the irregular particle sizes of Si and graphite. On the contrary, tuning the morphology, size, and surface area of graphite may increase the compatibility of graphite with Si via controlling the distribution of Si and graphite in the composite, but it is also a challenge to homogeneously distribute or embed the Si particles in the microsized graphite and retain the homogeneity of the Si/G composite morphology.

3 | INTEGRATION OF SI AND GRAPHITE VIA CARBON ADDITIVES FOR ACHIEVING HIGH-PERFORMANCE SILICON/GRAPHITE/CARBON COMPOSITE ANODES

Simple mixing of Si and graphite cannot provide an intact and robust matrix to alleviate the drawbacks of Si/G composite mentioned above, due to the loose connections among the graphite particles and the poor interface adhesion between graphite and Si, so that the improvement in performance is limited. To achieve a high-capacity and stable Si/G composite, it is critical to tailor the structure, morphology, and surface to maximize the benefits of the combination of Si and graphite. For this

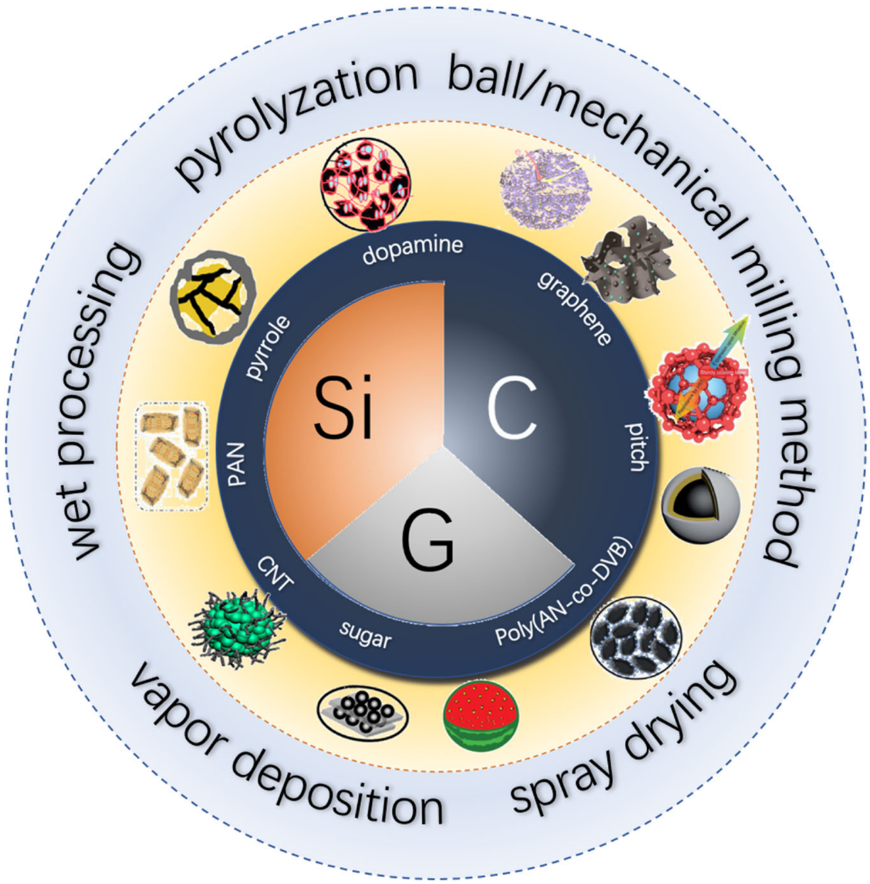

FIGURE 2 Strategies and structures of Si/G/C anodes prepared with diverse carbonaceous materials and various methods. Reproduced with permission: Copyright 2016, Royal Society of Chemistry[15]; Copyright 2017, Elsevier[16]; Copyright 2018, Wiley-VCH[17]; Copyright 2018, Wiley-VCH[18]; Copyright 2018, Royal Society of Chemistry[19]; Copyright 2013, Society of Powder Technology[20]; Copyright 2016, Wiley-VCH[21]; Copyright 2016, Elsevier[22]; Copyright 2019, American Chemical Society[23]; Copyright 2018, Royal Society of Chemistry[24]; Copyright 2017, Elsevier[25]

purpose, other various carbon additives have been widely introduced to construct this desirable structure, morphology, and surface via various scalable synthesis methods (Figure 2).

Compared with silicon, carbon materials have similar characteristics, and they can combine closely with each other. The addition of carbon additive within the Si/G composite can act as a glue to form strong interface bonding between the graphite and the Si, and enable a uniform distribution of Si particles on the graphite. On the other hand, different kinds of micrometer-sized hierarchical structures, originating from the introducing carbon additives or organic carbon sources, can be constructed with a uniform conductive network, good electrical conductivity, good adhesion, and high chemical stability, benefiting from better electrical conductivity and for a better ability to accommodate volume change. Furthermore, as one of few materials that have both electrical and ionic conductivity, carbon coating has been widely used to improve the interphase chemistry, conductivity, and mechanical integration of the Si/G composites. Therefore, carbon additives have been intensively used to prepare the Si/G/C composites with the combination of hierarchical structures and surface modification to maintain high-capacity and long-cycling stability.

Using different nanostructures to buffer the volume change of Si has achieved academic success, but their drawbacks such as low tap density, low CE, and complicated synthesis have hindered the real application. However, these delicate designs, such as core-shell and sandwich structures, have been leveraged to tune the morphology of secondary structures of Si/G/C composites. In these micrometer-sized structures, Si can be well distributed in the secondary structure, which not only retains the advantages of the nanoscale, but also eliminates its associated drawbacks to integrate nanosized Si with micrometer-sized graphite. Furthermore, the specific surface area of the micrometer-sized structures can be minimized to favor the formation and retention of a stable SEI upon cycling. It is also desirable to tailor appropriate voids inside the structures to buffer the volume change of Si and maintain the robust structure. Creating the pores on the carbon shell is also welcomed, which not only accommodate the volume changes in the composite, but also impregnate liquid electrolyte into the structure for ensuring a high electrochemical active surface area. Moreover, the secondary micrometer-sized Si structures usually exhibit a higher tap density than that of pure Si nanostructures, which is critical for the design of practical LIBs. The fabrication of micrometer-sized Si/G/C composites is mainly also relied on one simple, low-cost, and easily scaled up manufacturing method, such as ball milling/mechanical milling, spray drying, chemical vapor deposition (CVD), or wet processing, or on combinations of these methods, and the selection of raw carbon materials can also be broad.

In the last decade, tremendous efforts have been made to combine different forms of carbon additives with Si and graphite to form uniform conductive network structures and to prepare Si/G/C composite materials with good electrical conductivity, good adhesion, and high chemical stability. The various carbon additives create great differences in the contact between the Si nanoparticles, graphite, and carbon matrix, as well as the whole structure, which also has a profound effect on the electrochemical performance of the composites. Before constructing high-performance Si/G/C composite anode, the following critical issues should be addressed: the homogeneous distribution of Si particles on the graphite and the carbon matrix; the fabrication of microsized secondary structures consisting of uniform and clustered nanosized or microsized primary particles to achieve both high-gravimetric and high-volumetric energy densities; optimization of the ratio between Si, graphite, and carbon materials; and a facile and economical synthesis technique to achieve large-scale production. In the following sections, the progress on Si/G/C composites and their modifications in recent years are carefully discussed according to the type of carbon additive to reveal the architectural design and surface modification.

3.1 | Carbon nanotubes and reduced graphene oxide

Carbonaceous additives can be roughly classified into two types: the first one acts as a conducting matrix directly without further pyrolysis, such as carbon nanotubes (CNTs) and reduced graphene oxide (rGO); while the other type includes the pyrolyzed carbon derived from organic carbon sources, such as pitch, sugars, and so forth, that can act as a conductive and protective layer or network to enhance the contact between Si and graphite. CNTs are commonly used as a carbon additive to improve the performance of electrodes.[26,27] They not only have high electrical conductivity (resistivity, $<10^{-1}\ \Omega\,cm$),[28,29] but also show superior physical properties such as large aspect ratio, excellent mechanical strength,[30,31] structural flexibility, and tortuosity.[32] Therefore, combining Si/G with carbon nanotubes is a reasonable strategy.

