Synthesis of Doped Porous 3D Graphene Structures by Chemical Vapor Deposition and Its Applications

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Graphene doping principally commenced to compensate for its inert nature and create an appropriate bandgap. Doping of 3D graphene has emerged as a topic of interest because of attempts to combine its large available surface area—arising from its interconnected porous architecture—with superior catalytic, structural, chemical, and biocompatible characteristics that can be induced by doping. In light of the latest developments, this review provides an overview of the scalable chemical vapor deposition (CVD)-based growth of doped 3D graphene materials as well as their applications in various contexts, such as in devices used for energy generation and gas storage and biosensors. In particular, single- and multielement doping of 3D graphene by various dopants (such as nitrogen (N), boron (B), sulfur (S) and phosphorous (P)), the doping configurations of the resultant materials, an overview of recent developments in the field of CVD, and the influence of various parameters of CVD on graphene doping and 3D morphologies are focused in this paper. Finally, this report concludes the discussion by mentioning the existing challenges and future opportunities of these developing graphitic materials, intending to inspire the unveiling of more exciting functionalized 3D graphene morphologies and their potential properties, which can hopefully realize many possible applications.

1. Introduction

Since the extraction of graphene in 2004 via mechanical exfoliation,[1–3] also referred to as the scotch tape method, the material has fascinated the research community, due to its extremely high charge carrier mobility, superb thermal conductivity, and superior mechanical strength. In addition, graphene offers a high specific surface area, unparalleled flexibility, and high transparency. All these unmatched properties in a single material enable its use in a wide range of applications such as wearable and lightweight electronics as well as photovoltaic and supercapacitor devices.[3–8]

Historically, graphene has been reported in various forms classified as zero-dimensional (0D) to 3D, such as graphene quantum dots (QDs), nanobelts, and foams.[9–15] However, 3D graphene nanostructures are significantly different from other kinds, with their interconnected porous networks based on two-dimensional (2D) graphene sheets. Due to their hollow structure, 3D graphene has
shown exceptional performance in many useful applications, such as energy storage. Typically, 3D graphene can be in powder form or show a macroporous interconnected framework. Powder-form 3D graphene consists of individual nanosized pieces such as graphene nanoshells and nanocubes, while the latter consists of a continuous seamless monolith or hierarchical nanoporous graphene structure such as graphene nanofoam, graphene sponge, a graphene–carbon nanotube hybrid, or biomorphic graphene.\[12,16–29\]

Some 3D forms are shown in Figure 1b–j. Olszowska et al.\[19\] and Chen et al.\[20\] have elucidated the 3D graphene structure.

Graphene doping received attention mainly in researchers’ attempts to overcome the drawbacks presented by its inert nature and to generate a bandgap, which would help attain properties highly desirable in the catalysis and semiconductor industries, respectively. This could be achieved by exploiting the intrinsic nature of doped atoms (different in electronegativity and size) that resulted in charge polarization and a spin density upon integration in the graphene architecture.\[30–33\] In addition, doping also provides graphene with distinctive chemical, structural, electrical, optical, and magnetic characteristics.\[31,33–39\]

It has been demonstrated both theoretically and experimentally that doping contributes significantly to the properties of 2D graphene, as can be seen in Figure 2a–g.\[29,30,32,40–50\] Doping of 3D graphene is still considered an emerging topic of research and many investigations have been undertaken to utilize the properties of these unusual graphitic derivatives such as their large accessible surface area; high electron mobility due to the interconnected porous architecture; and superior catalytic, chemical, and biocompatible properties generated by doping\[31,33,51–53\] and, in the process, uncover exceptional synergy between 3D graphene forms and the doped elements.\[24,25,27,29,43\]

The doping of graphene has been summarized by many researchers and discussed from various perspectives.\[31,33,54–61\] Herein, we explicitly pay attention to the chemical vapor deposition synthesis (CVD) of doped 3D graphene (which is the first effort according to our understanding) by incorporating various foreign atoms (such as N, B, S, and P) into 3D graphene. Specifically, our goal was to cover the recent CVD-based development of doped 3D graphene, single- and multielement doping, and the applications of the resulting materials in various fields such as in energy generation, gas storage, and biosensors, as shown in Figure 3. Finally, a summary and prospects and outlook for the challenges in CVD synthesis and controlled doping are presented.

2. CVD Synthesis

Synthesis of 3D-doped graphene (3DDG) by many synthetic approaches has been reported so far (Table 1). It is worth noting that, since 2006, CVD has been considered a scalable, high-quality, and reliable production method.\[86–92\] In addition, CVD likely grows materials directly over the fabrication substrate (through the use of economic precursors)\[89,91,94\] and can guarantee high yield of good-quality products, which is crucial for large-scale practical applications.\[95,96\] As a result, CVD is now extensively used for 3DDG growth, which is the key focus of this review article.

