

From Molecular Precursors to Nanoparticles—Tailoring the Adsorption Properties of Porous Carbon Materials by Controlled Chemical Functionalization

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Nanoporous carbon materials (NCMs) provide the “function” of high specific surface area and thus have large interface area for interactions with surrounding species, which is of particular importance in applications related to adsorption processes. The strength and mechanism of adsorption depend on the pore architecture of the NCMs. In addition, chemical functionalization can be used to induce changes of electron density and/or electron density distribution in the pore walls, thus further modifying the interactions between carbons and guest species. Typical approaches for functionalization of nanoporous materials with regular atomic construction like porous silica, metal–organic frameworks, or zeolites, cannot be applied to NCMs due to their less defined local atomic construction and abundant defects. Therefore, synthetic strategies that offer a higher degree of control over the process of functionalization are needed. Synthetic approaches for covalent functionalization of NCMs, that is, for the incorporation of heteroatoms into the carbon backbone, are critically reviewed with a special focus on strategies following the concept “from molecules to materials.” Approaches for coordinative functionalization with metallic species, and the functionalization by nanocomposite formation between pristine carbon materials and heteroatom-containing carbons, are introduced as well. Particular focus is given to the influences of these functionalizations in adsorption-related applications.

1. Chemical Functionalization of Nanoporous Materials as a Versatile Tool to Tune Their Adsorption Properties

The nanometer-sized cavities present into nanoporous materials are the reason for their remarkably high specific surface area and thus a large interface area with the surrounding

matter.^[1] In consequence, such materials are attractive candidates for applications where interactions between species from a fluid phase with a solid surface (i.e., adsorption processes) play a crucial role.^[2] This can range from gas filtration,^[3] over the heterogeneously catalyzed conversion of molecules (in gas phase or in solution),^[4] to the selective adsorption of ions,^[5] molecules, or even larger species in water and blood filtration.^[6] Electrochemical energy storage in supercapacitors and batteries and related devices is as well often based on adsorption processes, however, in this case in combination with electron transport in the solid material and in some cases with electron transfer.^[7] Thus, in general, any porous material has the “function” of high specific surface area and can be regarded as being intrinsically functionalized.

From a thermodynamic point of view, adsorption processes on surfaces (not to be mixed with “absorption” in the volume of a material) are traditionally

subdivided into physical adsorption (“physisorption” based on weak and easily reversible van der Waals interactions that can be described by the Lennard–Jones potential with enthalpies in the range of typical condensation enthalpies usually below 50 kJ mol^{−1}) and chemical adsorption (“chemisorption” with the formation of covalent chemical bonds and thus higher enthalpies usually in the range between 50 and 500 kJ mol^{−1}). Crucial properties determining the strength of interaction between porous materials and a given adsorptive are the texture of the pore system (i.e., pore sizes and pore geometries) and the electron density (distribution) within the pore walls (i.e., their atomic construction motives). The architecture of a pore system as such provides a possibility for the physical functionalization of a material. For a given chemical composition of the pore walls, smaller pores (as long as they are still large enough to be entered by the guest species) will lead to higher adsorption enthalpies for one and the same adsorptive because the Lennard–Jones potentials of both pore walls are overlapping. The influence on the adsorption enthalpy remains however limited to either stronger (in case of decreasing pore sizes) or weaker (in case of increasing pore sizes) van der Waals interactions. In this context, it should be noted that when the size of the pores is approaching the size of the guest species, the adsorption process will reach its equilibrium slower and slower, that

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DOI: 10.1002/adfm.201908371

is, it takes longer time until all pores are filled with the species to be adsorbed. In such a case, a hierarchical pore structure combining smaller pores with a system of transport pores can be beneficial in order to enhance the mass transport within the bulk material and improve the accessibility of the smallest pores.^[8]

In a similar sense as organic chemists call a functional group in a molecule “functional” because it provides the molecules with a certain property/reactivity, “chemical functionalization” of porous materials is usually carried out to change the electron density and/or electron density distribution in the pore walls—in most cases the aim is to tune their strength and mechanisms of interaction with guest species.^[9] In other words, chemical functionalization of porous materials is translating the principle of functionalization from molecules to materials. Examples for chemical functionalization of porous materials include the decoration of the surface of porous silica materials (Figure 1A) with functional groups (e.g., hydrophobic surface groups, chiral groups, or Lewis acidic sites)^[9c,10] or the modification of the chemistry of the linkers in metal–organic frameworks (MOFs) (Figure 1B).^[11] Cation exchange and the change of the density of acidic sites in zeolites (Figure 1C),^[9d,12] as well as the introduction of specific functional groups into porous polymers, are further examples.^[9a,13]

Chemical functionalization is a very powerful “regulation screw” to tune adsorption properties of materials over a wide range by introducing specific electrophilic/nucleophilic, ionic, or chiral sites for enhanced interaction with the matter to be adsorbed. Even for species with low adsorption enthalpy specific interactions can contribute. For example, nitrogen molecules can have strong interactions with metal ions in zeolites, and it is thus recommended to analyze the porosity of those and other materials with nonpolarizable argon as the test gas.^[14] Well-defined structure motives causing specific interactions can, for instance, be implemented into metal–organic materials. As one example, Nugent et al. reported that the control over pore functionality and size in a series of metal–organic materials with coordinately saturated metal centers and periodically arrayed hexafluorosilicate anions (“SIFSIX”) (Figure 2A) enables a kinetic and thermodynamic “sweet spot” that offers high volumetric uptake of CO₂ at low partial pressure and high selectivity in adsorption over other gases (Figure 2B).^[11b] The reason for this strong interaction between CO₂ molecules and solid material is the particularly strong interactions between the electropositive carbon atoms of CO₂ molecules and electronegative fluorine atoms of SiF₆^{2−} anions. Long and co-workers reported that diamine-appended MOFs can even behave as “phase-change” adsorbents.^[11c] It has been found that the insertion of CO₂ molecules into metal–amine bonds induces a cooperative reorganization of the amines into well-ordered chains of ammonium carbamate (Figure 2C). Without chemical functionalization, such adsorption phenomena would remain unachievable.

Due to precise and a wide range of control over the adsorption enthalpies, it is not surprising that more and more approaches for the chemical functionalization of various kinds of porous materials are reported.^[15] The general requirement that a synthetic strategy for the chemical functionalization of a nanoporous material has to fulfill is that the functionalization motives are similar throughout the bulk material (e.g.,



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the basicity of newly introduced basic functional sites is of the same strength) and that other properties of the material such as the crystal structure, the pore size, or the macroscopic appearance can still be controlled.

What all the materials mentioned so far have in common is the fact that their chemical functionalization is rather precisely controllable considering the well-defined structure of the

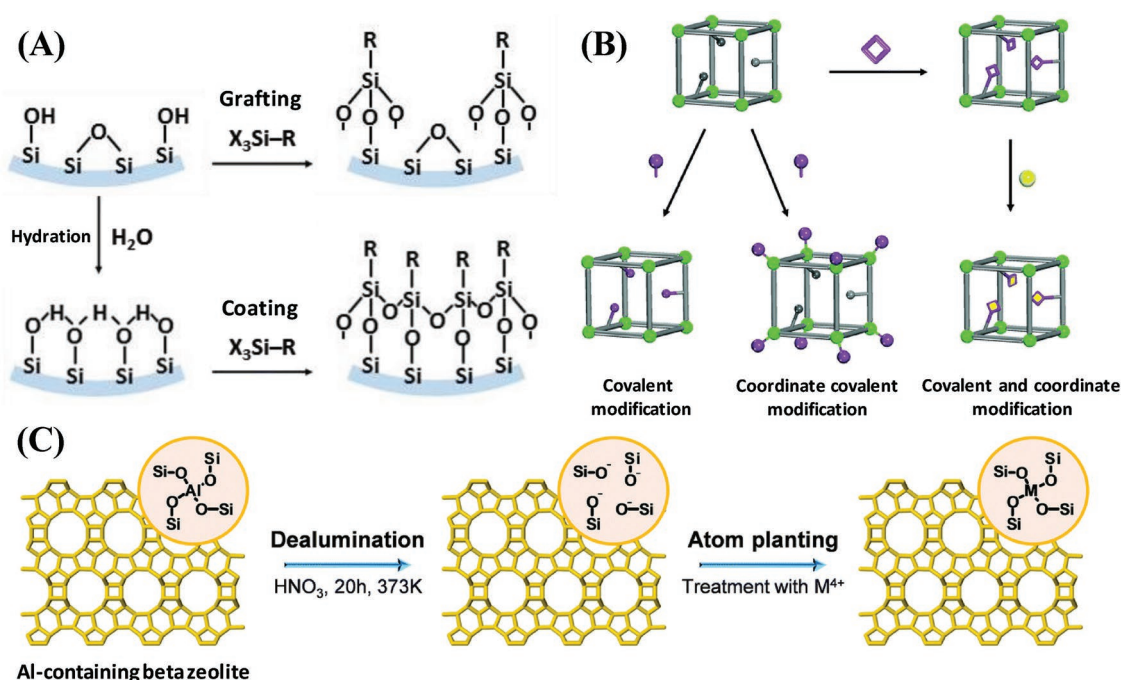


Figure 1. Examples for chemical modifications in porous materials. A) Chemical functionalization of silica surfaces by coating and grafting processes. B) Different postsynthetic strategies for chemical functionalization of MOFs. C) Two-step postsynthetic approach for the preparation of metal-containing zeolites. A) Adapted with permission.^[10a] Copyright 2000, Wiley-VCH. B) Reproduced with permission.^[9b] Copyright 2011, Royal Society of Chemistry. C) Reproduced with permission.^[9d] Copyright 2015, Royal Society of Chemistry.

starting materials. Porous framework materials like MOFs and zeolites have crystalline structures. Porous polymers and silica have in most cases a defined surface chemistry. The chemistry of functionalization is well controllable for such regular and ordered materials—not only from a synthetic but also from an analytical point of view.

Nanoporous carbon materials (NCMs) are not only different from the above-mentioned examples in their properties but also in their structure. They have the smallest voxel size of chemical construction and usually have a rather ill-defined local atomic arrangement rich of defects. In consequence, typical procedures as applied for the chemical functionalization of nanoporous materials with a regular atomic construction and defined structure cannot simply be applied for NCMs—at least not if the requirements for the chemical functionalization mentioned above are taken into consideration. The introduction of the desired functionality into this important class of materials requires special strategies and will also have effects which are not offhand comparable to other materials. It is therefore not surprising that the variety of existing methods for the functionalization of carbon materials has been summarized and described in numerous earlier review articles.^[16] It is the aim of this review article to summarize some fundamental concepts and recently developed strategies toward a controlled functionalization chemistry of NCMs. In the following sections, synthetic approaches for the controlled functionalization of nanoporous carbon materials with heteroatoms (covalent functionalization), with metallic species (coordinative functionalization), and with carbon materials of different structure and properties (composite functionalization) will be reviewed along

with their influence on the properties of the NCMs in adsorption-related applications. Advantages and disadvantages will be critically discussed (Scheme 1).

