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Blowing Route towards Advanced Inorganic Foams

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1. Overview of Cellular Solids

Growing energy demand and environmental issues put challenges upon new materials. Cellular solids are ensembles of packing cells with solid edges (and faces) in a space (Figure 1).\(^1,2\) Life has evolved diverse cellular patterns, \textit{e.g.} wood and bone.\(^3\) The low-density cellular structure supplies sufficient mechanical support and netlike channels for water and nutrition transports. The use of natural cellular solids (\textit{e.g.} wood) can be traced back to the beginning of humankind. Inspired by nature, since the 20th century, synthetic cellular solids have been engineered including polymers and inorganics (metal, ceramic, and \textit{glass} \textit{etc.} ). Cellular solids are a type of advanced materials with unique functionality. They extend significantly the range of properties/functions of the dense counterparts. Cellular solids play indispensable roles in consumption and industry, with extensive applications of providing lightweight support, impeding thermal flow, absorbing impact energy, damping noise, absorbing oil and ions, coating orthopedic implants, scaffolding biological tissues, and acting as electrochemical porous electrodes.\(^4,8\)

In light of dimension, cellular solids are classified into two-dimensional (2D) honeycomb and three-dimensional (3D) foam. A honeycomb is a cell array on plane. Regular hexagonal grids are the lowest-perimeter configuration for an equal-area division of a plane (as proved in 1999). A 3D cellular solid, \textit{i.e.} foam, is a porous material. According to International Union of Pure and Applied Chemistry, pores are categorized into micropores (<2 nm), mesopores (2-50 nm), and macro-pores (>50 nm). Surgical tape, activated charcoal, zeolite, and metal-organic framework are usual microporous materials.

Mesoporous materials appeared in the early 1990s,\(^9,10\) including mesostructured silicates, carbons, metals, and polymers.\(^11\) Macroporous materials were early engineered, yet their structure (how a foam is built from cells) was studied in the late 19th century. Artificial foams were manufactured, \textit{e.g.} rubber foams \textit{via} Dunlop process in 1929, aluminum foams developed in 1948,\(^12\) porous ceramic articles in 1963,\(^13\) and carbon foams in 1964.\(^14\)

From the aspect of pore forming, foams are fabricated \textit{via} top-down and bottom-up protocols.\(^15-19\) The former includes 3D lithography, 3D patterning, corrosion, dealloying, \textit{etc}. The latter includes:

i) Assembly of building blocks, \textit{e.g.} sintering of powders, powder metallurgy, sol-gel, emulsion polymerization, sintering of hollow spheres, 3D printing, and so on;

ii) Templating, \textit{e.g.} using soft templates, powdery or foamy hard templates, and ice templates (\textit{i.e.} freeze-casting);

iii) Blowing/foaming, including chemical and physical blowing methods.

Artificial foams have become significant engineering materials since the early 20th century. With developing nanotechnology, foams have been newly exploited over the last couple of decades. Foams taking advantages of nanosized building blocks are emerging as advanced functional materials. In spite of luxuriant application-based studies, the foam subdiscipline is in fact sparsely understood and theorized. In this article, we focus on a fabrication strategy, the blowing approach, discussing its fundamental physics, traditional practices, current progress, and constructive applications.
2. Fundamentals of Blowing Approach

2.1. Introduction to Blowing

Blowing is a general strategy, using gas to foam the flowable matter, to yield a large variety of foams. It consists of three steps (Figure 2): the admixing of blowing agents and precursors, the foaming (i.e. bubble nucleation and growth forced by external exertion), and the final stabilization (e.g. solidification, hardening, curing, cross-linking, or crystallization) to convert a fluidlike foam into a solid one. Gas comes from gas-releasable chemical reaction, physical boiling or volatilization, mechanical agitating, or precipitation of pre-dissolved gas. The blown matter stays in a fluidlike status, e.g. melts, mobilizable monomers, flexible macromolecules, and viscous liquids. The gas formats and expands bubbles, where gas enters into bubbles directly or via diffusion through the blown matrix from gas resources.

In a gas-liquid dispersion, if the liquid fraction is >35 vol% (the wet limit), the faces of packed polyhedron cells are reduced as geometrical points. Such a dispersion system looks like isolated bubbles in liquid sea, called as bubbly liquid or gas-liquid flow, which behaves different from foams with the liquid fraction of <35 vol%. With pouring gas continuously, the liquid bubbles appear, destruct, or grow up. Along with decreasing liquid fraction, the gas-liquid system undergoes the statuses of the bubbly liquid and then the fluidlike foam, owing to physically increasing surface tension, viscosity, etc. The fluidlike intermediate foam is usually unstable and weak, under tugging by the built-in pressure of gas. In this stage, the topological and dynamic evolutions, e.g. lamella-thinning, coarsening, rheology, and rupture, occur on mobilizable cells and cell components. Accompanying or following the foaming stage, the further hardening stabilizes the fluidlike foam into a solid foam. In the whole process, the foaming is the key to guiding the cellular structure at micro- to macro-scales, and the stabilization relates to the atomic-level crystallization. Both of them are crucial to realize high-performance foams.

