Doping carbons beyond nitrogen: an overview of advanced heteroatom doped carbons with boron, sulphur and phosphorus for energy applications

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Heteroatom doped carbon materials represent one of the most prominent families of materials that are used in energy related applications, such as fuel cells, batteries, hydrogen storage or supercapacitors. While doping carbons with nitrogen atoms has experienced great progress throughout the past decades and yielded promising material concepts, also other doping candidates have gained the researchers' interest in the last few years. Boron is already relatively widely studied, and as its electronic situation is contrary to the one of nitrogen, codoping carbons with both heteroatoms can probably create synergistic effects. Sulphur and phosphorus have just recently entered the world of carbon synthesis, but already the first studies published prove their potential, especially as electrocatalysts in the cathodic compartment of fuel cells. Due to their size and their electronegativity being lower than those of carbon, structural distortions and changes of the charge densities are induced in the carbon materials. This article is to give a state of the art update on the most recent developments concerning the advanced heteroatom doping of carbon that goes beyond nitrogen. Doped carbon materials and their applications in energy devices are discussed with respect to their boron-, sulphur- and phosphorus-doping.

Broader context

The research and design of novel materials that are applicable in various energy devices represent one of the central and most thriving subjects within today's scientific work. The challenges do not only rely on the tremendous need to overcome traditional fossil fuel based energy recovery. While a lot of sustainable concepts already exist, these require the development of high performance materials that are able to cope with certain challenges, *e.g.* the dependence on highly expensive and rather not abundantly available noble metals, and also a lack of long term stability of those. Researchers have been carrying out numerous studies concentrating on finding alternative materials that can be applied in novel energy devices. Those alternative materials should most preferably be free of noble metals, avoid expensive precursor systems, be sustainable and not rely on the fossil energy sources that are to be replaced, and of course exhibit high activity in the devices they are designed for. One class of materials in whose development and understanding researchers have put strong effort is heteroatom-doped carbon materials. By heteroatom doping the properties are altered compared to crude carbon materials. The by far most intensely studied doping candidate is nitrogen, capable of not only increasing electric conductivity, but also the catalytic activity of carbons. Such N-doped carbons have advanced tremendously in the past few years, especially by proving their usefulness as electrocatalysts for the reduction of oxygen in fuel cell cathodes, or as electrode materials in super-capacitors. Meanwhile the spectrum of doping has been widened, and novel doped carbons have been reported, indicating the promising potential of such materials in the field of novel forms of energy recovery. The envisaged aim of this research is contributing towards the solutions of the major global challenges of energy supply that are currently faced due to the severe problem of climate change, while at the same time a growing need for energy is encountered. This article is supposed to give an overview of the influence of doped carbons on the progress of novel energy devices, pointing out the significant importance of this class of materials for the future.

Introduction

Graphite and its related carbon structures – such as carbon nanotubes[1] or graphene[2,3] – represent a thriving class of materials, with a high potential to be applied in numerous promising fields, such as sensors or photovoltaics.[4-6] Nevertheless, the purest carbon materials are not always the most suitable

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candidates for certain applications. When it comes to different energy applications, such as electrocatalysis in fuel cells, an advanced modification of the pure carbon can lead to a significantly enhanced performance. One way to modify plain carbons is to dope the respective materials with heteroatoms, which basically means to chemically attach or incorporate them into the backbone of the respective carbon material. Many studies have been performed; while – especially regarding the design of materials for energy related materials – nitrogen is by far the most abundantly investigated heteroatom because – as a "neighbour" of carbon – it is chemically relatively easy to bring

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the two types of atoms together. The result is a colourful plethora of nitrogen containing carbon based materials that can exhibit variable property profiles. Basically, this class of material can be divided into two major groups with contrary properties: nitrogen rich carbon nitrides exhibiting a rather stoichiometric composition of $C_xN_{y \geq x}$ on the one hand, and nitrogen-doped carbon materials in which only a small percentage of the atoms in the carbon backbone are substituted by nitrogen atoms on the other hand. The development of stoichiometric nitrogen-rich carbon nitrides included the postulation of two different allotropes, namely cubic C_3N_4 and graphitic C_3N_4, of which especially the cubic structure was subject of theoretical studies, due to its predicted hardness being higher than that of diamond, while feasible synthetic procedures remain unknown.[7-9] Unlike its cubic counterpart, the graphitic allotrope g-C_3N_4 has been the subject of numerous synthetic approaches, based on the trimerisation of nitrile units, which actually dates back to 1834.[10] These carbon nitrides represent a class of materials on its own that lies beyond the scope of this manuscript. The reader is thus referred to early reviews on the subject,[11,12] and also to an overview focusing on the photocatalytic and generally heterocatalytic applications of carbon nitrides,[13] allowing for obtaining a complete picture of these semiconductors at the edge of inorganic and organic materials.

N-doped carbons for ORR and supercapacitors

From the semiconducting properties of graphitic carbon nitrides it already becomes obvious why the fundamentally contrary properties of N-rich carbon nitrides and N-doped carbons have been stated previously. The merely doped materials, with nitrogen contents of up to ~10%, rather retain the properties of their non-doped analogues, nevertheless finely tuning and thus – considering certain energy related applications – improving them. The roots of the development of N-doped carbons can be found in the field of fuel cell research and date back to 1964, when Jasinski et al. applied metal–phthalocyanine-complexes to catalyse the reduction of oxygen

electrochemically in the cathodic half cell, inspired by redox active enzymes.[14] Thermal treatment of related catalysts finally increased both activity and stability;[15] so the concept of N-doped carbons as electrocatalysts was born. It nevertheless took more than a decade to prove that also precursors not related to biological redox systems can successfully create ORR catalysts.[16] Up to this point of time it yet remained unclear whether the N-doping, the metals in the respective materials or a synergy of both are essential for good ORR activity. A complete overview of the development of such a metal complex mimicking catalysts can be derived from an accordant review provided by Zhang et al. in 2008.[17] As further progress was achieved, the necessity of metals in the ORR catalysts was more and more doubted, as experimental results gave more hints on an intrinsic electrocatalytic activity of N-doped carbons. In 2006 completely metal free catalysts were proven to be active ORR catalysts by Ozkan et al., finally evidencing the beneficial influence on the activity. While the possibility of a crucial influence of metals used throughout the synthetic procedure – that were removed afterwards – on the formation of C/N-sites with electrocatalytic activity was mentioned, the authors also already considered the idea of a favourably changed charge profile at the carbon atoms neighbouring the more electronegative nitrogen atoms, which might ease the interaction with molecular oxygen. Also the possibility that nitrogen atoms bound in pyridinic sites at the edges of carbon sheets play an important role was implied.[18] The design and improvement of now metal free catalysts for ORR are too complex to be discussed here in full detail, and an accordant review article by Shao et al. is hence recommended.[19] Later vertically aligned nitrogen-doped carbon nanotube arrays were presented by Dai et al., remarkably exceeding the activity of conventional Pt@C catalysts, while additionally exhibiting an outstanding ORR selectivity avoiding deactivation by crossover effects in an alkaline medium.[20] As for the first time Pt@C catalysts are left behind, at least under alkaline conditions; this can be considered as one of the most important breakthroughs in the research on N-doped carbon based electrocatalysts. The

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reasons for the electrochemical activity of such materials are meanwhile seen in the charge profile induced in the carbon backbone by the electronegativity of the doping atoms, and also in the influence of pyridinic nitrogen atoms with their free lone pair available for interaction with oxygen.[18,21–24] Furthermore, N-doped carbon materials can not only be used as ORR catalysts directly, but also improve the stability of classical Pt nano-particle catalysts. This could be proven on carbon nanotubes modified with ionic liquid derived N-doped carbon using time resolved *in situ* small angle X-ray scattering, clearly pointing out a significant increase of stability of the particles against coarsening and agglomeration achieved by the N-doping.[25] As the development of noble metal free catalysts might still be facing certain challenges, this concept shows that N-doped carbon can also be applied in a kind of bridging technology.

Apart from being applied as ORR catalysts, the second major energy related field of applications for N-doped carbons is found in supercapacitors. Carbon materials have been used widely as electrodes in supercapacitors, as they have been reviewed frequently.[26–30] It has been shown explicitly by Frackowiak *et al.* that nitrogen atoms induce favourable pseudocapacities, especially relying on the protonation of pyridinic nitrogen atoms at graphitic edges.[31] This influence of nitrogen was also correlated with the porosity of the respective materials.[32] It thus cannot be questioned that nitrogen-doping is one of the central keys in the design of supercapacitor electrode materials.