2. The Special Case of Chemical Functionalization of Nanoporous Carbon Materials

NCMs, in general, have high thermal/electric conductivity, chemical/thermal stability, and relatively low polarity.^[17] They are particularly useful for the application in fields where one or more of these properties have to be combined with adsorption processes. Such fields include electrochemical energy storage,^[18] catalysis,^[19] or storage/purification of gases.^[20] Similar as described above for other nanoporous materials, the most crucial factor that determines the properties of nanoporous carbon in adsorption-related applications is the strength of interaction with the atoms, molecules, or ions, to be adsorbed. The pore size provides a certain degree of control over the strength of interaction with guest species, but chemical functionalization of the carbon network can be used as a larger and stronger toolbox to tailor adsorption enthalpies on carbon surfaces.

Among the various families of nanoporous materials, there is hardly one with less defined local atomic arrangement than NCMs. Starting from the stacked crystalline graphite, substitution of carbon six rings by other structure motifs like five rings, seven rings, or defects leads to distortion of the structure. If the arrangement becomes completely random, a nanoporous carbon material is the result (Figure 3A,B). In this regard,

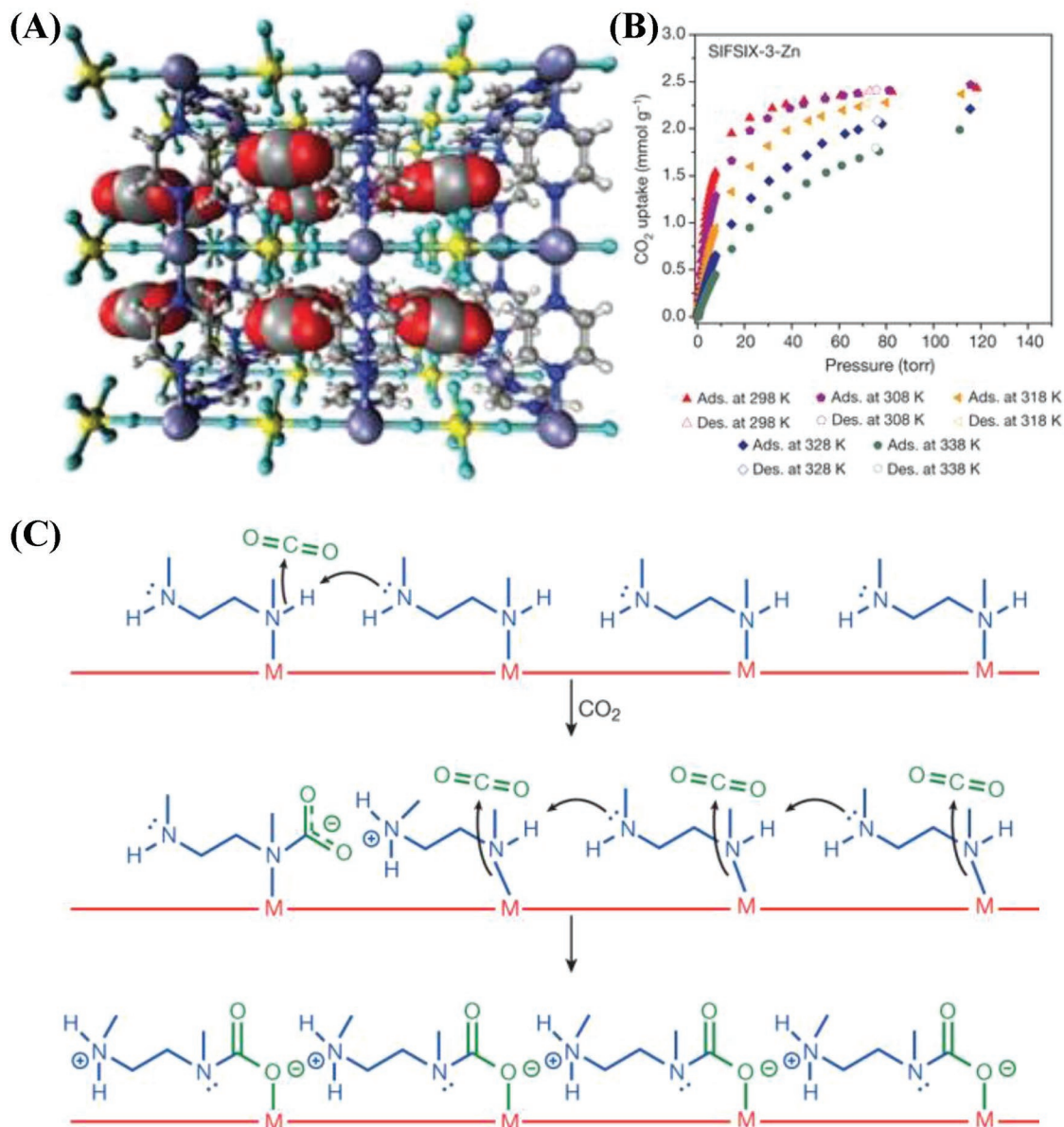
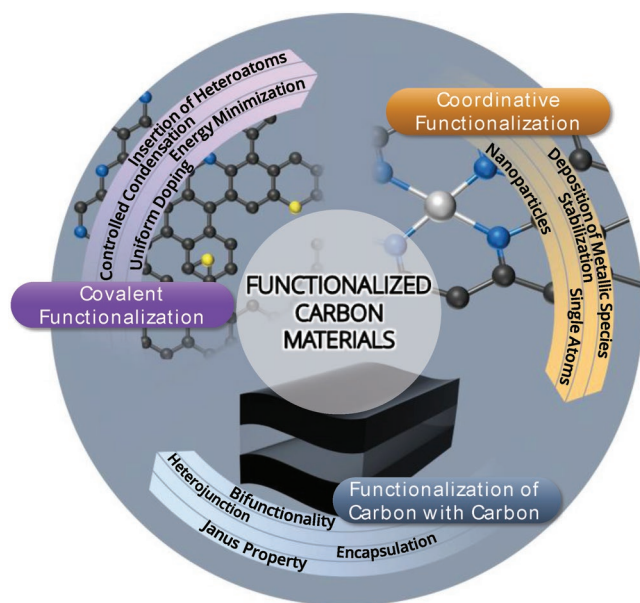


Figure 2. A) Modeled structure of SIFSIX-3-Zn, a metal–organic material with coordinately saturated zinc centers and periodically arrayed hexafluoro-silicate anions. Due to the presence of multiple binding sites, SIFSIX materials show an isosteric heat of CO₂ adsorption of up to 45 kJ mol⁻¹ and an ideal adsorbed solution theory (IAST) CO₂/N₂ selectivity close to 2000. Color code: C (gray), H (white), N (blue), O (red), Si (yellow), F (green), and Zn (purple). B) CO₂ adsorption isotherms of SIFSIX-3-Zn at different temperatures indicating remarkably strong binding between adsorbent and adsorbate. C) Functionalization of an MOF with N-donor functions leads to simultaneous proton transfer, and nucleophilic attack of nitrogen on a CO₂ molecule forms an ammonium carbamate species that destabilizes the amine coordinated at the next metal site, initiating the cooperative adsorption of CO₂ by a chain reaction. A,B) Reproduced with permission.^[11b] Copyright 2013, Springer Nature. C) Reproduced with permission.^[11c] Copyright 2015, Springer Nature.

already a “standard” porous carbon material (such as activated carbon)^[17b] can be regarded as being not only functionalized with porosity but also as being abundantly chemically functionalized. The chemical potential and reactivity of the individual atoms in the carbon network of typical sp²-rich NCM materials vary within a certain window. This fact will already be relevant in adsorption processes. For instance, the adsorption enthalpy and equilibrium distance of a nitrogen molecule adsorbed over a sp² carbon six ring will be (slightly) different in comparison

to the adsorption enthalpy over a five or seven ring because the electron density in the pore wall affects the Lennard-Jones potential of adsorption.

In order to tune crucial physicochemical properties of NCMs such as redox potential, electric conductivity, local electron density distribution, or polarity/acidity of surface, over a wider range, further chemical functionalization has to be applied. This can be achieved by the introduction of heteroatoms, such as nitrogen, boron, phosphorus, or oxygen,



Scheme 1. Toolbox for functionalization of nanoporous carbon materials discussed in this article.

into the carbon framework, and/or as surface functional groups,^[16b,e,f] or by the introduction of metallic species in form of nanoparticles,^[23] or single atoms/ions.^[24] In a wider sense, also composite materials between carbon and other materials or between carbon and a carbon material with different properties can be regarded as a method for chemical functionalization.^[25] The achievable range of properties and applications can be further broadened by using combinations of these strategies. Such chemically functionalized NCMs usually have adsorption properties, which are significantly different than those of pristine NCMs.

Nature is impressively showing how precisely adsorption properties can be tuned if these functionalization tools are wisely combined and site-specific interaction is provided. Some of the examples are an enzyme found in plants with the most selective CO₂ capture mechanism, Ribulose-1,5-bisphosphate carboxylase/oxygenase (RubisCO),^[20a,26] carbonic anhydrase that converts and transports CO₂,^[27] and metalloprotein hemoglobin that has the function to transport O₂ in vertebrates.^[27b,28] Inspired by the control that nature achieves, materials chemists are more and more focusing on the development of methods for transferring these principles from biology to carbon-based materials. For example, the self-cleaning effect on a lotus leaf and cicada wing attracted the attention of scientists for developing and tailoring biomimetic surfaces with super-hydrophobic properties.^[29] Lee et al. fabricated well-defined nanostructured polymeric surfaces with aligned nanofibers of controllable aspect ratio, which enables control over the wetting property by rendering nanometer-scale roughness.^[29a] Probably one of the best illustrations of biomimetic research is development of synthetic materials for molecular recognition. Because of the ease of functionalizing the pores and adjusting porosity, MOFs have emerged as superior materials for the recognition of small molecules.^[30] Pullen et al. adopted postsynthetic modification of the organic linker

in UiO-66 to introduce the same binding motif as present in [FeFe]-hydrogenase, for enhanced photochemical hydrogen production.^[30a] One approach for enhancing the properties of catalysts for oxygen reduction reaction (ORR) is including bio-mimetic porphyrine-like structures as the catalytically active site.^[31] Mehmood et al. used this strategy to embed iron into a nitrogen-doped carbon (NDC) framework, thus using NDCs as solid-state ligands and conductive supports at the same time.^[31a]

