The Functional Chameleon of Materials Chemistry—Combining Carbon Structures into All-Carbon Hybrid Nanomaterials with Intrinsic Porosity to Overcome the "Functionality-Conductivity-Dilemma" in Electrochemical Energy Storage and Electrocatalysis

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Nanoporous carbon materials can cover a remarkably wide range of physico-chemical properties. They are widely applied in electrochemical energy storage and electrocatalysis. As a matter of fact, all these applications combine a chemical process at the electrode–electrolyte interface with the transport (and possibly the transfer) of electrons. This leads to multiple requirements which can hardly be fulfilled by one and the same material. This "functionality-conductivity-dilemma" can be minimized when multiple carbon-based compounds are combined into porous all-carbon hybrid nanomaterials. This article is giving a broad and general perspective on this approach from the viewpoint of materials chemists. The problem and existing solutions are first summarized. This is followed by an overview of the most important design principles for such porous materials, a chapter discussing recent examples from different fields where the formation of comparable structures has already been successfully applied, and an outlook over the future development of this field that is foreseen.

1. Carbon Nanomaterials in Electrochemical Energy Storage and Electrocatalysis

For many years, sp^2-dominant carbon- and carbon-based materials have been playing a crucial role in electrochemical applications. This includes but is not limited to their use for electrochemical energy storage in battery[1–4] or supercapacitor electrodes,[5–10] as catalyst or catalyst support in electrochemical energy conversion,[11–14] or as a selective adsorbent in electrochemical sensing[15–17] and purification applications.[18,19] The most obvious point that all these applications have in common is that they rely on the transport of electrons combined with the interaction between carbon and a "guest species" from the environment. This can, but must not, include full electron transfer between them. The guest species can be intercalated as in graphite anodes of alkali metal ion batteries or they can be adsorbed on the carbon surface as is the case for substrate molecules in electrocatalysis or ions in electric double-layer capacitors. Electron transport and transport of the guest species as parts of such an electrochemical process have to work together, ideally with comparable time frames. Obviously, the slower process will be limiting the rate of the overall procedure.

From a generalized point of view, the most obvious attractive property of carbon-based materials, which qualifies them for these applications, is their high conductivity for electrons and the tailorability of their structure for the interaction with a given compound. It is often perceived that one has to choose between highly functional and highly conductive carbon. This perspective aims to show that this "functionality-conductivity-dilemma" can be overcome by combining two carbons and forming porous all-carbon hybrid nanomaterials where one phase serves as the electron conductor and the other gives carbon its functionality. Firstly, an overview of the "functionality-conductivity-dilemma" is given, followed by the thorough discussion regarding important consideration for the design of all-carbon hybrid nanomaterials. Next, selected examples of all-carbon hybrid nanomaterials are discussed as electrochemical energy storage materials and electrocatalysts followed by an outlook on the possible future development of the field.

We would like to point out that the present perspective article is explicitly not aiming to give application- or materials-specific guidelines. Our intention is to give a general overview over important aspects that materials chemists have to take into consideration for the synthesis and application of porous all-carbon hybrid nanomaterials in electrochemical applications. Specific requirements may of course differ from case-to-case.

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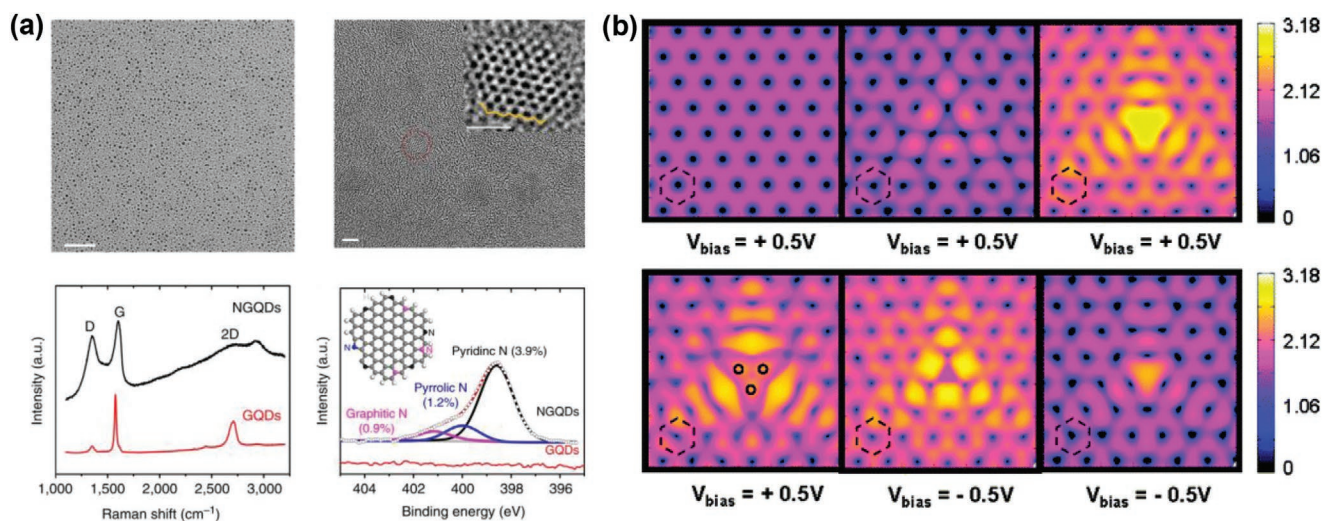NANO · MICRO
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Figure 1. a) Low- and high magnification TEM images (scale bars are 50 and 2 nm, respectively), Raman spectrum, and N 1s XPS spectrum with corresponding deconvolution into three subpeaks representing pyridinic, pyrrolic, and graphitic nitrogen of nitrogen-doped graphene quantum dots (NGQDs). The inset in the high-magnification TEM image (scale bar is 1 nm) shows a single NGQDs with zigzag edge. The Raman an XPS spectra of nitrogen-free graphene quantum dots (GQDs) are shown for comparison. Reproduced under the terms of the CC-BY license.[29] b) Computed Scanning tunneling microscopy images of pristine and doped graphene: pristine (top, left), pyridine (down, left, locations of 3N are denoted by black circles), nitrogen substitution (top and down, middle), and boron substitution (top and down, right). One dashed hexagon is represented on the different images to highlight the atomic network. The color scales for height are in Å. Reproduced with permission.[30] Copyright 2010, American Chemical Society.

2. The "Functionality-Conductivity-Dilemma" of Nanoporous Carbon Materials in Electrochemistry

One of the unique properties of carbon materials is that their physicochemical properties can be adjusted over a remarkably wide range depending on the nature of chemical bonds between the carbon atoms and on their functionalization.[20–23] This becomes evident by the differences between the macroscopic element modifications diamond and graphite. Nanostructured carbons can even have a variety of different properties within one and the same material depending on the local bonding situation.[24] For instance, in sp^2-based compounds like carbon nanotubes (CNTs)[25] the carbon atoms at the cap of the CNTs do already differ in chemical reactivity (e.g., in oxidation resistance) from the carbon atoms in the body of the tube. The same holds true for the terminal carbon atoms and the carbon atoms which are only bonded to other carbon atoms of a graphene sheet.[26] The sp^3-hybridized carbon atoms in the bulk and on the surface of nanodiamonds also differ significantly in their properties.[27] From these examples, it can be seen that such "ordered" carbon nanomaterials by geometry and chemical architecture already contain carbon atoms with different chemical properties. Notably, the members of each "group" of carbon atoms within the material remain rather similar in their properties and functionality. Taking the graphene sheet as an example, terminal carbon atoms with attached functional groups can chemically interact with other species while the carbon atoms within the sheet ensure electronic conductivity. The ratio between them could be adjusted within a certain range by changing the dimensions of the sheet and the edge groups can be chemically modified (**Figure 1**a).[28,29] The latter does not only introduce certain chemical functionalities but also changes the local density of states of the carbon atoms close to the defect (Figure 1b).[30]

