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3D porous graphene-based structures - synthesis and applications

Kamila Żelechowska^{*}, Izabela Kondratowicz, Wojciech Sadowski

Gdansk University of Technology, Narutowicza St. 11/12, 80-233 Gdansk, Poland

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Introduction

Porous carbon-based materials are of the great industrial and academic interest due to their high surface area, low density, good electrical conductivity, chemical inertness and low cost of fabrication. Up to now, the main approach to obtain porous carbon structures has involved the pyrolysis of carbonaceous natural or synthetic precursors. After the isolation of graphene, the interest in 3D porous graphene-based structures (called graphene foams, sponges, networks or frameworks) aroused and methods of their production were introduced [1-5]. Their high porosity alongside their chemical and biological inertness makes such 3D porous graphene-based structures good candidates as chemical adsorbents [6-14] and tissue-engineering scaffolds [15-17]. However, the main advantage, as compared to other carbon-based structures, is their high electrical conductivity, thus they are mainly examined as an electrode material in devices such as (bio)fuel cells, batteries, and supercapacitors [4, 18].

It should be noted that there can be found number of papers describing porous graphene being two-dimensional materials and we stress here that these should not be confused with bulk 3D structures, as will be reviewed herein.

Synthesis of 3D porous graphene-based structures

Two main approaches to synthesis of porous graphene-based structures exist in the literature, these are the "template method" and "template-free method". The template-free approach focuses mainly on the self-assembly of graphene oxide and its reduction to graphene under elevated temperature leading to hydrogel formation (so called hydrothermal gelation). Other methods used in the template-free approach include centrifugal vacuum evaporation [6, 19], vacuum filtration [20-21], leavening [22] and sugar blowing [23].

In the latter, hard and soft templates are often used to organize the graphene sheets into porous structures. The most frequently used hard templates are polystyrene and silica spheres, mesoporous silica or metal (Ni or Cu) foams. 3D carbonaceous structures can be obtained by chemical vapour deposition [24-27], assembly and reduction of graphene oxide [28-30] or vacuum filtration [31]. Soft-templating methods are based on the self-assembly of the template and the carbon precursor together in solution. The soft-templating materials typically include polymers, block copolymers, and surfactants [4, 32-34].

Template-free methods

Recent studies have shown that the self-assembly of graphene oxide (GO) upon reduction, leads to the creation of free-standing reduced graphene oxide (rGO) hydrogels [1,2]. This method, termed hydrothermal gelation, is one of the most commonly used methods to realize 3D graphene-based foams; it requires low-cost reagents processed using simple apparatus. Generally, graphene oxide is obtained from graphite, frequently by the Hummers' method and its modifications [3, 35, 36]. Briefly, graphite is treated with strong oxidizing agents (e.g. $KClO_3/H_2SO_4$ [35]; $KMnO_4/H_2SO_4$ [36]) to produce graphite oxide (GrO), which is then exfoliated to form single or multi-layered graphene oxide. The reaction scheme is presented in Fig. 9.1. It should be noted, that graphite can be obtained from reused batteries as our research group showed in a recently published work, making the process increasingly eco-friendly [3].



FIGURE 9.1 Scheme of graphene oxide synthesis

The produced graphene oxide is then dispersed in a polar solvent (more often than not, water) and reduced thermally or chemically under appropriate pressure and temperature to form free-standing graphene hydrogels. When an organic solvent is used as a gelation medium, the formed porous structure is called an organogel. During the reduction reaction hydrophilic GO is transformed into hydrophobic reduced graphene oxide (rGO). The hydrophilic-hydrophobic balance dramatically influences the rGO assembly, together with π - π stacking, and van der Waals interactions between the carbon sheets in the reaction mixture [37]. As a result, 3D porous structures are formed, made of interconnected rGO sheets with encapsulated water molecules forming hydrogen bonds with the residual oxygen groups on the flexible rGO layers (see. Fig. 9.2). The Figure 9.3 shows the results of hydrogel formation from the graphene oxide suspension obtained in our laboratory. The magnified view (Fig. 9.3 B), presents interconnected rGO sheets forming a hierarchical three-dimensional structure.



FIGURE 9.2 Scheme of self-supported graphene hydrogel formation



FIGURE 9.3

A. Optical image of a vial with GO suspension (left) and a vial with rGO hydrogel (right)

B. A typical scanning electron micrograph of a hydrogel structure. (Scale bar: 5 $\mu m)$

The graphene hydrogels are then subjected to a suitable drying process and a xero- or aerogel is formed. During the drying process, often at room temperature, the solvents evaporate leading to a structural collapse of the pore structures, due to the capillary stress and the subsequent creation of xerogels. Aerogels are formed after supercritical drying when the liquid solvent is transformed into gas beyond its critical point. The removal of solvent proceeds in the absence of surface tension therefore without destroying the fragile pore network. The prevention of gel shrinkage can be ensured by decreasing the pressure and temperature using a vacuum freeze-drying approach. Xie et al. reported that the pore size, pore shape, and pore wall thickness are strongly dependent on the temperature of the freeze-drying [5]. Thus, various properties of graphene aerogels (such as mechanical strength, and the water and oil adsorption ability) can be engineered by controlling the freeze-drying temperature.

An example of hydrogel, before and after drying by different methods is presented in Fig. 9.4. A noteworthy difference in the shrinkage can be observed.



FIGURE 9.4

Optical image showing different shrinkage of hydrogel after drying

- A. rGO hydrogel
- B. Vacuum freeze-dried rGO hydrogel,
- C. Room-temperature dried rGO hydrogel

Hydrothermal gelation

Different approaches to the formation of three-dimensional self-assembled graphene hydrogels (3D SGHs) can be found in the literature. Recently, a facile method was proposed by Xu et al. [1,6]. The 3D hydrogel was formed from homogeneous GO aqueous dispersion in a Teflon-lined autoclave at 180°C, in just one hour, without any additional reductants or linkers. The obtained 3D SGH showed high mechanical strength and thermal stability. Three-dimensional self-assembled graphene hydrogels can also be fabricated by chemical reduction of graphene oxide with common reductants, such as sodium ascorbate, citric acid, hydrazine, NaBH₄, urea, ethyl alcohol, hydroquinone and the noble metals [4, 38-40]. Generally, lower temperatures are needed to create SGHs, if reducing agents are used. Usually, reductants are mixed with the GO suspension in water, or other solvents, and the reaction mixture is then heated in the autoclave. It was observed, that gelation occurs even near room temperature, however this process can be very time-consuming (more than 24 h) making it industrially incompatible. For example, increasing the temperature to around 90°C shortens the SGHs formation time, in the presence of ascorbic acid, to 1.5 h.

The pH of the suspension also plays a critical role in hydrogel formation. It was reported, that gelation of graphene oxide suspension at pH 10 led to hydrogels with low porosity (when the density is compared to graphite), but with much higher compressive strength (6-times higher than that of graphite) [41]. More porous structures can be prepared in neutral or acidic environment, but it should be remembered that very low pH may cause carboxyl group protonation which ultimately hinders hydrogel formation. It is also worth noting, that in the case of chemical reduction, using an autoclave is not necessary and it is possible to form graphene hydrogels in the open vessels [1], manifesting a significant time and financial saving. Moreover, chemical reduction and functionalization can be performed in one-step processes, as was shown by Xu et al. [39]. Here they reported a convenient strategy to prepare SGHs incorporating hydroquinones in the 3D graphene framework via π - π interaction, where hydroquinone served as a reducing and functionalizing agent. Our group have obtained aryl modified hydrogels, where anthracene residues were covalently linked to carbonaceous skeletons [40]. Some variation of thermal gelation of rGO was proposed by Ahn and Jang [42]. Self-assembled foam-like graphene structures were formed using a simple nucleate boiling method, which is governed by the dynamics of bubble generation and departure in the grapheme colloid solution. The idea of the process is illustrated in Fig. 9.5. In the first step, the rGO platelets, suspended in water, precipitate to form a thin film on the substrate lying on the bottom of the reaction vessel. Then, when heated at a continuous boil, air bubbles are generated. These air bubbles serve as a dynamic template for pores creation and the assembly of rGO platelets occurs on their surface. The porous structure is created with the help of the bubbles via condensation and hydrogen bonding between rGO platelets. The porous films were successfully self-assembled on different substrates, including silica, glass, polydimethylsiloxane (PDMS), aluminum, fluorine tin oxide and copper foil.



