TOPICAL REVIEW — Low-dimensional nanostructures and devices

Preparing three-dimensional graphene architectures: Review of recent developments*

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The recent development of synthesis processes to assemble graphene sheets into porous three-dimensional (3D) macroscopic structures are reviewed, including our efforts on 3D graphene structures. Mechanisms for building 3D graphene architectures and their composite materials are also summarized. The functional systems based on 3D graphene architectures provide a significant enhancement in the efficacy due to their unique structures and properties.

Keywords: graphene, three-dimensional architecture, self-assembly, template method

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1. Introduction

Graphene is a one atom-thick, two-dimensional (2D) monolayer carbon material which possesses superior electronic, thermal, optical, and mechanical properties.[1–5] Graphene and its derivatives have sparked an explosion of interest in the applications of low-dimensional physics and electronic devices, energy related systems, sensors, catalysis, composite materials, etc. Interest is mainly focused on the materials' extraordinary electrical, chemical, optical, mechanical, and structural properties. Obviously, these excellent properties are relevant at the nanoscale so that to harness these properties for macroscopic applications. For exploring the advanced properties of individual graphene sheets for macroscopic applications, it is essential to integrate two-dimensional graphene components into three-dimensional (3D) functional architectures. To fully utilize and further explore new functions of graphene, both large-scale synthesis and integration of individual graphene sheets into advanced multifunctional structures are required. Several approaches, such as mechanical exfoliation,[1] epitaxial growth,[6] chemical vapor deposition (CVD),[7,8] and chemical exfoliation of graphite oxide,[9–12] have been successfully developed to produce individual graphene sheets and their functionalized derivatives. In addition, chemically derived graphene sheets, particularly graphene oxide (GO), have often been integrated with other materials such as nanoparticles and polymers to form composites owing to their ease of preparation and processing. The GO produced by Hummers' method has demonstrated its capability to provide novel structures and functionalities if aggregation during synthesis and processing is prevented.[13]

The integration of individual graphene sheets into a three-dimensional macroscopic assembly and then into a functional system is a significant strategy for macroscopic applications. Constructing 3D graphene-based structures has become one of the most active research fields in the last several years.[14–18] Here, we will focus on the development of methods for preparing 3D graphene, and the mechanism of forming 3D graphene frameworks will be discussed. Though lots of work has been done in this tremendously active field, we consider that a brief compilation of the preparation processes used for three-dimensional graphene can be of interest for readers working with 3D graphene-based architectures.

2. Preparation of 3D graphene

Graphene and its functionalized derivatives with unique 2D structures can be well used as the building blocks for self-assembly of 3D functional graphene-based materials.[19,20] It is believed that developing the 3D structures of graphene will further expand its significance in applications. For most solvents, graphene needs to be further functionalized in order to improve its solubility, and π–π stacking with hydrophilic aromatic molecules or coupling to diazonium salts is a good method. In this case, graphene is well dispersed into the gel medium by using the non-covalent π–π stacking interactions with the gelator peptide. Besides, graphite oxide developed by the Hummers method could be soluble in aqueous solutions to make homogeneous graphene suspensions. Good dispersion in an organic or aqueous suspension will benefit the subsequent chemical processing into 3D architectures through self-assembly. Besides, the template-directed approach is another useful strategy to make true 3D architectures, which will also be briefly summarized in this section. Both these two

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strategies (self-assembly and template directed) can make 3D macroscopic structures for practical applications.

2.1. Self-assembly of 3D graphene

Self-assembly has long been recognized as one of the most effective strategies for bottom-up nanotechnology. With its unique structure and properties, graphene naturally becomes a versatile nanoscale building block for self-assembly to achieve hierarchical microstructures and novel functionalities.[21] In colloidal chemistry, it is well known that gelation can be induced by simply changing the electrostatic repulsion forces between colloids. This principle can be applied to a GO dispersion as well. Graphite oxides are 2D amphiphilic conjugated polyelectrolytes featuring a hydrophobic basal plane and hydrophilic oxygenated groups, which can self assemble into 3D graphene architectures.[13] Besides, GO or other graphite derivatives as the starting materials not only can be scalable but also can provide these 3D structures with processability and new functions.