Figure 2. Scheme of blowing process: \(i\) heating or reducing-pressure induces the gas release from blowing agents; \(ii\) the gas initiates the bubbly liquid, then it foams fluidlike precursors; \(iii\) fluidlike foams are finally solidified into solid foams applicable for target scenes.
The blowing agent (known also as pneumatogen) features the blowing method, which is pre-blended in the matrix for releasing minute gas. In terms of the type of gas liberation, there are two mechanisms: chemical or physical blowing. Chemical blowing is capable of producing volatile resultants from endogenous or exotic resources via endothermic/exothermic reactions. For example, it can be the pyrolysis of organics like azodicarbonamide and stearic acid, the decomposition of inorganic salts like sodium bicarbonate and sodium benzoate, or the decomposition of metal hydride to release hydrogen. Physical blowing agents release themselves' gases on boiling, e.g. historically chlorofluorocarbons, hydrochlorofluorocarbons, pentane, butane, and CO\textsubscript{2}. The gas can also be precipitated by reducing the pressure, which is previously dissolved into the matrix at high pressures. Another variant is to jet gases, usually air, N\textsubscript{2} or CO\textsubscript{2} into the matrix via a nozzle. Beating egg whites follows the same mechanism, by forcing air into liquid, to form a froth. The frothing process is sometimes assisted by surfactants to resist thermodynamic collapse.

The ancient blown product should be bread about 14,500 years ago. The leavening agent in baking is yeasts or sodium bicarbonate (used since 1800s), to yield CO\textsubscript{2} within dough. In 1925, aluminum melt was foamed by M. A. De Meller via injection of inert gas or carbonate. The blowing engineering appeared for producing latex foams via either a chemical-blowing Dunlop process in 1929 or a physical-blowing Talalay process in 1936. It did then for polyvinyl chloride plastisol flooring in late 1950s. With arising 2D materials since 2004, the blowing method was introduced into the field of the 3D architecture of 2D materials, for synthesizing boron nitride (BN) foams in 2011,\textsuperscript{21} and 3D graphene foams in 2013.\textsuperscript{22} In last five years, a great deal of foam materials are developed, e.g. macroporous carbon monoliths, 3D doped graphenes, and carbon nitride foams. The blowing technology is well compatible with scalable industry due to ordinary facilities and low cost, which is pretty valuable for both fundamental researches and industrial practices. It is necessary to investigate and understand the blowing mechanism for controlling products. In next sections, we outline the geometry of foams which restricts possible topological configuration, the static equilibrium which points out the stable structure, and the kinetics as well as dynamics which greatly dominates the practical structure of foams.

2.2. Structure and geometry in blowing.

At a glance of cells of foams, the constitution seems disordered, but a close survey discloses plenty of orders. Foams present to be closed-cell or open-cell according to the interconnectivity of cells. A cell is a hollow polyhedron in geometry, and also a macropore in materials science. If all cells are separated into discrete gas pockets by cell walls, it is a closed-cell foam, e.g. ground pad and airplane cushion. If all cells are interconnected with losing walls, it is an open-cell foam, e.g. bath sponge. In geometry, face is the connecting part of every two cells, edge is the triad common of meeting three cells, and vertex is the convergent point of merging four cells (Figure 3). The face is a lamella in materials science, usually a solid membrane to seal off neighbors. The cell wall or pore wall denotes either the lamella or sometimes the sum of faces, edges, and vertex. The face misses in open cells for building continuous channels throughout the whole foam, which blank is called as window. The edge is known also as Plateau border. The vertex is called as node, junction, or tetrapod point, in physics, engineering, and materials science. The strut, a terminology in material science, contains usually both edge and vertex, because edge and vertex are structurally similar in contrast with voids or lamellae. Note that the strut signifies only the edge sometimes.
Figure 3. Terminology employed to characterize a foam structure. The right is a cross-sectional view cutting an edge, where the edge/face radiates (ideally at 120°) outward from the central axis.

The topology of cells of foams is a fascinating field (namely mathematical tiling, space filling, or close packing of polyhedrons), which has been lasting for centuries. The dry-foam is defined as a foam with the liquid fraction to be infinitesimal. Such idealized foam is discussed in topology.