FIGURE 9.5

Scheme of graphene hydrogel formation by nucleate boiling method

Next to the self-supported graphene hydrogels described above, the 3D porous structures can be obtained from GO with usage of cross-linking agents as polyhydroxides, peptides, DNA, polycationic polymers, tetralkylammonium salts or polyvalent metal ions [4, 32, 43]. Linkers can form hydrogen or coordinate bonds with adjacent GO sheets, regulate the electrostatic interactions and influence the hydrophobic-hydrophilic balance providing an additional bonding force for the gelation. Figure 9.6 shows schematically the idea of the GO gelation in the presence of the cross-linking molecules.



FIGURE 9.6

Scheme of graphene hydrogel formation in the presence of cross-linking molecules

Bai et al. examined hydrogel formation in the presence of poly(vinyl alcohol), concluding that the hydrogen bonds between –OH rich polymer and oxygen groups in GO stabilize the formed network [44]. In a similar manner, Wei et al. produced highly porous hydrogels reinforced with carbohydrates as dextrans or cyclodextrins. Ji et al. [45] employed three types of carbohydrates (chitosan, glucose, β -cyclodextrin) to facilitate the creation of 3D graphene with the simultaneous reduction of GO. The samples had cylindrical shape with the network of interconnected pores of sizes ranging from submicrons to microns. Composite made of cellulose/rGO (with different ratios) was prepared by Ouyang et al. [46]. Ball milling-assisted chemical reduction of GO was followed by a coagulation in the presence of H₂SO₄ and a subsequent vacuum freeze-drying. Wood pulp was used by the Xu group as a source of cellulose, which was mixed with GO and ionic liquid as a reaction medium to produce biocompatibile and non-toxic hydrogel [47].

Positively charged compounds such as, polycationic polymers or tetraalkylammonium salts have been also used as linking agents [32-34]. In order to investigate the electrostatic interactions between linker and GO sheets, polydimethyldiallylammonium chloride was used. Here the creation of hydrogen bonds was excluded. The results revealed that electrostatic interactions are a more effective driving force than hydrogen bridges for graphene gel formation [32].

Stable, polymer supported graphene hydrogels were obtained in the presence of nonionic commercially available Pluronic triblock copolymer and α -cyclodextrin (α -CD). The hydrophobic segments of the copolymer bind to the hydrophobic surface of the graphene *via* hydrophobic effects, whereas the hydrophilic chains extend into the water and form host-guest complexes with α -CD molecules, forming supramolecular graphene based hydrogels [33].

Cheng et al. demonstrated three-dimensional graphene oxide-based hydrogels and organogels obtained through the self-assembly of a series of amphiphilic molecules, which possess a polar carbohydrate head group attached to a nonpolar pyrene group. The possible driving force for the gelation was attributed to the π - π stacking interaction between the pyrene groups and the graphene oxide central planes, together with hydrogen bonds between the cross-linking molecules and oxygen groups on the GO [34]. The self-healing and unusual stability in a variety of harsh conditions was revealed for graphene oxide hydrogels cross-linked with two-stranded DNA. This unique observation was attributed to the various interactions, including π - π stacking and hydrophobic interaction between the DNA bases and the graphitic domains of the GO, as well as the electrostatic/hydrogen bonding interactions between the bases of DNA and the GOs oxygen-containing groups [43].

Polyvalent metal cations were shown to stabilize the graphene hydrogel network by forming coordination bonds. Di- and trivalent metal ions, such as Ca^{2+} , Pb^{2+} , Cu^{2+} and Fe^{3+} , Cr^{3+} , respectively, coordinate hydroxyl and carboxyl groups on graphene oxide sheets enhancing their assembly into hydrogels. On the contrary, monovalent metal ions (K⁺, Na⁺, Li⁺ or Ag⁺) did not induce gelation, as they reveal lower coordination stability constants as compared to the transition metal ions [32].

To date it has been seen that many supramolecular interactions play crucial roles in hydrogel formation in the presence of cross-linkers, including hydrogen bonds, electrostatic interaction, coordination bonds, hydrophobic-hydrophilic balance, π - π and van der Waals interactions. The formation of graphene hydrogels can thusly be controlled by several factors, as initial graphene oxide concentration, pH value, concentration, molar mass and linker type.

Vacuum filtration

Vacuum filtration, the technique used in all chemical laboratories to separate solids from liquids, can be implemented for controlled assembly of graphene flakes, as was reported by Ruoff et al. [20,21]. In this method, GO or rGO suspensions are prepared and vacuum filtered using a Büchner funnel, resulting in the formation of a filter cake hydrogel of GO or rGO. The individual carbon sheets interlock with one another in a near parallel fashion, forming lamellar, paper-like structures (Fig. 9.7). Water molecules, present between the graphene sheets, act as spacers and prevent the collapse of the porous structure. Ruoff et al. obtained graphene oxide paper by filtering GO colloid through an Anodisc membrane filter (0.2 mm pore size) and drying at room temperature [20,21]. The correlation between water content and mechanical properties of GO paper was hereby established. As the moisture content of the graphene oxide paper decreased, the mechanical strength increased, but with simultaneous loss in the porosity. To prevent the GO or rGO paper from significant shrinkage, controlled drying procedures were applied [48]. The hydrogel films, obtained by filtration of reduced graphene oxide dispersion on porous cellulose membranes, were immersed in a miscible mixture of volatile and nonvolatile liquids and left until the water within the hydrogel was exchanged. The volatile solvents were then removed from the hyrogels by vacuum evaporation. By changing the ratio of volatile and nonvolatile liquids, 3D graphene structures of varied density, from 0.13 to 1.33 g/cm³, were prepared.



FIGURE 9.7

Scheme of 3D porous structures preparation by vacuum filtration method followed by different drying approach

An interesting method, inspired by bread baking, was presented by Niu et al. [22]. A leavening strategy, involving hydrazine vapor, was used to obtain 3D porous structures of rGO from free-standing compact GO layered films. The GO paper was prepared by vacuum filtration and then subjected to reduction in hydrazine vapors. Hydrazine vapors chemically reduce GO to rGO, exhaling gaseous species, whose rapid evolution scarifies the carbonaceous structure. The density of the obtained structure (which was as low as 0.03 g/cm³) could be tuned by the hydrazine concentration and is much lower, as compared to previously reported values for graphene papers.

Rotary evaporation

Rotary evaporation is another technique frequently used in the chemical laboratory, which was adapted to 3D graphene structure preparation. Rotary evaporator is used to remove high boiling solvents by applying heat to a rotating vessel containing a sample at a reduced pressure (from several kPa to mPa). Here, GO colloidal suspensions are evaporated for 4 h at 40°C using a rotary evaporator (rotating speed of 1 800 rpm), producing GO sponges, which are afterwards converted into rGO sponges by annealing at 800°C under a hydrogen environment. Increasing the temperature of the evaporation leads to GO film formation instead of 3D porous structures. If the vacuum evaporation process is operated at low temperatures, the centrifugal force dominants over the solvent vapourisation forces, enhancing the GO flakes assembly into fluffy clumps. When the evaporation proceeds too rapidly, the GO sheets restack to form compact films [6, 19].