Another member of the carbon materials family is nanoporous carbon, a class of materials with disordered structure and high surface area available for physical adsorption of guest species (**Figure 2**a).[31,32] Different to ordered nanocarbons, confinement of a molecule or ion in a small pore and its interaction with one or more curved "walls" of the carbon typically leads to an increase of the adsorption enthalpy and (in many cases more important) the mass-specific adsorption capacity.[33–38] In contrast to CNTs and graphite, the local binding motives in nanoporous carbon materials are rather random. Such a structure is usually still dominated by sp^2-hybridized atoms and has a delocalized system of electrons, which leads to conductivity that is sufficient for most electrochemical applications but the chemical properties of the individual atoms can not be simply distinguished into one, two, or more specific groups.[39,40] Carbon atoms are instead bonded in a range of different motives. As one obvious consequence, this makes it difficult to achieve a homogeneous chemical functionalization of the pore walls in such materials in comparison to more ordered carbon structures. Such a chemical functionalization with so-called "heteroatoms" is often used to modify the intrinsic properties of carbon materials such as their polarizability and redox-activity and by that also their interaction with a given guest species (Figure 2b).[20,41–43] For example, the postsynthetic functionalization of CNTs with nitrogen-containing surface groups by controlled oxidation and ammonia treatment can be assumed to lead to homogenous functionalization.[44] Hummers' method is meanwhile a widely established tool for the homogeneous oxidation of graphite.[45] In the case of nanoporous carbon materials, homogenous functionalization is more difficult and indeed, post-synthetic modification of such materials often results in a broad distribution of bonding motives of heteroatoms.[46,47]
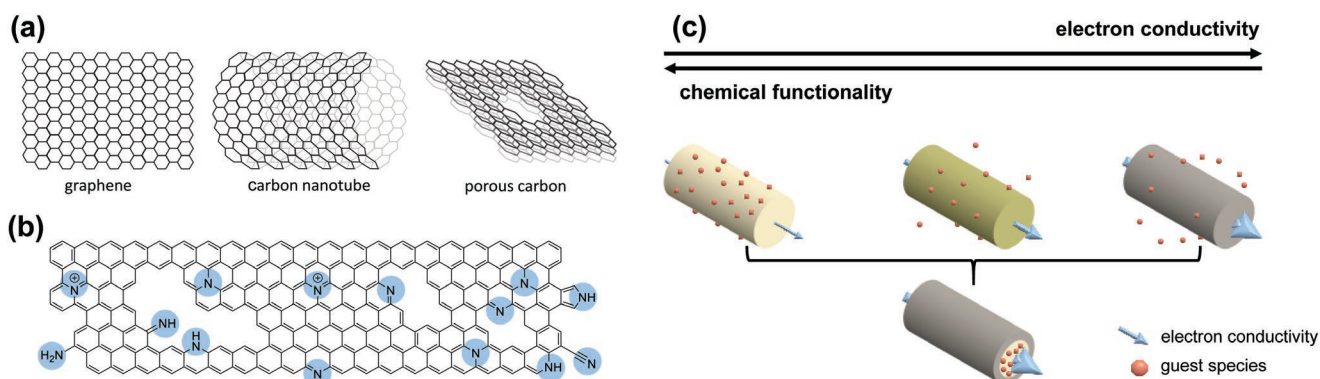
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Figure 2. a) Structure models of graphene, single-walled carbon nanotubes, and porous carbons. b) Possible bonding motives of nitrogen heteroatoms into a carbon network. c) Carbons with high electric conductivity often have a weak specific chemical interaction with guest species. It is possible to synthesize highly functionalized carbon providing stronger interaction but usually at the expense of conductivity. The formation of all-carbon hybrid nanomaterials can be a solution to overcome this dilemma.

Building the bridge to the application in electrochemistry, such chemical functionalization with heteroatom-containing functional groups is a powerful tool to tailor the strength of binding between carbon materials and a given guest species by using possible specific chemical or physical interaction (e.g., hydrogen-donor–acceptor couples, acid–base interaction, or coordinating effects).[48–51] To enable the desired functionality, the functional groups have to be present in high density and must be bonded in defined chemical motives. On the other side, the incorporation of such functional groups often leads to a change of the electron density in the carbon material, that is, a change of its Fermi-level.[29,52] It should be noticed that a negative or positive effect of heteroatom-doping on the conductivity of the carbon framework can hardly be generalized. For instance, a quaternary nitrogen atom doped into an sp^2 carbon structure would increase the conductivity whereas an electron-withdrawing amine group would decrease electronic conductivity. However, especially when carbon is functionalized with high concentrations of more electronegative heteroatoms like nitrogen or oxygen, the increased functionality is often at the

expense of electric conductivity. In many cases, researchers try to find a compromise between functionality and conductivity into one and the same material as the amount of heteroatoms can be for example controlled by heating at higher temperature or by fundamentally changing the functionalization method.[46,53]

All-carbon nanohybrid materials consisting of electrically conductive carbon-dominated domains and highly functionalized carbon-based domains can be a possible solution to overcome this "functionality-conductivity-dilemma" (Figure 2c). With this problem in mind, the physical mixing of materials with a chemical functionality but limited conductivity with CNTs or carbon black is already a widely applied method in the fabrication of electrodes for energy storage devices (**Figure 3**).[3,54–56] Also in electrocatalysis, the catalytically active particles are often deposited on a conductive substrate (in many cases carbon paper).[57] Although homogenous mixing is often supported by dispersing or ball-milling,[58–60] such "microscale mixtures" often suffer from the limited contact area and loose contact between both compounds. This, in turn, does not only lead to additional resistance but is also an intrinsic barrier for
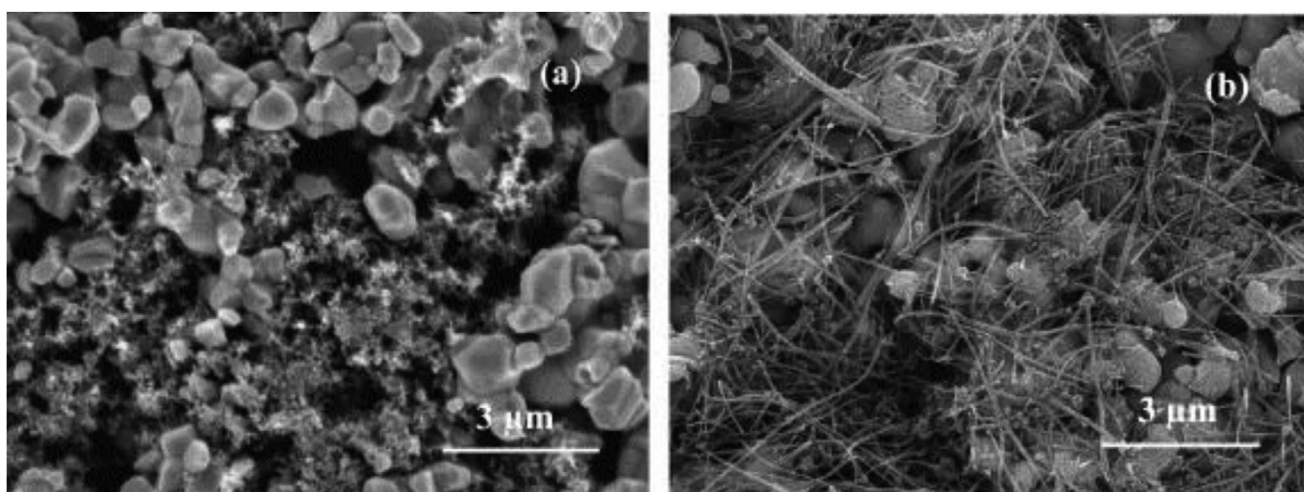

Figure 3. SEM images of composite cathodes of nickel-cobalt-lithium-based electrodes with (a) 5 wt% acetylene black and (b) 5 wt% multi-walled CNTs as condcutive additive. Reproduced with permission.[56] Copyright 2006, Elsevier.
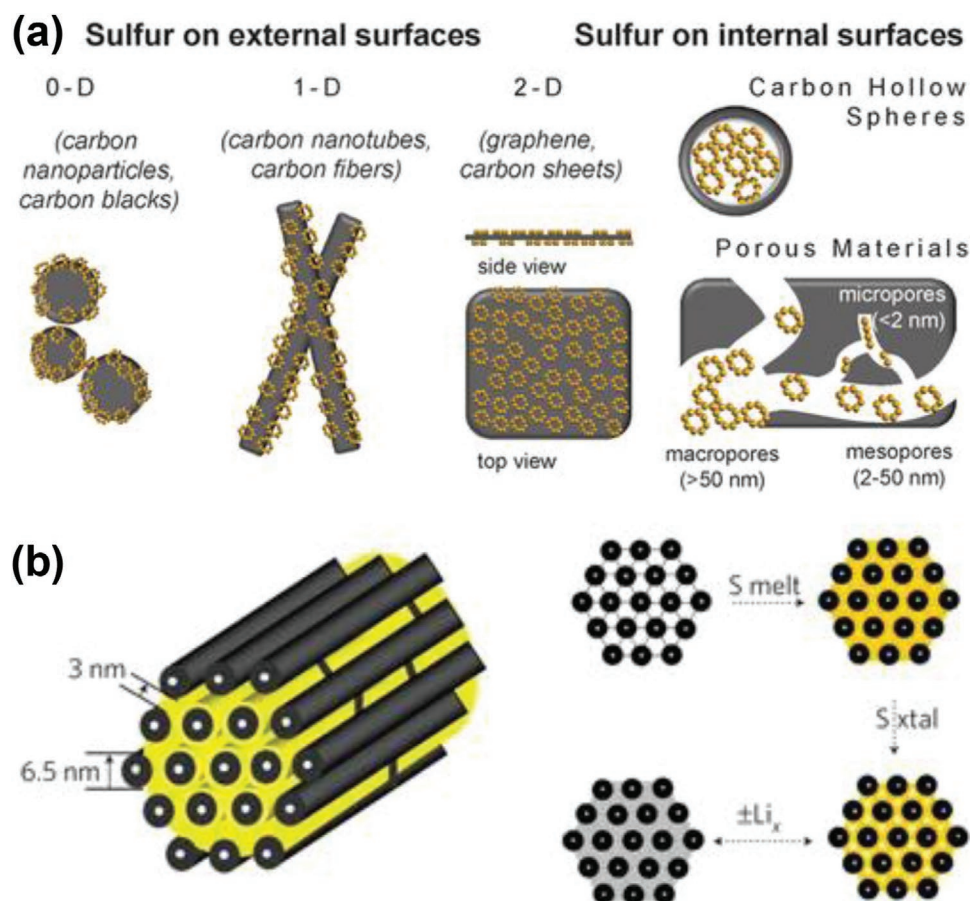
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Figure 4. a) Possible nanohybrid materials by combining sulfur and nanocarbon materials with with different textural properties for Li–S battery cathodes. Reproduced with permission.[4] Copyright 2016, Wiley-VCH. b) Schematic of sulfur (yellow) confined in the interconnected pore structure of mesoporous carbon CMK-3 (left) together with schematic illustration of composite synthesis by impregnation of molten sulfur, followed by its densification and battery cycling. Reproduced with permission.[62] Copyright 2009, Nature Research.

the homogenous distribution of an externally applied electric potential which is often intended to be applied to the chemically functional part of such a mixture.