Some rules have been studied to describe the relationships of faces, edges, and vertices, among which three laws are helpful to characterize a dry-foam:

i) Euler’s law.23 The numbers of vertices, \( V \), of edges, \( E \), of faces, \( F \), and of cells, \( C \) in a foam have the relationship,

\[ V + F - E - C = 1 \]  

An interesting inference regarding a polyhedral cell is

\[ \bar{e}_f = \frac{M_e M_f}{M_e - 2} \left( 1 - \frac{2}{f} \right) \]  

where \( \bar{e}_f \) is the average number of edges/sides per face, \( f \) is the number of faces in the cell, \( M_e \) is the number of edges meeting at a vertex (it is often 4), and \( M_f \) is the number of faces meeting at an edge (it is usually 3). Hence, \( \bar{e}_f \) is always about 5, no matter \( f \) is 10 or larger. In another word, most faces of foams possess 5 edges in statistics, regardless of the shape of polyhedral cells, which has been popularly observed.

ii) Aboav-Weaire law.24 It is

\[ \bar{f}_n = 13 + \frac{14}{f} \]  

where \( \bar{f}_n \) is the average number of faces of neighbor cells of a cell. It implies the more edges one cell acquires, the fewer have those surrounding it.

iii) Lewis’s law.25 It is written as

\[ \frac{V_f}{V_I} = \frac{f - f_0}{\bar{f} - f_0} \]  

where \( V_f \) is the volume of a cell having \( f \) faces, \( V_I \) is the average volume of cells, \( \bar{f} \) is the average number of faces of cells, and \( f_0 \) is a constant ~3. It indicates that the cell volume increases following the face number of the cell. The consequence via combining Aboav-Weaire’s and Lewis’s laws gives the topological insight: a bigger cell is always encircled by smaller neighbors. These topological rules can judge the existence of foam configurations.

2.3. Statics and equilibrium in blowing.

Besides the geometric constraints, the structure of foams is also forced by static, dynamic, thermodynamic, and kinetic factors. Competitive growth is a simple model, which is one of factors shaping foams. Supposing initial bubbles nucleate synchronously and grow in isogony, the grown bubbles meet with each other to form the polyhedral structure. The structure is called as Voronoi partition in tessellation subdiscipline, which can diagram the coral pattern to a large extent. The Voronoi foams have some curious angles, which aren’t energetically preferable.

The most obvious factor governing foams is surface tension. Because of surface tension in proportion to surface area, the stable state of foams is that minimizing the interior surface area. The equilibrium structure of foams is
proposed by Joseph A. F. Plateau in 1873. Plateau's laws are: three faces meet symmetrically (at 120°) in a Plateau border; four Plateau borders meet symmetrically (at 109.47°) in a vertex. The laws hold the essentiality of minimal surfaces. Structures other than Plateau's ones are unstable, which tend to conform to the restrictions via rearrangements. Taking a step forward, the reasonable stable structure should be the equal primitive-cells with minimal surface to fill the infinite space, which is known as Kelvin problem. In geometric measure theory, a spherical bubble has the least area enclosing a given space, as proved by H. A. Schwarz in 1884. The least-area way of double bubbles is that three spherical surfaces meet at 120° on the common circle, as proved in 2002. As for Kelvin problem, William Thomson proposed Kelvin structure in 1887, a truncated octahedron having 14 faces per cell (Figure 4a). It isn’t a least-area pattern. Sparked by the figure of β-tungsten clathrate, Weaire-Phelan structure was found in 1994 (Figure 4b). It bases on the A15 phase of close packing, as presented like Water Cube for 2008 Beijing Olympics. Weaire-Phelan structure has 13.5 faces per cell, which still isn’t least-area. The optimal solution to Kelvin problem should comprise 13.39 faces per cell and 5.1 edges per face, which isn’t clarified today. Kelvin problem limits possible regular structures of foams. The real foams are usually polydispersed, which structures are requiring progressive analytics.

![Figure 4](image)

Figure 4. (a) Kelvin structure, an elongated tetrakaidecahedron with delicately curved hexagonal faces. (b) Weaire-Phelan structure. The base has two types of polyhedrons: 2 tetrahedral-symmetry pyritohedrons and 6 Goldberg tetrakaidecahedrons.

The least-area model takes charge of surface energy, beautiful yet simple. In practice, more influencers must be considered, e.g. gravity and viscous force. The gravity plays a part in the gradient gas-liquid distribution, e.g. the phenomenon of gravitational rainbows, which should be useful for making functional gradient materials. The viscous force shows profound effect on the structure of practical foams. It actually dominates the speed of dynamic evolutions. For instance, the high viscosity retards the drainage speed, generating off-equilibrium structures.

At last, if some pressure difference exists between two neighbored cells, the middle lamellae are curved rather than flatted. Surface tension results in the overpressure in the interior of a curved surface, e.g. at the single surface of a gas bubble surrounded by liquid. Young-Laplace equation describes such overpressure as

$$\Delta p = \gamma \left( \frac{1}{R_1} + \frac{1}{R_2} \right)$$  \hspace{1cm} (5)

where $\Delta p$ is Laplace pressure, $\gamma$ is the surface tension, and $R_1$ and $R_2$ are two principal radii of a curvature. For a lamella separating two cells (or the wall of a free-standing bubble), two surfaces exist through the lamella. The caused total pressure is the same with equation (5), if the lamella is thin enough. The non-zero gas pressure difference between two neighbored gas pockets must be balanced by Laplace pressure, which thus determines the curvature of their middle lamella.