Sugar blowing

As shown in the previous section, food processing inspires scientists to develop new methods of materials manufacturing. An ancient food art, termed "blown sugar" gave rise to the commonly referred "sugar-blowing" technique used to produce 3D self-supported graphene [23]. The fabricated porous 3D graphene, called by authors "strutted graphene", consisted of graphene membranes connected and supported by networks of graphitic struts. The membranes are mainly large-area mono/few-layered graphenes and some multilayered graphite sheets. This "strutted graphene" was synthesized by controlled heating of glucose in the presence of NH_4Cl . During heating, glucose-derived polymers are formed, which are simultaneously blew into bubbles by gases released from ammonium chloride. Further temperature increase caused the subsequent

graphitization of membrane walls, leading to mechanically robust, but very light (density c.a. 0.003 g/cm³) three-dimensional carbonaceous structure.

Electrochemical methods

The reduction of GO suspensions can be carried out by electrochemical methods using different electrode types. Under appropriate conditions 3D porous graphene-based structures can be obtained, showing similar properties to those obtained by chemical reduction of GO. Chen et al. succeeded in depositing 3D porous graphenes with electrochemical reduction method on different electrodes, including platinum, graphene paper or porous nickel, revealing a somewhat universal character of the approach [49].

Electrochemical foaming of graphite paper, called "electrochemical leavening" has been presented by Zhang et al. [50]. Simply, the graphite paper, consisting of highly ordered graphite sheets stacked together, was electrochemically leavened in aqueous solution of sodium sulfate at a current density of 200 mA/cm². The applied electric field weakens the van der Waals interactions between the graphene layers, enabling the ions, present in the electrolyte, to fill in the interlayer space of the graphite structures. Here, the ions play a similar role as the gas molecules in common bread baking. The resulting foam-like structure can be considered as a transient state between graphite and graphene flakes obtained by complete graphite exfoliation.

Template methods

Although, template-free methods are generally less complicated, the control of the pore size distribution within the 3D porous graphenes is possible. Accurate control is challenging. Templating methods resolve this issue. Both hard-templates (silica and polystyrene spheres or metal foams) and soft-templates (polymeric or amphiphilic compounds) are widely used [24-34]. Different from chemical composition discussed previously, both hard and soft templates ensure uniform pore creation based on engineered templates that are easily removable after synthesis. Hard-template architectures can be either solid (non-porous) or porous. In the case of solid-type templates, spherical particles are mainly used [28,30,31]. Most frequently, colloids of silica or polystyrene spheres are mixed with graphene oxide and gelation is induced, with simultaneous or subsequent reduction of GO to rGO. In this process, GO/rGO sheets coat the templating surfaces, forming the bulk material with the template particles submerged in the interconnected carbonaceous matrix. Next, the template is removed, leaving the carbon structure with pore sizes determined by the template diameters. If the porous template is used, the carbon network is created inside its pores and after the template is removed, a negative replica is obtained. The template acts as the morphology determining agent. It can be used in various synthetic approaches, including selfassembly, electrochemical deposition, vacuum filtration and chemical vapor deposition [24-31].

Soft templates, in a form of polymers or low molecular mass amphiphilic compounds are used to organize porous structures and can be removed by thermal annealing following synthesis. Several examples of hydrogels obtained in the presence of cross-linking agents were given in the previous section. In most cases, it is difficult to ascertain the difference between gelating agents and soft-templates and generally they play dual roles in porous structure manufacturing. Thus, in this section only hard-template methods will be described.

Polystyrene and silica spheres

Polystyrene (PS) spherical particles are one example of hard templates used for 3D porous graphene synthesis. The positively charged PS spheres attract negatively charged GO or rGO (with negatively charged residual oxygen groups) inducing assembly of carbon sheets into interconnected networks. The driving force for the GO or rGO embedding on the template surface is the electrostatic interaction and hydrophobic-hydrophilic balance. Thus, the surface chemistry of the template is the key factor controlling the morphology of synthesized 3D structures.

Vickery et al. adapted a well-established layer-by-layer method to produce 3D porous grapheme [31]. In this layer-by-layer method thin films are formed by depositing layers of oppositely charged materials. Here, the negatively charged chemically modified graphene dispersions were deposited on the surface of the positively charged polymeric spheres; a process which was repeated several times to obtain the required height of the lamellar arrangement. After treatment with toluene the structure deflated and interconnected graphene microspheres were obtained. Choi et al. managed to create composite material by vacuum filtration method, using PS particles and rGO, which after etching the template in toluene gave 3D porous structure [51].

Similarly, silica particles are utilized in the hard-templating approach. The silica-graphene or silicagraphene oxide interactions have been studied in the literature [52,53]. The silica surface can be easily modified, modulating its hydrophobicity and electric charge, thus the silica wrapping by GO or rGO sheets can be controlled by various surface phenomena. For example, Huang et al. modified silica spheres with methyl groups, changing their hydrophilic character into hydrophobic [28]. Considering the hydrophobic nature of GO central planes, methyl group grafted silica spheres were chosen as the template to fabricate graphene foams. The hydrophobic nature of both, the silica templates and GOs central planes, induced self-assembly of the lamellar-like structures, which were subjected to a reduction and etching step, giving nanoporous rGO foams. Interestingly, nonporous materials were prepared using the silica spheres without -CH₃ group modification as a template under the same conditions.

Later, Cai et al. obtained porous structures, made of interconnected hollow spheres with very thin walls (5 nm), using a modified method as originally proposed by Huang [29]. The non-modified silica sphere colloids were mixed with graphene oxide suspension to form a hydrogel, which was then subjected to vacuum freeze drying. To reduce the graphene oxide and remove the template, the dry composite material was annealed at 800°C and the highly toxic silica etching agent, hydrofluoric acid solution was used to remove the underlying template. As a result of such multi-step procedure, ultrathin-shell hollow spheres were successfully obtained.

We have synthesized 3D porous graphenes of different pore sizes, using GO suspension and silica spheres of various diameters [30]. In contrast to procedures described above, in our approach the self-assembly of GO on silica templates, and its reduction to rGO, was entirely carried out in a one-step synthesis. Non-modified silica spheres of chosen diameters (from 50 to 300 nm and in micrometer range) were mixed with GO suspension and chemical reduction was performed, giving hybrid rGO-silica hydrogels. After template etching (with HF solution) and drying, free-standing porous graphenes were obtained, with pore sizes determined by the silica template diameters. In Fig. 9.8 scanning electron micrographs of hybrid rGO-silica material and 3D graphene after silica etching are shown. The diameters of the silica spheres used in this experiment were c.a. 300 nm, with narrow size distribution, as is evident in Fig 9.8. A. The interconnected graphene hollow spheres remaining after template removal, preserved the size and shape of the template, as can be seen in Fig 9.8. B. The inset in Fig 9.8 B shows the macroscopic size of the obtained structure. The

size and shape of the 3D porous graphene can be modulated by changing the volume of GO suspension and choosing different reaction vessels.



FIGURE 9.8

A. SEM imageof hybrid rGO-silica, presenting silica particles (300 nm) covered with thin graphene layer. Scale bar 1 μ m.

