Polymer-Derived Heteroatom-Doped Porous Carbon Materials

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Figure 1. Schematic illustration of two general routes for synthesizing polymer-derived HPCMs.

1. INTRODUCTION TO HETEROATOM-DOPED POROUS CARBON MATERIALS

Carbon materials are ubiquitous in our daily life. In retrospect, charcoal, a biomass-derived material, was utilized as medicine in ancient Greek times to relieve dysentery-like diseases, which, as we now understand, functions through the adsorption of bacteria and bacterial metabolites by nanostructured carbons. This guest molecule adsorption property was also used in the early 1900s in the form of filters in respirators for the prevention of toxicant poisoning. Currently, carbon materials are broadly used as adsorbents, supports, and even metal-free catalysts to address pressing global challenges, including, but not limited to, energy and environmental issues. Carbon is of rich abundance in nature, relatively low cost, and comparably high chemical and thermal stability. It possesses a tunable surface area and multiple structural forms at the atomic/nanoscale that define an unusually broad range of physicochemical properties to satisfy diverse applications. As the sixth element in the periodic table, carbon is sometimes referred to as an all-purpose material, even exceeding "quintessence" (the metaphoric fifth element) of alchemy.

The porous state of carbons no doubt profoundly impacts their properties and functions. Equipping carbons with pores of different sizes and shapes lowers their apparent density and expands their surface area to accelerate interfacial energy and mass transfer, a step that is crucial and decisive in many surface-related physical and chemical processes. The topic of porous carbons is particularly "fueled" by the recent trend to replace fossil fuels with affordable clean energy in the next few generations, as defined in the Sustainable Development Goal 7 (SDG7) by the United Nations. The concept of hierarchical structuration of carbons in terms of pore sizes ranging from micro- to meso- and macropores is well developed in the porous carbon community, since it balances both a high density of and a low diffusion resistance toward active sites. The macropores are literally transport highways, while the micro- and mesopores provide a large specific surface area bearing active sites for heterogeneous reactions.

Equally important is the effect of heteroatom doping of carbon materials with nonmetals, e.g., nitrogen (N), phosphorus (P), boron (B), sulfur (S), and selenium (Se).[1] These types of atoms can be solely or jointly incorporated into a carbon framework via either carbonization of heteroatom-rich precursors or chemical postmodification of parental porous carbons. Heteroatoms in turn can tailor the physicochemical properties of carbons and endow carbons with fascinating properties. Not only the electronegativity but also the charge density and size of heteroatoms are vital to the properties of porous carbons. Different types of heteroatoms, or even the same type of heteroatom in a different bond configuration, can impart carbons with distinctively different properties. Considering the potential of heteroatom-doped porous carbon materials (HPCMs) as metal-free catalysts that can replace costly noble/transition metal-based catalysts, as already observed for a number of key applications, and that are stable even under harsh conditions, i.e., at high temperatures, under sulfur species and carbon monoxide atmospheres, or in strong acid and alkali solutions, their research horizon has been significantly and will be further broadened in both academia and industry. HPCMs are discussed in reference to applications such as electrochemical devices, catalysts, fire-

retardant materials, seawater desalination devices, and many more.

In this context, the judicious choice of carbon precursors is of tremendous significance, among which polymers stand out due to the availability of a myriad of macromolecular and self-assembled (nano)structures, tunable chemical compositions, and versatile processing techniques. HPCMs in different forms have been produced through the rational choice of polymers, including spheres, fibers, thin films/membranes, foams, monoliths, and their hollow counterparts (Figure 1). The polymers are chosen from either biopolymers or synthetic polymers, ranging from traditional polyacrylonitrile (PAN) and conjugated polymers to the recently emerging well-carbonizable polymers, e.g., poly(ionic liquid)s (PILs) or polydopamine.

In the ongoing search for carbon (nano)materials exhibiting unconventional properties and important applications, studies of polymer-derived porous carbons in well-defined shapes doped by heteroatoms are a fast-growing focus area. Previous reviews and perspective articles in this area targeted the specific aspects of heteroatom doping effects, energy conversion/storage applications, and/or carbonization mechanisms.[2−7] In terms of polymer-derived HPCMs, there are only a few solid conclusions in the literature. With the ongoing advancement in polymer nanomaterials, we believe that polymers are excellent candidates for producing carbon materials with diverse morphologies. These polymers can be first processed into complicated structures and then build up selective porous networks via intrinsic phase separation. At the same time, with the aid of heteroatoms, the electronic structures of HPCMs can be rationally tailored for designated applications. The current review attempts to survey the progress in the entire field in a comparative fashion and discusses the state-of-the-art understanding of common denominators of these advances. We highlight the impacts of preformed polymer structures and the freedom in the choice of processing strategies on the production of carbons with diverse morphologies and tunable nanostructures and the related physiochemical properties and functions. We also share our views on challenges and opportunities for the synthesis and application of polymer-derived HPCMs. This Review aims to give comprehensive summaries of polymer-derived HPCMs based on their synthesis, morphology, heteroatom doping, and porosity. To be more focused in its content, it will not cover the development of metal atom doping, and interested readers can refer to other recent reviews.[2,3]

2. SYNTHETIC APPROACHES

Heteroatom-doped porous carbons can be prepared by pyrolysis of heteroatom-rich polymers as precursors or by subjecting preformed porous carbons to postsynthetic treatment with heteroatom-containing precursors.[4−8] The former can homogeneously add heteroatoms into the entire porous carbon matrix, whereas the latter mostly loads heteroatoms only onto the carbon surface. Sometimes both methods are combined to maximize the heteroatom loading. Each synthetic route may generate porous carbons in structures with distinct strengths and specific weaknesses.[9−11] In this section, the synthetic methods for polymer-derived HPCMs are systematically discussed. Two main strategies, including template and direct synthesis, are summarized in Figure 1. These strategies are detailed with a variety of examples in the following section.

2.1. Template Methods

Hard and soft template strategies are the most mature and widely used methods for preparing HPCMs with diverse pore structures from polymers (Figure 2). Hard templates are solid
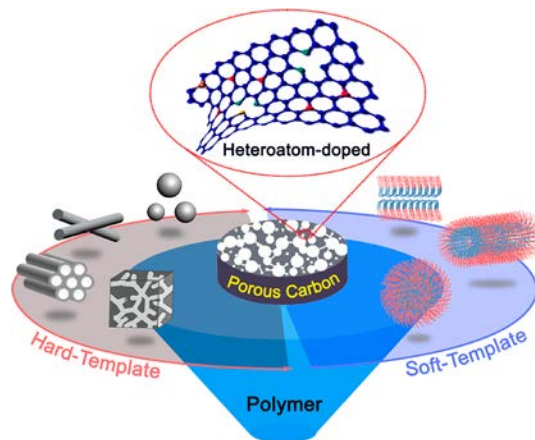
Figure 2. Schematic illustration of hard and soft templates for the synthesis of HPCMs from polymers.

compounds with pores or high surface areas, including zeolites and mesoporous silicas, as well as colloidal particles and their assemblies. Soft templates are organic nanostructures built up from micelles of ionic or nonionic surfactants, assemblies of block copolymers, liquid crystalline phases, soft droplets, biopolymers, or vesicles.[12−15] Despite the significant progress made thus far, precise control of the structure and morphology at low cost remains a persistent topic. To tailor the morphologies of porous carbons, a straightforward method is to adopt templates of the corresponding morphologies.

2.1.1. Inorganic Nanostructures as Templates. Utilizing inorganic nanostructures as templates for the synthesis of well-defined porous carbons is one of the most straightforward and popular methods. After infiltrating the template with a heteroatom-containing polymer or in situ polymerization of the monomer, followed by carbonization and template removal by appropriate chemicals, HPCMs that are an inverse replica of the original template will be obtained. Owing to the rapid synthetic progress of porous inorganic nanostructures, a variety of inorganic templates have been employed to produce carbons with well-defined pores. This approach involves templating with metal nanoparticles, silica nanoparticles or their opal crystals, silica gels, aluminosilicates, silica carbide, and nanostructured metal oxides, such as anodic alumina, calcium carbonate, and zinc oxide, which can be easily removed by a weakly alkaline or acid solution or vaporization.[16−23] Novel morphologies are accessible for porous carbon materials with such appropriate inorganic templates. Ideally, the template must be chemically inert to carbon and carbon precursors, thermally stable, and equipped with a chemical trigger for removal to leave pores behind in the template. It is worthwhile noting that the pore size of the resulting porous carbons is not always the same as that of the original templates because the carbonaceous material can shrink under further thermal processing at elevated temperatures.

Since the templating concept was demonstrated in 1982, colloidal silica particles and silica gels have been explored and widely adopted as molds for porous carbons.[24] Hyeon's group pioneered the synthesis of mesoporous carbon using colloidal
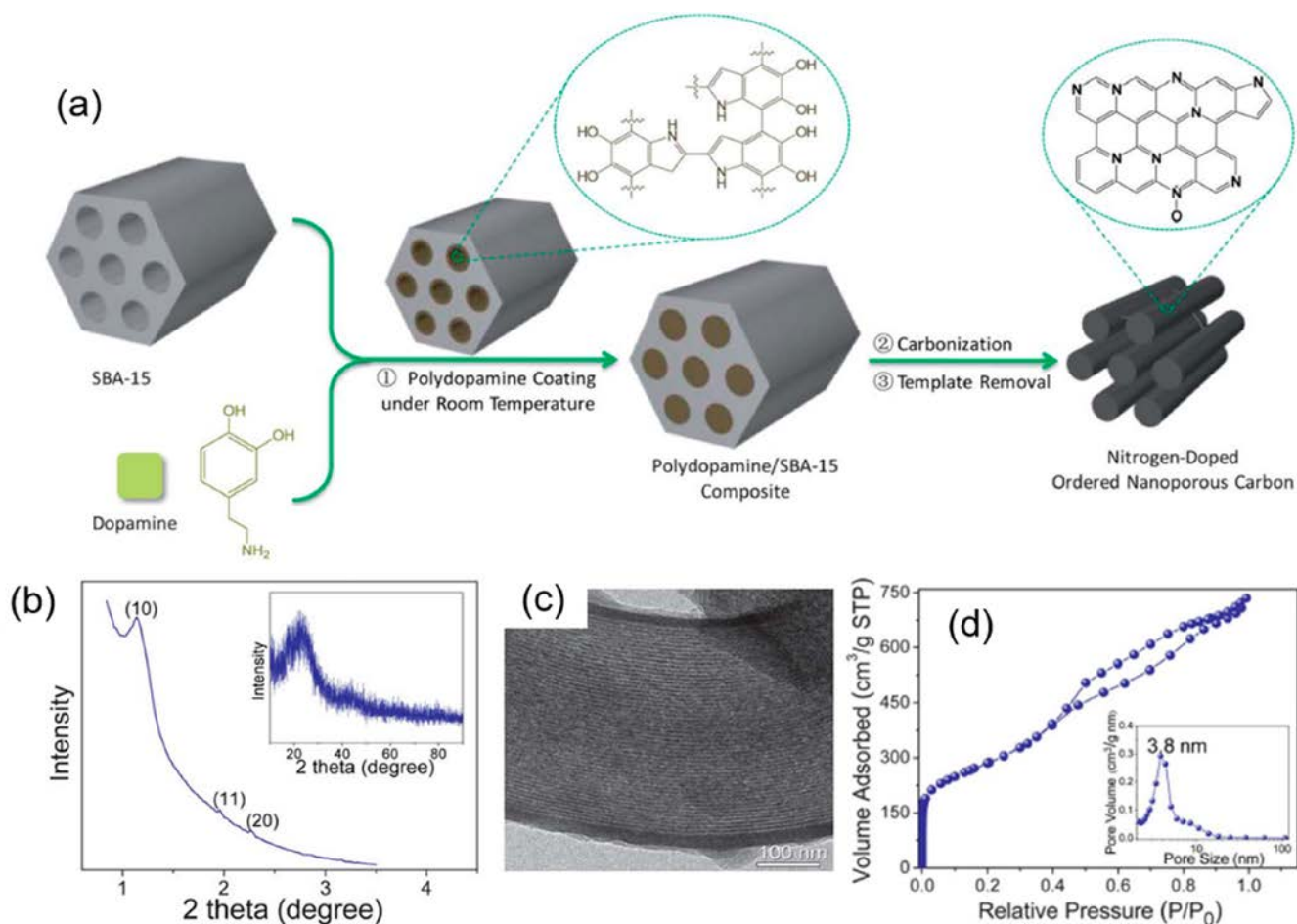
Figure 3. (a) Schematic illustration of the polydopamine-coating-directed synthesis of NONCs. (b) Low-angle XRD pattern and wide-angle XRD pattern (inset) of the NONC. (c) TEM image of the NONC. (d) N_2 sorption isotherms of the NONC and its pore size distribution. Reproduced with permission from ref 30. Copyright 2013 Royal Society of Chemistry.

silica particles as hard templates.[25,26] It was found that the pore size distribution of the carbon was significantly affected by the silica/polymer ratio. Stein's group further demonstrated the preparation of porous carbon with a periodic array of macropores, which was defined as three-dimensionally ordered macroporous carbon.[27] The pore size distribution of carbons templated by silica particles of a uniform size is not necessarily narrow, suggesting that carbon is not always a true replica of voids in silica nanoparticles. To minimize irregular agglomeration of silica particles, which produces nonuniform voids, the surfactant cetyltrimethylammonium bromide (CTAB) was used to stabilize silica particles in solution before processing them into a porous template.[25] The resulting nanoporous carbon showed an improved pore size distribution peaking at 12 nm, which well matched the size of the employed silica particles. Apart from the surfactants used, later studies found that the silica sol content and the pH value had significant impacts on the porous structures and textural properties of the resulting mesoporous carbons.[28,29]

It is important to note that ordered inorganic materials, such as mesoporous silica and zeolites, are also popularly used as hard templates to produce ordered porosity in carbon materials. In terms of silica templates, MCM-41, HMS, MSU-1, MSU-H, SBA-1, SBA-7, SBA-12, SBA-15, and SBA-16 are on the "hot list". For example, Wu et al.[30] reported the fabrication of N-doped ordered nanoporous carbons termed "NONCs" by pyrolyzing a polydopamine (PDA)/SBA-15 nanocomposite under N_2 at 800 °C for 3 h, followed by removal of the SBA-15 template to form NONCs with an S_{BET} value of 1013 m² g⁻¹ (Figure 3). At the same time, Zou et al.[31] synthesized nitrogenated graphitic ordered mesoporous carbons termed "G-OMCs" by using mesoporous nickel oxide as a catalytic template and dopamine as a precursor, which was carbonized at 900 °C for 4 h. The results revealed that G-OMC materials had a higher degree of graphitization than those prepared only from dopamine and the inert SBA-15 template, which suggested a catalytic graphitization process involving nickel oxide. The I_D/I_G value was 0.69, which was lower than that of ordered mesoporous carbon CMK-3 (0.84).

A major drawback associated with this approach lies in the multistep synthesis and the use of hydrofluoric acid (HF) or other toxic etching chemicals to remove the silica template. To mitigate this issue, inorganic nanostructures, such as porous anodic aluminum oxide (AAO), MgO, CoP, $CaCO_3$, and $Al(OH)_3$, that can be removed by relatively safe chemicals, e.g., HCl and NaOH, have been utilized as templates.[32] For example, Chen and co-workers prepared N-doped porous carbon nanocages (NCNCs) via an *in situ*-generated MgO template method using pyridine as a precursor.[33] The MgO template was etched away by a HCl solution at room temperature. The NCNCs exhibited an excellent oxygen reduction reaction (ORR) performance in alkaline solution
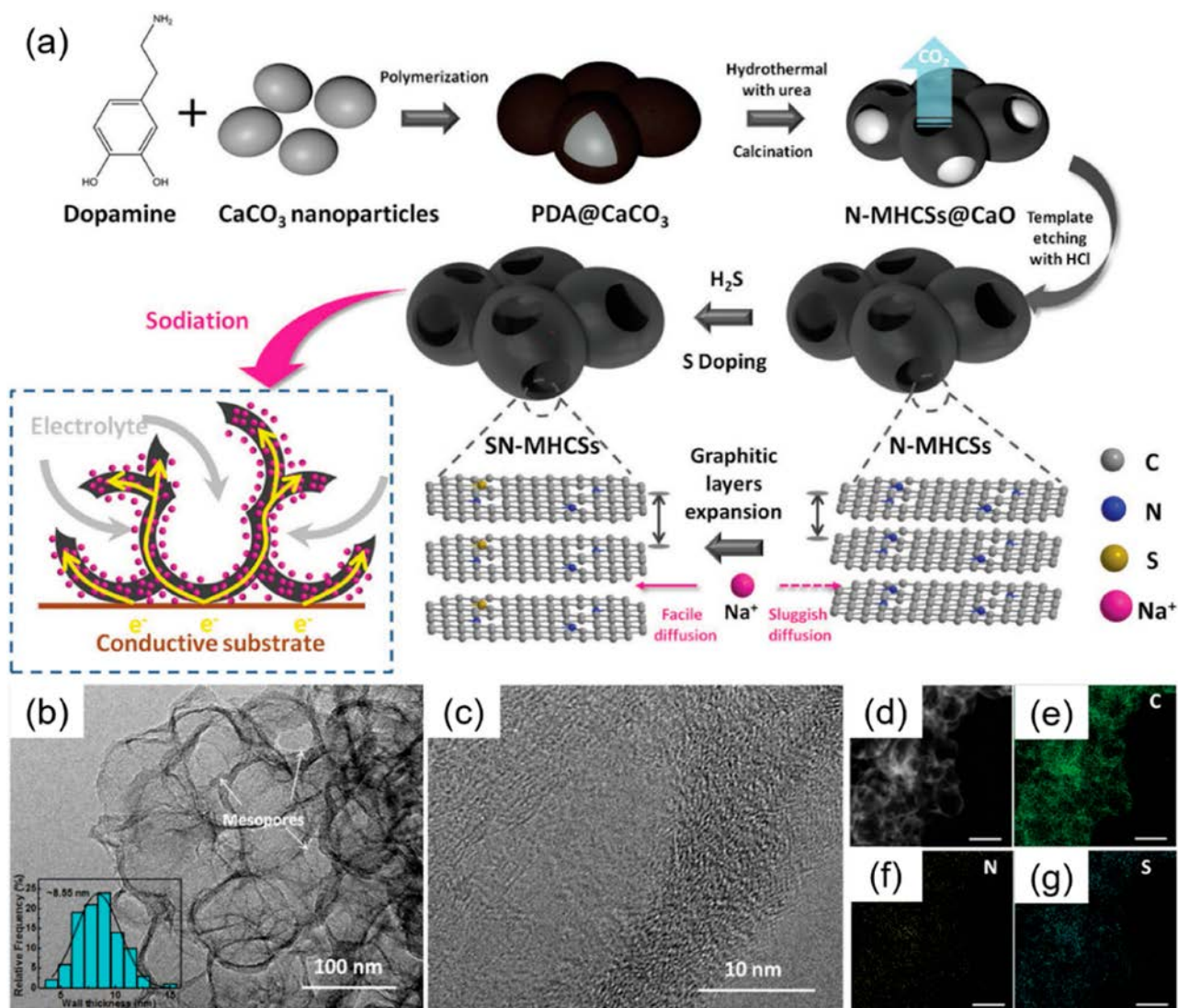
Figure 4. (a) Schematic illustration of the synthetic procedure for SNMHCSs using $CaCO_3$ as a template. (b, c) TEM image of SNMHCSs; the inset is a histogram of the carbon wall thickness distribution. (d) STEM image of SNMHCSs. (e−g) Corresponding distributions of the elemental C, N, and S. The scale bar is 100 nm. Reproduced with permission from ref 35. Copyright 2019 Wiley-VCH.

with superior stability toward methanol crossover and CO poisoning, at a level that could compete with the commercial Pt/C electrocatalyst. Similarly, Hu et al. reported a novel 3D hierarchical S- and N-codoped carbon nanocage termed "hSNCNC" as a bifunctional oxygen electrocatalyst, where MgO nanocubes were used as a template and a pyridine and thiophene mixture as a precursor.[34] The as-prepared hSNCNC exhibited a positive half-wave potential of 0.792 V (vs reversible hydrogen electrode, RHE) for the ORR and a low operating potential of 1.640 V at a 10 mA cm^{-2} current density for the OER. The reversible oxygen electrode index was 0.847 V, superior to those of commercial Pt/C and IrO_2. In another example, S- and N-codoped mesoporous hollow carbon spheres termed "SNMHCSs" were prepared by Sun's group using low-cost $CaCO_3$ nanoparticles as self-sacrifice templates and PDA as a precursor (Figure 4).[35] During the calcination process, $CaCO_3$ decomposed to CaO and released CO_2 gas, which facilitated the formation of small pores in the carbon walls. Urea was used during the carbonization process as a N-content enhancer, followed by an additional thermal annealing under H_2S to induce S doping. When the porous carbon

product was applied as an anode for sodium-ion batteries, excellent rate and cycling performance was achieved due to the interconnected mesoporous hollow sphere structure that provided a large electrode/electrolyte interface for reactions; this in turn facilitated the diffusion of electrolyte, increased the transport rate of electrons and sodium ions, and buffered the volumetric expansion of the electrode during cycling. S doping could increase the interlayer space between adjacent graphitic layers, enable the carbon electrode to accommodate more sodium ions, and promote ion transport, while N doping could add functional groups and defects to increase the capacity.

2.1.2. Polymer Nanostructures as Sacrificial Templates. Polymer nanostructures are popular templates in the synthesis of porous materials due to the ease of morphological control by well-established, mature polymer processing techniques and simple removal through dissolution, calcination, or other mild treatments.[36−40] It should be stressed here that the removal of a polymeric template by calcination is usually performed in combination with the carbonization process, an obvious advantage of soft templates in comparison with the inorganic hard counterparts. It should also be
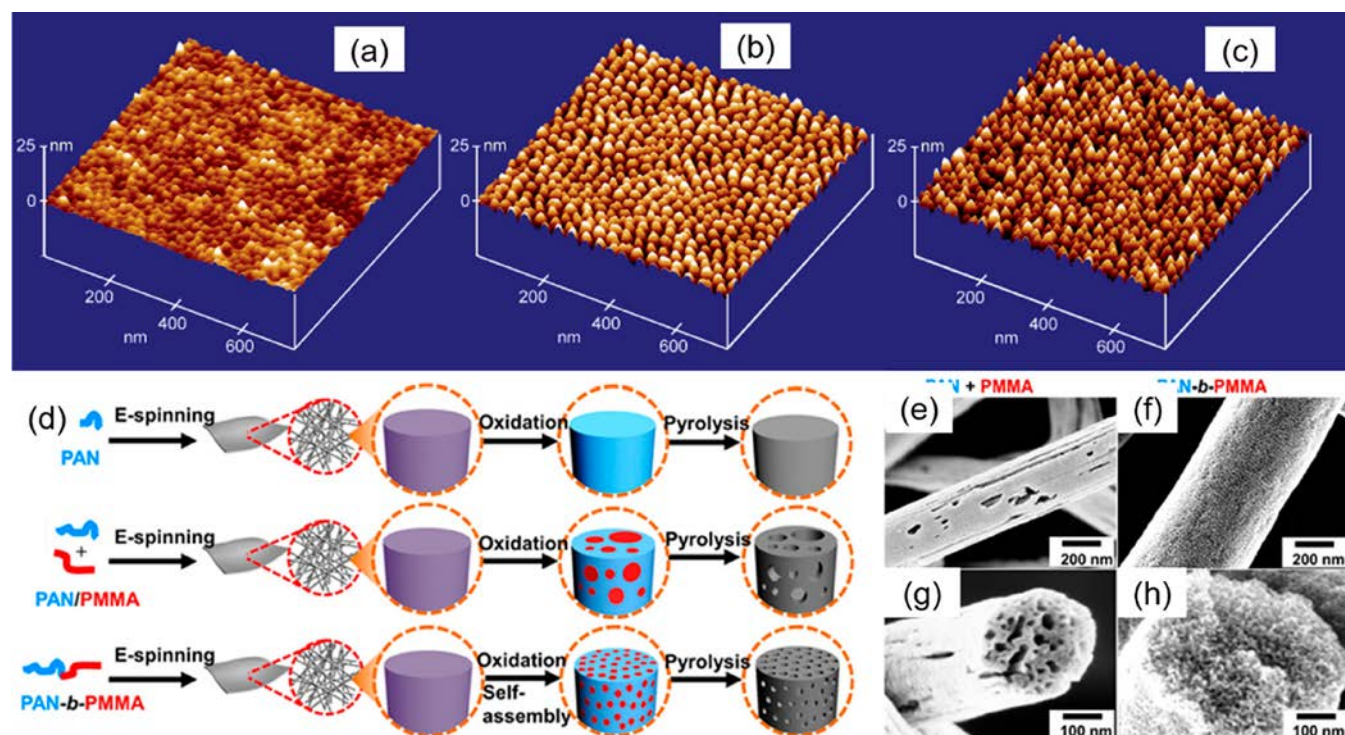
Figure 5. (a) $(AN)_{45}-(BA)_{530}-(AN)_{45}$ block copolymer film vacuum annealed for 2 h at 220 °C to equilibrate the morphology. Sample heated under N_2 to (b) 600 °C and (c) 1200 °C. Reproduced with permission from ref 42. Copyright 2002 American Chemical Society. (d) Fabrication scheme of N-doped porous carbon fibers from polymeric precursors: PAN (blue), PAN/PMMA (red) blend, and PAN-*b*-PMMA block copolymer. (e, f) SEM images of the carbon fibers derived from PAN/PMMA. (g, h) SEM images of the porous carbon fibers derived from PAN-*b*-PMMA. Reproduced with permission from ref 44, licensed under CC BY.

explained here that the polymer nanostructures included in this section (2.1.2) have at least one polymer component fully removed by thermal decomposition, dissolution, or etching to introduce pores. In the later section 2.2.1 "Direct Carbon-ization of Heteroatom-Rich Polymers", the polymer serves as the carbon source, even though one part (but not all parts) of such a polymer may decompose into pores.

To date, polymeric nanostructures ranging from 0D nanoparticles to 1D fibers, 2D sheets, and 3D bulk species have been successfully used to template the pyrolytic growth of HPCMs. For example, polystyrene (PS) latexes or "nano-spheres" are one of the most commonly used templates due to their easy scale-up preparation at low cost. The interplay between the template and the carbon precursor is vital to generating the target products. To provide the required affinity of templates to polymeric precursors, PS nanospheres are usually surface functionalized with, e.g., polyvinylpyrrolidone (PVP) as a bridging layer to accommodate intermolecular interactions, such as hydrogen bonding. Hao and co-workers fabricated hollow N-doped carbon microspheres termed "HNCMs" using polyaniline (PANI) as a source of nitrogen and carbon for grafting onto PVP-functionalized PS spheres as a template.[41] The organic PS core was burned off by carbonizing the core–shell microspheres under a N_2 atmosphere at 500 °C for 2 h to produce HNCMs.

Utilizing microphase-separated structures of polymer blends or block copolymers as templates, well-organized nano-structured carbon materials can be fabricated by pyrolysis accompanied by volatilization of the sacrificial phase. Matyjaszewski et al.[42] first demonstrated the success of such a strategy using the triblock copolymer of acrylonitrile (AN) and *n*-butyl acrylate (BA) with average composition $(AN)_{45}-$

$(BA)_{530}-(AN)_{45}$ as a precursor. For certain PAN/PBA ratios, the original morphology of the bulk precursor is well retained upon pyrolysis between 400 and 1200 °C (Figure 5a–c). Extension of this route to block copolymers with other morphologies (e.g., the gyroid phase) or polymer blends was also found to be successful and straightforward. The resulting carbon materials show a high surface area and accessibility of nitrogen functionalities, as inferred from their performance as electrodes for supercapacitors and sorbents for CO_2 capture as well as efficient electrocatalysts for the oxygen reduction reaction.[43] For example, in 2019, Liu's group[44] reported the fabrication of porous carbon fibers (PCFs) with well-controlled mesopores of ~10 nm or micropores of ~0.5 nm in size by employing the microphase-separated PAN/PMMA blend or block copolymer PAN-*b*-PMMA, respectively, as a template (Figure 5d–h). PAN can be directly converted to N-doped PCFs, sometimes with oxygen (O) codoping due to a necessary aerobic thermal cross-linking/stabilization step at 250–350 °C, while the porous structure is created by decomposition of the thermally labile PMMA domains. Such PCFs exhibited substantially reduced ion transport resistance and a high capacitance of 66 μF cm^{-2} in an electrochemical supercapacitor test owing to the advantageous interconnected porous network and the highly optimal bimodal-size-distribution pores.

As mentioned above, block copolymers are powerful templates because of their rich phase diagrams accessible via self-assembly, and some are commercially available.[45−48] Carbon materials with ordered mesopores and a narrow pore size distribution can be templated by micelles of amphiphilic block copolymers. The most common ones are poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide) tri-
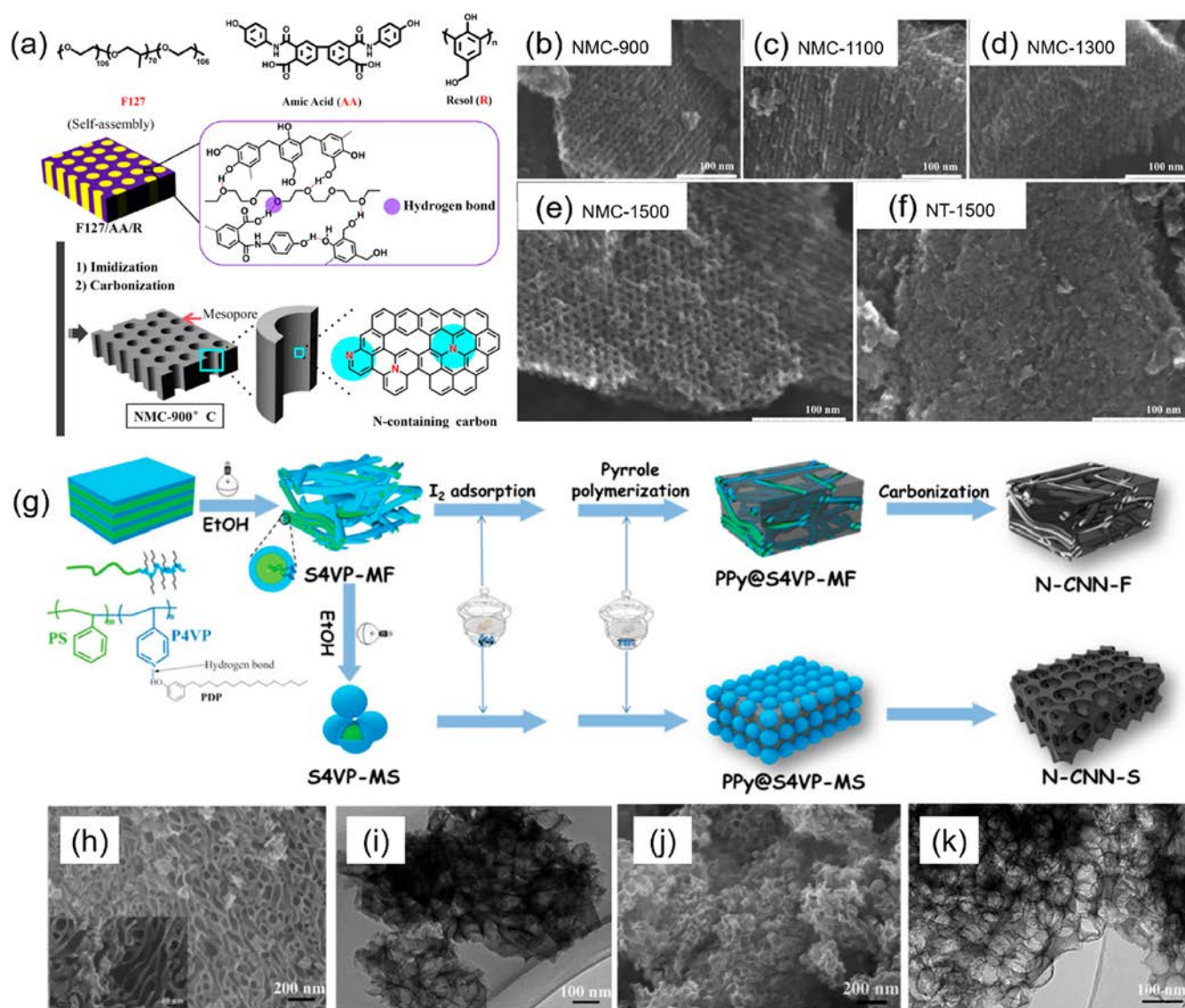
Figure 6. (a) Schematic illustration of the synthesis of NMCs (purple matrix, PEO block/AA/resol; yellow cylinders, PPO block) via the F127-block-copolymer-assisted self-assembly of an aromatic N-containing carbon precursor, amic acid (AA), and a cross-linker, a resol (R). (b–e) Porous structures of NMCs carbonized at different temperatures. The number represents the carbonization temperature (°C). (f) Morphology of disordered N-doped carbon (NF) as a comparison. Reproduced with permission from ref 50, licensed under CC BY. (g) Experimental procedure for the preparation of interconnected porous N-doped carbon networks (N-CNNs). (h, i) SEM and TEM images of N-CNNs templated from micellar fibers (N-CNN-F). (j, k) SEM and TEM images of N-CNNs templated from micellar spheres (N-CNN-S). Reproduced with permission from ref 37. Copyright 2018 Wiley-VCH.