In a few electrochemical applications, significant breakthroughs have been achieved in recent years, after nanohybridization strategies have been introduced. One case example where only one of the two compounds is carbon-based is the confinement of sulfur into carbon materials for lithium storage into lithium–sulfur (Li–S) battery cathodes (**Figure 4**).[4,61,62] Such carbon/sulfur hybrid materials combine sulfur as a compound that fulfills the chemical function of lithium-ion storage (i.e., the formation of Li_2S) with carbon as a compound that fulfills an electronic function (i.e., the delivery, storage, and transfer of electrons to sulfur). From this point of view, the often-used term "(electro)active material" is surely misleading as the electrons involved are part of both compounds of the composite. Only when both are homogeneously connected on a nanoscale, each compound can efficiently contribute to the overall function with its individual advantages and the problems of limited electric conductivity and utilization of sulfur for lithium storage can be overcome. Batteries utilizing redoxactive polymers as the functional material for charge storage are a field into which the fabrication of all-carbon hybrid materials has been widely applied to enhance the utilization of

redox-active sites of the polymers.[63–66] This can avoid potential gradients throughout electrodes, and enhances the stability of polymers against decomposition and dissolution throughout electrochemical cycling.

Notably, the concept of the formation of all-carbon-nanohybrid materials is already well established.[67–69] This is not surprising as nanocomposites have an interface area that can be orders of magnitude greater than in a physical mixture of two individual compounds. However, closing the cycle to the considerations made above, the majority of the formed materials are composed of ordered carbon materials like CNTs or graphene as the electron-conducting core. This is most likely again due to their more defined surface structure and simpler chemical functionalization that can be used for strong and homogeneous chemical coupling of the functional compound. In contrast, the combination of a chemically functional compound with a porous carbon is less investigated but at the same time, it provides a couple of possible advantages. Effects of nanoconfinement make it possible to influence the physicochemical properties of the chemically functional compound and an electric potential applied to the host structure is translated more uniformly to the hosted compound as the field can in principle be applied from all 3 dimensions. For the same reason, the contribution of physical interaction between both

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phases can be expected to be stronger as well. The possibility to control the pore architecture of the surrounding carbon enables the regulation of the loading of the second species with fewer gradient effects as when thicker and thicker layers are deposited on 1D or 2D carbon substrates. In contrast to the case of CNTs or graphite, at least one (in most cases the conductive) part of the hybrid material is continuously connected at least on a particle scale. In addition to the change of intrinsic properties of such a hybrid material when moving from hosts with large external surface area to porous carbons, confinement effects affecting the guest species and other matter in the pores (e.g., electrolytes) can occur as well.[70,71] This is hardly possible when mater is deposited on materials dominated by external surface area. Finally, when fabricated into an electrode, the grain boundaries between individual particles lead to less restricted electron conductivity on a microscale because the electronically conductive domains instead of those with the chemical function are getting connected.

Despite all these promises, the translation from CNT- or graphene-based carbon hybrid materials to those based on porous hosts is still in its infancy. To make this kind of materials useful for electrochemical energy storage and conversion, several considerations must be taken that are related to both parts of the hybrids, their interface, and the remaining porosity. In the following chapters, we will first summarize the considerations that we believe are crucial for the design and application of all carbon-hybrid materials. In the following, some case examples on the use of such hybrid materials in different electrochemical energy storage applications will be given and we will close with an outlook on the future of all-carbon hybrid materials based on intrinsically porous host materials with a special focus on the question how already existing knowledge can be transferred to the design of such compounds.

3. Crucial Considerations for the Design of All-Carbon Hybrid Nanomaterials

Before one can decide on which individual compounds to combine into an all-carbon nanohybrid structure, the requirements for the final material have to be defined depending on the intended application. These considerations are of course not limited to electrochemical applications but should be made for any materials scientific research and development project. From a chemical point of view, it seems more reasonable to first think about the process taking place in the part of the hybrid material containing the chemical functionality. Therefore, it is important to specifically design the chemical functionalities that suit the best the targeted application. First, it is needed to identify the chemical species that will participate in the electrochemical process and subsequently design the carbon material that can interact with these species in accordance to the requirements of the respective application. This is followed by the definition of ratios, geometrical considerations, and interface design. All these points have to work together when a synthesis strategy toward such a multifunctional material is developed.

The first important point that needs to be clarified before such a hybrid material is prepared is the function that the chemically functional part of the hybrid material has to fulfill. For instance, in a polymer-based battery, one would use a redox-active polymer material (**Figure 5**a).[64,65] In electrocatalysis, a carbon-based material that can activate the substrate molecules is the compound of choice (Figure 5b).[72,73] For the selective adsorption of ions, for instance, a functional carbon-based material with ligand-like chemical functionalities might be a suitable candidate (Figure 5c).[74] Most often, these compounds are not intrinsically providing the electronic conductivity that would be necessary to fully utilize their "chemical
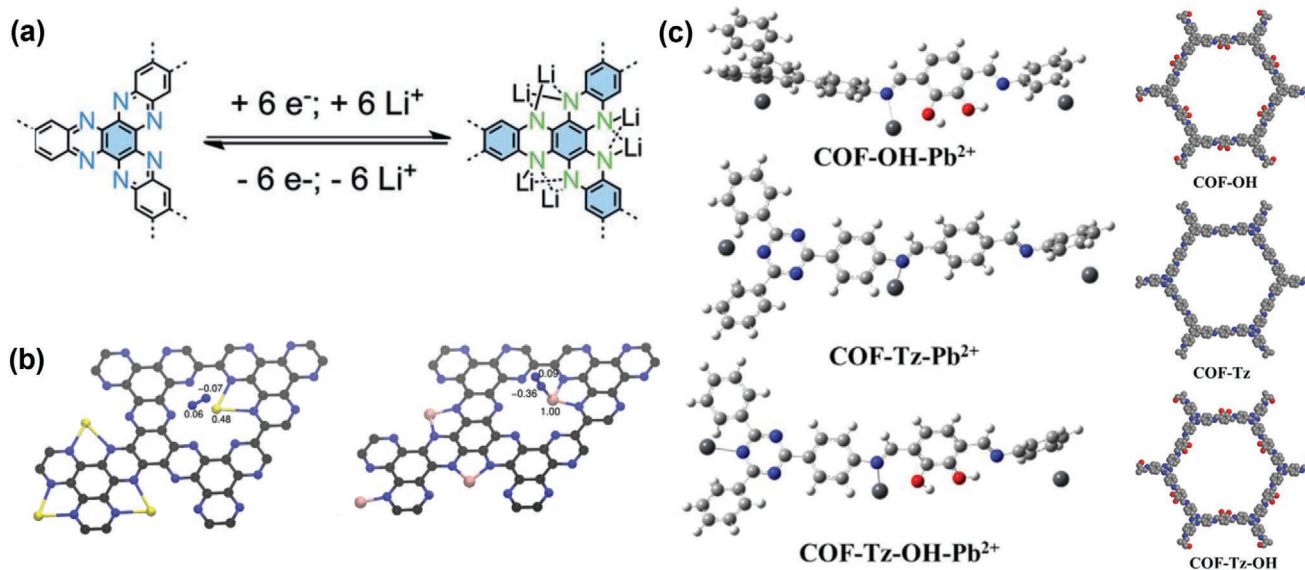