These and many other (bioinspired or non-bioinspired) examples represent the huge potential of chemical functionalization of NCMs for tuning their interaction strength with different guest species. What makes chemical functionalization of NCMs different from the other porous materials described above is their much less defined local atomic arrangement. The differences in the reactivity of carbon atoms in these disordered materials make it more difficult to establish synthetic routes for their controlled chemical functionalization. Many generally applicable synthetic routes have been developed for the functionalization of other nanostructured carbon materials with more regular construction motives like graphene,^[32] carbon nanotubes (CNTs),^[33] fullerenes,^[34] or even nanodiamonds (NDs),^[35] which consist of sp³ carbon atoms (Figure 3C–F). For example, nitrogen functionalization of CNTs can be easily accomplished and precisely tuned by the choice of precursor, metal catalyst, and synthesis temperature. In the study of Bitter and co-workers, increasing synthesis temperature leads to increasing C/N ratio, and the type of nitrogen in the graphene layer changed from predominantly pyridinic to quaternary nitrogen.^[36] In the work of Gogotsi and co-workers, covalent linking of ethylenediamine to the surface carboxyl groups of nanodiamond powder enabled covalent incorporation of ND particles into the polymer matrix. This straightforward modification is achievable due to ND's tailorable and defined surface chemistry, without compromising the properties of the diamond core. Obtained nanodiamond–epoxy composites showed superior mechanical strength properties, and by that opened up a range of possible applications.^[37]

In contrast, when an NCM would be treated under the same conditions as a CNT or ND in order to introduce oxygen or nitrogen heteroatoms postsynthetically, they will likely be less chemically defined because the carbon atoms have variable reactivity toward the functionalization agents. Depending on properties such as the degree of carbon ordering (i.e., the “graphitization degree”), pore structure, and particle size/morphology, this reactivity can span over a broad range. The strength of interaction of NCMs with metallic species for functionalization is also strongly dependent on their intrinsic properties like the pore size and the presence or absence of heteroatoms and is surely different than for nonporous carbon materials with more regular structure. In conclusion, the targeted chemical functionalization of NCMs comes with special challenges for materials chemists. Strong research efforts to develop advanced synthetic methods have been made recently, and it becomes more and more obvious that the huge potential of chemical functionalization of NCMs can only be accomplished in full when the functionalization fulfills the requirements mentioned above.

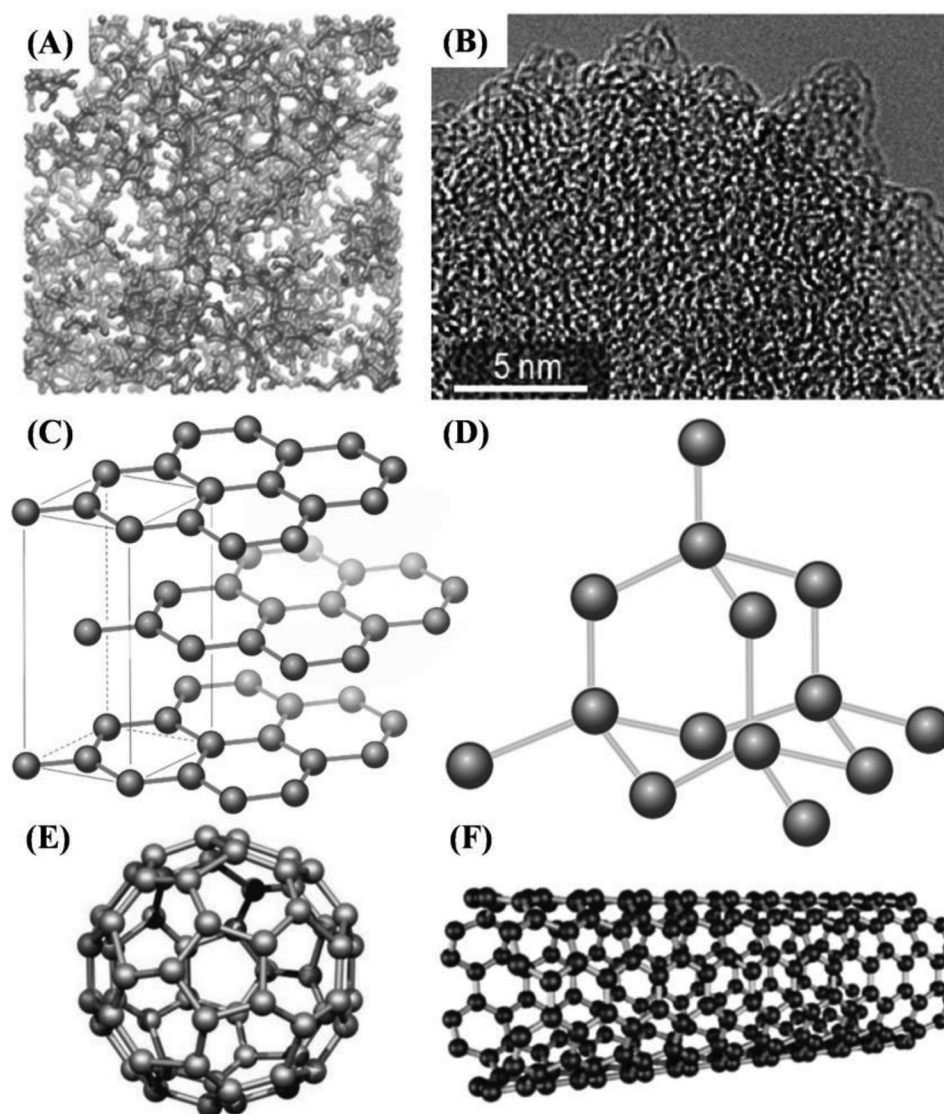


Figure 3. A) Model atomic structure of a nanoporous carbon material and B) high-resolution TEM microscopic image of an NCM. Atomic structures of C) graphite, D) nanodiamond, E) fullerene, and F) single-walled carbon nanotube. A) Adapted with permission.^[21] Copyright 2010, Elsevier. B) Adapted with permission.^[22] Copyright 2010, American Chemical Society.

3. Covalent Functionalization of Carbon Materials by Heteroatom Doping

3.1. Effects of Heteroatoms on the Properties of Carbon-Based Materials

“Heteroatom doping” of NCMs means the attachment of surface functional groups such as amine groups, nitrile groups, pyridinic groups, hydroxyl groups, or carboxylic groups on the surface of the carbons (Figure 4).

Nitrogen is the by the far most widely applied sort of atom doped into carbon materials,^[16i,38] but other elements like sulfur,^[39] oxygen,^[40] phosphorous,^[41] or boron,^[42] and combinations of different elements can play a role as well.^[16f,43] For nitrogen as the dopant, there seem to be a couple of

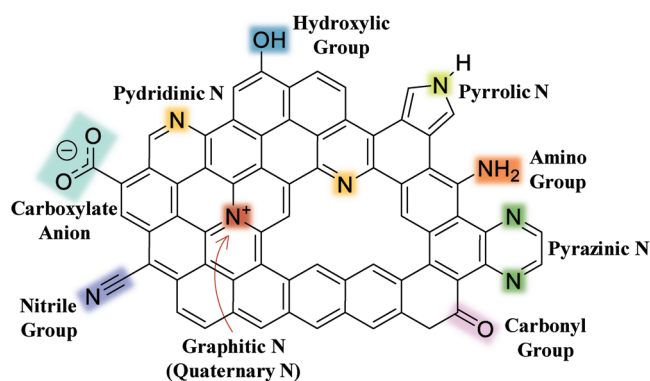


Figure 4. Some of the possible heteroatom-containing functional groups within NCMs.

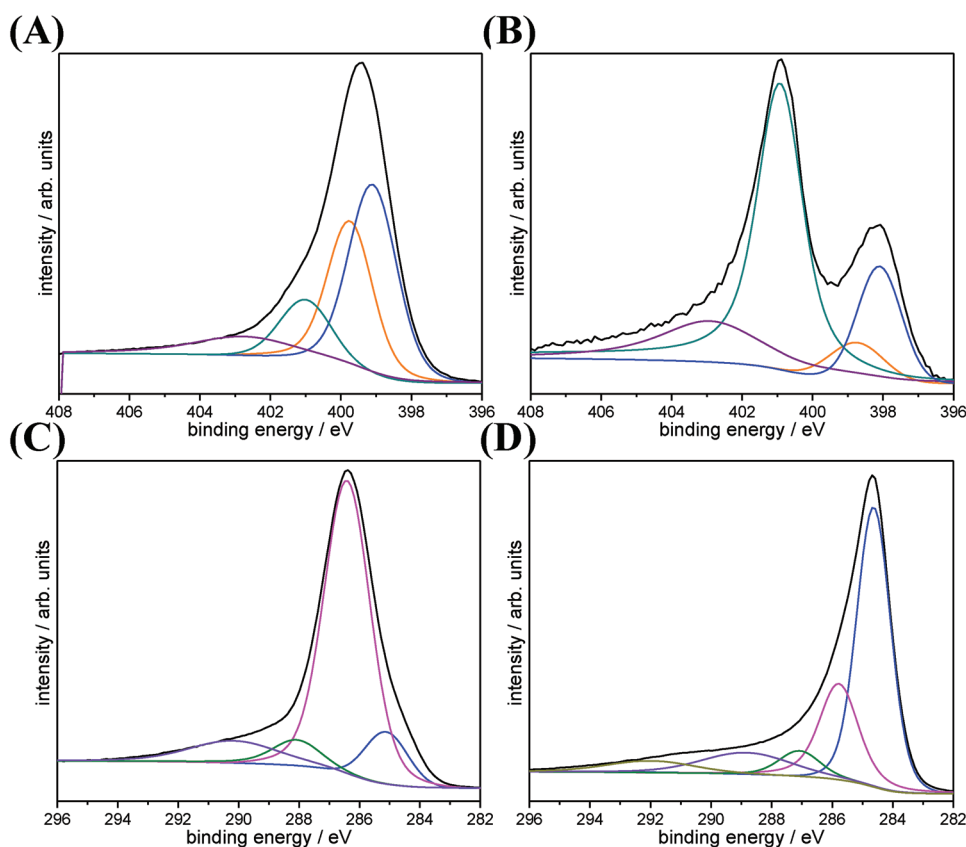


Figure 5. Fitted N 1s XPS line scans of A) C-HAT-CN-550, B) C-HAT-CN-1000, and fitted C 1s XPS line scans of C) C-HAT-CN-550 and D) C-HAT-CN-1000. Adapted with permission.^[45c] Copyright 2018, Wiley-VCH.

thermodynamically favorable stoichiometric nitrogen/carbon ratios, and there is the general tendency that the amount of nitrogen that can be doped into the carbon framework decreases with increasing temperature. Not only the amount, but also the binding motifs of nitrogen in NCMs are important because this directly affects the electron density distribution within the carbonaceous network. X-ray photoelectron spectroscopy (XPS) is a surface analysis technique that provides quantitative and chemical and electronic state information, which makes it suitable for characterization and for getting a profound understanding of adsorption phenomena in heteroatom-doped NCMs. Because of the unique ability of XPS to give an insight into local bonding environment of chemical species, the following section will focus on the information that one can derive from and the interpretation of XPS spectra of selected nitrogen-containing NCMs.

