



Graphene Nanofoam Based Nanomaterials: Manufacturing and Technical Prospects

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Abstract: This article fundamentally reviews progress in the design and manufacturing of threedimensional (3D) graphene-based nanocomposites for technical applications. The 3D graphene nanostructures have been manufactured using techniques like the template method, chemical vapor deposition, sol-gel, freeze-drying, hydrothermal technique, and other approaches. The nanofoam has been reinforced in polymers to achieve superior structural, morphological, and physical characteristics of the ensuing polymer/graphene nanofoam nanocomposites. The polymer/graphene nanofoam nanocomposites have been manufactured using the approaches like direct template method, in situ technique, infiltration process, and other methods. The 3D nanofoam- and polymer-based nanostructures have shown high specific surface area, suppleness, electron transport, thermal conduction, mechanical resilience, and other physical properties. The technical applications of hierarchical graphene nanofoams have been observed in the fields of radiation shielding, solar cells, supercapacitors, fuel cells, and other applications.

Keywords: graphene; nanofoam; manufacturing; nanocomposite; solar cell; supercapacitor

1. Introduction

Graphene is a two-dimensional nanocarbon nanomaterial with sp² hybridized carbon atoms [1]. It is a single-atom thick nanocarbon nano-allotrope. The van der Waals interactions may cause a nanosheet wrinkling effect [2,3]. Graphene has found potential applications in electronics, semiconductors, solar cells, and other technical fields [4]. In addition to two dimensional graphene, three dimensional (3D) graphene nanofoam has gained research attention [5]. The 3D graphene nanofoam or aerogel shows an excellent nano-porous structure and unique morphology. The graphene nanofoam not only exhibits the inherent properties of graphene nanosheet, but also reveals remarkable physical features [6]. Consequently, the 3D hierarchical nanofoam nanostructure possess high surface area, flexibility, robustness, porosity, and outstanding structural, mechanical, thermal, electrical, and other enhanced physical features [7,8]. Several approaches have been developed for the manufacture of graphene nanofoam such as template approach, chemical vapor deposition, freeze/supercritical drying, hydrothermal, sol-gel, and numerous other approaches [9–11]. The graphene nanofoam has been explored for the potential applications in the nanocomposites, electronics, supercapacitors, photovoltaics, batteries, energy, electronics, environment, and biomedical applications [12,13].

This state-of-the-art review presents advances in the design, manufacturing, and properties of 3D graphene nanofoam. Then, essential aspects of graphene nanofoam



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). based nanocomposites are discussed including the manufacturing approaches, essential properties, and application areas. The transformation of graphene nanosheet into 3D graphene nanofoam revealed remarkable structural and property innovations leading to promising application areas of the graphene nanofoam nanocomposite. Figure 1 shows the graphic of technical developments of graphene-to-graphene nanofoam and nanocomposite nanofoam for high-tech applications.

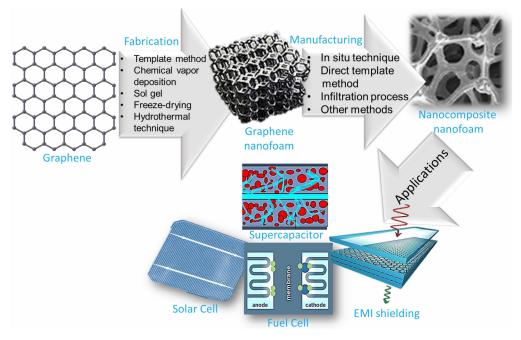


Figure 1. Schematic of technological developments of graphene-to-graphene nanofoam and nanocomposite nanofoam.

2. Nanofoam

Carbon nanofoam is a three-dimensional nano-allotrope of carbon [14,15]. In carbon nanofoam, the carbon atoms are arranged in a 3D hexagonal structure, which is often referred to as aerogel [16,17]. Initially, laser pulse technique was used to form the nanofoam using a carbon target in an inert atmosphere [18]. Carbon nanofoam exhibits high surface area and a transparent structure [19]. The three dimensional nanofoam has a C-C bond length of 5.6 Å [20]. The nanofoam usually possesses low density of $\sim 2 \text{ mgcm}^{-3}$, and so it is lightweight [21]. Due to unpaired electrons, carbon nanofoam displays ferromagnetic properties below 90 K. Due to the magnetic properties, the carbon nanofoam revealed applications in spintronic devices and bio-imaging [22–24]. According to scanning/transmission electron microscopy, the nanofoam consists of woven forms of graphene nanosheets [25,26]. The periodic patterns have been observed in the three dimensional cross-linked nanostructures [27]. The simulation or computational studies have been performed to investigate the nanofoam nanostructures [28]. Furthermore, the carbon nanofoam has been applied in high-performance thermal insulation materials [29–31]. In addition, the three-dimensional nanofoam shows high electrical conductivity, thermal conductivity, and optical absorption [32,33]. The nanofoam displays a low dielectric constant, necessary for significant electrical properties [34]. The low dielectric constant and high charge transportation of these materials were found important for electronics/microelectronics applications [35,36]. The structure of carbon nanofoam has been modified through the inclusion of carbon nanoparticles (carbon nanotube or carbon nanofibers) in the three dimensional structure [37]. The modified nanofoam may lead to improved structural properties and high-tech applications. Graphene is a unique two dimensional nanocarbon nanostructure [38,39]. It has a unique hexagonal arrangement of sp² hybrid carbon atoms with π bonding [40]. Owing to unique structure and superior physical properties, graphene presented potential for various advanced technical applications ranging from energy/electronics to biomedical devices [41–43]. The two dimensional graphene nanosheets can be arranged into a three dimensional nanostructures [44,45]. The 3D graphene is often referred as graphene nanofoam, graphene sponge, or graphene aerogel in the literature [46]. The three dimensional macroassemblies of graphene have been developed due to van der Waals interactions between the nanosheets [47]. The three dimensional graphene nanofoam shows the intrinsic features of graphene and also novel physicochemical properties [48]. Consequently, the three dimensional graphene nanofoam possesses a large surface area, thermal transport, electrical conductivity, mechanical stability, porosity, and flexibility [49]. Graphene nanofoam has a high specific surface area of 1000 m²g⁻¹ [50]. The three-dimensional graphene nanofoam has been developed using graphene and so novel physicochemical properties [49]. Graphene nanofoam has a sigh specific surface area of 1000 m²g⁻¹ [50]. The three-dimensional graphene nanofoam has a well as graphene oxide.