Figure 5. a) Proposed lithium storage mechanism of the redox-active unit in a two-dimensional sp^2-carbon-linked conjugated polymer framework with nitrogen-rich skeleton in lithium-ion battery cathodes. Reproduced with permission.[64] Copyright 2019, Wiley-VCH. b) Atomic structure of a dinitrogen molecule adsorbed over a gold-on-C$_2$N catalyst (left) and over an iron-on-C$_2$N catalyst (right) as the first step in electrochemical nitrogen reduction to ammonia. Reproduced with permission.[72] Copyright 2020, American Chemical Society. c) Optimized geometries of interactions between moieties of covalent-organic frameworks with Pb^{2+} cations (gray: carbon, blue: nitrogen, red: oxygen, black: lead) with graphic representations of the COF-based adsorbents. Reproduced with permission.[74] Copyright 2019, American Chemical Society.
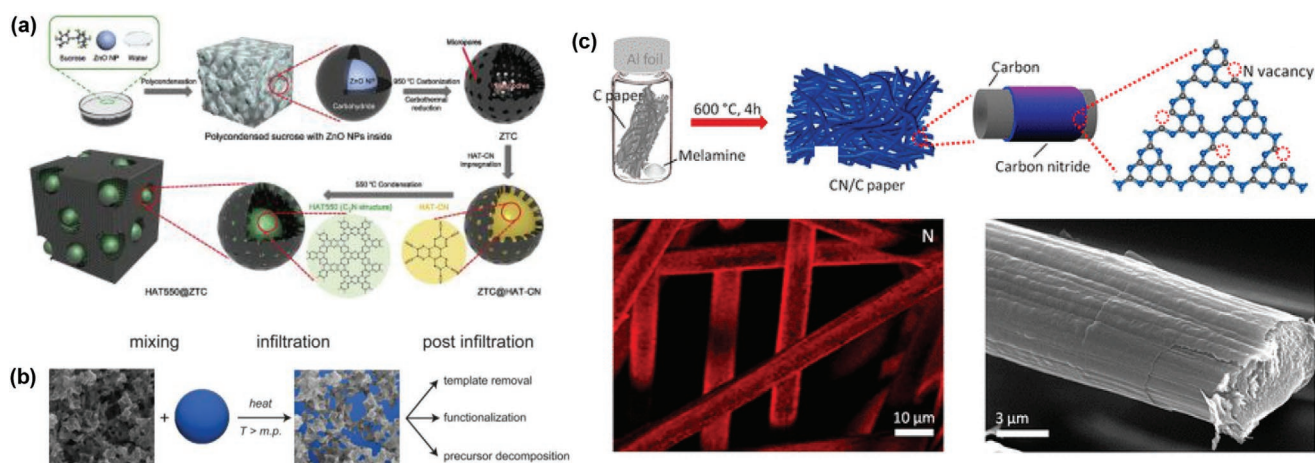
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Figure 6. a) Preparation of a carbon/nitrogen-doped carbon hybrid material by solution infiltration of the N-doped carbon precursor into porous carbon followed by thermal condensation. Reproduced with permission.[80] Copyright 2020, Elsevier. b) General steps involved in melt infiltration. Reproduced with permission.[82] Copyright 2013, Wiley-VCH. c) Vacuum-assisted synthesis of a carbon paper/nitrogen defective carbon nitride hybrid material (top) with SEM-EDX mapping of nitrogen and an SEM image of an individual fiber (bottom). Reproduced with permission.[57] Copyright 2020, American Chemical Society.

potential" and they must therefore be hybridized with a conductive compound.

The second important consideration for the materials design is the particle texture and pore architecture of the conductive carbon host. Both will be crucial not only for the filling with the chemically functional compound but also for the mass transport in the later targeted application. In general, the pore volume and the specific surface area should be high enough to allow for loading the targeted amount of the chemically functional material. After the combination, the remaining pores in the hybrid material should be large enough to allow for unrestricted transport of electrolyte ions in the electrochemical energy storage or educts/products in an electrocatalytic reaction. The dimensionality of the deposited chemically functional part (which can be itself intrinsically porous or not) should be small enough that its entire surface is also still accessible for those species and that the gradient of the electric potential applied remains as small as possible. In general, larger pores will allow the loading of a second material with larger dimensions. High pore volumes allow higher loading ratios of the chemically functional part or higher volume of remaining empty pores if necessary for the targeted application. Another important question is whether the porosity of the host is completely open or if it also contains larger pores that are only accessible for fluids through smaller entrances.[75,76] In the latter case, the chemically functional part of the hybrid material would be geometrically confined in addition to its stabilization on the surface of the conductive carbon. This is an already widely established principle in catalysis.[77] The possibility to use conductive carbons with hierarchical pore structure allows to selectively fill only one of the present pore systems with the functional material. For instance, in micro- and mesoporous conductive carbon material, the micropore system could be filled with a chemically functional compound to achieve strong contact and high surface area whereas the larger mesopores remain open and can ensure efficient materials transport if necessary.[78]

From these simple considerations, one important conclusion can already be drawn: parameters like those discussed above have to be adjusted depending on the targeted application. It

can for example be expected that a nitrogen molecule will have a different accessibility to the surface of the hybrid material as compared to a sodium ion.[79] First must be the application, then the material. In this context, aspects of volumetric efficiency and electrolyte loadings need to be considered as well. It is often required that the content of the chemically functional compound is maximized while the electric resistance and the remaining free volume should be as low as possible. Carbon–sulfur composites for Li–S batteries can again serve as a case-example here. This is as crucial in electrochemical energy storage as in electrocatalysis but is often overlooked.

The combination of both parts of the hybrid materials can be carried out in multiple different ways. Classical approaches would be infiltration of the functional part (or its precursor) from solution (**Figure 6**a).[80,81] Polymers and other substances melting before decomposition can often also be loaded by melt-infiltration (Figure 6b).[82] Another option is the loading of the chemically functional carbon from the gas phase, for instance by chemical vapor deposition (CVD, Figure 6c).[57,83] Here, individual building blocks are first infiltrated from the gas phase and then react to a larger network.

One other option would be the so-called "one-pot synthesis" in which the conductive carbon and the chemically functional carbon are formed in one step.[53,84] Although this seems to be an attractive approach avoiding multiple steps, there is always the possibility that both precursors and/or their decomposition products react with each other resulting in one material without two clearly distinguishable phases. To overcome this limitation, it is worth to consider alternative carbonization concepts. One example is laser-induced carbonization where a surface of precursor film is carbonized using a laser beam.[85] This method is of great interest for the development of carbon–carbon hybrid materials because the energy supply during carbonization depends on the depth of the sample the surface of which is in contact with the laser. The resulting materials would hence have more the characteristics of "gradient materials" instead of having clearly separated phases. This must not necessarily be a disadvantage but is instead more likely the "holy grail" of all-carbon hybrid materials design. Surface patterning becomes
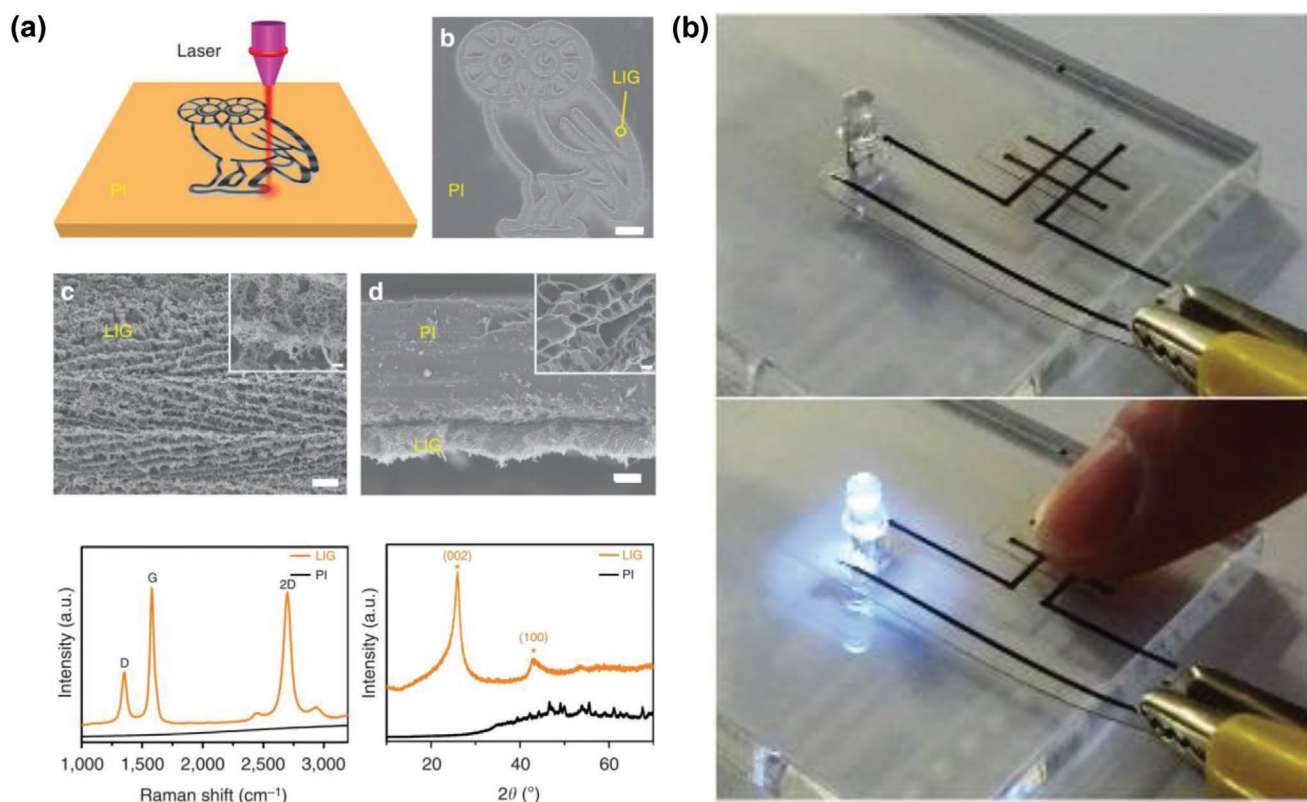
Figure 7. a) Schematic of the synthesis of laser-induced graphene (LIG) from a commercial polyimide (PI) film (top, left), SEM image (scale bar is 1 mm) of LIG patterned into an owl shape (top, right) with corresponding SEM image (scale bar is 10 µm) of the circled area (middle, left), cross-sectional SEM image (scale bar is 20 µm) of the LIG film on the PI substrate (middle, right) and Raman spectrum of LIG film and the starting PI film (down, left) as well as XRD pattern of powdered LIG scraped from the PI film (down, right). Reproduced with permission.[85] Copyright 2014, Nature Research. b) Photographs showing laser-patterned carbon conducting paths printed on a flexible, transparent PET substrate connecting an LED with a 6 V power supply being switched by applying pressure between the paths. Reproduced under the terms of the CC-BY license.[86]