Foam system isn’t intrinsically the lowest-energy state in thermodynamics. The aforementioned static equilibrium is actually thermodynamically metastable. The statics dominates foam structures via driving mobilizable foam components in the fluidlike stage in blowing processes.
2.4. Blowing kinetics.

Controlled foaming is critical for customizing high-quality foams. Blowing kinetics consists of the decomposition or vaporization of blowing agents, the dissolution, saturation, and diffusion of gas within liquid, the homogeneous or heterogeneous nucleation of bubble clusters, the growth of bubbles, the movement, merging, and final stabilization of cells of foams (Figure 5a).

Bubble nucleation occurs in a supersaturated gas-liquid solution spontaneously for lowering energy. A bubble cluster larger than the critical size tends to grow, while the smaller one collapses, owing to the trade-off between interfacial and volumetric free energy (Figure 5b). The critical size is usually at the level of nanometers. The nucleation can be homogeneous or heterogeneous. In normal blowing processes, blowing agents are exotic matter with rough surface, acting as the nucleating site where the bubble clusters preferentially initiate. The nucleation process is quick, owing the continuously increasing supersaturation in a real perturbed gas-liquid system.

Bubble growth is a rather complex microcosmic picture. It is simplified as models of single-bubble growth or cell growth (Figure 5c). In isothermal context, the bubble growth involves mass and momentum transfers between the bubble cavity and the surrounding solution. For a single cavity in the liquid sea, the radial growth is induced by gas feeding via diffusion. The more realistic picture is the swarm of bubbles growing in proximity in the liquid, which is the cell model dividing the liquid into spherical unit cells. The cell model can treat the end of growth when bubbles reach the ultimate size. Many thermodynamic and rheological factors work in the growth process, e.g. operation parameters including feeding, saturation pressure, depressurization rate, foaming temperature, shear rate, and relaxation time, as well as system properties including solubility, diffusivity, surface tension, and viscosity.

The cell size, the cell distribution, and the matching between foaming and hardening depend on the nucleation and growth kinetics, although the control of kinetics is still challenging due to complex thermodynamic and rheological mechanisms. In principle, larger pressure, quicker gas diffusion, less viscosity, and less surface tension of liquid deliver the faster growth rate of bubbles, which may deplete the driven gas and prevent the nucleation at nearby sites. Larger supersaturation and more gas feeding are often beneficial to the rapid nucleation and thus the fine-size bubbles.

Figure 5. (a) Sketch of blowing kinetics. (b) Free energy diagram in nucleating a bubble homogeneously. (c) Bubble growth models in foaming.

2.5. Blowing dynamics.

Dynamics of foaming describes the structural evolution of a metastable foam driven by diverse forces, which has been focused since 1970s. The first notable process is the liquor drainage driven by interfacial tension. If applying Young-Laplace equation to a cell, the Laplace pressures are different between regions at lamellae (a flat plane) and at Plateau borders (a cylindrical surface with an infinite principal radius and another small one), as shown in Figure 6a. The spatially different Laplace pressure drives a flow from lamellae to Plateau borders, making the lamellae thinner and thinner. The drainage attenuates if reducing surface tension or improving viscosity.

Another drainage is driven by gravity. Considering different densities between gas and liquid phases, the centroid of the foam system must fall down. The liquor drains from the top to the base of foams, and then out of the system.
The flow slows down by increasing viscosity. There is a balance between gravity and surface tension, giving a height limit of foams, i.e., capillary length. The capillary length is 2.7 mm for a clean-water-air foam, which is improved up to 4 m by the assistance of surfactants.

Coarsening is the degradation of cellular structures, including increased dimension and decreased number of cells. It is also known as ripening or Ostwald ripening. Gas diffuses across the middle lamella in orientation from small to large bubbles due to Laplace pressure difference (Figure 6b). As learnt from Lewis's law, a larger cell is always surrounded by smaller ones due to geometric constraint, so the local coarsening rate accelerates with time until smaller cells disappear. For terminological distinction, coalescence of cells denotes the association of two growing contiguous cells, resulting from the rupture of the middle lamella. The rupture is derived from the over-stretching by gas pressure or by the reduced surface tension due to ultimate drainage. Both coarsening and coalescence lead to the increasing average size of cells, and the progressive destruction of cells with decreasing quantity.

![Diagram](image)

Figure 6. (a) Scheme of drainage driven by interfacial tension. \( R_1' \) is small while \( R_1 \) and \( R_2 \) are infinity, so \( \Delta P_{\text{lamella}} \) is smaller than \( \Delta P_{\text{strut}} \). The larger internal pressure at lamellae drives the liquor motion to strut regions. (b) Least-area configuration of double bubbles, and scheme of coarsening (merging a smaller bubble into a larger one).