2.1.1. Gelation of GO as organogels

Monolithic graphene architectures can be prepared from either graphene or GO in organic or aqueous suspensions. After gelation, these organic 3D structures will form chemical or physical cross linkers between gelator molecules, monomers, or polymers with GO. For instance, the self-assembly of gelator molecules is a well-known process for the preparation of supramolecular gels, in which a large number of solvent molecules are immobilized by the network structure.[22] GO is the most common form of graphene with its soluble character conferred by the presence of hydroxyl, epoxide, and carboxylic groups at the basal planes and edges, which is used for the preparation of the network structures. The functional groups also provide the tethering sites for the linking of organic molecules. Thus, aqueous suspensions of GO stabilized with gelator molecules have been used for the preparation of organogels. For instance, Banerjee and coworkers incorporated unfunctionalized and non-oxidized graphene into transparent, stable, supramolecular fluorescent organogels formed by an N-terminally pyrene conjugated oligopeptide (Fig. 1).[23]

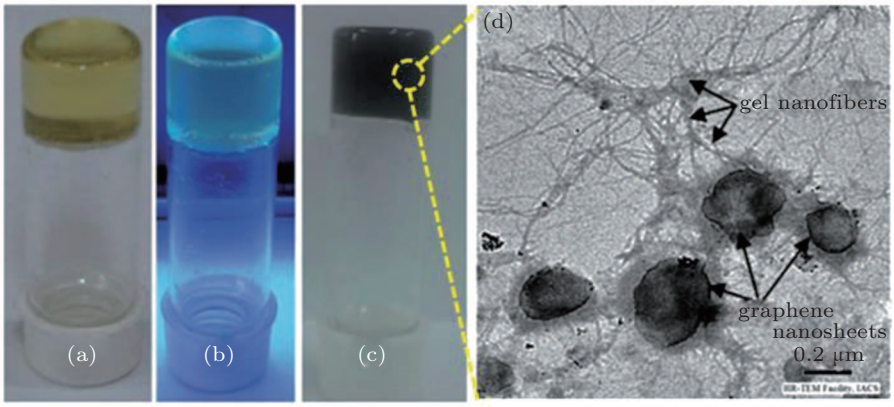


Fig. 1. Photographs of organogel in o-dichlorobenzene, (a) under exposure to daylight, and (b) under exposure to UV light (excitation at 365 nm). (c) Graphene-containing hybrid organogel under exposure to daylight. (d) TEM image of the hybrid organogel (in o-dichlorobenzene), showing the presence of both graphene nanosheets and peptidic gel nanofibrils.[23]

2.1.2. Gelation of GO as hydrogels

The hydrothermal treatment of a homogeneous GO aqueous dispersion is a method for preparing GO-based 3D architectures, either in the presence or in the absence of further additives. Wang and coworkers used a GO suspension that contained a noble-metal salt and glucose.[24] In the absence of noble metals, both the GO concentration in the suspension and the length of the hydrothermal treatment proved effective in tuning the morphology. Whereas Shi and coworkers prepared a GO hydrogel with no components other than GO.[25] The framework of which was formed upon physical cross-linking by the partial overlapping or coalescing of flexible graphene sheets (Fig. 2). Interestingly, the structure was always mechanically strong enough to support the weight of at least a few hundred grams even though the monolith itself only weighed some tens of milligrams. In addition to the excellent apparent mechanical strength, these monoliths exhibited a pretty decent electrical conductivity around 5×10^{-3} S·cm^{-1}.

Recently, Ruoff and coworkers described the production of graphene castings by a pH-mediated hydrothermal reduction of GO suspensions also containing ammonia or NaOH.[26] Combined with the molding methods, the process allowed the controllable fabrication of compact high-density graphene macrostructures with various shapes, e.g., triangular prism, quadrangular prism, joint ring, crucible, screw stem, and gears, among others (Fig. 3). The pH of

the graphene oxide dispersion was a key factor, which determined the properties of its product. The pH had a direct impact on the surface topography, internal structure, and the electrical and mechanical properties of the compact graphene (CG). The CG had the most solid structure and properties when the pH of reaction was adjusted to 10, i.e., smooth surfaces, dense internal structures, good electrical conductivity, and high compressive strength. The