Numerous manufacturing approaches have been applied for the formation of the three dimensional graphene [52]. Depending upon the fabrication strategy used, the graphene nanofoam may reveal different morphologies [53]. The template methods have been frequently used for the synthesis of graphene nanofoam [54]. Deng and co-workers [55] developed the three dimensional graphene on the nickel foam template via chemical vapor deposition technique (CVD). The graphene nanofoam has large surface area and mechanical robustness properties. Moreover, the graphene-nanofoam-based electrode showed high specific capacitance of 321 Fg⁻¹ for high performance supercapacitor. Zhang et al. [56] proposed a route to graphene nanofoam derived from the template method showed low density, high porosity, mechanical stability, and electrical conductivity [57].

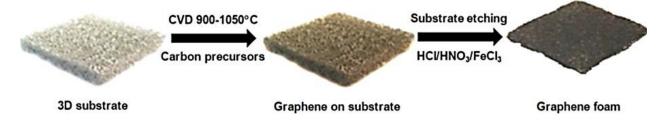


Figure 2. Schematic of synthesis of three dimensional graphene network through chemical vapor deposition. Reprinted with permission from Ref. [56]. 2022, MDPI.

Along with CVD, numerous other manufacturing methods have been used for the formation of graphene nanofoam [58]. Consequently, the freeze/supercritical drying approaches have been adopted to produce the 3D inter-linked graphene nanofoam [59,60]. The direct hydrothermal technique has also been applied for the formation of 3D graphene nanofoam with nanoparticles [61]. Zhang et al. [62] fabricated the 3D graphene nanofoam with titanium dioxide nanoparticles using the one-pot technique. The graphene nanofoam has efficient absorption properties [63]. Consequently, the nanofoam has been found useful for the adsorption-photo-electrocatalytic degradation of bisphenol A. The sol-gel technique was considered useful to prepare the 3D graphene oxide nanofoam [64]. The chemical cross-linking was observed due to reaction between hydroxyl, carbonyl, and epoxide functionalities of graphene oxide and the sol-gel precursor [65]. In this method, the heat/thermal treatment has been applied for the development of covalently linked 3D graphene structure [66]. During thermal treatment, the macro-assemblies of graphene oxide were reduced to graphene [67]. The sol-gel-derived graphene nanofoam revealed high surface area, porosity, electron mobility, and thermal conductivity properties [68,69]. The graphene nanofoam nanocomposites exhibited applications in catalysis, sensors, energy storage devices, absorbents, and biomedical fields [70]. Table 1 compares the various graphene nanofoam fabricated using numerous manufacturing approaches. All the mentioned methods have been efficiently used to prepare the high performance nanofoam.

Table 1. Essential properties of graphene nanofoam.

| Nanofoam | Fabrication | Properties/Applications | Ref. |
|---|---|--|------------|
| Graphene nanofoam | Chemical vapor deposition technique | Specific capacitance 321 Fg ⁻¹ | [55] |
| Graphene nanofoam | Template + catalyst method | Low density; high porosity; mechanical stability; electrical conductivity | [56] |
| Graphene nanofoam | Hydrothermal technique | Mechanical stability; electrical conductivity | [61] |
| Graphene nanofoam | One-pot technique Absorption properties | | [62] |
| Graphene nanofoam Sol-gel technique; heat/thermal treatment | | Chemical cross-linking; high surface area; porosity; electron mobility; thermal conductivity | [64,68,69] |
| Graphene nanofoam | Freeze-drying | Freeze-drying 1280 times higher elastic modulus than CVD nanofoam | |
| Graphene nanofoam | Freeze-drying | Average pore size 70–100 μm | [71] |
| Graphene oxide foam Freeze-drying | | Compression strength; recovery after 300 compression cycles | [72] |

4. Polymer/Graphene Nanofoam Nanocomposite

Numerous manufacturing approaches have been applied for the formation of 3D nanofoam nanoarchitectures [73]. The nanofoam-based nanocomposites displayed high surface area, low density, and high electronic, thermal, and mechanical characteristics [74]. Yao et al. [75] applied the simple one-pot surfactant-free technique to manufacture polymer/3D reduced graphene oxide nanofoam nanocomposites. The materials have been used for the supercapacitor electrodes. A significantly high specific capacitance of 952.85 Fg⁻¹ was obtained. Tang et al. [76] fabricated the three dimensional reduced graphene oxide using the hydrothermal method. Then, the polyaniline/three-dimensional reduced graphene oxide nanocomposite was manufactured using the in situ technique. Figure 3 demonstrates the formation of the polyaniline/three-dimensional reduced graphene oxide nanocomposite. The nanomaterial was developed as supercapacitor electrode with high specific capacitance of 243 Fg⁻¹.