block copolymers (PEO-*b*-PPO-*b*-PEO), i.e., the commercial Pluronic family,[49−51] polystyrene-*b*-poly(4-vinylpiridine) (PS-*b*-P4VP),[37] or polystyrene-*b*-poly(ethylene oxide) (PS-*b*-PEO).[52] The applied carbon precursors can be either heteroatom-containing or heteroatom-free polymers such as small clusters of phenol-formaldehyde, so-called "resol",[51−54] "RF resin" (resorcinol-formaldehyde),[55] or "PF resin" (phlor-oglucinol-formaldehyde).[49] Heteroatom-doped carbons can be synthesized by direct carbonization of heteroatom-containing polymers in the block copolymer template or post-treatment of carbons derived from heteroatom-free polymers. Fascinating porous carbon nanostructures have been produced from block copolymer nanostructures as sacrificial templates, including two-dimensional hexagonal (*p6mm*), three-dimensional bicontinuous (*Ia3d*), or body-centered cubic (*Im3m*) varieties.[49−55] For example, Hayakawa's group synthesized well-ordered N-containing mesoporous carbons (termed NMCs) with hexagonally arranged, uniform 4 nm mesopores via a block copolymer template. The NMC films were obtained from a blend of Pluronic copolymer F127 (M_w = 12600 Da, PEO$_{106}$-PPO$_{70}$-PEO$_{106}$), amic acid (AA) as a N-containing precursor, and a resol as a stabilizer (Figure 6a–f).[50] Well-ordered NMCs bearing large mesopore volumes (V_{meso} = ∼0.8 mL g^{-1}, V_{total} = ∼0.9 mL g^{-1}) and a moderate S_{BET} of 532 m^2 g^{-1} were achieved by pyrolysis of the self-assemblies of F127, AA, and the resol. Similarly, in 2018, Chen and co-workers reported 3D interconnected N-doped carbon networks (N-CNNs) with designable pore geometries (Figure 6g–k).[37] The authors applied a vapor-phase polymerization approach using self-assembled bicontinuous PS-*b*-P4VP membranes as templates. The template morphology was tuned by the addition of 3-*n*-pentadecylphenol (PDP) to PS-*b*-P4VP through ethanol
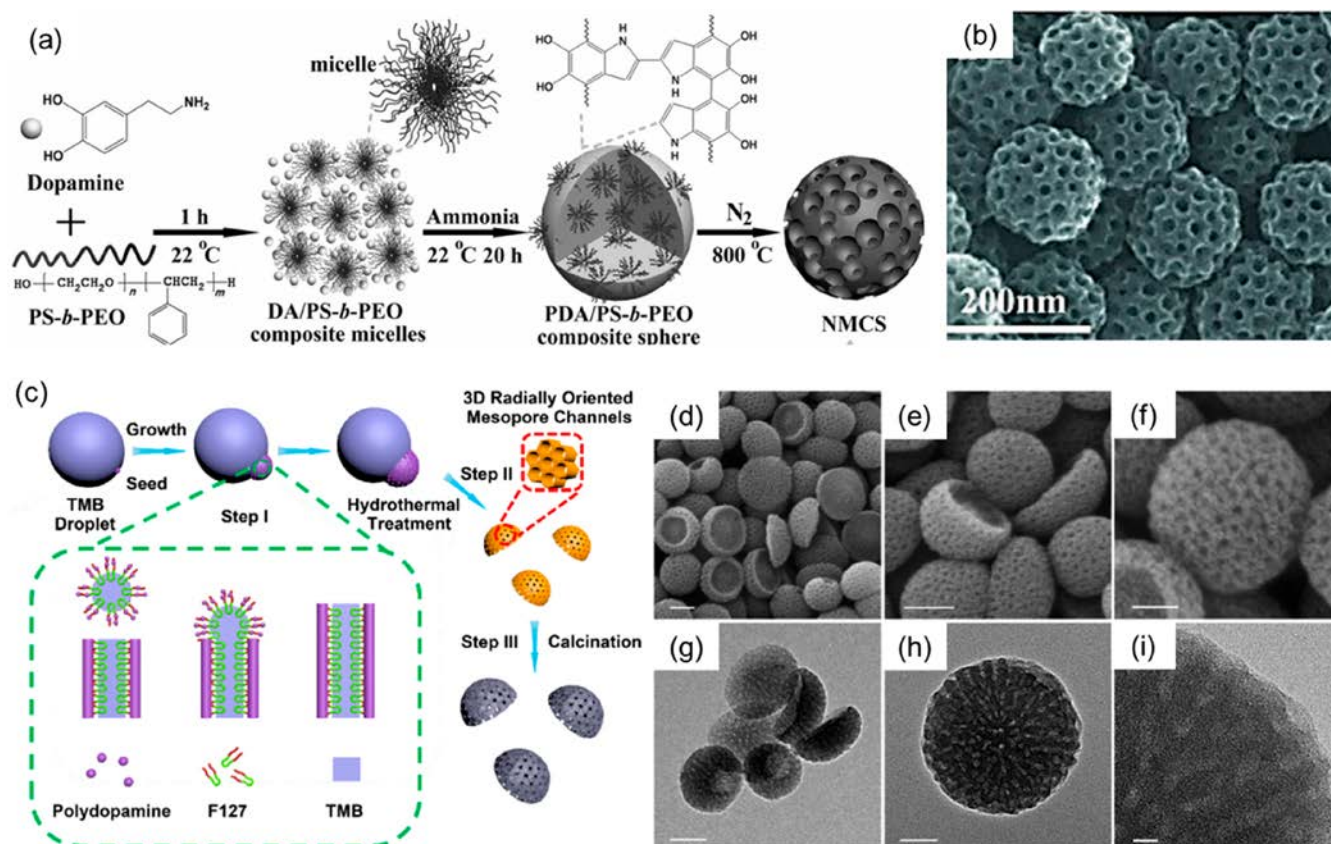
Figure 7. (a) Formation process and (b) SEM image of N-doped mesoporous carbon nanospheres (NMCSs) obtained via the self-assembly of block copolymer−PDA composite micelles followed by direct carbonization. Reproduced with permission from ref 56. Copyright 2015 Wiley-VCH. (c) Formation process of bowl-like mesoporous particles. Step I, formation of the block copolymer F127/TMB/PDA oligomer composite micelles and emulsion-induced interface anisotropic assembly of asymmetric bowl-like mesostructured PDA particles with radially oriented large mesochannels. Step II, hydrothermal treatment of the mesostructured PDA nanocomposites to stabilize the structure. Step III, carbonization at 800 °C for 2 h under N_2 to generate bowl-like mesoporous carbon particles with radially oriented mesochannels. (d−f) SEM images and (g−i) TEM images of the porous bowl-like carbon particles. Scale bars are 100 nm (d, e, g), 50 nm (f, h), and 10 nm (i). Reproduced with permission from ref 57. Copyright 2016 American Chemical Society.

swelling. This step formed hydrogen bonding of PDP with the P4VP block to increase the P4VP volume fraction in the block copolymer, which resulted in a microphase separation transformation from lamellar to interconnected micellar fibers or spheres with a PS@P4VP core−shell structure inside the PS-*b*-P4VP membranes. Different morphologies of block copolymer templates could be obtained by simple adjustment of the swelling time for the same PS-*b*-P4VP(PDP) system. Complexed iodine was used to initiate the polymerization of pyrrole to form polypyrrole on the outer surface of PS@P4VP core−shell micelles. Finally, the block copolymer template was removed after carbonization, and N-CNNs with different pore geometries were obtained. When applied as a metal-free oxygen reduction reaction (ORR) catalyst, the N-CNNs with interconnected network structures displayed a performance comparable to that of commercial Pt/C in alkaline media. The so-called vapor-phase polymerization approach using block copolymer assemblies as templates provides a synthetic alternative and important insights into the design of porous 3D networks.

In addition to the most commonly reported ordered porous carbon films, individual carbon spheres with internal ordered porous channels are also accessible by using a block copolymer as a template. As an example, N-doped mesoporous carbon spheres (NMCSs) were synthesized by Yamauchi et al. in 2015.[56] A pore size of up to 16 nm was engineered inside NMCSs through self-polymerization of dopamine (DA) and spontaneous coassembly of diblock copolymer micelles (Figure 7a). The resultant NMCSs featured characteristic mesopores of up to 16 nm and a uniform particle size of ∼200 nm (Figure 7b). Their high electrocatalytic activity in the ORR was related to the large mesopores and the small dimensions of the NMCSs, which promoted mass transport by reducing and smoothing the diffusion pathway. Similarly, an emulsion-induced interfacial anisotropic assembly approach was employed by Lou et al.[57] to produce N-doped porous bowl-shaped particles from a 1,3,5-trimethylbenzene (TMB)-in-water emulsion. Mesostructured PDA seeds were first produced through self-assembly of block copolymer F127/TMB/PDA composite micelles formed at the TMB/water interface. These micelles further anisotropically grew into bowl-like particles. The nucleation and anisotropic growth of PDA particles was then controlled by the TMB droplets as a soft template, which governed the mesoporous structure and particle morphology (Figure 7c−i). These bowl-shaped porous PDA particles were readily carbonized into mesoporous carbon particles with preserved morphology and mesostructure. This approach exemplifies a unique paradigm for the synthesis of dimensionally asymmetric porous carbon particles. At the same time, Feng and his group reported a coassembly method to
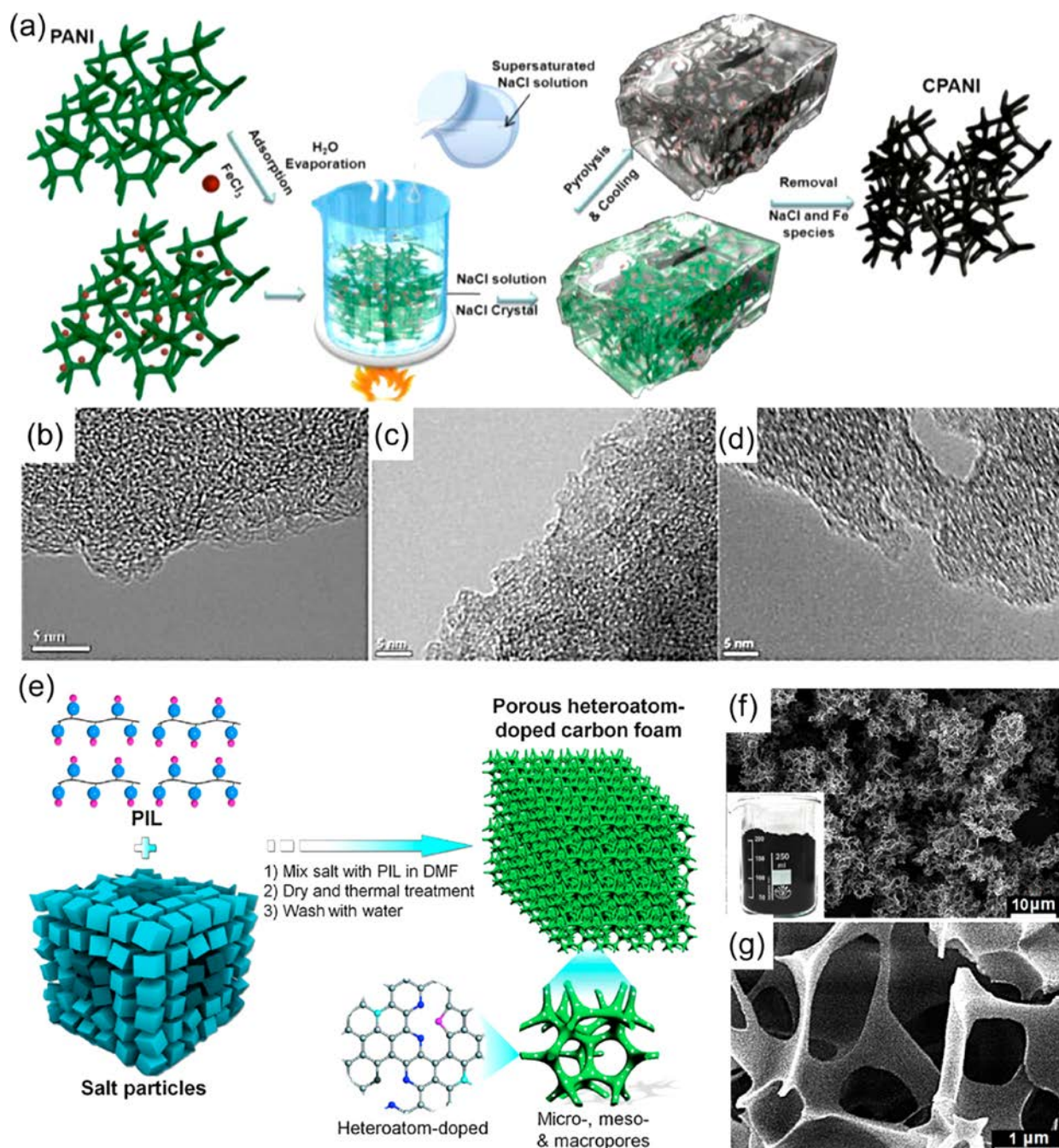
Figure 8. (a) Synthetic scheme for porous carbons via a salt recrystallization method. High magnification TEM images showing the porous structures and edges of CPANI (b), CPANI-NaCl (c), and CPANI-Fe-NaCl (d). Reproduced with permission from ref 61. Copyright 2015 American Chemical Society. (e) General fabrication procedure of hierarchically porous heteroatom-doped carbon foams using PILs as a N/C precursor and chemically inert solid salt as a template. (f, g) SEM images of PNCF with different magnifications. Reproduced with permission from ref 62. Copyright 2018 Elsevier.

synthesize N-doped mesoporous carbon nanospheres (MCNSs) with well-controlled pore sizes ranging from 8 to 38 nm by employing PS-*b*-PEO with varied PS block length as soft templates and dopamine as a N-rich precursor.[52] They introduced a linear equation to guide the quantitative control of the average pore size of MCNSs by adjusting the block length in the block copolymers, which precisely dictated the porosity of the PDA-derived carbon nanospheres. When these MCNSs were used as electrodes in supercapacitors, this group found that the capacitance normalized by S_{BET} remained invariable, whereas the specific capacitance of the MCNSs decreased linearly with increasing pore size.

2.1.3. Polymer/Inorganic Hybrids as Templates. If the inorganic template and the polymeric carbon precursor are incompatible, then a nonuniform interface will form during the molding/casting procedure. This inevitably produces a nonporous and/or ill-defined porous structure due to the weak template−precursor interaction, which leads to incomplete filling of the pores in the template and unfavorable deposition of carbon on the external template surface. As the formation of a highly uniform interface between the template and carbon
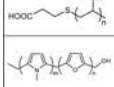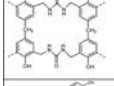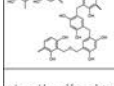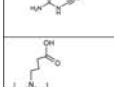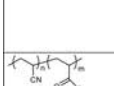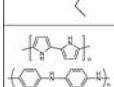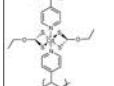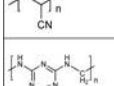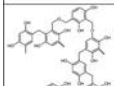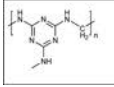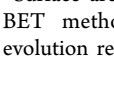
precursor is beneficial, the interfacial energies should be chemically controlled. Copolymerization of monomers with an alkoxide inorganic precursor, e.g., tetraethylorthosilicate (TEOS), is a practical approach to reach this goal.[58,59] For example, Zhang and co-workers synthesized Br-containing organosilica NPs <5 nm in size using a brominated organosilica precursor; the NPs were then grafted with PAN chains to prepare silica-g-PAN composites by surface-initiated atom transfer radical polymerization (SI-ATRP).[60] Porous carbons were obtained with an S_{BET} value of 1244 m^2 g^{-1} and a nitrogen content as high as 11.9 wt %.

As discussed above, the interaction of the carbon precursor with the template plays a vital role in governing the morphology of carbons. To optimize the precursor–inorganic interface in the templating method, other strategies employing inorganic salts or crystals as a template matrix and space confinement have been conducted. For example, Wei et al. demonstrated how to fix the precursor shape via a salt recrystallization method to synthesize N-doped carbon nanomaterials with a high density of active sites as an ORR catalyst (Figure 8a–c).[61] In their method, a NaCl crystal acted as a fully sealed nanoreactor, facilitating N incorporation and graphitization. As displayed in Figure 8a, they first fabricated a three-dimensional (3D) PANI network via a self-assembly process. After adsorption of FeCl$_3$, a supersaturated NaCl solution was poured into a beaker containing PANI networks. The water was then evaporated so that NaCl recrystallized onto PANI at the bottom of the beaker. To fully cover the 3D PANI network with NaCl, cycles of NaCl solution addition, water evaporation, and NaCl recrystallization were repeated until the whole PANI was buried by and tightly sealed inside NaCl crystals. The NaCl-crystal-sealed PANI was first dehydrated at 120 °C before annealing at 900 °C under N$_2$. A hot aqueous H$_2$SO$_4$ solution was applied to wash off the NaCl crystals and iron species. This method for synthesizing an Fe-doped catalyst benefited the formation of more FeN$_x$ sites in the inner pores and graphitic structure. Later, in 2018, Yuan et al. prepared hierarchically porous N-doped carbon foams (PNCFs) via a facile bottom-up strategy by using PILs as the N/C precu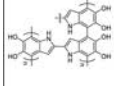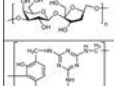rsor and common inorganic salts as the structural template, a method termed "cooking carbon in a solid salt" (Figure 8e–g).[62] In their work, a salt/PIL physical mixture was first prepared by dropwise addition of an aqueous salt solution into a PIL solution in DMF, followed by thermal evaporation of the solvent. The mixture was calcined close to but below the melting point of the salt to convert the PILs into carbon inside the solid salt matrix. The salt was washed away by water, leaving carbon foams with rich heteroatoms and hierarchical micro/meso/macropores. This approach is universal and can be applied to different common salts, such as NaCl, KCl, and Na$_2$SO$_4$.

2.2. Direct Synthesis

Although hard templates may enable synthesis of heteroatom-doped carbons with better pore control, most hard templates have to be synthesized and then removed, which is a time/labor-consuming procedure.[79−81] Beyond the costs of materials, labor, and time and toxic etching agents, the effect of these treatments on the carbon structure and catalytically active sites in particular remains a concern. For example, HF can remove oxygen functionalities from carbon nanotubes.[80] Similarly, to increase the surface area, "activating" steps with CO$_2$ or KOH can remove much of the nitrogen content.[73] By contrast, at the

Table 1. Polymer-Derived HPCMs Obtained by Template Methods Reported in the Literature

Precursor Polymer	Monomer	Template / T (°C)	^{a}Surface area (m^2 g^{-1})	Pore volume (cm^3 g^{-1})	Pore size (nm)	Content of heteroatom	Applications	Ref.
		SiO$_2$ spheres 800 °C	1056	2.56	1–30	N (8.2 wt%)	Supercapacitor	64
		SBA-15	1013	1.14	~3.8	N (4.5 wt%)	Supercapacitor	30
		CdS nanowires 1000 °C	1054.8	—	5.93	N (5.09 at%) S (2.99 at%)	Catalyst	63
		PS-b-PEO 800 °C	~350	~0.5	5.4–16	N (7.5 wt%)	Electrocatalyst for the ORR	56
		APTS@SBA-15 450–900 °C	790	0.86	5.12	N (0.6 at%) O (2.9 at%)	Supercapacitor	65
		Silica particles 900 °C	836	2.96	1.74 12.3	N (13.2 at%) O (3.9 at%)	Li-S batteries	66
		SBA-15 1000 °C	1012	0.91	2~7	N (4.0 at%) O (0.6 at%)	Catalyst supports	67
		Mesoporous silica (KIT-6) 850 °C	1152	1.7	3.9	N (~10 at%)	Electrocatalyst for the ORR	68
		Pluronic F127 600 °C	557	0.29	2.8	N (0.38 at%)	CO$_2$/SO$_2$ capture	69
		Pluronic F127 800 °C	638	0.66	1 7	B (0.42 wt%) O (3.83 wt%)	Supercapacitor	39
		TiO$_2$ 800 °C	2144	2.27	0.6 1.2 2.7 7~25	N (8.25 wt%) O (6.6 wt%)	Supercapacitor	23
		Pluronic P-123 800 °C	2369	0.88	< 2	N (8.0 wt%)	CO$_2$ capture	70
		Phytic acid 1000 °C	1663	1.42	<10	N (1.8 wt%) O (3.3 wt%) p (0.1 wt%)	Electrocatalyst for the ORR and OER	71
		PS spheres 500 °C	323	0.78	2~5	N (19.22 wt%)	Electrocatalyst for the ORR, Supercapacitor	41
		Co(OH)$_2$ 800 °C	236.8	—	1~30	N (3.4 at%)	Electrocatalyst for the ORR	72
		Poly(n-butyl acrylate) 700 °C	500	0.67	~13	N (18 at%) O (3.6 at%)	Electrocatalyst for the ORR, Supercapacitor	73
		Triton X-100 900 °C	3022	—	2.5	N (2.55 wt%)	Supercapacitor, Li-S batteries, Adsorbent	74
		CdS nanoparticles 1000 °C	2446	3.1	1.4, 4.8	N (2.79 at%) S (1.41 at%)	Electrocatalyst for the ORR	75
		Organosilica NPs 800 °C	1244	—	~2.5	N (11.9 wt%)	Supercapacitor	60
		Colloidal silica 700 °C	777	2.3	10–20	N (4.3 at%)	CO$_2$ adsorption	76
		Polyhedral oligosilsesquioxanes (POSS) and Pluronic F108 900 °C	2000	1.19	~1 ~4	N (~4 wt%)	Supercapacitor	77
		Pluronic P-123 and sodium silicate 900 °C	794	1.05	—	N (7.4 wt%)	Electrocatalyst for the ORR	78

^{a}Surface area calculated from the N$_2$ adsorption isotherm using the BET method. ORR, oxygen reduction reaction; OER, oxygen evolution reaction; HER, hydrogen evolution reaction

expense of less precise control of the porous structure, direct carbonization of polymers without an external template can reduce template-related etching procedures. By adjusting the pyrolysis program, the heteroatoms introduced into the carbon framework can be preserved at a relatively high content and are then also stable under harsh service conditions.[82,83] In general, direct carbonization of heteroatom-rich polymers or a mixture of heteroatom-free polymers and heteroatom-containing compounds allows the production of HPCMs. The former involves homogeneous doping of heteroatoms in the bulk, the contents and types of which are dominated by the polymers themselves. In the latter, heteroatom-free or -poor polymers can be mixed with heteroatom-rich compounds, e.g., NH_3, urea, melamine, cyanamide, and dicyandiamide, before carbonization.[82,84−87] However, compared with template methods, the control over the pore size distribution is usually weak due to potential phase changes of the mixture of the polymer and the heteroatom-containing compound. Recent progress in the synthesis of HPCMs directly from polymers without templates is summarized in Table 2. These studies include different types of polymeric precursors and heteroatom sources, S_{BET}, pore sizes, heteroatom contents, and carbonization conditions.

2.2.1. Direct Carbonization of Heteroatom-Rich Polymers. Heteroatom-rich polymers, such as the N-containing polymers of PAN, PI, PAM, PVP, PoPDA, PPy, PANI, PDA, and imidazolium-containing PILs and S-containing polymers such as polythiophene (PTh),[8,88−96] can be directly carbonized. Owing to their rich abundance of heteroatoms, the easy access to most of them, and the simple control of the morphology by classical polymer processing techniques, the direct carbonization route is popular for the preparation of HPCMs by direct carbonization in an inert atmosphere (e.g., N_2, Ar, or Ar/H_2). In a typical procedure, heteroatom-containing polymers with defined structures (e.g., nanospheres/nanotubes/nanofibers) are first prepared by organic reactions or polymerization of monomers under specific experimental conditions. Then, the as-prepared polymers are calcined in an inert atmosphere to generate porous carbons with partially, if not entirely, maintained micro/mesoporous structures from the polymers.

2.2.1.1. Conjugated Polymers (CPs) as Heteroatom-Doped Carbon Precursors. Conjugated polymers (CPs) usually possess highly conjugated polymeric main chains as well as a sufficient content of heteroatoms such as N and S.[97,98] Heteroatom-doped carbon materials derived from CPs have been considered for applications in energy devices owing to their high carbonization yield, high heteroatom content, and maintained or even increased conductivity.[99] Advantageously, the heteroatoms homogeneously introduced into the polymer in an sp^2 or sp hybridization state are better preserved than nonconjugated species under the same carbonization conditions and are more stable under the harsh working conditions usually applied to carbons. Direct carbonization of CPs also avoids extra steps of conventional carbonization methods, such as thermal annealing in the presence of NH_3, chemical vapor deposition, the arc-discharge method, and nitrogen plasma treatment.

PANI with its structure of phenyl rings connected via nitrogen-atom bridges can be considered the archetype of a conjugated-polymer-based precursor for N-doped carbons. Direct carbonization of PANI, which serves as both the carbon and nitrogen sources, could preserve the homogeneous distribution of N sites on the resultant graphitic carbon

Table 2. Summary of the Polymeric Precursor, S_{BET}, Pore Size, N Content, and Carbonization Conditions for Diverse Porous Carbons Obtained by Direct Synthesis Strategies

Precursor Polymer	Monomer	Temperature (°C)	Surface area (m² g⁻¹)	Pore volume (cm³ g⁻¹)	Pore size (nm)	Content of heteroatom	Applications	Ref.
		800 °C	1513	1.13	2.98	N (8.4 wt%)	Supercapacitors	
		900 °C	465	0.39	1.64	N (1.21 at%) O (4.61 at%)	Supercapacitors	139
		800 °C	20.35	0.03317	6.52	N (11.9 wt%)	Li-ion batteries	140
		1000 °C	1327	—	1~2	N (1.9 at%)	Supercapacitors	
		800 °C	753	—	2	N (6.0 wt%)	Supercapacitors	88
		600 °C	1203	0.641	0.5–1, 1.2–7	N (2.7 at%) O (5.4 at%)	Supercapacitors	
		600 °C	159.6	—	3.8, 14, 70	N (20.6 at%) O (6.4 at%)	Li-ion batteries	142
		800 °C	2279	0.177	2.23	—	Supercapacitors	
		700 °C	1852	0.964	0.5 1.0	N (1.72 wt%)	CO₂ capture	
		800 °C	815	0.733	10	P (1.62 at%)	Electrocatalyst for the ORR	
			38	0.022	—	N (1.3 at%) O (8.6 at%) S (1.7 at%)		
		800 °C	290	0.157	<1	N (2.4 at%) O (9.3 at%) S (2.4 at%)	Supercapacitors	
		600 °C	754	—	1~5	N (23.9 wt%)	Electrocatalyst for the ORR	
		1000 °C	907	0.79	15	N (5.7 wt%)	Electrocatalyst for the HER and OER	
		Direct synthesis (L-lysine) 800 °C	537	0.258	—	N (1.28 wt%) O (3.44 wt%)	CO₂ capture	136
		800 °C	215	0.26	1.81	N (5.63 wt%) B (3.34 wt%)	CO₂/CH₄ capture	147
			291	0.33	1.84	N (5.72 wt%) B (3.21 wt%)		
			268	0.23	1.72	N (4.89 wt%) B (2.91 wt%)		
		800 °C	1051	1.93	7.4	O (7.90 at%)	Supercapacitors	
		900 °C	1535	2.21	0.5–2, ~30	N (3.21 wt%) P (2.12 wt%)	Electrocatalyst for the ORR	127
		700 °C	496	0.25	10	N (12 at%) B (5.6 at%)	Electrocatalyst for the ORR	
		900 °C	683.7	—	3–9	B (8.07 wt%)	Li-O₂ batteries	

^aS_{BET} calculated from the N_2 adsorption isotherm. ORR, oxygen reduction reaction; OER, oxygen evolution reaction; HER, hydrogen evolution reaction.
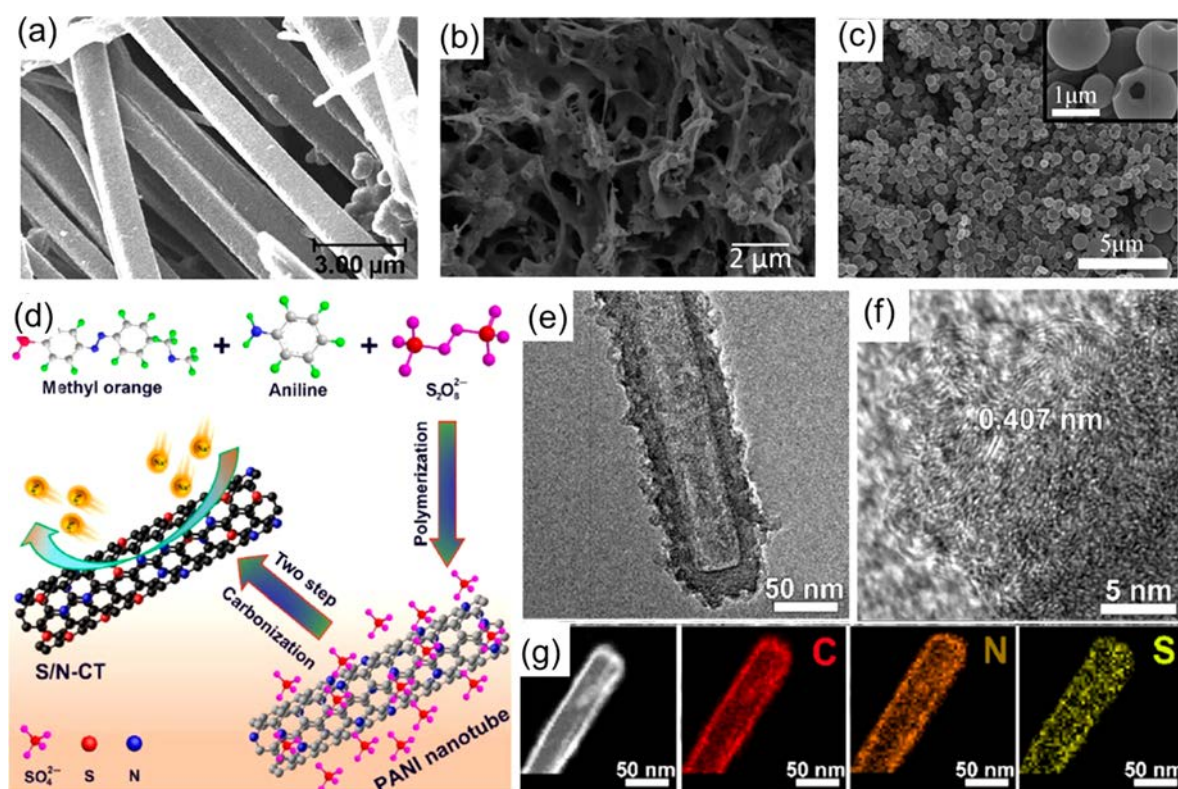
Figure 9. (a) SEM image of N-doped carbon fibers from PPy annealed at 800 °C. (b) SEM image of N-CNWs prepared from PpPD annealed at 700 °C. (c) SEM image of hollow carbon spheres obtained by annealing PoPD at 700 °C. (d) Synthetic schematic for PANI nanotubes *via* a soft template method and subsequent high-temperature conversion into S/N-CT samples. (e, f) TEM images of S/N-CT. (g) STEM image and energy-dispersive elemental maps of C, N, and S in S/N-CT. Reproduced with permission from ref 101, copyright 2012 Royal Society of Chemistry; ref 93, copyright 2014 American Chemical Society; ref 102, copyright 2015 Elsevier; and ref 105, copyright 2018 Springer.

surface.[100] In addition to PANI, PPy and polythiophene are other typical choices of conjugated polymers as carbon precursors. It is important to know that, beyond heteroatom doping, controlling the morphology and nanostructure is crucial to improving the functionality of CP-derived carbocatalysts.[97] For example, Jousselme and co-workers synthesized PPy with granular- and tubule-like morphologies and studied the relationship between the morphologies and the ORR performances of the resultant carbon materials (Figure 9a).[101] They found that the annealed PPy tubes showed better ORR performance, current density, and electron transfer number. Lei et al. prepared 3D porous N-doped carbon networks (3D N-CNWs) containing a high N content by carbonizing poly(p-phenylenediamine) (PpPD) through the integration of oxidative polymerization and catalytic carbonization procedures (Figure 9b).[93] The 3D N-CNWs obtained at 700 °C possessed a high S_{BET} value of up to 1513 $m^2 \cdot g^{-1}$. Similarly, to obtain N- and O-codoped hollow carbon spheres (HCSs), Yao's group directly carbonized PoPD submicron spheres with the assistance of a glycine dopant (Figure 9c).[102] The as-synthesized mesoporous HCSs displayed an S_{BET} value of 355 $m^2 \cdot g^{-1}$, a high specific capacitance of 210 $F \cdot g^{-1}$, and good cycling stability in supercapacitor tests.

Thiophene and thiophene-based compounds, especially the commercially available 2-thiophenemethanols, are the most common choices for the synthesis of S-doped carbons.[103,104] They are sufficiently thermostable to give a high yield under carbonization conditions. $FeCl_3$ is usually used to polymerize 2-thiophenemethanol into a thermostable, S-rich linear polymer. In polythiophene-derived carbons, the incorporated

S atoms predominantly form aromatic five-ring sulfides and are not eliminated due to their high thermal stability. High-temperature treatment of carbon precursors with S-containing gases, such as CS_2 and H_2S, is also efficient for increasing the S doping in carbon materials; such a method is commonly used for doping graphene with S.

Apart from a single type of heteroatom doping, Xu's group demonstrated conjugated-polymer-mediated synthesis of S- and N-codoped carbon nanotubes (S/N-CT) *via* carbonization of S-containing PANI nanotubes (Figure 9d–g).[105] In their work, ammonium persulfate $(NH_4)_2S_2O_8$ was applied as both an oxidant and a dopant. Their results indicated that the selected carbonization technique as well as the $(NH_4)_2S_2O_8$ content had a great impact on the construction of the carbon framework, S_{BET}, pore volume, and relative contents of the S and N species, which can in turn alter the Na^+ storage performance of the S/N-CT materials.