Foams can conduct rheological behaviors, e.g., T1 process. T1 topological rearrangement is the neighbor swapping between four cells. The entire foam elongates in the direction where two originally neighbored cells depart, and it contracts in the direction where two originally separated cells meet newly. It supplies the plasticity upon the ensemble. The deformation of a cell and the viscoelasticity of liquids also contribute to the macroscopic rheological properties. They work in the blowing process especially if using melt feedstock.

Fluidlike foams collapses eventually in the end of evolutions. Drainages cause the continual thinning of lamellae. When a lamella becomes a black-film (ultrathin liquid membrane), the disjoining pressure weakens the surface tension, resulting in rupture. The lamella disappears, and a bubble destructs or two neighbored cells merge into a bigger one.

The foam system is thermodynamically unstable, which ends up to be several huge cells after setting and finally destructs. Though controlling kinetic growth and dynamic evolutions, the foams with appropriate structures can be optimized and be temporarily fixed for the next stabilization for expected goals.

3. Advanced foams fabricated via implements of blowing strategy.

The geometric constraint, thermodynamic and kinetic controls, static and dynamic evolutions govern the structure, while the structure further determines the property of foams. Although the understanding and controlling about foaming is slowly developing, there have been blooming researches about the productions and applications of traditional and emerging foams. The blowing strategy has been used for manufacturing advanced BN and graphene
foams in 2011 and 2013, respectively. Due to the fertility of diverse polymers based on hydrogen, boron, carbon, nitrogen, oxygen, sulfur and phosphorus elements, the blowing method has been extensively explored for producing B-C-N-system foams for the past five years. It is especially meaningful to synthesize 2D materials which were fabricated difficulty by other methods, such as C$_3$N$_4$, BN, and BC$_3$N (Figure 7). In next sections, we survey the blown foams made of “traditional” plastics, metals and ceramics, and the newly developed macroporous carbons, 3D graphene foams, C$_3$N$_4$ foams, BN foams, and doping/hybrid ones.

Figure 7. Ternary diagram of B-C-N compositions, in which some compounds are emerging in 2D material field.

3.1. Plastic, metallic, and ceramic foams.

Plastic foams are the first blown foams industrially due to relatively easy manufacture. Gas was introduced into the liquid monomer or hot polymer melt, to allow bubbling, foaming, and finally stabilizing via cross-linking or cooling. Worldwide demand for light-weight materials pushes the continuous development of plastic foams. A huge variety of plastic foams have been produced, e.g. rubber, ethylene-vinyl acetate, polyolefin, polyethylene, polychloroprene, polypropylene, polystyrene, polyurethane, polyimide, polyvinyl chloride, silicone, acrylonitrile butadiene styrene, and degradable biopolymers. For example, a porous polylactic acid scaffold was generated via physical blowing of high-pressure CO$_2$. Foamed plastics processes a wide spectrum of excellent properties such as high strength-to-weight ratio, high weight-specific stiffness, electrical, and acoustic insulation.

Metallic foams are constructed via either injecting gas into melt, or mixing chemical blowing agents (e.g. metal hydride) into melt, or releasing the pre-dissolved gas in melt. The low-melting metal foams, such as aluminum, magnesium, zinc, lead, and copper, have been widely studied. The high-melting ones, e.g. foamed nickel and iron, are minorly explored. A variant is the investment casting (or lost-foam casting) using a plastic foam as the template, where the space occupied by plastics was replaced by metals. Metallic foams have been extensively applied to building, aerospace, dampener, thermal or electromagnetic shielding, heat exchange, and environmental science.

Ceramic foams are made by either a sponge-based slurry-coating method or a direct foaming method. In the former, ceramic slurry was spread upon the internal surface of open-cell plastic foams, which was then fired into ceramic foams. In the latter, the foaming was either to blow ceramic melts, e.g. using H$_2$S to blow glass melt, or to pump air into a fine-powder suspension. In the suspension, the colloidal ceramic particles can stabilize gas-liquid interfaces in Pickering emulsion. They attach to and replace a part of liquid-gas interfaces into solid-gas interfaces for lowering high-energy solid-liquid area. The suspension is thus foamable with/without the assistance of surfactants. Alternatively, the implement of foaming is to heat a pre-designed precursor. For example, in cationic polymerization of organic carbonates with oxasiline and oxysilane, the chemically release CO$_2$ directly foamed the resin/silica hybrid, which resultant was further calcined into a silica foam. Ceramic foams can act as lightweight stiff support in aerospace. They are especially suitable for high-temperature applications, e.g. thermal catalysis, refractory insulation, and filtrations of molten metal, hot corrosive gas, or exhaust gas.
3.2. Carbon foams.