Very nitrogen-rich carbon nitride materials (C_3N_4) are usually stable up to 550 °C and start to decrease in nitrogen content at higher temperatures.^[44] Recently, materials with a C_2N stoichiometry have been reported which are stable up to around 700 °C.^[45] At higher temperature, the nitrogen content decreases, and typical nitrogen-doped carbon materials with the thermodynamically most stable graphitic nitrogen atoms are obtained. NDCs prepared at high temperatures have typically nitrogen contents of 10 at.% or lower, and in contrast to the nucleophilic, electron-rich heteroatoms present at low temperature, the nitrogen atoms are stabilized in the form of electron-

deficient quaternary/graphitic nitrogen (green peak at ≈ 401 eV in **Figure 5B**). The ratio between different binding motifs of nitrogen in the carbon framework can be controlled by the synthesis temperature. The decrease of nitrogen content at higher temperatures is mainly due to decrease of cyano and pyrazine groups (blue and yellow peaks at 400–398 eV; **Figure 5A,B**), whereas quaternary N with higher binding energy remains in the material at temperatures as high as 1000 °C (**Figure 5A,B**). Cyano/pyrazine peaks for C-HAT-CN-550, a material with a C_2N stoichiometry (presented in **Figure 6A**), emerge at a binding energy of ≈ 399 eV, and quaternary nitrogen signal with relatively low intensity is located at 401 eV (**Figure 5A**).^[45c] In C-HAT-CN-1000, a nitrogen-doped carbon material with around 5 at.% of nitrogen, all of the fitted peaks are shifted and their intensity ratio changes (**Figure 5B**). From these considerations it gets evident that nitrogen atoms incorporated into carbon materials have quite different chemical properties and work functions of their electrons depending on how they are bonded to the carbon atoms. In a C_2N material, very electron-rich nitrogen atoms are present whereas the heteroatoms in the high-temperature material are more electron deficient. That will result in different adsorption properties for both materials, and one NDC material hardly has the same properties as another one.

These heteroatoms affect the electron density and electron density distribution of the carbon framework and therefore also the macroscopic properties like surface polarity, acidity/basicity,

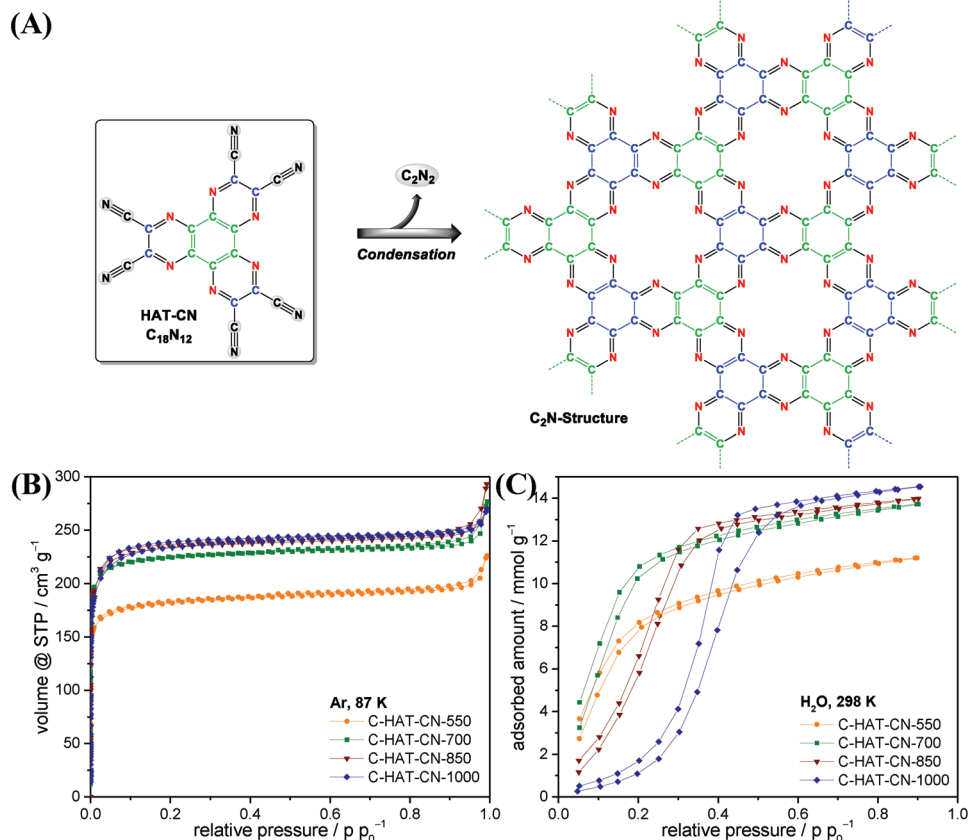


Figure 6. A) Idealized model for the formation of a C₂N structure by condensation of an HAT-CN precursor, B) argon physisorption isotherms (87 K), and C) water vapor physisorption isotherms (298 K) of C-HAT materials. Reproduced with permission.^[45c] Copyright 2018, Wiley-VCH.

or electric conductivity.^[46] These influences are also observed in C 1s line scans in XPS of NDCs (Figure 5C,D). A peak corresponding to carbons bonded to electron-rich nitrogen atoms (pink peak at ≈ 286.5 eV) emerges as a dominant species in C₂N material, while graphitic C=C carbons (blue peak at ≈ 285 eV) have only a minor contribution (Figure 5C). In C-HAT-CN-1000 this ratio is reversed, due to the continuing development of a nitrogen-free graphitic carbon phase at higher synthesis temperature (Figure 5D). As in the case of nitrogen scans, not only the relative intensity of different binding modes changes with increasing temperature, but also the position of the peaks. All single peaks as well as the full line scan are shifted almost 2 eV to lower binding energies with increasing synthesis temperature, thus making the carbon atoms more electron rich. This essentially implies that the heteroatom doping has the same effect on the carbon atoms in the NCM network as if a positive or negative electric potential of 2 V would be applied. In a figurative sense, the electron density in the C₂N network is transferred from carbon to nitrogen atoms. In principle, the same happens when an anion is adsorbed on a carbon surface that is positively charged by 2 V—as long as this adsorption process is mirrored by a counter electrode as it would be the case in a supercapacitor. In this context, it should be noted that the simple presence of heteroatoms does not necessarily enhance the electric conductivity of NCMs. The change will depend on the binding motives and content of heteroatoms, and the often

generalized view that nitrogen enhances the electric conductivity of carbon is surely misleading. Another consequence of the incorporation of large amounts of nitrogen atoms into NCMs at high local order is that they stand out by a remarkable oxidation resistance due to their almost “ionic character.”^[47]

Very important for applications including adsorptive processes, the presence of an inhomogeneous electron density distribution further increases the strength with in particular polar guest species such as water or carbon dioxide molecules or ions in solution or from ionic liquids (ILs). Binding a carbon atom to a nitrogen atom instead of another carbon atom will cause a positive partial charge on this atom due to the higher electronegativity of nitrogen and the high mobility of electrons in a sp²-dominated system of carbon atoms. The larger the number of these nitrogen atoms and the more defined the repetition units are, the stronger is their impact on the properties of the carbon atomic framework. For instance, in a C₂N material, every carbon atom is bonded to at least one nitrogen atom. Such a binding situation will cause a “cascade effect” that maximizes the electron density on the heteroatoms. In contrast, an inhomogeneous doping of heteroatoms into carbon materials cannot affect the electron density of all carbon atoms with a similar strength. As an additional consequence, these surface functional groups can serve as anchoring points for further modification by adding complexes,^[48] biomolecules, or nanoparticles by covalent bonding, electrostatic interactions, or via

hydrogen bridges. In many cases, functionalization of carbon materials does not only enhance the interaction with species to be adsorbed but also with compounds that are useful for further chemical functionalization of the carbon.

3.2. Synthetic Concepts for the Controlled Functionalization of Carbon Materials with Heteroatoms

The following section will give a brief introduction on approaches for the controlled functionalization of nanoporous carbon materials with heteroatoms which is presumably the most widely applied method to tailor their adsorption properties. Special focus will be given to molecular precursors for the doping of nitrogen. As nanoporous carbons are usually rich in defects, heteroatoms can be introduced by relatively simple methods. In most cases, nitrogen doping is achieved by adding a nitrogen source (such as urea or organic matter with nitrogen-containing functional groups) to the carbon precursor before carbonization,^[4a,49] or the carbonization of a nitrogen-containing nanomaterial such as porous polymers,^[50] or MOFs with N-containing organic ligands.^[51] Postsynthetic treatments under ammonia atmosphere are also applied to substitute atoms at defect sites with nitrogen-containing groups.^[52] Oxygen doping can be achieved by boiling the carbon materials in nitric acid, supplying nitric oxide vapors to them, or by simple heating in air.^[4a,53] Such strategies are relatively simple and can be carried out in a way that the porosity of the carbon materials is not much affected.^[54] Whether the porosity will be affected finally depends on the degree of order of the carbon material on an atomic scale. In particular, well-ordered and stable materials like CNT or graphene will not suffer from altered porosity, whereas typical disordered activated carbon can significantly increase in microporosity under such conditions. On the other side, this kind of postsynthetic treatment suffers from the limited number of heteroatoms that can be incorporated, especially at high temperatures. Furthermore, as mentioned above, the nonuniform reactivity of atoms in porous carbon materials often leads to multiple different binding motives of the incorporated heteroatoms. It is therefore not surprising that in particular postsynthetic methods for the incorporation of heteroatoms are most often applied for materials with a defined structure such as carbon nanotubes.^[55] In the particular case of NCMs, such methods are most often unsuitable for the controlled incorporation of heteroatoms. In consequence, synthetic strategies for controlled incorporation of heteroatoms into carbon materials with atomic control are necessary. Synthetic principles which are offering higher degrees of control over heteroatom doping of carbons will be reviewed in the following sections.