B. SEM image of 3D graphene after silica etching, showing hollow spheres left after template removal. Scale bar 1 $\mu m.$

Inset presents macroscopic size of obtained 3D structure. Scale bar: 1 mm

Porous templates

Metallic foams are very porous materials. They have numerous applications, for example in heat exchange, energy absorption and lightweight optics. Nickel and copper foams are also frequently used as hard templates in 3D porous graphene synthesis by chemical vapor deposition (CVD) method as both metals are well-know catalytically active metals for the growth of all of the members of the graphitic nanocarbon family. Indeed, layered graphene is synthesized by the CVD on Cu and Ni foils, as these elements catalyze graphene formation [54]. During CVD, gas species (for example methane or acetylene) are thermally decomposed in the reductive environment to form carbon radicals at the metal surface, which then form single-layer and few-layers graphene on the metallic support. The template can be removed after synthesis by mineral acid treatment, leaving graphene foam-like structures. It should be mentioned here, that the mechanism of graphene formation, and the underlying catalysis on which this is based, differs between Ni and Cu. This difference principally arises from the different carbon solubility in these two metals and the different interaction and recombination of hydrogen on Cu and Ni surfaces. Nickel has a relatively high carbon solubility (> 0.1 atomic %) at elevated temperatures, whereas Cu has ultralow carbon solubility (<0.001 atomic %) [54]. The role of hydrogen in graphene formation is more complex. It lies outside of the scope of this chapter and will not be discussed here. A more detailed description of the role of hydrogen in CVD can be found in [54,55]. Typically many multilayer graphite flakes are synthesized on Ni supports, while on Cu, uniform single-layer graphene is often produced. Understanding the substrate-dependent graphene growth chemistry is required in order to control the morphology of the produced 3D structures. The porous metallic foams enables the 3D

graphene synthesis and serve as both the template and the catalyst, controlling the deposition mechanism and influencing the structural and mechanical properties of the resultant foam. Three-dimensional conductive graphene networks grown by chemical vapor deposition on the Ni foams were presented for the first time by Chen et al. [24]. Since then, numerous papers described synthesis of 3D graphenes by CVD, including plasma-enhanced chemical vapor deposition [25]. Ruoff et al. improved the proposed method in order to obtain free-standing graphene foams, contrary to the polymer supported structure presented by Chen [26,27]. Several hybrid structures, that is graphene foams (GF) decorated with different types of nanostructures, were also successfully prepared by CVD and their sensing and catalytic properties have been evaluated. Examples generally include metallic nanoparticles (Au, Pd, Pt and bimetallic) [4,46,57], metal oxides (MnO₂, Fe₃O₄, Cu₂O etc.) [58-60], lithium compounds (LiFePO₄, Li₄Ti₅O₁₂) [61,62], other forms of [18] and conducting carbon (carbon nanotubes) polymers (polyaniline, poly(3,4ethylenedioxythiophene), polypyrrole) [49,55,63].

As the commercially available nickel foams possess rather large pores (200-500 µm), and wide branches (c.a. 50 µm) their morphology cannot be easily tuned. As a result novel methods for porous nickel fabrication have been researched. Xia et al. developed a hydrogen dynamic method to produce highly porous 3D nickel films, with pore and branch sizes much smaller than those of commercial Ni foam template [63]. The 3D porous Ni film was prepared by facile electrodeposition methods in a two electrode system (nickel foil as the working electrode and platinum as the counter-electrode) at room temperature. The typical pore size of the Ni films was about 5–10 μ m and the free-standing interconnected Ni branches were in the same range (5-10 μ m). The above electrodeposited 3D porous Ni films were used as the 3D scaffold templates for the CVD growth of ultrathin graphite foams, whose pore and branch sizes were similar as for the template. An alloying-etching approach was used to strategically porosify commercially available 3D Ni foams [64]. The 3D Ni foams were coated across their entire surface with an alloying metal, such as Cu, by electrodeposition. Next, the Cu-Ni composite was annealed at 1100°C for interfacial atomic diffusion and then etched electrochemically to obtain arrays of micropores (c.a. 5 μ m) on the 3D surfaces of these Cu-Ni foams. The pore morphology, size and density was controlled by the applied potential, etching rate, pH values, reaction time, and temperature. Perhaps most noteworthy, 3D porous carbon structures were synthesized on such template by CVD method at only 600°C, which could be attributed to the higher catalytic activity of the Cu-Ni alloys than those of their pure counterparts. Moreover 3D carbonaceous nanostructures with multilevel porosity (pores of 100 μ m and 5 μ m) were obtained, however; these were formed from thin graphite films rather than graphene.

According to Li et al., Ni foam-based approaches are beneficial for the preparation of lightweight grapheme materials, but they are limited in their yield and the mechanical strength required in some real-world applications [65]. Thus, they presented high-density 3D grapheme obtained by CVD process at atmospheric pressure using nickel chloride hexahydrate as a precursor of porous Ni skeleton. The density of the obtained carbonaceous structure was one order of magnitude larger than that of commercial Ni foam-grown graphene, with pore sizes being one or two orders of magnitude smaller. The mechanical strength and density of 3D graphene synthesized by this method increased linearly with the growth time.

Metallic foams are generally used to prepare graphene foams *via* CVD, however; Yin et al. succeeded in 3D graphene preparation on nickel templates using a hydrothermal method [66].

Simply, nickel foam was immersed in a GO suspension and then reduced by hydrazine in an autoclave. After template removal, by a HCl treatment, porous rGO structures were obtained. A multistep procedure, using amorphous porous carbon as both a template and graphene precursor, have also been used to prepare 3D graphenes of excellent electrochemical properties [67]. Amorphous porous carbon templates were sputtered with nickel to form a smooth nickel coating on the carbonaceous surface. This was subsequently annealed at 750°C, followed by an acid etching to remove the Ni. It is known, that amorphous carbon can easily diffuse in to Ni at elevated temperature and concomitantly graphitize at the nickel surface. In this process, 3D amorphous porous carbon templates were converted, with help of Ni catalyst, to 3D porous graphene structures.

Properties of 3D porous graphene-based structures

The properties of 3D porous graphene structures strongly depend on the method of their fabrication and can be tuned within a wide range, making them useful for a diverse range of applications. Table 9.1 summarizes the various properties of 3D porous graphenes obtained by different methods.

TABLE 9.1

Chosen properties of 3D porous graphenes obtained by different methods

Method/	Template	Pore size	Mass	Surface	Electrical	Mechanical	Ref
precursor		μm	density	area	conductivity	properties	
			g/cm ³	m²/g	S/cm		
Hydrothermal	No	Submicrometer	-	-	10 ⁻²	-	[2]
gelation/GO		to several					
		micrometers					
Hydrothermal	No	0.002-0.07	-	1260	5·10 ⁻³	Storage	[1,39]
gelation/GO						modulus	
						450-490	
						kPa	
Hydrothermal	No	-	1.4-1.6	-	7.1-8.2	Compressive	[41]
gelation/GO						strength 361	
						MPa	
Nucleate boiling	No	1-3	-	-	11.8	-	[42]
method/GO							
Rotary	No	0.5-50	0.003-	-	-	-	[19]
evaporation/			0.009				
GO							()
Vacuum	No	-	1.8	-	-	Tensile	[20]
filtration/GO						modulus	
						32 GPa	
Vacuum	No	<10	0.03	-	5-8	Tensile	[22]
filtration-						strength	
leavening/GO						3.2 MPa	
Vacuum	PS	0.1-2	-	-	-	-	[51]
filtration/GO	spheres						

Self-assembly/GO	PS	Micro-, meso-	-	440	-	-	[68]
	spheres	and					
		micropores					
Self-assembly/GO	SiO ₂	0.003-0.25	-	~248	$2.4 \cdot 10^{-4}$	-	[29]
	spheres						
Self-assembly/GO	Methyl	0.03-0.12	-	851	-	-	[28]
	grafted						
	silica						
	spheres						
Electrochemical	No	-	-	1000	60	-	[49]
deposition/GO							
Sugar	No	20-200	0.003	1005	10 ⁻²	-	[23]
blowing/glucose							
and NH₄Cl							
CVD/ethylene	Cu-Ni	~ 5 and ~ 100		19.2	9	-	[64]
	foam						
CVD/CH ₄	Ni foam	several	0.022	560	12	-	[65]
	produced						
	in situ						
	from						
	NiCl ₂						
CVD/ethanol	Electro-	5-10	0.004	980	-	-	[63]
	deposited						
	porous Ni						