Wang et al. [77] manufactured the polyaniline/3D graphene oxide and reinforced in the epoxy matrix through the in situ oxidative polymerization. Figure 4 depicts the synthesis of epoxy and polyaniline/graphene oxide nanofoam derived nanocomposites. The graphene oxide nanofoam has been prepared using the freeze-drying method. The 3D graphene oxide nanofoam was reduced to the 3D graphene nanofoam. The in situ oxidative polymerization of aniline was performed on the 3D graphene nanofoam to form the nanocomposite. The resulting polyaniline/3D graphene nanofoam was reinforced in the epoxy matrix. The interface bonding between the polymer and nanofoam has been observed. The 0.39 wt.% nanofoam loading enhanced the electrical conductivity to 0.036 Scm^{-1} . Figure 5 shows the interfacial bonding mechanism for the formation of the nanocomposite. The π - π stacking interactions have been observed between the polyaniline and graphene structure.

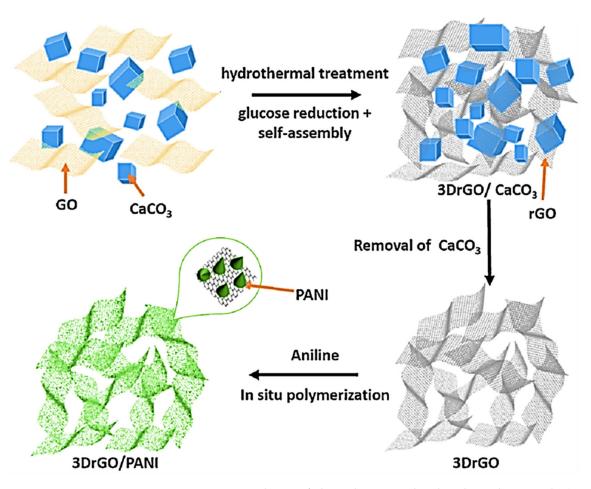


Figure 3. Preparation scheme of three dimensional reduced graphene oxide (3D-rGO) and three dimensional reduced graphene oxide/polyaniline (3D-rGO/PANI). GO = graphene oxide; PANI = polyaniline. Reprinted with permission from Ref. [76]. 2015, Elsevier.

Li et al. [78] performed the manufacturing of graphene nanofoam by hydrolytic condensation technique. The 3D polypyrrole/graphene oxide nanofoam was developed using the in situ route [79]. The 3D nanofoams were applied for oil and solvent adsorption. The sorption capacities were found to be high, >100 gg⁻¹, due to 3D covalent network formation in the nanofoams [80]. Salvatierra [81] reported on the preparation of polythiophene/graphene nanofoam nanocomposite through the one-pot in situ route.

Wang et al. [82] used the infiltration technique for the formation of the epoxy and graphene-nanofoam-based nanocomposite. Jia and co-workers [83] manufactured the graphene nanofoam reinforced epoxy derived nanocomposites using the infiltration method. The nanocomposite had high fracture toughness of $1.78 \text{ MPa} \cdot \text{m}^{1/2}$. Moreover, the 0.2 wt.% nanofoam loading revealed the electrical conductivity of 3 Scm^{-1} . Ormategui et.al. [84] proposed the epoxy and reduced graphene-oxide-nanofoam-based nanocomposite with superior electrical conductivity and mechanical properties.

Rinaldi [85] manufactured the poly(dimethyl siloxane) (PDMS) and graphene-nanofoambased nanocomposite using direct template method. The PDMS/graphene-nanofoam-derived pressure sensor was developed, which detected pressure variations ~1 Pa. The nanocomposite sensing material had compressive stress ~10 kP. Zhao and co-workers [86] manufactured the poly(dimethyl siloxane) nanocomposites with graphene nanofoam and graphene sheet nanofillers. The nanocomposites were formed through the solution and infiltration routes. Figure 6 depicts the scanning/transmission electron microscopy images of the graphene nanofoam and graphene sheet. The graphene nanofoam had a three-dimensional structure, whereas the graphene sheet possesses a wrinkled structure. Figure 7 shows the thermal conductivity of neat PDMS and nanocomposite with graphene nanofoam and graphene nanosheet. Neat PDMS revealed thermal conductivity of $0.19 \text{ Wm}^{-1}\text{K}^{-1}$. The graphenenanofoam- and graphene-nanosheet-based nanocomposites had high thermal conductivity of 0.46 and 0.56 Wm⁻¹K⁻¹, respectively. The better graphene dispersion and inter-linked network formation led to better thermal conductivity and electron transportation properties.