One promising way toward controlled insertion of heteroatoms at high content is the use of stable molecular building blocks such as (poly)ionic liquids (PILs) or other hardly oxidizable organic molecules to translate certain molecular motifs into carbonized materials. The idea behind this principle is to achieve controlled condensation and coordination of these building blocks to obtain porous heteroatom-functionalized carbonaceous frameworks. While this method has proven to be suitable to obtain materials with the desired construction

motives, it remains complicated to precisely adjust their porosity at the same time because established templating methods as used in standard carbonization processes can often not be simply adapted to such alternative precursors. Maybe even more importantly, the purification of heteroatom-rich carbon materials can be problematic as their interaction with the templates is stronger than for pristine carbon materials. Inorganic salts such as ZnCl_2 , NaCl , LiCl , KCl , and their mixtures are commonly used as salt templates for porous carbon materials.^[54,56] However, by introducing heteroatoms in their backbone, the nucleophilic character of the heteroatom-containing sites is strengthening the interaction of the material with electrophilic metal cations. This practically means that metal ions from the salt are stabilized by heteroatoms in the material, which leads to difficult removal of the template.^[45b]

Template-free approaches for the synthesis of such porous molecular carbons are thus desired. One way of achieving this is to use well-established process of sol-gel polycondensation and adding a heteroatom-containing compound in the first step of the synthesis. Depending on the drying method, the obtained materials are either obtained as aerogels, cryogels, or xerogels, formed by supercritical, freeze, or vacuum drying, respectively.^[16e] However, it is difficult to obtain high degree of control over the condensation of single smaller molecules, because of several possible condensation pathways. In that sense, it is more beneficial to select a starting material which is structurally and energetically closer to the final product.^[57] A suitable example of this principle is direct condensation of electron-deficient hexaazatriphenylene-hexacarbonitrile precursor (HAT-CN) into porous carbon materials with high nitrogen content in absence of any template (Figure 6A,B).^[45c] The atomic construction of the materials is predicted by the HAT-CN precursor, and uniform nitrogen doping can be achieved with the nitrogen content and binding motives being controllable by the condensation temperature. These materials reach specific surface areas of up to $1000 \text{ m}^2 \text{ g}^{-1}$ as well as very high H_2O adsorption capability (Figure 6C) even at relative pressures below $p/p_0 = 0.2$ (6000 ppm). This strong interaction with water at high nitrogen-doping level is caused by the presence of extremely electron-rich nitrogen atoms in direct neighborhood to electron-deficient carbon atoms. This “ionic character” of C_2N in combination with the narrow micropores is comparable to the properties of zeolites, and the strong water adsorption is a logical consequence of that.

With this molecular design concept for carbons, the porosity and the atomic construction can be further controlled by the condensation temperature.^[45d] Condensation of HAT-CN starts at a temperature of $\approx 500^\circ\text{C}$, where the pore size of these nitrogen-rich carbon materials is large enough to host CO_2 , but without notable N_2 adsorption leading to a molecular sieving effect (Figure 7A,B). HAT-CN-derived carbons undergo specific interactions with polar guest molecules, such as H_2O and CO_2 , and thus high isosteric heat of adsorption is observed. Theoretical calculations confirm that CO_2 molecules adsorbed on the material are oriented orthogonal to the C_2N planes in an idealized structure occupying every second vacancy in a checkerboard-like fashion (Figure 7C,D). This results in energy minimization since the nitrogen atoms in the C_2N layers are surrounding the carbon atom in the CO_2 molecule, and the carbon

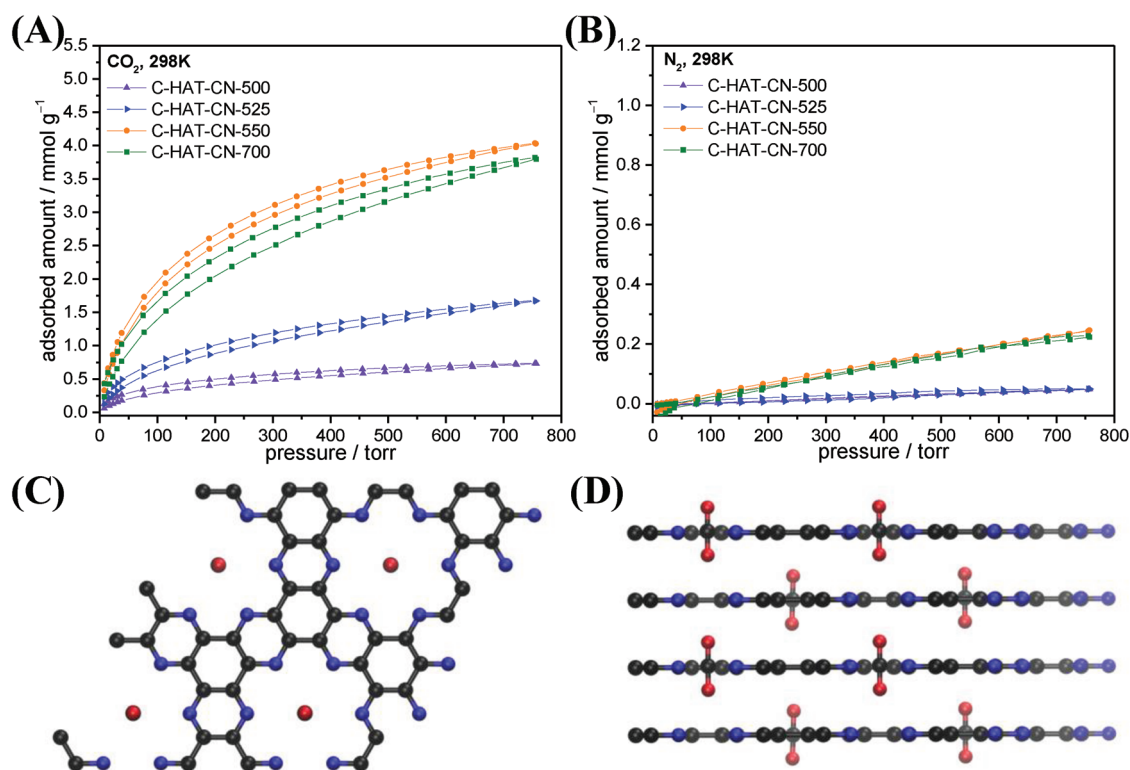


Figure 7. A) CO₂ and B) N₂ physisorption isotherms of C-HAT-CN-500, C-HAT-CN-525, C-HAT-CN-550, and C-HAT-CN-700 measured at 25 °C. C,D) Lowest energy structure of C₂N with maximum amount of CO₂ molecules adsorbed: C) top view and D) side view. Reproduced under the terms of the Creative Commons Attribution 3.0 Unported Licence.^[45d] Copyright 2019, The Author(s). Published by the Royal Society of Chemistry.

atoms from C₂N are in close proximity to the oxygen atoms in the CO₂.

In a similar sense, control over multiple factors by tuning cation and anion pairs is provided by using functionalized or task-specific ionic liquids (TSILs) as carbon precursors.^[58]

The obvious advantage of this class of compounds is that they provide high carbonization yield and are liquids with negligible vapor pressure, which simplifies their processing. Many works in this field make use of nitrogen-containing cations and cyano-functionalized anions that can undergo crosslinking during heating, leading to high nitrogen content into the final material.^[59] Polymerizable groups within the ILs are further necessary to avoid complete thermal decomposition,^[59a,60] but this can also be prevented by either using a spatial confinement (i.e., templates),^[60c,61] or employing (pre)polymerized ILs (PILs).^[62] When polymerizable groups are used, porosity in the resulting carbons can be achieved by sacrificial ions, meaning that non-crosslinkable counterions serve as templates to generate pores.^[60b] An advantage of using hard templates for obtaining porosity is that the IL interacts strongly with the polar surface of inorganic oxides, which are commonly used as templates.^[60c,61] Nanocasting porous silica leads to successful replications, since the precursor can homogeneously fill the pores of the template. Another way to introduce porosity into IL-derived carbons is salt templating, where inorganic salts (or eutectic salt mixtures) act as porogens, resulting in high porosity and high carbon and heteroatom yield.^[63] Poly(ionic liquids) are expanding the possibilities of chemical moieties

used as carbon precursors, and by that enabling the incorporation of classically noncarbonizable groups into the carbon backbone.^[58b,64] Furthermore, processing of these materials can be accomplished by typical polymer operations such as molding, coating, and extrusion.^[47,62d,65] It is also possible to obtain heteroatom-doped carbon membranes by using PILs as carbon precursors.^[25a,62d]

One of the pioneering works in this field from the group of Dai and co-workers describes a carbonization of nitrile-functionalized imidazolium TSILs, where the importance of crosslinkable functional groups was pointed out (Figure 8).^[59a] Moreover, it was shown that the nature of the anion influences not only the thermal stability of IL, but also the overall porosity of the resulting carbons. Materials derived from bulky anions showed high surface areas, meaning that anions function as a template in this case. For example, materials derived from 1,3-bis(cyanomethyl)imidazolium cation ([BCNIm]⁺) had significantly higher surface area when bis(trifluoromethylsulfonyl) imide ([Tf₂N]⁻) was used as an anion (640.4 m² g⁻¹), then when chloride was used (15.5 m² g⁻¹). Nitrogen content reached only up to 3 at.%, but the approach from this work was used in followup studies where higher values of nitrogen doping could be achieved.^[59b,60b,c] The formation of these carbons resembles mechanism previously illuminated by Antonietti and co-workers for highly porous organic materials via the formation of polyaryltriazine networks.^[66]

Materials obtained by direct pyrolysis of ILs usually have high nitrogen content, and a very stable backbone due to the

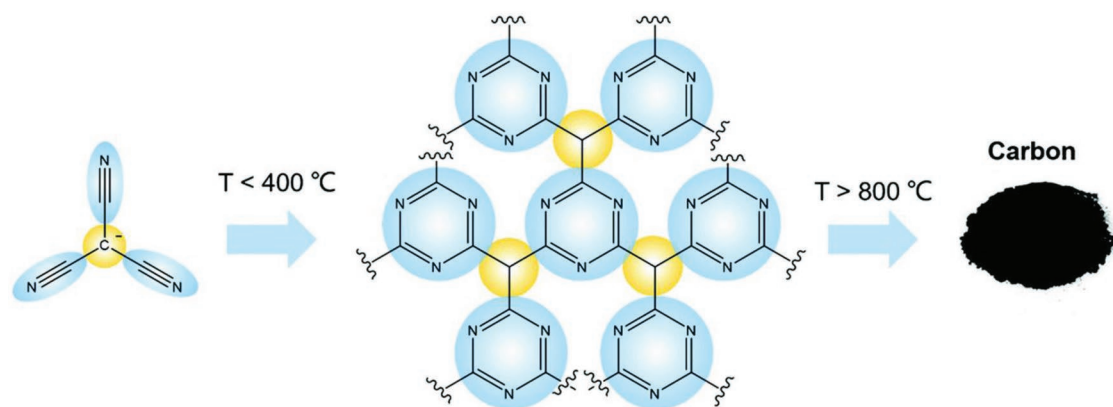


Figure 8. Typical synthesis of N-doped carbons from cyano-containing ions in ILs. Reproduced with permission.^[59c] Copyright 2018, Royal Society of Chemistry.

graphite-like local structure with pyridinic and quaternary nitrogen. Pyridinic nitrogen acts as a Lewis base, whereas quaternary nitrogen enhances the conductivity. These kinds of structural N-doping also increase the oxidation resistance, which is beneficial for utilization of these materials for production of electrochemical devices^[61a,b] and in electrocatalysis.^[67]