2.2.1.2. Polydopamine (PDA) as a Heteroatom-Doped Carbon Precursor. PDA is an alternative conjugated polymer for preparing N-doped porous carbons because it has not only rich N-containing groups but also a nearly 60% carbonization yield under N_2 at 800 °C.[106−109] The first evidence of the high potential of PDA as a N-doped carbon precursor was demonstrated by Dai et al. in 2011, where PDA was used as a nitrogen and carbon precursor and silica nanospheres as a hard template to produce uniform hollow carbon spheres.[108] Shortly after this work, in 2013, Lu and colleagues produced size-controlled monodispersed porous carbon submicron spheres (SMSs).[109] These authors identified that dopamine could directly polymerize into PDA in a submicron sphere
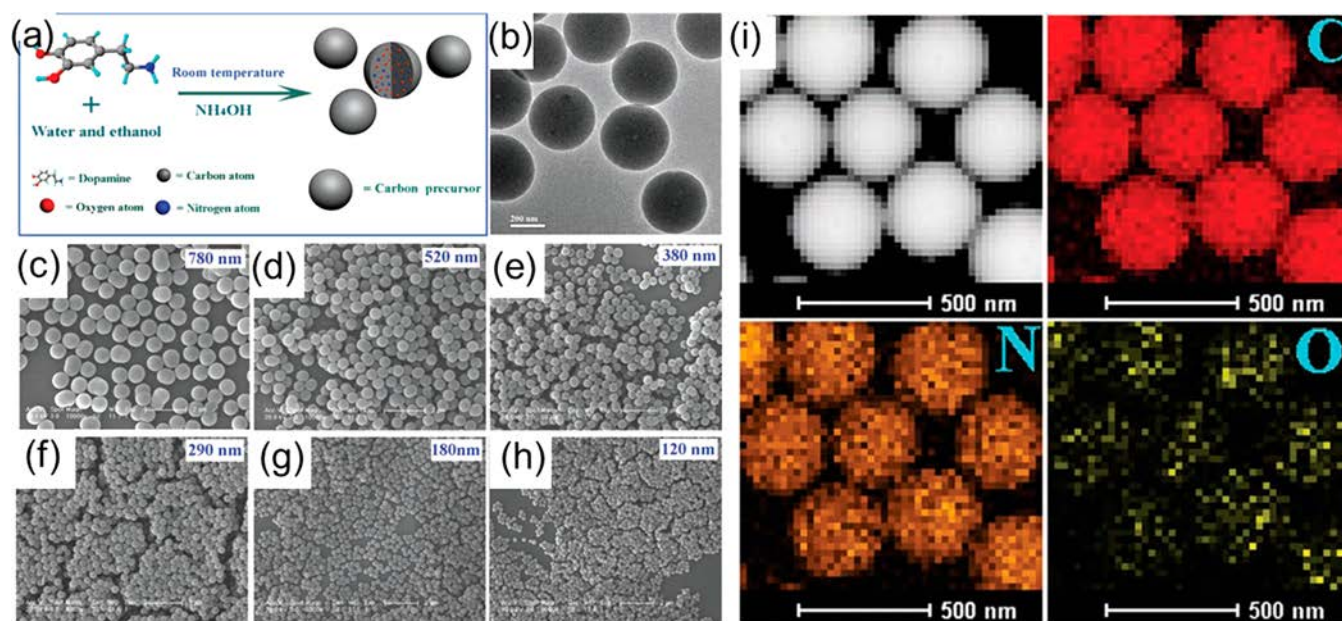
Figure 10. (a) Schematic illustration of the synthesis of PDA submicron spheres (SMSs). (b) Typical TEM image of PDA SMSs with an average diameter of 380 nm. (c−h) SEM images of PDA SMSs with different diameters prepared at different ratios of ammonia to dopamine. (i) EELS mapping analysis of PDA-based carbon spheres. Reproduced with permission from ref 109. Copyright 2013 Wiley-VCH.

state without any template in a mixture of ethanol, water, and ammonia at room temperature (Figure 10). After carbonization at 800 °C, the PDA spheres were converted into carbon spheres. Furthermore, the sizes of the carbon spheres could be precisely adjusted over a wide range, even down to below 200 nm, by varying the ratio of ammonia to dopamine. In comparison to the phenol/formaldehyde resin-derived carbon spheres, the PDA-derived ones contain a higher degree of sp^2 carbon (graphitic carbon) as well as a high content of N active sites, thus exhibiting enhanced electron conductivity and catalytic activity. It should be noted that the functional groups of PDA, such as catechol and N−H, make it convenient to coat PDA on various solid surfaces to form hybrid materials with specific properties.

Apart from the structural regulation of PDA, different heteroatoms, such as S and B, can be easily introduced into the PDA matrix to obtain dual-doped carbons in combination with the intrinsic nitrogen in PDA. PDA can react with thiol groups under ambient conditions *via* Schiff base or Michael addition reactions, with the rate constant ranging from 4×10^5 to 3×10^7 $M^{-1} \cdot S^{-1}$ in the case of cysteine at pH 7.[110,111] For example, Qiao et al. reported that, by reacting 2-mercaptoethanol with PDA, a 2.5 nm-thick PDA−GO hybrid could graft approximately 16.7 at. % S, which, after pyrolysis, yielded mesoporous N, S-codoped carbon nanosheets (N, S-CNs).[112] This S doping strategy could realize *in situ* and uniform N, S codoping and simultaneously achieve much higher doping efficiencies (4.1 at. % N and 6.1 at. % S) than those achieved by the post-treatment methods. The resultant N, S-CNs exhibited excellent performance as bifunctional electrocatalysts for the ORR/OER, which was attributed to the high level of dual doping, abundant pores, and favorable electron transfer ability. In addition, boronic acid can bind the catechol groups of PDA by boronic acid−diol complexation.[111] This strategy was utilized by Ahmed and co-workers to construct a N, B-codoped carbon, which showed enhanced ORR activity due to the synergy of B and N codoping in the carbon framework.[113]

To date, the shapes of PDA-derived HPCMs have been limited mainly to nano- or macroparticles due to the difficulty in morphology control without templates. When templates are applied, PDA can be easily manufactured into desired nanostructures depending on the utilized substrates. The unmatched adhesive properties, flexible component tunability, and structural regulation are the best features exclusive to PDA. In general, heteroatom-doped carbons with richly tailored structures can be synthesized from 0D nanodots, 1D fibers, 2D films, and 3D membranes by using different types of templates.

2.2.1.3. Poly(ionic liquid) (PIL) as Heteroatom-Doped Carbon Precursors. In recent years, the synthesis of HPCMs from PILs has become an increasingly growing topic.[114] PILs are the polymer products of ionic liquid monomers. The interest in applying PILs as carbon precursors lies in the unique structural properties and functions of PILs, such as negligible vapor pressure and high thermostability and heteroatom content, in addition to the ease of shaping and processing.[115−117] Thus, porous carbon materials with different morphologies can be obtained from PILs. The approach of doping carbons with heteroatoms using PILs is very efficient for adjusting the electrical conductivity, basicity, oxidation stability, and catalytic activity of PIL-derived carbons. The requirements on the chemical structure and the formation mechanism of porous structures from PILs are similar to those of ILs, which were reviewed previously.[118,119] PILs bearing nitrile or cyano groups generally produce N-doped carbons with a higher yield than PILs without them because these nitrile/cyano groups undergo cyclization into triazine networks that stabilize the carbon intermediate to limit fragmentation, thus boosting the carbonization yield. Cyano groups can be easily incorporated into PILs either by attaching a nitrile group onto the polymer chain or *via* anion exchange to load nitrile/cyano-containing anions, such as dicyanamide (dca), tricyanomethanide (tcm), and tetracyanoborate (tcb). These condensable anions can couple different cations, such as
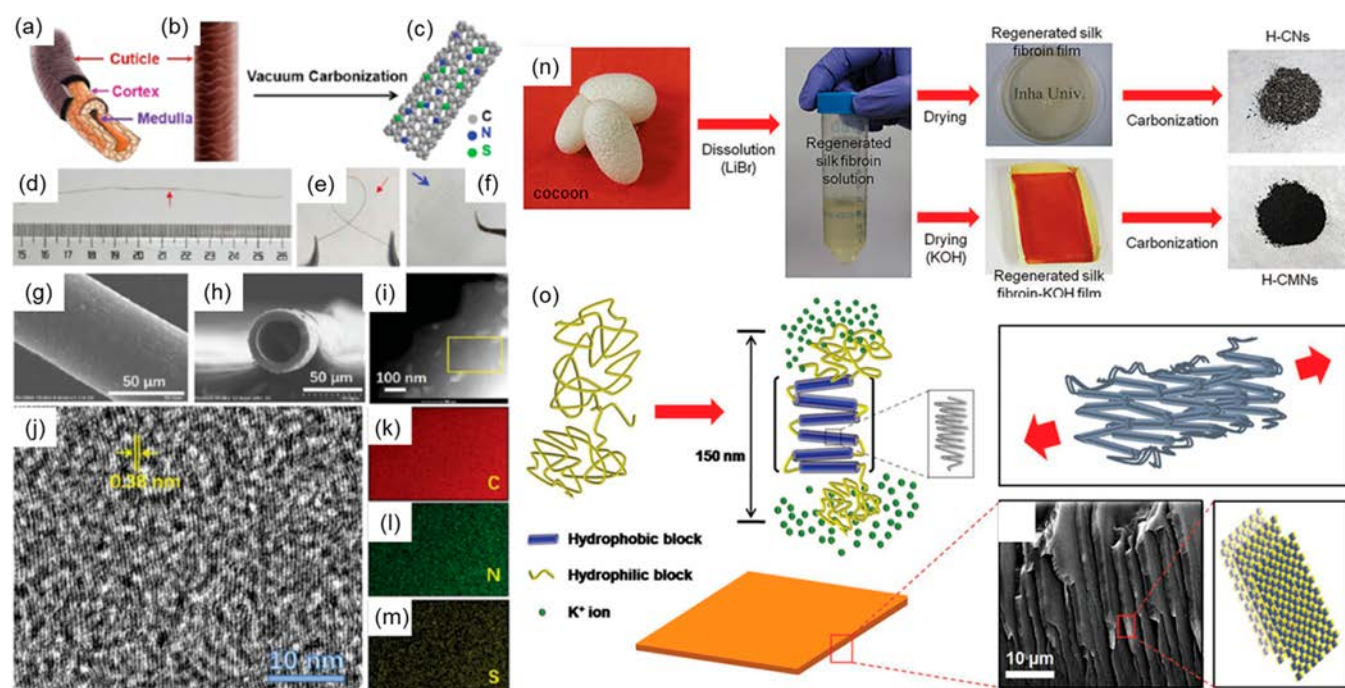
Figure 11. (a−c) Cartoon illustration of a heteroatom-doped graphitic carbon fiber derived from "human hair". (d−f) Digital photographs of linear and bent carbon fibers and textile. (g, h) Surface and cross-sectional SEM images of carbon fibers. (i) HRTEM image of carbon fibers. (j−m) STEM image and corresponding elemental mappings. Reproduced with permission from ref 133. Copyright 2019 Royal Society of Chemistry. (n) Fabrication process of HCMNs from silk fibroin fibers. (o) Schematic model of *Bombyx mori* silk fibroin lamellar-like layer formation in water by self-assembly. The inset is an SEM image of regenerated silk fibroin film after thermal treatment at 200 °C. Reproduced with permission from ref 134. Copyright 2013 Wiley-VCH.

pyridinium, pyrrolidinium, or imidazolium derivatives, to generate N-doped carbons in high yield.

In 2010, Yuan et al. demonstrated the first example of using PILs as carbon precursors to produce highly graphitic, mesoporous, and conductive carbon nanostructures by the pyrolysis of IL monomers or PILs at 900 °C without a template under nitrogen in the presence of iron(II) chloride.[120] This synthetic route involved metal salts that catalyzed the growth of folded-up or stiff graphite plates with thicknesses in the range of 5−20 nm and therefore enabled template-free synthesis of porous carbons. The employment of metal chloride in this carbonization process improves the graphitization degree of carbons at the expense of a low nitrogen content due to the dissolution−precipitation mechanism during carbonization, which is not active for nitrogen. As a significant N content is essential for enhanced electronic conductivity and (electro)catalytic activity, in most of the following research activities, efforts were directed to carbonization processes without Fe/Co/Ni metals or metal salts to maintain the high nitrogen content in the final products. In addition, to use the advantages of the polymeric nature and rich processing approaches, various morphologies of PILs were pursued and converted into the corresponding carbons with well-designed shapes and structures. For example, Wang et al. reported the synthesis of porous carbon nanoparticles through a hydrothermal carbonization (HTC) method (160−200 °C), using sugars as a carbon source and PILs as an additive.[117] In this template-free process, the PILs acted as a stabilizer for the primary nanoparticles formed in the initial stage and allowed for only growth through the further addition of monomers. This occurred due to the electrostatic repulsion exerted by the PIL attached to the nanoparticle surface, which minimized agglomeration, lowering the particle size to <50 nm. In addition, the PILs further improved the porous structure of the final materials in the post-HTC carbonization step. The porous carbon nanoparticles obtained *via* this template-free approach showed a high surface area of up to 572 m²·g⁻¹. Porous functional carbon monoliths can be generated from sugar-based molecules and polysaccharide biomass at comparably low temperatures of 400 °C under a N₂ atmosphere. PILs act as "soft activation agents" with their own structural contribution and effectively promote the conversion and pore generation even at a low addition amount of 7 wt %. The obtained monolith can still preserve its natural shape, high porosity, and good mechanical performance. In addition, all aforementioned template methods can be applied to PILs owing to their extremely good affinity and compatibility with most template surfaces.

2.2.1.4. Porous Polymers. Porous organic polymers (POPs) are a family of multidimensional porous network materials with covalently bonded stable backbones that exhibit high specific surface areas and nanometer-scale pores.[5,121] According to their degree of long-range order, POPs can be generally divided into two categories: amorphous polymers (such as most covalent organic frameworks, hyper-cross-linked polymers, and polymers of intrinsic microporosity) and crystalline polymers such as conjugated microporous polymers. They can be easily designed at the molecular level and synthesized from abundant monomers with desired active sites and porous properties. POPs have been emerging as alternative precursors for the preparation of HPCMs because of their intrinsic porous structure, ease of preparation, and diverse heteroatom-containing monomer units.[122,123] POP-based self-templating has many merits, such as potential preservation of high surface
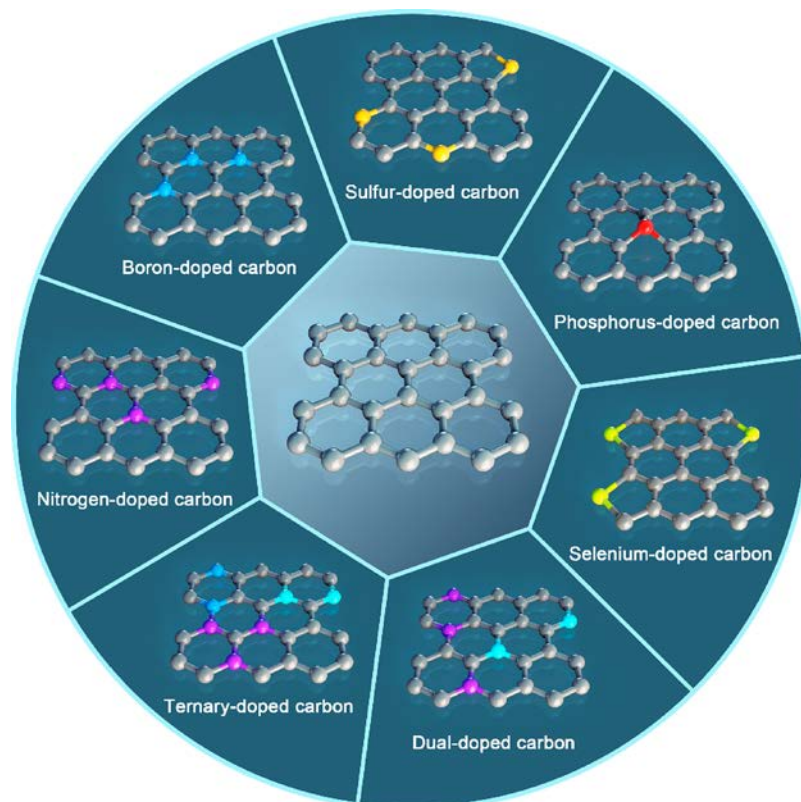
Figure 12. Schematic diagram of the structures of various heteroatom-doped carbons.

area and porosity and uniform heteroatom doping. Various POPs have been used to fabricate HPCMs for high-performance electrochemical devices, such as imine and benzimidazole-linked polymeric frameworks[5,124−126] As an example, Tan and co-workers prepared N, P-codoped carbon materials from an imine-linked POP.[127] Imine-linked POPs were first synthesized in one step with a high yield *via* Schiff base condensation in DMSO under catalyst-free conditions. N, P-Codoped carbons with a hierarchical porosity traversing the micro-, meso-, and macropore ranges with a high S_{BET} value of 1535 m^2 g^{-1} were obtained by straightforward pyrolysis of imine-linked POPs. These N, P-codoped porous carbons displayed superior electrocatalytic activity in the ORR, along with excellent stability and high tolerance to methanol. Although numerous heteroatom-doped POPs have been reported as carbon precursors, large-scale preparation at low cost remains one of the greatest obstacles for practical applications. Another challenge could be the synthesis of "strictly" metal-free HPCMs because metallic catalysts or metal-containing starting materials are usually needed to prepare POPs and trapped in part if not entirely in POPs.

2.2.1.5. Biomass Polymers as Heteroatom-Doped Carbon Precursors. From an economic and environmental viewpoint, the use of renewable precursors to synthesize HPCMs is a rational choice. Pyrolysis of biomass or biomass waste into biochars has attracted increasing interest due to their availability and recyclable nature.[128,129] Biomass in different forms, such as bean shells, pomelo peel, chicken feathers, waste coffee grounds, silk, amino acids, and willow catkins, has already been carbonized.[128,130,131] The porosity and capacitance of the resulting carbons can be balanced by optimizing the carbonization conditions. The type and content of heteroatoms, morphology, and structure of carbons can be tuned by the choice of biomass with or without chemical activation. For example, Qu et al. demonstrated green and scalable synthesis of N-doped porous carbon spheres by using fermented rice as the starting material, leading to a high S_{BET} value of 2105.9 $m^2 \cdot g^{-1}$ and a high porosity of 1.14 $cm^3 \cdot g^{-1}$.[132] When used as an active electrode in supercapacitors, the carbon spheres presented a capacitance as large as 219 $F \cdot g^{-1}$ at a high discharge current density of 15 $A \cdot g^{-1}$ and a good cycling ability of over 4400 cycles at 1 $A \cdot g^{-1}$ in a three-electrode system, using 6 M KOH as the electrolyte. More recently, Wang et al. successfully fabricated macroscopic heteroatom-doped graphitic hollow carbon fibers at scale by vacuum carbonization of "human hair" (Figure 11a−m).[133] These fibers are highly flexible and display a remarkable conductivity of 257 S cm^{-1}, suggesting great promise for a large variety of applications from wearable to electrochemical devices. Jin et al. fabricated microporous carbon nanoplates with a high surface area and numerous heteroatoms (HCMNs) by using regenerated silk fibroin as a precursor, followed by KOH activation (Figure 11n).[134] The carbon nanoplates could form lamellar-like layers in water by self-assembly (Figure 11o) due to their uniform 2D structure. The obtained HCMNs showed potential applications in supercapacitors with high energy and power density. It should be mentioned that a low concentration of metal species, e.g., Fe and Cu, originally exists in the enzymes or cofactors of biomass, which can be unaffectedly incorporated into carbons. Although these metal species are typically at the ppm level in the biomass, their potential catalytic effect in the carbon product should not be overlooked.

2.2.2. Carbonization of Heteroatom-Free Polymers with Heteroatom-Rich Coreactants. Although the direct carbonization of heteroatom-containing polymers is more

straightforward for producing HPCMs due to its simple operation, the types and contents of heteroatom elements within porous carbons rely largely, if not exclusively, on the polymers. By contrast, mixing heteroatom-containing compounds with heteroatom-free polymers provides more flexibility in manipulating the type and content of heteroatoms. In this regard, the raw material can be carbonized either by mixing heteroatom-free polymers with heteroatom-rich small organic precursors, such as N-containing arginine, dicyandiamide, melamine, adenine and urea,[85] P-containing phosphoric acid and phytic acid,[135] B-containing boric acid and boron trioxide, and S-containing thiophene and ammonium persulfate, or by carbonization in an active gas such as NH_3 and H_2S.[84] The former is usually done in a "one-pot" approach. For example, Hao et al. fabricated N-containing carbon monoliths through direct pyrolysis of a mixture of resorcinol, formaldehyde, and lysine.[136] These carbon products possess a higher nitrogen content in the bulk than on the surface. The authors found that the carbon monolith obtained at 500 °C exhibited a CO_2 adsorption capacity of 3.13 mmol g^{-1} at room temperature by balancing the N content and porosity *via* optimization of the carbonization conditions. In another example, Guo et al. prepared a N, B-codoped hierarchical carbon monolith using poly(benzoxazine-*co*-resol) and ionic liquid $[C_6mim][BF_4]$ assemblies, in which $[C_6mim][BF_4]$ acted as a structure-directing agent and a heteroatom source of N and B.[137] The obtained porous carbon monolith had a high skeleton density and fully interconnected macro/meso/micropores that facilitated the diffusion of electrolyte ions by minimizing the diffusion resistance. The nanostructure of the N, B-codoped carbon (CNB) contained a random combination of graphitic and turbostratic stacking with a short-range order and displayed a graphite-like microstructure with good electrical conductivity due to the multilength-connected carbon framework, showing promise as an electrode material for supercapacitors with a high gravimetric capacitance of 247 F g^{-1}.

Apart from direct "one-pot" synthesis by mixing heteroatom-rich precursors with heteroatom-free polymers, post-treatment methods, such as thermal annealing in active gas, i.e., NH_3, are powerful approaches for introducing heteroatoms. Most commonly, N doping is conducted in a NH_3 atmosphere.[1] It has been demonstrated that the N content and N doping environments could be controlled by changing the temperature or flow rate of NH_3.[138] Note that post-treatment methods generally lead to surface doping rather than full interior (bulk) doping. In addition, NH_3 thermal treatment results in relatively low doping levels, i.e., below 3 wt % for annealing between 800 and 900 °C. To increase the doping level, researchers often employed N precursors such as melamine for direct doping in combination with a postcarbonization NH_3 thermal treatment.

3. HETEROATOM DOPING EFFECT ON POROUS CARBONS

Chemical doping is one of the most popular strategies to modulate carbon materials (Figure 12).[151,152] The integration of heteroatoms into the carbon matrix inevitably causes structural distortions and changes the electronic band structure, which alters physicochemical characteristics, such as the thermal stability, electronic and optical properties, surface chemistry, and magnetic properties. This endows carbon materials with adjustable functions for catalysis, environmental, and energy technologies.[153−155] In this section,

doping by heteroatoms to tailor the function of porous carbons will be extensively discussed from the perspectives of synthesis, theoretical simulation, and applications, providing a solid understanding of how to dope carbon materials for target functions. The doping effects discussed here will exclude those of metal atoms, although they are important for applications in the energy and catalysis fields. Oxygen doping is also excluded, as many porous carbon materials when produced already contain oxygen due oxidation of carbons to a certain extent by air at high temperatures.

3.1. Characterization of Heteroatom-Doped Porous Carbons

To discuss the specific doping effects for various heteroatom-doped carbons and the related applications, it is important to begin with the characterization techniques that have been utilized for determining the dopant type, content, state, location, distribution, and atomic configurations in the carbon framework. It is meaningless to claim that the higher the dopant content, the better the material performance. Even at the same dopant content, the binding state and locations of the dopant elements can be drastically different. Beneath, several key instrumental methods currently employed to characterize heteroatom-doped carbons are discussed.

Elemental analysis (EA) is one of the most basic techniques to determine the dopant type and content in carbon materials. The advantage of EA characterization is that this method is widely available in many chemical laboratories because it serves multiple subfields of chemistry. Combustion EA is among the most popular methods. By careful combustion of carbon materials under designed conditions, organic elements, such as C, N, hydrogen (H), and S, that can be converted into oxidized volatiles, such as CO_2, H_2O, NO_2, and SO_2, can be detected, whereby the heteroatom concentrations in the carbon materials can be readily acquired based on the corresponding volatiles. For elements such as B, P, selenium (Se), or other elements, their corresponding oxidized species are not volatile, and other procedures are required to quantify their presence with EA.

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) equipped with energy-dispersive X-ray spectroscopy (EDX) are frequently employed to describe the elemental compositions as well as their distributions in carbons.[156] When bombarding a heteroatom-doped carbon sample with high-energy X-rays or γ-rays, the electrons in the inner shell of every atom will be "kicked out", thus producing vacancies, and then, electrons from a higher energy level fill the empty lower energy levels. This process emits characteristic X-rays that can be detected by the EDX system. Different elements display different characteristic X-ray signals. In this way, the types, quantities, and distributions of the as-expected elements in the sample can be monitored by collecting the emitted X-ray signals. Moreover, the emitted characteristic X-rays of heavy atoms are simpler to detect than those of light atoms, and EDX is hence a very effective tool for determining the contents and distributions of heavy dopants, such as Se, Sb, and Te, in carbons. In comparison to combustion EA, EDX analysis works at the local nm or μm scale. The electrons in SEM typically enter the sample to depths of tens of nm; thus, the technique is surface-sensitive. In this context, samples with a homogeneous distribution of heteroatoms will provide close results when comparing EA and EDX data. Care should be taken for samples with nonhomogeneous or site-specific

distributions of heteroatoms, as the EDX analysis results can then be significantly different from the combustion EA method results.

Beyond the elemental composition and spatial distribution in the carbon scaffolds, the chemical nature and the binding environment of the heteroatoms are also relevant. Generally, nuclear magnetic resonance (NMR) spectroscopy is widely employed to probe the local chemical structure of dissolved molecules. Similarly, solid-state NMR (SSNMR) could provide us with useful structural information of carbons. It is indeed one of the most powerful techniques, but with condensed carbon samples, some typical mistakes arise that often are not considered by the layman. First, one has to be sure that the sample is neither metallic nor contains unpaired electrons, which would greatly distort the signals, in the worst case causing loss of the entire or parts of the spectrum. Second, solid-state ^{13}C NMR is mostly performed with cross-polarization; that is, the carbon atom to be detected should be bound to a hydrogen atom, which in fact is often not the case in carbonaceous materials. The aromaticity is thereby massively underrepresented, as are carboxylate groups. This NMR problem in quantifying solid-state spectra of highly condensed organic materials can be resolved by using direct ^{13}C NMR and/or special pulse sequences. For more information on this topic, we point to the inspiring work of Schmidt-Rohr and co-workers.[157]

As a practical example, by utilizing ^{13}C cross-polarization magic-angle-spinning SSNMR (^{13}C CPMAS SSNMR), Mao and co-workers differentiated various C species in carbonized polymers (Figure 13).[158] The carbon resonance at 37.4 ppm is
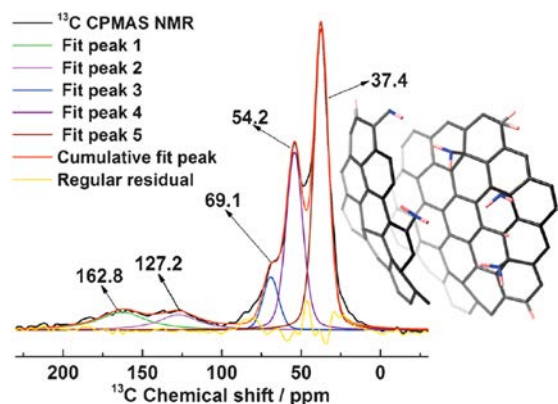
Figure 13. ^{13}C CPMAS SSNMR of a graphitic polymer condensate. Note that such SSNMR spectra are not quantitative, as they rely on cross-polarization. Reproduced with permission from ref 158. Copyright 2016 Wiley-VCH.

attributed to aliphatic carbons, i.e., methylene or methine carbons. The signals at 54.2 and 69.1 ppm can be attributed to heteroatom-bound aliphatic carbons, such as the alpha-position of aliphatic amines or alcohols. The chemical shifts at 127.2 and 162.8 ppm correspond to benzene-like aromatic carbons and electron-poor aromatic carbons, respectively. It can be nicely seen here that, in these cross-polarization SSNMR spectra, the carbons not directly connected to hydrogen atoms are massively underrepresented. Notably, SSNMR spectroscopy can also be used to probe other NMR-active heteronuclei, such as ^{31}P, ^{11}B, ^{15}N, ^{19}F, ^{27}Al, and ^{77}Se.

Undoubtedly, X-ray photoelectron spectroscopy (XPS) is the benchmark and most popular spectroscopic tool for qualitatively and quantitatively investigating the chemical compositions, chemical states, and electronic binding states of elements on carbon surfaces. XPS spectra are obtained by irradiating a sample with a beam of X-rays while simultaneously recording the kinetic energy (KE) and number of electrons that escape from the top surface, i.e., from approximately 1 to 10 nm depths of the sample.[159] A typical XPS spectrum is a plot of the number of electrons vs the binding energy of the electrons detected. Each element produces a characteristic set of XPS peaks at specific binding energies that directly identify each element on the surface. These characteristic peaks correspond to the electron orbitals of the electrons within the atoms, i.e., 1s, 2s, 2p, 3s, etc. The number of detected electrons in each of the characteristic peaks is directly related to the amount of elements within the irradiated area, which corresponds to the atomic percentage values. For example, Joo et al. investigated the function of the N contents in carbons vs the carbonization temperature by XPS.[160] As illustrated in Figure 14a, the N 1s spectra clearly showed four fittable peaks at 398.0, 399.3, 400.7, and 402.1 eV, which were assigned to pyridinic N (N1), pyrrolic N (N2), graphitic N (N3), and oxidized N (N4), respectively. With increasing pyrolysis temperature, the peak area of N3 increased, while the peak area of N1 decreased, which indicates that graphitic N is more stable than pyridinic N at high temperature. The relative ratios of the deconvoluted peak areas of the N 1s spectra were further analyzed to quantify the atomic percentage ratio for each N configuration, in which the percentage of N3 increased from 41.3 to 58% and that of N1 decreased from 41.7 to 20.3% with increasing pyrolysis temperature from 800 to 1000 °C (Figure 14b). Care should be taken that the amount of quaternary N in the aromatic systems is approximately constant; i.e., aromatic carbons can take only a limited amount of N atoms within the planes without destroying or significantly weakening their aromaticity. Despite this fact, in many literature figures, researchers prefer to draw carbon frameworks with a relatively high content of N atoms, which is merely for educational purposes and does not represent the reality in carbon materials. Indeed, N is mostly an edge-termination element. In comparison with N atoms, other heteroatoms are even more edge-preferring in terms of their positions in the aromatic carbons.

With the rapid development of advanced characterization techniques, the possibility of directly visualizing the atomic configuration in heteroatom-doped carbon has become reality. Atomic-resolution scanning transmission electron microscopy (STEM) uses a scanning beam mode that can be focused to a diameter as small as 0.1 nm by condenser lenses, which means that STEM can achieve the finest possible probe size of 0.5 Å with the maximum current available.[161] This merit allows for atomic scale resolution in imaging and chemical analysis of heteroatom-doped carbons. The STEM images are formed by filtering the scattered electrons over a certain angular range of the diffracted beam, which usually allows differentiation between bright-field (BF) and dark-field (DF) imaging modes. If the analyzed region in the sample contains a higher atomic number element, then the STEM image will appear relatively dark in the low-angle annular BF (LAABF) or relatively bright in the high-angle annular DF (HAADF).

For example, in a Se-doped carbon material, the heavy Se atoms have considerably higher Z than the light C atoms; therefore, in the HAADF images, these atomically dispersed Se
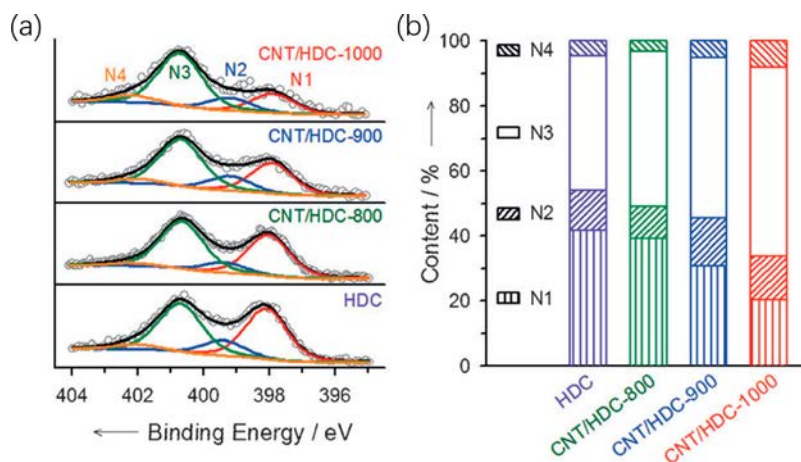
Figure 14. (a) High-resolution N 1s XPS spectra of heteroatom-doped carbon (CNT/HDC-X, where X represents the annealing temperature). (b) Relative ratios of the deconvoluted peak areas of the N 1s XPS spectra. Reproduced with permission from ref 160. Copyright 2014 Wiley-VCH.

atoms can be clearly visualized as individual bright dots (Figure 15a).[162]
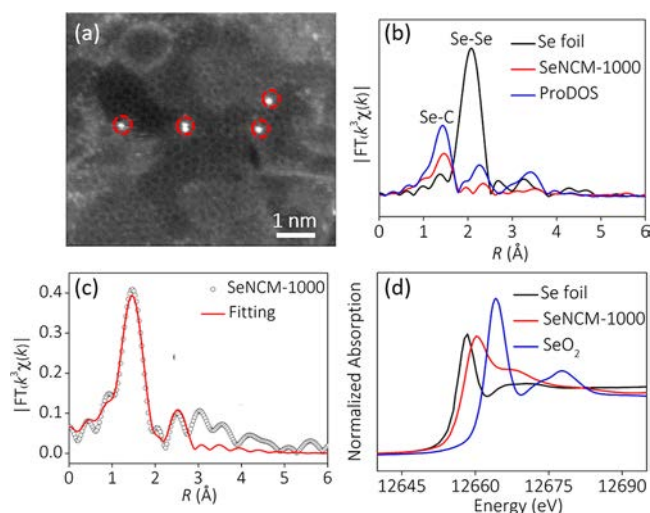
Figure 15. (a) Representative STEM-HAADF image of N, Se-codoped carbon. The Se atoms are highlighted by red circles. (b) Se K-edge Fourier transformed EXAFS spectra in the R space of the N, Se-codoped carbon compared with two other references. (c) Fourier transformed EXAFS spectrum of N, Se-codoped carbon and the corresponding simulation curve; the inset is a model structure of N, Se-codoped carbon. (d) Se K-edge XANES of the N, Se-codoped carbon as well as Se foil and SeO_2 as references. Reproduced with permission from ref 162. Copyright 2019 Wiley-VCH.