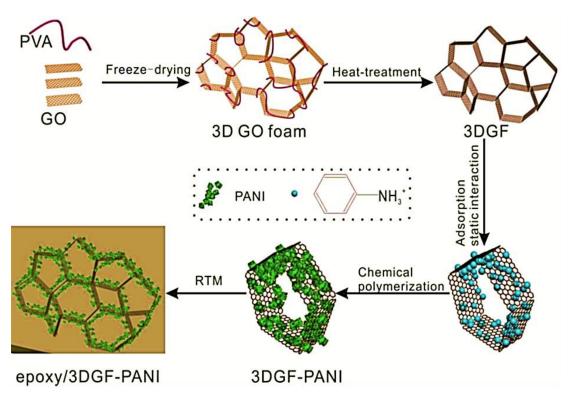


Figure 4. Schematic of preparation of three dimensional graphene oxide-polyaniline (3DGF-PANI) and epoxy/three dimensional graphene oxide-polyaniline (epoxy/3DGF-PANI) nanocomposite. Reprinted with permission from Ref. [77]. 2018, Elsevier.

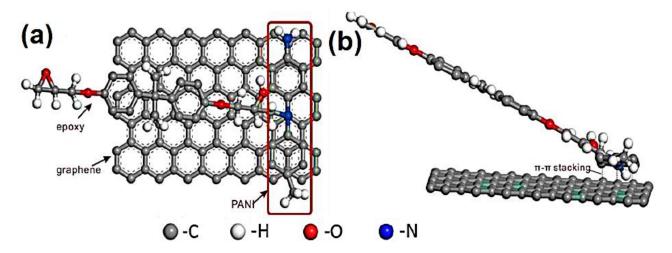


Figure 5. Schematic of proposed interfacial bonding mechanism (**a**) vertical view and (**b**) front view. Reprinted with permission from Ref. [77]. 2018, Elsevier.

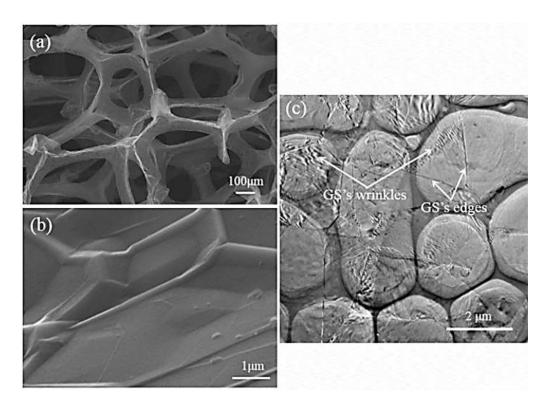


Figure 6. Scanning electron microscopy images of (**a**) graphene nanofoam; (**b**) graphene sheet; and (**c**) transmission electron microscopy image of graphene sheet. PDMS = poly(dimethyl siloxane); GF/PDMS = /poly(dimethyl siloxane); GS/PDMS = poly(dimethyl siloxane). Reprinted with permission from Ref. [86]. 2015, Elsevier.

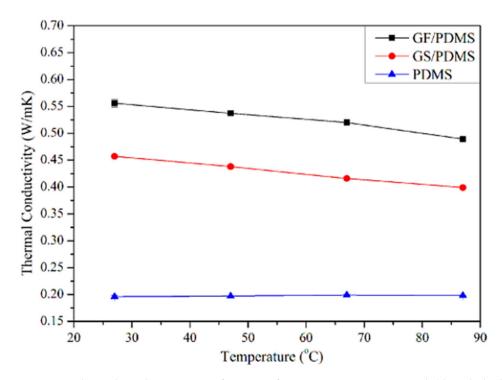
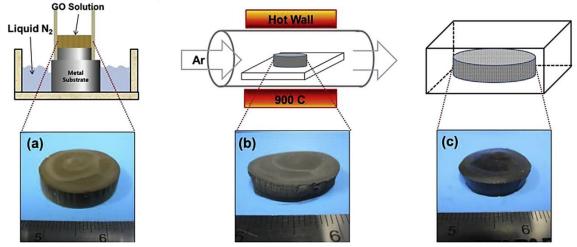


Figure 7. Thermal conductivity as a function of temperature. PDMS = poly(dimethyl siloxane); GF/PDMS = graphene nanofoam/poly(dimethyl siloxane); GS/PDMS = graphene sheet/poly(dimethyl siloxane). Reprinted with permission from Ref. [86]. 2015, Elsevier.

Jun et al. [87] manufactured the poly(dimethyl siloxane)/graphene nanofoam nanocomposites using the freeze-drying and infiltration methods. The small flake and large flake graphite nanosheets have been used to form the graphene nanofoam. Figure 8 demonstrates the manufacturing processes for the formation of graphene nanofoam by a freeze-drying technique. Later, the infiltration of PDMS resin through the nanofoam led to the formation of nanocomposite. Figure 9 depicts the in-plane electrical conductivity of the poly(dimethyl siloxane)/graphene nanofoam nanocomposites. The 1.9 wt.% large flake graphite led to high electrical conductivity of 102 Sm⁻¹, due to better dispersion and interconnecting matrix-nanofiller network formation.



Step I. One-directional Freezing Step II. Thermal Reduction in the Furnace Step III. Infiltration with PDMS

Figure 8. Schematic illustrating manufacturing procedure for (**a**) reduced graphene oxide nanofoam; (**b**) poly(dimethyl siloxane)/graphene nanofoam nanocomposite (**c**), and sliced slab of poly(dimethyl siloxane)/graphene nanofoam on probe fixture PDMS = poly(dimethyl siloxane); LFG = large flake graphite; SFG = small flake graphite. Reprinted with permission from Ref. [87]. 2015, Elsevier.