Generally, CVD involves a one-step synthesis based on the breaking of precursor molecules (gas, liquid, and solid) in the gaseous state and their reforming over a substrate/catalyst surface (Figure 4).\[97–100\] Conventionally, template-assisted CVD is used for the synthesis of doped 3D graphene nanomaterials to obtain a perfect and tunable morphology in which graphene grows around a 3D or porous template and then the template is dissolved by an etchant. Subsequently, pristine freestanding 3DDG
with a truly 3D morphology are obtained (unlike that produced by other synthetic methods for which the morphology is not so pure),[21,26,101,102] and the sample is usually given the name of the template morphology. In addition to determining the final morphology, the template also works as a catalyst. Its role in this case is to significantly help reduce the activation energy of precursor molecules decomposition. However, there have also been reports of noncatalytic template-assisted CVD growth of porous graphene.[15,21,26,87] Generally, metallic frameworks (e.g., Ni foam), oxides (e.g., MgO powders/nanoparticles), biomorphic templates (e.g., seashells), minerals (e.g., zeolites), as well as, dielectric substrates (e.g., Al₂O₃) are employed as a sacrificial growth surface (template).[20,21,24,27,29,31,33,87] In CVD, some parameters critically affect the development of doped 3D graphene nanomaterials, such as the template/substrate, which determines the 3D morphology of the developed material; the dopant/carbon ratio, which significantly controls the doping content; the flow rate, which determines the thickness or number of layers; and the final temperature, which can affect several features such as the doping configuration, doping content, and morphology of the 3D materials produced. In addition, in CVD the cooling step can also play significant role, especially in case of high solubility substrates, e.g., Ni, which is important for controlling the film thickness (number of layers) since the C (and dopant) solubility is high. Typically, fast cooling is employed for good quality growth. Film thickness can also be adjusted through the growth time. Moreover, the contribution of the precursor to the resulting product is also significant but is generally considered to be secondary.[87,90,103,104] The advantage is that these parameters can be controlled externally, which can lead to controllable growth. Thus, herein, we intend to highlight the effects of various CVD parameters on the synthesis of single-element- and multielement-doped 3D graphene.

2.1. Single-Element Doping

Single-element (e.g., N and S) doping has significantly improved the attributes of 3D graphene, such as its electrochemical and storage properties. Interestingly, due to the inherent features of the foreign atoms, a variety of bonding configurations[105,106] are observed for graphene with a single dopant (Figure 1a), which could be beneficial for different applications.[31,107] For instance, N has three common bonding configurations with graphene: in-plane and out-of-plane. The former is graphitic while the latter is nongraphitic (bonding with dangling carbons, which leads to boronic and borinic ester functionalization).[53] A theoretical study has predicted various bonding configurations for S although thiophene- and oxide-based configurations are commonly observed.[108] Similarly, experiments have clearly showed that P exhibits two bonding configurations, namely, P=O and P=C. Due to the different bonding configurations each dopant shows, the materials produced can potentially shows diverse properties as a function of each distinctive configuration and their concentration, e.g., graphitic N is significant for carrier
mobility while pyridinic N and pyrrolic N are essential for storage purposes. Additionally, in the case of small dopants (N and B), structural defects are marginal[31,104,109] whereas the defects are substantial for large dopants (S and P). This feature could be useful if deliberate; therefore, a detailed insight into the effects of doping and properties of the resulting materials has been provided in references.[31,33]

CVD is an efficient and direct (since it avoids multiple synthetic steps) method for producing high-quality single-element-doped 3D graphene with perfect morphologies (such as that obtained by template-assisted CVD). [110–112] Precursors in diverse forms (single- and multiprecursor approaches as well as solid, liquid, and gaseous precursors) and a variety of templates (metallic and metallic oxide ones such as Ni and MgO, respectively) under different growth parameters have been employed to produce distinctive 3D graphene morphologies with different doping contents and configurations (Figure 4).[110,112–114] In the following sections, CVD synthesis of N-, B-, S-, and P-doped 3D graphene will be discussed, which have also been listed in Table 1.

2.1.1. Nitrogen-Doped 3D Graphene

N-doped 3D graphene forms have been studied extensively because of their similarity in size with carbon and thus their

Figure 2. Graphene characteristics induced by incorporation of foreign atoms (doping). a) Source–drain current ($I_{ds}$) versus various back gate voltages ($V_G$) for the N-doped graphene FET (field effect transistor) device. Adapted with permission.[40] Copyright 2009, American Chemical Society. b) $I_{ds}/V_G$ characteristics for B-doped graphene (red curve) and pristine graphene (black curve) devices. Adapted with permission.[41] Copyright 2013, Wiley-VCH. c) Band structure of monoatom B-doped graphene (blue ball signifies B atom) with d) corresponding geometry. Adapted with permission.[42] Copyright 2013, The Royal Society of Chemistry. e) N and S codoped porous graphene possible catalytic mechanism. Adapted with permission.[43] Copyright 2015, Wiley-VCH. f) Tridoped graphene (N, S, and P codoping) expected geometry with unified defects at curvature. Adapted with permission.[29] Copyright 2016, Wiley-VCH. g) Temperature dependent electrical transport of N-doped graphene. The inset corresponds to the changing ln($R$) with respect to $T^{-1}$ within the temperature window of 100–300 K). Adapted with permission.[44] Copyright 2011, Wiley-VCH.

Figure 3. High-quality single- and multielement-doped 3D/porous graphene synthesis by CVD, which is significant for energy generation/conversion, gas storage, and biomedical applications.
high compatibility with a graphene matrix, and different research groups have reported different morphologies for it. Recently, Wang et al. employed a single-solid-precursor CVD approach to develop N-doped porous graphene. They pressed a mixture of melamine (melamine (C₃H₆N₆) as both C and N source) and Ni nanoparticles (as the template) to a large single piece (pellet), which they later on annealed in a CVD reactor: the schematic for the growth can be seen in Figure 5a. The obtained sample was a highly crystalline interconnected network of few-layered graphene (Figure 5b–d). Additionally, N existed in pyridinic, pyrrolic, and graphitic forms, the presence and content of which showed a dependence on the growth temperature. It was demonstrated that the N concentration was low at high temperatures.\[110\] In a similar way, Li et al. for the first time, obtained highly N-functionalized graphene–carbon nanotube (CNT) hybrid architectures (with N doping levels of up to 12.7 at%) with a substantial pyridinic configuration. Interestingly, the authors claimed a unique role of the Ni substrate, wherein they provided Ni nanoparticles that caused the formation of N-doped CNTs over the N-doped graphene.\[111\]