A class of materials which can be considered a subgroup within ILs is deep eutectic solvents (DESs). These eutectic mixtures are molecular complexes typically formed between solid ionic hydrogen bond acceptor, e.g., choline chloride or tetraethylammonium chloride, and a hydrogen bond donor, such as urea or phenols.^[68] The advantages of DESs over conventional ILs as heteroatom-doped carbon material precursors are their lower costs, simple synthesis, and greener nature.^[58b,59c,69] However, they are often thermally instable and thus not suitable as NCM precursor.^[70] This problem can be addressed by co-condensation of DES with, for example, phenolic resins.^[71]

We have shown until now how different heteroatom-containing building blocks can form a network of doped NCM upon heating. However, another important approach for incorporating heteroatoms in NCMs, which has been excessively used in recent years, is “top-down” strategy starting from crystalline precursors such as MOFs. An advantage that MOFs offer is their versatility of organic linkers, as well as intrinsic ordered porosity of these frameworks, that gets translated into a final carbonized product.^[16d,72] First reports were using MOFs as sacrificial templates,^[73] but it was later found that heteroatom-doped carbonaceous materials can be prepared without additional carbon sources. Carbonization of MOFs often results in materials with extremely high porosity, making them suitable for applications in adsorption,^[8c,73c,74] catalysis,^[72,75] electrochemical energy storage,^[76] and many others.^[77] For a number of these applications, presence of heteroatoms enhances the performance of NCMs, and MOFs are often chosen as precursors for high loading and uniform distribution of heteroatoms. The fact that these precursors contain metals further provides the opportunity to incorporate metals or metal oxides into the final material, or alternatively, to use the metals as a hard template, providing additional porosity to the resulting NCM. The latter is easily accomplished with Zn-containing MOFs, because of the low boiling point of this metal.^[8c,78] Possibility to extend the properties of obtained NCMs is given by the formation of

core-shell composite MOFs, and their subsequent carbonization.^[79] These materials can then benefit from both sets of characteristics, such as different polarity, bimodal porosity, as well as potential cooperative effects between the components of the composite. Nevertheless, the control over the carbonization pathways is lower than in the case of condensation of smaller molecules which can be seen as a “bottom-up” approach, making MOFs less suitable precursors for the “from molecules to materials” design approach.

4. Coordinative Functionalization of Carbon-Based Materials with Metallic Species

The immobilization of metallic species in the form of nanoparticles or single atoms/ions is another form of chemical functionalization which can significantly impact the properties of NCMs. Especially in the field of heterogeneous catalysis, NCMs have proven to be suitable as so-called “supports” for metal containing nanoparticles. Like other porous materials, NCMs can help to stabilize the particles and slow down their growth during the catalytic reaction. This principle is established for a long time, and many studies have investigated the influence of the carbon on the properties and stability of the nanoparticles because this is crucial for catalysis which is usually taking place on the surface of the particles.^[80] Most of these studies confirmed that the properties of the carbon support have indeed a significant influence on the nanoparticles. For example, nitrogen groups often lead to stabilization of particles by binding them more strongly to the carbon surface.^[52a]

The other way, that is, the influence that the nanoparticle has on the properties of the NCM, is by far less often considered and investigated, but in a similar sense as for heteroatom doping, the deposition of metallic nanoparticles can cause significant changes of the properties of carbon materials and thus of their adsorption behavior. For instance, if a species that tends to be reduced by carbon is immobilized on it, a flow of electron density from the carbon to the particle or at least to the contact area will occur. That causes the change of electron density distribution in the carbon in a similar sense like heteroatom doping. One recently reported example of such an effect is the

use of ordered mesoporous carbon materials decorated with metal oxide nanoparticles as electrode materials in supercapacitors with ionic liquid electrolytes.^[39a,41a] Although the specific surface area of the carbon after loading with metal oxide nanoparticles decreases, the specific capacitance of the functionalized materials as supercapacitor electrodes increases due to the stronger adsorption of electrolyte ions at the carbon–metal oxide interface.

Due to their structural similarity to the solutions nature has developed, single atoms or ions embedded into heteroatom-doped carbons are an intensely studied field as well. Metal atoms or ions can be “complexed” by the heteroatoms leading to very stable compounds. In simple words, the carbon materials act here as a “porous system of chelating ligands.” As for

heteroatom doping itself, the uniform incorporation of heteroatoms in high number is of crucial importance to enable the deposition of single atoms/ions.

Single-atom catalysts (SACs) have recently attracted significant interests due to their potentially desirable catalytic performance in different chemical reactions.^[81] Compared with traditional heterogeneous catalysts, every metal atom in SACs is exposed as a potential catalytically active site.^[82] This is of particular importance for noble metal-catalyzed reactions.^[82b] SACs can be stabilized and well dispersed on heteroatom-doped carbons functioning as ligands.^[83] Recently, carbon-based materials have exhibited their unique advantages to stabilize SACs thus enabling to translate principles from homogeneous to heterogeneous catalysis.^[84] As

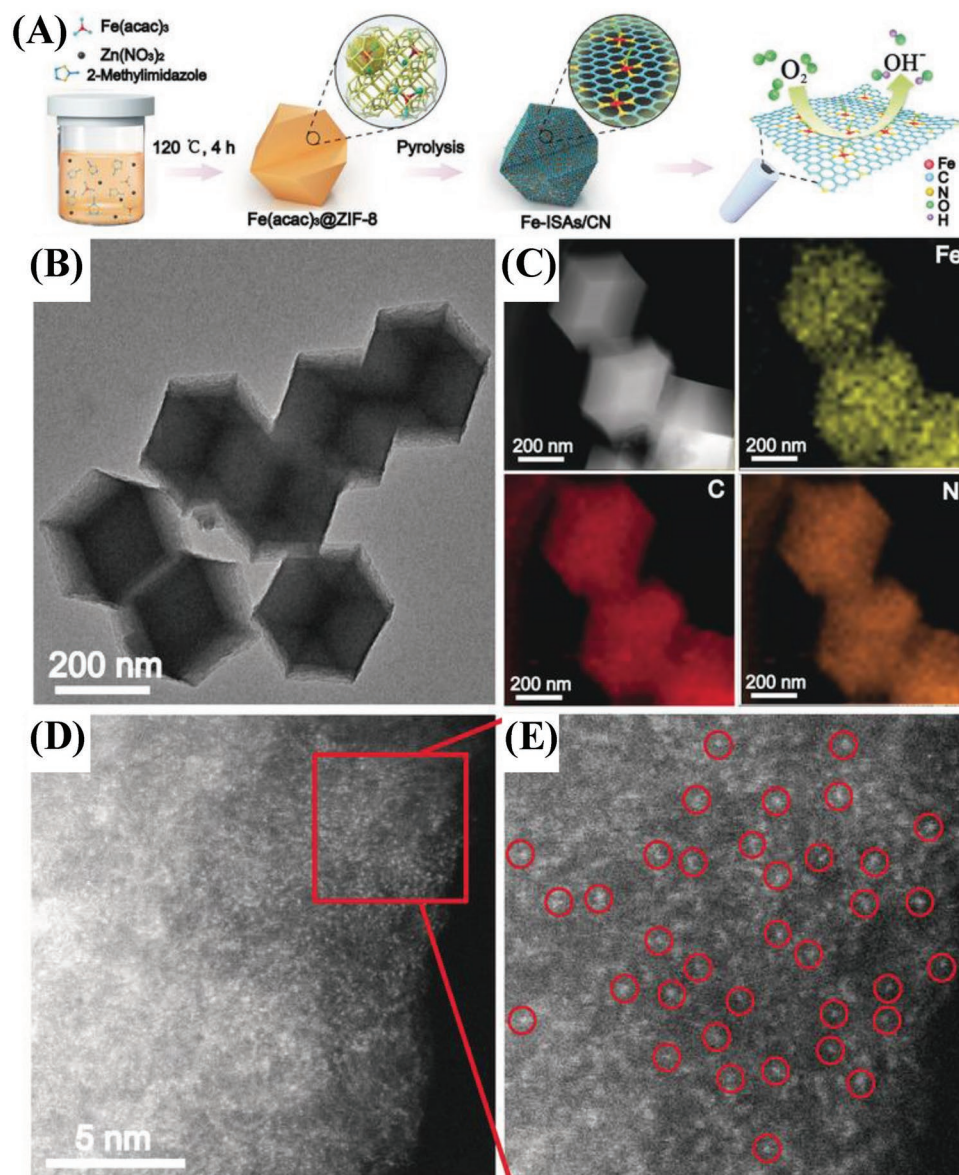


Figure 9. A) Schematic illustration of the formation of Fe-ISAs/CN, B) TEM, C) high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image, corresponding element maps showing the distribution of Fe (yellow), C (red), and N (orange). D,E) HAADF-STEM images and enlarged images of the Fe-ISAs/CN. Single Fe atoms are highlighted by red circles. Reproduced with permission.^[87a] Copyright 2017, Wiley-VCH.

this is one of the major focuses of catalysis research, it is not surprising that carbon-supported SACs have been widely studied.^[85]

Synthetic methods toward carbon-supported SACs include but are not limited to wet chemistry,^[86] pyrolysis,^[87] and chemical vapor deposition (CVD).^[88] The extensively used pyrolysis is normally carried out at high temperatures under the protection of N_2 , Ar, H_2 , or NH_3 by using a mixture of carbon and metal precursors.^[87] Different types of carbon precursors can be used in order to achieve desirable structure for stabilization of the single sites. Among those, metal-organic frameworks can be suitable candidates due to their crystalline and porous structure. For example, Chen et al. successfully synthesized Fe isolated single atoms supported N-doped carbon (Fe-ISAs/CN) using the mixture of Zn^{2+} , 2-methylimidazole, and $Fe(acac)_3$ (Figure 9A). At the first step, zeolitic imidazolate frameworks (ZIF-8) are obtained with the confined metal precursor of $Fe(acac)_3$ in the pore.^[87a] After pyrolysis under Ar atmosphere at

900 °C, Zn can be evaporated and N-doped carbon forms from ZIF-8, while $Fe(acac)_3$ is reduced to Fe single atoms, anchored by N species (Figure 9B–E).