Li et al[33] compared Si/G composites with and without CNTs (commercial CNTs) as anode for LIBs. In This study, Si/G/CNTs composite was synthesized by ball milling-dried nano Si, graphite, and CNTs, followed by carbonization. The Si/G/CNTs exhibited a better reversible capacity (1900 mAh/g) and capacity retention (86%) than those of Si/G (1800 mAh/g and 43%) at 350 mA/g in the first 35 cycles. Nyquist plots indicated that the Si/G/CNTs electrode had much smaller resistance than that of Si/G, demonstrating that CNTs could provide strong compensation for poor electronic conductivity of Si/G, increasing the charge transfer, and improving the cycling efficiency.[34] Similarly, in the work of Zhang et al,[35] a composite of Si/G/CNTs was also prepared, but CNTs were multiwalled CNTs (MWNTs) from a catalytic decomposition method.[36] The denoted Si/G/MWNTs presented an average reversible capacity of 584 mAh/g in the first 20 cycles. These two works highlighted the superior conductive function of CNTs for Si/G systems, but also indicated that it was not sufficient to address the drawbacks of Si/G by simply adding CNTs alone. On the contrary, the selection of the proper type of CNTs may be also a critical point for further enhancing the electrochemical performance of Si/G.

To increase the functionality of CNTs, Li et al[23] pretreated the silicon and then combined it with CNTs and graphite. In this study, the product B-Si/CNT@G, wherein the porous Si was doped with boron and wedged tightly by CNTs (Figure 3A), presented an average capacity of 450 mAh/g with 83.4% cycling retention for over 100 cycles. Although the role of boron is not clear, the sea-urchin-like composites with numerous spine-like CNTs could not only provide superior structural compatibility of Si with the graphite matrix to enhance the structural integrity of B-Si/CNT@G during long cycling, but was also favorable to ion diffusion and electrical conductivity. On the contrary, Yang et al[37] added pitch together with CNTs (Figure 3B). In this study, a ~5-μm spherical structure was constructed where the graphite was fully and evenly coated with Si powder and CNTs, and the silicon was encapsulated well by a carbon layer derived from pitch with a thickness of 4.5 nm. In this structure, the carbon layer could buffer the volume changes of Si and enhance the interface stability, while the CNTs acted as an interconnected conductive network and also helped the dispersion of Si particles. As a result, one of the products, denoted as pitch-C3, showed the best reversible capacity (810 mAh/g) with a capacity retention of 81.3% after 100 cycles at 100 mA/g when the amount of pitch was optimal. Compared with the previous work only using CNTs,[35] adding another organic carbon source such as pitch along with the CNTs was beneficial to further improve the electrochemical performance of Si/G/CNTs materials, but the added amount and type needed subsequent optimization.

rGO is a two-dimensional (2D) carbon nanomaterial and its sp^2 hybrid orbitals construct a hexagonal honeycomb-like lattice, which has received continuous

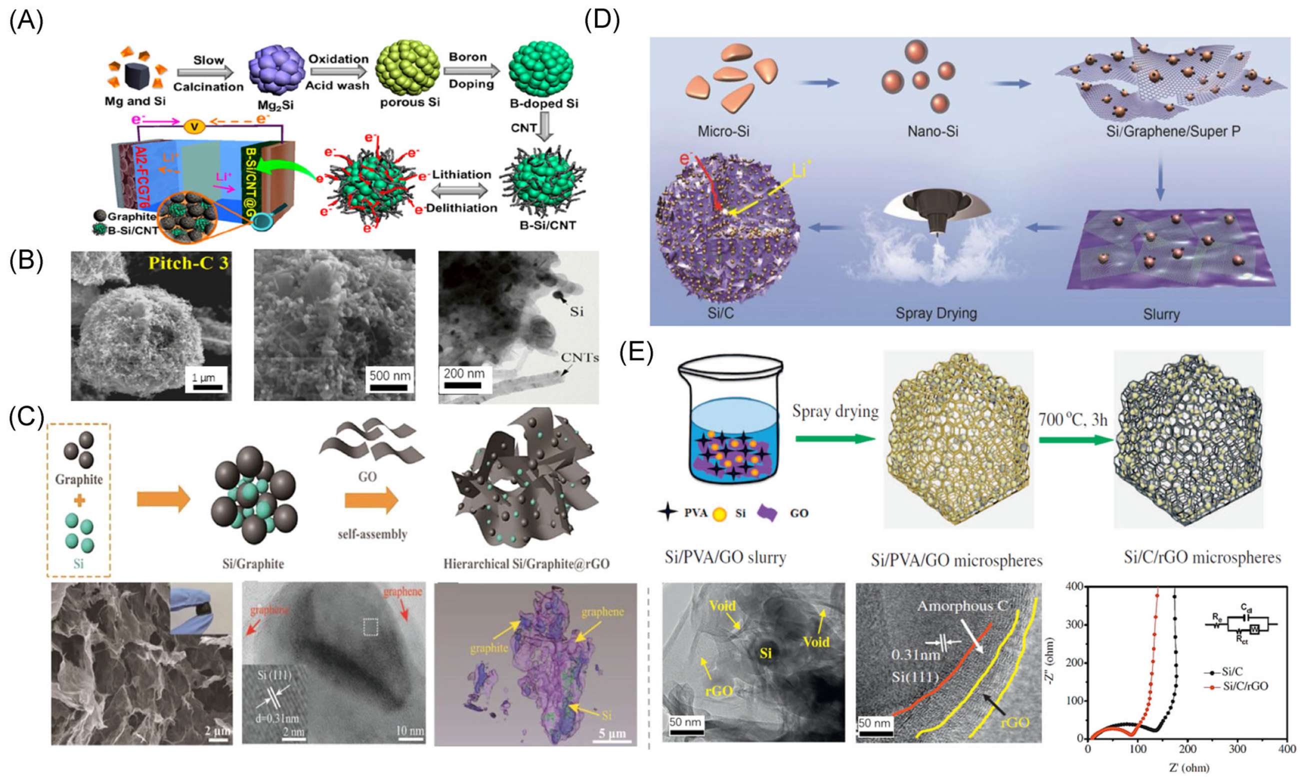

FIGURE 3 A, Schematic illustration of the preparation of B-Si/CNT@G. Reproduced with permission from Reference,[23] Copyright 2019, American Chemical Society. B, Scanning electron microscope (SEM) images of pitch-C3 at different magnifications and its transmission electron microscope (TEM) image. Reproduced with permission from Reference,[37] Copyright 2017, Elsevier. C, Fabrication of hierarchical Si/G@rGO and its SEM image, with the inset a photograph of Si/G/GF-5 hydrogel; corresponding high-resolution TEM (HRTEM) image, with the inset the characteristic (111) plane of Si; illustration of three-dimensional microstructures of Si/G/GF-5. Reproduced with permission from Reference,[17] Copyright 2018, Wiley-VCH. D, Synthesis of spherical Si/C granules. Reproduced with permission from Reference,[16] Copyright 2017, Elsevier. E, Preparation of porous Si/C/rGO microspheres; TEM and HRTEM images of Si/C/rGO; Nyquist plots of Si/C/rGO and Si/C before cycling with the equivalent circuit in the inset. Reproduced with permission from Reference,[38] Copyright 2017, Elsevier

attention and enthusiasm in the field of energy conversion and storage due to its admirable electronic conductivity, large specific surface area, outstanding structural flexibility, superior surface to volume ratio, and ultra-thin thickness.[39-41] Besides these, graphene is also an ideal 2D matrix for supporting nano-Si, similar to the conventional carbon matrix.[42,43] Therefore, graphene has also been well used in building Si/G/rGO composites.

Zhu et al[17] designed a three-dimensional (3D) hierarchical structure, wherein Si powders were dispersed evenly on commercial graphite and then encapsulated with a hierarchical rGO scaffold (Figure 3C).[44] The Si/G/GF-5 with Si nanoparticles (NPs) in a weight ratio of 5 wt% exhibited a reversible capacity of 445 mAh/g after 300 cycles at 372 mA/g, with only 0.07% capacity fading per cycle. The superior electrochemical performance of the Si/G/rGO composite could be attributed to the unique hierarchical structure resulting from the addition of rGO. The highly interconnected 3D graphene framework with porous structure not only promoted the transportation of electrons and Li^+ ions, but also effectively avoided the aggregation of Si NPs and alleviated their volume expansion. Considering the scale of production at the industrial level, Xu et al[16] utilized micron-sized Si as raw material to fabricate affordable Si/G/rGO composite, which contributed to reduced cost and prevented the oxidation of nano-Si (Figure 3D). In This study, micron-sized Si powder was sand milled into nanosized Si, first by using phenolic resin, polyvinyl pyrrolidone (PVP), and sodium alginate as grinding aid reagents. Then, the Si/G/rGO composite was synthesized via ball milling, spray drying, and heating processes. The Si/G/rGO spheres showed an initial CE of 75.64% and high cycling stability at the mass loading of 4.0 mg/cm^2. A capacity retention of 86% could be maintained even after 500 cycles. Tao et al[38] also prepared porous Si/C/rGO microspheres with double carbon layers via a scalable synthesis method that involved spray drying and carbonization process (Figure 3E). In this study, polyvinyl alcohol (PVA) was used as a cross-linking agent and source material for amorphous carbon (AC). The Si/C/rGO electrode showed high-capacity retention of 98% after 70 cycles, retaining about 928 mAh/g. The increased electrochemical performance of Si/C/rGO was confirmed by electrochemical impedance spectroscopy according to the Nyquist plots, where the charge-transfer resistance of Si/C/rGO (73 Ω) was lower than that of Si/C (127 Ω), benefiting from the hierarchical structure as well as the large number of voids and double carbon layer from the carbonization of PVA and rGO.