Doping 3D graphene with nitrogen can result in versatility arising from the use of solid as well as liquid precursors. In a typical experiment, Shi et al. cracked a mixture of pyridine (C₅H₅N) and methane (CH₄)—used as nitrogen and carbon sources, respectively—and reported a unique 3D N-doped graphene morphology in which the N-doped graphene was coated around porous pristine graphene. Initially, methane led to the growth of porous graphene over a MgO template at an elevated temperature (900 °C) and then the system was cooled to 750 °C, following which pyridine was injected to develop the N-doped graphene coating over porous graphene. Interestingly, this scaffold left most of the N dopants exposed as well as retained the conductivity of porous graphene: both of these factors are essential for catalytic applications. In addition, the obtained porous sample was a few layers thick and exhibited a high surface area (1531 m² g⁻¹) as well as a dominant pyrrolic N configuration (1.3 wt% N content), which could be attributed to the lower growth temperature of the coated layer.\[112\]

Table 1. Summary of synthetic approaches (non-CVD and CVD) for fabricating doped 3D graphene.

| Doped 3D graphene material | Synthesis method | Ref. |
|----------------------------|-----------------|-----|
| N-doped Hydrothermal, pyrolysis, solvothermal, ball milling | [62–68] |
| B-doped Hydrothermal, annealing | [69–71] |
| S-doped Hydrothermal, annealing, ball milling-annealing | [72–74] |
| P-doped Hydrothermal-annealing, ball milling | [75,76] |
| N/B codoped Hydrothermal, calcination | [77,78] |
| N/S codoped Thermal method | [79,80] |
| N/P codoped Thermal method, hydrothermal-microwave treatment | [81–84] |
| N/S/P codoped Pyrolysis | [85] |
| N-doped Chemical vapor deposition | [25,27,110–117,133–135,151,158] |
| B-doped Chemical vapor deposition | [120] |
| S-doped Chemical vapor deposition | [24,121,122,152] |
| P-doped Chemical vapor deposition | [123,124] |
| N/B codoped Chemical vapor deposition | [120,127] |
| N/S codoped Chemical vapor deposition | [43,128,129] |
| N/P codoped Chemical vapor deposition | [130] |
| N/S/P codoped Chemical vapor deposition | [29] |

Figure 4. Schematic illustration of a CVD reactor (template-assisted thermal CVD approach), with various growth aspects and growth steps indicated. Different forms (solid, liquid, and gas) of precursors are fed into the hot CVD reactor, which helps decompose and form different carbon/dopant species under controlled growth conditions. Various control parameters: for example, temperature, time, pressure, flow rate, and carrier gas allow the deposition of sp² carbon and doping agent (e.g., N) over 3D/porous template. Templates include metal frameworks (e.g., Ni foam), or powder (e.g., MgO nanoparticles). Finally, the template is dissolved away by an etchant which result to high-quality graphene (doped) with a 3D architecture.
In order to avoid the use of multiple precursors, two separate groups (Feng et al. and Chen et al.) utilized ethylenediamine (C$_2$H$_8$N$_2$) as a single precursor for both C and N feeding, which led to 3D N-doped graphene over Ni foam as a template. Both groups separately reported the same range of pore diameters (200–600 µm) for the obtained materials although the materials they obtained were multi- and few-layers thick, respectively. Furthermore, XPS analysis demonstrated the presence of the three dominant N configurations, i.e., pyridinic, pyrrolic, and graphitic. [113,114] Recently, Ito et al. successfully developed N-doped nanoporous graphene by cracking pyridine as a sole liquid precursor over a porous Ni template on a CVD setup. The resultant materials were a few layers thick with a high surface area (1000 m$^2$ g$^{-1}$) and variable porosity (100 nm–1.5 µm). Importantly, it was observed that growth temperature and time significantly affected the as-grown material porosity, which decayed as both the parameters evolved. It has also been demonstrated that the temperature significantly influences the N doping content, which declines with a rise in temperature. [115]

Similarly, Mo and his coworkers followed the same sole precursor (pyridine) and template approach for developing 3D N-doped graphene foam at an elevated temperature. The as-grown sample was porous with a significant surface area of 392.8 m$^2$ g$^{-1}$, which was then post-treated for encapsulation of Ge quantum dots (QDs) for application as a lithium-ion battery anode material. [116] Uniquely, Muñoz-Sandoval et al. reported the use of aerosol-assisted CVD for developing a sponge-shaped N-doped graphene material. The authors used benzylamine (C$_7$H$_9$N) as a single precursor with both carbon and nitrogen, including ferrocene and thiophene. The ferrocene acted as a catalyst while the presence of S resulted in the 3D morphology of the growing material. The experiments were carried out at different locations inside the CVD reactor and it was found that samples grown at the hottest zone showed a perfect sponge topography and included a substantial N content displaying a quaternary N configuration, which agreed well with the assumption that a high temperature promotes the graphitic N configuration. [25]

A gaseous precursor has the advantage of controlling the flow rate and dopant/carbon ratios, which can adjust the film thickness and doping concentration. Recently, Wang et al. demonstrated the CVD synthesis of a N-doped mesoporous graphene framework by cracking a gaseous mixture of ammonia (NH$_3$) and methane over MgO as the template substrate with a doping level of up to 3.41 at%. Binding energy analysis confirmed various N configurations as well as a high specific surface area of 1440 m$^2$ g$^{-1}$. [117] In another report, Tian et al. used a metal alloy as the growth substrate and ethylene (C$_2$H$_4$) and ammonia as precursors to form a N-doped graphene/CNT hybrid material. They reported high specific surface areas of 812.9 m$^2$ g$^{-1}$, as determined by Brunauer–Emmett–Teller isotherms, and the coexistence of graphitic, pyrrolic, and pyridinic N configurations with a total doping of 0.58 at%. Importantly, the Raman spectrum of the sample clearly showed radial breathing modes.