Carbon foams are porous carbon which can be manufactured into monolith state. Carbon foams have usually macroporous structure and relatively large surface area. They show popularly open cells or interconnected channels through breaches of faces, for interacting with exotic mass. Some carbon foams are closed-cell for purposes such as thermal insulation. Compared with polymers or metals, carbon foams are distinguished by lighter weight, high thermal and chemical stability, relatively high strength, and natural hydrophobicity. Thermal and electrical conductivities of carbon foams can be tuned via controlling topological structure and sp²/sp³ hybridization. Carbon foams are comparatively low-cost, which are applied to the adsorption of heavy oil and gases as well as the environmental recovery. They are newly emerging as efficient thermal management materials for high-density electronics. Literally, 3D graphene foams, belonging to carbon foams, are discussed in next section. The fabrication ways of carbon foams include the sintering of hollow carbon spheres, the template-assisted carbonization, and the direct blowing method.

The blowing method is practiced earliest and widely to produce carbon foams. The organic precursors serve as both carbon resources and blowing agents in heating, e.g. phenolic resin, phenylethylene, and mesophase pitch. The released CO₂, CO, and volatile hydrocarbons blow viscous carbonaceous matter into polymeric foams. The polymeric foams themselves are either thermoplastic or thermoset for different targets, while the intermediate polymeric foams need be thermostet in case of producing further carbon foams. An alternative way is to add gas into fluidlike organic under high pressure, and the foaming occurs when removing the pressure. The polymeric foams are afterwards converted into the carbon foams in amorphous, glassy, or graphitic states at carbonization or graphitization temperatures. Historically, carbon foams were initiated from phenol-formaldehyde resin in 1964, which showed brittle characteristic. Since 1992, activated by navigation and aviation demands, carbon foams have been extensively studied via foaming pitches. Typically, pitches were heated in a closed vessel above the softening point (~280 °C), during which the pressure increased up to a few MPa. When releasing the pressure, a green polymeric foam was generated. It was then carbonized over 1000 °C. Polyarylacetylene was also used due to the high carbonization yield. For example, via heating arylacetylene prepolymer with a blowing agent of pentane, a bubble stabilizer of Tween 80, and a catalyst of sulfuric acid, a high-strength carbon foam was produced. Considering difficult graphitization in the free pyrolysis of organics, metals may be involved in the blowing process to catalyze the graphitization reaction. For example, an acrylic-type cation-exchanged resin was pretreated by Ni²⁺, and then heated for foaming and carbonization to generate graphene-like carbon networks.

Many studies focus on the direct carbonization of industrially available plastic foams. Melamine foams are made by formaldehyde-melamine resin, which were popularly used. A 3D elastic carbon foam was achieved via directly carbonizing a melamine foam (Figure 8a,b). The elasticity came from the increased aspect ratio of struts in foams, which was as high as 26.7. The carbonized melamine foam showed relatively high surface area and hydrophobic property, used as flexible electrochemical electrodes and as removers of waste organics or oil out of water. When applying heating rates of 5~10 °C min⁻¹, the secondary blowing process occurred within the vertex region of melamine foams. The scissoring of ether linkage would soften the resin, and the release of ammonia and hydrogen cyanide could blow the resin (Figure 8c,d). The secondary blowing further hollows and lightens the carbon foam, which facilitates the transportation of potassium ion and electron as the anode of potassium ion battery.
Figure 8. (a) Photo of a melamine foam with the size of $70 \times 18 \times 20$ mm$^3$ and the derived elastic carbon foam of $46 \times 10 \times 13$ mm$^3$ obtained over 800 °C at a heating rate of 5 °C min$^{-1}$. (b) SEM image of the carbon foam. The inset is the cross section with concave triangle shape. Reproduced from ref. 41. (c) SEM image of a melamine foam. (d) SEM image of directly carbonized foam from (c), obtained at 1300 °C at a heating rate of 5 °C min$^{-1}$. The insets show the cross sections at the tetrapod joints, which was inflated and hollowed by the secondary blowing in pyrolysis. Reproduced from ref. 44.

3.3. 3D graphenes.

3D graphenes can be viewed as the ultimate of carbon foams, where the foam skeleton is thinned as mono-atomic layers. In practice, the cell wall of 3D graphenes is often a few of graphitic layers, i.e. few-layered graphenes (10 graphitic layers still show some unusual band structure). 3D graphene was proposed in graphene field. In graphene powders, the weak hand-in-hand interconnectivity breaks the continuous pathway for electron and phonon transports, suppressing intrinsic conductivity and mechanical strength. The face-to-face restacking and agglomeration diminishes the accessible surface area. 3D graphene is expected to overcome the problems, for delivering extraordinary nanoscale properties of individuals upon macroscopic architectures. The terminology of graphene aerogels or carbon aerogels were also employed, viewed from the aspect of ultralight solids (with density of <10 mg cm$^{-3}$). 3D graphenes are vital for graphene-based massive applications, such as electrodes, elastomers, and conductive fillers of composites. The blowing technology is reliable for producing 3D graphenes, which is discussed in light of different feedstock.