Synthetic routes towards N-doped carbons

The synthetic pathways leading to such N-doped carbons are nevertheless incredibly manifold, and are thus not limited to a single standard procedure. Classically, post-treatment of crude carbons with reactive nitrogen sources, such as urea, nitric acid or especially ammonia, is one way of obtaining N-doped carbons.[33–37] Another dominant approach is the pyrolysis or chemical vapour deposition of nitrogen and carbon containing precursors, such as heterocycles, melamine or aminated sugars, by which a direct incorporation of the nitrogen atoms into the forming carbon backbone becomes possible.[38–40] Actually the examples of nitrogen-doped carbons are nearly uncountable, also due to numerous studies on nitrogen-doped graphene, which have been reviewed by Wang *et al.* in 2012 (ref. 41), and on nitrogen-doped nanotubular structures, about which overviews can also be found elsewhere.[42,43] A very recent overview of nitrogen-doped porous carbons has just been presented by Shen and Fan.[44] Nevertheless we would like to introduce some more unconventional routes towards N-doped carbon materials that do not follow the classical pathways. One way is hydrothermal carbonisation that has meanwhile become a well-established procedure for deriving carbonaceous materials from carbohydrate rich biomass.[45–47] Using nitrogen-containing biomass related precursors and treating them hydrothermally yield nitrogen-containing carbonaceous materials that offer different possibilities for further treatments and applications.[48–54] Another approach is based on a study on the thermal stability of ionic

liquids from 2006 in which the potential of nitrile functionalised ionic liquids is indicated, as they do not decompose completely to volatile products under an inert gas.[55] This led to profound and detailed studies on how these ionic liquids can be used as a nitrogen-doped carbon source, ranging from mechanistic and fundamental points of view[56–60] to more application oriented studies, as the derived materials are promising candidates, *e.g.* for fuel cell applications.[25,61–63] Also supramolecular types of ionic liquids can form systems suitable for N-doped carbon synthesis.[64] Meanwhile also nitrogen rich organic networks and frameworks have been thermally treated to give nitrogen-containing carbon materials[65–67] with promising properties, *e.g.* for supercapacitor applications[66] or as cathodic materials in lithium batteries.[67]

As we tried to show throughout this introduction, nitrogen-doping is nowadays a widely applied concept in carbon material research. Although it is almost impossible to provide an overview truly covering the entire field, we tried to focus on the most central steps in the history of N-doped carbons. While these N-doped carbons have become a well-established approach to face challenges in energy related applications, interest has also arisen concerning the doping of carbons with other heteroatoms. The chemical preconditions of the other heteroatoms might not be as perfectly fitting for incorporation into a carbonaceous backbone, as is the case for nitrogen. Nonetheless the electronic situation in boron or the size of second row elements like sulphur and phosphorus and thus induced structural effects represent a pool of possibilities to tune carbon materials into even more versatile directions. In the following chapters we will therefore give an overview of highly advanced carbon materials, doped with boron, sulphur or phosphorus. Therein we will highlight the first goals that could be reached in energy applications of such materials that are however still at the very beginning of their successful development.

Boron

Boron is an element with unique and basically incomparable properties within the periodic table. It is thus a highly interesting candidate for the doping of carbon materials, modifying the properties of pure carbons as will be discussed in detail throughout this article. Early works on boron doped carbons were inspired by the fascination of stoichiometric boron nitride compounds that can form hexagonal patterns enabling sp^2-carbon-related structures, such as stacked sheets or nanotubes, as has been reviewed *e.g.* by Rhenzi *et al.* or Goldberg *et al.*[68,69] Early works on B/N/C-materials with graphite like structure and a composition of $B_{0.35}C_{0.3}N_{0.35}$ have been reported by Bartlett *et al.* in 1987, who used a chemical vapour deposition approach with boron trichloride, acetylene and ammonia as the precursor mixture.[70] Instead of chemical vapour deposition, Ajayan *et al.* applied an electric arc discharge base synthetic procedure, in which elemental amorphous boron and elemental graphite powder served as precursors, yielding a mixture of different boron containing carbon nanostructures, such as thin graphitic sheets, tubes and filaments.[71] A similar pathway was followed

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for B/N/C-nanotubular structures by Redlich et al.[72] Over the years many boron-doped carbons and – due to the fundamental proximity to the aforementioned stoichiometric boron nitride materials – also boron- and nitrogen-codoped carbons have been synthesised, some examples of which can be found in the reference list, reaching from chemical vapour deposition and arc discharge approaches over pyrolytic procedures towards the carbonisation of ionic liquid based precursors.[73–80] Meanwhile research groups have started focusing on not only fundamental studies on boron-doping, but also on applying the obtained materials and exploiting their beneficial properties in energy related applications. In the following, we would like to briefly introduce the readers to boron-doped or boron- and nitrogen-codoped carbon materials used as fuel cell catalysts, as electrodes in supercapacitors and as materials for lithium intercalation in batteries.

Boron-doping for fuel cell applications

When it comes to fuel cells, some studies have focused on the use of merely boron-doped carbon electrocatalysts. E.g. Sun et al. presented boron-doped carbon nanorods derived by a spray pyrolysis chemical vapour deposition process. Yet the authors did not directly use these nanorods as ORR catalysts, but as a support for electrochemically active platinum nanoparticles. The boron doping succeeded in significantly enhancing the durability of this noble metal based ORR catalyst, in comparison to crude carbon hosts, which is attributed to a direct Pt–B-interaction and the high stability of the nanorods themselves: only 13.2% of the electrochemical surface area of the boron-free catalyst is retained after 3000 electrochemical cycles, while boron doping increases this value to 47.7%.[81] A similar idea has been adopted recently by Manthiram et al. who distributed platinum nanoparticles as catalysts for methanol oxidation in the anodic compartment of fuel cells on boron doped carbon nanotubes derived from a chemical vapour deposition process with toluene, ferrocene and triethyl borate as the precursor–catalyst-system. In comparison to non-doped reference nanotubes, boron functionalised tubes allowed for a more homogeneous distribution of the Pt particles with fewer tendencies towards agglomeration, which is illustrated in Fig. 1. Thus also the electrochemical surface area has been enhanced. Besides this effect the authors have most noteworthily observed a significant increase of stability of the Pt catalyst against carbon monoxide poisoning, for which a favoured interaction of the CO with the boron sites on the host compared to the electrocatalytically active particles is considered as responsible.[82]

Of course boron-doped carbon materials are not only suitable as hosts for rather classical noble metal catalysts, but also serve as fuel cell electrocatalysts themselves, as has been demonstrated by Hu et al. whose Boron doped carbon nanotubes were directly tested for their ORR activity. Upon increasing the boron content, also an increase of the ORR activity has been observed, indicating the importance of the boron moieties in the catalytic process. Also excellent ORR selectivity and resistance against methanol crossover qualify the B-doped nanotubes as promising ORR candidates. Additional theoretical calculations performed by the authors have closely elucidated the reason for the beneficial influence of the boron doping, which is based on two synergistic effects: on the one hand boron has a lower electronegativity than carbon, and the positively polarised boron atoms attract the negatively polarised oxygen atoms leading to chemisorption. On the other hand, boron sites can also act as electron donors for the reduction reaction, as the electron density of the graphitic π-electron system can be transferred to the free p_z orbital of the boron.[83] This electronic tuning adds a general promising potential to B-doped carbons as ORR catalysts, as could be further shown by Xia et al. who annealed graphene oxide in the presence of B_2O_3 yielding B-doped graphene. This material has proven to exhibit remarkable ORR activity with long-term stability of the catalyst under alkaline conditions.[84] Also other ideas on the influence of boron-doping have been discussed, as those recently by Nabae et al. Their resin-based B-doped carbons have shown improved ORR activity compared to the non-doped equivalent material, which is attributed to the enriched presence of oxygen species due to the reactivity of their boron source. The reasons have hence not yet been fully illuminated, and the concept seems to be limited to the very specific example of the type of material presented in their study.[85]

Dual doping with boron and nitrogen for ORR

While hitherto only merely B-doped carbons have been discussed, also B- and N-codoped carbons have been developed and applied for ORR, exploiting synergistic effects of the beneficial influences of the two contrarily profiled heteroatoms. Carbonisation of polymer particles with melamine and boron trifluoride as reactive agents was e.g. used by Ozaki et al. to obtain B–N-codoped carbon with interesting ORR activity boosted in comparison to only nitrogen doped carbons. The activity does however not reach values of conventional Pt@C catalysts. The authors suggest that this effect is not only due to the addition of both doping effects, but also due to a crucial role of B–N–C-type moieties throughout the catalyst.[86] The authors intensified their study by performing directly comparative measurements of purely N-doped, purely B-doped and B–N-codoped carbons, all derived from the carbonisation of polymerised furfuryl alcohol under the influence of the respective reactive additives. Once more the pronounced synergistic effect of the codoping on the B–N–C-type moieties was pointed out.[87]
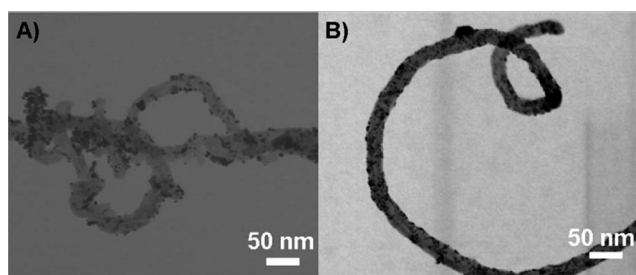

Fig. 1 Scanning transmission electron micrographs of Pt particles loaded on non-doped nanotubes (a) and B-doped nanotubes (b). [Reprinted with permission from ref. 82; copyright © 2012 Royal Society of Chemistry.]