As a characterization technique complementary to STEM, X-ray absorption fine structure spectroscopy (XAFS) measurement could offer the coordination environment and chemical state of heteroatoms in carbons.[159] The fine structure is commonly divided into two regions: the near-edge region (XANES or NEXAFS, within ca. 50 eV) and extended fine structure (EXAFS), which may extend to more than 1000 eV above the edge. The XANES is very sensitive to the electronic binding structures, while the EXAFS region is focused on the distance and number of neighboring atoms. Taking Se-doped carbon as an example again, the EXAFS spectrum of Se-doped carbon membranes revealed that the Se atoms were indeed only bonded to C atoms, and no Se−Se bond was detected

(Figure 15b). Moreover, the atomic configuration of Se atoms was determined to be at the edge of graphitic planes (Figure 15c). The XANES also revealed the adsorption edge to be located between those of Se foil and SeO_2, indicating the positively charged character of the Se atoms (Figure 15d).

With the rapid development of various characterization methods, it is believed that the intrinsic relationship of the unique electronic structure of heteroatom-doped carbons with the material performance will be more clearly revealed and understood. This advance will help rationally design and prepare desirable functional heteroatom-doped carbons for specific applications.

3.2. Molecular Doping Effect of Heteroatoms on Porous Carbon

Heteroatom doping aims to tailor and adjust the bulk and/or surface properties of carbons to further optimize their performance toward a specific usage. In the case of molecular doping, the heteroatom is covalently and uniformly embedded in the carbon framework, which could readily disturb the sp^2 carbon network, inducing defects, bending individual graphitic planes, enlarging the interlayer spacing, and/or causing an uneven charge distribution in the carbon framework.[163] These structural parameters are usually considered to dictate active sites for various applications. In the following, the doping effects of N as the most widely used doping element in carbons and of non-N atoms, such as B, S, P, and Se, on tailoring the intrinsic structures/properties will be systematically discussed.

Charge redistribution induced by the electronegativity difference between a heteroatom and carbon is the most straightforward molecular doping effect.[151] In a simplified model, a heteroatom with strong electronegativity, such as N, will drag electrons away from the adjacent carbons, making them partially positively charged. The density of the positive charge depends naturally on how strongly the heteroatom pulls the electron cloud away from the carbon atoms. This pulling effect is directly reflected in the classic characterization techniques, such as XPS, EELS, or SS NMR. For example, a difference of several eV is readily seen in the XPS spectrum. By contrast, a heteroatom of lower electronegativity, such as B, will endow adjacent carbons with electron density, resulting in partially negatively charged carbon.[152,164] This uneven electron distribution creates active sites that are drastically different from the rest of the carbon framework, alters the collective

electronic band structure, and subjects carbons to easier adsorption of or interaction with nucleophiles or electrophiles. The ORR of N- and B-doped carbon materials is a good illustrative example. Both theoretical calculations and experimental data have demonstrated that B- or N-doped carbons exhibit a higher oxygen (O_2) molecule adsorption energy, while a much lower adsorption energy is measured for pristine carbons.[154,165] Density functional theory (DFT) calculations revealed that substitutional B in carbon nanotubes is present in a three-bonded form (BC_3), which exhibits sp^2 hybridization characteristics in the B−C bonds. The electronegativity difference between B and C induces a sufficient positive charge on B, which facilitates chemisorption of O_2 on B-doped carbon nanotubes.[166] For N-doped carbons, the larger electronegativity of N can induce a positive charge on the adjacent C atoms. These two different positively charged atoms in the different materials act as active sites to capture O_2 molecules and play an important role in enhancing the ORR catalytic activity.[154] According to theoretical calculations, different heteroatoms (N, B, S, and P) in graphene display different binding energies for O_2, in which B- and N-doped graphenes exhibit the lowest overall reaction free energy at U^0, suggesting a high ORR performance.[167] The exchange current density predicted for ideal heteroatom-doped graphene (x-graphene) is calculated to be 2.12×10^{-6} A/cm^2, which is 5 times that of conventional Pt/C catalysts under the same test conditions, underlining the great potential of heteroatom-doped graphenes as metal-free electrocatalysts for the ORR.

Unlike B and N, heteroatoms such as S and Se have a similar electronegativity as carbon, which means that the charge redistribution in carbon planes induced by these heteroatoms is negligible within this simplified local description. However, their considerably larger atomic size turns out to be the decisive factor in the doping effect. First, incorporating large-sized heteroatoms inevitably distorts the carbon framework and enlarges the graphitic spacing, which could create numerous defects and strain inside the carbon framework. These structural defects in carbon materials are responsible for breaking the symmetry of the charge density (or spin density) distribution, causing the electrons to be localized at specific locations and thus resulting in active sites. Meanwhile, the enlarged interlayer spacing can effectively enhance intercalation. These parameters are crucial for multiple application purposes.

Apart from creating active sites and defects in the carbon matrix via heteroatoms, the introduction of strong coordination heteroatoms, such as N and P, enables the anchoring of metal ions or nanoparticles (MNPs) as catalytic centers.[168] These ligand-type interactions can maximize the dispersion of MNPs, avoid their agglomeration, and promote strong and direct carbon−metal interactions to establish an efficient metal−ligand electron transfer between MNPs and carbon. MNPs supported in heteroatom-doped carbons have a huge potential in electrocatalysis, organic transformation, photocatalysis, etc. Though how the interaction of heteroatom-doped carbons and MNPs determines their performance in these applications is still under debate, the specific mechanism of a Mott−Schottky layer between MNPs and heteroatom-doped carbon appears to be the most widely accepted mechanism.[169]

3.3. N-Doped Porous Carbons

3.3.1. Bulk Doping. To give a better view of the N doping effect inside carbons, in this section, the concept of bulk and surface doping will be discussed separately. Bulk doping mainly focuses on the ability to modulate the electronic band structure such as the Fermi level, bandgap, and charge distribution, while surface doping modulates surface properties such as the basicity, chelating power, and wettability of the carbon materials. For heteroatom-doped graphene, bulk and surface doping are identical, as the boundary between the bulk and surface vanishes in 2D structures.

N, as one of the neighboring elements next to C in the periodic table, can form stable covalent bonds with carbon. It has been the most studied foreign element in carbon materials over the past decade. The main reason is closely associated with its abundance and the easy synthesis, unique properties, and outstanding performance of N-doped carbons.[170]

N has a similar atomic size to C, which makes the C−N bond length (1.41 Å) very close to the actual C−C bond length (1.42 Å). These similar atomic sizes between N and C atoms can effectively minimize the structural distortion of the carbon network and, thus, to a large extent, maintain the geometry of the carbon network. As discussed above, N has a much stronger electronegativity than carbon, in most scenarios increasing the electron density around N. Depending on the structural binding in the carbon framework, the configuration of N can be divided into pyridinic, pyrrolic, and graphitic N.[171] Other configurations, such as oxidized N, quaternary N, or N atoms located near a vacancy, are also possible. In this section, the specific effect of different N configurations inside the carbon framework will be analyzed.

Pyridinic N is sp^2 hybridized and bonded to two C atoms at the edge of the hexagonal carbon units; it contributes one p-electron to the π system. Electronically, the lone electron pair on pyridinic N is in an sp^2 orbital and is not a part of the delocalized π system but creates an edge termination. Thus, it is significantly basic and displays a strong electron donating character. The pyridinic N configuration is on top negatively polarized, while the surrounding C atoms are positively charged. The valence band as such moves to more positive values.[172] N-Doped carbons tend to oxidize other compounds instead of being oxidized and combusting.

As an illustrative example, Wang et al. recently demonstrated the excellent high-temperature oxidative stability of a N-doped porous carbon membrane. Its original state can be well preserved even in a butane flame (~1300 °C) in air for at least 60 s (Figure 16).[173] In the recent review by Antonietti et al., the ability of N-doped carbons to protect against oxidation is named "nobility", and multiple doping effects are summarized.[174]

Similarly, quaternary N substitutes C atoms in hexagonal rings and adopts an sp^2 hybridization bound to three carbon neighbors. However, the electronic structure is completely different compared to pyridinic N.[175] Experimentally, the chemical shift of graphitic N is approximately 401.1 eV in XPS.[176] This value is comparable to that of a pyridinium ion $C_5H_5NH^+$ (401.2 eV) and an ammonium ion NH_4^+ (401.5 eV), suggesting a positive charge character of such N. This can be explained by the fact that the lone electron pair is now contributing to the π system.[177] In addition, the positively charged N atoms indicate that the surrounding C atoms should be negatively polarized due to Coulomb screening. Then, the energy levels of the carbon materials are shifted to more
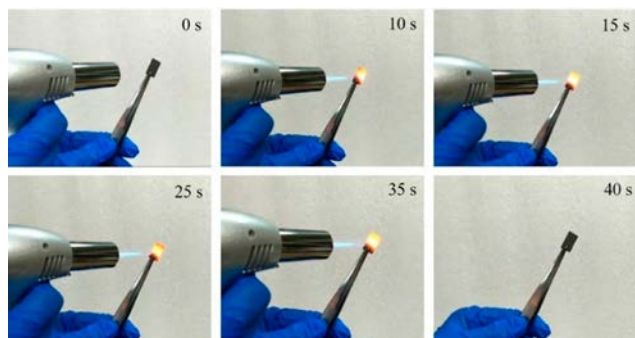
Figure 16. Fire retardancy of a N-doped porous carbon membrane. Reproduced with permission from ref 173. Copyright 2018 American Chemical Society.
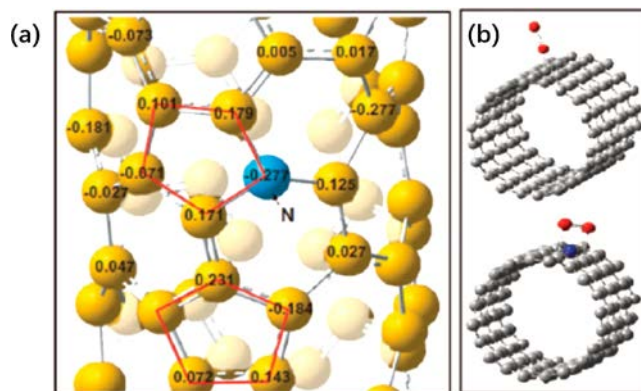
Figure 17. (a) Calculated charge density distribution of N-doped carbon nanotubes. (b) Schematic representations showing the O₂ adsorption mode change from end-on to side-on. Reprinted with permission from ref 185. Copyright 2009 AAAS.

negative values, which is consistent with the theoretical calculation.[178]

The different N configurations are all possible and can be beneficial for different purposes. Therefore, selectively constructing carbons with solely one N configuration can be both interesting and important, as it will provide a solid understanding of the material performance attributed to N doping. As an example, Wang et al. constructed mesoporous carbons with exclusively the graphitic N configuration from chitin by utilizing TiO_2 as a catalyst.[179] At the same time, by changing the catalyst to $Fe(NO_3)_3$, carbons with solely pyridinic N were obtained. Lin et al. achieved pure pyridinic N doping by thermal CVD of hydrogen and ethylene on Cu foils in the presence of NH_3.[180] Interestingly, by adjusting the flow rate of NH_3, the atomic ratio of N and C could be rationally tailored. Other strategies, such as hydrofluoric acid etching[181,182] and a solution-based method,[183] have also been reported to achieve pyridinic N-dominated carbons. For pyrrolic N-doped carbon, steam etching has shown some potential to increase the level of pyrrolic N content among all N species.[184] It is noted that, since N is mostly an edge-termination element, pyridinic N is usually more feasible than other configurations.

For the ORR, it is generally believed that positively polarized atoms facilitate the interaction with electron-rich reaction species and act as active centers in chemical reactions, e.g., in the electroreduction of O_2, CO_2, and N_2. Theoretical studies suggest that the binding energy of O_2 is stronger in N-doped carbons due to the overall positive charge on carbon atoms adjacent to N, which changes the O_2 adsorption mode from end-on to side-on (Figure 17).[185] This is regarded as crucial to breaking the O–O bond to finally facilitate the ORR. However, the precise active site for the ORR in N-doped carbon materials is still under debate. Kang et al. suggested that charge back-donation from the electron-rich N atom to O_2 significantly increased the adsorption energy of O_2 on the pyridinic N-rich carbon surface in comparison to N-free pristine carbons.[175] The binding energy per O_2 is considerably larger for higher N content. In many of the studies, the specific active sites for the ORR were closely related to graphitic N. This may be a reasonable assumption because the lone pair of N in graphitic coordination is partly donated to the π^* antibonding orbitals of the carbon, making the nitrogen formally positive and the carbon negative. This provides efficient active sites for the ORR. Pyridinic N only has one electron for the p_z orbital and negligible occupation in the π^* antibonding orbitals.[186,187] In a recent theoretical calculation

by Li et al., graphitic N induced n-type doping, while pyridinic N and pyrrolic N led to p-type doping in graphene nanosheets. The n-type doping favored the adsorption of O, and the p-type doping favored the adsorption of H.[188] Although the additional pyridinic N might not be the active sites for the ORR in this model, studies do suggest that the intrinsic locations of pyridinic sites nevertheless increase the kinetics of electro-catalytic reactions. Therefore, the widely accepted view is that graphitic N can improve the limiting current density, while pyridinic N can determine the onset potential for the ORR[189] (4e⁻ pathway). However, by precisely engineering the active sites of carbons, it is possible to selectively manipulate the ORR pathway. Recently, Harris et al. utilized the metal organic framework (MOF) amino-MIL-101(Al) as a carbonization precursor to construct N-doped carbons with a specific N configuration.[190] By changing the carbonization condition, carbons with and without quaternary N were obtained. According to their study, the presence of quaternary N sites can exclusively catalyze ORR via the 4e⁻ pathway, while pyridinic and pyrrolic N were ineffective. For the 2e⁻ pathway, Antonietti et al. obtained mesoporous N-doped carbons by direct carbonization of an ionic liquid.[191] Interestingly, the obtained carbons displayed production of H_2O_2 with a remarkable faradaic efficiency of 65.15%. In this work, the production of H_2O_2 was attributed to the high level of pyrrolic N and the "radical" character induced by the low degree of delocalization. Fornasiero et al. developed N-doped graphi-tized carbon nanohorns for H_2O_2 production with a faradaic efficiency as high as 98%.[192] In their study, the presence of microporosity was believed to favor the 2e⁻ pathway, as the residence time of H_2O_2 was short, preventing further reduction to water. At the same time, the ratio of pyridinic N and pyrrolic N also played a significant role in achieving high productivity of H_2O_2.

Recently, N-doped carbons as metal-free, low-cost electro-catalysts for the CO_2RR have received increasing attention in both academic and industrial fields. Harada et al. demonstrated that the localized electronic state of carbon materials induced by N atoms played a crucial role in achieving high CO_2 adsorption and facilitating the subsequent reduction reac-tion.[193] Particularly, the authors suggested that the edge pyridinic N and plane-located graphitic N sites could effectively stabilize the adsorbed CO_2 through an efficient charge transfer between N sites and CO_2. This point was
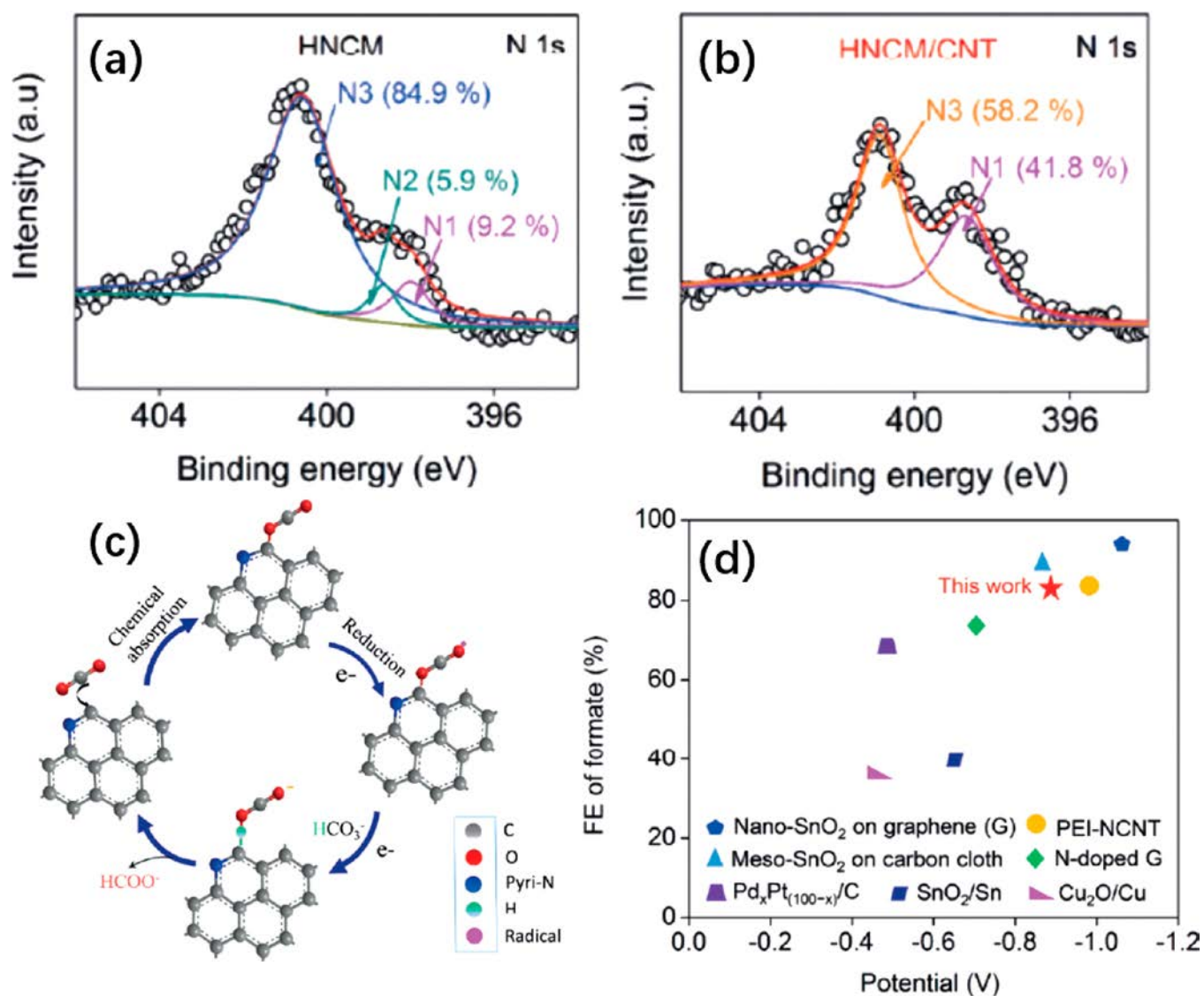
Figure 18. (a, b) High-resolution N1 XPS spectra of HNCMs and CNT-doped HNCMs/CNTs. (c) Proposed mechanism of the CO_2 RR. (d) Comparison of the potentials and faradaic efficiencies for the formation of formate on HNCMs/CNTs with those on other electrocatalysts. Reproduced with permission from ref 197. Copyright 2017 Wiley-VCH.

further confirmed by Yuan and coauthors. They constructed biphasic N-doped porous carbons by direct carbonization of PIL-coated porous carbon fibers.[194] The unique biphasic structure NPCFs could serve as a high-performance CO_2 adsorption material. The main reason why the NPCFs exhibited a miraculously high CO_2 uptake value was mainly attributed to the biphasic heterojunction that amplifies the interaction between the carbon material and CO_2. Such a heterojunction structure is similar to previously reported heterojunction systems and may be beneficial for other applications.[195,196]

In 2017, Wang et al. reported efficient electrocatalytic reduction of CO_2 to formate in 0.1 M $KHCO_3$ by hierarchically structured N-doped nanoporous carbon/CNT hybrid membranes.[197] The formed carbon on the surface of CNTs is rich in defects and short-range ordered micropores. The introduction of CNTs into the N-doped carbon membranes (HNCMs) could substantially increase the relative content of pyridinic N from 9.2 to 41.9%, as shown in the XPS spectrum analysis (Figure 18a,b); that is, the presence of

nanotubes promotes the formation of edge termination. It is noteworthy that the reported selectivity and catalytic efficiency are some of the highest for the metal-free CO_2RR and even comparable to those of the state-of-the-art tin oxide nano-crystals (Figure 18c,d). In another example, Zheng et al. specifically constructed N-doped carbons with pyrrolic N as the dominant N configuration by water steam treatment of N-doped carbon nanotubes (NCNs). The authors found that NCNs with a pyrrolic N domain show excellent electrocatalytic CO_2 reduction performance but very low hydrogen evolution reaction activity.[198]

The exact electronic effect of different N configurations in the carbon matrix for the CO_2RR is still controversial. For example, Ajayan et al. analyzed the Gibbs free energy for each configuration of N in CNTs for the CO_2RR by employing DFT simulations.[199] The results showed that pyridinic N exhibited the lowest adsorption barrier for the *COOH intermediate during the CO_2RR. The conclusion from Guo and colleagues was that the carbon atoms adjacent to the graphitic N in graphene were the most active sites for CO_2
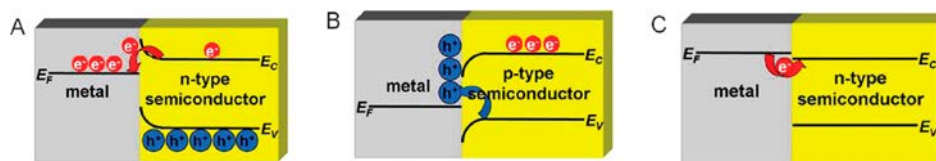
Figure 19. Schematic view of typical (a) rectifying metal−n-type semiconductor contact, (b) rectifying metal−p-type semiconductor contact, and (c) metal−semiconductor ohmic contact. Reproduced with permission from ref 169. Copyright 2013 Royal Society of Chemistry.
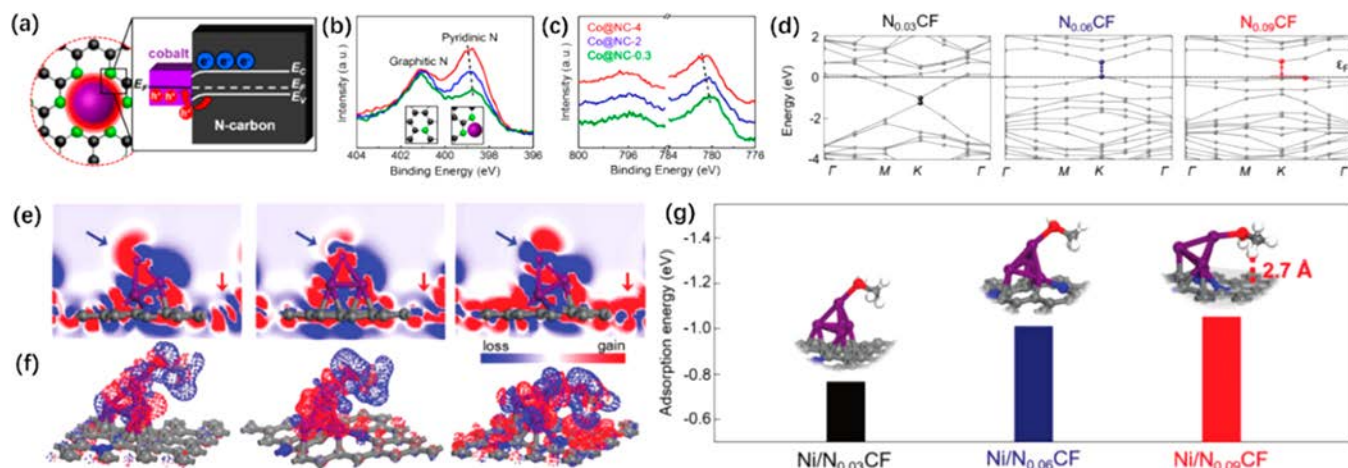
Figure 20. (a) Schematic illustration of the Mott−Schottky-type contact in a Co@NC-4 sample. (b) N 1s and (c) Co 2p XPS spectra of Co@NC-x. Reproduced with permission from ref 201. Copyright 2017 American Chemical Society. (d) DFT calculations of diverse N-doped carbons and opening of the bandgap. (e, f) Electron densities of an adsorbed model Ni_4 cluster and methanol adsorbed on the diode. (g) Methanol adsorption energies and molecular conformations of the bonding states with diverse N doping levels. Reproduced with permission from ref 202. Copyright 2018 Wiley-VCH.

adsorption.[200] In this regard, future works are required to alleviate the confusion and reveal the catalytic mechanism of different N configurations.

Apart from utilization as metal-free electrocatalysts, N-doped porous carbons can act as catalyst supports. The incorporation of N can cause the work function of electrons to be more positive than those in undoped carbons. The positive work function implies that these then "noble" carbons are more likely to accept rather than donate electrons. Thus, when MNPs are loaded onto the N-doped carbon supports, the electron density inevitably moves from the electron-rich MNPs toward the N-doped carbons, making the MNPs more positive (or reactive). In solid-state physics, such electronic interaction between a metal and a semiconductor is described as the Mott−Schottky effect, and electrons in the system will flow until the Fermi levels on both sides of the interfaces are equal (Figure 19).[169]

The Mott−Schottky effect between MNPs and N-doped carbon supports is somehow analogous to the function of a ligand in homogeneous catalysts, and the electron density on the MNPs can be rationally tailored by using different carbon supports. For example, Chen et al. constructed a Mott−Schottky type of heterogeneous catalyst for oxidation of alcohols by covering cobalt nanoparticles with N-doped carbon shells.[201] It is important to note that incorporation of N atoms into the carbon matrix can effectively lower the valence band (p-type) and elevate the conduction band (n-type), enlarging the bandgap (work function) of the carbon materials. Therefore, with a higher flat band potential than the metallic cobalt nanoparticles, the N-doped carbon shell can readily withdraw electrons from the cobalt nanoparticles to balance the Fermi levels (Figure 20a). Such Mott−Schottky electron

flow across metal−carbon interfaces can obviously redistribute the electron density at the interface between cobalt and N-doped carbon, causing the metallic cobalt to be more positively charged to attract and activate O_2. Such electron redistribution is supported by the XPS analysis, as the binding energies of N and Co increase gradually (Figure 20b,c). In this regard, the N atoms on the carbon surface can behave as a base to constitute an overall mild and additive-free catalytic system. Later, in 2018, the same group constructed N-doped carbon-supported Ni nanoparticles for highly efficient dehydrogenation of gas-phase methanol.[202] The observed enormous catalytic rate and long-term stability were attributed to the Mott−Schottky effect and Mott−Schottky barrier across the N-carbon interfaces. In addition, DFT calculations demonstrated that electrons transferred from the nickel nanoparticles to the N-doped carbon supports due to the enlarged bandgap of N-doped carbon induced by the N atoms (Figure 20d). Therefore, the enhanced electron deficiency of the Ni nanoparticles led to a much stronger interaction with the O−H bond in methanol, thereby promoting the dehydrogenation reaction (Figure 20e,f). Furthermore, the relatively "electron-rich" carbons also showed unusual binding to the electron-deficient methyl group, enhancing the binding energy (Figure 20g).

The introduction of coordinative heteroatoms, such as N, P, or S, into carbons can coordinate metal ions or MNPs to effectively prevent their agglomeration and coarsening. This feature is highly important in the controllable synthesis of specific morphology size and lattice. For example, Li et al. constructed single-atom Co−N$_5$ porous carbon spheres with nearly 100% selectivity for the CO_2RR by immobilization of cobalt phthalocyanine (CoPc) in N-doped porous carbon spheres.[203] The N atoms in the carbon network provide CoPc
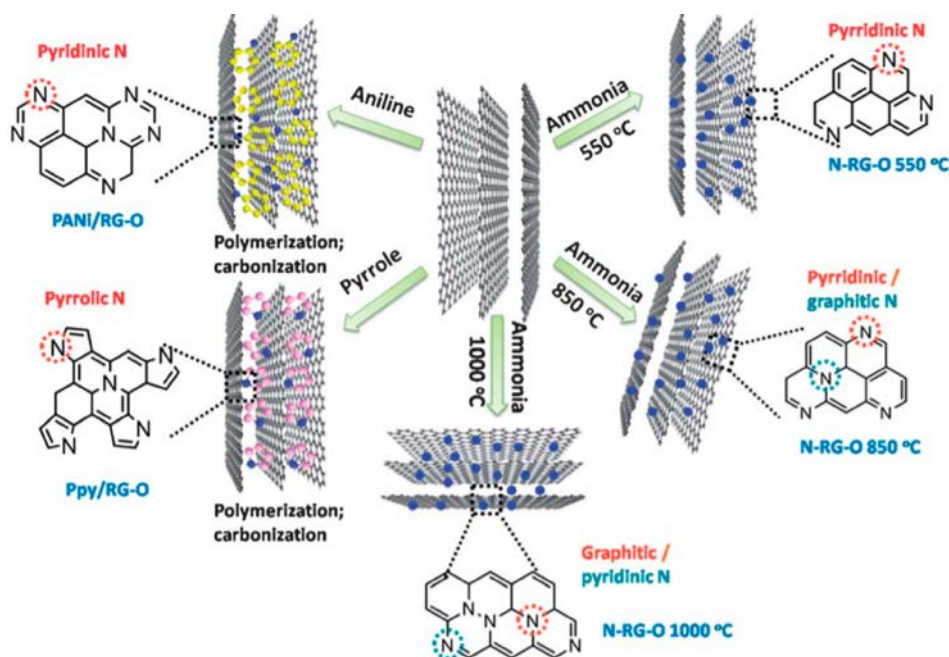
Figure 21. Surface doping of graphene using selective polymer precursors and temperatures. Reproduced with permission from ref 206. Copyright 2012 Royal Society of Chemistry.

chelating sites. It is noteworthy that utilizing N-doped carbon as a support for preparing single-atom catalysts is a simple yet versatile strategy, which is currently a topic under intensive research.

3.3.2. Surface Doping. Surface doping is the second heteroatom doping strategy to tailor the surface properties of carbon, i.e., the basicity, chelating capability, wettability, and roughness, as these properties are important for applications.[6,204,205] For instance, in energy storage applications, N atoms on the carbon surface can considerably increase the surface hydrophilicity, which helps a polar electrolyte wet the electrode surface. In the adsorption and separation field, the strong basicity of surface N atoms could promote the adsorption efficiency for various acidic molecules.

Post-treatment of carbon materials in the presence of N-containing precursors is a simple yet effective route to engineer carbon surfaces with heteroatoms (Figure 21).[206] As mentioned previously, NH_3 has been thus far the most popular source of N to dope carbons. At high temperature, NH_3 will decompose into reactive $\bullet NH_2$ or $\bullet NH$ radicals to etch carbon fragments into a N-containing functional group such as $-NH_2$, $-CN$, or pyrrolic entities. This etching process could alter the surface properties, electronic structure, and porosity of the carbon materials.

Economy et al. found that NH_3-activated carbon fibers could act as efficient adsorbents of acidic gases, i.e., SO_2.[207] The NH_3 treatment could not only basify the carbon surface but also substitute and remove oxygen-containing moieties. At elevated temperatures, the oxygen moieties on the carbon surface formed lactams, imides, and other active nitrogen groups, which improved the surface basicity of the carbon materials. This was shown to be favorable for the diffusion of a polar electrolyte into the carbon electrodes in supercapacitor devices.[208] The quantum chemical calculation by Thrower et al. demonstrated that the introduction of pyrrolic N and $-NH$ groups by ammoxidation also improved the charge mobility inside the carbon matrix by bringing electron-donor character-

istics to enhance the electron transfer behavior, thereby impacting the performance in energy devices.[209] The N configurations in a carbon framework are a function of the post-treatment temperatures. Mangun et al. confirmed that NH_3 treatment below 600 °C generates amide, imide, imine, amine, and nitrile groups, while thermally stable aromatic rings, such as pyrrole and pyridinic N, form above 600 °C.[210] This is particularly important, since different N configurations play different roles for task-specific applications.