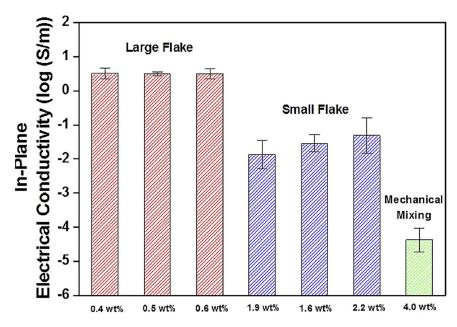


Figure 9. In-plane electrical conductivity of poly(dimethyl siloxane) nanocomposites produced from LFG and SFG, respectively. LFG = large flake graphite; SFG = small flake graphite. Reprinted with permission from Ref. [87]. 2015, Elsevier.

Zhao et al. [88] filled the PDMS matrix with the graphene nanofoam and carbon fiber fillers using high speed shearing and stirring techniques. The filler contents were varied up to 10 wt.%. The 10 wt.% filler addition enhanced the tensile strength and Young's modulus by 52% and 71%, respectively, relative to neat PDMS (Figure 10). The increase was credited to the strong interfacial bonding between the PDMS and the fillers. Moreover, the thermal conductivity of $0.55 \text{ Wm}^{-1} \text{ K}^{-1}$ was observed, that is, ~162% higher than the neat PDMS. Yuan and co-researchers [89] manufactured the polystyrene and graphene-nanofoam-based nanomaterials through the vacuum filtration technique. The polystyrene/graphene nanofoam was used to form the supercapacitor electrode and own large specific capacitance of 141–206 Fg⁻¹. Figure 11 shows the varying trend of specific capacitance as a function of current density for the graphene nanofoam nanocomposite.

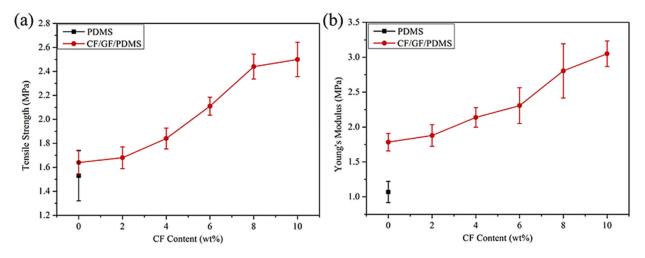


Figure 10. (a) Typical tensile strength and (b) Young's modulus of nanocomposite materials PDMS = poly(dimethyl siloxane); CF/GF/PDMS = carbon fiber/graphene nanofoam/poly(dimethyl siloxane). Reprinted with permission from Ref. [88]. 2016, Elsevier.

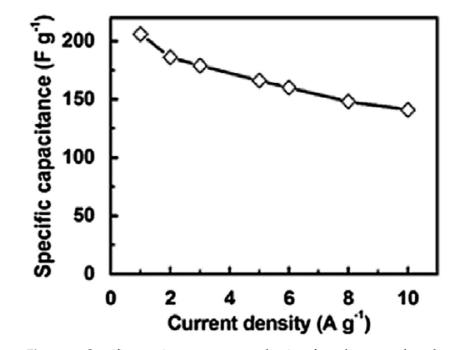


Figure 11. Specific capacitance vs. current density of graphene-nanofoam-based nanocomposite electrode. Reprinted with permission from Ref. [89]. 2014, Elsevier.

Gnanasekaran and co-workers [90] manufactured the polybutylene terephthalate/ graphene nanofoam nanocomposite using the infiltration method. The nanomaterial was utilized for the printing of electrically conducting structures. Among other polymers, polyamide 6 has been composited with the graphene nanofoam through in situ polymerization [91]. The polyamide 6/graphene nanofoam nanocomposite had high thermal conductivity of 0.891 Wm⁻¹K⁻¹ [92]. Thus, various combinations of polymers with graphene nanofoam, graphene oxide nanofoam, and reduced graphene oxide nanofoam have been manufactured through facile routes. The nanofoam designs have been explored for the enhanced morphological, conducting, capacitance, thermal, and mechanical properties.

5. Significance of Polymer/Graphene Nanofoam Nanocomposite

The manufacturing and property exploration of the polymer/graphene nanofoam architectures have attracted considerable research attention in numerous technical fields [93,94]. Table 2 compares the essential polymer- and nanofoam-based nanomaterials with fabrication techniques, properties, and application areas. It has been observed that the conducting polymer-based nanocomposites revealed enhanced electrical conductivity properties for suitable applications. However, thermoplastic polymer/graphene nanofoam nanomaterials also revealed high performance and technical uses. Consequently, by manufacturing 3D graphene nanofoam instead of two-dimensional graphene nanostructures, high performance and industrial applications have been achieved.