Additional computational studies have implied that indeed certain B–N–C-sites may cause enhanced ORR activity; yet the activity is highly sensitive to the actual arrangement of these moieties within the carbon backbone, *e.g.* boron and nitrogen atoms directly bound to each other do not seem to represent a favourable binding concept.[88] Woo *et al.* who used a chemical vapour deposition approach for the synthesis of B–N-codoped carbon using a precursor and catalyst system composed of dicyandiamide, boric acid and iron or cobalt chloride, also observed a beneficial effect of the codoping on the ORR activity of their materials.[89] Beneficial effects on ORR activity of B–N-codoping in carbons have also been observed by Chisaka *et al.*, nevertheless depending on the presence of iron species.[90]

B–N-codoping for ORR has furthermore been applied recently for two highly advanced carbon allotropes: graphene and carbon nanotubes. Regarding the latter, Dai *et al.* have used melamine diborate as a single precursor for vertically aligned carbon nanotubes doubly doped with boron and nitrogen, finally synthesised by a chemical vapour deposition approach with metal catalysts, while metal residues were eliminated from the final product by acid treatment. The aligned nanotubes (see Fig. 2 for electron micrographs) have been successfully tested as electrocatalysts in ORR, in which the B–N-codoped systems clearly exceeded both mono-doped nanotubes used as a reference system; the current densities of the dually doped tubes get close to those of conventional Pt@C electrodes. Given the fact that XPS measurements show that no metal residues are present in the catalyst, this observation clearly underlines the synergistic effect of both dopants.[91] The results of Hu *et al.* further allow for an even more detailed elucidation of the B–N-codoping synergistic effects. The authors have therefore prepared two types of codoped carbon nanotubes. One approach was performed by chemical vapour deposition under direct incorporation of boron and subsequent post-treatment of the tubes under ammonia to additionally introduce nitrogen atoms, preserving the antecedently established binding sites of boron. Thus B and N are separate and not directly bound to each other in this carbon material. In contrast, the authors used a chemical vapour deposition procedure using precursors allowing for a simultaneous and direct inclusion of both heteroatoms into the forming carbon nanotube structures, yielding neighbouring N and B

atoms in the resulting material. The electrochemical measurements of the ORR activity of the as-synthesised materials offer a profound insight into the mechanistic details; measurements were performed with varying doping degrees of boron, in comparison to purely N-doped analogous materials. The exclusively N-doped materials have shown – as expected – enhanced ORR activities compared to pristine CNTs. Upon a stepwise increase of the boron content, a decrease of the maximum reduction current has been observed in the case of the doping concept with neighbouring boron and nitrogen atoms. Contrarily, an enhancement of the current has been observed in the case of boron and nitrogen atoms incorporated into the carbon isolated from each other. These data explain that the beneficial effects of both boron and nitrogen on the ORR activity of carbons sensitively depend on their chemical environment. Due to the opposite properties of both dopants, their effects can be mutually compensated, while most fruitful synergies can be achieved when thoughtfully designing the doping procedures.[92] This is in good agreement with aforementioned calculations.[88] The effects have also been similarly observed in studies on B–N-codoped graphene: Dai *et al.* have published their approach that allows for the synthesis of B–N-codoped graphenes by thermally treating graphene oxide with boric acid in an atmosphere of ammonia. The authors have thereby obtained BCN-materials with stoichiometries of $B_{38}C_{28}N_{34}$, $B_7C_{87}N_6$ and $B_{12}C_{77}N_{11}$ and outstanding thermal stabilities. Already XPS measurements have indicated the easy adsorption of oxygen on the graphene surface, pointing out a high potential of the materials as ORR catalysts. $B_{38}C_{28}N_{34}$ nevertheless could not be shown to be a useful electrocatalyst, probably due to a lack of conductivity, attributed to the low carbon content, and a mutual compensation of the effects of B and N atoms directly bound to each other – in agreement with the previously discussed aspects of the binding environment of B and N in doped nanotubes. Hence the accordant electrochemical measurements for the other candidates could indeed show the outstanding behaviour of the B/N-graphenes as ORR catalysts under alkaline conditions, while $B_{12}C_{77}N_{11}$ even exceeds the current density of a conventional Pt@C catalyst throughout the major part of the scanned potential range. Also, good electrochemical stability, high ORR selectivity and an electron transfer number of almost 4 (see Fig. 3) complete the
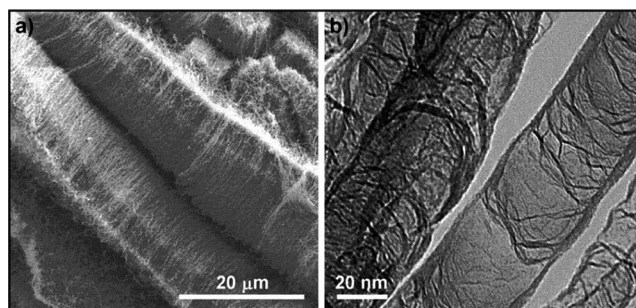

Fig. 2 (a) Scanning electron micrograph and (b) transmission electron micrograph of boron/nitrogen-doped vertically aligned carbon nanotubes. [Reprinted with permission from ref. 91; copyright © 2011 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.]
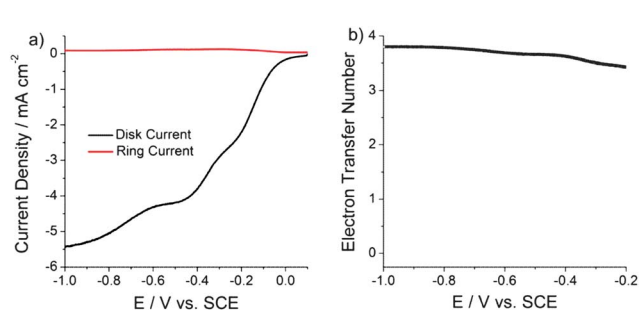

Fig. 3 RRDE testing on a BCN graphene ($B_{12}C_{77}N_{11}$) sample in an oxygen-saturated 0.1 M KOH solution (a) and the corresponding electron transfer number of ORR on the BCN graphene (b). [Reprinted with permission from ref. 93; copyright © 2012 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.]

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picture of a remarkable ORR catalyst, based on heteroatom doping of carbon. The authors have further supported their experimental data by calculations, showing that in the case of $B_{12}C_{77}N_{11}$ the values of maximum spin densities and maximum charge densities are higher than those for the other tested graphenes. This is thus considered as one crucial factor for ORR activity enhancement by B–N-codoping.[93] In a similar approach, with varied N- and B-sources during thermal treatment of graphene oxide, Woo et al. have presented a work supporting the previous results discussed here. Also their B–N-codoped graphene has proven itself as a good ORR catalyst, even under acidic conditions.[94]

It can be summarised that boron-doped carbons represent a promising class of ORR catalyst candidates. The results discussed throughout this article speak for themselves, giving numerous examples of advanced ORR catalysts based on this concept, using different ways to achieve synergies of the two contrary doping heteroatoms boron and nitrogen.