The surface wettability of carbons is an important factor that affects the performance of carbon materials in practical applications because it can effectively enhance the diffusion of electrolytes into carbon structures and promote ion transport. Previously, Yu et al. constructed N-doped carbon nanofibers by pyrolysis of polypyrrole-coated carbon nanofibers, in which the N content, surface area, surface wettability, and pore size could be well controlled by the pyrolysis temperature.[211] They found that the performance of these N-doped carbon nanofibers in supercapacitor devices is closely dependent on their structural features because the surface wettability of these N-doped carbon nanofibers controls the ion transport. Wang and co-workers developed a type of freestanding and hydrophilic N-doped carbon foam by direct carbonization of melamine sponges (Figure 22a−c).[212] The dynamic water contact angle measurements demonstrated a highly hydrophilic nature of the N-doped carbon foams with an initial contact angle of 31.5°, while a commercial carbon cloth was very hydrophobic with a higher water contact of 107.6° (Figure 22d−f). Similarly, Kaskel et al. constructed carbon materials with an amphiphilic surface as a supercapacitor electrode by post-treatment of carbon nanotubes and graphenes with bipyridine and boronate at elevated temperatures.[213] The synthesized carbons were composed of sp^2 carbon with a hydrophobic inner layer and a hydrophilic outer layer due to the N and B functionalities there. The unique bipolar surfaces and high heteroatom doping level rendered excellent wettability to promote the energy density
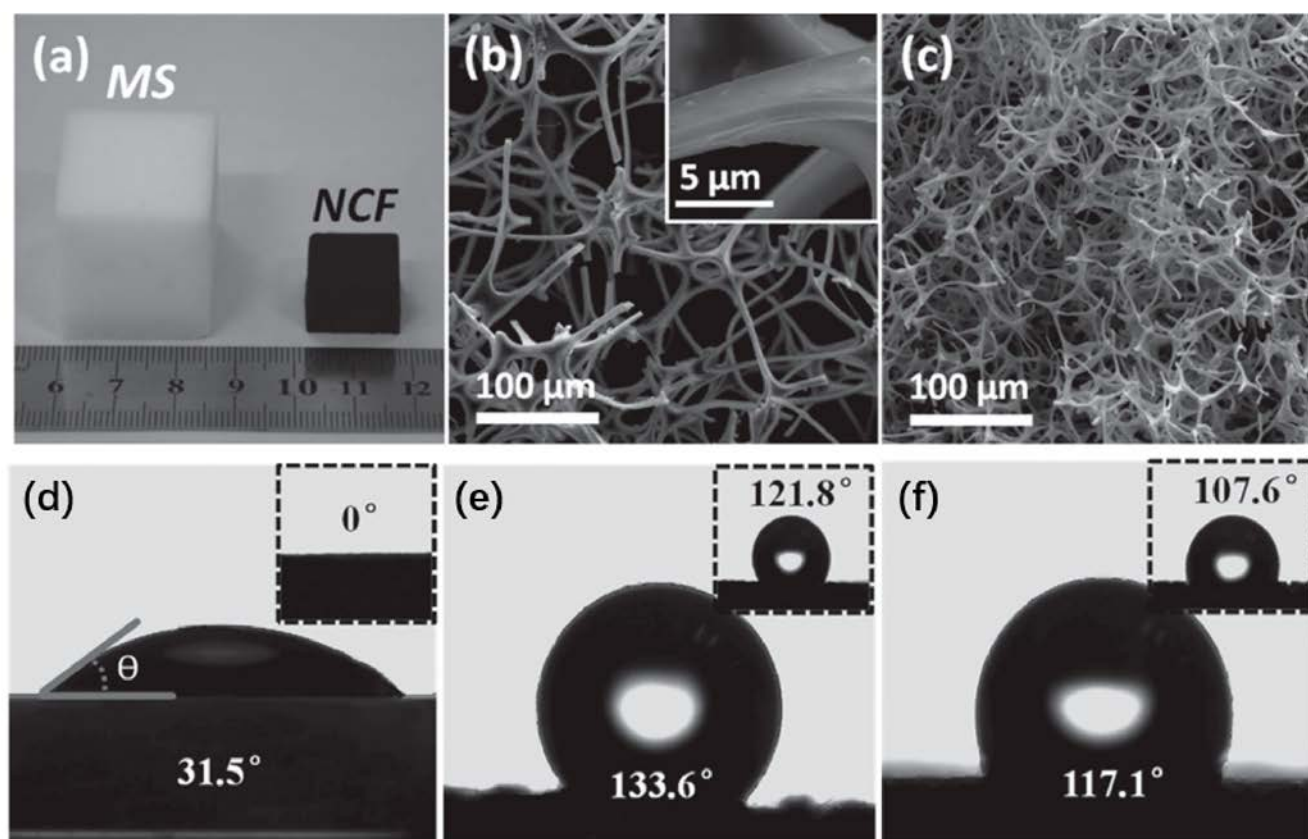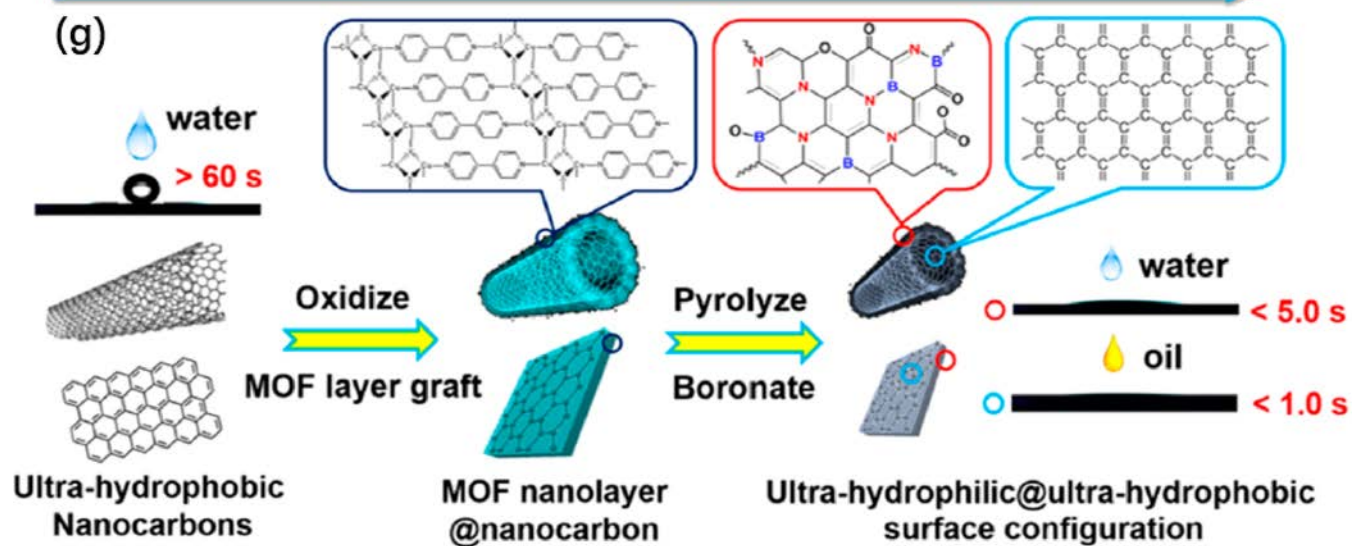
Figure 22. (a) Photographs of a melamine foam and a N-doped carbon foam. (b, c) SEM images of the melamine and carbon foams. Water contact angles of (d) N-doped carbon foam, (e) nickel foam, and (f) carbon cloth. Reproduced with permission from ref 212. Copyright 2016 Wiley-VCH. (g) Synthesis schematic of bipolar nanocarbon hybrids with a hydrophilic@hydrophobic surface configuration. Reproduced with permission from ref 213. Copyright 2016 American Chemical Society.

by 2−3 times compared with typical benchmark materials (Figure 22g).

We can state that N doping is clearly able to modulate the electronic structure, defects, and surface properties of carbon materials. N-Doped porous carbon materials as metal-free catalysts and electrodes are promising for modern energy conversion applications. Moreover, the unique electron donating nature of N could help anchor MNPs. This feature successfully widens N-doped porous carbon applications to catalyst supports and the construction of single-atom catalysts.

3.4. Non-Nitrogen-Atom (B, S, Se, and P)-Doped Porous Carbons

In addition to N, the introduction of other heteroatoms, such as B, S, Se, and P, into carbon materials has also been widely
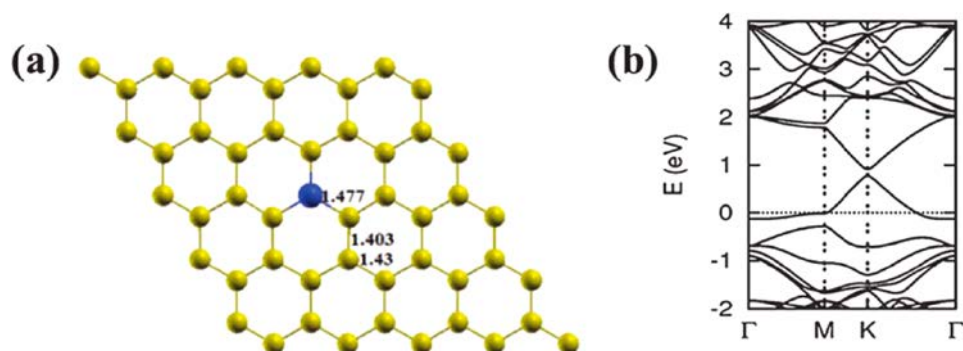
Figure 23. (a) Substitutional doping of B (blue ball). (b) Band structure of a single B-doped graphene sheet. Reproduced with permission from ref 214. Copyright 2013 Royal Society of Chemistry.
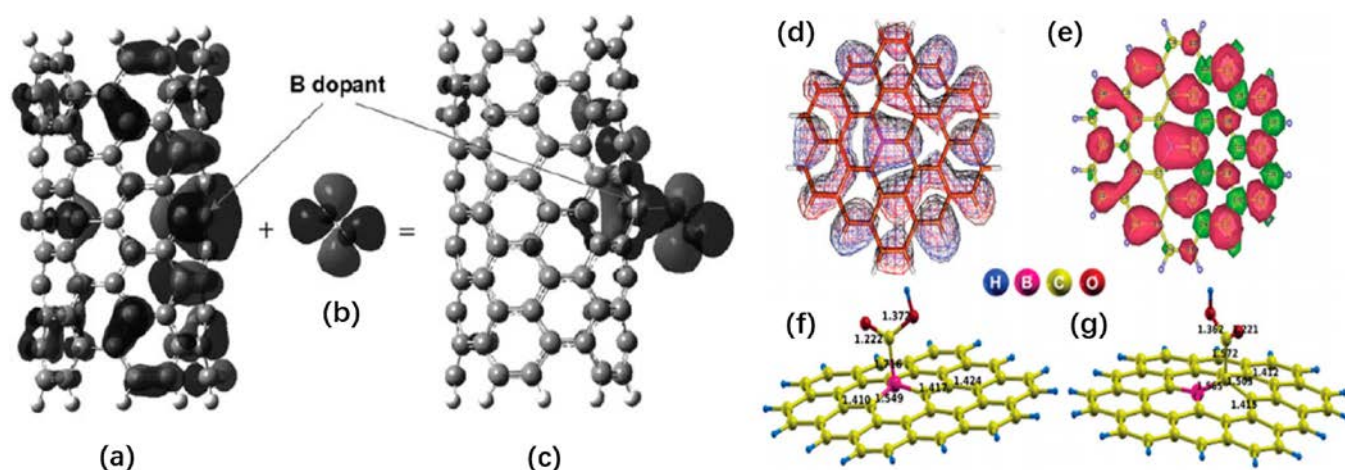
Figure 24. Molecular orbitals involved in O_2 adsorption on B-doped CNT (5,5). (a) Spin-down HOMO−1 of B-doped CNT (5,5). (b) LUMO of triplet O_2. (c) Spin-down HOMO−2 of O_2 adsorbed on B-doped CNT (5,5). Reproduced with permission from ref 166. Copyright 2011 Wiley-VCH. (d) HOMO and (e) spin density mapping of constructed B-doped carbons. Chemisorption of *COOH on B-doped carbons via B atoms (f) and C atoms (g). Reproduced with permission from ref 218. Copyright 2015 Royal Society of Chemistry.

investigated. For example, B-doped carbons are particularly useful in heterogeneous organocatalysis due to their electron-deficient characteristic. S- and P-doped carbons can enlarge the graphitic spacing and are popular in battery and supercapacitor devices. Se, as one of the latest doping elements, has begun to stand out in carbon-based heterogeneous catalysis. In the following, the properties of these non-N element-doped porous carbons from polymers will be detailed.

3.4.1. B Doping. The B atom with an outer electron shell of $2s^2 2p^1$ is, similar to nitrogen, a second row element in the periodic table. The electronic structure of B is opposite to that of N. B has only three valence electrons with three covalent bonds, which can only bring up to six electrons in total, being an electron-deficient element that always hungers for two more electrons to form a stable four-coordinate bond (or adduct), as occurs with most Lewis bases. When B is doped into carbons, the most stable form is planar, which is also referred to as in-plane doping. For the in-plane doping, B can maintain the sp^2 hybridization of the carbon network in the form of BC_3 and join the π system (Figure 23a).[214] With stable substitution patterns, e.g., phenyl groups, it can also enter sp^3 hybridization, here negatively charged BC_4. Note that BC_4 as an out-of-plane structure would eventually relax to the in-plane BC_3 structure due to thermally induced elimination.[215] Although the bond length of the C−B bond (∼1.50 Å) is longer than that of an sp^2 C−C bond (1.42 Å), the strong polarization between

neighboring C atoms and electron-deficient B can minimize the mechanical stress on the host carbon structure.[216] The empty orbital of B can readily withdraw electron density from the carbon network via pi-bonding, which inevitably increases the work function of the carbon materials to more negative values (Figure 23b).

Previously, several groups found that moderate B doping could enhance the ORR performance.[217] The DFT calculations by Hu et al. showed that the intrinsic electron-deficient nature of B can readily withdraw electrons from the pi-system and act as a bridge for a fast electron process toward O_2 in the ORR. Upon adsorption, the protruding lobe of the spin-down HOMO (highest occupied molecular orbital) of a B-doped CNT (BCNT(5,5)) maximized the overlap with the LUMO (lowest unoccupied molecular orbital) of triplet O_2 to create end-on adsorption, thereby facilitating the ORR process (Figure 24a−c).[166] Similarly, B-doped carbons also displayed exceptional catalytic performance for the CO_2RR. In the calculation from Phani's work, the electron delocalization symmetry is broken in B-doped carbons (Figure 24d,e).[218] The introduction of B also induces asymmetric charge and spin density distributions, making B-doped carbons function in the electrocatalytic CO_2RR (Figure 24f,g).

In addition to catalysis, B-doped porous carbons have also been applied in energy storage systems. For instance, Zhang et al. prepared B-doped OMCs by direct carbonization of self-
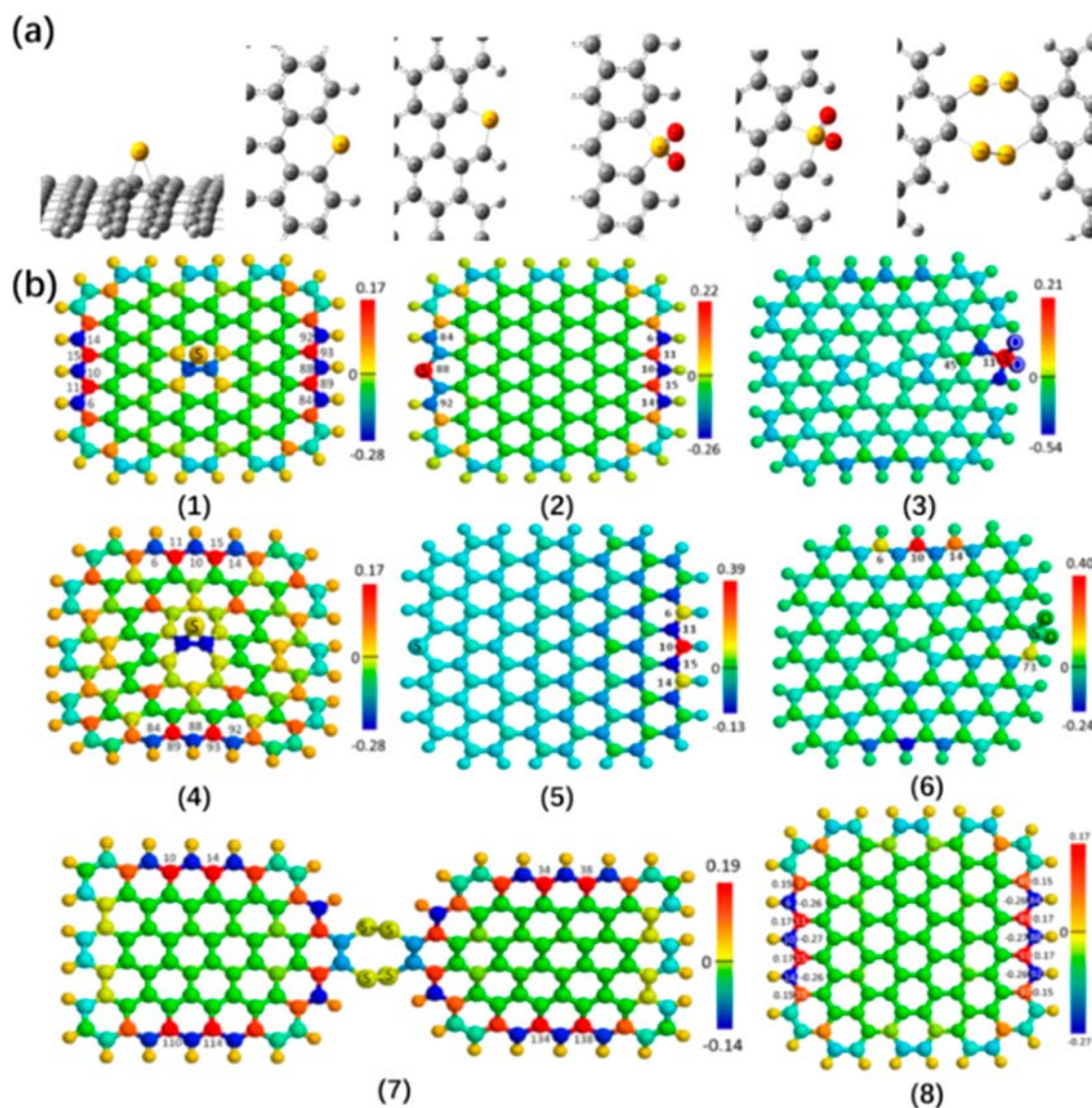
Figure 25. (a) Different mathematical models of S-doped graphene clusters. Small white, gray, yellow, and red spheres represent hydrogen, carbon, sulfur, and oxygen, respectively. (b) Atomic charge density distribution on S-adsorbed graphene clusters with (1) a perfect structure and (2) one Stone–Wales defect; (3) atomic charge density and (4) spin density distributions on a perfect graphene cluster with S substituting at the zigzag edge; (5) atomic charge density and (6) spin density on SO_2-doped graphene with a Stone–Wales defect; atomic charge density on (7) a sulfur ring cluster connecting two pieces of graphene clusters and (8) a pure graphene cluster. The colors of the balls represent relative values of charge and spin density; the density decreases linearly from positive to negative values in the color order of red, orange, yellow, green, and blue. Sulfur and oxygen atoms are labeled with S and O, respectively. The unlabeled small and large balls represent H and C, respectively. Reproduced with permission from ref 225. Copyright 2014 American Chemical Society.

assembled resorcinol and formaldehyde (RF resin) with the triblock copolymer Pluronic F127 as a soft template in the presence of boric acid. The obtained carbon materials exhibited a moderate S_{BET} value of 700 m^2 g^{-1} with a uniform micropore size of 0.6 nm. The incorporation of B atoms into the carbon framework rendered a carbon surface with surface oxygen groups. These functional groups can conduct faradaic reactions with a wide range of onset potentials, thus enhancing the pseudocapacitance of supercapacitor devices.[219]

Although B is one of the interesting doping elements in fundamental chemistry, effectively utilizing B in carbon materials is challenging, since it can be easily oxidized into boron oxide in air owing to its oxyphilic nature. Therefore, how to precisely synthesize B-doped carbon rather than oxidized B-doped carbon is being actively pursued.

3.4.2. S Doping. Unlike N and B, the S atom ($\chi = 2.58$) has a similar electronegativity to C ($\chi = 2.55$), which indicates that the covalent bond between S and C atoms is basically not polarized. However, the C–S bond length is 1.78 A, which is approximately 25% longer than the C–C bond.[220] This structural mismatch between S and C atoms makes five-ring species (i.e., thiophene and thiazole) the preferred species. In other cases, it can also bend the sp^2 flat configuration of graphenes and distort the aromatic system to a certain extent. In addition, carbons with higher S contents were found to become ribbon-like,[221] which means that sulfur preferentially contributes to extended edge termination. Such structural expansion and worsened packing are beneficial for mass transfer.[153] Theoretical calculations showed that introducing S atoms in a mathematical way into graphitic carbons opens a bandgap of the materials. S Doping (n-type dopant) could also
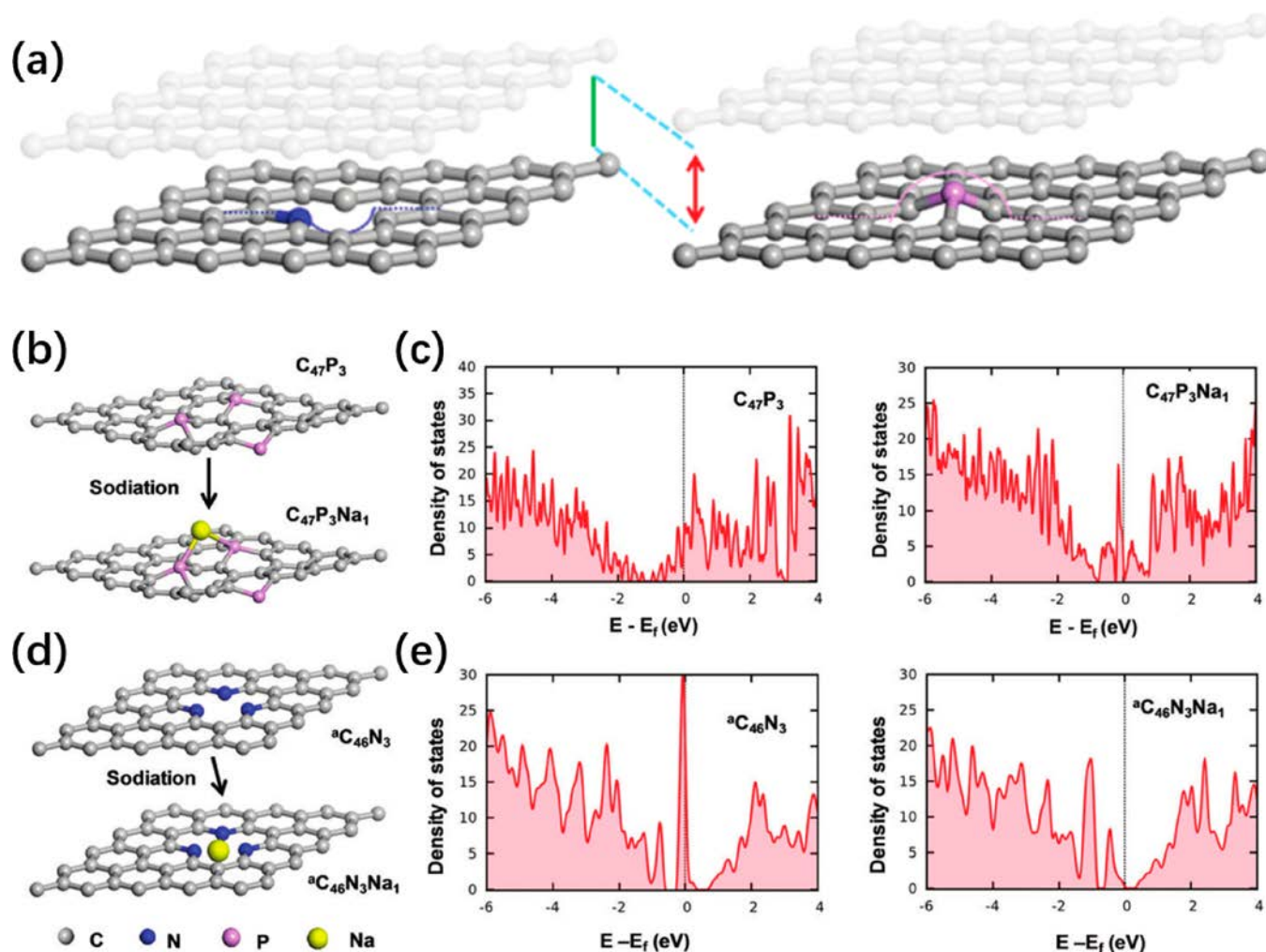
Figure 26. (a) A model in-plane "hole" defect induced by pyridinic N doping (blue) and an out-of-plane "protrusion" defect caused by P doping. (b) Schematic illustrations of P-doped states in graphene before and after sodiation. (c) Partial density of states (PDOS) of P-doped states in graphene before and after sodiation. (d) Schematic illustrations of N-doped states in graphene before and after sodiation. (e) PDOS diagrams of N-doped states in graphene before and after sodiation. Reproduced with permission from ref 229. Copyright 2017 Royal Society of Chemistry.

increase the polarization and, when charged, enhance the electronic conductivity of carbons, making S-doped carbons suitable as anodes in batteries.[222] For example, Huang et al. demonstrated that S-doped carbons performed better than their N-doped counterparts in Na-ion batteries, which mainly stems from the large interlayer distance of S-doped carbon (0.39 nm) compared to the value of 0.36 nm in N-doped carbon, thereby facilitating the insertion and extraction of Na.[223]

S-Doped carbon materials were also capable of promoting the ORR. In 2012, Huang et al. prepared S-doped carbons by thermal annealing of graphene oxide and benzyl disulfide in an argon atmosphere.[224] They found that S-doped carbons are better catalysts in the ORR than commercial Pt/C in alkaline media. This finding was particularly interesting, as S has a similar electronegativity to C, which excludes the traditional explanation of a charge redistribution effect induced by the electronegativity difference causing an improved ORR. In light of DFT calculations from Xia and co-workers, S could substitute C atoms at the graphene edges in the form of sulfur, sulfur oxide, or sulfur cluster rings (Figure 25a).[225] Mathematical replacement of C by S atoms at the edges of graphitic layers enhanced the charge and spin density. The

most effective catalytic active sites were identified to be located at the zigzag edge or the neighboring carbon atoms of the doped sulfur oxide, which also possessed a large spin or charge density (Figure 25b). Thus, the larger atomic radius of S atoms was believed to result in a mismatch of the outermost orbitals between S and C, leading to a nonuniform spin density distribution and an increase in the catalytic activity. In addition, the polarized environment of the S−C bonding will improve the interaction with O_2, and the greater strain on the polarized O_2 will promote the ORR.[226]

3.4.3. P Doping. P as a group V element has a similar binding shell electron configuration as N. However, the significantly larger atomic size of P and vacant 3d orbitals endow P-doped carbons with different features. For example, the P−C bond length is ∼24% longer than the C−C bond length, again resulting in a serious structural distortion of the carbon frameworks.[227] Moreover, the smaller electronegativity is sufficient to induce charge redistribution between P and C atoms, a property that is interesting for energy storage applications. Yu et al. introduced P atoms into carbons and found that more edges and topological defects were created in P-doped carbons, which accelerated efficient lithium ion diffusion and thus led to superior lithium ion storage
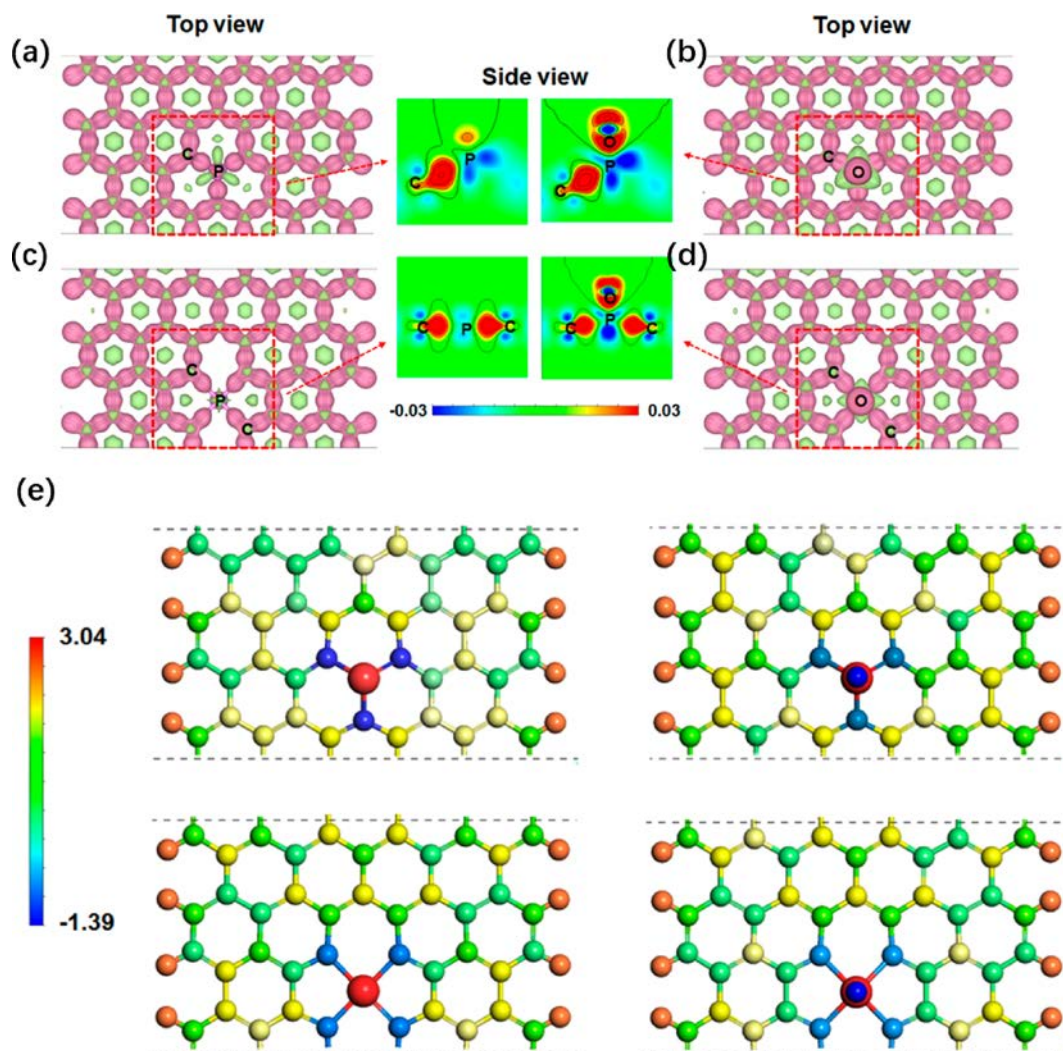
Figure 27. Deformation electronic density of hypothetical (a) PC3G, (b) OPC3G, (c) PC4G, and (d) OPC4G. The pink and yellow regions represent the areas of electron accumulation and loss, and the red and blue regions in the side view signify the areas of electron gain and loss. (e) Bader charges of the constructed models. Red and blue indicate positive and negative charges, respectively. The gray, white, red, and pink spheres represent the C, H, O, and P atoms, respectively. Reproduced with permission from ref 232. Copyright 2017 American Chemical Society.

performance.[228] These results are in agreement with the study by Wang's group, in which the "protrusion" type P-doped graphene exhibited better performance in Na batteries than N-doped graphene (Figure 26a).[229] From their DFT calculation, the maximum theoretical capacity of Na for P-doped graphene is calculated to be ∼770 mAh/g, which is much larger than the values for the N-doped versions (225.6 mAh/g for pyridinic N and 406.1 mAh/g for pyrrolic N) in a hypothetical $C_{46}N_3$ structure. In addition, the metallic properties of P-doped graphene remain mostly unchanged after sodium adsorption, which results in fast electron transport during sodium-ion insertion and extraction (Figure 26b−e).

In 2011, Yang et al. reported the first metal-free P-doped porous carbons as an efficient catalyst for the ORR.[230] The as-obtained porous carbons were flake-like graphitic layer structures with convex cuplike structures on the surface of each layer. The P-doped carbons exhibited high electrocatalytic activity, long-term stability, and outstanding tolerance to the crossover effects of methanol in the ORR compared to conventional Pt/C in alkaline media. Similarly, Yu et al. prepared P-doped carbons with an ordered mesoporous architecture by employing triphenylphosphine and phenol as

P and carbon sources and SBA-15 as a hard template.[231] The obtained porous carbons exhibited the morphology of microspheres with an S_{BET} value of 1182 m^2 g^{-1}. The XPS spectrum confirmed the existence of P−C and P−O bonding with a total P content of 1.36 at. %. Despite this low P content, the P-doped porous carbons displayed outstanding performance toward the ORR and long-term stability.

From a theoretical calculation point of view, Wei et al. explained the influence of different P configurations on the electronic structures of graphene for the ORR.[232] The oxidized P atom with three P−C bonds (OPC3G) was found to possess the highest stability, followed by the oxidized P atom with four P−C bonds (OPC4G), P atom with four P−C bonds (PC4G), and P atom with three P−C bonds (PC3G). The deformation electronic density showed substantial electron accumulation around the O and C atoms because the P atom had the lowest electronegativity (χ = 2.19) compared to O (χ = 3.44) and C (χ = 2.55) (Figure 27a−d). The C atoms adjacent to P atoms have a partial negative charge and can act as active sites for the ORR (Figure 27e). Similar effects have also been proposed in the oxidation of alcohol with P-doped porous carbons, where the enhanced

catalytic activity is attributed to the existence of P—OH/P=O moieties.[233] Moreover, the PBE (Perdew−Burke−Ernzerhof) DFT calculations showed that the binding energy of O_2 for P-doped graphene is much larger than that for N-doped graphene. The magnetic moment was found to vanish upon O_2 adsorption, thus drastically enhancing the electrical conductivity. Furthermore, P has vacant 3d orbitals, which were speculated to accommodate the lone pairs of O_2 to initiate the ORR.[154,163,230,234] Studies are still ongoing to understand the role of the vacant 3d orbital in altering the properties of P-doped porous carbons.

3.5. Codoping Effect of Heteroatoms on Porous Carbons

Each heteroatom can contribute its distinct characteristics to optimize the carbon materials for specific tasks. Codoping involves doping of two different heteroatoms into the carbon network, which could bring structural synergy. However, codoping is less studied than single-heteroatom doping in the porous carbon field due to its complexity, and future work is needed.

3.5.1. N, B Codoping. N and B-codoped carbons have been applied in fields such as catalysis and energy storage. In the previous sections, studies showed that single doping of N or B can readily adjust the electronic structure of carbons. The similar atomic sizes of B, C, and N can effectively minimize the structural distortion, but the contrary electronic properties between B and N could induce a distinct electronic effect. For example, the intrinsic electron-deficient nature of B atoms could lead to p-type doping, while the electron-rich N atoms could lead to n-type doping. Taken together, these unique features have numerous unexpected synergistic merits for multiple applications.