3.3.1) 3D graphenes foamed by blowing agents of ammonium salts.

3D graphenes were early studied based on gelation in colloidal chemistry. Polymer or ion linkers were used to glue graphene sheets into an assembly, which is actually a composite. The performance wasn’t maximized owing to the non-covalent interconnection. A more intimate way of joining graphene sheets was the chemical vapor deposition of graphenes on nickel foam templates, yet the cycling of nickel foams was a heavy burden against low cost. In 2013, Wang et. al introduced the blowing strategy to 3D graphenes (Figure 9). The ammonium-assisted chemical blowing (i.e. sugar-blowing) debuted to synthesize a 3D self-supported strutted graphene (Figure 9a). In heating glucose and NH$_4$Cl, the syrup was polymerized into melanoïdin, whereas released gases (NH$_3$ and HCl) blew the melanoïdin into foams. The walls of melanoïdin foams were observed as thin as 20 nm (Figure 9k-m), because of the blowing dilation, the drainage, and the elimination reactions of pyrolysis. Such thermoset walls were annealed into graphenes at 1350 °C (Figure 9l). At the same time, melanoïdin struts became graphitic struts in the 3D graphene foam.

Ammonium-assisted chemical blowing relies strongly on the match between the decomposition of ammonium salts and the polymerization-curing of sugars. Their decoupling resulted in rudimentary or broken bubbles. Glucose,
sucrose, or house-hold sugars are available carbon sources. Residue-free ammonium salts can be selected, e.g. \((\text{NH}_4)_2\text{CO}_3\) decomposed at 50–80 °C at moderate heating rates, \(\text{NH}_4\text{NO}_3\) at 150–200 °C, \(\text{NH}_4\text{Cl}\) at 200–270 °C, and \((\text{NH}_4)_2\text{SO}_4\) at 330–380 °C.\(^2\) Other blowing agents can be urea decomposed at 170–220°C or oxalic acid at 190–220°C.\(^2\) Besides the feeding, the kinetics can also influence the foaming. At quicker heating rates, smaller-cell foams were got owing to boosted nucleation (Figure 9b-e). The duration of gas release can assist the foaming. The additionally added \((\text{NH}_4)_2\text{CO}_3\) helped keep the uniform dispersion of \(\text{NH}_4\text{Cl}\) in syrup, contributing to shaping elegant foams.\(^4\)

Geometrically, strutted graphenes were the packing of polyhedrons, which facets were mainly pentagons and minorly quadrangles, hexagons and heptagons (Figure 9h). The size of facets, the width of struts, and the diameter of cells were 80 μm, 3.5 μm, and 186 μm in average, respectively. Strutted graphenes showed high conductivity of 1 S m\(^{-1}\), compressible mechanics, and large specific surface area (SSA) of 1005 m\(^2\) g\(^{-1}\) (Figure 9f). Struts serve as fixers to integrate facets, as connectors to conduct electrons and phonons, and as supporters to prevent restacking (Figure 9j). Strutted graphenes show thus better interconnectivity. The blowing route is capable of low-cost production on a large scale. The cost-effective strutted graphenes are suitable as supports, catalysts, sorbents, gas reservoirs, filters, fillers, sound absorbers, and electrodes for substituting current porous carbon papers.

In addition, \(\text{NH}_4\text{Cl}\) is a gentle residue-free blowing agent, which can also foam other organics. 3D carbon nitride frameworks were got via heating hexamethylene tetraamine and \(\text{NH}_4\text{Cl}\).\(^{48}\) Ferric citrate also replaced sugars to make N-doped hierarchical porous carbons after additional acid washing.\(^{49}\) The nitrogen constituents were teen percentages at low-temperature annealing around 700 °C, which were useful electrodes in electrocatalysis, supercapacitors, etc.

Figure 9. (a) SEM images of glucose and \(\text{NH}_4\text{Cl}\) crystals, subsequent melanoidin bubbles, and final strutted graphenes in ammonium-assisted chemical blowing (i.e. sugar-blowing) route. (b-e) SEM images of strutted graphenes grown at heating rates of 1, 4, 20 and 100 °C min\(^{-1}\), respectively. The inset is topological reconstruction of marked region: a decahedron (faced by 8 pentagons and 2 quadrangles) and a dodecahedron
(by 8 pentagons, 3 quadrangles, and 1 heptagon). (f) SSA and the ratio of cell perimeter to strut width versus heating rates. (g,h) Photo and optical image of 3D strutted graphenes. (i) High-resolution transmission electron microscope (HRTEM) image of two graphene sheets. Reproduced from ref. 22. (j) Optical image of a graphene face braced by graphitic struts, showing their intimate connection in strutted graphenes. (k-m) SEM images of intermediate polymeric bubbles and their thin walls in the chemical blowing of sugars. Reproduced from ref. 47.