B-doped and B–N-codoped carbons for supercapacitors and lithium ion batteries

Due to their interesting property profiles, such materials have heretofore also been applied in other energy related fields, e.g. as electrodes in supercapacitors. A main focus has also been on boron- and nitrogen-codoped carbon materials, as presented e.g. by Gao et al. The authors have followed a relatively unconventional synthetic pathway using citric acid as the carbon source, boric acid as the boron source and claim to have succeeded in the incorporation of nitrogen into their structures by simply executing the carbonisation reaction in a nitrogen atmosphere that is – despite its estimated role in the reaction – referred to as an inert gas atmosphere. Application of the derived hierarchically porous materials as supercapacitor electrodes has been reported as successful, indicating that the favourable pseudocapacitance effects are not only achievable by nitrogen-, but also by boron-doping.[95] As mentioned before, Dai et al. have synthesised B/C/N-nanotubes from chemical vapour deposition using melamine diborate as a single precursor. The authors have – additionally to the fuel cell application tests – focused on the applicability of the material in supercapacitors, too. The first interesting observation is a significant enhancement of the specific capacitance of the nanotubes, from 83.8 F g^{-1} for pristine nanotubes to 162.5 F g^{-1} for the doped tubes (in acidic media). This is attributed to induced pseudocapacitance contributions, and also a thickened electrochemical double layer due to an improved wettability of the doped structures. A second finding is that not only the doping itself, but also the nanomorphology of the electrode material influences the capacitance drastically. Using vertically aligned B/C/N-nanotubes a specific capacitance of 312.0 F g^{-1} is reached, which is almost doubled compared to the non-aligned tubes.[96] A new step in the ongoing process of B/N-doped carbon materials for supercapacitors has further been reached by Müllen et al. who presented a study on using a B–N-codoped graphene aerogel in all-solid-state supercapacitors. The graphene aerogels were obtained by hydrothermally treating graphene oxide with ammonia boron

trifluoride and subsequent freeze-drying. The morphology of the interconnected doped graphene sheets giving monolithic structures allows for a targeted shaping of the material to fit the requirements of the supercapacitor device. Electrochemical measurements performed in direct comparison to N-doped, B-doped and pristine derivatives of the material have pointed out that significant synergies can be achieved by dual doping, as the highest specific capacitances of up to >60 F g^{-1} could be observed for the dually doped samples. Nevertheless, also pure B-doping is shown to exhibit a remarkable supercapacitor performance, getting close to the results of the codoped sample.[97] This result further proves that not only is codoping with boron and nitrogen a promising concept for the design of novel supercapacitor electrodes, but also the mere doping with boron can pave the way towards interesting electrode materials, as Cheng et al. have shown using an ordered mesoporous carbon derived from a hard templating approach with sucrose as the carbon source and SBA-15 as the template. Already minimal boron doping in amounts of 0.2 atom% – achieved by boric acid used as an additive during synthesis – was capable of boosting the specific capacitance strongly.[98] Furthermore Park et al. could recently point out similar results in their study on boron-doped graphene nanoplatelets. The authors have derived their B-doped graphene from a solution process, simply giving dispersed graphene oxide the possibility to react with a borane–tetrahydrofurane adduct (as reducing agent and dopant) and subsequently drying the sample in a vacuum under gentle conditions. This mild procedure yielded materials with ∼1 atom% of boron incorporated into the graphene platelets. They thereby reached a conclusion that specific capacitance can reach values of >200 F g^{-1}, which can be almost fully retained after 4500 electrochemical cycles.[99]

As a last example of energy related applications of boron-doped carbon materials, we would like to provide a short overview of lithium ion batteries. Nevertheless, in comparison to the aforementioned application fields, studies of lithium ion batteries using B-doped carbons as electrodes are still relatively rare. An early overview has been provided in 2000 by Endo et al., pointing out difficulties that have been faced with B-doped carbons as lithium battery anodes, as in many cases the formation of boron carbide or nitride sites in carbonaceous materials has prevented beneficial effects of real boron doping.[100] Later some examples have shown that boron-doping obtained by graphitisation of pitches or fossil coals with boron sources at temperatures >2000 °C can yield potential anode materials for lithium ion batteries, still partially encountering the aforementioned problem.[101–104] A recent breakthrough for B-doped carbons could be presented in a study by Cheng et al. The authors have focused on graphene to be doped with boron for enhanced performance as an anode material in lithium ion batteries. Thus graphene is post-functionalised at 800 °C using boron trichloride as a doping agent, yielding a doping level of 0.88 atom% in the material. High electrode capacities of 1549 mA h g^{-1} at low charge/discharge rates and 235 mA h g^{-1} at very high rates represent a remarkable result, attributed to numerous effects of the boron doping regarding electrode/electrolyte wetting properties, interlayer distances, electrical conductivities or heteroatom induced defect sites, thus leading

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to enhanced performance of the material concerning its Li^+ absorption and diffusion properties.[105] It can be followed that boron doping is indeed a promising concept for the design and development of new anode materials for lithium ion batteries, and that there certainly are ways to overcome the previously encountered problems of the formation of unfavourable boron binding situations. Boron is thus already a relatively profoundly studied dopant for carbon materials that has entered numerous energy related applications and will play a significant role in the further ongoing process within this field.

Sulphur

In comparison to boron, sulphur doping in carbon materials is hitherto still quite rare and represents an emerging field within carbon material research. While nowadays the high potential of such materials for energy applications in fuel cells, super-capacitors or batteries is continuously discovered and exploited, until only a few years ago, only little had been known about such sulphur-doped carbonaceous species. The knowledge mainly ranged from graphite–sulphur-composite materials and their superconductive behaviour[106,107] towards theoretical studies about the effects of single sulphur atoms in carbon nanotubes or graphene sheets.[108–112] Sulphur–carbon composites have also entered the field of lithium–sulphur batteries.[113–118] Nonetheless, synthetic concepts establishing doped carbons with sulphur atoms firmly and covalently incorporated into the carbon structures have only been developed since 2011, when Schmidt et al. used a microporous polymer network containing thienyl building blocks as a precursor for intrinsically microporous S-doped carbon with variable sulphur contents of ~7 wt% up to ~20 wt% depending on the carbonisation temperature.[119–121] Comparable to this concept, Spange et al. developed an approach linking thienyl monomers covalently to silica precursors. This dually functionalised precursor system allows for the synthesis of silica/S-doped carbon composites yielding additional porosity after silica removal. The authors further induced mesoporosity within this type of material applying hard templates.[122]

S-doped activated carbons for hydrogen storage

Fuertes and Sevilla et al. acknowledged the potential of the thienyl group as a central tool in the synthesis of S-doped carbon, and polymerised thiophene using an oxidative approach, followed by carbonisation under activation of the forming carbon with potassium hydroxide. Thus a rather classical approach for the preparation of activated carbons has been successfully transferred to the design of modern materials. The as derived S-doped carbons exhibit a microspherical morphology and remarkable microporosities with BET surface areas of up to ~3000 m^2 g^{-1} and micropore surface areas of up to ~2600 m^2 g^{-1}, depending on the polythiophene–KOH-ratio and the carbonisation temperature applied. The sulphur atoms are firmly bound to the carbon backbone, mainly in C–S–C binding motifs, in amounts from ~4 wt% up to ~14 wt% – again depending on the reaction temperature.[123,124] Due to the high surface areas and pore volumes of their materials, the author initiated first tests on their application

in the field of energy as hydrogen storage media. The hydrogen uptake in these S-doped carbons can reach 5.71 wt% at −196 °C under a pressure of 20 bar and 2.41 wt% at a pressure of 1 bar. The calculated hydrogen uptake density of this specific sample was 9.5 μmol m^{-2}. The materials with surface areas lower than 3000 m^2 g^{-1} can reach up to 12.7 μmol m^{-2}. Although a sulphur-doped carbon type material has been used in this study, the authors tend to assign the hydrogen uptake behaviour to the porous structure and the high active surface area, but do not see a clear beneficial influence provided specifically by the sulphur atoms within the material.[123] This has been discussed in different manners by Xia et al. Their approach included a template based synthesis of microporous sulphur-doped carbon using 2-thiophenemethanol as a polymerisable precursor and a zeolite as a hard template. The as synthesised S-doped carbons exhibited one of the highest hydrogen uptake densities reported for nanoporous carbons at this point of time of 14.3 μmol m^{-2}. According to the authors, this is due to the sulphur atoms that induce a stronger interaction between the carbon host and the hydrogen molecules, which has been derived from measurements of the isosteric heat of the hydrogen adsorption that is – in the case of the template derived S-doped carbon – up to 8.9 kJ mol^{-1} significantly higher than those for comparable N-doped or non-doped carbons and also those for metal organic frameworks.[125] Thus the real influence of the sulphur atoms is still controversially discussed; yet their promising potential as a dopant is obvious and will be subject of future studies. Other works of S-doped activated carbon – with S-doping in the ppm range – have been performed by Bandosz et al., focusing on other types of applications as adsorbent materials[126,127] or photoactive substances for light harvesting.[128]

S-doped graphene based materials for ORR

Another carbon allotrope that is currently the subject of different studies in the field of sulphur doping is graphene. The general feasibility of S-doping in graphene has been predicted theoretically by Denis et al. S-doping should be more difficult than doping with e.g. nitrogen, taking into account the size and the different binding behaviour of sulphur atoms. Nevertheless it was calculated that S-doping should allow for a targeted tuning of the graphene bandgap, depending on the amount of sulphur atoms incorporated into the sheets.[110,129] Practically it is e.g. possible to synthesise S-doped graphene by a chemical vapour deposition approach using a solution of elemental sulphur in hexane as the precursor.[130] As can be derived from data published by Yang et al., another way to obtain sulphur-doped graphene is to blend graphene oxide homogeneously with benzyl disulfide, followed by subsequent annealing (compare the scheme in Fig. 4).