Figure 5. a) Schematic illustration of porous N-doped graphene fabricated by CVD. b) SEM image of porous N-doped graphene. c,d) Low- and high-magnification TEM images of porous N-doped graphene, respectively. The inset shows the selected area electron diffraction pattern. Adapted with permission.[110] Copyright 2018, Elsevier. e,f) SEM images of S-doped graphene not subjected to Ar plasma treatment and subjected to Ar plasma treatment, respectively. g,h) TEM images of S-doped graphene not subjected to Ar plasma treatment and subjected to Ar plasma treatment, respectively; the yellow circles show the holes generated by plasma treatment. i) Raman spectra for pristine, untreated, and plasma-treated S-doped graphene. Adapted with permission.[24] Copyright 2018, Springer Nature.
which usually suggest the presence of a single-walled carbon nanotube network.[27]

2.1.2. Boron-Doped 3D Graphene

2D B-doped graphene produced by CVD has been widely investigated.[48,118,119] However, 3D B-doped graphene fabricated by CVD has been rarely reported. According to our understanding, only one report exists of a work wherein Xue et al. obtained 3D B-doped graphene for the first time by template-assisted CVD in conjunction with B and N codoping (which will be discussed later in Section 2.2.1). The obtained sample showed inferior boron doping (2.1 at%) with an obviously porous morphology,[120] which could be useful in many applications, e.g., in gas sensing and energy storage devices.

2.1.3. Sulfur-Doped 3D Graphene

CVD procedure is inferior in terms of integration of S atoms in porous graphene: this could be due to the large size and high growth temperature of S, which make it thermodynamically unstable and leads to a poor doping content. Despite this, researchers have developed S-doped porous graphene by CVD that have shown great potential in energy-related applications and storage purposes. For instance, Hassani et al. used S powder with acetylene (C2H2) as the dopant and carbon precursors, respectively, over Fe/CaCO3 as the catalyst/substrate over a mild growth temperature window. Subsequently, doped multilayered graphene nanostructures were produced with a maximum doping level of 5 at% that showed a thiophene bonding configuration.[121] Han et al. reported few-layered highly crystalline S heterographene with a doping level of 1.0 at%. Their work used a sole precursor (thiophene (C4H4S) provide both C and S) at a high growth temperature (800 °C) over a nanoporous nickel substrate. The S dopant existed in the forms –C=S–C=–, –C=S–, and those containing oxide moieties (–C=SO2=–), as confirmed by compositional and binding state analysis (XPS). As expected, the grown sample was nanoporous and showed a large surface area of 775 m2 g−1 and high discharge capacitance (4920 mAh g−1) when used as electrode materials.[122] Similarly, Zhou et al. used a single precursor (thiophane (C3H3S2) supply both carbon and sulfur) to develop a S-doped graphene foam (Figure 5e,f) that was Ar plasma treated to create more defects or active sites, which are crucial for the hydrogen evolution reaction (HER). The S-doping content was 2.9 at% with uniform S distribution across the sample, as confirmed by EDS mapping. The plasma effect was clearly observed in the form of pores (after plasma treatment) in the TEM image and extra evolution of the D peak in the Raman spectrum (Figure 5h,i). However, Ar plasma treatment did not significantly disturb the covalent bonding between C and S.[24]

2.1.4. Phosphorus-Doped 3D Graphene

Generally, preparing P-doped porous graphene by CVD is considered challenging. This is because the large size of P makes it challenging to incorporate the element in the 3D graphene matrix under harsh growth conditions and therefore an inferior doping content is usually observed. Recently, Xu et al. demonstrated the successful growth of porous P-doped graphene using Mg3(PO4)2 as the template at a high temperature (900 °C) in a vertical-ambient-pressure chemical vapor deposition (APCVD) strategy. Methane gas provided carbon while Mg3(PO4)2 functioned as both the template and P dopant. The resultant sample was inferiorly doped (0.71 at%) with a substantial P–C doping configuration. The authors pointed out that such a low doping could be either due to size mismatch between P and C atoms or the high growth temperature, which does not favor P incorporation due to the low P–C binding energy.[123] Interestingly, Li et al. reported a single precursor CVD methodology wherein triphenylphosphine (C18H15P) was used as both the C source and the P source. Topological study clearly indicated the 3D architecture of the as-fabricated samples while compositional study demonstrated uniform P doping of 2.71 at% with P–C and P–O doping configurations.[124]

2.2. Multielement Doping

Recently, multielement doping has drawn substantial attention in attempts to achieve the concomitant coupling of the features of codopants in one material, thus establishing superior properties in terms of several attributes as opposed to the advantages offered by the single doping components, such as the ability to undertake catalysis of important reactions.[30,31,33] However, in the case of N and B codoping, they usually incline to integrate together, promoting B–N configurations, which counter the synergistic effect, and thus the graphene behaves similarly to a pristine architecture in the case of such bonding configurations. Other common coding configurations tend to randomly position the multiple elements in the graphene skeleton.[105,125,126] Moreover, it has been predicted that P and N codoped graphene is more stable than P-doped graphene: this effect is observed when both the dopants are in close vicinity.[31]

Similarly, codoped 3D graphene fabricated by various synthetic approaches have been widely reported, as summarized in Table 1. Yet, control over the doping is among the major concerns, apart from the film thickness, distinctive 3D morphologies, and inferior quality of the material produced. Interestingly, CVD has the potential to overcome these challenges, producing high-quality graphene with controlled thickness and uniform allocation of foreign atoms: this is due to CVD route being capable of significantly affecting the growth conditions.[58,120,127,128] Generally, the same CVD strategies and growth conditions have been adapted for codoping as those used for single-element doping.