possible with such a method. For example, a so-called "precarbonized material" produced from urea and citric acid at 300 °C was reported as a precursor for laser-induced graphitization forming a film with good conductivity on the surface and a high amount of functional groups in the lower layers (**Figure 7**).[86]

Recently, numerous all-carbon hybrid materials were prepared using interesting novel techniques such as emulsion-templated polymerization where reduced graphene oxide is used as an emulsifier. Upon carbonization of the formed polymer a high surface area material is formed where remaining graphene sheets support the transportation of the electron resulting in the materials of high conductivity.[87] Similarly, glucose-impregnated carbon nanotube aerogels have been used as a carbonization precursor to form graphene-coated carbon nanotube aerogels.[88] Another novel technique worth mentioning is a top-down technique, formation of holey graphene, as functionality is introduced in well-conductive graphene sheets.[89,90]

In any case, a nanoscale homogenous hybrid material can only be formed if both materials do not form separated domains on the micrometer scale, which would result in characteristics that are rather close to those expected for the mechanical mixtures as usually obtained by top-down approaches such as ball-milling. Thus, from a chemical perspective, an attractive interaction between both parts is necessary. Chemical functionalization of the surface of the conductive carbon is one option to

minimize this problem as it can serve as a nucleation point for the growth of the second phase if there is an attractive interaction between them. A small pore in the wall of a larger pore can as well serve as an "anchoring point" for the deposition of the chemically functional carbon.

The interface formed between both parts of the hybrid material is of huge importance for the properties and the stability of the hybrid material—especially under operating conditions. Depending on their chemical structure, the interaction between both can be based on rather weak van der Waals forces or stronger π-π interactions or hydrogen bondings. Even stronger connection would be based on ionic interactions and covalent bondings. In most cases, it might be assumed that a stronger interaction is preferable because this would lead to lower electric resistance at the interface and higher stability. For example, a polymer that is sensitive against dissolution will be more stable when it is covalently bonded to the carbon surface instead of being just physically embedded. A looser contact between both parts of one and the same hybrid material might also be of advantage in several cases. For instance, when the process taking place in the functional material leads to large volume changes and mechanical stress that needs to be balanced or when the structure of this material at the interface is so much distorted that the targeted functionality can not be fulfilled anymore.
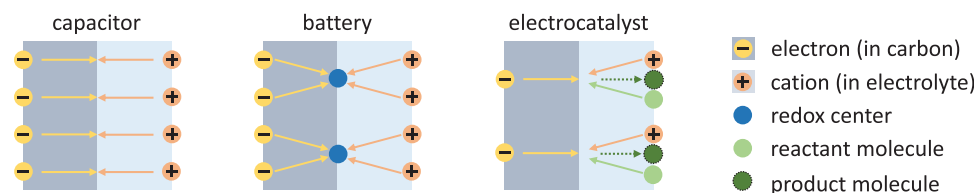
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Figure 8. Simplified illustration of electrochemical processes occurring in capacitors (here cation electrosorption), batteries (here the electron transfer to a cation), and electrocatalysts (here the reduction of a small molecule).

One important effect that has to be considered in this context is that the combination of two materials (especially on the nanoscale) will affect their individual physicochemical properties and that they will thus be different from the pristine compounds after a nanocomposite is formed. Heterojunctions between a metal and a semiconductor change the work functions of electrons in both materials.[52,91] Important for practical applications is their mutual influence on chemical stability. In many cases, nitrogen-rich carbon materials are much more stable against oxidation with oxygen than pristine carbon.[21] However, when the latter gets oxidized at elevated temperature, the formed carbon oxide can possibly contribute to the decomposition of nitrogen-doped carbon. Even such indirect cross-effects should always be considered when an all-carbon nanohybrid material is formed and applied.

Nanoencapsulation alone often changes the properties of the encapsulated material.[92] If the bulk chemically functional material is a metal it can become a semiconductor and its bandgap will depend on the size of the domains.[93] Similar to the changes of the physicochemical properties of a given material when it is downscaled to nanodimensions, other important properties like redox-potential, solubility, or melting point are size-dependent as well.[94]

From all these considerations it can be seen that the design of all-carbon hybrid nanomaterials is not trivial at all as many considerations have to be made. On the other side, they are showing the enormous potential of this approach as many possible "regulation screws" exist to tune their properties. The combination of two different carbon-based materials gives the resulting materials a higher "dimensionality" in terms of achievable properties. More synthesis pathways can be chosen and optimization work is becoming more complicated and complex because in principle all individual properties can be changed independently of each other.

4. From Redox-Reactions to Electrocatalysis—Versatile Applications of All-Carbon Hybrid Nanomaterials

Carbon-based materials have been dominating the world of electrochemical energy conversion and electrochemical energy storage for many years. Researchers often make use of their versatile properties and new physicochemical phenomena have been observed with this family of nanomaterials. On the other hand, it is not at all surprising that examples into which all-carbon hybrid nanomaterials have shown advanced properties over a single compound or simple physical mixtures

have already been reported many times. Compared to ordered carbon materials, hybrids based on at least one nanoporous carbon material are still underrepresented in this field but first examples exist. Just as described above, the likely reason for the preferred use is that an energetically homogeneous surface is easier to be homogeneously functionalized with another compound. On the other side, the use of 1D or 2D substrates limits the geometrical versatility of hybrid materials. Confinement effects can not be utilized and depending on the relative thicknesses of both compounds, unwanted gradients can appear. This chapter will give a brief overview of the state-of-the-art and describes some selected examples and concepts for the use of all-carbon hybrid nanomaterials in different electrochemical applications including electric double-layer capacitors, batteries and electrocatalysis. These three applications all rely on different fundamental electrochemical processes (**Figure 8**).