| Polymer | Nanofoam | Fabrication | Properties/Applications | Ref. | |
|-------------------------|------------------------------------|---|---|---------|--|
| Polymer | 3D reduced graphene oxide nanofoam | One-pot surfactant- free technique | Supercapacitor; specific capacitance 952.85 Fg ⁻¹ | [75] | |
| Polyaniline | 3D reduced graphene oxide | Hydrothermal method; in situ technique | Supercapacitor; specific capacitance 243 Fg ⁻¹ | [76] | |
| Polyaniline | 3D graphene oxide | Freeze-drying; In situ oxidative polymerization | π-π stacking interactions; electrical conductivity 0.036 Scm ⁻¹ | [77] | |
| Polypyrrole | Graphene oxide nanofoam | Hydrolytic condensation; in situ route | Oil/solvent adsorption; sorption capacities >100 gg ⁻¹ | [76,78] | |
| Polythiophene/ | Graphene nanofoam | In situ route | Electrical conductivity | [81] | |
| Epoxy | Graphene nanofoam | Infiltration method | Fracture toughness 1.78 MPa·m ^{1/2} ; electrical conductivity $3 \mathrm{Scm}^{-1}$ | [83] | |
| Poly(dimethyl siloxane) | Graphene nanofoam | Direct template method | Pressure sensor; pressure variations ~1 Pa; compressive stress ~10 kP | [85] | |
| Poly(dimethyl siloxane) | Graphene nanofoam | Solution and infiltration route | Thermal conductivity $0.56 \text{ Wm}^{-1}\text{K}^{-1}$ | [86] | |
| Poly(dimethyl siloxane) | Graphene nanofoam | Freeze-drying; infiltration methods | Electrical conductivity 102 Sm ⁻¹ | [87] | |
| Poly(dimethyl siloxane) | Graphene nanofoam | High speed shearing and stirring techniques | Increase in tensile strength 52%; Young's modulus 71%; thermal conductivity 0.55 Wm ⁻¹ K ⁻¹ i.e., increase by 162% | [88] | |

Table 2. Specifications of polymer/graphene nanofoam nanocomposites.

| Polymer | Nanofoam | Fabrication | Properties/Applications | Ref. | |
|---|-------------------|---|---|-------|--|
| Polystyrene | Graphene nanofoam | Vacuum filtration technique | Supercapacitor; specific capacitance 141–206 Fg ⁻¹ | [89] | |
| Polybutylene terephthalate | Graphene nanofoam | Infiltration method. | Thermal conductivity 0.891 Wm ⁻¹ K ⁻¹ | [90] | |
| Poly(3,4- ethylenedioxythiophene): poly(styrenesulfonate) | Graphene nanofoam | Drop coating technique | High porosity 98.8%; ultralow density ~18.2 \times 10 ⁻³ g/cm ³ ; EMI shielding effectiveness 91.9 dB; electrical conductivity 43.2 Scm ⁻¹ | | |
| Poly(vinylidene fluoride) | Graphene nanofoam | Hot pressing technique | EMI shielding effectiveness ~20 dB; electrical conductivity 10^{-4} S m ⁻¹ | [96] | |
| Polyurethane | Graphene nanofoam | Hydrothermal method | EMI shielding effectiveness 969–1578 dBcm ² g ⁻¹ | [97] | |
| Polymer | Graphene nanofoam | CVD; spin coating techniques | Dye sensitized solar cells; AM 1.5 illumination | [98] | |
| Polymer | Graphene nanofoam | Solution/ coating | Power conversion efficiency 6.58%; short-circuit current density 15.4 mAcm ⁻² ; dye absorption efficiency ~1.28 \times 10 ⁻⁷ mol cm ⁻² | | |
| Polypyrrole | Graphene nanofoam | Solution dispersion; chemical/hydrothermal reduction routes | Specific capacitance 253–520 Fg ⁻¹ | | |
| Polyaniline | Graphene nanofoam | One-step electrochemical deposition | Specific capacitance 751 Fg ⁻¹ | | |
| Poly(methyl methacrylate) nanofoaming | Graphene | Thermal annealing method | Polymer electrolyte membrane fuel cell; high power density ~967 mW cm ⁻² | [102] | |

Table 2. Cont.

Consequently, significant technical application areas of the polymer/3D graphene nanofoam nanomaterials have been discovered [94]. The electromagnetic pollution, due to intensive use of electronic devices, has caused serious environmental issues [103]. In this regard, the electromagnetic interference (EMI) shielding nanocomposites were manufactured through the three dimensional graphene nanofoams [104]. Owing to high electrical conductivity, the graphene-nanofoam-based nanocomposites revealed fine EMI shielding performance. The graphene-nanofoam-based nanocomposites possess high durability, flexibility, and radiation protection features [105]. Such materials have been found very useful in the aerospace sector for radiation shielding [106]. Important research attempts have been found on the conducting polymer/graphene nanofoam nanocomposites for EMI shielding applications [107,108]. Wu et al. [95] manufactured the ultralight poly(3,4ethylenedioxythiophene):poly(styrenesulfonate)/graphene nanocomposite nanofoam using the drop coating technique. This method resulted in enhanced wettability and interfacial interactions between the poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) matrix and graphene nanofoam. The nanocomposite nanofoam revealed high porosity (98.8%) and ultralow density ~18.2 \times 10⁻³ g/cm³. Due to a finely interlinked 3D network structure, high electrical conductivity of 43.2 Scm⁻¹ was obtained. Consequently, the nanocomposite nanofoam revealed significantly high EMI shielding effectiveness of 91.9 dB. In addition, thermoplastic polymer/graphene nanofoam has been developed for