Applications of 3D porous graphene-based structures

Many papers have reported the use of 3D graphene-based porous structures in various fields of research. Due to their high specific surface area and porosity, graphene-based materials exhibit greater adsorption capabilities than other known adsorbents. Very often, the surface of graphene needs to be first chemically modified (covalently or non-covalently) in order to prevent the agglomeration of the sheets and to enable further manipulation of the graphene in different solvents. The surface of graphene can act as a support for other materials such as metal oxides/hydroxides, metal nanoparticles, polymers, and therefore 3D graphene found its place in many fields [4,56-63]. Numerous examples show its promising applications in the adsorption of metal ions as well as the removal of oils and organic solvents from wastewater [6-14,69,70]. In addition, the biocompatibility of graphene enables its use as a new-generation scaffold for tissue engineering, or as a platform for biosensing [15-17]. There are ongoing efforts to implement graphene foams/aerogels as supports for thermal energy storage [71-77]. Indeed, the unique set of excellent properties including good electrical conductivity, great chemical stability, and the possibility to obtain free-standing structures allow such graphene-based structures to be used in electrochemical energy storage and conversion devices such as: fuel and biofuel cells, lithium ionbatteries, supercapacitors [4,18]. Herein, we review common examples of the non-templated and templated, versatile graphene-based structures in the above-mentioned applications.

Water remediation

Effective removal of organic solvents and dyes, oily contaminants, and heavy metal ions from water is of importance for water source protection. To purify drinking water, the removal of

microbiological contaminants is also necessary, thus different sterilization methods are applied. 3D porous graphenes were used in water remediation processes and the results are summarized in this chapter.

Ion adsorption

The adsorption of different species, for instance heavy metal ions $(Cd^{2+}, Pb^{2+}, Cu^{2+}, Ni^{2+})$ or noble metal ions (Ag^+, Au^{3+}) on carbon surfaces has been of interest for the last few decades. Due to their high surface area and interconnected porous structure, some of the carbon forms show great adsorption potential for different cations. Adsorption that takes place on the carbon surface is usually a physisorption process. It is a sorption of molecules through the weak van der Waals forces between the surface of the sorbent and the sorbate [78]. The importance of heavy metal ion removal from water is driven by the increasing awareness of the need for environmental protection.

Graphene-based materials show much promise for this application. Various groups have demonstrated that graphene surfaces can act as binding sites for metal ions, subsequently enhancing their adsorption. For this reason, graphene is considered to be one of the few viable next-generation materials for effective water remediation. Lei et al. [69] demonstrated the use of three-dimensional graphene sponges for the removal of a wide range of heavy metal ions. The adsorption of zinc, iron(III), cadmium, and lead(II) ions on graphene were studied by analyzing the adsorption isotherms at different ion concentrations. According to the Langmuir model of adsorption, the maximum adsorption capacity for zinc ions was evaluated to be 326.4 mg/g; much higher than for other typically used adsorbents such as zeolites or activated carbon. The regeneration of materials after several adsorption-desorption cycles was also studied and is a technologically critical parameter in assessing the usefulness of an emerging device. In the study of Lei et al., 0.2 M HCl solution was used to desorb the ions. The results suggest good recyclability with 85% of the maximum capacity retained after 5 cycles. Chen et al. [25] fabricated 3D graphene on nickel foam with poly(methyl methacrylate) as a growth-supporting agent. They subsequently studied the adsorption of As(V) and Pb(II). These ions are some of the most toxic and readily pass through the food chain via contaminated water supplies. Graphene foams were prepared using PECVD on nickel foam. Then 3D foams were directly oxidized to produce 3D graphene oxide structures, which exhibited excellent As(V) and Pb(II) removal efficiency. The abundant oxygen groups on the GO foams were shown to contribute to the adsorption process. A synergic mechanism, that is electrostatic attraction and ion exchange between hydroxyl groups and metal ions was proposed. The adsorption capability of the GO foam was strongly dependent on pH and temperature, and reached 232.1 mg/g for As(V) and 485.9 mg/g for Pb(II).

Water-cleaning tea bags containing a 3D porous graphene-based foam were developed by researchers in Portugal and tested toward Hg removal from water. The teabag prototypes can remove 96% of the Hg dissolved in pure water in one day, which is significantly improved compared to activated carbon [70].

Adsoprtion of organic compounds

Oil pollution of surface waters, mainly seas and oceans, is most often caused by the spill of fuel oils from ships and tankers as well as by waste release from petroleum industries. Oily wastewater is an important global environmental issue. Proper treatment is necessary to avoid serious ecological impacts and the loss of valuable water resources. Many strategies to remove oil from water have

been considered, including chemical, physical, and electrochemical methods [79]. Nevertheless, adsorption techniques remain some of the most widespread, with many scientists actively researching more suitable adsorbing materials. To date, natural materials such as zeolites, sawdust, and wool fibers have been widely used but their efficiency remains poor due to the adsorption of both the water and oil phases. Consequently, synthetic adsorbents are produced with the highest interest in the microporous polymeric structures, silica aerogels and carbonaceous gels and foams. Graphene, with its high surface area and hydrophobicity, is a versatile building block for oil adsorbents. Many texts have reviewed in detail the use of graphene-based materials in the wastewater treatment [7,8].

The adsorption capacity (Q) is very frequently calculated using the mass (m) of a material before and after adsorption, as given by:

$$Q = \frac{m_{after} - m_{before}}{m_{before}}$$

There are two methods to determine the adsorption capacity; the first being the "soak method". In this case, the porous material is soaked with the adsorbate and the mass before and after determined to allow for the adsorption to be measured. Another method, called the "drop method", involves the dropping of the adsorbate on a porous material (one drop after another) until it becomes fully saturated and cannot accept additional adsorbed material. Then the weight before and after adsorption is compared.

Niu et al. [22] prepared the free-standing, porous graphene slices using the leavening method. They studied the adsorption ability of the material towards oil and organic solvents. rGO slices were brought into contact with oil on the water surface and exhibited the high affinity to oil whilst repelling water. They reported an uptake capacity of 37 for the adsorption of motor oil and 26 for organic solvents (cyclohexane, chlorobenzene, toluene). Such materials can also be easily regenerated by immersing them in hexane to release the adsorbed oil. Li et al. [9] prepared amino-functionalized graphene hydrogel that was reinforced with tri-isocyanate for enhanced crude oil adsorption. The material showed low density (0.08 g/cm³) and good adsorption capability for crude oil.



FIGURE 9.9

Step by step preparation of three-dimensional graphene hydrogels obtained through the reduction of amino-functionalized graphene oxide sheets, followed by the hydrogel reinforcement with tri-isocyanate

He et al. [8] produced graphene oxide (GO) and reduced graphene oxide (rGO) foams with superior oil adsorption capacity. Three different methods of drying were applied, which resulted in a formation of three different graphene oxide foams that were subsequently thermally reduced giving reduced graphene oxide foams. They used both 'drop' and 'soaked' methods for organic liquids and oils. They considered olive oil, pump oil, petrol, chloroform or toluene. The results showed that the oil adsorption capacity of the rGO foams was better than that of the GO foams and was, impressively, higher than 100 g/g for all test liquids.

Adsorption experiments in our laboratory have been conducted using various types of commercially available oils (e.g. rapeseed oil). The 3D graphene, prepared by hydrothermal method was placed in a Petri dish filled with a dyed-water/oil mixture. Figure 9.10 shows images acquired in time intervals of 1 minute. The entire process of adsorption typically takes a few minutes to be completed. The experiments (data not published) show the adsorption capacity of such material to be around 10-15. The results are comparable to those obtained by other groups [10,11].