As an example, Antonietti et al. prepared B/N-codoped carbons with a high S_{BET} value of 978 m^2 g^{-1} by direct carbonization of a constructed B/N-codoped monolithic precursor under N_2 for selective oxidation of amine.[235] The synergistic effect of B and N could uniquely modulate the carbon electronic structure, in which B atoms (electron acceptors) could lower the valence band (or HOMO) and N atoms (electron donors) could elevate the conduction band (LUMO), thus relocalizing electrons to activate the substrate and oxygen molecules for oxidation reactions.

Previously, Oya et al. found that a N, B-codoped carbon material exhibited higher ORR catalytic activity than individual N- or B-doped carbons. The authors attributed this ORR phenomenon to a synergistic effect of B−C−N-type moieties in the carbon network.[236,237] This suggestion was confirmed by Qiao et al. through DFT calculations. In the constructed models, the 2p orbital of C in the B−C−N heteroring is polarized by adjacent N atoms, which inevitably donate extra electrons to the adjacent B atoms.[238] The activated B atoms could facilitate the adsorption and bonding of HO_2. This charge transfer induced by the B and N doping synergy was believed to account for the enhanced catalytic activity in the ORR. In 2011, Dai et al. demonstrated that the catalytic performance of B/N-codoped carbon in the ORR was largely related to the concentration of the dopants.[239] First-principles DFT calculations with four different models, pure graphene, $B_7C_{87}N_6H_{26}$, $B_{12}C_{77}N_{11}H_{26}$, and $B_{38}C_{28}N_{34}H_{26}$, were performed to understand the relationship between the dopant concentration and the catalytic capability of B/N-codoped carbons. As shown in Figure 28, the $B_{38}C_{28}N_{34}H_{26}$ model exhibited overloaded B and N atoms in the carbon network,
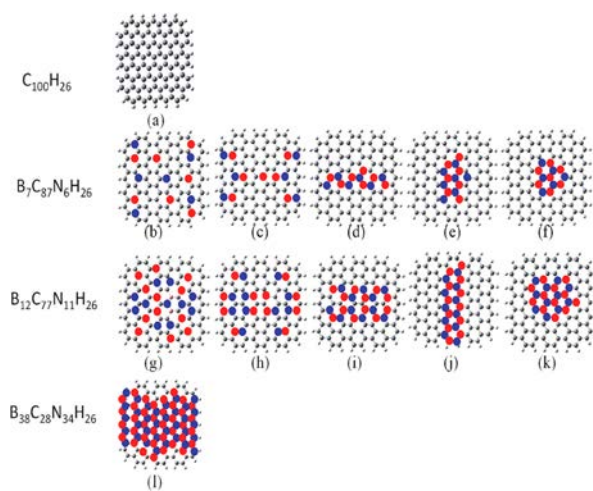
Figure 28. Different constructed B/N-codoped models. Reproduced with permission from ref 239. Copyright 2012 Wiley-VCH.

resulting in a low electrical conductivity due to the largely formed BN clusters. The $B_{38}C_{28}N_{34}H_{26}$ model displayed the highest energy gap for the ORR owing to the low conductivity, which inevitably hindered efficient electron transfer. In the $B_7C_{87}N_6H_{26}$ and $B_{12}C_{77}N_{11}H_{26}$ models, randomly distributed B/N atoms or a smaller amount of BN clusters exist, and their energy gap was found to be significantly smaller than that of the $B_{38}C_{28}N_{34}H_{26}$ carbon. Therefore, the electrocatalytic activity of moderately B/N-doped carbons was expected to be higher than that of pristine or overdoped $B_{38}C_{28}N_{34}H_{26}$ carbons. In addition, $B_{12}C_{77}N_{11}H_{26}$ has higher B and N contents than $B_7C_{87}N_6H_{26}$; thus, more carbon atoms with relatively high spin density and charge density are created, which could act as active sites toward the ORR. Taken together, the electrocatalytic activity of the moderately doped $B_{12}C_{77}N_{11}H_{26}$ was calculated to be the highest in the ORR, which was later proven experimentally. Feng et al. found that the introduction of B and N atoms into the carbon network could induce the formation of dipole moments in the scaffold of the materials due to the uneven electronegativities among B, N, and C moieties.[147] Such an uneven charge distribution is beneficial for absorbing quadrupolar CO_2 through dipole−dipole interactions. Therefore, the B/N-codoped carbon exhibited high selectivity for CO_2/CH_4 adsorption with a ratio of more than 5:1 at 298 K, showing great promise in gas separation and purification.

In 2006, Stephan and colleagues reported the first example of main group elements other than metals that could reversibly activate H_2.[240] The chemistry of such unique activation of small molecules is referred to as a "frustrated Lewis pair (FLP)", where the Lewis acid and Lewis base are separated from each other by steric hindrance. In solid-state chemistry, an FLP-like configuration anchored on catalyst supports is also found to be successful in catalyzing various reactions.[241,242] Recently, several carbon-based FLP catalysts, such as Au@N-doped carbon[243] and particularly graphene,[244] have been reported in the literature. In a theoretical calculation, Su et al. predicted that, with a suitable space between N and B atoms, codoped carbons can overcome the energy barrier and heterolytically dissociate H_2.[245] However, challenges remain, as the synthesis of FLP-like codoped carbons has to be precisely controlled.
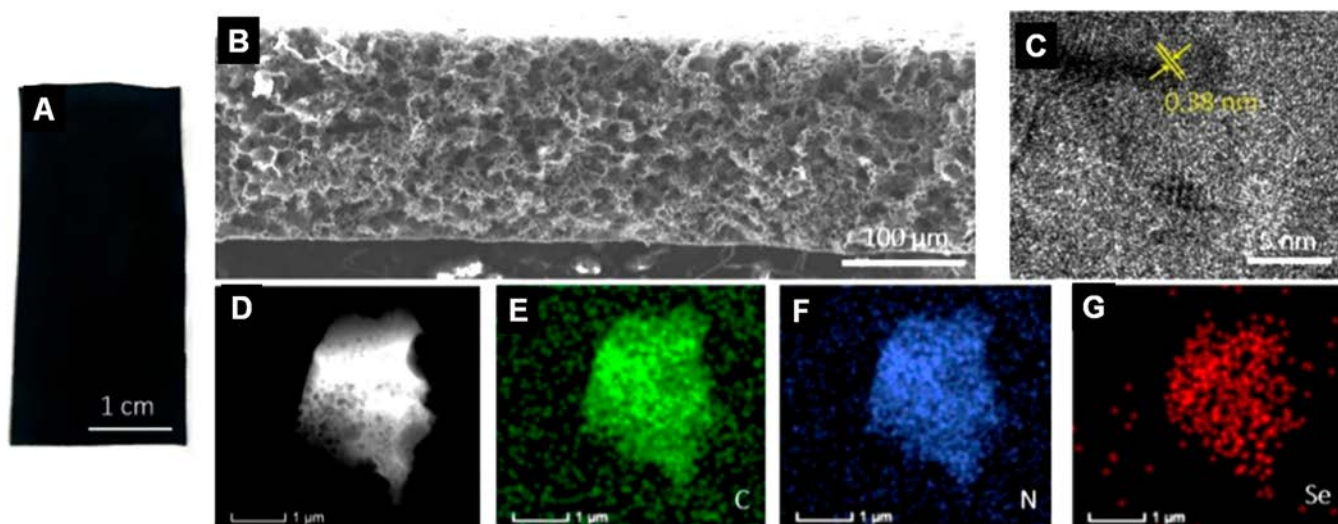
Figure 29. (a−c) Digital photograph, cross-sectional SEM image, and HRTEM image of carbon membranes. (d−g) STEM image and corresponding elemental mapping. Reproduced with permission from ref 162. Copyright 2019 Wiley-VCH.

3.5.2. N, S Codoping. N/S-codoped porous carbons are exotic materials for electrochemical applications. Not only can the N atoms effectively increase the carbon electrode conductivity, but also, the S atoms can enlarge the carbon interlayer spacing, thus boosting the charge mobility and accessibility to reactive species.

As an example, Yan et al. constructed N/S-codoped porous carbons from direct thermal annealing of human hair with KOH activation for electrochemical supercapacitors.[246] The KOH-activated N/S-codoped carbons possessed micro/meso-pores with an S_{BET} value of 1306 m^2 g^{-1} and a high N/S content, delivering outstanding specific capacitances of 340 F g^{-1} in 6 M KOH and 126 F g^{-1} in 1 M LiPF$_6$ organic electrolyte at a current density of 1 A g^{-1}. Incorporation of N and S atoms can significantly improve the electrical conductivity and surface wettability and provide multiple redox active sites, thus enlarging the pseudocapacitance and specific capacitance.

In addition, N/S-codoped porous carbons are potential anode materials for batteries, i.e., Na-ion batteries, because the enlarged interlayer spacing is beneficial for ion transport, while the introduction of N atoms can increase the first cycle Coulombic efficiency through improved electronic conductivity. This point was further confirmed by dispersion-corrected DFT calculations. Yang et al. indicated that N/S codoping could effectively enlarge the adsorption capacity and mobility of Na ions.[247] According to their calculations, the N/S-codoped carbons carried the highest spin density to promote the adsorption capacity of Na ions compared to other constructed models. They found that the adsorption capacity of Na$^+$ will be weakened with excess O atoms in N/S-codoped carbons. The increased interlayer spacing induced by the S atoms could significantly lower the energy barrier for the diffusion of Na ions from 126.83 to 97.87 meV.

In addition to applications in energy storage, N/S-codoped porous carbons are known catalysts. Feng and co-workers prepared N/S-codoped porous carbons directly from the carbonization of conjugated polymer nanosheets.[248] These porous carbons are catalytically active and stable in zinc-air batteries compared to conventional Pt/C. According to the DFT calculations from Qiao and colleagues, the codoping of N

and S could induce asymmetrical spin and charge density, which are responsible for catalytic reactions.[249] In addition, due to the large size of the S atom in the carbon matrix, the orbital mismatch between S and C will create active sites that catalyze the ORR. Similarly, N/S-codoped porous carbons are also active catalysts for the HER. For example, Chen et al. found that the introduction of S atoms led to more defects within carbons.[250] These defect sites could create a negative charge character on the S atoms, while the N atoms generated a positive charge inside the carbon matrix. Both positively and negatively charged species in the carbon framework could provide a fast electron transfer pathway for the HER. In a theoretical study from Qiao et al., N/S-codoped carbons displayed the highest HER performance compared to N-, N/B-, and N/P-(co)doped carbons.[251] These results implied that the hydrogen adsorption energy was crucial to determining the HER process.

Even though S atoms have the same electronegativity as C atoms, their large atomic size and unique electron configuration could lead to numerous unexpected properties, i.e., redistribution of the spin density and creation of defects inside the carbon framework. At the same time, incorporation of N atoms could further bring about favorable electronic properties, making N/S-codoped porous carbons promising in the field of electrochemical applications.

3.5.3. N, Se Codoping. Selenium, as one of the chalcogen elements, has similar chemical properties but a larger atomic size and a higher polarizability compared to sulfur.[252] Very recently, Wang's group successfully achieved molecular doping of Se atoms into carbon membranes by direct carbonization of a PIL porous membrane bearing a Se(CN)$_2^-$ anion (Figure 29).[162] As a semimetal, the Se atoms were found to bond to adjacent carbons with a uniform atomic dispersion throughout the carbon framework (Figure 15). Analogous to bulk doping, it is crucial to tune the electronic structure of carbons because covalent incorporation of Se atoms can readily induce strain, defects, and charged species into the carbon matrix. The XRD spectra confirmed that molecular doping of Se could enlarge the interlayer spacing (d_{002}) of graphitic domains, which is favorable for ion transfer. EXAFS spectra and STEM images confirmed that each Se atom existed individually in the carbon
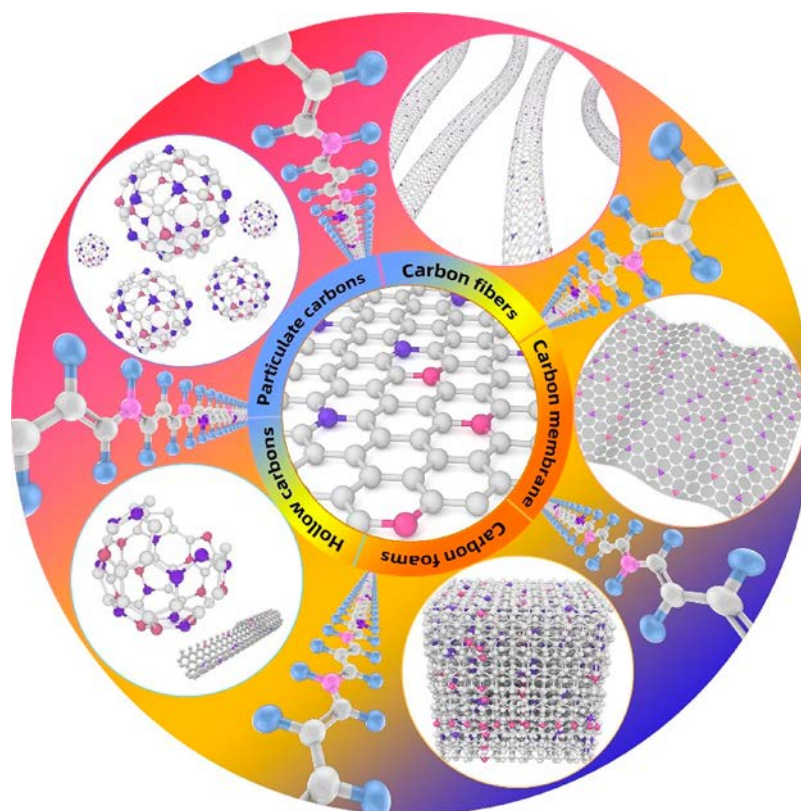
Figure 30. Schematic illustration of carbon materials with different morphologies.

framework, located at the edge of graphic domains in the membrane. The valence state of Se was between 0 and +4 according to XANES, indicative of a positive charge characteristic. The enlarged graphitic layer, positively charged Se atoms, and hierarchically porous membrane structure endowed the membrane with striking hydrazine oxidation performance in practical hydrazine fuel cells.

As an emerging doping element, Se is starting to become relevant in various applications. It is important to note that how the large atomic size and "semimetal-like" properties of Se could impact intrinsic carbon properties remains largely unknown. Therefore, it is possible that synergistic interplay between Se doping and other heteroatoms might lead to unexpected results.

3.5.4. N, P Codoping. Yuan et al. constructed N/P-codoped microporous carbon spheres by direct carbonization of self-assembled PDA with diphosphonic acid.[253] The utilization of diphosphonic acid was particularly interesting because it not only initiated the self-polymerization of dopamine but also induced the acid–base interaction with amine to incorporate P moieties into the polymer backbones. During the carbonization process with F127 as the porogen, the P/N moieties inevitably fused into the carbon matrix. These P/N-codoped porous carbons demonstrated a high performance in the ORR and HER. In 2015, Dai and colleagues reported the first N/P-codoped porous nanocarbon foams as efficient bifunctional electrocatalysts for the ORR and OER in Zn-air batteries.[71] The porosity and N/P doping level of porous nanocarbon foams could be well tailored by the carbonization temperature to optimize the electrocatalytic performance (e.g., NPMC-1000 or NPMC-1100). The first-principles DFT calculations revealed that the N/P-codoped carbons exhibited the lowest ORR and OER overpotentials compared to those of individual N- or P-doped carbons and even the state-of-the-art Pt and RuO_2 electrocatalysts in alkaline media. Later, in 2018, the same group constructed microporous N/P-codoped graphitic nanosheets by thermal annealing of conjugated microporous polymers in the presence of phytic acid.[254] Interestingly, incorporation of P was found to enhance S_{BET} due to a carbon-etching process. The XRD profiles indicated an increased interlayer spacing, suggesting that P atoms were doped into the carbon matrix. The enhanced I_D/I_G ratio in the Raman spectra was also attributed to the P doping and edge defects associated with the porous structures of the carbon network. As a consequence, through the synergistic effects between N and P, the enhanced microstructures of N/P-codoped porous carbons presented superior electrocatalytic activity for the ORR with a low overpotential, a high current density, and good stability over the entire pH range.

3.5.5. Ternary Doping by Three Types of Heteroatoms. Ternary-doped porous carbons are rarely reported. In early 2012, Woo et al. reported post-treatment of synthesized N-doped carbons with boric acid and phosphoric acid to construct N/B/P ternary-doped carbons.[255] This work showed that B effectively reinforced the sp^2 structure of carbon, N increased the portion of pyridinic N, and the larger atomic size P could severely distort the carbon framework to add edges. Therefore, the N/B- and N/P-codoped carbons showed 1.2 and 2.1 times higher ORR activity than that of N-doped carbons, while N/B/P ternary doping further improved the ORR activity, as the additional doping of B and P was expected to promote an asymmetric atomic spin density as well as charge localization of the carbon atoms.

Recently, Song et al. developed N/S/P ternary-doped carbocatalysts by carbonization of poly(cyclotriphosphazene-
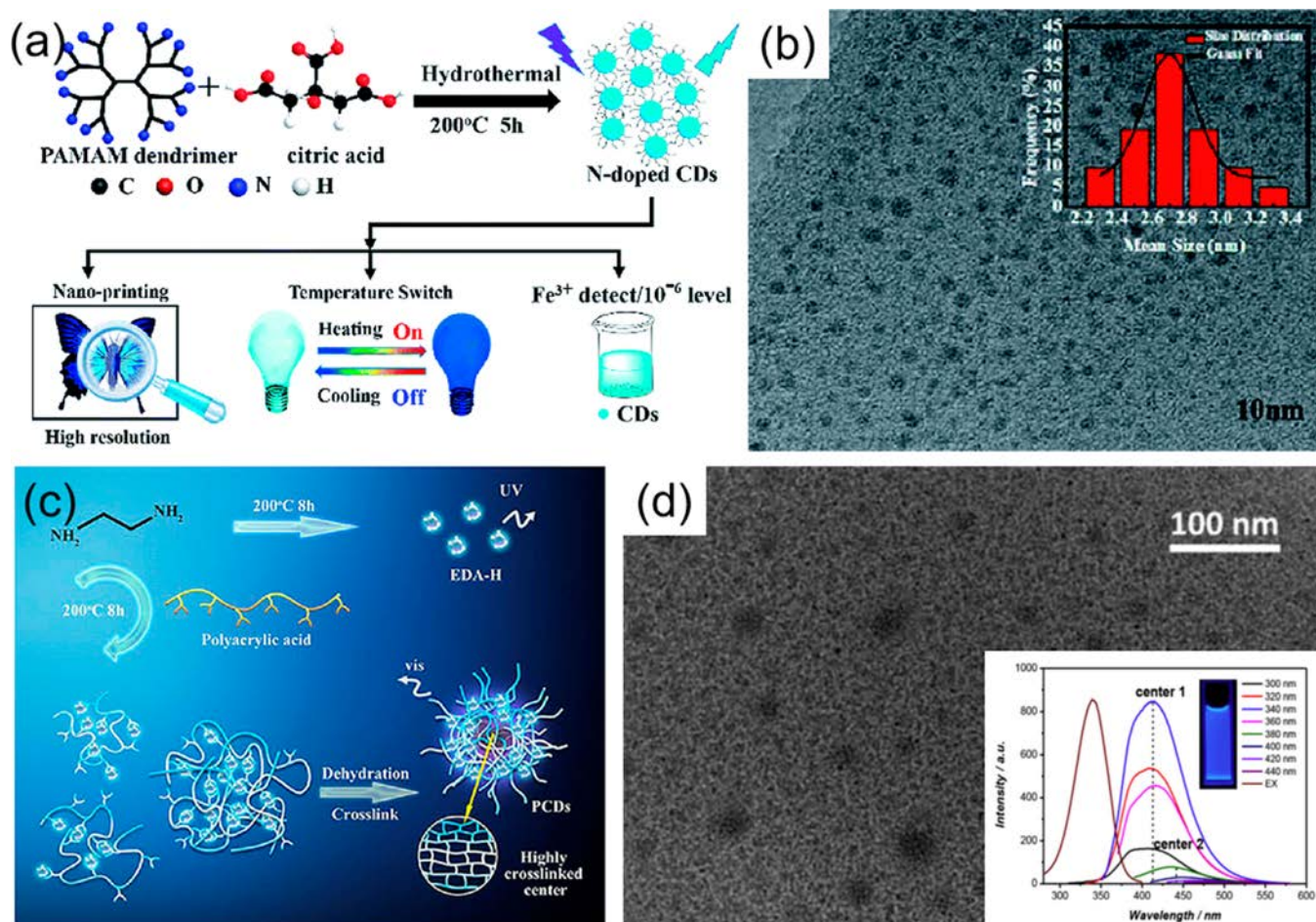
Figure 31. (a) Schematic diagram of the synthetic procedure for CQDs from PAA and EDA. (b) HRTEM image of the CQDs. The inset shows the photoluminescence excitation and emission (300−440 nm) spectra. Reproduced with permission from ref 268. Copyright 2016 Royal Society of Chemistry. (c) Schematic illustration of the synthesis of CQDs from a PAMAM dendrimer and their exemplary applications. (d) HRTEM image of CQDs along with a particle size distribution plot (inset). Reproduced with permission from ref 269. Copyright 2017 Elsevier.

co-4,4′-sulfonyldiphenol) (PZS)-coated ZIF-67 followed by acid etching to remove metals.[256] The TEM images of ZIF-67 displayed a typical polyhedral structure, which was well maintained after coating with PZS and carbonization. After acid etching, hollow carbon shells of ca. 20 nm in thickness were obtained. Remarkably, the hollow carbon shells exhibited a high S_{BET} value of 1020 m^2 g^{-1} with a pore size of 4.3 nm. Moreover, the introduction of heteroatoms readily changed the surface wettability of the carbon materials, which made them well dispersed in aqueous solution. In addition, the incorporation of N into the carbon materials was considered important to activate the C−H bond, while the N/S codoping could modulate the carbon electronic structure. Therefore, the N/S/P-codoped carbon exhibited high selectivity in the oxidation of aromatic alkanes in an aqueous solution.

Multiheteroatom doping of porous carbons is apparently also beneficial for a variety of applications. N Doping can change the electronic structure and promote the conductivity; B doping can increase the in-plane defects and even act as electron-deficient sites for various reactions; and P, S, and Se doping can enlarge the interlayer spacing and cause significant lattice distortion and defects, thus making carbons chemically more active. Furthermore, the asymmetrical spin and charge density induced by these large heteroatoms could functionalize the carbon materials. Therefore, carefully designed multi-

heteroatom doping can work synergistically, and the detailed interplay mechanism has yet to be fully understood.

4. MORPHOLOGICAL CONTROL OF POROUS CARBONS

In addition to the intrinsic chemical composition, the morphology of heteroatom-doped carbons is related to their electronic properties and corresponding electrochemical performances. The surface areas and mass transport capabilities vary greatly among 0D nanoparticles, 1D fibers and tubes, 2D sheets, and 3D bulk. Therefore, the choice of the carbon morphology has been widely studied in the literature. In this section, we highlight some particularly interesting morphologies involved in porous carbons derived from polymers ranging from porous particles to fibers, nanotubes, films, and freestanding membranes along with their corresponding processing techniques and their specific applications (Figure 30).

4.1. Heteroatom-Doped Porous Carbon Particles

Porous carbon particles, such as nano/microspheres, bubble-like hollow particles, and particles with anisotropic/asymmetric morphologies, are unique in terms of a low apparent density, a low percolation threshold, a high surface-to-volume ratio, and high thermal and chemical stability.[257] Comparably, porous carbon particles have obvious merits such as being easier to
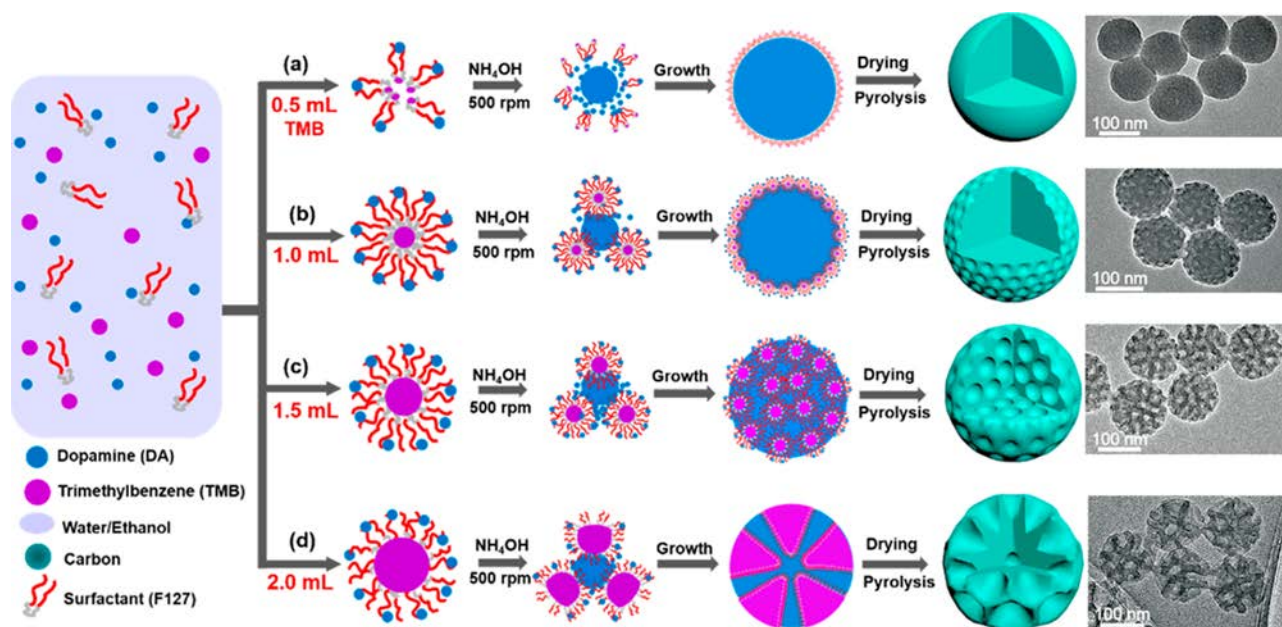
Figure 32. Formation process for the N-doped mesoporous carbon nanospheres with various morphologies prepared by the versatile nanoemulsion assembly approach and corresponding TEM images of the carbon nanospheres. Reproduced with permission from ref 274. Copyright 2019 American Chemical Society.

disperse, having shorter pathways from the bulk to the particle surface for electron transfer, and having more accessible active sites.[258] To date, polymer-derived porous carbon particles have been prepared *via* different approaches, including hard and soft template methods, controlled polymerization methods, and Stöber-based methods.[257−260] In this section, porous carbon particles with different structural features, including nano/microspheres, hollow porous particles, and anisotropic/asymmetric porous carbon particles, will be discussed.

4.1.1. Carbon Quantum Dots (CQDs). Though the chemical nature and origin of the optical properties of carbon quantum dots (CQDs) are still under debate, they have emerged as innovative carbon-based sub-10-nm nanoparticles with interesting properties due to the quantum confinement effect, i.e., a carbonaceous version of classic quantum dots in nanoscience. CQDs feature unique properties, including a small size that is rather unusual for carbons, fluorescence emission, chemical stability, water solubility, easy synthesis, and the possibility of surface functionalization, plus geographically unlimited access to carbon precursors globally. Because of the combined property profile, CQDs are a rising star in the field of nanostructured carbon materials widely studied for imaging, sensing, drug delivery, optics, and catalysis.[261] Multiple techniques have been developed to prepare CQDs simply and inexpensively, such as the hydrothermal method, electrochemical synthesis, the arc-discharge method, and microwave pyrolysis.[261−263] These top-down or bottom-up methods involve several categories of precursors covering bulk carbon, small organic molecules, natural polymers, and synthetic polymers. Among them, natural and synthetic polymer precursors provide more synthetic flexibilities on the basis of their tunable structures to define their positive, negative, zwitterionic or nonionic, and hydrophilic or hydrophobic features.

Many natural polymers have been reported for the synthesis of CQDs, including chitosan, xylan, citrus pectin, silk fibroin, gelatin, and polysaccharide.[264] As an example, CQDs of 4−7 nm in size with a remarkably high quantum yield (QY) of 43%, excellent photostability, and low cytotoxicity were hydrothermally synthesized from chitosan at 180 °C for 12 h and used as a cell imaging agent.[265] The high QY was possibly attributed to the inherent nitrogen doping effect endowed by the chitosan precursor. In addition to chemically pure natural polymers, direct use of crude natural materials (including biomass) as CQD precursors has appeared as a hot topic due to their renewable feature with little to no involvement of toxic chemicals. For instance, amphibious CQDs of 2−5 nm could be prepared by hydrothermal treatment of peach gum polysaccharide at 180 °C for 12 h.[266] The obtained CQDs exhibited strong photoluminescence and excellent dispersibility both in water and in organic solvents. More natural polymeric precursors, e.g., cashew gum, peanut shell, sweet potato, pomelo peel, grass, egg white or egg yolk, bagasse, paper ash, plant leaf, and plant peel, used to generate CQDs were summarized in earlier reviews.[264,267]

Compared to abundant, diverse natural polymer precursors, by taking advantage of the controllable chemical structures of synthetic polymers, CQDs for target applications can be designed and synthesized from different types of synthetic polymers, including negative/zwitterionic/neutral and hydrophilic/hydrophobic ones.[264] Typically, N-doped CQDs can be generated from N-containing polymers, such as polyethylenemine, polyacrylamide, polydopamine, and polyamidoamine dendrimers. Using a polyamidoamine (PAMAM) dendrimer as a precursor, CQDs with a QY of 40% were synthesized through a hydrothermal process. They were further hybridized with poly(N-isopropylacrylamide) and used for sensitive detection of Fe^{3+}, as printing ink, and in thermosensitive devices (Figure 31a,b).[268] Tao et al. reported the synthesis of fluorescent CQDs (20−30 nm) with an absolute QY of 44% by hydrothermally cross-linking poly(acrylic acid) (PAA, MW = 3500 g/mol) and ethylenediamine (EDA).[269] The fluorescence mechanism was studied by investigating the optical properties of individually or co-treated PAA and EDA
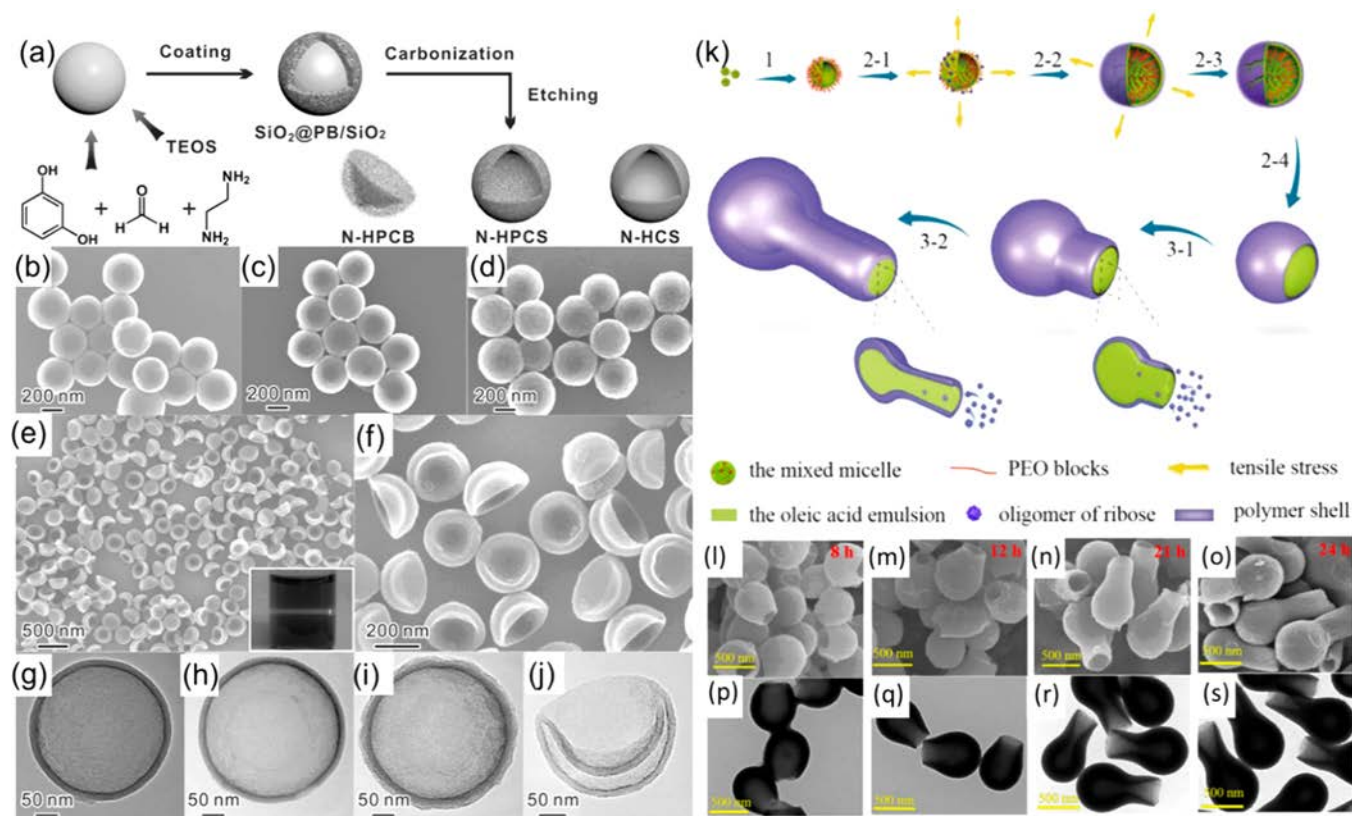
Figure 33. (a) Schematic illustration of the silica-assisted PB coating strategy for the synthesis of N-HCSs, N-HPCSs, and N-HPCBs. SEM images of (b) HCSs, (c) N-HCSs, (d) N-HPCSs, and (e, f) N-HPCBs. TEM images of (g) HCSs, (h) N-HCSs, (i) N-HPCSs, and (j) N-HPCBs (inset: optical image of the dispersed solution of N-HPCBs and the corresponding Tyndall effect). Reproduced with permission from ref 282. Copyright 2016 Wiley-VCH. (k) Schematic mechanism of the growth of HOCFs. (1) Formation of nanoemulsions. (2) Formation of openings: (2−1, 2−2) PEO blocks caused the nanoemulsions to swell. (2−3, 2−4) The shells were cracked by the tensile stress. (3) Formation of necks: the derivatives filled in, and the nanoemulsion flowed out gradually. (l−o) SEM and (p−s) TEM images of the HOCFs prepared with different hydrothermal times: (l and p) for 8 h, (m and q) for 12 h, (n and r) for 21 h, and (o and s) for 24 h. Reproduced with permission from ref 283. Copyright 2017 American Chemical Society.

products. It was revealed that the synergistic effect of PAA chains and fluorescence centers in EDA might contribute to the fluorescence. Specifically, the PAA chains were considered to decrease the motion freedom and provide a solvation effect by cross-linking and wrapping the fluorescence centers of EDA, leading to improved QY and red-shifted emission (Figure 31c,d).