The result is an interesting material, composed of graphene sheets exhibiting partially wrinkled and folded morphological motifs. The sulphur with contents of up to ~1.5 wt% is homogeneously distributed throughout these sheets, also at their edges, according to the elemental mapping data provided. The chemical environment of the sulphur atoms could be further elucidated by XPS, indicating covalent bonding between carbon
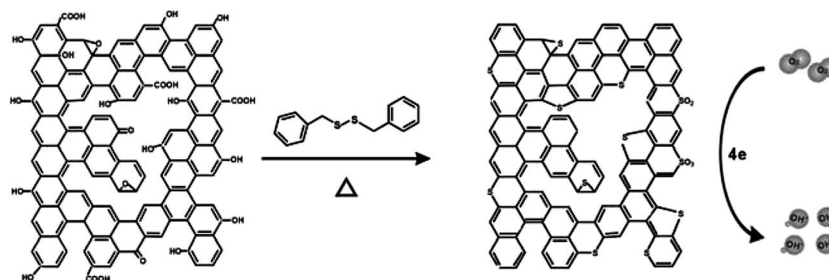
Fig. 4   Schematic representation of a S-doped graphene synthetic approach using graphene oxide and benzyl disulfide as precursors. Application as an ORR catalyst is also indicated. [Reprinted with permission from ref. 131; copyright © 2012 American Chemical Society.]

and sulphur and thus the usefulness of this method for the synthesis of S-doped graphene. The authors have further reported the good performance of their S-doped graphene for ORR catalysis under alkaline conditions. Therefore, different doped graphenes obtained at different reaction temperatures in the synthetic process were compared to their non-doped equivalents, synthesised without the addition of benzyl disulfide. In all cases, the ORR activity was significantly enhanced by S-doping. The electrocatalytic activity of S-doped graphene synthesised at 1050 °C even exceeds the activity of a conventional Pt@C catalyst, while additionally exhibiting higher selectivity for oxygen reduction and thus avoiding well crossover effects. Koutecky–Levich-plots further revealed that an almost ideal four electron transfer occurred in the S-doped graphene catalysts, once more accentuating the powerful character of the S-doping method within the field of fuel cell catalyst research. The reason is suggested to be found in the increased spin density in the graphene achieved by sulphur doping.[131] Müllen *et al.* applied a similar approach in their S-doped graphene synthesis, using graphene oxide as the starting material. In a first step, ultrathin silica–graphene oxide composite sheets were produced. In a second step, annealing in an atmosphere of H_2S allowed for the formation of S-doped graphene that was isolated by subsequent removal of the silica. The tests on the materials' ORR activities were successful; like Yang *et al.* the authors observed good electrocatalytic activities, electron transfer numbers close to 4 and – especially in comparison to conventional Pt@C catalysts – good resistance against crossover effects, tested by the addition of methanol. Thus S-doped graphene also in this study is accentuated as a promising candidate for electrocatalysis; nevertheless the authors discuss a bit more considerately that – in comparison to nitrogen doping – a homogeneous doping with sulphur atoms is still difficult; sulphur atoms – due to their different chemical binding behaviour – tend to cumulate at graphene edges. A potential source of further improvement of S-doped graphenes as ORR catalysts is thus seen in achieving a more homogeneous distribution of the sulphur throughout the graphene sheet.[132]

S-doped carbons for lithium ion batteries and supercapacitors

Beyond fuel cell applications, sulphur also plays a role as a dopant for carbon materials in other electrochemical devices. Therefore graphene-based materials have also been applied; yet in this case – reported by Guo *et al.* in 2012 – non-doped

graphene is one part of a composite, while the other part is a sulphur-doped porous carbon. This composite was obtained by ionothermal condensation of glucose in a sulphate containing ionic liquid with the addition of graphene oxide. The thus obtained gel was carbonised in an atmosphere of an inert gas at 800 °C to yield the S-doped porous carbon–graphene composite. With a surface area >900 m^2 g^{-1} and a bimodal pore size distribution – with a hierarchical structure exhibiting micro- and mesopores (more details about the nanomorphology of the composites are available in Fig. 5) – the material exhibits ideal preconditions for its application in lithium ion batteries. Accordant experiments have revealed good performance of this material, exhibiting a stable reversible capacity of 1400 mA h g^{-1}, a long life cycle and remarkable rate performance. The authors attribute this behaviour at least partially to the sulphur doping that is supposed to increase interlayer distances in the stacking of graphene sheets and to increase the amount of nanopore moieties. Nevertheless, in this complex composite material, of course sulphur doping is not the only factor that plays a crucial
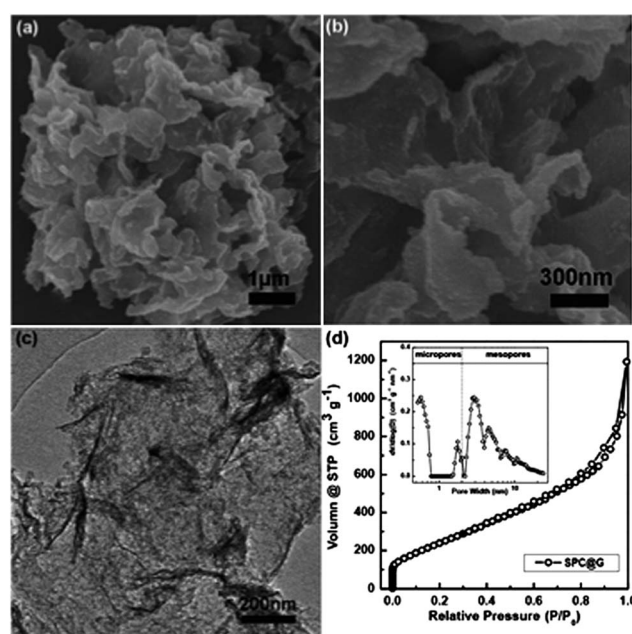
Fig. 5   (a and b) SEM images of a sulphur-doped porous carbon–graphene composite; (c) accordant TEM image; (d) nitrogen sorption isotherm and pore size distribution. [Reprinted with permission from ref. 133; copyright © 2012 Royal Society of Chemistry.]

role determining its performance.[133] S-doped carbon has further been applied as a coating on porous silicon electrodes, showing that it can also serve as a functionalising agent to other lithium ion battery anode materials.[134]

Furthermore sulphur-containing carbonaceous materials are on their way to achieve an important role also as electrodes in supercapacitors. As in this field monolithic materials are preferred, Kanamori et al. have used divinylbenzene as a precursor and polydimethylsiloxane as a phase separation inducing agent, enabling a spinodal decomposition and thus macroporous monolith formation upon polymerisation of divinylbenzene. The thus obtained polymer monolith was washed, sulphonated using concentrated sulphuric acid, carbonised under nitrogen and finally activated thermally using carbon dioxide as an activating agent, yielding a sulphur functionalised carbon monolith (with 0.83 atom% S) with a complex porous structure, containing a microporous, a mesoporous and a macroporous stage, with a surface area >2400 m^2 g^{-1}. This monolithic carbon showed significantly higher specific capacitances (103 F g^{-1} at a scan rate of 200 mV s^{-1}/175 F g^{-1} at a scan rate of 5 mV s^{-1}) than crude activated carbon electrodes without sulphur functionalities, further having negligible degradation over 2000 cycles. The scientific background of this influence of sulphur is still under investigation by the authors.[135]

Carbon materials dually doped with sulphur and nitrogen

Merely sulphur-doped or sulphur-functionalised carbon materials are the central subject of all the studies discussed so far throughout this article. Besides that, numerous groups have also started concentrating on codoped carbon materials that not only have sulphur, but simultaneously also nitrogen incorporated into their structures. One class of materials in this context is again based on the carbon allotrope of graphene: Qiao et al. have used – comparable to aforementioned graphene experiments – benzyl disulfide to introduce sulphur atoms into graphene by annealing it with graphene oxide. At the same time, melamine was applied as the nitrogen source, and additionally colloidal silica to induce a template derived mesoporosity of the resulting sample. The as synthesised mesoporous graphene-based material contains sulphur (2.0 atom%) and nitrogen (4.5 atom%) and has proven its applicability as a highly promising electrocatalyst due to its ORR activity that is – with a reaction current of −3.3 mA cm^{-2} – higher than that for merely S- or N-doped graphenes that have been used as the reference. With an electron transfer number of up to 3.6, the ORR process is also close to the desired complete reduction of oxygen to water; and further a good ORR selectivity was also discovered. As the results for this dually doped graphene exceed the ones of mono-doped graphenes, a synergistic effect is concluded and evidenced by density functional theory calculations, based on the changes of charge and spin density at the different sites of the dually doped materials, enhanced by the different behaviours of nitrogen and sulphur.[136] Similar results could be presented by Guan et al. who also investigated the ORR activity of dually doped graphene. In their approach, few-layered graphene was doped with N and S at the same time using pyrimidine and