FIGURE 9.10

Pictures taken after time intervals of 1 minute showing the adsorption of oil (not dyed) and the repelling of water (blue-dyed) by the graphene aerogel. First photo shows the mixture of blue dyed-water and the oil stain which gradually disappeared by being soaked with graphene hydrogel

The hydrophobic rGO basal plane is an excellent substrate for different dyes adsorption. As most of the dyes belong to the family of aromatic compounds, the π - π interaction of graphene and dye molecule is the driving force for the adsorption process. This may be enhanced by other interactions (e. i. electrostatic, hydrogen bonds) occurring between residual functional groups of rGO and dye molecule. Previously, suspensions of GO or rGO flakes were reported for dye removal

from wastewaters, however; in such approaches centrifugation or filtration is necessary to separate adsorbent from the purified liquid. The usage of bulk porous graphene based structures is beneficial as it can be simply removed following water remediation.

The 3D rGO-based hydrogels showed excellent removal capabilities for methylene blue (100%) and rhodamine B (c.a. 97%), with no loss in adsorption capacity after regeneration using ethylene glycol [7]. Different functionalization approaches were also undertaken to improve adsorption properties of 3D porous graphenes. Polycationic polymer was integrated with graphene porous matrix to produce efficient adsorbent for anionic dyes, as ponceau S and trypan blue [12]. Sulfonated graphene was gelated with the help of polyvinyl alcohol into 3D porous structure, which was proved to efficiently separate cationic dyes from anionic dyes in water [13].

The three-dimensional TiO_2 -graphene hydrogel revealed a significant enhancement in the photodegradation reaction of methylene blue and brilliant blue [14,80]. Similarly, 3D graphene decorated with ZnO nanorods exhibited excellent methylene blue removal efficiency [81].

Silver nanoparticles are known to be an outstanding antimicrobial agent. Combining them with 3D porous graphenes lead to a composite material with high antibacterial activity against *Escherichia coli* which can be used as a novel nanofilter for water disinfection [82]. Benzalkonium bromide, popular biocide was mixed with GO to produce antimicrobial hydrogel. Thanks to the synergistic effect of graphene oxide and benzalkonium bromide, the resultant hydrogels demonstrated strong antibacterial activities against both Gram-negative and Gram-positive bacteria [83].

Scaffolds for tissue engineering

Nowadays tissue engineers focus on the production or regeneration of tissues and organs, using living cells and scaffolds to promote their growth. Many synthetic and natural materials (such as collagen, fibrin, chitosan) are used as scaffolds which provide a suitable 3-dimensional microenvironment for cellular attachment. For the tissue to be reconstructed, the scaffolds must meet many chemical, biological, and mechanical conditions. The high porosity within the interconnected network of pores, a well-accessible surface area, and biodegradability are all essential. Critically, the scaffolds should not elicit any immune response and should provide a mechanically durable platform during cell growth and surgical manipulation [84].

The application of graphene-based structures for advanced tissue engineering is still in its infancy, however; much effort has been made to stimulate their adoption in the biomedical sciences. Low toxic, biocompatible, lightweight, and mechanically and thermally stable three-dimensional graphene-based foams seem to be an excellent scaffold material for stem cells proliferation [15-17]. Moreover, the presence of graphene can accelerate the differentiation of stem cells into specialized cells for instance: bone, muscle, and cartilage cells [15].

Crowder et al. [16] employed three-dimensional graphene foams (GF) as substrates for human bone marrow-derived mesenchymal stem cells. These kind of cells promoted osteogenic differentiation in the presence of osteogenic growth factor. GFs were grown by CVD on nickel foams which were subsequently removed by immersing the materials in FeCl₃ etchant. The cell viability and protein adsorption on graphene foams were investigated. Cells were treated with two markers to stain live and dead cells. The GF maintained the viable stem cells with very few dead cells observed after 2 weeks. The study also showed that 3D GFs promote spontaneous osteogenic differentiation of human mesenchymal stem cells without any extrinsic manipulation. It may be a result of the high stiffness of graphene foams that induces stress between foam and the cells, causing the guided cell behavior. Lower protein attachment, as compared to the commonly used scaffolds made of polyglycolic acid, was observed. Graphene-based 3D structures can also offer a favorable substrate for neural tissue engineering [17]. Li et al. reported the use of GFs as a new scaffold for the neural stem cells (NSC). These cells are the source of neurons and glia; they hold great promise in regenerative medicine for neural repair and restoration of cognitive function following injury or disease. Graphene porous structures were prepared, by a known CVD method with nickel foam as a template. The pore size was 100-300 µm with a porosity of 99%. The neural stem cells adhesion to graphene surface was determined by immersing GF coated with laminin in the cell culture medium. After 10 hours, no cells were detected in the remaining solution. The highresolution SEM imaging confirmed the formation of neural network on the skeleton. The proliferation and differentiation of NSC were also studied. The expression of a cellular marker for proliferation was examined, and the phenotypic changes within the cells was investigated. The macroporous structure of the GFs likely facilitates cell proliferation due to the large surface area available for the nutrition for NSC. After 5 days of differentiation, neural cells with elongated shapes covered nearly the whole surface of graphene. Differentiation into all three types of neural cells was observed. Owing to the high electrical conductivity of graphene, the GF acts as an impressive conductive scaffold for electrical stimulation of neural cells. The electrochemical properties of these materials was studied using cyclic voltammetry (CV) within the potential window from -0.3 V to +1.0 V. For this material, the charging and discharging processes occur at the interfacial double layer which can be considered as a capacitor. This is suitable for neural stimulation, as no chemical reactions take place, therefore no changes of tissue or electrodes were observed. CV measurement results indicated that for the potential window ranging from -0.2 V to 0.8 V, the electrical stimulation of cells through charge injection can be performed.

Thermal energy storage

Thermal management has become an important issue for many applications, especially in the context of industrial waste heat recovery (e.g. for controlling the temperature in the electronic devices), building and vehicle energy saving, and intermittent energy sources (e.g. solar energy). According to the International Renewable Energy Agency (IRENA), "thermal energy storage" (TES) is a technology that stocks thermal energy by heating or cooling a storage medium so that the stored energy can be used at a later time for heating and cooling applications and power generation" [71]. Phase-change materials (PCM) are commonly used for this application. They can easily store and release latent heat during a phase change. The most widely used substances are polyethylene glycol (PEG), octadecanoic acid (OA), paraffin, and many more [72,73]. The list of required properties of such materials includes a high heat storage density, high phase change enthalpy, and small temperature variation (constant temperature during the phase change).

Preparing the shape-stabilized PCM is of great scientific interest as it solves many problems that thermal management encounters. First of all, the leakage of the liquid above its melting point is hindered. PCMs usually show low thermal conductivity and its improvement can be achieved by the use of thermally conductive fillers. Polymers, metal and carbon foams, nanospheres, expanded graphite etc. have all been employed as such supporting materials [74,75]. With the progress in nanotechnology, all the above suggest the use of novel nanomaterials. Three-dimensional graphene-based structures can be utilized as the supports for phase-change materials. With its high thermal and electrical conductivity and good mechanical properties, graphene serves as a leading material for thermal management applications.

Ji et al. [74] have prepared ultrathin graphite/graphene foams by CVD on nickel foam that was chemically etched away after the synthesis. The addition of a small volume of graphitic material-

0.8-1.2 vol% - allowed them to obtain a composite with 18 times improved thermal conductivity, with no significant change in the PCMs melting temperature. GFs are hydrophobic; they can be used as nanocontainers for hydrophobic PCMs. Chemical modification of graphene to introduce oxygen functional groups and thusly stimulate the formation of hydrophilic surfaces was suggested. The thermal stability of GFs during the phase change was investigated. One of the requirements for the nanofillers is their stability after serious of melting and solidification processes. The electrical resistance (ER) for foams filled with paraffin and erythritol was found to change by less than 2% during multiple cycles, confirming the materials robustness and mechanical and thermal stability.