In other studies, efforts have been made to address the aggregation problem of CQDs,[270] which hinders their applications in imaging and drug delivery. To this end, "zwitterionic polymers" containing equimolar anionic and cationic groups in their structures have been recently explored through a simple microwave heating method.[270] In addition to their well-known superhydrophilic and antifouling properties in resisting nonspecific binding of proteins, cells, and microorganisms, zwitterionic polymers have also been demonstrated to efficiently protect nanoparticles from aggregation.[271,272]

4.1.2. Porous Carbon Spheres. Carbon nanospheres are widely used in drug delivery, heterogeneous catalysis, and encapsulation of support and electrode materials. Precise control of the particle size, chemical composition, pore size, and dispersity of carbon nanospheres has been enabled by the rapid progress in synthesis. A number of strategies, such as extended Stöber synthesis, templating routes, and organic−organic self-assembly *via* different binding methods, have been

widely reported. Stöber synthesis is a typical sol−gel approach for preparing monodisperse silica spheres, which has been extended to prepare porous carbon spheres by ammonia-catalyzed polymerization of resorcinol and formaldehyde in the ethanol−water phase, followed by carbonization in an inert atmosphere.[260] By using suitable precursors, heteroatom-rich carbon spheres with unique porous structures can be fabricated *via* the extended Stöber-based method.[273] As discussed in section 2.1.1, by using the micelles of block polymers as a soft template, a coassembly strategy was developed by Yamauchi et al. to prepare N-doped carbon spheres with large mesopore sizes.[56] This unconventional templating and coassembly method sheds light on the role of the interfacial interactions between soft templates and carbon precursors, which allows the synthesis of various carbon nanospheres with tunable pore sizes and chemical components. Very recently, Zhao et al. extended this method to prepare N-doped carbon nanospheres with high uniformity and large tunable pore sizes ranging from 5 to 37 nm (Figure 32).[274] In this work, dopamine was used as the carbon precursor and F127 as the soft template. TMB was used to control the formation of a uniform Pluronic F127/TMB/dopamine microemulsion in the ethanol/water system. They showed that TMB not only plays an important role in the evolution of pore sizes but also significantly affects the interfacial interaction between the soft template and carbon precursor. After the polymerization of dopamine and

subsequent carbonization, N-doped carbon nanospheres with diverse novel structures, such as smooth, golf ball, multi-chambered, and dendritic architectures, could be obtained. The uniform dendritic mesoporous carbon nanospheres showed a large pore size (∼37 nm), a small particle size (∼128 nm), a high surface area (∼635 m^2 g^{-1}), and abundant N content (∼6.8 wt %) and delivered a high current density and an excellent durability for the ORR in alkaline solution. This microemulsion strategy provides new insights into the interfacial assembly and synthesis of mesoporous carbons beyond conventional block copolymer templating.

Other methods, such as spray carbonization, autogenic pressure carbonization, or hydrothermal carbonization of biomass-based resources, are available to construct carbon spheres.[275−277] Utilizing polymers as carbonization precursors is particularly intriguing, as it demonstrates a facile, versatile strategy for manufacturing carbon materials with tailored morphologies (in this case, carbon spheres) along with heteroatom doping without complicated post-treatment.

4.1.3. Hollow Porous Particles and Anisotropic/Asymmetric Porous Carbon Particles. The template approach also provides opportunities for developing various anisotropic or asymmetric porous carbon particles, such as bowl-like, concave, Janus, rattle-type, and patchy particles.[57,277−280] Strategies involving hard, soft, and self-templating methods have been successfully explored for the fabrication of heteroatom-doped carbon particles with anisotropic or asymmetric shapes.[277−281] The hard template method has been used frequently owing to the well-established preparation of solid anisotropic polymer nanostructures through approaches ranging from stretching to controlled deformation methods, microfluidic and photolithographic approaches, single-phase swelling reformation, and seeded polymerization.[281] Compared with polymer templates, the creation of anisotropic/asymmetric inorganic templates, such as silica, remains a challenge, especially by wet chemical approaches owing to the natural primary principle of symmetry that leads to isotropic morphologies. Very few works have been reported on the fabrication of asymmetric carbon particles by employing isotropic silica nanospheres as templates. One example was given by Zheng et al. in 2016. They synthesized N-doped hollow carbon spheres (N-HCSs) and their bowl-like (N-HCB) counterparts by applying polybenzoxazine (PB) in the Stöber coating method for template synthesis.[282] In their work, SiO$_2$ spheres were used as a template, and resorcinol/formaldehyde/ethylenediamine (EDA) was used as the PB precursor. PB-coated SiO$_2$ spheres (SiO$_2$@PB) were first obtained via a modified Stöber coating process, i.e., a one-pot polymerization of the PB precursors in a mixture containing TEOS, ethanol, and H$_2$O. N-Doped hollow porous carbon spheres (N-HPCSs) and bowls (N-HPCBs) could be obtained after calcination and removal of the hard template (Figure 33a−j). The ratio of TEOS to EDA was crucial to determining the morphology of the carbon particles. In comparison with N-HPCSs, a higher concentration of TEOS was required to synthesize N-HPCBs. The formation mechanism of N-HPCBs was proposed to be that, after the removal of SiO$_2$, the porous carbon framework in N-HPCBs was not rigid enough to support the hollow structure due to its high porosity, and the carbon shell thus collapsed into its internal cavity and finally formed a bowl-like structure.

Most recently, new insights have been provided into the synthetic methodology beyond conventional hard and soft template methods. A mechanism of synergetic interactions between the template and biomass was applied by Wang's group to synthesize hollow open carbonaceous nanoflasks (Figure 33k−s).[283] In this work, P123 copolymer and sodium oleate (SO) were chosen as double surfactants, while ribose acted as a carbon source. The asymmetric carbon nanoflasks were obtained via hydrothermal carbonization (HTC) treatment of ribose in aqueous P123 and sodium oleate (SO). During the HTC process, mixed micelles were first formed due to the strong interaction between the two surfactants, which were then transferred into nanoemulsions at high temperature. These nanoemulsions were not stable at 160 °C due to the vulnerable P123, which could be easily swollen by the hydrophilic PEO blocks of P123, leading to cracking of carbonaceous polymer shells at the interface, facilitating the anisotropic deposition of biomass polymers. The necks of the nanoflasks could be derived from the anisotropic growth of carbonaceous shells at the newly formed interface of the broken nanoemulsions driven by the gradual filling by oligomers from the biomass. The resulting carbonaceous nanoflasks showed a narrow size distribution and excellent performance in supercapacitor devices. Their proposed dynamic process induced by the synergetic interactions between the template and biomass would enable access to novel inspirational methodologies for fabrication of carbonaceous materials of high structural complexity.

4.2. Heteroatom-Doped Porous Carbon Fibers and Tubes

4.2.1. Porous Carbon Fibers. With the rapid development of portable and wearable electronics, carbon fibers are receiving increasing attention due to their light weight, high conductivity, large surface area, high chemical stability, and outstanding mechanical strength.[284] In fact, fibrous carbon materials have already been applied in the field of flexible devices as sensors,[285−290] actuators,[291−296] energy storage materials,[297−301] and many more. Although conventional carbon fibers can be made from CNTs or graphene, these processes usually require transition metals as catalysts, which causes concerns in applications where even trace fractions of metals are a problem. Furthermore, the high price of CNT-based fibers hinders their daily usage. In this regard, direct carbonization of polymers to fabricate carbon fibers aims to provide a low-cost yet versatile approach to produce carbon fibers for diverse applications. In this section, we will highlight some of the representative heteroatom-doped porous carbon fibers derived from polymers.

CNFs can be prepared mainly by two methods. One is catalytic thermal chemical vapor deposition growth, and the other is electrospinning followed by thermal annealing. As a versatile, cost-effective and simple technology for preparing polymer-derived CNFs as well as their composites with controllable architectural parameters, electrospinning is already widely applied in both industrial production and research laboratories. The principle of electrospinning has been well introduced in several previous reviews on electrospun materials for energy-related applications.[297] To date, the polymer fibers that serve as carbon fiber precursors can be polyacrylonitrile (PAN), polyimide, poly(vinyl alcohol), poly(vinylidene fluoride), and pitch. Among them, PAN is one of the most common because it can rearrange into thermally stable pyrazine ladder polymers prior to carbonization at elevated temperature. Recently, Wu et al. fabricated carbon fibers by carbonization of electrospun polymer fibers using PAN and
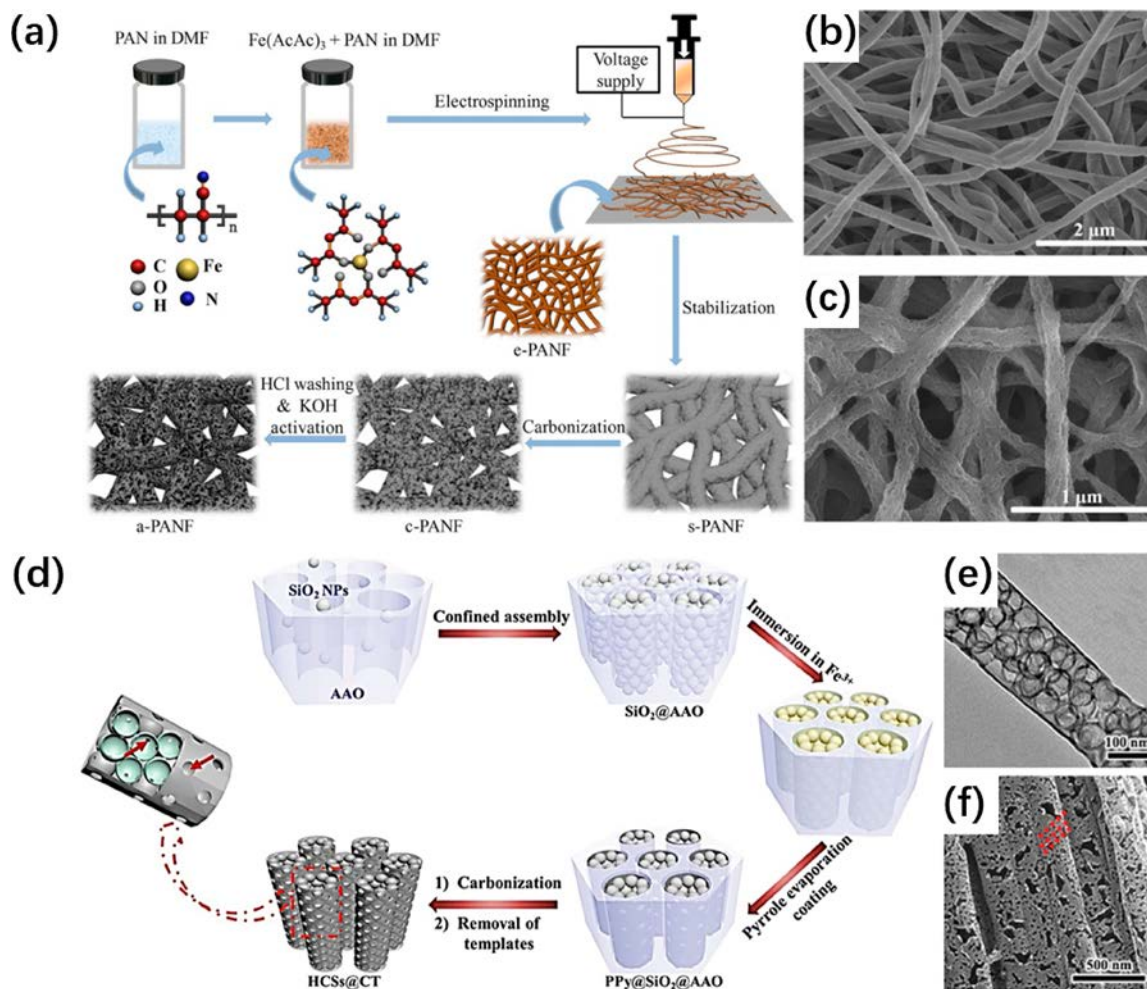
Figure 34. (a) Synthesis scheme of N-doped carbon fibers and membranes by electrospinning. (b, c) SEM images of N-doped carbon fibers prepared from electrospun fibers. Reproduced with permission from ref 303. Copyright 2018 Wiley-VCH. (d) Schematic illustration of the production of HCSs@CT with the assistance of the dual template formed by confined assembly. In the enlarged view of HCSs@CT, meso/macropores are visualized between the interconnection of HCSs and the connection of the CT and HCSs (green spheres show the internal circumstances of HCSs). (e) TEM and (f) SEM images of the obtained HCSs@CT. Reproduced with permission from ref 307. Copyright 2018 Wiley-VCH.

H_3PO_4 as precursors.[302] The as-obtained carbon fibers possessed more defects and less long-range order in the carbon network, and the interlayer spacing was significantly expanded by the incorporation of P. This enlarged d-spacing and defect-laden N, P-codoped carbon fiber exhibited excellent performance in sodium batteries as a fiber electrode. It was demonstrated that adding inorganic salts into the spinning solution is an effective route toward the preparation of advanced carbon fiber composites. For example, PAN and $Fe(acetate)_3$ can be directly codissolved in N,N-dimethylformamide (DMF) and electrospun into $Fe(acetate)_3$–PAN composite fibers (Figure 34a–c).[303] Fe NP-functionalized carbon fibers could be readily prepared by carbonization of $Fe(acetate)_3$–PAN fibers.

PILs have recently emerged as a new type of carbon precursor. Their tunable chemical compositions and structures endow them with a myriad of opportunities to fabricate advanced carbon fibers. For instance, Yuan et al. first synthesized a PIL with dicyanamide counteranions, which are known for undergoing condensation reactions at 280–300 °C to stabilize the carbon network. N-Doped carbon fibers with a high conductivity of 200 ± 60 S cm^{-1} could be easily obtained by direct carbonization of PIL-based fibers under rather moderate conditions.[304]

Owing to their light weight, high conductivity, and chemical stability, macroscopic flexible carbon fibers are extremely appealing for flexible devices. It is believed that the development of thermally stable polymer fibers that can be converted into carbon fibers could provide a versatile platform to fabricate fiber electrodes for conduction, electron storage, and energy conversion.

4.2.2. Porous Carbon Tubes. Heteroatom-doped carbon micro/nanotubes used as electrode materials for batteries have shown significant advantages compared to fiber materials due to their enhanced surface-to-volume ratio for the electrode–electrolyte interface.[305,306] Moreover, these 1D hollow carbon tubes can be easily functionalized with various secondary structural components to meet the requirements of energy conversion and storage devices for real-life applications. For instance, Lee et al. successfully fabricated N-doped hollow CNFs by carbonization of polymer fibers. They first prepared core–shell structured polymer fibers utilizing the coaxial electrospinning technique, in which PS-co-PAN (SAN) was the core and PAN was the shell material.[140] Before
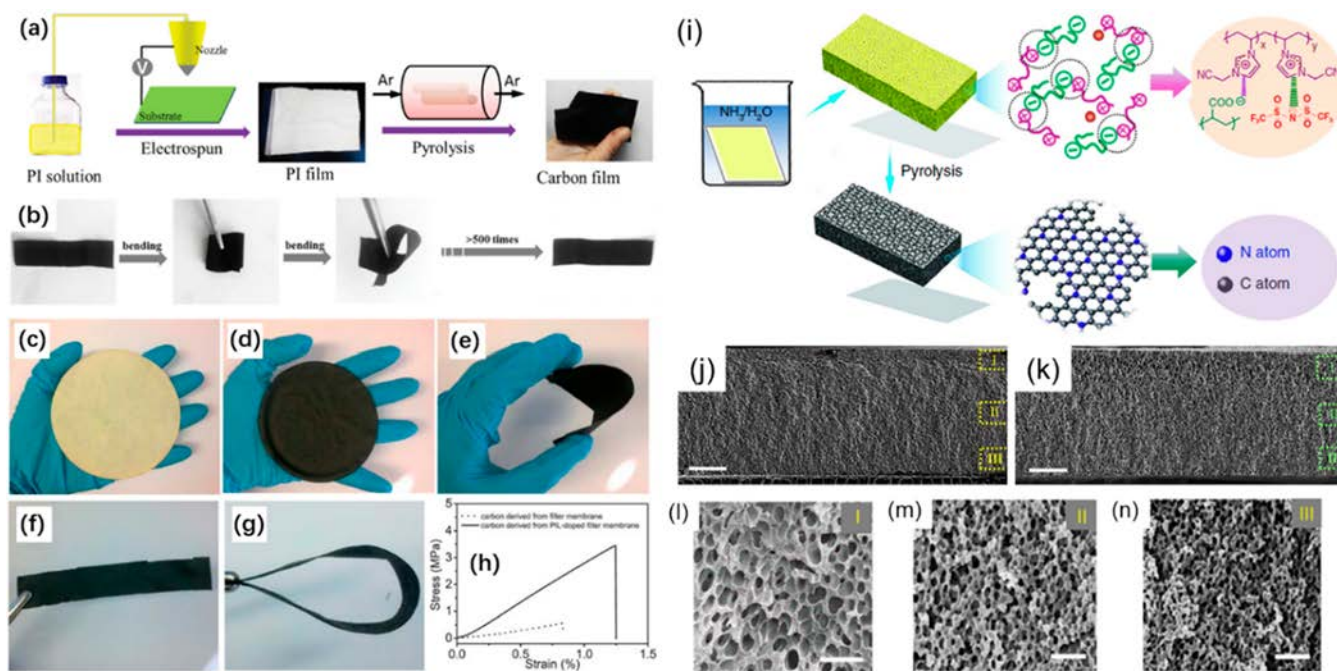
Figure 35. (a) Schematic illustration of the fabrication of nanoporous carbon fiber films. (b) Photographs of the resultant flexible nanoporous carbon fiber films. Reproduced with permission from ref 324. Copyright 2016 Wiley-VCH. Photographs of (c) PIL wetted filter paper, (d) the paper after carbonization at 400 °C, (e) bending test of the carbonaceous membrane paper, and (f) a carbonaceous strip cut from a carbonaceous membrane. (g) Bending test of the strip. (h) Plots of the tensile testing experiments of carbon membranes derived from a pure cellulose filter membrane (dotted line) and from a PIL-doped filter membrane (solid line). Reproduced with permission from ref 325. Copyright 2013 Royal Society of Chemistry. (i) Preparation procedure of HNDCMs. (j) Cross-section scanning electron microscopy (SEM) image of HNDCM-100000 calcined at 1000 °C. (k) SEM image of the cross section of HNDCM-250000 calcined at 1000 °C; the scale bars in parts j and k are 20 μm. (l−n) High-magnification images of part k. The scale bars represent 500 nm. Reproduced with permission from ref 146, licensed under CC BY.

carbonization, these as-spun nanofibers were first stabilized at 270−300 °C for 1 h in air and then pyrolyzed at 800, 1000, 1200, and 1600 °C for 1 h under nitrogen. During thermal treatment, the core component burned out, and linear PAN molecules could be transformed into ladder structures and then further carbonized into N-doped hollow carbon fibers. The large continuous central porous structure in the N-doped hollow carbon fibers facilitates the penetration of Li⁺-carrying electrolyte into the inner part of the carbon fibers, thus promoting the full use of the active lithium-storage part and improving the performance of the lithium battery.

Apart from the electrospinning technique, porous carbon tubes were also achieved in the laboratory by template methods. For example, heteroatom-doped carbon nanotubes can be produced using anodic aluminum oxide (AAO) membranes (200 nm in channel size) as hard templates. The inner channel of AAO was filled with a heteroatom-rich polymer solution driven by capillary force, where a thin polymeric coating layer formed upon evaporation of the solvent. The thickness of the coating layer could be fine-tuned by the polymer concentration. The polymer tubes on the walls of AAO were then carbonized into heteroatom-doped carbon nanotubes. Furthermore, by introducing a second inorganic template into the AAO channels, hierarchical porous carbon tubes could be obtained after removal of the template. For instance, Yang's group constructed a sphere-in-tube structure by using AAO and SiO₂ nanoparticles as co-templates, where hollow carbon spheres were encapsulated in a carbon nanotube (HCSs@CT) after removal of the AAO and SiO₂ nano-particles.[307] In their approach, confined assembly of SiO₂ nanoparticles in the channels of AAO generated a SiO₂@

AAO co-template for subsequent filling with polypyrrole, followed by carbonization and template removal to form N-doped HCSs@CT (Figure 34d−f). At the same time, Zhang's group similarly prepared porous carbon tubes as cathode materials for Li−S batteries.[308] This novel architecture combines several merits for electrode application: (1) optimized utilization of the carbon nanotube intracavity to improve S_{BET}; (2) a hierarchical porous structure (micro/meso/macropores) for rapid electrolyte access; (3) a high charge transport capability; and (4) a N doping effect resulting from the N-rich carbon precursor. In this context, heteroatom-doped carbon materials with such architectures function not only in lithium batteries but also in supercapacitors due to their high surface area, well-defined porous structures, good electrical conductivity, and long-term stability.

4.3. Heteroatom-Doped Porous Carbon Thin Films and Membranes

Porous carbon films and membranes with large sizes are highly valued, especially for electronics and electrochemical applications, catalysis, separation, and purification, due to their structural integrity, continuity, and purity.[309] Such applications require carbon materials with a large and easily accessible surface. Additional requirements could be good conductivity, efficient mass transport of chemical species to and from the surface, or the capability to deform through bending, buckling, twisting, rotation, and so on. In this regard, a well-defined porous structure should be taken into account. To date, porous carbon membranes have been synthesized via different methods, including pyrolysis of block copolymer−colloidal silica hybrids and direct carbonization of self-assembled
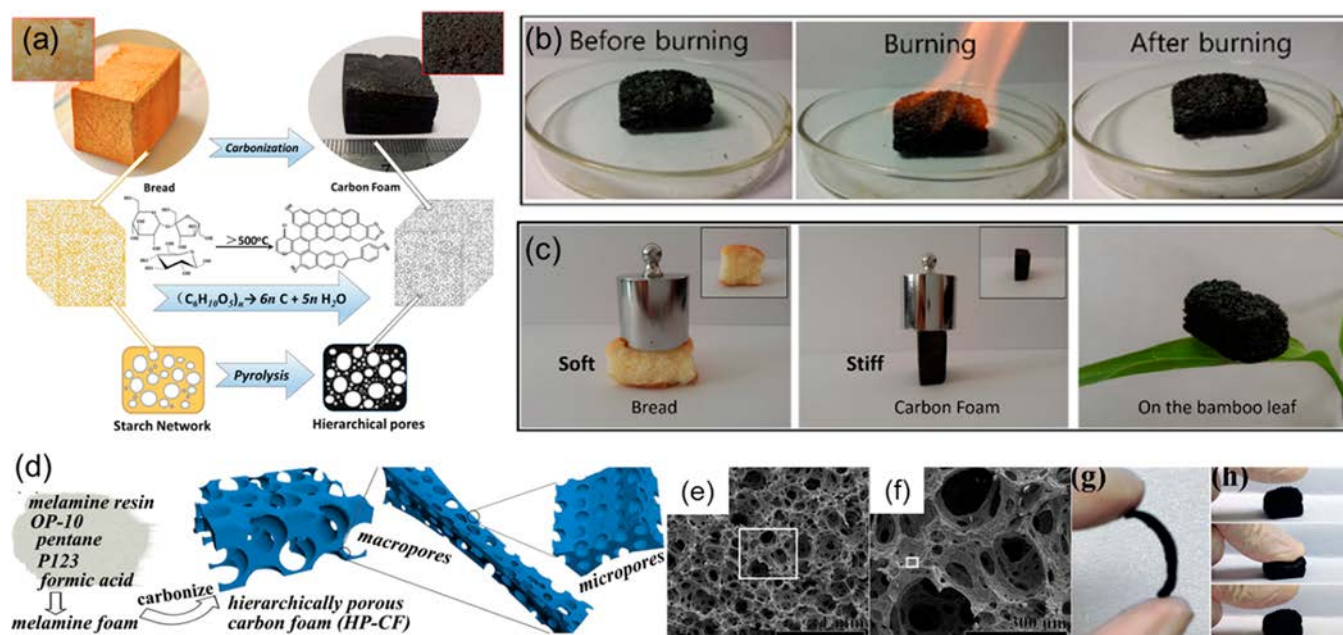
Figure 36. (a) Schematic illustration of porous carbon foams derived from bread. (b) Photographs illustrating the mechanical properties and light weight of the carbon foams. (c) Photographs illustrating the thermal stability of the carbon foams. Reproduced with permission from ref 338. Copyright 2016 American Chemical Society. (d) Synthetic route toward porous carbon foams using P123 as a soft template. (e, f) SEM images of the porous carbon foams. (g, h) Photograph illustrating the mechanical strength of the porous carbon foams. Reproduced with permission from ref 340. Copyright 2016 Elsevier.

heteroatom-rich polymer films and electrospun fiber-based polymer films.[310,311]

Porous carbon films derived from carbon fibers are indeed widely applied in catalysis,[312−316] energy storage,[301,317−319] separation,[320−323] and so forth. Owing to the interconnected fiber network, these carbon films are composed of numerous macropores, which facilitate mass diffusion but also enable a sponge-like elasticity. For example, Yao et al. prepared nanoporous carbon fiber films by direct carbonization of an electrospun polyimide (PI) film under Ar (Figure 35a).[324] Due to the highly aromatic nature of PI, the structural integrity of the polymer films was largely maintained during carbonization. In addition, the as-obtained carbon films were flexible with an electrical conductivity of 147 S cm^{-1} and as such are useful in wearable devices (Figure 35b).

As mentioned in the previous section, precursors to be carbonized in high mass yields and under structural preservation are rather limited to only a few polymers, which significantly hinders broader applications. To this end, Yuan et al. utilized ILs/PILs as efficient carbonization/activation coating agents to promote the co-conversion of diverse biopolymers.[325] For example, commercially available cellulose filter membranes can be coated with ILs/PILs and are then sufficiently stable to undergo carbonization to form carbon membranes. Remarkably, such hybrid polymer carbon membranes display outstanding flexibility and high thermal stability (Figure 35c−h). Moreover, the introduction of N atoms by the IL/PIL coating significantly improves the oxidation stability of the final carbon membranes.

In addition to fiber-based carbon films, a series of hierarchically structured porous carbon films/membranes have been synthesized via different techniques. For instance, Muench and co-workers synthesized hierarchically porous N-doped carbon membranes featuring continuously organized macro- and mesopore channels.[326] This was achieved by pyrolysis of ion-track-etched polyimide. In another example, Wang and co-workers developed a bottom-up approach for the fabrication of N-doped, hierarchically structured, graphitic nanoporous carbon membranes (termed HNDCMs) through morphology retaining carbonization of a porous PIL membrane as a sacrificial template and a N/C precursor (Figure 35i−n).[146] Assembly of the polymeric precursor occurred directly by interpolyelectrolyte complexation between the cationic PIL and anionic neutralized poly(acrylic acid) (PAA), thus resulting in parental porous polymer membranes. In particular, the obtained carbon membrane exhibited an unusual single-crystal-like carbon orientation in the wall and a gradient size distribution of the pores along the membrane cross-section. Moreover, the N-doped nanoporous carbon membranes could be loaded with cobalt nanoparticles and function as an active carbon-based bifunctional electrocatalyst for overall water splitting. This promising strategy was then extended as a scalable synthetic approach for multiheteroatom-doped porous carbon membranes and applied for photo-thermal conversion in seawater desalination.[173]

Considering the diverse structures of PILs, it has been demonstrated that taking PIL-based assemblies as precursors to manufacture heteroatom-doped porous carbon membranes is promising. These membranes have already exhibited advantages over their powdery counterparts in electrocatalytic fields because they can be directly employed in devices, avoiding the use of binders and powder grain surface polarization.

4.4. Heteroatom-Doped Porous Carbon Foams and Monoliths

"Bulk" carbons, such as porous carbon foams and monoliths, have macroscopic 3D porous structures while being mechanically robust and can operate even under extreme conditions (high pressure or stress). Moreover, these 3D structured

carbons have a higher volume to take up guest molecules for capacity-limited real-life applications, such as energy storage,[327−330] gas separation or storage,[331,332] environmental remediation,[333−337] and so forth.

One of the most straightforward strategies for fabricating "bulk" porous carbon materials is direct carbonization of bulk biomass pieces. Li et al. prepared hierarchically nanoporous carbon foams by carbonization of (porous) bread (Figure 36a).[338] The porous architectures of carbon foam could be controlled by the amount of yeast and the strength of gluten. The carbon foam produced under optimized conditions exhibited an outstanding compressive strength of 3.6 MPa with a density of 0.29 g/cm^{-3}, excellent thermal stability (Figure 36b,c), and a high S_{BET} value of 988 m^2/g. Carbonization of biomass with PILs could also lead to 3D porous carbon foam. Yuan et al. prepared porous carbon foams by carbonization of natural cotton in the presence of PILs.[325] In this process, the PILs effectively preserved the overall morphology and microtexture of the cotton. These sponge-like carbon foams removed methylene blue and crystal violet quickly from their aqueous solutions.

In addition to the construction of porous bulk carbons from biomass polymers, synthetic polymers are an alternative. For example, Lu et al. prepared porous carbon monoliths through the self-assembly of poly(benzoxazine-co-resol) with the soft template Pluronic F127 followed by thermal annealing.[339] The as-obtained porous N-doped carbon monoliths displayed a hierarchical nanoporous architecture with an S_{BET} value of 670 m^2 g^{-1}. Similarly, Wong et al. constructed N-doped hierarchically porous carbon foams by direct carbonization of soft template (P123)-cast melamine foams (Figure 36d−f).[340] In this process, the pyrolysis of P123 created micropores, while the macropores resulted from the release of volatiles at elevated temperatures. With an S_{BET} value of 1231 m^2 g^{-1}, these hierarchically porous carbon foams were flexible and compressible (Figure 36g,h).

One of the most unique features of carbon foams and monoliths is their 3D morphology and mechanical robustness, which facilitates reusability for practical handling. This unusual behavior can be mainly attributed to the hierarchically porous structure; as polymer-derived carbon materials are usually brittle and can sustain little compressive deformation. To date, both experimental and theoretical analyses have indicated that hierarchically porous structures are critical for the mechanical properties.

5. PORE ENGINEERING IN HETEROATOM-DOPED CARBONS DERIVED FROM POLYMERS

A key feature of activated carbons is their high surface area and pore structure, which increases the absorption capacity for guest molecules. In this regard, porosity plays a pivotal role in determining their material performance. The pore size distribution (micro-, meso-, and macropores and hierarchical pores) is an intrinsic characteristic that determines the surface area and mass transport capability beyond the outer morphology. In this section, we summarize strategies to engineer pores in heteroatom-doped carbons derived from polymers.

5.1. Control of Microporosity

5.1.1. Activation Approach to Construct Microporous Structures. We discussed above that the usage of template methods and the intrinsic nature of precursors generally create

meso- and macropores in carbons.[11,341] The micropores in carbons are usually formed by in situ activation during carbonization or postsynthetic activation by gases (mainly H$_2$O steam or CO$_2$) and alkalis, i.e., KOH.[342−344] The first technique is activation by gases at elevated temperature, which is referred to as "physical activation". The second technique is activation by heating the solid mixture of carbon and KOH or other chemicals in an inert atmosphere, which is known as "chemical activation". It is industrially well established that the activation of carbon materials enhances their porosity and pore-related performance.

Physical activation of nonporous or less porous carbon materials by CO$_2$ is well-known. Boudouard equilibrium between CO$_2$ and carbon produces CO gas at moderate (600 °C) to high (approximately 1000 °C) temperatures, which can be expressed as C + CO$_2$ = 2CO (ΔH = +159 kJ/mol). Significant amounts of carbon are thereby lost. Note that the porosity is closely dependent on the activation temperature, degree of burnoff, and CO$_2$ flow rate. Apart from CO$_2$, activation gases such as water vapor[345] and ammonia (NH$_3$)[346] are also popular in industry. Water vapor activation could lead to a large amount of micropores, accounting for 45−62% of the total surface area of carbons. This value is higher than that of CO$_2$-activated carbon but still lower than that of KOH-activated carbon. NH$_3$ activation is another efficient way to increase the S_{BET} value and pore volume, as well as the N content, of carbons. Note that NH$_3$ activation can generate extremely toxic HCN during the activation reaction and thus should be avoided in the laboratory.

KOH is widely utilized to activate carbon material to create micropores. The activation can be performed by heating a physical mixture of carbon materials with solid KOH under N$_2$ at a desired temperature (400−1000 °C). During this process, KOH first melts and dehydrates into potassium oxide (K$_2$O) at approximately 400 °C. K$_2$O is further reduced into intercalated K by carbon at higher temperatures. Therefore, the consumption of carbon during the reaction with K$_2$O and the intercalation of K into the graphitic stacks are considered the two major factors for developing microporosity and a higher S_{BET}. This simple yet powerful chemical is broadly employed in industry to construct well-defined micropores. The textural properties of the carbons can be greatly varied by tuning the quantity of KOH and the activation temperature. Generally, the micropore volume, S_{BET}, and total pore volume increase with increasing mass ratio of KOH/carbon or activation temperature. More KOH and a higher activation temperature can cause high carbon burnoff, which is undesirable from both economic and environmental perspectives. Therefore, the trade-off between S_{BET} and the carbon yield is usually considered.