thiophene as precursors in the chemical vapour deposition type synthesis of graphene. The resulting graphene sheets are homogeneously doped with nitrogen and sulphur atoms and show remarkable ORR activity for noble metal free catalysts, even reaching electron transfer numbers of 3.7.[137] A very different pathway towards S–N-codoped carbons has been followed by Wohlgemuth et al. using the hydrothermal carbonisation method. Combining glucose as the main starting compound in the hydrothermal carbonisation process with sulphur functionalised amino acids yields soft amorphous carbons with high sulphur contents of up to ∼12 wt% and nitrogen contents of up to ∼4 wt% exhibiting a microspherical morphology. These carbon spheres can be further pyrolysed to increase the aromatisation and condensation of the carbon backbone, yielding a more graphitised S- and N-doped carbon with sulphur contents of up to ∼7 wt% and nitrogen contents of up to ∼4.5 wt%.[138] In a subsequent study the authors modified their hydrothermal approach by adding albumin to the precursor mixture; the morphology of the S–N-codoped carbons could be drastically altered and aerogel-like monolithic structures with surface areas of up to 321 m^2 g^{-1} (after additional pyrolysis at 900 °C under nitrogen) were achieved. The S/N-doped aerogels were tested for their ORR activity, giving good results under alkaline conditions and reasonable activity under acidic conditions, while in the latter case at least showing a better stability than platinum based conventional catalysts. The authors – like the ones of the previously discussed reports – see the reason for the enhancement of ORR activity compared to crude carbons e.g. in the charge density profile induced by the different electronegativities of the different atoms involved. Furthermore, the bigger size of the sulphur atoms will induce structural defects and thus sites with enhanced catalytic activity. Finally, also the increase of polarisability due to the large sulphur lone pairs should favour the interaction with oxygen.[139] Most recently also S- and N-codoped carbon foams were synthesised by Huang et al. The foams exhibit a continuous and hierarchical structure and also show promising results as ORR catalysts.[140] The field of S–N-codoped carbons thus represents a thriving area of materials research, and numerous studies can be expected in the near future, contributing to a quick progress and development. Meanwhile, another synthetic approach, based on nitrile functionalised thiazolium salts, has been published, showing a novel concept allowing for an easy tuning of both nitrogen and sulphur contents, simply by a variation of the carbonisation temperature. Furthermore, combining this approach with hard templating yields S–N-codoped carbons with high active surface areas of almost 1200 m^2 g^{-1}, whose open sponge-like structures can be followed in the electron micrographs depicted in Fig. 6.[141] In this context we would like to introduce the reader to another class of materials in which nitrogen and sulphur appear side by side. Nevertheless it is a carbon nitride with an idealised stoichiometry of C_3N_4, doped with sulphur atoms partially substituting N atoms in the nitride lattice, using thiourea as a single precursor. By this sulphur doping the photocatalytic water splitting activity was enhanced; according to the authors a change in the optical properties of the carbon nitride because of the sulphur doping is one factor that promotes this effect.[142]
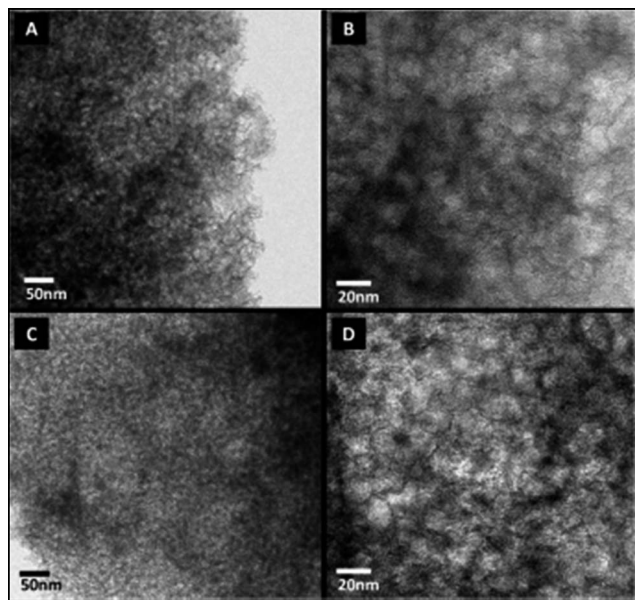
Fig. 6 Transmission electron micrographs of S–N-codoped carbons from different thiazolium salts, templated with colloidal silica spheres. [Reprinted with permission from ref. 141; copyright © 2012 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.]

In summary sulphur doping is a young concept; nevertheless already the very first studies presented here prove its promising potential. Influences of the sulphur atoms on the spin density, the polarisability and structural defects seem to especially promote highly beneficial properties in the field of electrochemical applications.

Phosphorus

When it comes to phosphorus, research has mainly focused on the investigation of phosphorus-doped carbon materials with diamond-like binding motifs. A detailed discussion of this entire class of materials is beyond the scope of this overview and can be found elsewhere.[143–146] In this reviewing article we are yet concentrating on carbon materials with sp²-hybridised binding motifs, and their tuning upon doping with different heteroatoms. Within this field, until now examples with phosphorus as a dopant are relatively rare. Computational studies have predicted an influence of phosphorus doping on the bandgap of graphene, with a more pronounced effect than that calculated for sulphur, while also the incorporation of phosphorus should be energetically more favourable.[110,112] Furthermore, calculations have shown that phosphorus doping is to improve the electron-donor properties of a carbon material, conclusively accompanied by an increased catalytic activity, *e.g.* in ORR.[147]

First synthetic approaches and fuel cell applications of P-doped carbons

A truly synthetic and not computational approach of using phosphorus for adding a function to a crude carbon has been presented by Lee *et al.* in 2003: the authors have used crude

carbon fabrics intending to increase their stability against oxidation applying phosphoryl chloride or methyl phosphonic acid, respectively, as activating agents. After the treatments the samples contained up to 6.7 wt% phosphorus, which yielded a significantly increased stability against oxidation. Thus hitherto the motivation has not been directly related to energy applications; furthermore the synthetic approach using a kind of an activating agent rather favours the formation of surface functional groups, but not a direct incorporation of phosphorus atoms into the carbonaceous backbone of the materials.[148] More recent approaches have established different synthetic pathways towards phosphorus-doped carbon materials, proving themselves as very promising candidates for the application as ORR catalysts. In 2011 Peng *et al.* reported a phosphorus-doped graphite material capable of catalysing the electrochemical reduction of oxygen in an alkaline medium: therefore toluene containing 2.5 wt% of triphenylphosphine was pyrolysed in a tubular furnace, yielding graphite flakes whose phosphorus content was determined by EDX and XPS. XPS further allowed for an insight into the binding states, proving the true incorporation of the phosphorus atoms into the graphite sheets, besides some P–O binding sites, most likely at the material's surface. The material was successfully tested as a catalyst in ORR, in direct comparison to a non-P-doped reference – derived from an analogous synthesis without the addition of triphenylphosphine to the toluene – and to conventional Pt@C-catalyst materials. RDE experiments clearly show how significantly the P-doping boosts the catalytic activity in ORR, while nonetheless not totally reaching the values of Pt@C (compare Fig. 7 for illustration). It is yet noteworthy that the P-doped carbon is remarkably capable of avoiding crossover effects that occur in the case of methanol as fuel. In this context the P-doped graphite clearly outclasses the conventional Pt@C-catalysts. Moreover an average of 3 electrons is transferred during the oxygen reduction, indicating that at least partially a full reduction of oxygen to water occurs.[149]