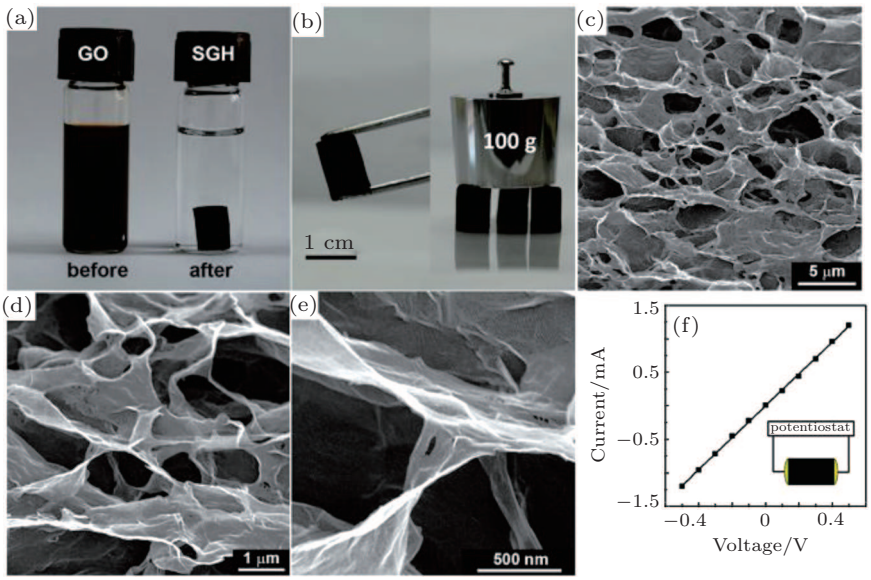


Fig. 2. (a) Photographs of a 2 mg/mL homogeneous GO aqueous dispersion before and after hydrothermal reduction at 180 °C for 12 h. (b) Photographs of a strong rGO hydrogel allowing easy handling and capable of supporting weight. (c)–(e) SEM images with different magnifications of the SGH interior microstructures. (f) Room temperature *I*–*V* curve of the SGH exhibiting Ohmic characteristic, inset shows the two-probe method for the conductivity measurements.[25]