2.2.1. N/B Codoped 3D Graphene

Xue et al. reported N and B codoped graphene foam for the first time, which they prepared using Ni foam as the template and melamine borate as the single precursor for both the dopants. A 3D porous morphology was clearly visible under SEM with a thickness of few layers. Moreover, XPS and FTIR analyses
confirmed the presence of covalent attachment of N and B atoms in each case as well as the uniform distribution of N and B (Figure 6h–k). The doping concentrations achieved for N and B were 4.5 and 3.0 at%, respectively.[120] Similarly, Jin et al. developed crumpled N and B bidoped graphene sheets by noncatalytic APCVD. Urea (CH4N2O), boric acid (H3BO3), and polyethylene glycol (C2nH4n+2O2n+1) were used as the N, B, and C sources, respectively, in the temperature window of 800–1000 °C. The group observed three competing growth configurations: C–B, C–N, and B–N. It was also demonstrated that high temperatures favored the first two configurations, while the third was favored by low temperatures, although this assumption is true for the particular range of precursor ratios studied.[127]

2.2.2. N/S Codoped 3D Graphene

Considering the significant properties of pristine graphene and single-element-doped graphene, multielement-doped graphene will likely exhibit unique properties. Inspired by this idea, N and S dual-doped graphene materials have been developed. Xu et al. proposed the successful few-layer N and S bidoping of graphene (oxide) by employing liquid precursors. The authors cracked a mixture of thiophene and pyrimidine (C4H4N2) as S and N suppliers and subjected them to bimetallic (Fe–Co/γ-Al2O3) catalyst-assisted vertical wall CVD at a relatively mild growth temperature (700 °C). The resultant sample showed uniform distribution of both S and N dopants throughout the sample, as confirmed by XPS and elemental studies. Importantly, it was observed that graphitic N was favored at high temperatures but it was compromised by a low N content because of the inferior thermodynamic stability of the material at high temperatures.[128] Recently, another group adopted the template CVD route, employing pyridine and thiophene (as C, N, and S sources) and obtained high-quality N and S dual-doped nanoporous graphene at various temperatures (Figure 6a–c). Furthermore, binding energy analysis evidently detected dominant graphitic N and thiophilic S configurations as well as other minor configurations within the working temperature window.[43] Interestingly, Chen et al. obtained a unique architecture of graphene that could be described as a skin of doped graphene coating nanoporous pristine graphene in a two-step CVD approach (such architecture has also been reported by Shi et al.[112]). In this work, first, nanoporous graphene was developed at an elevated temperature of 900 °C...
and subsequently treated with Ni salt; then, it was treated with pyridine and thiophene as N and S sources, respectively. The as-fabricated porous materials showed a N and S codoped blistered skin supported by porous graphene. Formation of the blistered bi-dopant coat could be attributed to the conversion of Ni salt into Ni nanoparticles during the growth, which was deliberate and can be helpful in energy-related contexts, e.g., the HER.[129]

2.2.3. N/P Codoped 3D Graphene

N/P codoped 3D graphene has been widely reported to have been synthesized by other synthesis protocols[82–84] but has been rarely developed by CVD. One of the first reports that dealt with the growth of N and P codoped porous graphene was made by Mai and co-workers, who used methane and (NH₄)₃PO₄ as the carbon and N and P sources, respectively. MgO (as the template) and the (NH₄)₃PO₄ composite were calcined up to 900 °C under a flow of methane in a vertical CVD reactor setup. The as-grown samples were porous in nature and their textural properties are clearly demonstrated in Figure 6d–g, which shows reasonable N and insignificant P doping (2.6 and 0.6 at%, respectively). Interestingly, the authors claimed that P dopants were more effective as Li ion storage sites, suggesting that they are more favorable for use in battery anode materials.[130]

2.2.4. N/S/P Codoped 3D Graphene

CVD growth is not limited to single- or bielement doping but tri-elemental doping of 3D graphene has also been achieved in attempts to facilitate superior synergy among three dopants, although this field of work has not been explored sufficiently. Recently, Ito et al. reported N, S, and P tridoped nanoporous graphene prepared by CVD. The group employed benzene, pyridine, thiophene, and triphenylphosphine over a NiO substrate at a temperature of 750 °C (Figure 7a). Notably, the porosity was clearly visible under SEM (Figure 7b–d) and uniform doping was evident in electron energy loss spectroscopy mapping. It was demonstrated that the curved region, which had more topological defects, favored more chemical functionalization; in other words, the curved regions were dopant-rich areas (Figure 2f) in the as-grown porous graphene that could be useful for catalytic purposes.[29]

Although high-quality and realistic 3D morphology of doped 3D graphene has been achieved using CVD, certain disadvantages have been reported for the method, such as harsh growth conditions that will increase the total cost, trivial doping contents, and low yield. In addition, the use of a template, the template etching process, and presence of system residues reduce the quality of the product and further increase costs. For these reasons, doped 3D graphene may be less common than other materials.[20,110,123,128] However, this area is emerging, and various improved CVD techniques are necessary to achieve tunable products and to realize a significant balance between the quality and quantity of developed 3D-doped graphene.