In general, both CNTs and rGO can positively optimize the electrochemical performance of the Si/G/C composites. CNTs play the role of a "highway," connecting the whole of the Si/G bulks and greatly improving the efficiency of electron conduction. Choosing CNTs of the proper type and size can further optimize and upgrade the performance of Si/G/C composite anodes. It is highly recommended to use CNTs in conjunction with other carbonaceous materials. The price advantage of CNTs is obvious compared to rGO, but rGO is effective in constructing 3D-conducting networks and for designing porous structure, which is beneficial to achieve high performance. However, the wide use of rGO is limited by the difficulty and cost of large-scale preparation. Although rGO has already been commercialized, the price is still high, especially for high-quality rGO. This may be unaffordable for battery manufacturers.

3.2 | Carbon derived from pitch

In the case of the pyrolyzed carbon, pitch, as one of the most economical carbonaceous precursors, is widely used to integrate the Si/G composite. Pyrolyzed carbon from pitch offers the following advantages to the Si/G system: (a) it has sufficient elasticity to effectively inhibit the volume expansion of Si during long-term lithiation-/delithiation-cycling processes; (b) it acts as a glue in the construction of a 3D network structure, which can effectively connect the graphite and the Si, and firmly keep Si in the network during charging and discharging processes; and (c) as a by-product of industry, pitch is inexpensive and easy to obtain.[45-47]

In early 2006, Uono et al[48] reported a "surface-coat-type" composite of Si, carbon (pitch), and graphite, fabricated by a milling process and heat treatment. They concluded that the small particle size of Si (100 nm) and the large particle size of graphite (30 μm) were beneficial for decreasing the composite's surface area, leading to low irreversible specific capacity. In 2008, Lee et al[49] designed spherical Si/G/C composites based on pitch via a ball milling method. The composite presented a high reversible capacity (700 mAh/g) and a superior initial CE (86%). In 2010, Jo et al[50] compared two types of existence of Si in the composites (Si-G-C_{pitch}): in one, the Si particles existed on the surface of graphite (type A), and in the other, the Si particles were embedded in the graphite (type B). It was found that the charge (657 mAh/g) and discharge (568 mAh/g) capacities of type B were both higher than for type A, but these two types had the same cycling CEs. However, these early works mainly dealt with a dry ball milling process, in which Si and graphite were mixed in the solid state without other additive solvents, which might lead to the agglomeration of Si particles, the demolition of the graphite, and insufficient adhesion between Si and graphite, resulting in a limited cycle life.

For improving the electrochemical performance, several different synthetic methods for using pitch in composites were explored and compared. So, Kim et al[51] designed a facile strategy for carbon-coated Si/G spherical composites via wet processing. As shown in Figure 4A, the transmission electron microscope (TEM) images indicated that Si was loaded on the surface of graphite successfully and fully encapsulated by an AC layer as well. The Si-C-G-20 composite exhibited a specific capacity of 805 mAh/g at 130 mA/g, and maintained more than 81.7% of its initial capacity after 50 cycles. Moreover, reducing the Si content in the composite decreased the reversible capacity while the initial CE increased. It was also demonstrated that the AC could tolerate the volume expansion of the embedded Si NPs and maintained the structural integrity of the Si-C-G composites. The reported number of cycles was limited to only 50 cycles, which was not ideal. It indirectly reflected the problem that it was difficult to achieve good dispersion by stirring and ultrasound, where the agglomeration of silicon particles is detrimental to the cycling performance of the battery. To achieve good dispersion, in addition to using the mechanical stirring, Li et al[52] explored the merits of pretreating silicon and graphite before mixing (Figure 4B). In their work, both the graphite and silicon were first treated by polydiallyldimethylammonium chloride (PDDA) and poly(sodium 4-styrenesulfonate), respectively, to become surface-charged because of the dissociation of the polymer salts. After further coating with PDDA and poly(acrylic acid), the multiply coated sample, denoted as P&C-Si@G, showed substantial enhancement in long-term cycling stability, with 95% of initial capacity retained even after 200 cycles. It could be clearly seen that the pretreatment of Si and graphite helped to achieve better dispersion. Unlike the "pretreatment", Yang et al[53] proposed the concept of "posttreatment" with CH_3COOLi and NH_4F (Figure 4C). They introduced a comodified silicon/graphite (SG) with pitch

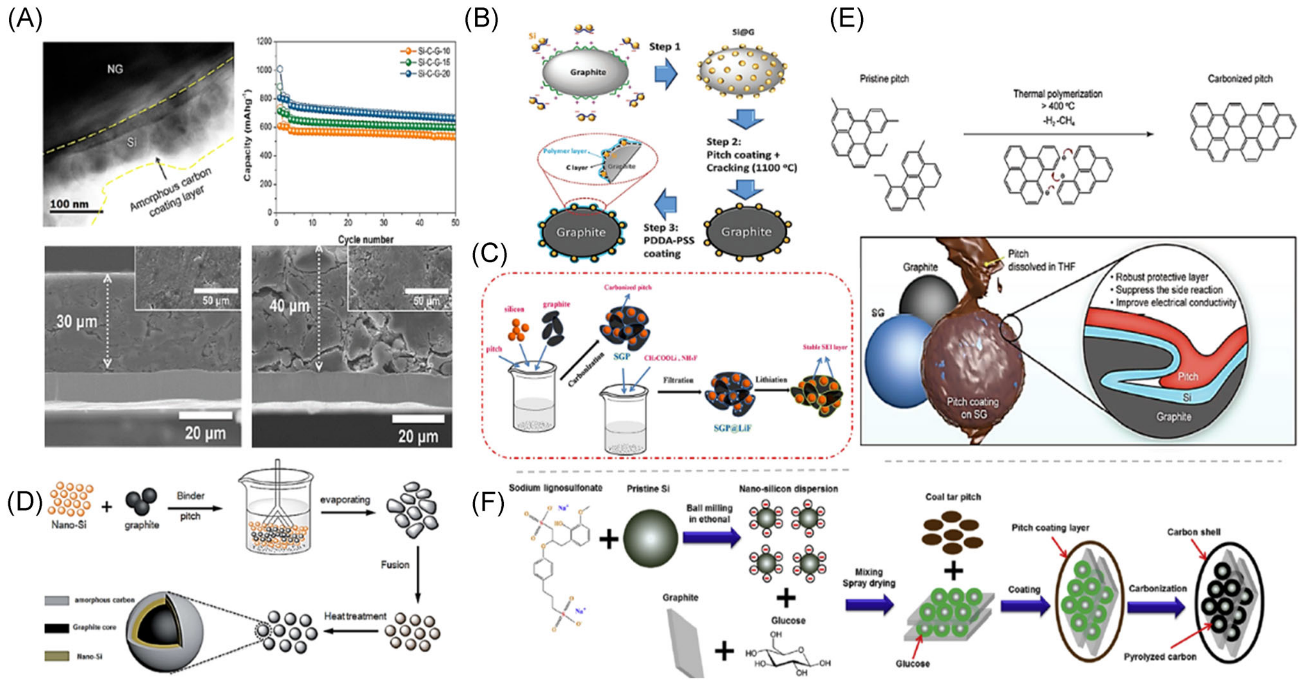

FIGURE 4 A, Bright-field transmission electron microscope (TEM) image of Si-C-G composite and its cycling performance at 0.2 C for 50 cycles; cross-sectional scanning electron microscope images of Si-C-G-15 in the pristine state and after the 50th cycle. Reproduced with permission from Reference,[51] Copyright 2016, American Chemical Society. B, Schematic illustration showing the synthesis process of the polymer–carbon-coated Si-on-graphite (P&C-Si@G) powder. Reproduced with permission from Reference,[52] Copyright 2016, Royal Society of Chemistry. C, Schematic illustration of the SGP@LiF preparation. Reproduced with permission from Reference,[53] Copyright 2017, Elsevier. D, Schematic illustration of the preparation of Si-G/C. Reproduced with permission from Reference,[19] Copyright 2018, Royal Society of Chemistry. E, Schematic illustration of the transformation mechanism for pitch during carbonization and the detailed structural features of pitch in SGC_{pitch}. Reproduced with permission from Reference,[18] Copyright 2018, Wiley-VCH. F, Synthesis procedure for G/Si@C. Reproduced with permission from Reference,[22] Copyright 2016, Elsevier

and lithium fluoride (LiF), which synergistically helped to accommodate the volume changes, reduce the side reactions, and form a stable SEI layer. As a result, their sample, denoted as SGP@LiF, delivered a capacity retention of 82.3% after 100 cycles. These results suggested that the "posttreatment" method should also be considered feasible, where the pitch carbon layer greatly buffered the volume changes and helped to provide good electrical conductivity, while LiF was helpful for forming a stable SEI, reducing the decomposition of electrolyte on the surface.