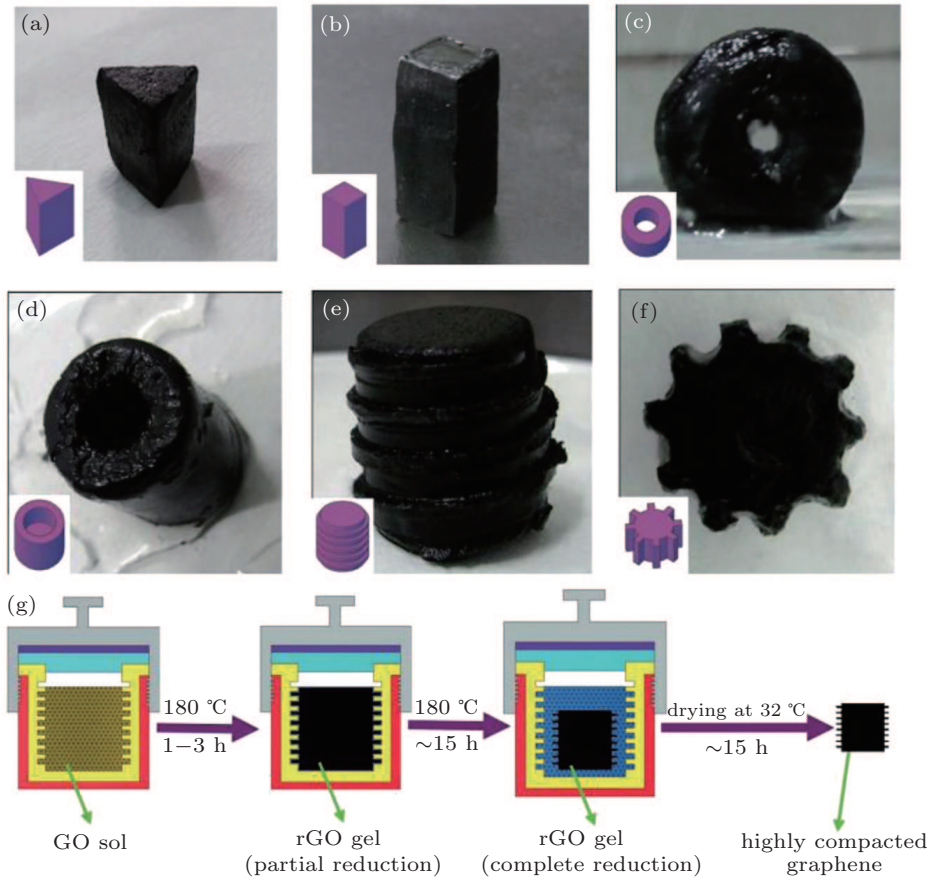


Fig. 3. Different castings of the graphene before drying: (a) triangular prism, (b) quadrangular prism, (c) joint ring, (d) crucible, (e) screw stem, (f) gear. The insets at each photo's bottom-left corner are their three-dimensional concept maps. (g) Diagram of the casting procedure, which comprises four steps: 1) GO dispersed in H_2O, 2) rGO gel with partial reduction indicated by the local magnified image, 3) rGO gel with complete reduction, 4) final casting with densified structure.[26]

density, compressive strength, and electrical conductivity could be further improved (1.6 g·cm^{-3}, 361 MPa, and 7.6 S·cm^{-1}, respectively) by high temperature annealing at 900 °C. This work points toward a new route for preparing highly compressed and super strong three-dimensional carbon macrostructures based on graphene.

2.1.3. Gelation of GO as aerogels

Graphene aerogels can be assembled through the formation of physical cross links between graphene sheets using sol–gel chemistry. Sol–gel chemistry involves the reduction of graphene oxide to form a highly cross-linked hydrogel, which can then be freeze-dried or supercritical-CO_2-dried to form a graphene aerogel. For example, Markovic and coworkers reported the formation of carbon based graphene 3D aerogels.[27] However, the use of freeze-drying provided aerogels in which both the electrical conductivity (e.g., 0.13 S·cm^{-1}) and the surface area (e.g., 240 m^2·g^{-1}) were lower than those of aerogels obtained from supercritical CO_2 drying. Besides, Zhang and coworkers developed an easy method to create graphene aerogels from graphene hydrogel precursors obtained by the chemical reduction of GO using L-ascorbic acid as a reducing agent.[28] The resulting graphene aerogels showed low density (12–96 mg·cm^{-3}), high conductivity (∼10^2 S·m^{-1}), and developed porosity (Brunauer–Emmett–Teller surface area of 512 m^2·g^{-1} and pore volume of 2.48 cm^3·g^{-1}). Note that such a graphene aerogel can support more than 14000 times its own weight (Fig. 4). Recent intensive work has revealed that the self-assembly method is a practical way to prepare either bulk graphene or GO macroassemblies.

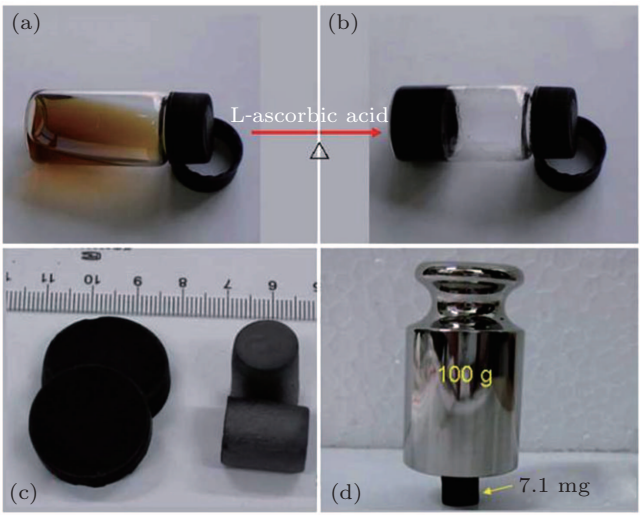


Fig. 4. (a) Photos of the aqueous suspension of graphene oxide. (b) Graphene hydrogel in a vial prepared by heating the mixture of graphene oxide and L-ascorbic acid without stirring. (c) Supercritical CO_2 dried (left) and freeze-dried (right) graphene aerogels. (d) A 7.1 mg graphene aerogel pillar with diameter of 0.62 cm and height of 0.83 cm, supporting a 100 g counterpoise, which is more than 14000 times its own weight.[28]

Recently, Gao and coworkers developed a template-free, synergistic assembly strategy for the scalable fabrication of macroscopic, multiform (1D, 2D, and 3D), ultralight aerogels with controlled densities (Fig. 5).[29] The all-carbon aerogels with a monolith 3D framework were constructed with cell walls of giant graphene sheets and carbon nanotube (CNT) ribs. The ideal combination of the giant size of constituent graphene sheets and the cooperative effect between graphene and CNTs offered the as-prepared aerogels integrated properties, such as outstanding temperature-invariant elasticity, ultralow density, excellent thermal stability, extremely high absorption capacities for organic liquids and phase-transformation materials, and good electrical conductivity.