EMI shielding applications [109]. Eswaraiah et al. [96] manufactured the poly(vinylidene fluoride)/graphene nanofoam nanomaterials using the hot pressing technique with a foaming agent. Due to fine compatibility between polymer–graphene nanofoam and conducting network formation, the electrical conductivity of nanomaterial $(10^{-4} \text{ Sm}^{-1})$ was found to be higher than the neat polymer $(10^{-16} \text{ Sm}^{-1})$. Consequently, the 0.5 wt.% graphene nanofoam contents led to EMI shielding effectiveness of ~20 dB in X-band (8–12 GHz). Furthermore, the polyurethane and graphene nanofoam nanocomposites have been manufactured through the hydrothermal method [97]. Due to superconductivity features, the polyurethane/graphene nanofoam nanocomposites own high EMI shielding effectiveness of 969–1578 dBcm²g⁻¹. Future research attempts have been found desirable for lightweight high-performance polymer/graphene-nanofoam-based EMI shielding materials for X-band. Additionally, the mechanism of EMI shielding in these nanomaterials need to be explored in the future.

Another important application of 3D graphene nanofoam has been observed in photovoltaics [110]. By converting the 2D graphene to 3D graphene nanofoam network, remarkable solar cell performance has been observed for solar cells [111]. In this regard, graphene-nanofoam-based dye sensitized solar cells (DSSC) have been developed and analyzed for environmental stability, toxicity, cost-effective, and commercial uses. Lee et al. [98] designed the 3D nanofoam using CVD and spin coating techniques on the polymer/nickel. The photovoltaic performance of DSSC was measured with AM 1.5 illumination (100 mW cm²). Tang et al. [99] manufactured DSSC using graphene nanofoam and CVD system. The graphene nanofoam was applied as the photoanode to enhance the photovoltaic functioning (Figure 12 and Table 3). Inclusion of 1 wt.% graphene nanofoam resulted in high power conversion efficiency and short-circuit current density of 6.58% and 15.4 mAcm $^{-2}$, respectively. The graphene-nanofoam-based material had high dye absorption efficiency of ~ 1.28×10^{-7} mol cm⁻². The nanomaterial depicted competent solar cell efficiency, dye absorption, and electrode lifetime. However, limited research attempts have been seen in the field of polymer/graphene-nanofoam-based DSSC and need to be further explored.

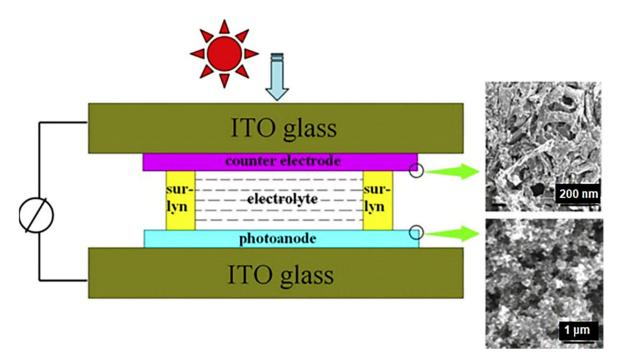


Figure 12. DSSC with graphene-nanofoam-based photoanode. DSSC = dye sensitized solar cell. Reprinted with permission from Ref. [99]. 2013, Elsevier.

| Photoanode | Short Circuit Current Density (Jsc) (mAcm ⁻²) | Photovoltaic Bias (Voc) (mV) | Fill Factor (FF) (%) | Efficiency η (%) | Absorbed Dye ($\times 10^{-7}$ mol cm ⁻²) |
|----------------------------------|--|---------------------------------|-------------------------|---------------------|--|
| 3D graphene nanofoam 0.5 wt.% | 13.6 | 671 | 63.4 | 5.79 | 1.03 |
| 3D graphene nanofoam 1 wt.% | 15.4 | 673 | 63.5 | 6.58 | 1.15 |
| 3D graphene nanofoam 2 wt.% | 11 | 674 | 63.2 | 6.01 | 1.28 |

Table 3. Results of photovoltaic properties and dye loading of the DSSC with varied photoanodes. DSSC = dye sensitized solar cell. Reprinted with permission from Ref. [99]. 2013, Elsevier.

Supercapacitors are an efficient energy storage device exhibiting ultrahigh capacitance, power density, and long cycle life [112]. The supercapacitor materials have been researched for low cost, high specific surface area, mechanical robustness, and chemical stability properties [113,114]. Especially, graphene is an emerging carbon material used in the field of energy storage. The graphene nanofiller has been reinforced in the polymers for enhanced supercapacitance features [115]. For supercapacitors, the 3D graphene-nanofoam-based electrodes have also been used [116]. The polypyrrole/3D graphene nanofoam derived electrodes had elevated specific capacitance of ~300 F/g [117]. Graphene nanofoam exposed capacitance of \geq 95% over 1000 galvanostatic charge/discharge cycles. Moreover, the epoxy/graphene nanofoam with nanoparticles have been used to form the supercapacitor electrode capacitance [118,119]. The supercapacitor electrode showed capacitance of 38 mFcm⁻² and current density of 0.67 mAcm⁻². The resulting supercapacitors possess high power efficiency and long lifetime [120]. Ye et al. [100] formed the 3D polypyrrole/graphene nanofoam using solution dispersion and chemical/hydrothermal reduction routes. The π - π stacking interactions were observed between the polypyrrole and graphene nanofoam. The nanocomposite nanofoam possess high specific surface areas and uniform porosity. The 3D interlinked hierarchically porous nanostructure led to high specific capacitance of 253–520 Fg^{-1} and excellent cycling stability [121]. Yu et al. [101] prepared the 3D polyaniline/graphene nanofoam using one-step electrochemical deposition technique. The highly ordered 3D nanostructure of polyaniline/graphene nanofoam electrode had high specific capacitance of 751 Fg^{-1} and capacitance retention of 98.2% after 1000 charging/discharging cycles. Future research attempts must focus the design of chemically/thermally stable conducting polymer/graphene nanofoam and use of green nanomaterials for advanced supercapacitors for commercial applications.