As a representative of the industry, Xiao et al[19] of BTR New Energy Materials Inc reported a Si-G/C composite with core-shell structure that was synthesized via a feasible three-step process including stirring-evaporation, fusion, and heat treatment (Figure 4D). The as-prepared Si-G/C composite anode demonstrated a first-cycle capacity of about 650 mAh/g, over 90% CE, and high-capacity retention of 96.7% after 50 cycles. More importantly, the commercial viability was certified via a full cell with battery capacity of around 3000 mAh, using Co-Al co-doped lithium nickel oxide (NCA) as the cathode material and Si-G/C as anode. The full cell exhibited a high cycling CE of 99.5% and superior cycling stability with more than 81% capacity retained for over 1200 cycles. This reported method was simple and scalable, without additional "pretreatment" or "post-processing", and the obtained Si-G/C showed excellent performance in the full cell, although the details of the synthesis process and fusion were not described clearly, so more comparison of the transformation from the amorphous structure to the spherical structure is needed.

Compared with the mechanical and wet-mixing methods, CVD has unique merits. Apart from the relative simplicity of the process, it is also favorable for obtaining a nanoscale coating layer with a uniform and controllable thickness. In the earlier work of Ko et al,[54] they used high-purity silane gas to obtain the homogeneous deposition of silicon on graphite powder, and then coated it with carbon via the decomposition of acetylene gas to synthesize SGC composite. In their later work, the same method was employed to prepare Si/G, in which they replaced acetylene with pitch as the carbon coating material to achieve $Si/G/C_{pitch}$ (Figure 4E).[18] For comparison, $Si/G/C_{acetylene}$ and $Si/G/C_{sucrose}$ were also prepared by the same process. They found that the $Si/G/C_{pitch}$ showed better performance than $Si/G/C_{acetylene}$ and much better performance than $Si/G/C_{sucrose}$, indicating that the coating effect of pitch was better than those of acetylene and sucrose. Moreover, the pitch was safer than acetylene, as the acetylene was prone to explosion and might cause significant damage or even be dangerous.

In addition to the strategy of using one type of carbonaceous material, the use of two or more carbon material sources is also an interesting concept. Li et al[22] reported a core-shell structured G/Si@C based on glucose and pitch, which were produced via scalable and economical methods, including ball milling, spray drying, and pyrolysis. In this structure, internal pyrolyzed-carbon obtained from glucose could be well used to marry silicon and graphite, providing good physical and electrical connections; while external pyrolyzed-carbon obtained from pitch could effectively hold the whole structure of G/Si@C together (Figure 4F). The G/Si@C presented capacity of 570.5 mAh/g after 100 cycles with 89.5% capacity retention and a high CE (99.5%). Therefore, in addition to a simple single-layer coating method, a double- or multiple-layer coating method can also be considered, wherein silicon and graphite were first coated with a layer of carbon and then the whole structure were coated with another layer of carbon. The internal glucose carbon and the external pitch carbon played different roles, with the former serving the function of connecting Si and graphite, and the latter serving to support the entire structure. The details of the positive effect of internal glucose-derived carbon were not given, and there was no comparison between the composite with and without glucose-derived carbon under the same conditions.

In summary, numerous experimental results have proved that pitch can effectively integrate the Si/G composite and also significantly improve its electrochemical properties. By selecting a suitable synthesis method, as well as a suitable strategy, such as pretreatment or posttreatment, the electrochemical performance of Si/G/C can be further enhanced. Moreover, it is a worthwhile strategy to use two or more carbonaceous materials, rather than being limited to pitch as the only carbon source. In addition, the source of the pitch has not been highlighted, as pitch can be classified as natural or manufactured; derived from petroleum, coal tar, or plants. Various forms of pitch (such as tar, bitumen, or asphalt) may lead to different coating effects, which may attract more attention.

3.3 | Carbon derived from sugar

Sugars such as glucose and sucrose are also often chosen as carbonaceous precursors because they are relatively available, nonpolluting, and economical. In 2012, Lai et al[55] reported a Si/G/C composite prepared via spray drying and subsequent pyrolysis (Figure 5A). This composite contained glucose-pyrolyzed carbon as a protective layer. They also investigated and compared the performances of different materials, such as glucose-pyrolyzed carbon, flake graphite, and Si/G/C composite. Among them, the Si/G/C composite had the largest reversible capacity of 600 mAh/g, which benefited from two main reasons: the nano Si was well coated by flake graphite and glucose-pyrolyzed carbon, and micron-sized pores in the composites could effectively buffer the volume changes of silicon during cycling.[58] Similarly, in 2013, they[59] designed a silicon/flake graphite/carbon (Si/FG/C) composite via carbonizing glucose. The difference from their previous work was that two kinds of dispersants were added to avoid agglomeration of Si and the flotation of graphite in this study. The initial CE of Si/FG/C was 69.71%, and the average cycling capacity was 602.68 mAh/g over 20 cycles. From the above discussion, the glucose-derived carbon could increase the specific capacity of Si/G composite, but both of these works only tested up to 20 cycles, and the addition of dispersants brought no apparent benefits; so it was hard to know whether glucose carbon is helpful for maintaining the long-term stability of Si/G.

Unlike the former sugar-derived AC, Jeong et al[56] used sucrose as a carbon source and fabricated hard-carbon-nano-Si/graphite (HC-nSi/G) through a hydrothermal process and carbonization step (Figure 5B). The obtained HC-nSi/G exhibited agglomerated secondary particles with a size of around 10 μm, and the hard carbon layer thickness was around 1 μm. The HC-nSi/G with 14.6 wt% silicon showed an areal capacity of 1.5 mAh/cm^2 at 0.05 C during the first few cycles, and it reached 1.43 mAh/cm^2 at 0.2 C with capacity retention of 86% for over 150 cycles. However, the direct use of commercial nano-silicon powder is extremely expensive and if the initial raw material is micron-sized silicon, the production cost will be greatly reduced. Sui et al[57] made an attempt in this regard. They reported a ternary core/shell SiGC composite, wherein micron-sized Si powders were ball milled in alcohol to form nanosilicon, and then milled with graphite and sucrose (Figure 5C). The Si/G/C exhibited a reversible capacity of 736 mAh/g at 500 mA/g and excellent stability over 300 cycles (83.6% capacity retention), which was superior to similar reports in literature.[60,61] The excellent results came from the AC shell, which relieved the pressure of Si expansion and promoted stability. The carbon shell could also strengthen the connections between the active material and the current collector to maintain the integrity of the electrode.[62,63] This study uses micron-sized silicon instead of the much more expensive nanoscale silicon,