3. Applications

3.1. Energy Generation

3.1.1. Fuel Cells and Catalytic Reactions (Oxygen Reduction Reaction (ORR), Oxygen Evolution Reaction (OER), and HER)

Developing an effective catalyst that is highly efficient, economical, and environmentally friendly is imperative in attempts to
resolve the global energy crisis. In this context, 3D graphitic materials should be prioritized because of their superior conductivity, high surface area, low density, and pliability (low density and pliable features are significant for wearable technologies). However, both experimental and theoretical studies have demonstrated that pristine graphene shows ordinary catalytic responses. Interestingly, chemical doping of graphene can address this issue by integrating foreign atoms into the graphene matrix, which results in a desirable charge polarization and spin density across the graphene nanostructure.\[31,33\]

An electrocatalytic process is a surface phenomenon. For example, in the ORR, an O$_2$ molecule is chemisorbed on the surface of a catalyst, which is followed by its conversion to OH$^-$ (Figure 8a).\[20,131\] In addition to the effects of single-element doping and geometrical defects, codoping offers the advantage of exploiting dual doping, which significantly enhances the catalytic performance.\[24,29,127,129\] Interestingly, 3D N-doped graphene showed bifunctionality in that it promoted both the ORR and the OER.\[20,117\] These effects were observed in the form of an increase in the values of parameters such as the onset potential, current density, stability, selectivity, and electron transfer number (Figure 8b–f).\[27,120,124,127\] Different theories have aimed to clarify the mechanism by which doped graphene catalysts function. Because of the different bonding configurations involved and trace amounts of metal residues in the doped graphene, predicting the possible catalytic mechanism undertaken by the doped graphene is challenging. It is likely that the mechanism for codoped graphene catalysis is even more complex.\[20,131\]

It has been established that the doping level and bonding species largely enhance the HER activity. Importantly, it has been predicted that the Gibbs free energy of H* adsorption can be highly reduced by the binary effects of chemical doping and textural defects, which can account for the exceptional activity of HER activity.\[20,29,43\] Single-element doping (e.g., S-doping) and codoping (e.g., N and S) have both largely improved HER yields.\[24,43,129,132\] Recently, Ito et al. reported superior HER results by exploiting tridoped graphene (N, S, and P), as can be seen in Figure 9a,b.\[29\] All these reports suggest that chemically functionalized 3D graphene materials are exceptional candidates for substantially improving the catalytic activity compared to that offered by metal-based catalysts.

3.1.2. Batteries

Meeting the increasing demand of energy, high energy density, a long cycle life, and high rate performance for wearable battery devices is an urgent requirement. Different from conventional electrochemical electrode materials (e.g., graphite), the 3D graphene architecture provides a large accessible surface area, high electrochemical stability, and superior conductivity; these
properties endow graphene with ideal electrode properties. More importantly, doping with foreign atoms provide graphene with enhanced storage capacities and prominent electrochemical cycling stabilities while preserving its lightweight, highly spacious nature; excellent conductivity; and mechanical robustness and flexibility.[20,33,110,112,116,133] In this context, many experimental efforts have been conducted to explore the potential of single-element (e.g., N and S)-doped and codoped (e.g., N and P codoping) nanoporous graphene. Recently, Han et al. employed CVD-grown highly textured S and N individually doped graphene as Li–O2 battery cathode materials. The S-doped graphene and N-doped graphene samples showed high discharge capacities of up to 4920 mAh g\(^{-1}\) and 10 400 mAh g\(^{-1}\), respectively, which had never been achieved to that point according to the authors. Interestingly, the group further observed that N-doped graphene offers a high-discharge capacity while S-functionalized graphene cathodes show high cycling stability for up to 300 cycles, which signifies a long battery life. It was proposed that a high cycling stability of S-doped graphene could be due to the slow degradation of the S-doped architecture until 300 cycles contrary to that noted for N-doped and pristine graphene.[122] Reddy et al. reported the use of CVD-grown N-doped graphene (doping level of up to 9 at%) as Li-ion battery cathode materials. Importantly, the as-grown few-layer N-functionalized graphene demonstrated a higher reversible discharge capacity (0.05 mAh cm\(^{-2}\)) against graphene, which could be attributed to an excess of textural defects emerging due to nitrogen incorporation in the graphene architecture. The enhanced specific capacity can also be exploited by the N pyridinic bonding configuration in the graphene matrix.[134] Interestingly, Li et al. used biomorphic N-doped graphene, grown by noncatalytic biotemplate-assisted CVD, as a polysulfide cleaner, thus reducing the shuttle effect, which subsequently enhanced the electrocatalytic stability. Importantly, the biomorphic 3D N-doped device also showed remarkable thermal as well as mechanical stability and retained a high storage capacity (Figure 10a–d). This could be attributed to its large surface area, unique morphology, and tunable N-integration, which suggests that such a material can be applied to practical devices to obtain a superior performance.[135] Ma et al. developed few-layered P and N codoped 3D graphene (0.6 and 2.6 at%, respectively) using CVD as a Li-ion battery anode material in order to exploit the synergy effect of the elements. The resulting material, P and N codoped graphene, demonstrated excellent reversible capacity (2250 mAh g\(^{-1}\)) and cycling stability (stable even after 1500 cycles). The improved performance could be attributed to the increase in the electrical conductivity owing to P and N incorporation and generation of superior textural properties (large number of defects, high porous nature, and large surface area) by the doping and template synthesis method. Interestingly, the team concluded that the contribution of P doping to the high Li ion storage (referred to as a high storage capacity) was higher than that of their codopant (N).[136]