4.1. Electric-Double-Layer Capacitors

Porous sp^2-dominated carbons are especially appealing as electrode materials for electric-double-layer capacitors as they fulfill two basic requirements for this application—they possess high electric conductivities and surface areas.[6,10] Conductivity allows fast electron transport through the carbon network while a high surface area makes sure that a large number of ions can be adsorbed to stabilize the charge of the carbon network through coulombic mirror charges. No electron transfer is involved in the energy storage mechanisms in EDLCs. This, in turn, means that either the electron or the ion transport is the rate-determining step. From this perspective, both the electronic conductivity of the carbons and the ionic conductivity of the electrolyte and the functional part of the hybrid material should be as high as possible to ensure full utilization of the capacity, especially under high power conditions. The high electronic conductivity of carbon is crucial, especially in aqueous electrolytes, as water has a rather high ion conductivity. However, the capacitance and rate performance of aqueous EDLCs is usually limited by the fact that pure carbon materials (even when an electric potential is applied) have a lower ability to stabilize ions than water molecules and that surfaces of pristine carbons are rather hydrophobic. The possibility to remove at least a part of the solvation shell or counter-ions when an ion enters a small carbon pore is widely accepted for organic electrolytes with less strongly coordinating solvent molecules[33] and ionic liquid electrolytes[95] but it remains difficult to design a single carbon material with pore walls that are also "stronger ligands" for ions as compared to water molecules and that is at the same time sufficiently conductive. High nitrogen content in
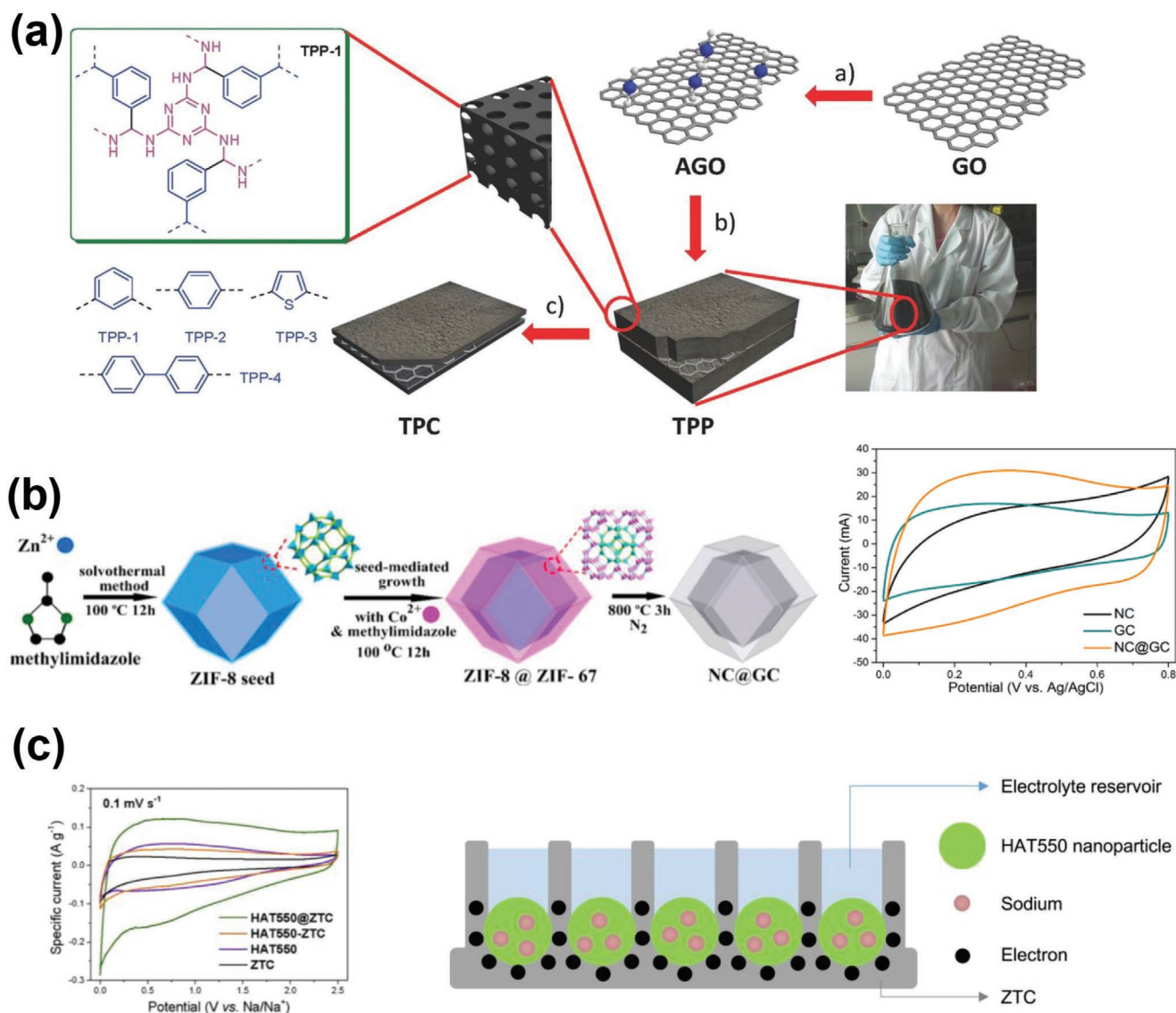
Figure 9. a) Synthesis of N-doped carbon on top of graphene oxide sheets. Step a) shows the introduction of amine groups on top of graphene oxide, b) is the synthesis of a Schiff-base-type porous polymer on top of aminated graphene oxide, and in step c), the formed material is carbonized. Reproduced with permission.[69] Copyright 2014, Wiley-VCH. b) Left: Formation of a core–shell ZIF-8@ZIF-67 hybrid material and subsequent carbonization for the formation of ZIF-8 derived carbon (NC) on top of ZIF-67 derived carbon (GC). Right: Electrochemical comparison of different carbons via cyclic voltammetry. Reproduced with permission.[84] Copyright 2015, American Chemical Society. c) Left: Comparison of HAT-550, ZTC, their hybrid material, and their physical mixture as anode materials sodium-ion capacitors via cyclic voltammetry. Right: Schematic for the explanation of the electrochemical performance of the formed hybrid material. Reproduced with permission.[80] Copyright 2020, Elsevier.

the carbon framework can increase the strength of ion adsorption as it polarizes the surface of the carbon. Depending on the bonding motif of the heteroatoms, it is well known that a small amount of graphitic nitrogen doping may increase the conductivity of the carbon. This is usually the case after treatment at temperatures above 800 °C. In contrast, high content of pyridinic or pyrazinic nitrogen usually reduces the conductivity of the carbons as they introduce defects into graphitic domains and lead to a decrease of the electron density in the conductive carbon framework.[96] As a possible solution to overcome these opposing trends, deposition of N-doped carbon on graphene has proven to be beneficial. Graphene provides a conductive backbone while highly N-doped carbon provides an attractive surface with high enthalpy for adsorption of ions.

As one example, Feng et al. showed that melamine-terephthalaldehyde networks are a suitable source to synthesize highly N-doped carbon. Growth of a melamine-terephthalaldehyde network on the top of aminated graphene and subsequent carbonization provided a carbon–carbon (**Figure 9**a) hybrid nanomaterial with strong covalent connection that showed extraordinary performance as a supercapacitor in 6 M KOH aqueous solution reaching a specific capacitance of up to 424 F g^{-1} at 0.1 A g^{-1}. This remarkable performance was exhibited by the sample that, prior to carbonization, contained 10% of aminated graphene oxide and that was carbonized at 800 °C. The resulting material was characterized by high surface area, namely, 364 m^2 g^{-1} and nitrogen content of 8.8 wt%. The hybridization strategy leads to composites that showed

superior capacitance in comparison to N-doped carbon without graphene presumably due to the low conductivity of highly N-doped carbons.[69]

Following a comparable approach, the same group showed that polytriazine carbonaceous networks can be derived from dicyanobenzene using an ionothermal zinc chloride-melt approach. The molten salt served as a solvent and catalyst for trimerization of the nitrile groups of dicyanobenzene. As this reaction occurs at elevated temperature (above 290 °C which is the melting point of zinc chloride) the resulting network is carbonaceous, but with rather high nitrogen content. Such a carbonaceous polymer was grown on top of nitrile-functionalized graphene. The material was tested as a cathode material for lithium hybrid capacitors. The capacity grew with the porosity of the material and the nanoscale dimensions of the polymer layer together with the strong covalent coupling were proposed to be responsible for the superior rate capability and cycle stability of the coupled graphene/porous polymer materials. The most remarkable performance was reached by a hybrid material that was carbonized firstly at 400°C and subsequently at 600 °C. Such a material had a high nitrogen content of 6.6 wt% that, along with a high amount of micro and mesopores, allowed for the high capacity above 600 mAh g^{-1} at 0.05 A g^{-1}.[67]

Another carbon–carbon hybrid material with core–shell structure and excellent properties as electrode material for EDLCs has been prepared by Yamauchi et al. using an approach into which both carbons are obtained simultaneously from a precursor material with different domains. ZIF-8, a metal–organic framework consisting of 2-methylimidazolates connected with zinc cations can be readily carbonized at 800 °C yielding carbons with high nitrogen content and surface area but limited conductivity. On the other hand, ZIF-67, a cobalt analog of ZIF-8, gets readily carbonized at the same temperature yielding highly graphitic carbons with excellent conductivity but with low nitrogen content and surface area. Core–shell particles of ZIF-8@ZIF-67 were carbonized yielding a core–shell material that consisted of highly conductive graphitic carbon as core and high surface area nitrogen-rich carbon shell that outperformed both ZIF-8- and ZIF-67-derived carbons as supercapacitor electrode in 1 M H$_2$SO$_4$ aqueous solution due to composite design that allowed both good conductivity and strong interaction with the electrolyte (Figure 9b). ZIF-8 derived carbon has a capacity of 239 F g^{-1} and ZIF-67 derived carbon has 119 F g^{-1}. A hybrid carbon material prepared with only 5% ZIF-67 core showed a capacity of 270 F g^{-1} at 2 A g^{-1} pointing to the importance of highly conductive carbon regions, even in very small amounts.[84]

Electric double-layers formed on the surface of charged carbons found their application not only in the field of energy storage but also for metal removal from solutions as the ions can reversibly absorb on the surface of porous carbon material.[97,98] Just like in EDLCs, the interplay between adsorption of ions and electronic conductivity also plays a crucial role in this capacitive deionization (CDI) technology. As one major difference, selectivity toward a certain ionic species is a fundamental requirement in CDI. For just the removal of sodium and chloride ions, mesoporous nitrogen-doped carbon grown on graphene sheets showed excellent properties due to the increased adsorption sites and rapid electron transportation pathways

showing that the hybridization strategy is also promising for CDI. These materials were able to remove up to 18.4 mg g^{-1} of sodium chloride from 0.5 g L^{-1} sodium chloride solution at 1.4 V.[99]