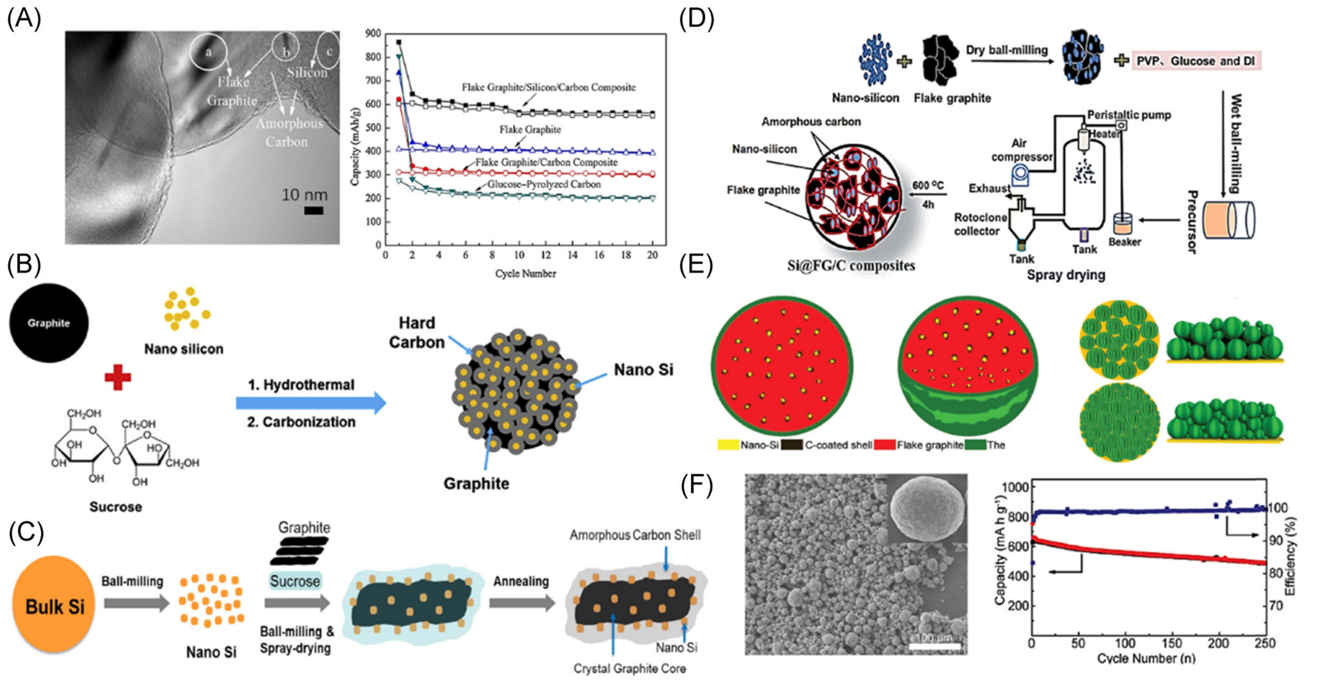

FIGURE 5 A, High-resolution transmission electron microscopy image of Si/G/C composite; charge/discharge plots of flake graphite, glucose-pyrolyzed carbon, flake graphite/carbon composite, and flake graphite/silicon/carbon composite. Reproduced with permission from Reference[55] Copyright 2012, Elsevier. B, Synthesis of HC-nSi/G via a hydrothermal process and carbonization step. Reproduced with permission from Reference[56] Copyright 2016, Elsevier. C, Synthesis of SiGC with graphite core, nano Si, and carbon shell from graphite, bulk Si, and sucrose. Reproduced with permission from Reference[57] Copyright 2018, Elsevier. D, Schematic illustration of the synthesis process for Si@FG/C. Reproduced with permission from Reference[15] Copyright 2016, Royal Society of Chemistry. E, Schematic illustration of watermelon-like Si/C microspheres; packing model of Si/C, and optimized model of Si/C with better size distribution. F, Scanning electron microscope image of Si/C and cycling performance of densely compacted Si/C anode at 55℃, with the current density 0.1 C for the first five cycles and 0.5 C for the remaining cycles. Reproduced with permission from Reference[21] Copyright 2016, Wiley-VCH

and the preparation method is easy to scale up, making it suitable for future industrial production. However, for practical application, the parameters of various aspects, such as the ratio of active materials to other additive agents and the areal density of the anode electrode slurry, should meet the industrial standard. In 2016, Wang et al[15] reported a controllable and scalable method to prepare silicon@flake-graphite/amorphous carbon (Si@FG/C) composite. Their preparation method was similar to that of Sui et al,[57] mainly including dry/wet ball milling, spray drying, and carbonization (Figure 5D), but two carbonaceous materials, glucose and PVP, were used. The binding effect of glucose and PVP was not only responsible for the formation of the spherical structure, but also induced a strong AC layer, which not only fixed the Si particles but also absorbed the mechanical strain arising from the volume changes during cycling. It was also pointed out that a higher AC content would be favorable for cycling stability but cause a low initial CE. Therefore, the ratio of Si, FG, and AC was a vital factor in achieving more optimized electrochemical performance.

In the following year, Xu et al[21] used glucose and PVP as carbon sources to prepare watermelon-inspired Si/C microspheres, as depicted in Figure 5E. Just like the watermelon, the silicon resembled watermelon seeds embedded in the red flesh graphite, and then the outside was wrapped by the melon peel-AC. The synthesis was performed by vigorous stirring of the silicon, flake graphite, glucose, carboxymethyl cellulose and PVP by ball milling, which was followed by the spray drying. The Si/C reached areal capacity of 2.54 mAh/cm^2, and it remained above 1.91 mAh/cm^2 after 500 cycles. More interestingly, superior performance was achieved at both high temperature (55°C) and low temperature (−20°C) (Figure 5F). This superior performance over a wide range of temperature showed that batteries containing this Si/C anode could be used to some extent in extreme environments. Therefore, space-efficient packing, that is, mixing different sizes of active particles properly, could increase the tap density and thus enhance the energy density, which was worth learning. Moreover, exploring the influences of different temperatures on the battery should not be ignored by researchers for wide applications.

To sum up, thanks to the richness of sugars, in addition to the above, there are maltose,[64] lactose,[65] fructose,[66] and so forth, as well as complex sugars such as starch,[67,68] chitosan,[69-71] and cellulose,[72,73] which are also used in the field of battery research. Moreover, sugars are readily available, and the methods of collection and synthesis are mature. Sugars are more recommended for use with other carbon sources such as PVP, to improve the comprehensive performance of silicon-graphite materials. As a pyrolytic carbon source, sugars can effectively improve the stability of silicon-graphite composites, although the selection of suitable sugars and their amounts still needs to be optimized. In addition, compared with pitch, sugars lack the structure of aromatic hydrocarbons, and the degree of graphitization of the products after high-temperature carbonization is low, which is not efficient for increasing the conductivity of the anode materials. Carbonized sugars are less polluting than carbonized pitch because the latter substance is prone to generate carcinogens.

3.4 | Carbon derived from heteroatom polymers

Polymers containing heteroatoms, with the "electron imbalance" effect of heteroatoms, have shown extra benefit to conductivity, and we discuss them here, particularly in connection with polymers containing nitrogen atoms. In fact, the pitch, sugar, and PVP mentioned above actually contain nitrogen as well, but the nitrogen content of their pyrolyzed products has not been emphasized and analyzed by the authors. In addition, polydopamine (PDA) is a kind of heteroatom (nitrogen) doped carbon material with excellent electrical conductivity.[74] It could be self-polymerized from dopamine, easily adheres to the surface of different kinds of substances[75] and thus facilitates lithium ion transmission on the interfaces of the active material with the electrolyte.[76,77] Zhou et al[78] prepared a spherical Si/G/PDA-C material in a composite with N-doped carbon via a dopamine polymerization process and subsequent pyrolysis (Figure 6A). Energy-dispersive spectroscopy mapping of N element indicated that the Si/G/PDA-C was homogeneously coated by an N-doped carbon layer, which could not only prevent direct contact of the active material with the electrolyte, but also could help to improve the electronic conductivity of the composite. The Si/G without carbon coating faded dramatically, while the Si/G/PDA-C retained capacity of 457.1 mAh/g after 100 cycles at 1 A/g. This study illustrates that nitrogen-