### 3.1.3. Solar Cells

Doped 3D graphene has shown great potential in realizing the fabrication of cost-effective, lightweight, flexible, and—more importantly—high-power-conversion photovoltaic solar cells to a greater extent than other materials such as transition metal compounds, conductive polymers, and graphitic materials.[136,137] For instance, Xu et al. used cross-linked P-doped graphene nanoflakes (Figure 11a) as the counter electrode in dye-sensitized solar cells (DSSCs).[123] Among available choices, e.g. N-, S-, and Si-doped graphene, the 3D P-doped graphene form has been the most successful in improving the catalytic reduction of I\(^3^-\) to I\(^-\) and achieving a commendable power conversion efficiency (7.08%) when compared to that of the benchmark Pt counter electrode (CE, 7.19%), as confirmed by the high photocurrent density of P-doped interconnected nanoflakes of graphene shown in Figure 11b.[123,138–140] This can be attributed to the insignificant electronegativity and large size of P compared to those of the carbon atom, which create a local charge gradient and more topological defects upon integration to graphene and thus lead to more catalytic sites and a higher catalytic activity. These features strongly suggest that P-doped graphene with controlled architectures and doping levels can potentially replace commercial Pt CEs.

### 3.1.4. Supercapacitors

Graphene-based supercapacitors or ultracapacitors have drawn extensive attention due to their high-power density, high
charge/discharge rates, and long durability including flexibility which is promising for the fabrication of wearable technology. For this reason significant research has and is devoted to graphene technology as a storage material exploring both 2D and 3D graphene materials.[141–143]

Recently, coupling foreign atoms (doping) with 3D porous graphene is allowing for a new trend to exploit the superior synergy of doping and the void nature as energy storage materials including supercapacitors.[144–148] These materials have also demonstrated remarkable performance in other energy-related applications such as fuel cells, batteries and solar cells (discussed in earlier sections).[31,33,122,123] Dopant integrated porous graphene has been synthesized by various different approaches (see Table 1) although the true promise of 3D morphology can be better realized by CVD.[20,141,148] Despite this, CVD developed doped 3D graphene materials as supercapacitor active electrode material has so far been poorly explored despite its enormous potential. Ma et al., reported CVD grown S-doped porous graphene and employed it as an active electrode material in supercapacitors. The devices exhibited remarkable storage capacity and capacity retention working long periods (Figure 12a, b). Furthermore, the group revealed that the high performance is due to the joint effect of both S-doping (promoting conductivity) and the high porous architecture, which demonstrate

Figure 10. a) Schematic of Li–S battery using N-doped biomorphic graphene separator. b) Charge/discharge capacity retention at different rates at 50 °C. c) Rate performance of the battery at 50 °C (thermal stability). d) Performance of the battery in a wearable device. Adapted with permission.[135] Copyright 2018, American Chemical Society.

Figure 11. a) Schematic of synthesis and corresponding N₂ adsorption–desorption isotherm for P-doped cross-linked graphene nanoflakes and pristine graphene. b) Photocurrent performance of DSSCs with porous P-doped, porous pristine graphene, and Pt as counter electrodes. Adapted with permission.[123] Copyright 2017, Elsevier.
that doped porous graphene has the potential to complement or substitute batteries in the practical applications.[141,148]

3.2. Gas Storage

Carbon dioxide (CO₂) emissions are rapidly growing because of combustion processes and causing significant global warming by promoting the greenhouse effect: thus, its storage is currently a matter of global concern. Similarly, storing hydrogen is also important because it is an efficient and clean energy source as well as essential in many other practical applications. Therefore, enormous efforts have been devoted to developing promising storage materials that exhibit high selectivity, substantial thermal and mechanical stability, as well as high porosity and can host a large content of an adsorbate such CO₂ and H₂. Various host materials (adsorbents) have been employed, e.g., metal nanoparticles decorated graphitic materials, to successfully improve the storage capacities of such systems. Generally, such materials suffer from poor thermal and mechanical stability, low storage capacity, lack of storage selectivity, and lack of adsorption reversibility.[33,149,150] In order to overcome these challenges, Xia et al. employed template-assisted CVD-grown N-doped nanoporous graphene for CO₂ accommodation: the material exhibited excellent storage performance. The adsorbent—the N-doped carbon network—showed superior textural properties, inherited from the substrate/template and a large adsorbate (CO₂) uptake capacity, which suggested that surface voids play a crucial role in CO₂ lodging. Importantly, adsorption interaction (adsorption energy, $E_{ad}$), which is the measure of the adsorbate–adsorbent bond strength, plays an important role in storage stability. The authors pointed out that, in the case of high CO₂ uptake, N doping substantially affects the adsorption energy, while at low coverage both the textural properties and N doping affect the adsorbate interaction. Furthermore, the N-doped adsorbent showed high reproducibility, exhibiting no change in its performance, which suggests adsorption stability. Importantly, selectivity is also a key property of the adsorbent, since it helps decide the acceptance of a desired species out of many. In order to investigate the selectivity, the material was tested using both CO₂ and N₂ and a ratio of 9.5 was obtained for their uptake, clearly demonstrating the adsorbent preference toward CO₂. These results conclude that both textural properties and N incorporation in carbon influence the CO₂ storage, an observation that could be extended to other materials in the future.[151] Later on, the same group reported a S-doped mesoporous carbon architecture grown using the same template methodology as a storage material. In this case, they employed two guest materials: CO₂ and H₂. The results were slightly different for each guest material, as in the case of H₂, the uptake capacity was influenced by textural properties and CO₂ uptake was affected by both the surface properties and S doping (Figure 13a,b). The researchers proposed that H₂ has a high adsorption energy due to generation of polarization by S across the carbon framework, unlike the CO₂ interaction, which is predominantly dependent on the textural properties and S functionality. These results suggest that both S incorporation and textured void spaces significantly contribute to the performance of the hosting adsorbate in terms of selectivity.[152]