Graphene nanofoam has also been applied in electronics such as batteries, sensors, etc. [122,123]. To advance the existing lithium–sulfur batteries for the current energy storage marketplace, it has been found essential to increase the electrochemical stability of the sulfur electrodes [124]. In this regard, graphene nanofoam has been designed as a current collector for the lithium–sulfur battery cathode. The graphene nanofoam may develop tortuous conducting network to enhance the conductivity of sulfur cathodes. CVD technique has been used to form graphene-nanofoam-based electrodes for lithium–sulfur batteries [125]. Few attempts have also been observed on the graphene-nanofoam-based strain sensors [126]. Electron transportation through these sensors has been analyzed [127]. The potential application of graphene nanofoam in straintronics may result in further advances in this field [128]. Nevertheless, few polymer/graphene-nanofoam-derived nanomaterials have been applied for electronics, and further efforts are needed to explore the full potential of these materials in this application.

For fuel cell applications, latest advances have revealed the use of graphene-based nanomaterials in the bipolar plates, electrodes, and electrolytes [129]. In this regard, the novel graphene-based nanomaterials and related structure-property relationships have been explored. Accordingly, the graphene nanofoam has been applied as catalyst supports [130]. Especially, graphene nanofoam has been used as anode electrode for the microbial fuel cell [131]. High power density of 427.0 W/m³ of fuel cell was observed.

Research efforts have been performed for improving the operational stability and lifetime of the polymer electrolyte membrane fuel cell (PEMFC) [132]. Nevertheless, the corrosion of metal bipolar plates has been observed as a major challenge in PEMFC, which may lead to low fuel cell efficiency and durability [133]. Sim et al. [102] designed the 3D nanostructure based on the poly(methyl methacrylate)/multilayer graphene using the rapid thermal annealing method. The 3D poly(methyl methacrylate)/graphene nanofoam was used to form the bipolar plate for fuel cell. The resulting PEMFC revealed significantly high power density of ~967 mW cm⁻² at cell potential of 0.5 V. Moreover, the interfacial contact resistance of 9.3 m Ω cm² was observed at 10.1 kgf cm⁻². Future efforts on manufacturing the novel polymer/graphene nanofoam designs may help to overcome the limitations of present PEMFC systems and to further enhance the efficiency of these energy conversion systems.

In future, the graphene-nanofoam-derived nanofibers can be developed for various unexplored technical application areas [134–136]. Moreover, large-scale production of polymer/graphene nanofoam materials need to be focused on in the future. In addition, the polymer/graphene nanofoams nanocomposites need to be explored in numerous uncovered areas like separation/purification applications, dye adsorption, oil–water separation, tissue engineering, and other biomedical fields [137–139]. Here, the choice of appropriate fabrication technique, in addition to the graphene-nanofoam-derived nanocomposite design led to high-tech applications.

6. Conclusions

The two-dimensional graphene has been applied to manufacture the 3D network structure of graphene nanofoam. The intrinsic features of graphene have been embodied in the graphene nanofoam architecture along with several exceptional properties of 3D nanostructure. Therefore, the graphene nanofoam show numerous beneficial features, relative to the neat graphene. The graphene nanofoam was manufactured using efficient techniques. An important use of graphene nanofoam has been observed in nanocomposite manufacturing. Here, the developments in design, features, and application areas of polymer and graphene nanofoam nanocomposite have been discussed. The graphene-nanofoam-derived nanocomposites, obtained through facile manufacturing techniques, led to high performance advanced uses. Graphene nanofoam has been found as a true wonder material that promises much in a variety of applications. Different facile methods have been discovered for the synthesis of graphene nanofoam and related nanomaterials, leading to viability and practicalities for the different practical relevance. Consequently, the modification of graphene-to-graphene nanofoam and polymer/graphene nanofoam has a marked impact in manifold applications including radiation shielding, energy storage/production devices, and electronics. Consequently, the current state-of-the-art graphene nanofoam research revolves around the EMI shielding, energy, and electronics fields. The development of 3D graphene nanostructures offers large surface area, porosity, electron transportation, charge passage, specific capacitance, current density, and radiation shielding effectiveness. Here, the interactions between the polymers and 3D graphene nanofoam are essential to improve the nanocomposite performance. Furthermore, the precise control over the pore size/distribution, flexibility, morphology, conductivity, and mechanical/chemical stability, and structure-property relationships of the materials may lead to future high-tech potential of unique graphene-nanofoam-based nanocomposites.

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