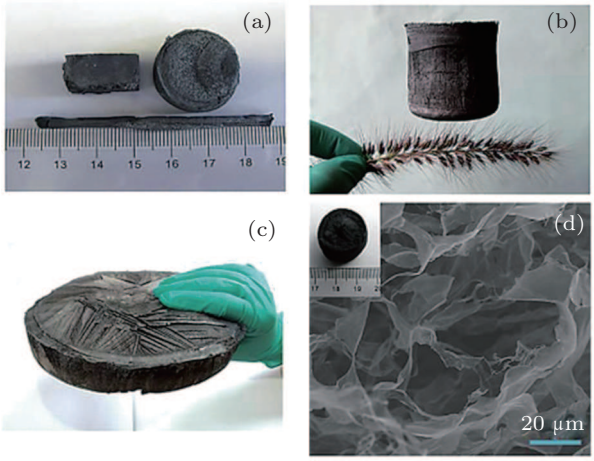


Fig. 5. Macroscopic and microscopic structures of ultra-flyweight aerogels (UFAs). (a) Digital photograph of UFAs with diverse shapes. (b) A 100 cm^3 UFA cylinder standing on a flower-like dog's tail. (c) A ∼ 1000 cm^3 UFA cylinder (21 cm in diameter and 3 cm in thickness). (d) SEM image and photograph (inset) of the lightest neat graphene aerogel (ρ = 0.16 mg·cm^{-3}, i.e., 1.38 mg in 8.6 cm^3).[29]

2.1.4. Flow directed self-assembly

The individual graphene sheets tend to irreversibly aggregate and restack, owing to the strong π–π stacking and the van der Waals force between the planar basal planes of graphene sheets. Therefore, preventing the aggregation of graphene sheets in the macroscopic structures is a critical challenge in constructing functional graphene-based macroscopic structures. Filtration, an efficient technique for the separation of solids from fluids, has been adopted for fabricating GO and rGO papers,[11,30,31] which has been denominated as flow-directed self-assembly. GO papers are prepared through vacuum filtration of their dispersions followed by drying. In the dried papers, the individual graphene sheets are stacked in a nearly parallel fashion to form compact films with an oriented structure. More recently, another approach based on the flow-directed self-assembly of GO followed by a leavening strategy to prepare 3D interconnected macroporous structures was developed.[32] Inspired by the leavening technique, Chen

et al. developed a proof of concept method for transforming compact GO films to porous rGO structures. Autoclave leavening and steaming of GO layered films create paper-like, lightweight, and electrically conductive rGO foams with open pores and continuously cross-linked structures. Thermal steaming of GO layered films with hydrazine appears to be the key to the formation of rGO foams. It is believed that the rapid evolution of gaseous species (such as H_2O and CO_2) in the film during the chemical reduction transforms the compacted GO layers into rGO foams, like the process of making bread from dough. Those continuously cross-linked structures overcome the restacking of graphene sheets and provide better conductive contacts between the sheets, lowering the resistance of foams.

2.1.5. Breath figure method

Although a porous structure can be obtained from random assembly procedures, it is still a challenge to achieve hierarchical architectures with an ordered porous structure in controlled chemical and assembly processes. The "breath figure" method can assemble graphene sheets into bioinspired honeycomb structures.[33,34] In order to use this method, the GO sheets must be modified and transferred into a water-immiscible solution. When the GO solution is cast on a substrate under high humidity, hexagonally packed water microdroplets form by cooling condensation on the solution surface. After solvent evaporation, the honeycomb-patterned film forms, with novel multilevel architectures on the surface.[35] It is important to highlight that the fabrication process of such hierarchical structures is easy, low-cost, green, and scalable, providing a universal approach and new opportunities for the rational design and engineering of electrode materials with enhanced performance.

2.1.6. Mechanism for self-assembly

The self-assembly behavior of functionalized graphene as the 2D molecular building block will inspire more novel designs of hierarchical and functional materials based on graphene. Furthermore, the assembled superstructures have novel collective physiochemical properties that differ from those of the individual components and the bulk material, which enriches the species in the material fields and improves their capacities for practical applications.[36,37] Different interactions, such as dipole interactions, electrostatic attractions or repulsions, hydrophilic/hydrophobic interactions, and hydrogen bonding, have been involved in the driven self-assembly process.[38,39] The hydrophilic–hydrophobic balance between inter planar van der Waals force and electrostatic repulsion of GO regulates their solution properties, and accounts for the self-assembly behavior of GO in aqueous media.