Similar to KOH activation, post-treatment or carbonization in the presence of NH$_3$ could also lead to microporosity and favorable in situ N doping. As mentioned in the previous section, NH$_3$ will decompose into various radical species at high temperature, which effectively etch the carbon framework and create defects and a microporous structure. At the same time, this process can also lead to in situ N doping. In an early study, Jaouen et al. activated pristine carbons in the presence of NH$_3$.[347] This process can simultaneously create micropores and N functionalities inside carbons. In another study, NH$_3$-pyrolyzed carbons displayed remarkable ORR activity compared to Ar-pyrolyzed carbons, which was attributed to their highly basic N functionalities and the existence of
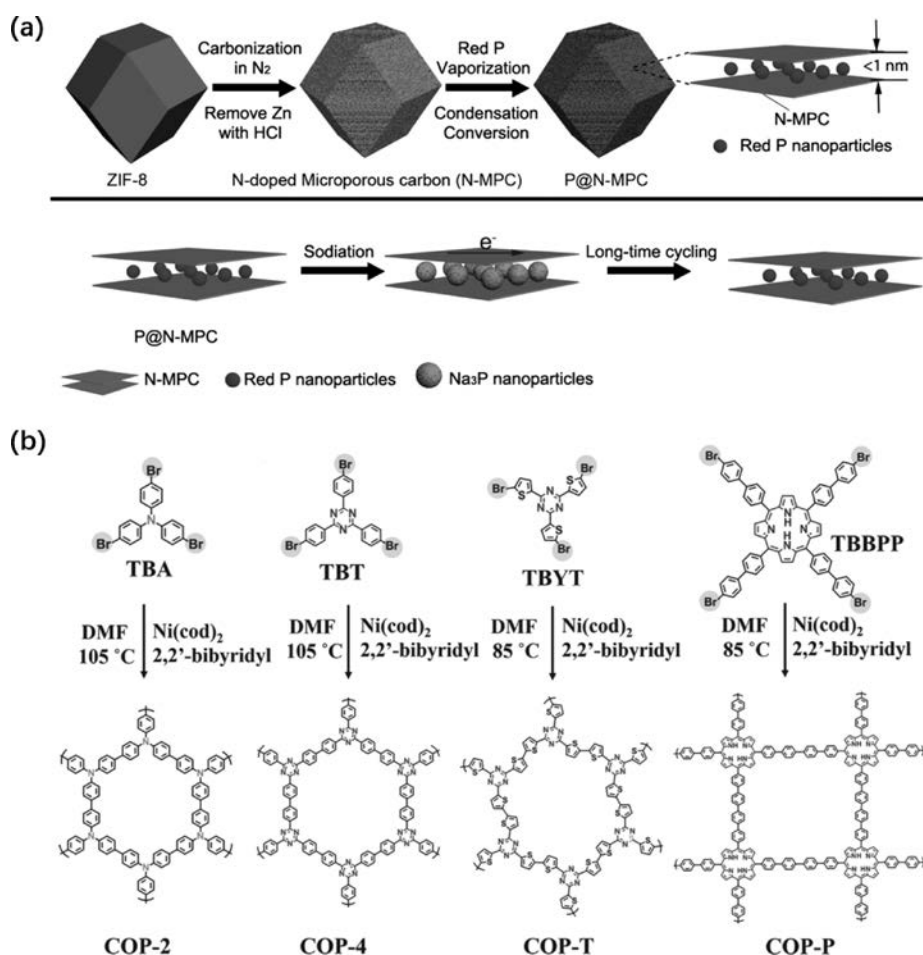
Figure 37. (a) Synthetic route toward microporous carbon materials derived from ZIF-8. Reproduced with permission from ref 356. Copyright 2017 Wiley-VCH. (b) Schematic diagram of the synthesis of COPs as carbonaceous precursors. Reproduced with permission from ref 358. Copyright 2014 Wiley-VCH.

porphyrin-like FeN_4C_{12} moieties.[348] Mukerjee et al. utilized a similar approach to activate carbon materials.[349] During heat treatment with NH_3, the remaining amorphous carbons were etched, and N functionalities were doped into the carbon scaffold. Other examples have also been reported, and improvements in various catalytic performances were observed.[350,351] This strategy, compared to KOH activation, is less corrosive.

To bypass the dilemma of using corrosive agents, the "salt templating" strategy was recently developed as an alternative solution to produce porous carbon materials with more micropores and small mesopores. As an example, Antonietti et al. employed different eutectic mixtures as a porogen in combination with an ionic liquid as a carbon source to construct porous materials with high surface areas ranging from 1000 to 2000 m^2 g^{-1}.[118] The porogen salts included eutectic $LiCl/ZnCl_2$ (S_m 294 °C), $NaCl/ZnCl_2$ (S_m 270 °C), and $KCl/ZnCl_2$ (S_m 230 °C), which can be recovered for further use, rendering sustainable salt recycling. Similarly, Matyjaszewski and colleagues utilized an aqueous solution of low molecular weight PAN and $ZnCl_2$ as a template and effectively functionalized various carbonaceous materials. By templating in the presence of SiO_2, nanoporous carbons with a high S_{BET} up to 1776 m^2 g^{-1} were reported.[352] Other examples, such as utilizing potassium oxalate,[353] molten KCl,[354] and molten $ZnCl_2$,[355] to endow carbon materials with micro-

porosity have also been presented. These methods are highly effective yet less corrosive, meaning that the overall morphology and functionality of the materials could be well retained after carbonization, especially compared to the rather destructive KOH activation.

5.1.2. Utilization of the Polymeric Structure and Composition to Construct Microporous Structures. A straightforward strategy to effectively construct a microporous architecture in carbon without losing too much material is desirable. The utilization of microporous polymeric structures to construct microporous carbons is one of the most commonly used methods. In particular, direct pyrolysis of organic frameworks (MOFs, COFs, or COPs) to produce porous carbons has recently stimulated much interest because their intrinsic micropores could be partially retained during carbonization. In addition, these organic polymeric frameworks usually contain a high content of heteroatoms, which simultaneously functionalize the product upon carbonization. For example, Yu et al. prepared P-doped microporous carbon by direct pyrolysis of ZIF-8 followed by encapsulation of red P into the microporous carbon (Figure 37a). The textural morphology of the MOF was well preserved after the carbonization process, and a polyhedron-like carbon material was isolated.[356] After the removal of metallic Zn with HCl washing, the S_{BET} value of the polyhedron-like carbon reached 1135.1 m^2 g^{-1} with a uniform narrow pore size distribution of
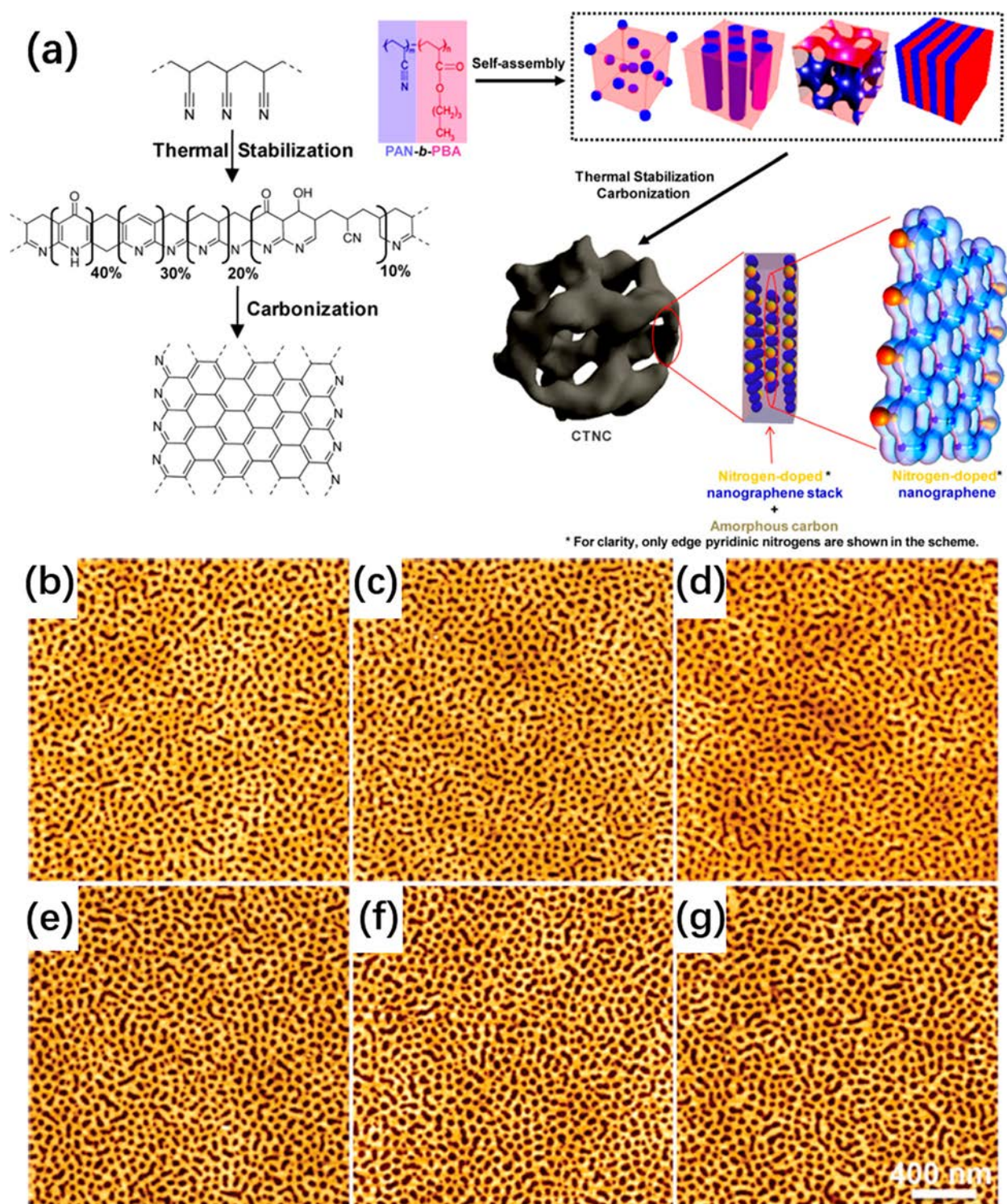
Figure 38. (a) Synthetic route toward N-doped nanoporous carbons from phase-separated block copolymers. Reproduced with permission from ref 73. Copyright 2012 American Chemical Society. AFM height images of PAN-*b*-PMMA-derived mesoporous carbon thin film after thermal annealing at (b) 100 °C, (c) 140 °C, (d) 180 °C, (e) 220 °C, (f) 260 °C, and (g) 300 °C for 1 h before carbonization. Reproduced with permission from ref 369. Copyright 2017 Wiley-VCH.

approximately 0.5 nm. Such microporous architectures are favorable for the diffusion of guest molecules. Similarly, Park and colleagues presented the synthesis of highly porous carbons derived from a MOF with a narrow pore size centered at 1.3 nm.[357] These microporous carbons exhibited BET specific surface areas as high as 3447 m^2 g^{-1} and showed great promise in H$_2$ storage. Despite the great potential of MOFs in

the synthesis of N-doped porous carbons, we will not expand upon this area in this Review, as, strictly speaking, MOFs as a rising group of carbon precursors are not directly related to polymers.

In addition to MOFs, Dai et al. specifically designed and synthesized a series of COPs with different N distributions and hole sizes (Figure 37b).[358] The subsequent carbonization of

these COPs created well-controlled N-doped holey graphitic carbon materials with average pore sizes below 1 nm. Similarly, Shiraki et al. constructed microporous N-doped carbons by direct carbonization of COFs with an azine-linked 2D molecular network.[359] Interestingly, the carbonized COFs displayed a higher S_{BET} value (1596 m^2 g^{-1}) than pristine COFs (1168 m^2 g^{-1}). The pore size was found to be reduced from 0.97 to 0.68 nm after carbonization, indicating partial shrinkage of the porous structure during the carbonization process. Recently, Bai and colleagues utilized a thermally stable covalent triazine framework and constructed a microporous carbon nitride-like material through direct carbonization.[360] Remarkably, the as-obtained carbon nitride displayed a uniform pore size distribution of approximately 0.5 nm and a maximum surface area of 401 m^2 g^{-1}. These examples prove that carbonization of predesigned microporous precursors is a valid method to directly prepare microporous carbons.

Composition engineering is another effective strategy to construct microporosity inside carbons. Previously, Dai et al. demonstrated that, by engineering the counteranion of an ionic liquid, well-developed microporous structures can be achieved without using either templates or activating agents.[361] In this regard, by carefully tailoring the composition of PILs with certain anions, e.g., bis(trifluoromethane sulfonyl)imide (TFSI), Yuan et al. demonstrated that direct pyrolysis of poly(3-cyanomethyl-1-vinylimidazolium TFSI) can effectively afford microporous N-doped carbons.[145] Remarkably, micropores of the size of the counterion were dominant, coexisting with only a small amount of mesopores less than 5 nm, while mesopores larger than 5 nm and macropores were essentially absent. It is believed that the bulky counteranion TFSI was aggregated and evaporated in protonated form during carbonization, thereby creating micropores in the carbons. This feature was particularly important because the polymeric cation could be utilized as both carbon and heteroatom sources, while the counteranion could simultaneously act as a molecular template of sufficient size. Taking advantage of the ionic nature of PILs, Wang et al. utilized electrostatic cross-linking of the cation of PILs with poly(acrylic acid) and constructed porous PIL membranes.[146] The subsequent carbonization ultimately led to hierarchical N-doped porous carbon membranes. Notably, the large macroporous structure was constructed by electrostatic cross-linking, while the micropores were simultaneously derived from the counteranion TFSI upon carbonization. Moreover, these PILs could be used as activating agents to create micropores in various carbonaceous species upon carbonization. Wang et al. utilized PILs as surface active agents and effectively constructed nanoporous N-doped carbon materials with S_{BET} up to 496 m^2 g^{-1} by hydrothermal carbonization.[362] Without PIL additives, the as-obtained carbons showed small S_{BET} and were basically nonporous. Similarly, PILs could also be utilized to activate already condensed carbon materials. Yuan et al. prepared N-doped nanoporous carbon composites by incorporating PILs and carbon nitride as precursors.[363] Remarkably, the carbon nitride became highly porous, and the S_{BET} was boosted up to 1120 m^2 g^{-1} with the addition of PILs.

Utilizing the polymeric structure and composition to directly obtain carbon materials with microporous structures is efficient and avoids the drawbacks of the other techniques discussed above. With their highly tunable chemical composition and surface activating nature, PILs have proven to be an especially promising carbonaceous precursor to build microporous

carbon materials with various morphologies. More importantly, these PILs are by their construction rich in heteroatoms such as N, S, or P, which can in turn be incorporated into carbon materials without any postsynthetic treatment, providing a versatile platform to design microporous carbon materials with desirable heteroatom doping.

5.2. Control of Mesoporosity

One of the most fundamental characteristics of block copolymers is their ability to form versatile morphologies *via* phase separation in selective solvents. Especially, with different chemical compositions, a variety of beautiful mesostructures, such as cubes, cylinders, or lamellae, can be well constructed. In this regard, porous carbon materials derived from block copolymers are particularly interesting, as no activation steps or post-treatments are required, and a variety of carbon morphologies can be readily copied from the original block-copolymer-derived structures.

As previously demonstrated, Yamauchi and colleagues directly constructed N-doped mesoporous carbon spheres through self-polymerization of DA and spontaneous coassembly of diblock copolymer PS-*b*-PEO micelles.[56] The as-obtained carbon spheres displayed a remarkably uniform mesopore size of 16 nm. Similarly, Zhao et al. utilized the micelle fusion-aggregation assembly method and successfully constructed mesoporous carbon materials.[364] Notably, by utilizing the phase separation of PS-*b*-PEO as a template, ordered mesoporous carbon materials with pore sizes ranging from 26.2 to 36.3 nm were rationally fabricated. This method is facile yet powerful for constructing mesoporous carbons with different morphologies with a narrow pore size. At the same time, other block copolymer templates, such as PS-*b*-PAA[365] or poly(ethylene oxide-*b*-caprolactone) (PEO-*b*-PCL),[366] are also possible.

In addition to thermally labile diblock copolymers, PAN-containing block copolymers are one of the most commonly used carbonaceous precursors for constructing organized N-doped mesoporous carbons. In 2012, Kowalewski et al. successfully fabricated N-doped mesoporous carbons by direct carbonization of the self-assembled block copolymer poly(n-butyl acrylate)-*b*-PAN (PBA-*b*-PAN).[73] In the carbonization process, the PAN chains underwent a cyclization reaction to form stable pyrazine ladder networks, while the thermally unstable PBA chains underwent thermolysis, leaving mesopores inside the carbon matrix (Figure 38a). Recently, the same groups also extended this method and fabricated mesoporous N/S-codoped carbons for supercapacitor applications.[367] By carefully adjusting the length of PBA blocks, the mesoporous structures were found to be highly tunable with a narrow pore size distribution ranging from 5.6 to 21.7 nm in a surprisingly linear fashion. To construct more ordered mesoporous structures, Kim et al. utilized a prestabilization method and obtained N-doped mesoporous carbon materials with an S_{BET} value of 860 m^2 g^{-1} and an average mesopore size of 8.1 nm by carbonization of a PAN-*b*-PMMA block polymer.[368] Interestingly, thermal stabilization at 250 °C prior to carbonization to stabilize the self-assembled structure was a prerequisite for successful preparation of the ordered mesopores; i.e., the polymer must be cross-linked before the template vanishes. Liu et al. further investigated the assembly behavior of PAN-*b*-PMMA during thermal and solvent annealing.[369] Interestingly, as the thermal annealing temperature increased from 100 to 300 °C, the pore size increased by
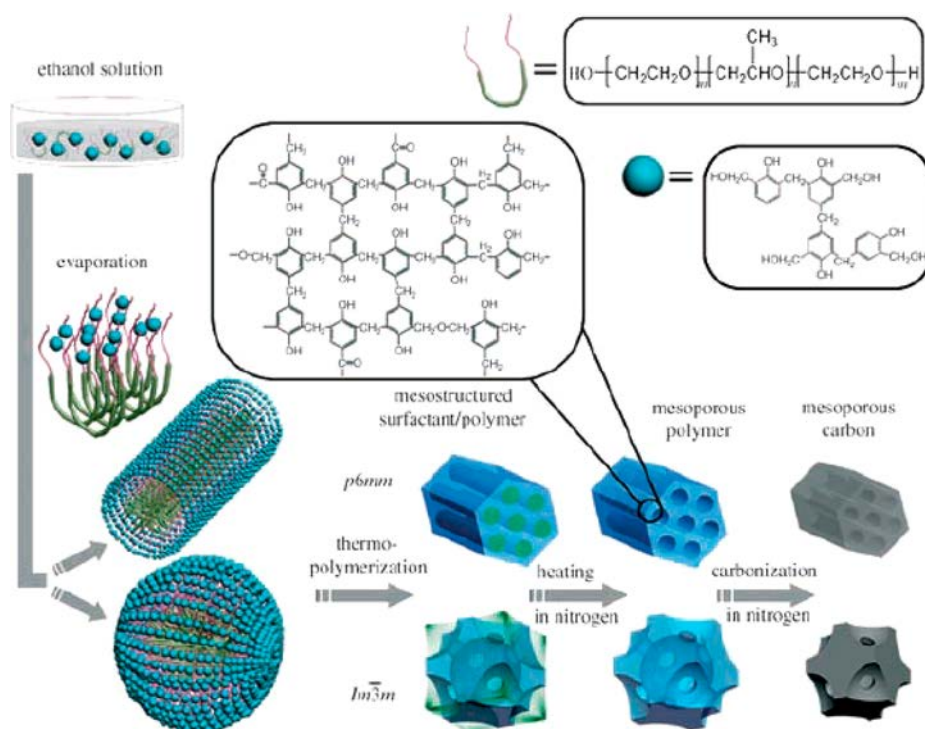
Figure 39. Schematic illustration of utilizing surfactants to construct different mesoporous polymers and corresponding carbon materials. Reproduced with permission from ref 53. Copyright 2005 Wiley-VCH.

approximately 25% (Figure 38b–g). At the same time, the pore size also varied as the solvent was changed from dimethyl sulfoxide to chloroform. Other examples of utilizing a thermal stabilization strategy prior to carbonization, such as PBA-*b*-PAN, were also recently presented by Matyjaszewski.[370,371] These N-doped porous carbons displayed uniformly distributed mesopores and could be applied in various energy storage applications.

In another example, Zhao et al. prepared ordered mesoporous polymers by solvent-induced self-assembly of amphiphilic triblock copolymers with phenol and formaldehyde resin as building blocks (Figure 39).[53] The resol contained a large number of hydroxyl groups, which could interact strongly with the triblock copolymers through the formation of hydrogen bonds. These features made the polymers particularly stable and permitted direct transformation into homologous carbon frameworks upon carbonization. Interestingly, by simply changing the concentration of surfactants, 2D hexagonal (FDU-15) and 3D cubic (FDU-16) structures were obtained, while a lamellar mesostructure was prepared by P123. Further carbonization of precalcined polymers led to mesoporous carbons with a slight shrinkage of the carbon network. The S_{BET} value of the carbon materials derived from FDU-15 and FDU-16 at 900 °C was found to be 968 and 778 m^2 g^{-1} with narrow pore size distributions around 2.9 and 3.7 nm, respectively.

5.3. Control of Macroporosity

Compared to the active pursuit of micro/mesopores in carbon materials, macropores are generally less studied because they generally contribute less to the surface area. However, creating macropores in carbon materials is sometimes needed for enhancing mass transport in specific applications. This point was detailed in Sung et al.'s work, as they systematically investigated the specific relationship between macroporous and micro/mesoporous carbon materials in the ORR by electrochemical analysis.[372] According to their electrochemical measurements, the macroporosity greatly enhanced the mass transport efficiency, and the interplay between micro/mesoporosity and macroporosity should be considered in the design of active-site-laden carbon materials.

One effective strategy to construct macropores is to use large-sized (>50 nm) templates, which could either be hard or soft. Inspiring works were reported by Stein's group using colloidal silica particles and silica gels as templates for the synthesis of ordered macroporous carbon.[27] A series of related approaches were developed in the following years. Yu et al. utilized polystyrene (PS) spheres and silica as nanocomposite templates to direct the polymerization of divinylbenzene.[12] The PS spheres in this case acted as a soft template, which could be readily removed by postsynthesis calcination to leave macroporous architectures. Satcher Jr. and Baumann prepared carbon aerogels with periodic macroporous architectures by utilizing a RF sol–gel solution as a carbon source along with PS spheres as a template.[13] The sol–gel solution was infused into the interstitial voids of the PS sphere template with the assistance of a filtration technique. After the formation of the gel, the RF/PS composites were soaked in toluene to dissolve the PS template and further dried by supercritical CO_2 into an aerogel. This RF aerogel displayed hexagonally ordered domains of spherical cavities close to the size of the PS template. The RF aerogel was finally carbonized into a periodic macroporous monolith. In a recent study, PS spheres were directly mixed with precursors of N-doped carbon and carbonized into P-doped well-ordered 3D porous networks (Figure 40a).[373] Tang et al. constructed hollow carbon spheres by utilizing colloidal PS spheres as sacrificial templates (Figure 40b,c). Upon carbonization at high temperature, the inner templates were thermally fragmented, leaving a N, P-codoped
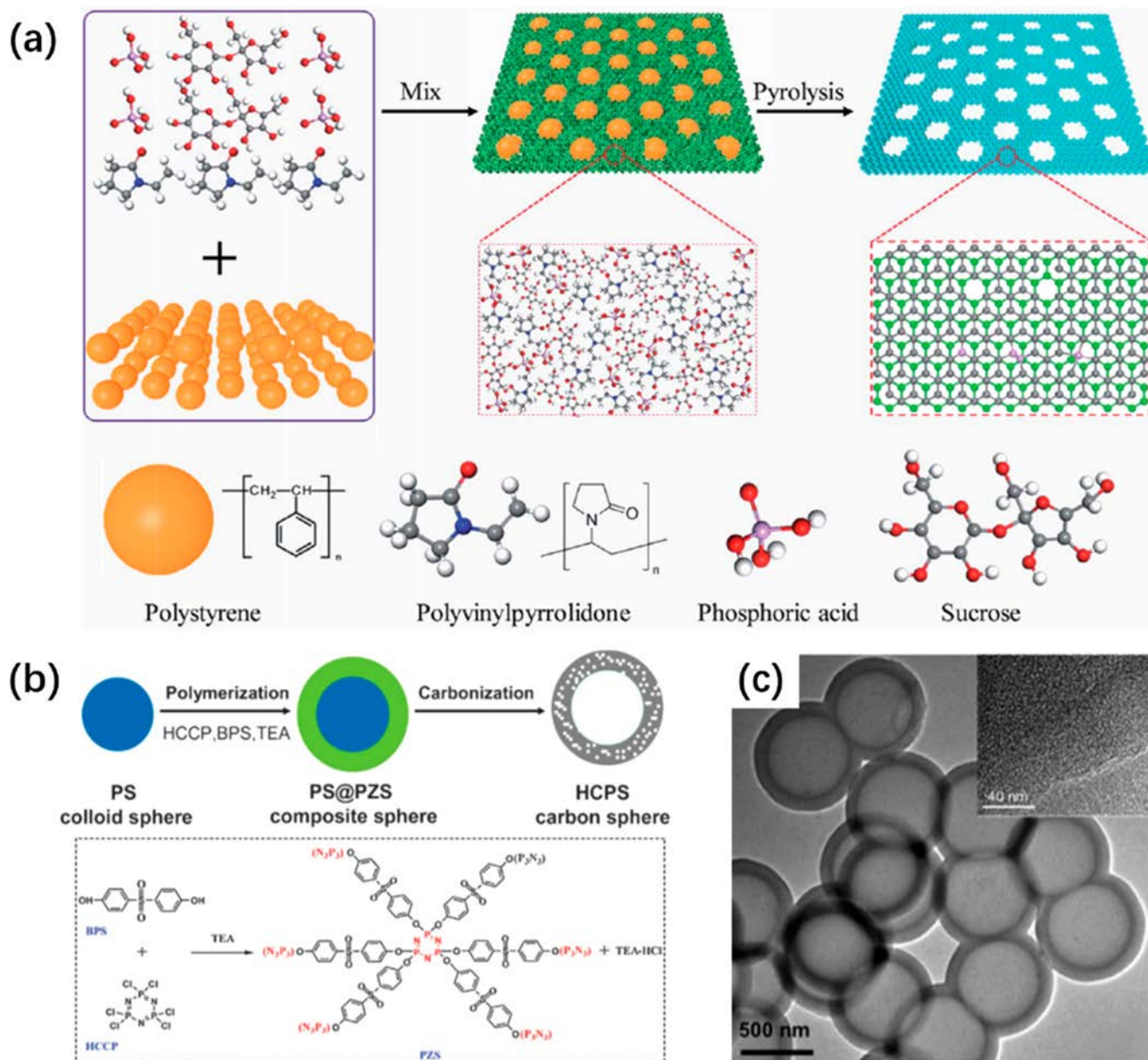
Figure 40. (a) Schematic illustration of the preparation of macroporous carbon aerogels utilizing PS spheres as a template. SEM images of the replicated RF aerogel before (b) and after (c) carbonization. Reproduced with permission from ref 373. Copyright 2019 Royal Society of Chemistry. (d) Schematic illustration of the preparation of hollow carbon spheres utilizing PS as a template. (e) Representative TEM images of hollow carbon spheres. The inset shows an HRTEM image of the carbon shell. Reproduced with permission from ref 374. Copyright 2010 Royal Society of Chemistry.

carbon shell. More importantly, by adjusting the mass ratio of PS by a comonomer, the thickness of the shell could be rationally tailored.[374]

PMMA nanospheres are excellent alternatives for constructing macroporous carbon materials because of their ease of preparation and low cost, as well as their ability to depolymerize completely at slightly elevated temperatures. Zhu et al. reported highly ordered macroporous N-doped carbon materials obtained by assembly and sequential carbonization of PMMA–PAN core–shell nanoparticles.[375] Prestabilization before the carbonization of the PMMA/PAN nanoparticles was important for the formation of the ordered macropore architectures, since the PAN molecule chains needed to be cross-linked and cyclized to form the carbon framework upon heating prior to the thermal decomposition of PMMA.

In addition to templating methods, electrostatic cross-linking of polymers can establish macroporous structures. As previously demonstrated, the electrostatically cross-linked PIL membranes displayed porous architectures, in which the size of the macropores was closely related to the cross-link density. Recently, Wang et al. demonstrated that the macropore size could also be regulated by the diffusion rate of NH_3 solution.[173] Generally, as the hydrophilicity of the PIL increased, the diffusion rate of NH_3 solution into the PIL-containing polymeric blend was enhanced. As a result, the accelerated infiltration of NH_3 solution induced fast, poorly regulated phase separation, forming irregular large macropores.

On the other hand, increasing the hydrophobicity of PILs effectively lowered the diffusion rate of NH_3 solution, and much smaller pores were formed. Upon vacuum carbonization, these macroporous structures were well retained and transformed into hierarchically porous carbon membranes.

Dai and Liang demonstrated a spinodal polymer decomposition strategy to manufacture bicontinuous macroporous carbon.[376] They synthesized polymer rods by assembly of phloroglucinol/formaldehyde copolymer and triblock copolymer F127 under various reaction conditions. The as-obtained polymer rods further underwent carbonization to form a bimodal meso/macroporous carbon monolith. With carefully designed preparation conditions (concentration, temperature, etc.), the pore architectures of the final carbon can be rationally tailored.

6. CONCLUSION

Porous carbons are one of the major research areas of materials science. This comprehensive Review discusses porous carbons that are derived either partially or exclusively from polymers and are simultaneously doped with heteroatom(s). One of the most important properties of such porous carbon materials is their large porosity and high specific surface area, which has led to many applications ranging from adsorption/separation to fire protection, energy management, and catalysis. Both template-based and template-free strategies are utilized for controlling the porosity and pore shape of carbons. Because of the multifarious hard templates and their easily tunable surface functionality, size, and porosity, the hard template method is popular for replicating HPCMs with a range of desirable ordered porous structures. However, a major drawback associated with this approach lies in the multistep synthesis and the involvement of etching chemicals to remove the template, which is generally considered a time/labor-intensive process inhibiting technical scale-up. The soft template method is straightforward and less time/work-demanding in terms of the template removal process at the expense of less precise control of the porous structure and morphology at the nano/microscale. The direct carbonization of pristine polymers without an external template is preferred for large-scale production of HPCMs, where, typically, the required control of the porous structure is less important for their applications. Note that polymers in the direct carbonization method may have a part of their molecular structure used as an internal template. For example, ion clusters formed by ionic polymers can serve as porogens to produce micropores or small mesopores in HPCMs.

It has been well-established in the carbon materials community that heteroatom doping is a promising strategy to selectively modulate the physicochemical properties of HPCMs and endow them with targeted catalytic activities. At the beginning of section 3, we interpreted in detail the techniques utilized to characterize HPCMs to help illustrate how to determine their structures down to an atomic level. Nitrogen-doped porous carbon materials first came into the view of researchers in the 1980s and sparked wider interest in 2009 with the discovery of the unusual activity of N-doped carbon nanotubes for the ORR. Meanwhile, recent studies demonstrated that codoping of two or more heteroatoms in carbon frameworks could endow HPCMs with structural synergy, showing great promise for the field of electrocatalysis in general. Codoping is much less studied and understood than single-heteroatom doping in the porous carbon field due to its

complexity. It is believed that, by pairing judicious polymeric precursor choices with appropriate polymer processing techniques, desirable HPCMs can be readily fabricated to contribute to efforts to mitigate the current energy and environmental issues.

Because the morphology of HPCMs plays an essential role in determining their application spectrum, studies have been devoted to controlling the local architectures. By employing template methods and rich polymer processing tools, HPCMs in the form of spheres, fibers, sheets, and membranes were created as functional materials for the adsorption/separation and energy conversion fields. In this regard, considering that many applications of HPCMs are currently centered around the energy-related electrocatalysis field, fibers or membranes of HPCMs might be prioritized, since they can be directly utilized as electrodes without the traditionally complicated processing of powdery carbocatalysts for gluing by electronically insulating polymeric binders. The challenges lie in their scalable fabrication with robust electrochemical and mechanical stability and flexibility.

It is necessary to state that the selection of polymers is crucial in determining the local binding properties of the final carbons. For example, the pyrolysis of PAN and cellulose at 1000 °C only leads to amorphous or poorly crystalline carbons, while carbonization of PILs at 1000 °C readily produces heteroatom-doped carbons with medium-to-high yields, and their atomic structure has a particularly high short-range order, which is needed for improving their conductive properties, bringing about fire-retardant properties as well as catalytic activity.

Currently, the state-of-the-art research on HPCMs is application-oriented and covers the adsorption/separation, catalysis, and energy conversion fields. We believe that the use of HPCMs could be easily expanded into other fields, e.g., water purification and electrosynthesis of valuable organics, as well as to "smart" actuators and flexible electronics, by careful design of their structures at all scales. Furthermore, utilizing polymers as carbonization precursors enables more complicated carbon morphologies to be achieved, such as anisotropic, hierarchical, and chiral carbons, to name a few. These morphologies are usually hard to obtain by other polymer-free methods. By carefully engineering the composition of polymers, it is also possible to systematically manipulate the electronic structures of the resulting carbons. Recent advancements in controlling electronic structures, including via SACs, Mott−Schottky effects, or even FLP chemistry, are all possible by utilizing predesigned polymers as carbon precursors. Therefore, we encourage researchers to further explore this exciting field, discover more interesting carbon materials, and hunt for their novel applications.

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