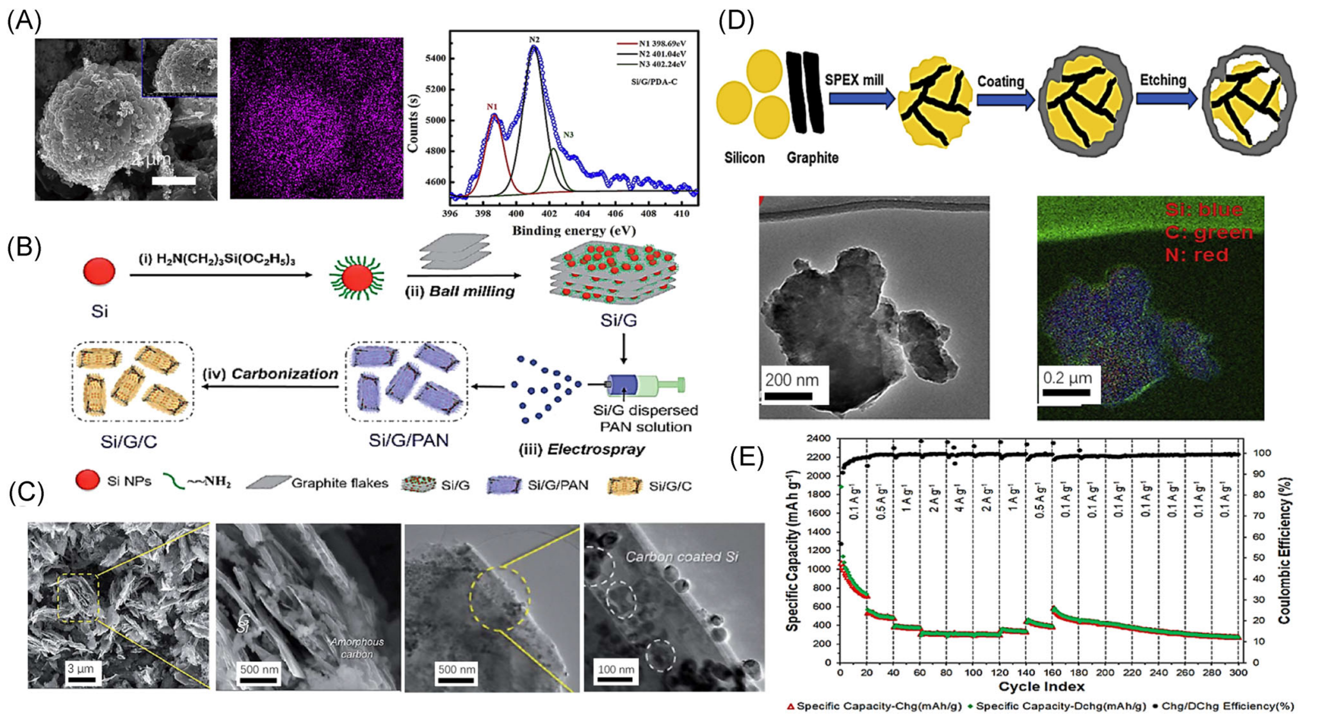

FIGURE 6 A, Field emission scanning electron microscopy (FESEM) images of Si/G/PDA-C and X-ray photoelectron spectroscopy (XPS) investigation of N element. Reproduced with permission from Reference,[78] Copyright 2016, Elsevier. B, Synthesis of Si/G/C via ball milling, electrospray, and carbonization. C, SEM and transmission electron microscope (TEM) images of Si/G/C at different magnifications. Reproduced with permission from Reference,[24] Copyright 2018, Royal Society of Chemistry. D, Synthesis of Si/Gr@void@C via a SPEX ball mill, carbonization, and chemical etching; SEM image of Si/Gr coated by pyrrole as precursor; energy-filtered TEM (EFTEM) and elemental mapping image of Si/Gr@void@C. E, Electrochemical performance of Si/Gr@void@C. Reproduced with permission from Reference,[25] Copyright 2017, Elsevier

doping could modify the properties of carbon such as electrical conductivity, but it would be better if there was a comparison of different nitrogen doping amounts.

Polyacrylonitrile (PAN) has high nitrogen content and can be obtained by radical polymerization of monomeric acrylonitrile. Moreover, PAN-based disordered carbon (PAN-C) could act as a diffusion barrier to prevent the interfacial reaction of graphite and silicon to form electrochemically inactive SiC during prolonged milling of graphite and Si.[79,80] Si/C composite coated with PAN-C was also proposed as a suitable anode material for lithium ion batteries. Liu et al[24] reported an electrosprayed Si/G/C composite, with the carbon derived from PAN (Figure 6B). SEM and TEM characterization indicated that the graphite in the Si/G composite was smooth and densely packed after ball milling, while the Si/G particles were coated well by the pyrolyzed carbon from PAN (Figure 6C). The Si/G/C exhibited excellent reversible Li^+ storage capability with a competitive capacity of 832 mAh/g at 200 mA/g and considerable capacity of 400 mAh/g at 500 mA/g after 200 cycles. The superior performance of Si/G/C benefited from its well-designed structure and AC layer derived from PAN, which formed a protective and elastic coating on the outside of the hybrid to bind/fix nano-Si onto graphite and prevent the formation of unstable SEI.

Polypyrrole (PPy) also has been considered as one of the candidates for an N-doped carbon source material because of its high electrical conductivity. It has been used with Si based anode martials,[81] contributing its dual-function as a binder and a conducting additive. Ashuri et al[25] reported nanostructured composites (designated as Si/Gr@void@C, where Gr is graphite) with a thin carbon shell and engineered voids via SPEX ball milling, carbonization, and chemical etching (Figure 6D). The carbon shell with the thickness of 5 to 20 nm was derived from the decomposition of pyrrole, and the voids were achieved after etching Si with NaOH solution. The batteries made with this tailored nanostructure exhibited superior electrochemical performance and a specific discharge capacity of~1800, 580, and 350 mAh/g at the first, 40th, and 300th cycle, respectively (Figure 6E). Two main advantages could be summarized from this study: (a) the carbon coating on the whole structure provided a long-range electrical network and good structural integrity with strong adhesion; (b) the voids inside the composite partially accommodated the huge volume expansion of Si during cycling, offering a stable particle/electrolyte interface for SEI layer formation around the particles, postponing particle pulverization and avoiding loss of electrical contact with the conductive additive.

Briefly, N-doped carbon derived from nitrogen-containing polymers has been successfully used to prepare Si/G/C composites for further tuning of the properties of carbon. In addition to nitrogen, there are also other elements such as phosphorus and sulfur that as members of the heteroatom-doping elements for the pyrolytic carbon family, have been recently reported for the preparation of silicon-based anode materials. Most of them also presented improved electrochemical performance.[82,83] The heteroatom-doped carbon can not only effectively protect the internal Si/G material, but also can enhance the conductivity, tune the surface activity, and thus improve the electrochemical properties of the composite. However, the most suitable content of heteroatoms has not yet been concluded and choosing the right type of heteroatom polymer with suitable content still lacks sufficient research.

3.5 | Other polymer-derived carbon

In addition to these typical carbonaceous materials mentioned above, there are still thousands of uncovered carbonaceous materials. It can be said that, whether they are natural or artificial, all carbon-containing materials may have their own characteristics and be useful to enhance the Si/G composites. Nevertheless, these potential treasures still require more exploration to prove whether they have practical value.

Phenolic resin (also named phenol formaldehyde resin) is a mature industrial synthetic polymer with low toxicity and a low price, which is obtained by the reaction of phenol or substituted phenol with formaldehyde. Su et al[20] reported a silicon, flake graphite, and phenolic resin-pyrolyzed carbon composite, denoted as Si/C. The SEM and TEM images (Figure 7A) exhibit an irregular morphology with a particle size less than 50 μm and three clear phases of Si, G, and phenolic resin-C. The Si/C exhibited an initial charge capacity of 640.51 mAh/g at 100 mA/g with a CE of 73.82%, which was higher than those of pure silicon and Si/C without annealing, as shown in the inset figure. This could be attributed to the good structure of the Si/C and further annealing of the electrode, which maintained a uniform electronic conducting network and had stronger cohesion between the binder and the current collector. The coated disordered carbon layer (5-nm thickness) on the Si/graphite powders could also provide an extra effective buffer during the insertion/extraction of lithium ions. By using LA132 ($-[-R_1-R_2-CH_2-CH(CN)-]-_n$), a kind of aqueous binder with strong adhesion and good dispersion capability, as the carbon source, Zhou et al[86] achieved better performance in their parallel work. The Si/G/L-C exhibited better capacity retention (73.68% in 40 cycles) than that of the composites containing phenolic resin-pyrolyzed carbon (52.63% in 40 cycles), although the cycling CEs and capacities