FIGURE 9.11

Schematic presentation of heat release and heat absorption by phase-change material in a conductive support made of porous carbons

Zhong et al. [76] presented work concerning graphene aerogel and its use as a thermal enhancer and a container in PCMs. They assembled GO sheets in a three-dimensional structure using a hydrothermal method. The graphene interconnected porous structure was impregnated with molten octadecanoic acid and the heat transfer through OA was studied. The thermal diffusivity and the specific heat for the sample were measured at room temperature using a laser flash technique and the thermal conductivity was calculated. The latent heat of the samples was tested by differential scanning calorimetry (DSC). The thermal conductivity of GA/OA was about 2.635 $W/m \cdot K$, which is higher than other common container materials. The latent heat of the material however was 181.8 J/g (slightly lower than for OA). On the other hand, due to the small pores in GA, the leakage of OA, the main problem in TES, was inhibited. All the results show that the graphene aerogel can be used as an effective holder for PCMs and can be a suitable part of nextgeneration thermal management systems. Li et al. [77] reported, for the first time, the simultaneous improvement of both thermal conductivity and latent heat of a phase-change composite made of graphene foam as a stabilizer and docosane as a PCM. Docosane was melted at 80°C and the GF was immersed in this long-chain carbohydrate at low pressure. The graphene sponge acted as a nucleating agent for the crystallization of docosane, which formed layers on the graphene surface. The latent heat of the composite increased from 256.1 J/g to 262.8 J/g, and the thermal conductivity increased twofold for a low graphene concentration of only 3 mg/ml.

Sensors and biosensors

Graphene has been widely used in biosensors and diagnostics for the detection of a wide range of analytes [85-90]. The unique electrochemical behavior and large surface area of graphene makes it a promising electrode material for electrochemical sensing devices. Several reviews can be found in the literature concerning graphene-based sensors, including biosensors [85-87], however; 3D porous graphenes have not, as yet, been frequently used.

GFs were successfully used to construct nonenzymatic sensors of small molecules. Zhang et al. [88] presented work on 3D graphene foam as a novel electrode architecture for electrochemical dopamine sensing. Such an approach lead to a sensor with remarkable sensitivity and low detection limit, as compared to other known approaches. Similarly, detection of ascorbic acid (AA) on 3D graphene foam decorated with CuO nanoflowers was studied [89]. CuO nanoflowers can further increase the electrochemically active surface area and catalyze the oxidation/reduction reactions of AA. As a result, low detection limit and excellent specificity towards AA (measurements conducted in presence of dopamine, uric acid, glucose etc.) was obtained, which is promising for practical applications. Detection of glucose and hydrogen peroxide (H_2O_2) in serum and food samples (e. g. the UHT milk) can be also achieved with the use of graphene porous foams. Si et al. [90] integrated Mn₃O₄ with the graphene foam synthesized by the templated CVD method, and studied the electrochemical performance of such structures. The presented enzymeless sensors exhibited excellent performance for real-time detection of glucose and H_2O_2 in serum and food samples.

Three dimensional graphene has been decorated with bimetallic PdCu nanoparticle for its use in non-enzymatic amperometric glucose sensors [57]. PdCu alloy was chosen due to its high catalytic activity, eco-friendliness, and low cost. Hybrid hydrogels with uniformly distributed PdCu were synthesized during the hydrothermal reduction of graphene oxide and Pd(II) and Cu(II) ions in an autoclave. The PdCu/GE composite showed improved electrocatalytic activity toward glucose oxidation (in the range up to 18 mM) with a detection limit of 20 μ M.

Other frequently used electrochemical sensors are enzymatic biosensors. Here enzymes act as the sensing component, catalyzing specific redox reactions. Enzymes are mostly physically or chemically immobilized on the electrode surface. Thus, increasing the electrode surface area will result in an increase in sensor performance. Chu et al. [91] achieved homogeneous enzyme immobilization on graphene nano-grids. 3D porous graphene structures were prepared on gold surfaces using polystyrene beads (of 500 nm) as templates. The template was subsequently etched away when the thickness of obtained graphene structure was c.a. 500 nm. Glucose and lactate oxidase were immobilized in the cavities created after the polystyrene beads were removed. The glucose biosensor constructed using this architecture exhibited much higher sensitivity as compared to layered structures.



FIGURE 9.12

Preparation of 3D graphene nano-grid on gold substrate for the enzyme immobilization

Not only biomolecules can serve as the sensing element. The whole bacteria cell can be immobilized on the graphene oxide hydrogel, as was shown by Liu et al. [92], to obtain biochemical oxygen demand sensor. The loading of microbes for graphene hydrogel was much higher (3.3 times) than for other commonly used carbons (e.g. activated carbon) and the immobilized microbes exhibited high viability and activity.

Fuel cells and biofuel cells

Fuel cells are devices that directly convert chemical energy into electrical energy. The electrodes (anode and cathode) support catalysts that promote redox reactions. Electrochemical reduction of oxygen to water with high current efficiency and small over potential is one of the main challenges facing modern fuel cell technologies. For an electrode material, carbon black is commonly used to support metal catalysts (usually platinum or platinum-based catalysts) [93, 94], facilitate four electron reduction of oxygen to water. Although, the catalyst performance is crucial for fuel cell efficiency, the material of which the electrode is made of plays also an important role in the device operation. The requirements for such electrode material in fuel cells are: 1) high surface area,

2) good electrical conductivity and 3) proper porosity and 4) good stability under fuel cell conditions (e.g. higher temperature, oxidative conditions). Carbonaceous materials are some of the most frequently used and the graphene-based three-dimensional structures appear to be the most promising among them.

The hybrid structure with platinum-ruthenium nanoparticles anchored on 3D graphene was reported for its use in direct methanol and ethanol fuel cells [95]. Due to the high surface area, active for reactants, and low resistance towards charge transfer, the material showed high catalytic activity for methanol and ethanol oxidation. In another approach, GF was loaded with one-dimensional NiCo₂O₄ nanoneedles [96] and studied for the electro-oxidation of methanol. The results revealed the high stability of the composite caused by the good electrical connection between the catalyst and GF. Defective GFs were synthesized using sodium ethoxide combustion process with subsequent heat treatment at 800°C [97]. SEM images of samples revealed that the surface consisted of thin graphene walls and a porous framework. Platinum nanoparticles were deposited on such surfaces. They were tested as electrodes in polymer electrolyte fuel cells. Better performance, when compared with carbon black and commercially available graphene was noted.

Several examples of 3D porous structures made of nitrogen-doped graphene, that served as cathodes in the fuel cells, can be found in the literature. The presence of heteroatoms in the carbon network creates the new adsorption and reaction centres for oxygen reduction, facilitating the four electron process. As a consequence, the fuel cell performance was markedly improved. Decoration of N-doped graphene foams with noble metal or noble-metal free catalysts were also reported. More details are given in [98-100].

A special type of fuel cell is the biofuel cell. Here, biomolecules such as enzymes or whole microorganisms play the role of the catalyst. The oxygen reduction is catalysed at the cathode by redox enzymes, mainly copper-containing oxidases. Research in the biofuel cell field is currently focused on improvement of the electrode structure, which should result in a decrease in the dioxygen reduction over potential, improvement of durability, and higher current densities. Graphene-based 3D structures with hierarchical pore network can serve as desirable, ready-to-use electrode material. Nevertheless, literature concerning this topic is still lacking, however; the idea of using graphene is promising for further development. It should be noted here, that graphene was proved to enhance direct electron transfer between the electrode and the enzyme, which is in other cases not efficient. The porous structure enables high protein loading and provides large

surface areas for chemical functionalization, which may additionally influence the electrode performance.