Peng *et al.* continued their work on phosphorus-doped carbons for ORR. The synthetic approach using toluene and triphenylphosphine as the precursor system was altered by adding metal catalysts aiming at the thermolytic formation of P-doped carbon nanotubes. The as prepared multiwalled P-doped CNTs showed excellent performance as ORR catalysts under alkaline reaction conditions, exceeding the electrocatalytic activity of a conventional Pt@C catalyst used as a reference material.[150] Also in comparison to the previously discussed P-doped graphite the electrocatalytic activity is increased, which is – according to the authors – due to the nanostructural motifs of the CNT morphology. Nevertheless it must also be considered that ferrocene is used as a catalyst during the thermolytic P-doped CNT synthesis, while no details on any acidic rinsing or other metal removing steps are reported; so the influence of the residual metal might require more profound consideration.[150] The ORR activity in acidic media still falls behind the activity observed under alkaline conditions.[151] In an additional study the authors observed another beneficial effect of the P-doping, upon loading Pt nanoparticles on the P-doped CNTs for electrocatalysis. The P-doping – in agreement
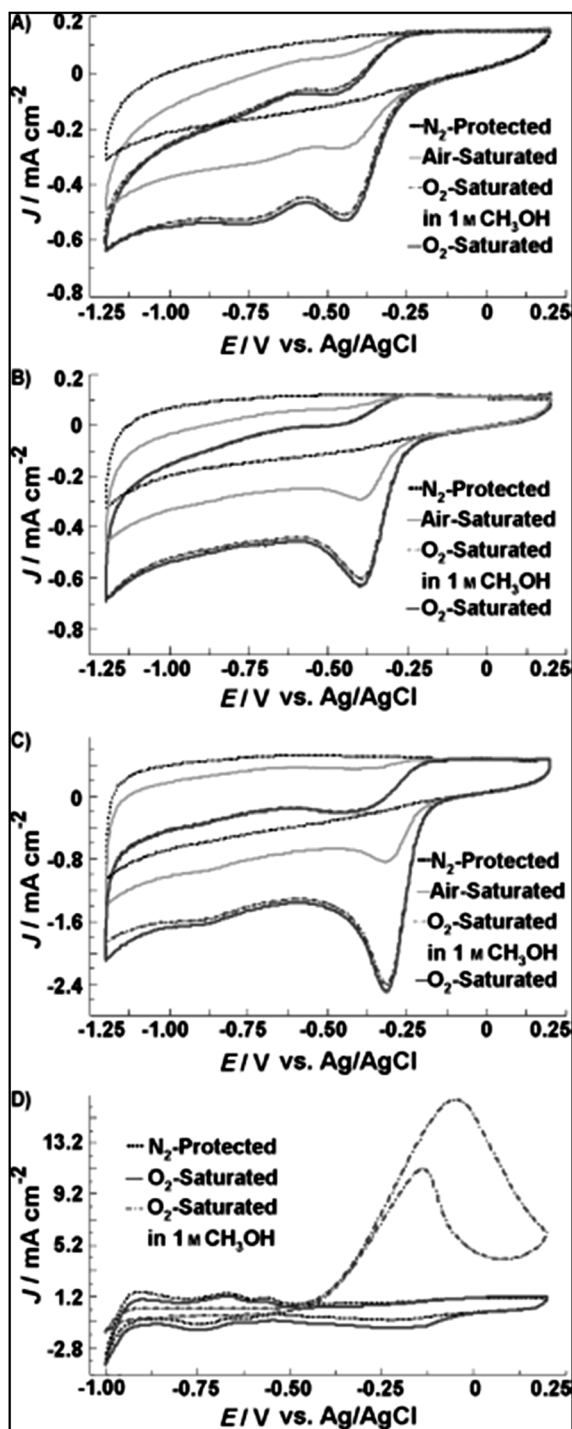
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Fig. 7 Cyclic voltammograms for the ORR at the bare glassy carbon electrode (A), the non-phosphorus-doped graphite electrode (B), the phosphorus-doped graphite electrode (C) and a conventional Pt@C electrode under alkaline conditions. [Reprinted with permission from ref. 149; copyright © 2011 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.]

with the results for nitrogen-doping discussed in the previous sections of this manuscript[25] – provides a better dispersion of the particles on the CNTs, and better stability during methanol oxidation that also occurs with higher efficiency compared to Pt particles loaded on non-functionalised CNTs.[152]

P–N-codoped carbons as electrocatalysts and further codoping

Apart from carbon materials doped exclusively with phosphorus, a lot of effort has been put on the design of materials using phosphorus as a codopant, mostly in addition to nitrogen doping. Interesting work in this context has been performed most recently in 2012 and 2013 by Woo *et al.* The work is related to their aforementioned studies on B–N-codoped carbons. The P–N-codoping was achieved by pyrolysing mixtures of dicyandiamide, phosphoric acid and metal salts and subsequent elimination of metal residues using aqua regia. The authors focused on the application of P/N-doped carbons as ORR electrocatalysts in acidic reaction media, which proves the high degree of practicability of the approach. Additional P-doping does increase the ORR activity of the carbons in direct comparison to merely N-doped materials. Furthermore the P-doping seems to guide the redox process towards the desired four electron transfer, making it more feasible to avoid hydrogen peroxide formation. These outstanding effects are observed despite a relatively low phosphorus content in the carbon material of below 0.6 wt%. The authors nevertheless see the reason for the enhanced ORR activity in the P-doping and the thus induced asymmetric charge density (due to the opposite character of the electronegativities of nitrogen and phosphorus compared to the electronegativity of carbon), in the enhanced asymmetric spin density of carbon atoms and in the increased charge delocalisation. It is also noteworthy that combining boron and phosphorus as codopants, yielding N–B–P-codoped carbon seems to lead to even enhanced synergetic effects of all doping induced modifications of properties, as this material showed the highest ORR activity in an acidic medium within this codoping study.[89] In additional works Woo *et al.* could further prove – besides novel experiments once more underlining their good ORR activities – that their dicyandiamide/phosphoric acid derived P/N-doped carbon material also exhibits a reasonable behaviour regarding its performance degradation. There was a performance loss of −30% after 10 h of treatment under harsh acidic conditions (also in nitrogen-, phosphorus- and sulphur-codoped systems), which is hence much lower than that for conventional Pt@C carbons exhibiting accordant values of −59%.[153] The authors have further presented a detailed study on the influence of the amount of P-codoping on the characteristics of P–N-codoped carbon materials. Going from purely N-doped carbon to additional P-doping of <1 atom% and further up towards 2.3 atom%, not only the ORR activity, but also the morphology of the material is altered. This crucial change comes along with (and also relies on) changes in the morphology. While their merely N-doped dicyandiamide derived carbon shows a horn-type morphology, an increase of the phosphorus content shifts the morphologies to more tube-like structures, with strongly uneven surfaces that are also wrinkled. Ongoing increase of the P-content yields lumps of carbon, whose morphology is described as "crumbled carbon sheets with a thickness of approximately 5 nm." TEM micrographs of the respective samples are depicted in Fig. 8. As can already be intuitively guessed from the micrographs in Fig. 8d/e, the surface area is also enhanced by codoping with phosphorus, reaching values of up to 578 m^2 g^{-1},

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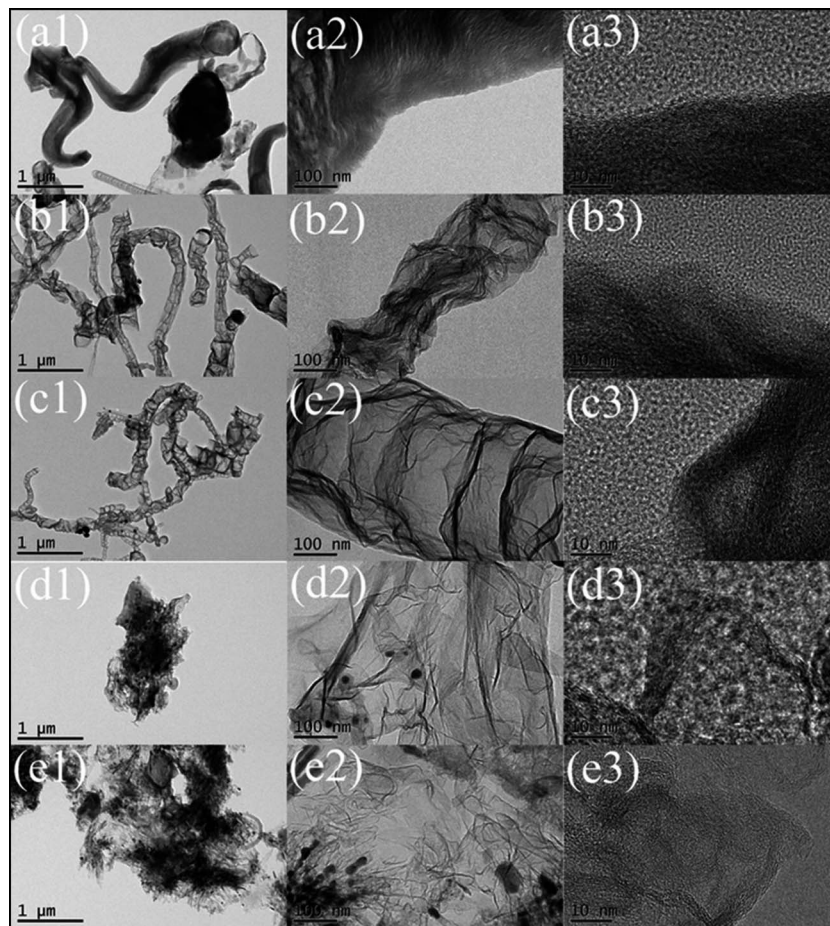*Energy Environ. Sci.*, 2013, **6**, 2839–2855 | **2849**

Fig. 8 TEM images of N-doped or P–N-codoped carbons, illustrating morphological alterations induced by phosphorus codoping. P-content increases from (a) to (e). [Reprinted with permission from ref. 154; copyright © 2012 Royal Society of Chemistry.]

compared to 108 m^2 g^{-1} in the merely N-doped derivative. As already discussed, the authors had observed enhanced ORR activity already at low doping amounts of P. Herein it can be seen that tuning the P-doping content can even further enhance this activity, and further direct the electron transfer processes towards a 4 electron transfer mechanism, yielding only little amounts of peroxide. The entire discussion has nevertheless to be considered with thoughtful care. All effects might also rely on varied N-contents, as the degree of N-doping is influenced by the amount of P-doping, and significant metal residues are found in all samples.[154]