4.2. Battery Applications

In addition to purely physical electrochemical energy storage as in EDLCs, carbon–carbon hybrid materials were also utilized for redox-based energy storage, for example by growing a conjugated redox-active polymer (which we can still regard as the functional part of an all-carbon hybrid material) on top of a conductive carbon backbone. Such a mechanism now involves electron transfer (which is a rate-determining step in most cases) and it can be assumed that low resistance between both compounds of the hybrid material is of crucial importance in such a case. For example, an electrode slurry was prepared by mixing porous carbon with a nitrile-rich, redox-active monomer. Upon casting of the slurry on the carbon collector and subsequent drying, polymerization was initiated by exposure of the composite to trifluoromethanesulfonic acid vapor. This method yielded a hybrid structure with superior performance for lithium storage compared to the electrodes prepared from the same porous carbon and the polymer, with up to 30% capacity improvement and a total capacity higher than 90 mAh g^{-1} at 0.05 A g^{-1}. This improvement was ascribed to the superior contact between carbon and polymer in the nanocomposite as compared to the simple physical mixture.[65]

This hybridization strategy is quite versatile in terms of the applied redox-active polymer. As another example, dopamine was hydrothermally polymerized in the presence of graphene oxide to prepare graphene coated with polydopamine. Such a composite performed very well as a cathode for lithium- and sodium-ion batteries, exhibiting capacities over 175 and 150 mAh g^{-1}, respectively. However, upon subsequent calcination of the composite at 200 °C, the performance improved, exhibiting capacities over 230 and 210 mAh g^{-1} for lithium- and sodium-ion cathodes. In addition to the removal of redox inactive heteroatoms at higher temperatures as proposed by the authors, this could also be ascribed to a stronger contact between graphene and polydopamine after calcination. Nevertheless, calcination at 650 °C significantly reduced the performance of the composite leaving no trace of redox-active behavior due to the complete removal of redox-active groups upon carbonization.[66]

Carbon–carbon composites were also used as anodes for alkali metal batteries where a cation gets (at least partially) reduced and stored on the surface or in the bulk of a carbon. Ion storage, electron transport, and electron transfer all remain difficult to be optimized within one and the same material.[100] For example, a nanocomposite was prepared by carbonization of hexaazatriphenylene–hexacarbonitrile, a novel class of precursors for the template-free synthesis of nitrogen-rich porous carbon and conjugated frameworks,[96,101] inside the mesopores of a more conductive carbon (Figure 6a). The obtained materials were tested as anodes for sodium-ion capacitors and the nanocomposite exhibited a capacity higher than 350 mAh g^{-1} while the physical mixture of precarbonized hexaazatriphenylene

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and mesoporous carbon exhibited low capacities, a bit higher than 200 mAh g^{-1}. In addition, the composite showed much better rate capabilities. The functional carbon was able to store sodium ions while the highly conductive carbon was simultaneously storing electrons (Figure 9c).[80] A comparable monomer was recently cross-linked to obtain a conjugated polymer framework. Its hybridization with CNTs increased the electric conductivity by several orders of magnitude and by that to a much higher utilization of the redox-active sites when used as a cathode material for lithium-ion batteries.[64]

The aforementioned N-doped carbon from melamine-terephthalaldehyde networks was prepared by growing the network on carbon nanotubes and subsequent carbonization at temperatures as low as 450 °C yielding composites with ultra-high nitrogen content and excellent capacity for lithium storage. Carbonization at higher temperatures, namely 600 °C did not improve the performance of the composite as electron transfer was not improved, due to the already high conductivity of carbon nanotubes, while the nitrogen content was reduced.[102]

As a slightly modified approach for the synthesis of carbon–carbon composites, a mesoporous amorphous carbon can be covered with N-doped graphitic carbon via chemical vapor deposition. The prepared composite was characterized by very low surface area, while its conductivity was extraordinary. Such a composite showed improved lithium storage capacity at high current densities compared to nonmodified hard carbons.[103]

4.3. Electrocatalysis

In electrochemical energy storage as in lithium- and sodium-ion batteries, carbon surfaces are often utilized as the substrate for redox reaction of species dissolved in the electrolyte. However, the ability of carbon materials to promote electron transfer processes is not limited to alkali ions, but they can also serve as efficient electrocatalysts, transforming also more complex species from one oxidation state to another. Such processes in electrochemical conversion reactions usually involve the transfer of multiple electrons and also species from the electrolyte to a given intermediate on the electrode surface. In order to minimize overpotentials, maximize conversion rates, and to achieve a certain selectivity in a process, educts often have to be catalytically activated by an electrocatalyst. Heteroatom-doped carbon materials are promising candidates as electrocatalysts in many reactions like the electrocatalytic reduction of nitrogen or oxygen[104–107] but their electronic conductivity is usually limited which can lead to an incomplete utilization of catalytically active sites and/or potential gradients throughout the electrodes. Just like in electrochemical energy storage, all-carbon hybrid materials can also be part of the solution for this dilemma of electrocatalysis.

This principle was demonstrated well by Feng, Müllen, and their coworkers on the example of self-standing carbon nitride nanosheets and carbon nitride nanosheets grown on graphene oxide. Carbon nitride-graphene nanohybrid prepared at 800 °C exhibits high nitrogen content of 10%. The nanohybrid structure was able to completely reduce oxygen in a four-electron process, while carbon nitride nanosheets promoted the incomplete reduction in a two-electron process. This difference can be directly ascribed to improved conductivity of the overall catalyst when the carbon nanosheets are combined with a conductive carbon backbone.[108]

Electrocatalytically active carbons may contain a variety of heteroatoms, not only limited to nitrogen. Conjugated microporous polymers grown on bromine-containing graphene sheets were used as precursors for highly active electrocatalysts (**Figure 10**a). Depending on the polymer chosen, carbon–carbon hybrids doped with nitrogen (3.8 wt%), sulfur (7.7 wt%), or codoped with both (3.0 and 5.9 wt%, respectively) were prepared upon heat treatment at 800°C and tested as electrocatalysts for oxygen reduction. Sulfur doped carbon on carbon composites showed the best performance with the half-wave potential (potential at which the oxygen reduction occurs) only 72 mV higher than Pt/C catalyst, a reference catalyst for the oxygen reduction reaction. Furthermore, carbons prepared only from microporous polymers, without graphene, showed significantly worse performance, with the halfway potential 52 mV higher than carbon–carbon hybrids showing the benefit of the introduction of highly conductive carbons in the composite.[109]

Another clear advantage of composite formation gets obvious when looking at ionic liquid-derived carbons which often show extremely good performance for many electrochemical applications including electrocatalysis. However, the high price of ionic liquids makes these carbons unsuitable for widespread applications. Composites of ionic liquid derived carbons on the surface of cheap activated carbon could provide a solution for this problem (Figure 10b). Such composites were developed by a chemical coating of different ionic liquids on activated carbons and subsequent thermal treatment at 900 °C. Additionally, changing of ionic liquid precursors allowed for versatile heteroatom doping. Therefore, nitrogen-doped carbons (2.35 wt%) were developed along with nitrogen and boron (6.61 and 3.44 wt%, respectively), nitrogen, and phosphorus (1.39 and 2.87 wt%, respectively), and nitrogen and sulfur (2.82 and 0.88 wt%, respectively) codoped carbons. Additionally, the addition of iron species to the precursors resulted in the iron-containing sulfur–nitrogen codoped carbon with excellent properties for oxygen reduction reaction, with mass activities of almost 40 mA g^{-1} of catalyst in the alkaline media and virtually no reduction in mass activity after 9000 cycles.[110]

Taking another electrocatalytic reduction reaction as an example, carbon dioxide was successfully reduced by carbonaceous networks rich in triazine groups grown on top of oxidized carbon nanotubes. The networks were prepared from nitrile rich precursors by trimerization reaction in zinc chloride melt, as discussed above. Formed networks showed excellent Faradaic efficiencies (ratio of the obtained product and theoretically obtainable product from the amount of electrons applied in the reaction) above 80% at −0.5 V versus reference hydrogen electrode (RHE) for carbon dioxide reduction. This is significantly better as compared to simple physical mixtures of carbonaceous triazine networks and oxidized carbon nanotubes (Figure 10c).[68]