Considering the high catalytic activity of single atoms, it is a challenge to stabilize those sites on the carbon supports to avoid aggregation. The insertion of defect sites into graphene can be a solution here.^[89] For example, Zhang et al. reported the use of defect-rich graphene (DG) to anchor Ni single atoms (A-Ni@DG).^[90] Except pure carbon, N-doped carbons have also been widely studied as supports, because nitrogen-carbon units (N-C) can help to stabilize single atoms to form M–N–C structure (M represents metal).^[87b,91] Until now, M–N–C structures with various metal centers have been successfully synthesized and show desirable catalytic performance.^[81d,h,85a,88,90–92] Recently, Qu et al. reported a novel strategy to achieve large-scale synthesis of SACs (Figure 10A).^[91a] In detail, different from normal-used metal precursors, bulk metals are used as precursors and can be emitted at high temperature. The use of NH_3

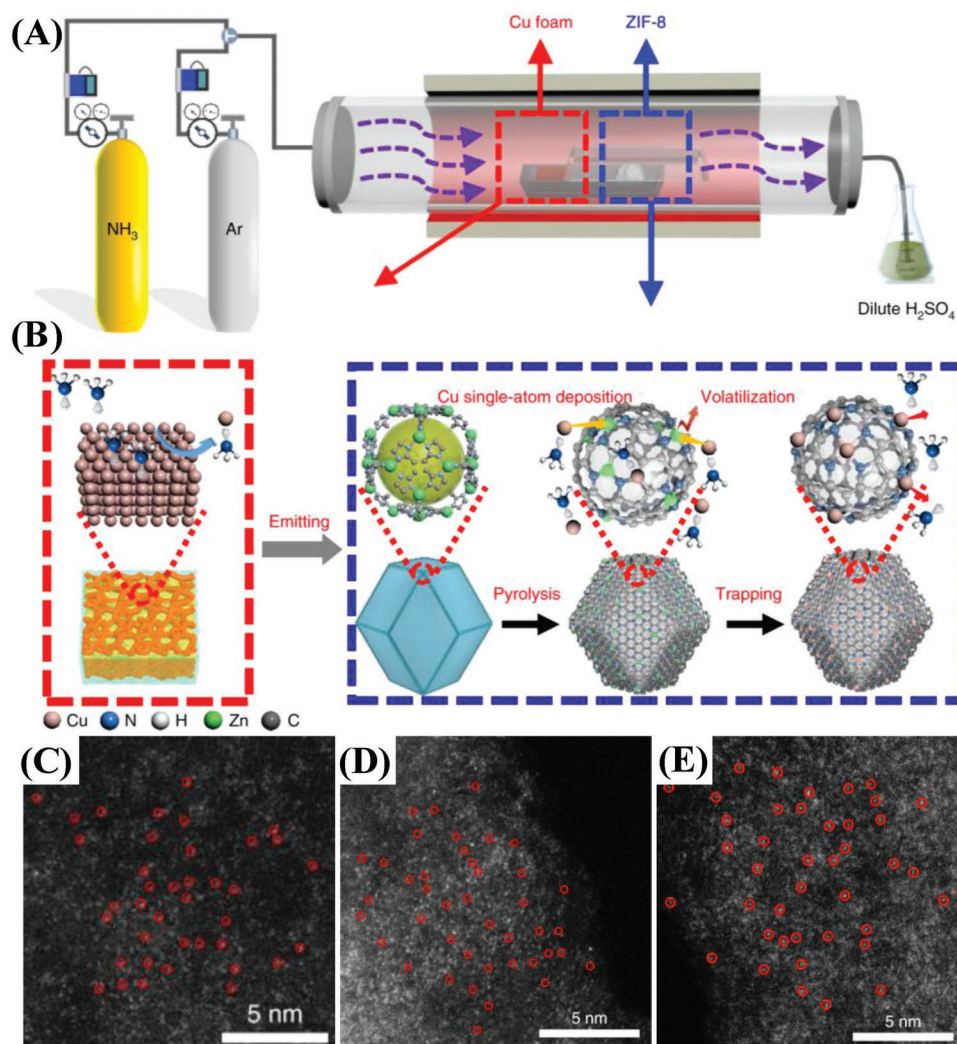


Figure 10. A) Apparatus scheme, B) proposed reaction mechanism, and magnified HAADF-STEM images of C) Cu-SAs/N-C, D) Co-SAs/N-C, and E) Ni-SAs/N-C. Reproduced with permission.^[91a] Copyright 2018, Springer Nature.

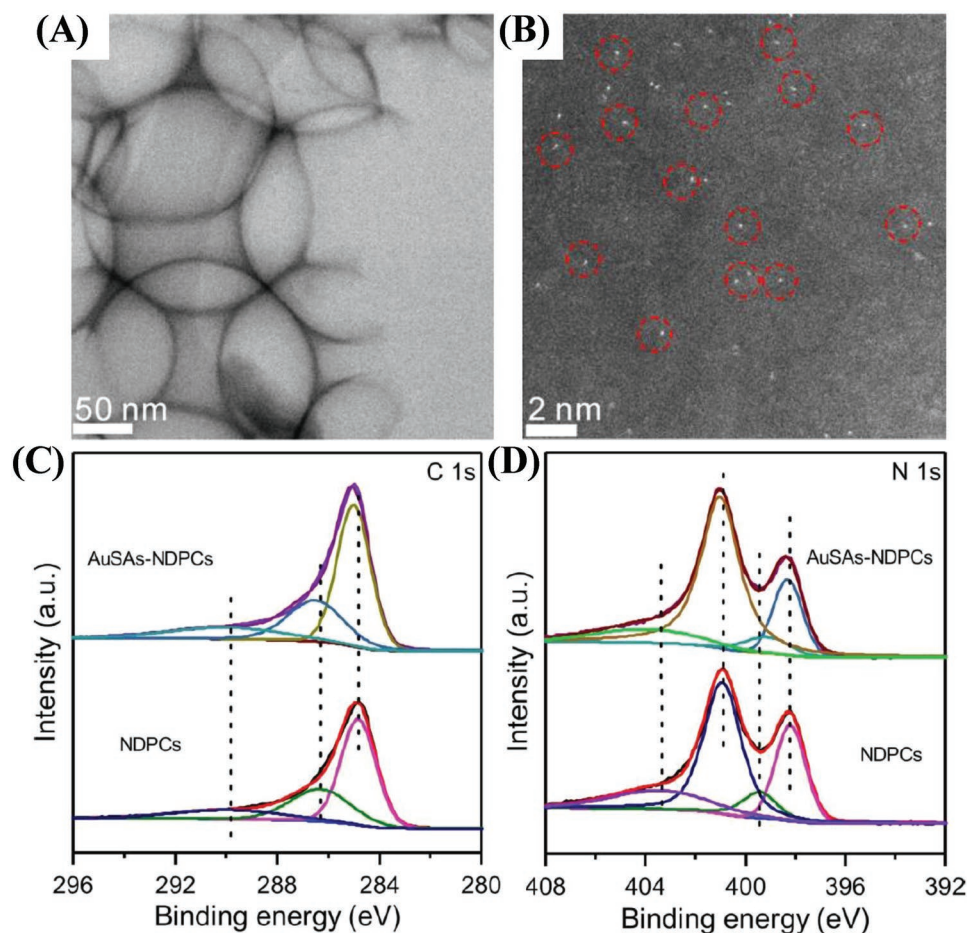


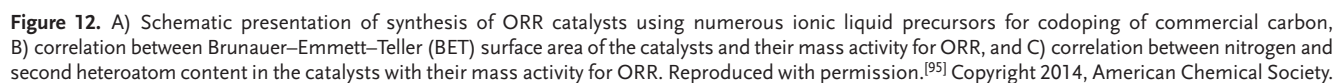
Figure 11. A) Representative TEM image, B) high-magnification HAADF-STEM image of AuSAs-NDPCs, and XPS spectra of C) C 1s and D) N 1s, obtained from AuSAs-NDPCs and NDPCs. Reproduced with permission.^[93] Copyright 2018, Wiley-VCH.

as protection gas is really important as it can trap Cu due to the strong Lewis acid–base interaction to form coordinated $M(\text{NH}_3)_x$ species and then transport formed $M(\text{NH}_3)_x$ species to the defects on the N-doped carbon supports to form SACs (Figure 10B). Similarly, Zhang et al. reported the synthesis of Ru single atoms on N-doped graphene, where single Ru atoms are coordinated and thus stabilized by N atoms.^[87b] As-obtained Ru–N₄ structures are responsible for excellent performance in the ORR.

Recently, the synthesis of Au single ions (AuSAs) by using HAT-derived N-doped porous carbon as supports (NDPCs) has been reported (Figure 11A,B).^[93] NDPCs are able to stabilize gold species in a quasi-positive way. This would hardly be possible without heteroatoms. The changed electron density in XPS spectra of both N and C atoms in AuSAs-NDPCs in comparison to the metal-free N-doped carbons indicates the strong electronic interaction of Au atoms with N and C atoms (Figure 11C,D). Thus, the electron transfer from the Au “cation” to the support “anion” can be achieved, which can be used to stabilize Au single ions, and this units can act as frustrated Lewis pairs (FLPs). Thanks to this structure, as obtained AuSAs-NDPCs catalysts exhibit desirable activity in electrochemical N₂ fixation to produce NH₃.

5. Functionalization of Carbon-Based Materials with Heteroatom-Containing Carbon Materials by Nanocomposite Engineering

Heteroatom doping of NCMs has numerous advantages for different applications of these materials. However, sometimes by tuning a certain property of the material (e.g., heteroatom content and polarity), other important properties are lost (e.g., conductivity or porosity). This is often a limiting factor in the utilization of novel materials. In order to overcome these problems, and fully benefit from the assets that NCMs offer, functionalization of carbon-based materials with heteroatom-containing carbon-based materials through formation of composites is a very useful approach to create materials with desired properties contributed from individual components with their respective advantages. Although both constituents are predominantly composed of the same element, their physicochemical properties and interaction with guest species can be substantially different. This behavior is well known from Janus particles, which bear two different types of chemistries occurring on the same particle.^[94] Following this principle, materials scientists can make use of the entire range of different morphology, porosity, polarity, and conductivity of NCMs with and



Pyridinic nitrogen is typically present in NDCs which are postsynthetically modified, as well as in NDCs synthesized through a low-temperature condensation of