Enlightened by the recent studies on the preparation of a 3D graphene hydrogel,[40] we now know how to prepare composites of embedded 3D graphene nanoparticles if the nanoparticles are dispersed homogeneously in a GO aqueous suspension during the reduction and self-assembly. As shown in Fig. 6, the capture of nanoparticles is similar to fishing with a fishing net, where the fish is the nanoparticles and the fishing net is composed of graphene/graphene oxide nanosheets that can be self-assembled together to form a network during reduction.[41] The nanoparticles can be captured into the graphene network in a simple one-step process during the network formation. Theoretically, any nanoparticles homogeneously dispersed in the aqueous suspension could be embedded into the graphene network to form a 3D graphene/nanoparticles gel.

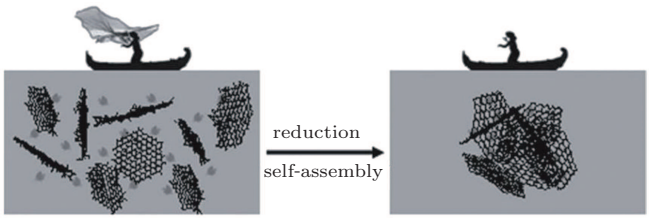


Fig. 6. The proposed self-assembly and wrapping mechanism for 3D graphene/nanoparticle architecture formation during the chemical reduction of GO in an aqueous suspension in the presence of nanoparticles.[41]

2.2. Template-directed approach

Template-guided methods are also effective for the construction of 3D graphene architectures. This approach can produce 3D porous graphene networks with well-defined and shaped structures in 3D scaffolds.[42–46] In the following section, we will review different templates that have been applied as the 3D structure scaffolds to form graphene stereostructures.

2.2.1. Template-directed CVD approach

Although rGO can be readily produced in large quantities without the need for specific equipment, in some cases, its application is limited due to its relatively poor conductivity. Chemical vapor deposition is an alternative method to produce graphene with high quality. Cheng and coworkers first developed a general strategy for the synthesis of 3D graphene foams using template-directed CVD.[42] The procedure consisted of the decomposition of CH_4 at 1000 °C under ambient pressure in the presence of a highly interconnected 3D scaffold of nickel. Graphene films were then precipitated on the surface of the nickel foam. These graphene-foam monoliths exhibited a continuous and interconnected graphene 3D network in which all the graphene sheets were in direct contact with each other without breaks, copying and inheriting the interconnected 3D

scaffold structure of the nickel-foam template, despite the occurrence of a small shrinkage of the graphene skeleton. The high quality of the graphene sheets and their perfect connection in three dimensions gave the material outstanding electrical conductivity, superior to that of macroscopic graphene structures made from chemically derived graphene sheets.

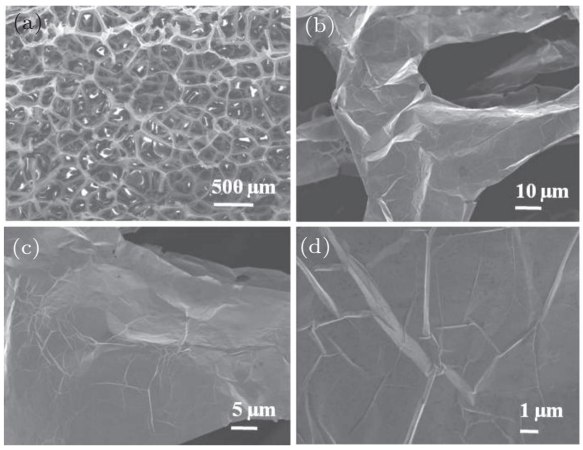


Fig. 7. SEM images of graphene foam made by template-directed CVD.

The 3D architectures endow graphene-based materials with large accessible specific surface areas, interconnected conductive networks, and a special microenvironment. In recent years, our group prepared 3D graphene foams by taking this template-directed CVD approach (Fig. 7). The porous, interconnected network is beneficial to ion diffusion and transfer kinetics, and provides a special reaction microenvironment and multiplexed conductive pathways for rapid charge transfer and conduction. We use the graphene foam as an ideal substrate to support a catalyst, and some ongoing studies on water-splitting through electrocatalysis or photocatalysis are now underway.