Carbon nitride grown on the top of carbon fiber (Figure 6c) paper proved an efficient electrocatalyst for nitrogen reduction reaction producing up to 3 mg of ammonia per gram of catalyst in 1 h in acidic conditions at −0.3 V versus RHE, with a Faradaic efficiency of around 20%.[57] This was ascribed to
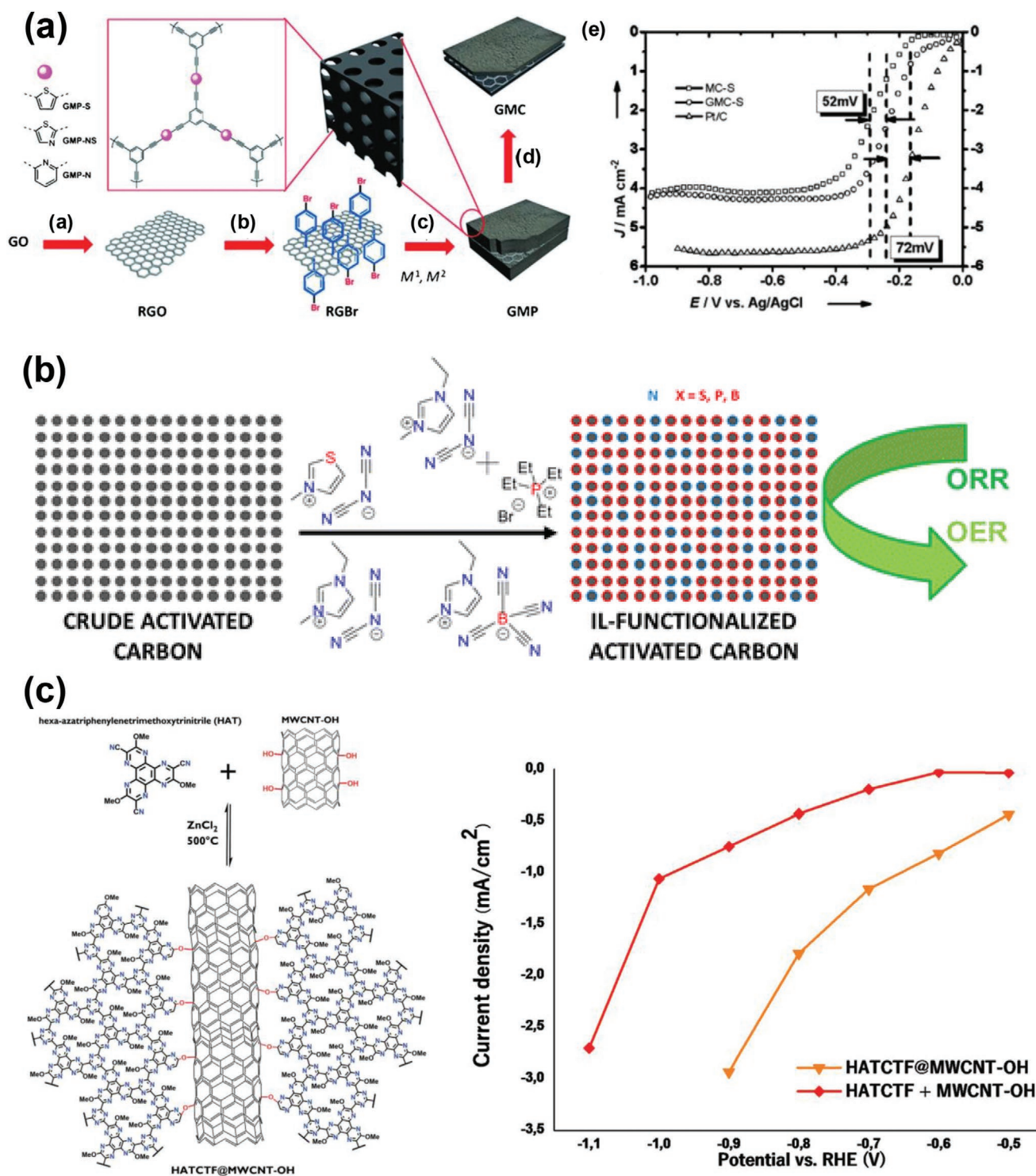
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Figure 10. a) Left: Synthesis pathway towards carbons derived from microporous polymers grown on graphene oxide, including reduction of graphene oxide, functionalisation of reduced graphene oxide, anhoring of microporous polymers on graphene oxide, and carbonization. Right: Electrochemical performance of the sulfur-doped carbon-carbon hybrid nanocomposite (GMC-S), as compared to graphene-free carbon (MC-S) and Pt/C, a reference catalyst, in the reduction of oxygen. Reproduced with permission.[109] Copyright 2013, Wiley-VCH. b) Synthesis of all carbon hybrid materials by functionalization of porous carbon with ionic liquid derived carbon. Reproduced with permission.[110] Copyright 2014, American Chemical Society. c) Left: Covalent coupling of triazine-based frameworks on surface-oxidized CNTs (HATCTF@MWCNT-OH). Right: Geometric current density in electrocatalytic CO_2 reduction of HATCTF@MWCNT-OH compared to a mixture of HATCTF + MWCNT-OH obtained by mixing individual compounds in a mortar. Reproduced with permission.[68] Copyright 2020, The Royal Society of Chemistry.

the combination of the intrinsic catalytic properties of carbon nitride[105] with excellent conductivity of carbon paper. Neither could carbon paper alone catalytically activate nitrogen nor is the electric conductivity of C_3N_4 high enough to allow for homogeneous application of electric potential and full utilization of all catalytically active sites. Additionally, composites prepared at 600 °C performed better than those at 500 °C, with the ammonia yield up to 6 times higher, due to the introduction of nitrogen defects in the carbon nitride material. This shows that a relatively small change in synthesis temperature can already have a significant impact on the properties of the chemically functional part of such a composite.

5. An Outlook for Porous All-Carbon Hybrid Nanomaterials

Following the success in the previous years, we believe that there will be ever-increasing use of all-carbon hybrid materials in the coming period. The ongoing development of more and more porous carbon structures and heteroatom-doped carbons alone will lead to an exponential rise of possible combinations. In addition, novel challenges in energy storage and conversion will cause new demands to materials chemists. This will automatically trigger the development of additional composite materials. It is a matter of fact that the majority of recent reports showing the advantages of carbon–carbon hybrid material engineering for a given application are rather phenomenological feasibility studies. Examples into which structure-property relationships are profoundly investigated (especially under working conditions) and optimization works are rather rare but still hold great promise from many different viewpoints including but not limited to raw material use, energy demand for synthesis, production cost, possible production volume, and electrochemical performance (gravimetric and/or volumetric).

All aspects discussed above are showing that the combination of two carbon-based materials on the nanoscale is a powerful method to combine their advantages. In contrast to the use of single compounds, there is no or less need to "make compromises." As most of the fundamental processes in electrochemical energy storage and electrocatalysis take place on the nanoscale it makes sense to overcome present limitations on the same scale instead of preparing microscale physical mixtures. However, the targeted design of advanced all-carbon hybrid nanomaterials might not only influence elementary steps in the respective fields but can also lead to new possibilities in electrode fabrication. For example, if we can think about a redefinition of the term "conductive additive" in battery electrode fabrication and if we start to understand the current collector as an integrative part of an electrocatalyst, such processes could be driven with much higher efficiency.

While materials chemists start to understand the advantages of carbon nanomaterials and novel all-carbon hybrids better and better, their synthesis is often still dominated by traditional infiltration and heat-induced condensation methods. Less conventional methods like laser-induced carbonization or deposition of one compound from the gas phase offer new synthetic possibilities in this field which are still rarely explored. Just like the physicochemical properties of the confined compound, the synthetic

mechanism and individual steps (e.g., the vapor pressure of molecular precursors) also differ significantly from the bulk. The lack of understanding for this fact is still leaving a lot of potential in the field of carbon–carbon hybrid materials unexplored.

In general, characterization of the individual compounds of such hybrid materials and their interface is much more complicated than for the individual compounds due to often unavoidable interference effects. However, structure-property relationships can only be accurately concluded, if a realistic and clear image about the entire structure of the hybrid material is available. Therefore it is reasonable to work with model compounds that are as defined as possible. The pristine carbon should be chosen with a uniform particle size and shape and a narrow pore size distribution. Preorganized precursors with controlled condensation mechanisms should be used to obtain functional carbon materials with a well defined chemical construction. This might be more far away from practical application on the first view but allows for easier interpretation of characterization data and thus more profound insights into the real structures and structure-property relationships of the hybrids.

Finally, we would like to emphasize that most of the principles discussed and summarized here are not at all limited to all-carbon hybrid materials. In many cases, similar fundamentals apply as well to hybrid materials between conductive carbons and noncarbonaceous materials with a chemical function or a noncarbonaceous electron conductor and a functional carbon. However, carbon is the only known element with a chemistry that is so versatile (at least under relevant conditions) that it can capture such a broad range of properties. Nevertheless, the rapidly expanding community of scientists producing all-carbon hybrid nanomaterials should learn lessons from previous works on inorganic functional materials—conductive carbon hybrid materials, particularly when it comes to design of the interaction between the functional and conductive carbon. For instance, we firmly believe that formation of core–shell precursor structures and their subsequent carbonization, as was done previously numerous times with inorganic-carbon hybrids is still little explored in all-carbon hybrids and approaches like the above-mentioned carbonization of core–shell particles of ZIF-8/ZIF-67 will receive more attention for the design and synthesis of all-carbon hybrids in the future.

Conflict of Interest

The authors declare no conflict of interest.

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