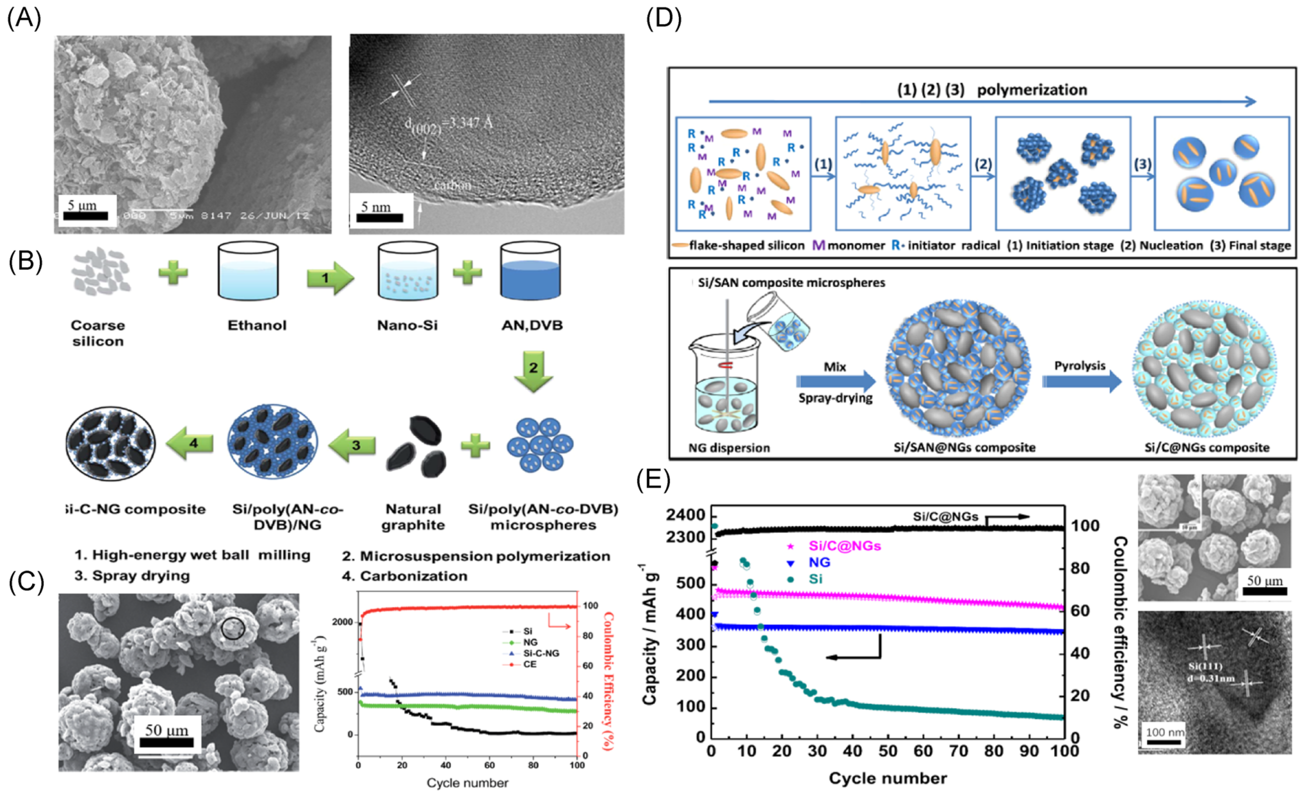

FIGURE 7 A, Scanning electron microscope (SEM) and transmission electron microscope (TEM) images of Si/C. Reproduced with permission from Reference,[20] Copyright 2013, Society of Powder Technology. B, Synthesis of Si-C-NG composite. C, SEM image and cycling performance of nano-Si, NG, and the Si-C-NG composites at 100 mA/g. Reproduced with permission from Reference,[84] Copyright 2016, Royal Society of Chemistry. D, Synthesis of Si/SAN composite microspheres and Si/C@NGs composite. E, The cycling performance of Si/C@NGs, NG, and Si for 100 cycles at a current density of 0.1 A/g; SEM image of Si/C@NGs and high-resolution TEM image of Si/C@NGs, with higher magnification in insets. Reproduced with permission from Reference,[85] Copyright 2016, Elsevier

of these two works were not competitive compared with the previously mentioned carbonaceous materials.

Mixing multiple polymers as carbon precursors is also one of the rational strategies for developing carbonaceous additives. Wang et al[84] reported a Si-C-NG composite, where NG is natural graphite, with two polymers—poly (acrylonitrile-co-divinylbenzene) (denoted as Si/poly(AN-co-DVB)) synthesized through ball milling, spray drying, and subsequent pyrolysis (Figure 7B and 7C). Through microsuspension polymerization, nano-Si was well encapsulated in chemically cross-linked poly(AN-co-DVB) microspheres, which could effectively restrict the agglomeration of Si and strengthen the bonding between Si and graphite via the conjugated carbon backbone from the pyrolysis of poly(AN-co-DVB). This Si-C-NG delivered a first charge capacity of 471.5 mAh/g and CE of above 96% for over 100 cycles at 100 mA/g. Wang et al[85] synthesized a silicon/carbon@natural graphite (Si/C@NGs) composite via spray drying-assisted self-assembly and a pyrolysis process by using two polymers (styrene-acrylonitrile copolymer [SAN]) as carbonaceous precursor (Figure 7D). The Si/SAN composite microspheres were obtained from flake silicon and the mixed monomers (styrene and AN) via step-by-step polymerization, and then they were thoroughly mixed with a natural graphite, followed by spray drying to form the Si/C@NGs composite. The Si/C@NGs exhibited an initial CE of 82.8% and capacity retention of 428.1 mAh/g after 100 cycles at 0.1 A/g (Figure 7E). This good electrochemical performance was ascribed to their multilayer carbon coating as well as their voids, which could alleviate the structural changes in Si during charging/discharging. These two innovative works used two polymers as carbonaceous coating materials, but both experimental steps were cumbersome and complicated. The performance of the obtained anode materials was also not so eye-catching, which is undoubtedly disadvantageous for achieving industrial production.

In short, there are many choices among the carbonaceous materials, but in the first choice of a suitable carbonaceous material, it needs to be considered whether they can be industrialized. Complex synthetic methods will increase the cost of production, and thus, not all carbonaceous materials are suitable. Therefore, the selection of superior carbonaceous materials requires longer uninterrupted exploration. In addition, their structural properties, whether they offer an appropriate carbon skeleton, the difficulty of carbonization, their cost, and their environmental friendliness are all considerations that must be taken into account for real commercial value.

4 | SUMMARY AND PERSPECTIVES

It is clear that there is a strong market demand for LIBs with higher energy, but commercially available LIBs with graphite anode have almost reached their theoretical capacities. Replacing graphite with Si, which has much higher capacity, has attracted intensive research interest for many years, but co-utilization of Si and graphite has been recently regarded as the most feasible pathway to commercial high energy LIBs in the short term. The co-utilization of Si and graphite could provide a higher specific capacity than that of graphite due to the capacity contribution of Si, and a longer cycle life than that of Si because graphite can impart electrical conductivity to the Si and mitigate its severe volume changes, thus creating synergy for market success.

The co-utilization of Si and graphite suffers from the incompatibility and the lack of sufficient bonding between Si and graphite. The unbound Si particles can easily lose their connections with graphite due to the repetitive volume change and SEI growth, resulting in poor cycling performance. Various carbonaceous materials have been widely introduced for creating more efficient conductive and protective network structures to promote the co-utilization of Si and graphite. Carbon additives are not only helpful for forming strong interface bonding between the graphite and the Si, but also build micrometer-sized hierarchical structures with good electrical conductivity, good adhesion, and high chemical stability. Furthermore, carbon coating on the whole structure can further improve the interphase chemistry, conductivity, and mechanical integration of the Si/G/C composite. In this review, we have reviewed the research progress on Si/G/C composites, and elucidated the influence of the different carbon sources, as well as the synthesis methods and structures in terms of electrochemical performance. The electrochemical performances of various Si/G/C composites synthesized by using different methods and carbonaceous additives are summarized in Table 1.

Although the addition of a variety of carbonaceous additives is a superior strategy to integrate the Si and graphite to maximize their respective advantages, these lower capacity carbon reduces the whole capacity and introduces irreversible capacity into the composite. Therefore, the weight ratio between Si, graphite, and carbonaceous materials is also a vital factor. At present, the Si content is basically recognized as low content, while graphite is properly high. However, the optimal value of the carbonaceous material content has not yet been definitively determined. Compared to the CNTs and rGO, pyrolytic carbon has poor conductivity, and thus, too much pyrolytic carbon material will not only reduce the capacity, but also lead to poor conductivity. Conversely, a low content of pyrolytic carbon can hardly support the integrity of the electrode during long cycling. Therefore, exploring the proper content ratios in different Si/G/C systems is critical to achieve acceptable performance.