2.2.2. Ice template

A freeze drying approach employing ice template-guided assembly has been used for fabricating 3D porous graphene materials in aqueous solution.[43,44] This unidirectional freezing is a well-known wet shaping technique to form porous materials. The technique has been explored by Mann and co-workers to produce 3D graphene macroporous scaffolds. The preparation process is shown in Fig. 8, wherein the aligned 3D architectures and macroscale porosity are controlled by freezing temperatures. Estevez and co-workers demonstrated the preparation of electrically conductive, macroporous hybrids comprising graphene and platinum nanoparticles.[44] After freezing and structure formation, the frozen sample composed of an aqueous suspension of Nafion, GO sheets, and chloroplatinic acid was treated with hydrazine or monosodium citrate to allow *in situ* reduction of GO and chloroplatinic acid to rGO and Pt nanoparticles, respectively (Fig. 8(b)). It was indicated that this strategy can be extended to prepare graphene composite materials, such as graphene–polymer and graphene–nanoparticles.

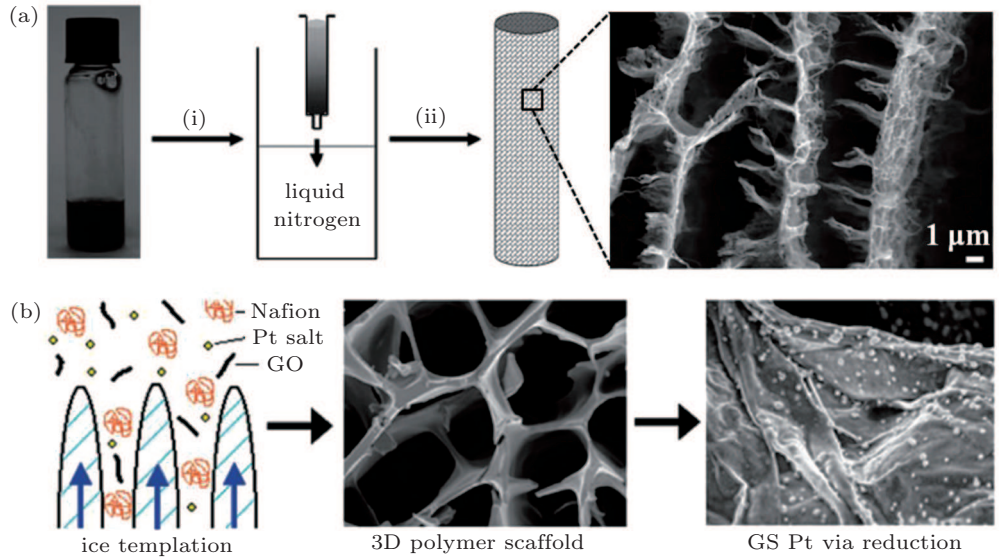


Fig. 8. (a) Schematic diagram showing the formation of macroporous polystyrene sulfonate-stabilized graphene sheets (PSS-G)/poly(vinyl alcohol) (PVA) monoliths using ice-segregation-induced self-assembly. (i) Homogeneous aqueous mixture of PVA and PSS-G (optical image) is transferred into an insulin syringe and unidirectionally frozen by controlled immersion into liquid. (ii) The frozen scaffold is then freeze-dried to sublime the ice crystals to produce a macroporous monolith (shaded cylinder).[43] (b) Schematic diagram showing ice templation to synthesize a Nafion scaffold with Pt and graphene nanosheet precursors, revealed upon reduction.[44]

2.2.3. SiO_2 template

The pores in 3D graphene architectures are usually in the range from hundreds of nanometers to several micrometers depending on the synthesis method. However, the large pores increase the volume and decrease the mechanical properties of the resulting materials. So 3D graphene architectures with nanometer scale pores remain a challenge. In recent years, Zhao and coworkers have developed a novel hydrophobic-interaction-driven hard templating approach to synthesize nanoporous graphene foams with controlled pore size, high surface area, and ultra-large total pore volume.[45] The choice of hydrophobic silica spheres as the templates has proved to be important for the preparation of nanoporous graphene foams (Fig. 9). Such graphene foams have the largest total pore volume (~ 4.3 $cm^3 \cdot g^{-1}$) of all reported porous graphene materials. Furthermore, it has been demonstrated that metal oxide nanoparticles can be easily decorated on the pore walls due to the ultra-voluminous open porosity and the homogeneous hydrophobic surface.