Cui et al. investigated the use of 3D graphene as a bioanode for direct electrochemistry of glucose oxidase [101]. Three-dimensional graphene was prepared by electrochemical reduction of graphene oxide suspension directly on glassy carbon electrodes. Chitosan was used as a matrix for glucose oxidase (GOD) immobilization and an homogeneous film with good adhesion was formed. The hydrogen bonds formed between residual oxygen groups on the graphene planes, enzyme and chitosan groups stabilized the whole structure and provided good contact with all the components-which is necessary for the efficient electron exchange. The electrochemical method of 3D structure manufacturing allowed for the fabrication of a material with high electrical conductivity, well defined size, and a surface easily accessible by the electrolyte. The electrochemical studies confirmed good electrochemical behaviour of the material showing a pair of well-defined redox peaks. No mediators were needed for the enhanced electron transfer.

glucose oxidase with chitosan



FIGURE 9.13

Electrochemically-reduced graphene oxide deposited on glassy carbon electrode. The porous structure and well-developed surface area enables more efficient enzyme adsorption

We reported the use of graphene aerogels obtained through hydrothermal reduction of graphene oxide for their use as bio-cathode in enzymatic biofuel cells [40]. The materials were chemically modified with anthracene residues in order to create a "bridge" for enhanced charge transfer between the active centre of the enzyme, buried deep inside the protein shell, and the electrode surface. The choice of these moieties was driven by the hydrophobicity of aromatic moieties that

are compatible with enzyme active centre, as well as their conjugated double bonds that facilitate the electron mobility [102,103]. The materials show good electrical conductivity and well-developed outer surface areas that was used as a platform for the adsorption of laccase for bio-electrode construction.

Lithium-ion batteries (LIBs)

At present, the most widely used batteries are rechargeable lithium-ion batteries. The World battery market is estimated to be around 120 billion USD; with 37% of all batteries being LIBs. They possess many desired properties such as high energy density, high operating voltage, lack of memory effect and long cycle life. They are commonly used in portable electronic devices, for instance as power sources for laptops and mobile phones. LIBs are composed of a cathode, anode and electrolyte. The anode, usually consists of layered structures (e.g. graphite) allowing the intercalation of lithium ions. Many materials were chosen as good candidates for an anode and cathode materials. Different electrolytes were also examined [104].

Graphene-based materials can serve as an effective electrode material, as well as porous support for other commonly used electrode materials. Many researchers report their use as the anode material, with less documentation referring to implementation of 3D graphenes as the cathode [105]. Because of the interconnected channels with large pores and high electrical conductivity, 3D graphene architectures can provide a suitable pathway for lithium ions and electrons, during the charge and discharge cycles. Moreover, the mechanical robustness of the flexible, lightweight, and free-standing material holds great promise for its use as the physical support and current collector.

Generally, 3D graphene based electrodes for LIBs were produced by different methods and their electrochemical behaviour was studied. However, they did not outperform graphite, which is commercially used in LIBs. Self-supported 3D graphene structures can successfully act as a scaffold for different active components, such as metals [106], non-metals [107], metal oxides [108] and chalcogens [109] or conducting polymers [110]. The synergic effect and improvement of ion/electron transfer is expected. Because of the continual interest, there has been a plethora of reports concerning graphene and graphene composites as LIBs components, and it is a field of significant breadth that requires a large review. Some details can be found in [4,18,110-112].

Supercapacitors (SC)

Supercapacitors (sometimes called ultracapacitors or hybrid capacitors) are electrochemical capacitors that exhibit high capacitance values, c.a. 10¹⁰ higher than electrostatic capacitors. They store energy efficiently by charge accumulation in an electric-double layer created on the surface of (usually) carbonaceous electrodes in aqueous electrolytes. Their advantages are numerous, including high power densities, environmental benignity, safety in use, and lightweight. Their industrial applications are wide. To obtain higher capacitance, a high specific surface area of the electrode is needed. It was shown [113] that micropores contribute to a higher electrical double layer, whereas macro- and mesopores act as pathways for ion transfer. The hierarchical porous structure can thus provide a great architecture for energy storage devices based on supercapacitors. Graphene-based materials have subsequently sparked interest in this field. Many papers review the use of graphene aerogels in supercapacitors, including free-standing GFs, nitrogen doped graphene foams, and hybrid structures, where 3D porous graphene supports function in conjunction with other active materials [4,114]. For example, supercapacitors implementing free standing non-modified 3D graphene electrodes revealed specific capacitance in

the range of 100-400 Fg^{-1} . Integration of 3D porous graphenes with other active components, as metal oxides (MnO₂, ZnO, Co₃O₄, NiO, RuO₂, CoMoO₄), metal hydroxides (e. g. Ni(OH)₂) or polymers (PANI, PPY) is expected to increase these values and most successful approaches allowed to obtain specific capacitance exceeding 1000 F·g⁻¹[4].

Graphene-based frameworks can be also applied in lithium-ion capacitors. This combination of both LIB and SC described above, consists of a LIB-type anode (where reactions of Li ions take electrochemical double laver capacitance (EDLC)-type place) and an cathode (adsorption/desorption of ions in an organic electrolyte). Ye et al. constructed Li₄Ti₅O₁₂/C hybrid as the anode and 3D porous graphene macroform as the cathode [106]. PGM was synthesized by hydrothermal reduction of a graphene oxide suspension with subsequent freeze-drying. The device showed an improvement in energy density (both in value and retention) as well as good reversible capacity.

Conclusion

Significant research has taken place on three-dimensional porous graphene-based structures, such as foams, sponges, aerogels/hydrogels, and papers. Their well-developed, accessible surface area, good conductivity and biological and chemical inertness make them outstanding candidates for replacing other hitherto used carbonaceous materials, such as graphite, activated carbons, and glassy carbons. A variety of techniques have been developed including simple, low-cost chemical reactions with graphene oxide as a precursor, as well as more complicated deposition methods with other carbon sources. The choice of synthesis strategy is driven by the actual device needs and can lead to materials with diverse properties and forms. In addition, the control over the morphology of porous graphenes can be achieved using template or template-free methods. It has been shown that by implementing different template skeletons, desired graphene frameworks can be constructed. Consequently, the final structure of graphene can be tailored to obtain demanded porosity and pore size distribution, suitable for the adsorption of different species, able to fit into the engineered pore voids. Although, the most commonly used templates are porous metal foams and spherical particles of different sizes, other shapes can also be used and the possible designs of carbon structures are limited only by the imagination.

Self-assembled graphene structures seem to be promising for many areas including water remediation, tissue engineering and regenerative medicine, sensors, biosensors and thermal energy storage. Significant scientific and industrial interest has grown for their use as free-standing electrodes for electrochemical devices such as batteries, fuel and biofuel cells, supercapacitors. Nevertheless, the challenges in the development of graphene-based materials for some applications still exist. The properties of traditional carbon electrodes are generally more satisfactory, thus graphene-based materials need to be, for example, decorated with other compounds (such as metal/metal oxide particles, simple carbohydrates, polymers) to enhance their performance. Based on this review, it is clear that the possibilities of modification are endless and graphene structures are the near ideal substrates in different hybrid composites. The described materials show highly promising industrial applications, however they are still far from commercial ventures. Scientific concerns should focus on the optimization of the material production, in particular its scalability and reproducibility which, in some cases still face difficulties. Nonetheless, three-dimensional graphene-based structures are rapidly gaining traction as an attractive alternative for conventional carbon-based materials.

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