From the perspective of commercialization, both the synthesis and raw materials should be cost-effective. It is good to see that the fabrication of micrometer-sized Si/G/C composites mainly relies on simple, low-cost, and easily scaled-up manufacturing methods such as ball milling/mechanical milling, spray drying, CVD, wet processing, and combinations of these methods. However, the whole synthesis processes are generally complicated. It would be better to achieve a balance between simplifying the synthesis and achieving good electrochemical performance. For carbonaceous additives, it is vital to choose the right and proper carbonaceous material. The various carbon additives can not only make a difference to surface activity and electrical conductivity, but also create great differences in the contact between the Si nanoparticles, graphite, and carbon matrix, as well as the whole structure, so that they have a profound effect on the electrochemical performance of the composites. CNTs and rGO are considered good choices with their superior abilities to improve conductivity and perform as a buffering matrix. CNTs can efficiently improve the conductivity of Si/G/C materials, while rGO is effective for constructing 3D-conducting networks and designing porous structures. However, the wide use of rGO is limited by the difficulty of large-scale synthesis with high quality. Also, the contributions of CNTs and rGO to the development of silicon/carbon composites has not met expectations. Pitch, sugars, polymers that can offer heteroatom doping, and most of other carbonaceous polymers have been mainly used for providing carbon protective networks and acting as glues to build micrometer-sized hierarchical structures. Thanks to its low cost and unique aroma-containing structure, pitch has become the most preferred carbonaceous material. Sugars are rich in variety and easy to collect. The price of these sugars is also acceptable, and they are less polluting than pitch, although a detailed comparison of the different varieties is lacking. Polymers that can provide heteroatom doping are beneficial to improve the conductivity of carbon. There are still many carbonaceous polymers that can be explored to improve the electrochemical performance of the

TABLE 1 Summary of Si/G/C composites with electrochemical performance, various carbonaceous additives and synthesis methods

Material	Silicon	Graphite	Carbonaceous material	Synthetic method	First discharge specific capacity, mAh/g	Initial CE, %	Current density	Retention %/cycles	Reference
Si/G/CNTs	Nano	–	CNTs	Grinding mill, pyrolyzation	2326	92.99	350 mA/g	86/35	Li et al[33]
Si/G/MWNTs	1-1.5 μm (BM)	20 μm	MWNTs	Ball milling, pyrolyzation	2274	–	35 mA/g	26.4/20	Zhang et al[35]
B-Si/CNT@G	100-200 nm (BM)	–	CNTs	Ball milling, pyrolyzation	670	80.00	225 mA/g	83.4/100	Li et al[23]
Pitch-C1	30 nm	Flake	CNTs, pitch (10 wt%)	Ultrasonication, spray drying, pyrolyzation	1220	80.80	100 mA/g	67.1/100	Yang et al[37]
Pitch-C2	30 nm	Flake	CNTs, pitch (15 wt%)	Ultrasonication, spray drying, pyrolyzation	1098.4	81.90	100 mA/g	70.5/100	
Pitch-C3	30 nm	Flake	CNTs, pitch (20 wt%)	Ultrasonication, spray drying, pyrolyzation	1057.84	81.60	100 mA/g	81.3/100	
Pitch-C4	30 nm	Flake	CNTs, pitch (25 wt%)	Ultrasonication, spray drying, pyrolyzation	998.68	83.20	100 mA/g	76.0/100	
Si/G/GF-5	<200 nm	–	Graphene oxide	Ball milling, stirring, pyrolyzation	739	75.64	372 mA/g	90/100	Zhu et al[17]
Si/C	100 nm (BM)	Flake	Graphene, phenolic resin, PVP	Sand mill, pyrolyzation	520	88.40	450 mA/g	86/500	Xu et al[16]
Si-C-G-15	50-100 nm	Microsphere, 12-15 μm	Coal tar pitch	Stirring, ultrasonication, pyrolyzation	712	80.50	72 mA/g	80/100	Kim et al[51]
P&C-Si@G	50 nm	20 μm	Pitch, PDDA, PSS	Stirring, pyrolyzation	480	93.75	90 mA/g	95/200	Li et al[52]
SGP@LiF	30 nm	Flake, 1 μm	Pitch	Ultrasonication, carbonization	760	81.50	100 mA/g	82.3/100	Yang et al[53]
Si–G/C-1	30-50 nm	3-6 μm	Pitch (10.5 wt%)	Agitation, fusion, pyrolyzation	820.8	87.60	500 mA/g	93/50 (1 A/g)	Xiao et al[19]
Si–G/C-2	30-50 nm	3-6 μm	Pitch (21.9 wt%)	Agitation, fusion, pyrolyzation	784	88.50	500 mA/g	95.6/50 (1 A/g)	
Si–G/C-3	30-50 nm	3-6 μm	Pitch (34.3 wt%)	Agitation, fusion, pyrolyzation	759.2	90.60	500 mA/g	96.7/50 (1 A/g)	
SGCpitch	<20 nm (layer)	Spherical, 10 μm	Pitch	CVD, pyrolyzation	523	90.90	0.5 C	97.5/50	Choi et al[18]

(Continues)

TABLE 1 (Continued)

Material	Silicon	Graphite	Carbonaceous material	Synthetic method	First discharge specific capacity, mAh/g	Initial CE, %	Current density	Retention %/cycles	Reference
SGCacetylene	<20 nm (layer)	Spherical, 10 µm	Acetylene	CVD, spray dryer, pyrolyzation	524	91.40	0.5 C	98.6/50	
SGCsucrose	<20 nm (layer)	Spherical, 10 µm	Sucrose	CVD, spray dryer, pyrolyzation	525	86.70	0.5 C	90.5/50	
G/Si@C	50-150 nm (BM)	Flake, 3-6 µm	Pitch, glucose	Ball milling, spray drying, pyrolyzation	820	78.04	0.1 C	89.5/100	Li et al[22]
Si/G/C	30 nm	Flake, 0.5 µm	Glucose	Stirring, ultrasonication, spray drying, pyrolyzation	860	69.71	60 mA/g	92/20	Lai et al[55]
Si/FG/C	30 nm	Flake, 0.5 µm	Glucose	Ultrasonic vibration, spray drying, pyrolyzation	864.54	69.7	60 mA/g	91.58/20	Lai et al[59]
HC-nSi/G	50 nm	10 µm	Sucrose	Hydrothermal reaction, carbonization	1100	80.00	120 mA/g	86/150	Jeong et al[56]
SiGC	100-200 nm (BM)	Flake, 2-10 µm	Sucrose	Ball milling, spray drying, pyrolyzation	1016	80.50	500 mA/g	83.6/300	Sui et al[57]
Si@FG/C-1	80 nm	Flake	Glucose, PVP	Ball milling, spray drying, pyrolyzation	587	74	500 mA/g	90/300	Wang et al[15]
Si/C	50-100 nm	Flake	Glucose, PVP	Stirring, ball milling, spray drying, pyrolyzation	710	89.20	300 mA/g	83.3/500	Xu et al[21]
Si/G/PDA-C	80 nm	Flake, 1 µm	Polydopamine (PDA)	Sonification, stirring, pyrolyzation	741.2	78.10	300 mA/g	82.4/100	Zhou et al[78]
Si/G/C	<70 nm	Flake, 0.4 µm	Polyacrylonitrile (PAN)	Electrostatic spray, pyrolyzation	1300	53.80	200 mA/g	97/100	Liu et al[24]
Si/Gr@void@C	Micro	Flake, 5-10 µm	Polypyrrole (PPy)	Ball milling, pyrolyzation, etching	1750	74.30	100 mA/g	–	Ashuri et al[25]
Si/C	30 nm	Flake, 0.5 µm	Phenolic resin	Magnetic stirring, pyrolyzation	867.6	73.82	100 mA/g	89/40	Su et al[20]
Si/G/L-C	Nano	–	LA132	Stirring, ultrasonication, pyrolyzation	909.8	76.80	100 mA/g	73.68/40	Zhou et al[86]
Si–C–NG	60-150 nm (BM)	Flake, 10 µm	Poly(AN-co-DVB)	Ball milling, spray drying, pyrolyzation	601.3	78.41	100 mA/g	87.9/100	Wang et al[84]
Si/C@NGs	28-342 nm	Flake, 10 µm	Styrene-acrylonitrile copolymer	Ball milling, hydrophobic treatment, pyrolyzation	550	82.80	100 mA/g	93.75/100	Wang et al[85]

Abbreviations: BM, ball milling; CE, coulombic efficiency; CNT, carbon nanotubes; CVD, chemical vapor deposition; PDDA, polydiallyldimethylammonium chloride; PVP, polyvinyl pyrrolidone.

Si/G/C materials, but their cost and large-scale availability should be considered as well for real application.

Together with the flexible and scalable fabrication processes, the use of carbonaceous materials to integrate Si and graphite improves the prospects of Si/G/C composites for industrial applications. Although it is a huge challenge to completely solve all the issues for Si/G/C composites such as volume changes and unstable SEI in a single system, engineering of micrometer-sized hierarchical structures and a suitable morphology with proper controls on distribution of components, conductive networks, sizes, voids, shells, and so forth would lead to competitive performance in terms of capacity, efficiency, and cycling stability for commercial success. It should also be noted that the integration of the Si/G/C composite with a suitable binder at the electrode level is also critical for maintaining the integrity of the electrode and achieving superior performance. A wide range of polymeric binders with functionalities such as cross-linking, enhancing conductivity, and self-healing are being explored for silicon electrodes,[87-94] and this knowledge can be leveraged to develop Si/G/C electrodes. Considering the abundance of carbon sources and the variety of Si/G/C composites, an integrated design with multicomponent interlinking among the Si/G/C composite and the binder (such as hydrogen bonding, ion-dipole interactions, covalent bonding, etc) could create a synergy for achieving high-capacity Si/G/C electrodes with high cycling stability.[95]

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