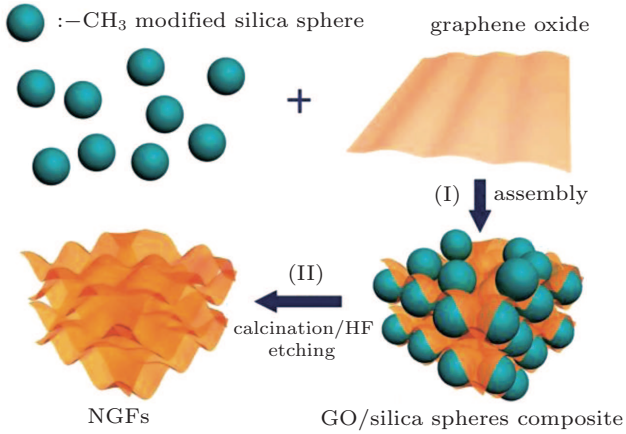


Fig. 9. Schematic diagram of the synthesis procedures of nanoporous graphene foams (NGFs). (I) The self-assembly occurs between GOs and hydrophobic silica templates. (II) Calcination and silica etching to produce NGFs.[45]

2.2.4. Lithographical template

Polsky and coworkers described the conversion of predefined 3D pyrolyzed photoresist films (PPFs) into well-defined 3D porous graphene with dimensions two orders of magnitude smaller than that previously reported for interconnected 3D graphene films.[46] The conversion follows the three-step process presented in Fig. 10, wherein 3D amorphous carbon structures are conformally sputtered with nickel and then annealed, converting the material into 3D graphitic monoliths. Acidic etching removes the remaining nickel, leaving hollow structures that consist of multilayered graphene. PPFs have been used as highly versatile electrode materials which are generated by the pyrolysis of a commercially available microfabrication quality photoresist in a reducing atmosphere. The conversion of PPFs into graphene is an intriguing and novel methodology to create 3D graphene structures using a host of already available lithographic patterning techniques. Moreover, the large concentration of catalytic edge sites implicit in 3D multilayer graphene makes the present material particularly attractive as an electrode material applicable in energy and sensor devices.

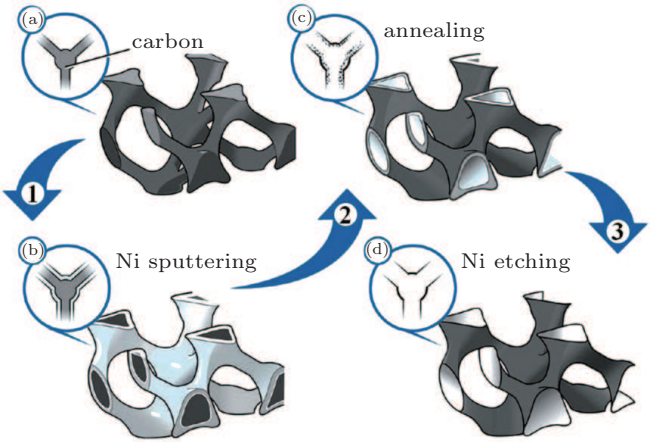


Fig. 10. Steps and mechanism for chemical conversion of amorphous porous carbon to 3D graphene: (a) porous carbon, (b) conformal Ni coating, (c) diffusion of carbon into Ni top surface during thermal annealing, (d) hollow 3D graphene after Ni etching.[45]

3. Conclusion

3D structures provide graphene materials with high specific surface areas, strong mechanical strengths, and fast mass and electron transport kinetics due to the combination of 3D porous structures with the excellent intrinsic properties of graphene. The two main strategies for 3D graphene architectures, self-assembly and template-direction, have been summarized in this paper. Graphene-assembled architectures have a tunable hierarchical morphology with a large surface area and can form macroscopic, large-size monolithic materials. The 3D graphene functional systems have provided a new platform to offer great technological promise for a variety of sustainable applications. Though considerable progress has been achieved in recent years, the large scale production of complex and hierarchical graphene materials with high conductivity, high mechanical properties, and controllable microstructures is still a great challenge.

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