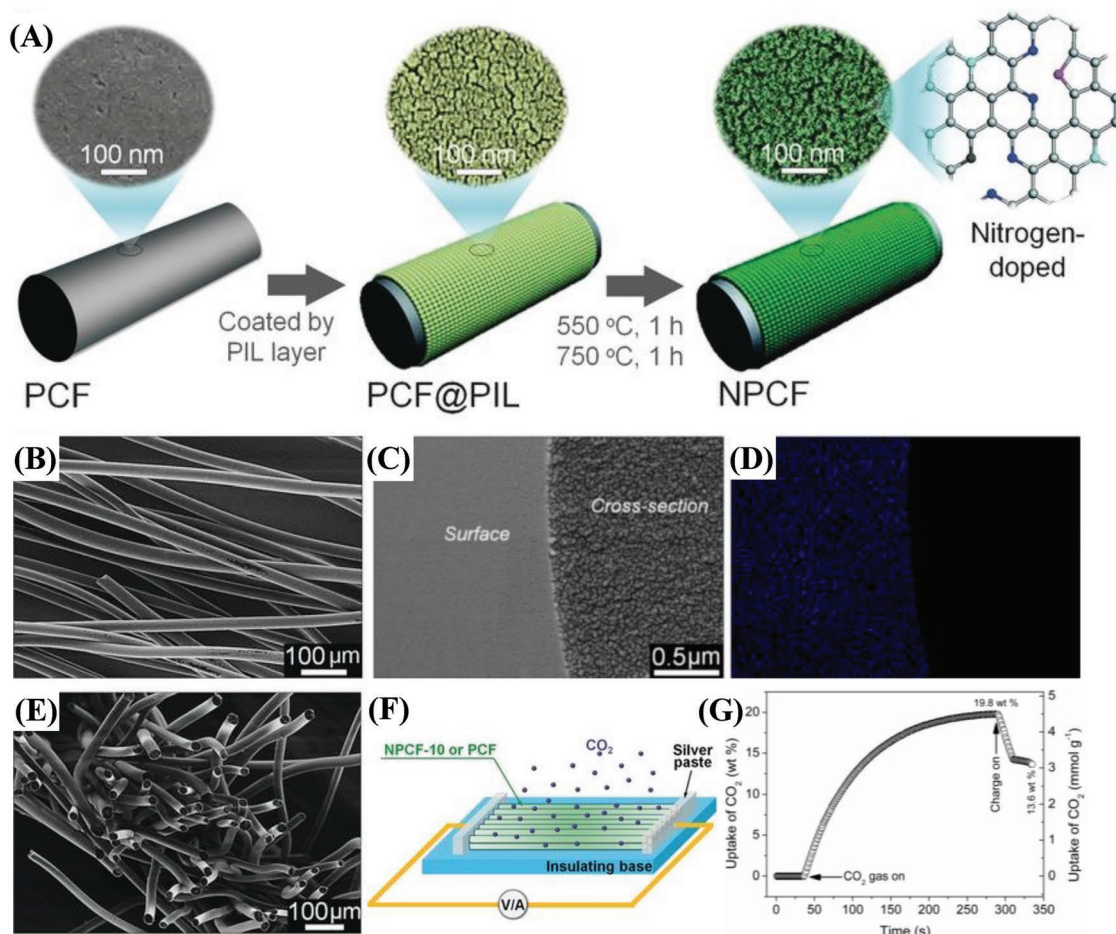


Figure 13. A) Schematic presentation of NPCF preparation, SEM images of NPCF: B) front view, C,E) cross-sectional view, and D) energy-dispersive X-ray spectroscopy (EDX) mapping showing uniform distribution of nitrogen (blue color) within the surface carbon nanolayer. F) Scheme of a CO₂ sensor based on NPCF array. G) Plot of CO₂ uptake on NPCF versus time at 298 K, presenting the effect of charge on the CO₂ uptake: applying potential on the material neutralizes the positive charge in NPCF, causing a drop of 30% in the uptake. Reproduced with permission.^[97] Copyright 2017, Wiley-VCH.

nitrogen-rich precursors. This species of nitrogen, however, is not responsible for increased conductivity of NCMs, often resulting in poorly conductive materials, unsuitable for electrochemical applications. On the other hand, it is known that NDCs have superior performance in comparison to their nitrogen-free counterparts, when applied in electrochemical energy storage devices, due to adsorption of metal ions or other electrolyte constituents on nitrogen-containing functionalities. Therefore, in this case a composite of nitrogen-doped carbon and carbon is an optimal solution, providing suitable active sites through NDC, as well as electrical conductivity through a pristine carbon material. As one example, Yan et al. recently combined a nitrogen-rich carbon material and pristine carbon domains within electrospun fibers.^[98] The free-standing fibers HAT-CNF-700, HAT-CNF-850, and HAT-CNF-1000 were obtained by condensation of the precursor fibers at 700, 850, and 1000 °C, respectively (Figure 14). It has been found that the combination of the strongly interacting nitrogen-containing material with a conductive compound enhanced the rate capability and energy storage capacity in sodium-ion capacitor anodes as compared to the individual compounds and that the content and binding motives of the

heteroatoms are crucial for the electrochemical energy storage properties.

6. Conclusions and Outlook

There is no doubt that the chemical functionalization of porous carbon-based materials is a powerful approach to adjust their properties and tailor the performance for a given application based on the interaction with surrounding matter. Incorporation of heteroatoms or metallic species can be applied to change the electron density and electron density distribution into the carbon materials and thus their properties as adsorbents or catalysts. In order to achieve a homogeneous structure, precise control over the atomic construction and porosity of the carbon materials is needed. Synthesis from defined molecular precursors seems to be a more promising method toward well-defined heteroatom-doped carbon materials than mixing precursors or postsynthetic treatments. Advanced carbon materials with defined and controllable atomic composition have been synthesized in the past years but simultaneous control over their porosity and/or the synthesis of heteroatom-containing carbons

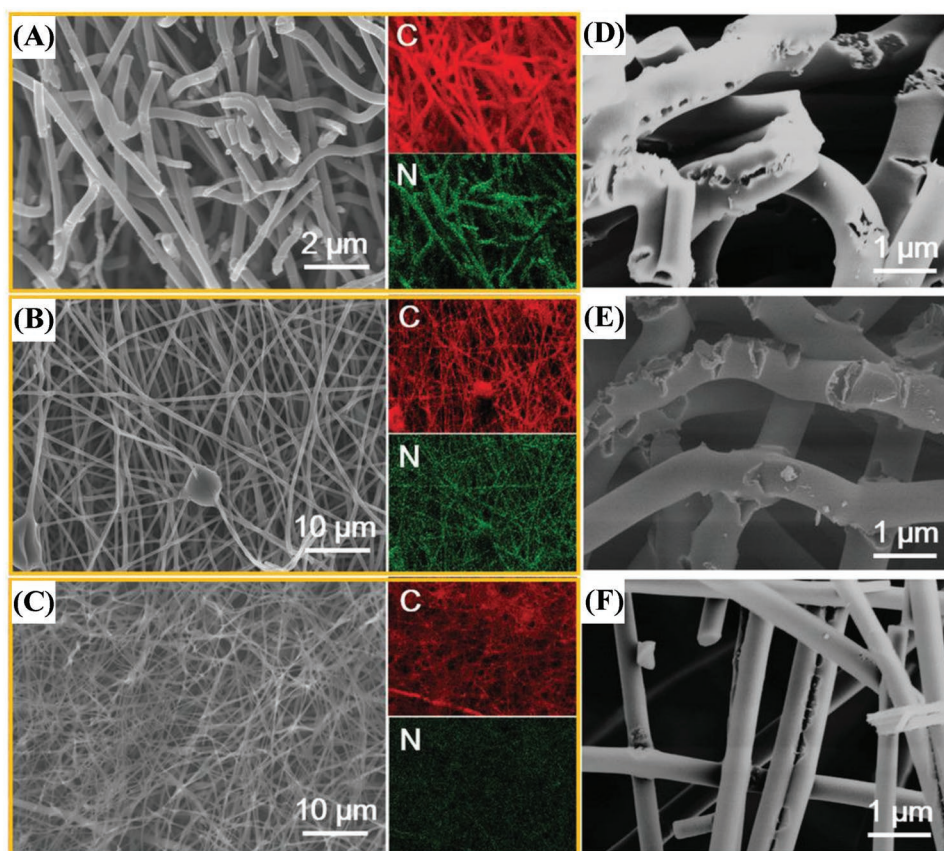


Figure 14. SEM images and EDX mapping of A) HAT-CNF-700, B) HAT-CNF-850, and C) HAT-CNF-1000, and SEM images of D) HAT-CNF-700, E) HAT-CNF-850, and F) HAT-CNF-1000 at higher magnification. Reproduced with permission.^[98] Copyright 2019, Wiley-VCH.

with hierarchical pore architecture from molecular precursors remains a grand challenge and requires continuous attention of materials chemists.

The incorporation of metal atoms or metal(oxide) nanoparticles is important for the field of catalysis but received less attention for chemical functionalization of carbon than doping carbon materials with heteroatoms. However, as strong interaction between the two compounds takes place, it can be expected that this strategy will become more important in the near future because adsorption processes or catalytic activation on the carbon/metal interface can be precisely controlled depending on the properties of carbon and metal.

It is our belief that the requirements to the carbon materials in many applications (especially in electrochemical energy storage and conversion) are so complex that one material alone can often not satisfy all of them with one and the same compound. Composite materials between carbon materials and chemically functionalized materials can be a solution to overcome that problem. Furthermore, the deposition of, for instance, a nitrogen-doped carbon on the surface of a porous pristine carbon can solve the problem of the difficult control over morphology and porosity of chemically functionalized carbon materials.

One often overlooked field that will become more and more important in the future is the structural characterization of chemically functionalized porous carbon materials. Currently

X-ray spectroscopy methods are often applied as they are important for the characterization of local binding motives. Standard characterization methods and models applied for other methods like spectroscopy, electron microscopy, or gas physisorption are often applied in the same way as for nonfunctionalized carbons but not necessarily applicable after chemical functionalization. For example, the incorporation of heavier heteroatoms induces vibrational dissymmetry and thus carbon D and G bands in Raman spectroscopy cannot be analyzed and interpreted in the standardized way. In physisorption, established density functional theory models are not as precise as in absence of heteroatoms, especially when polarizable molecules such as carbon dioxide are used as adsorbate. As a profound understanding of the structure of chemically functionalized carbon materials is of utmost importance to draw accurate conclusions on structure–performance relationships, new methods and models for their structural characterization have to be developed in the future. Theoretical calculations have already proven to be useful to provide a better understanding about the interaction between functionalized carbon materials and various guest species, and we foresee that they will increase in importance in the future.

Last but not least, a comparable consideration as for the characterization holds true for the application and the device design for chemically functionalized carbon materials. From a general point of view, intelligent design of reactors and devices is, in many cases, more useful to improve processes

than simple materials design. Carbon scientists should always consider if the functionalization of the materials may need a change of device design on another length scale. We are sure that only if materials science goes hand in hand with chemical engineering, the full potential of chemical functionalization (not only of carbon materials) can be utilized and will lead to meaningful improvements in adsorption related applications.

Acknowledgements

The authors thank Prof. Markus Antonietti from the Max Planck Institute of Colloids and Interfaces (Potsdam) for the continued support and outstanding mentoring. This work was financially supported by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) under Germany's Excellence Strategy—EXC 2008/1 (UniSysCat)—390540038. M.O. acknowledges financial support by a Liebig Stipendium from the German Chemical Industry Fund. M.P. and M.O. acknowledge financial support from the German-Israeli Foundation for Scientific Research and Development (GIF, Grant No. I-87-302.10-2015).

Conflict of Interest

The authors declare no conflict of interest.

Keywords

composites, heteroatoms, metal species, porous carbon materials, surface functionalization

Received: October 10, 2019
Revised: November 28, 2019
Published online: January 9, 2020

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