3.3. Biosensors

Biosensors are diagnostic tools used to provide information about biosystems and are thus extremely useful in determining measures for disease prevention. The efficiency of biosensors is determined by their sensitivity, target selectivity, response time, and stability and performance retention upon repetitive use: optimization of all these parameters can pave the way for the practical application of such a sensor.[19,153,154] Graphitic materials, either solo or in composites with other materials, have been widely used in such sensors although 3D doped graphene comprises an emerging area and a lot of research is being undertaken to unveil the full potential of this novel class of materials. Insertion of foreign atoms endows graphene with remarkable biocompatibility, high selectivity, and extremely low detection limits while allowing improvement in the intrinsic features of graphene such as its charge carrier mobility, tunable electronic properties, and surface area.[19,33,155–157] In this regard, N-doped graphene is often studied because of its stable interaction with graphene and excellent electrochemical sensing properties. For instance, Feng et al. developed N-doped
graphene foam by a facile template-assisted CVD method and used it to fabricate a dopamine biosensor. The sensor showed an extremely low detection limit of $1 \times 10^{-9}$ m, which is superior to that of similar sensors. Additionally, it demonstrated high stability and performance preservation after several times of use and, more importantly, it was highly selective in experiments undertaken in the presence of other coexisting molecules such as glucose, ascorbic acid, and uric acid. Similarly, Liu et al. reported $\beta$-cyclodextrin ($\beta$-CD)-loaded 3D N-doped graphene substrate as a dopamine and acetaminophen biosensor and observed exceptionally high sensitivities (5468.6 and 2419.2 $\mu$A m$^{-1}$ cm$^{-2}$, respectively), greater than previously reported values. These results suggest that 3D doped graphene are exceptional materials for use in biosensors that can be used in practical biological sensing purposes. Recently, Chen et al. once again, proposed a porous N-functionalized graphene-based material; however, this time, it was used as a deoxyribonucleic acid (DNA) electrochemical sensor, the working mechanism and detection results for which are shown in Figure 14a,b. The biosensor detected extremely low concentrations of target DNA of up to $2.38 \times 10^{-15}$ m and responded even to a single-base DNA mismatch, suggesting the superior sensitivity and selectivity of the sensor. Furthermore, the biosensor exhibited high performance retention and reproducibility when used in the case of analyzing human blood serum samples. These results clearly suggest a strong interplay between the large specific surface area (which leads to high sensitivity to low DNA loading) and the high electrical conductivity of 3D N-doped graphene materials, which endow the material with excellent sensing properties.

4. Summary and Perspectives

In summary, high-quality CVD-grown doped 3D graphene materials have been reported as efficient candidates for use in...
in energy generation, gas storage, and biomedical contexts. Their porous nature, interconnected architecture, and high accessible surface area favors electron mobility and diffusion of guest species (such as ions or gas molecules), which remarkably improves the catalytic and storage potentials. Importantly, the integration of foreign atoms (N, B, S, and P) endows graphene with new or enhanced catalytic and chemical properties by introducing desirable charge polarization and spin densities.

Despite significant improvements made in the high-quality large-scale production of 3D-doped graphene, control over the doping configuration and concentration and the growth mechanism remain major concerns. High temperatures and harsh conditions hinder large-scale production using CVD and consequently commercialization of the technique. Apart from this, parameters of CVD such as the substrate used and etching residues significantly influence the traits of the graphene obtained. Therefore, it is highly desirable to develop a feasible and clean synthesis methodology capable of addressing these challenges. In addition, the doping configuration is known to play a significant role in the synthesis and, in the case of codoping, the scenario becomes even more complex. The controlled synthesis of doped graphene and reproducibility for a single doping configuration is highly desirable to determine the effect of a specific configuration on a particular property. Moreover, to ensure superior catalytic, chemical, and biocompatible properties for the 3D-doped graphene materials, its benchmark counterparts need to overcome considerable challenges, especially in terms of cost and prospect for commercialization. Current understanding of the synthesis and properties of doped graphene is far from complete and sometimes even comprises contradictory ideas because of the large and uncontrolled heterogeneity of the materials obtained using current synthesis approaches. The emerging applications of CVD-grown 3D-doped graphene materials for energy generation, gas storage, and biomedical applications have been surveyed in the present study. We are optimistic that a better understanding of the doping mechanism and doping properties based on both theoretical and experimental investigations can further development of a controllable synthetic procedure and incorporations of new dopants can greatly extend the application scope of doped graphene materials.

Graphene research will continue to thrive because of the new opportunities provided by heteroatom doping and 3D morphologies. This article aims to provide useful clues for developing new and controllable CVD methods as well as a better understanding of the growth mechanism and properties of doped graphene materials. We also hope that it will inspire more exciting applications of this growing family of nanomaterials.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

3D graphene, biocompatibility, CVD, doping, energy generation

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