P–N-codoping of carbonaceous materials for fuel cell applications has been the subject of further studies, already introducing different synthetic concepts, and focusing on different states of the carbon backbone. Woo *et al.* could *e.g.* synthesise a P–N-codoped graphene-type material, combining their aforementioned concept of simultaneous pyrolysis of dicyandiamide and phosphoric acid with graphene oxide. Excellent ORR activity under acidic conditions has been evidenced.[94] Dai *et al.* presented vertically aligned carbon nanotube arrays that are codoped with phosphorus and nitrogen. Chemical vapour deposition assisted growth of such doped CNTs was achieved using pyridine and triphenylphosphine as precursors and ferrocene as the catalyst. Under alkaline conditions these

aligned arrays of doped CNTs show excellent ORR activity, getting close to the performance of conventional Pt@C catalysts. It is most noteworthy that they also exhibit a good tolerance against methanol crossover and CO poisoning, and electron transfer numbers of up to 3.88 can be derived from Koutecky–Levich plots, which is definitely close to the desired complete reduction of oxygen to water. The authors of this study also report a synergetic effect of the dual doping with two beneficial heteroatoms, as reference measurements using solely doped nanotube arrays – either with P or N – show enhanced ORR activity compared to non-doped materials, but still do not reach the performance of the codoped version.[155]

P-functionalised carbons in other electrochemical applications

Thus phosphorus-doping of carbons – either as a single dopant or as one heteroatom in codoping approaches – is a highly promising concept for the development of novel ORR catalytic systems. In the following we would nevertheless like to show that P-doping is by far not limited to this, but also allows for other applications in the wide field of electrochemistry and energy. Therefore we will further introduce some other concepts, also emphasising the promising potential of phosphorus as a doping

agent: on the one hand phosphorus-functionalised carbons in supercapacitors and on the other hand phosphorus-doped carbon nitride materials. Already in 2009 Hulicova-Jurcakova *et al.* have presented first results on P-functionalised carbons as supercapacitor materials. The authors used phosphoric acid as a reactive agent during the carbonisation of various carbon precursors, yielding P-functionalised microporous carbons with outstanding behaviour in supercapacitors. One special and most remarkable observation was the increase of the voltage range tolerated by the electrode material.[156] Furthermore, phosphate-functionalised carbon monoliths have been presented recently by del Monte *et al.* who modified their meanwhile well established concept of deep eutectic solvent based carbon synthesis[64,157–160] in a way that allows for the incorporation of phosphorus. During the acid catalysed condensation reaction towards monolithic resins and thus carbons, the authors have used phosphoric acid as the catalyst. Carbonisation without antecedent washing of the catalyst yielded phosphate functionalised carbon monoliths with a phosphorus content of ~8 wt% according to EDX analysis; furthermore the results were supported by solid state ^{31}P NMR spectroscopy. The monoliths with their hierarchical porosities – including a macroporous level and an ultramicroporous level (compare Fig. 9) – have shown remarkable properties as supercapacitor electrodes, reaching energy densities of up to 13 W h kg^{-1} and power densities of up to 10 W kg^{-1}. These values are unique within the class of such monolithic carbon materials.
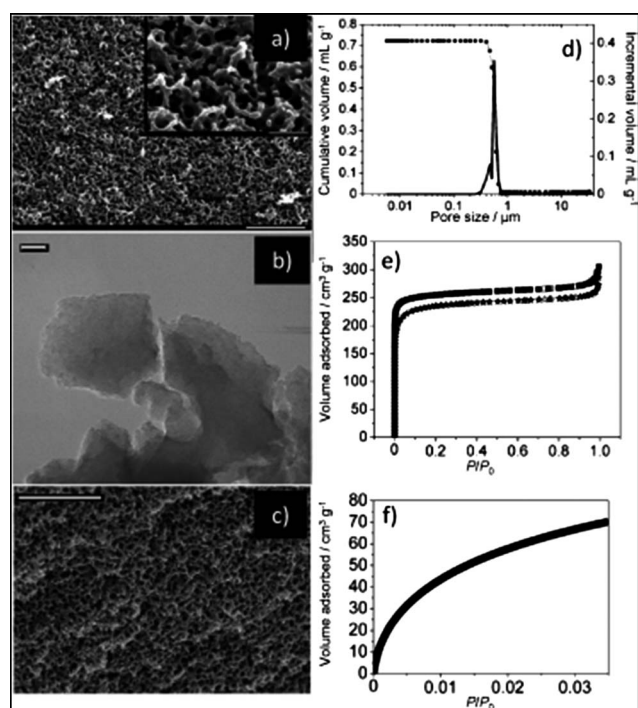

Fig. 9 (a) SEM micrograph of PfCM. The inset shows a detail of the morphology. Bars are 5 and 1 μm, respectively. (b) TEM micrograph of PfCM. Bar is 60 nm. (c) SEM image of nfCM (obtained from the pyrolysis of a washed resin). Bar is 5 μm. (d) Mercury porosimetry of PfCM. (e) Nitrogen adsorption–desorption isotherms registered at −196 °C of PfCM (★) and nfCM (■) obtained by calcination of non-washed and washed phenolic resins, respectively. (f) CO$_2$ adsorption isotherm of PfCM registered at 0 °C. [Reprinted with permission from ref. 161; copyright © 2012 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.]

Hence, by far the most remarkable effect of the phosphate functionalities is – in agreement with the previously discussed study – the widening of the electrochemical window the monoliths are persistent in towards a range of 1.4 V.[161] Su *et al.* chose a different way of producing their phosphorus containing carbon electrodes for supercapacitors. In a multicomponent self-assembly process under hydrothermal conditions phosphorus- and boron-codoped resins have been obtained and subsequently carbonised. Thereby ordered mesoporous doped carbons have been synthesised, showing good supercapacitance properties.[162] Meanwhile also a phosphorus-doped exfoliated graphene has been tested successfully as the electrode material in supercapacitors.[163] The other concept concerning phosphorus doping beyond electrocatalytic application in ORR is a study on phosphorus doping of graphitic carbon nitride, presented by Zhang *et al.* in 2010. Graphitic C$_3$N$_4$ was synthesised by thermal condensation of dicyandiamide with 1-butyl-3-methylimidazolium hexafluorophosphate added in amounts of up to 30 wt% to direct the condensation reaction towards an incorporation of the P-atoms into the forming graphitic carbon nitride polymeric lattice. The chemical incorporation of the phosphorus into the backbone of the material could be evidenced by solid state ^{31}P NMR spectroscopy and XPS. By this P-doping, the electric conductivity of the carbon nitride material is significantly enhanced by several orders of magnitude.[164]

Throughout this section we could show that phosphorus is a highly interesting and promising, however still young, candidate for doping or codoping carbon materials. Especially electrocatalysis of ORR is a thriving field of application for such materials; nevertheless these are not limited to this at all. It is most likely that in the very near future numerous studies will be published. On the one hand this will be to create a manifold synthetic toolbox – most recently an ionic liquid based approach for the synthesis of P–N-codoped carbons has already been reported. By using phosphonium halide additives in the carbonisation of ionic liquids, the codoped carbons become accessible. Furthermore they exhibit an intrinsically enhanced BET surface area which can be tuned by the amount of additive applied.[165] On the other hand, more elaborate and advanced applications in the field of energy recovery can be foreseen.

Conclusions

Despite the importance of nitrogen-doped carbon materials, this overview has clearly shown that there is an entire class of doped carbons that lies beyond nitrogen. Also boron, sulphur and phosphorus enable advanced doping concepts for carbon materials. While boron changes the electronic structures of carbon materials in the opposite way, but just as beneficially as nitrogen does, using both dopants at the same time even can yield synergistic effects. Therefore nonetheless the synthetic procedure must be finely tuned to avoid mutual compensation of the effects that are so beneficial for especially fuel cell applications. When it comes to sulphur and phosphorus, the caused effects are attributed more to the formation of structural defect sites or favourable spin densities throughout the

carbons, as here the electronegativities of carbon and the dopants are closer to each other. Regarding the wide spectrum of numerous synthetic routes and application profiles, it is still difficult to foresee which candidates will have the chance of a long-term breakthrough and will finally enter industrial scales of production. A lot of the materials exemplarily shown throughout this article can be obtained by simple annealing of crude carbons or carbon precursors in a reactive atmosphere. Furthermore the reactants, such as phosphoric acid or boric acid, are relatively cheap and might allow for an economic use of the as derived materials. Nevertheless the entire field is still very young, and one can be curious about what kind of materials' properties and application profiles will be developed in the future based on this concept. Already now the potential is undoubtful, and it will be highly interesting to follow the further progress in advanced heteroatom doped carbons, and how such materials will begin to revolutionise the field of materials for energy applications.

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