3.3.2) 3D graphenes foamed by blowing agents of organics or metal-contained salts.

A wide variety of organics are potential blowing agents, making the foaming-curing match easier. Melamine served often as an impurity-free all-leachable gas-releaser. The heating of pentaerythritol melamine phosphate involved the decomposition of melamine, the carbonization, and the dehydration-type activation by phosphorus (Figure 10). It resulted in a polymeric foam and further a carbon foam with high SSA of 2668 m² g⁻¹, rendering absorption for oil. The chemical blowing can be carried out delicately in some confined space. Through heating the mixture of ammonia borane and dimethylethanolamine within the channels of anodic alumina oxide, sausage-like carbon bubbles with diameters about 400 nm were formed.

Figure 10. (a) Photo of producing a carbon aerogel via heating pentaerythritol melamine phosphate. (b-d) Photo of the carbon aerogel placed on a dandelion, and SEM images. Reproduced from ref. 50.

Blowing agents shouldn't be limited within ammonium salts. Other decomposable salts contain often metal ions, which are still available. The enwrapped metals, e.g. iron-family elements, are expected as catalysts to improve the graphitization degree of carbons. The metals, e.g. potassium, sodium, and zinc, are expected to corrode the graphitic structure for high surface area. The metal species are removed via the additional rinse in hydrochloric or nitric acids. Fe(NO₃)₃, Ni(NO₃)₂, KHCO₃, and ZnCl₂ were used to foam hydrolyzed starch, cellulose, glucose, and maltose, respectively, producing graphene-like foams. The heating of basic copper carbonate and polymethyl methacrylate underwent the templating of copper and the gas liberation, yielding 3D porous graphene-like carbon. These pristine carbon foams were explored as electrodes of supercapacitors, capacitive deionization, fuel cell, lithium-sulfur battery etc.

Metal-incorporated 3D graphene foams can supply new functions, so it isn't always necessary to wash away the metal residues of blowing agents. Fe(NO₃)₃ blew the polyvinylpyrrolidone melt to be a foam, which was further converted into Fe₂O₃-contained carbon frameworks (Figure 11). The Fe₂O₃-contained carbon was favorable as the anode of lithium ion battery. CrCl₃ assisted the chemical blowing of glucose-NH₄Cl system, which finally yielded CrN-embedded graphene networks after ammonia annealing. The product worked for oxygen evolution reaction (OER) for water splitting.
3.3.3) RGO-based foams via blowing strategy.

Graphene oxide (GO) flakes in suspension behave like a macromolecule. They are mobilizable and can be dilated in the slurry or wet agglomeration of GO. Through adding NH₄Cl into GO suspension, the negatively charged GO adsorbed ammonium ions to form sandwich-like structures. In subsequent heating, GO was reduced into RGO, and released gas corrugated and expanded GO flakes simultaneously (Figure 12). The porous 3D RGO was finally fabricated. The 3D RGO was enhanced by adding glucose: glucose-derived carbon acted as glue to strengthen the interconnectivity. If functional lithium titanate was incorporated, the final titanate-loaded 3D RGO supplied rapid lithium-ion diffusion for the high-rate anode in lithium ion battery.

![Figure 12: Scheme of producing 3D RGO by an ammonium-assisted blowing method.](image)

GO hydrogel can be self-foamed by deoxygenation reactions, which process was called as "leavening". When heating a GO film (pre-fabricated via filtering) in hydrazine atmosphere, the decomposition of oxygenic groups resulted in the evolution of H₂O and CO₂ (Figure 13a-c). The gas expanded the original GO film by 50 fold to generate porous RGO. The deoxygenation of GO can also be induced by photothermal effect. The laser radiation into a GO film triggered the reduction reaction into RGO and the rapid liberation of gases, so porous RGO was yielded. The porous graphene-like carbons were also produced by laser radiation into polyimide film, wood, and pre-thermolyzed citric acid and urea (Figure 13d-j). 3D porous RGO was useful for the absorption of oil and...
organics, and for promising electrochemical capacitors.

Figure 13. (a) Scheme of leavening process for 3D porous RGO. (b,c) SEM images of 3D RGO via leavening in an autoclave at 90 °C with hydrazine. Reproduced from ref. 63. (d) Scheme of laser scribing for synthesizing the porous laser-induced graphene (LIG) from polyimide (PI). (e) SEM image of LIG pattern. (f) SEM image of LIG on PI substrate. The inset shows the porous morphology of LIG. Reproduced from ref. 66. (g) SEM image of expanded RGO network via laser scribing of GO films on polyethylene terephthalate substrate. Reproduced from ref. 65. (h) SEM image of hierarchical porous graphene via laser irradiation of woods. The inset shows the depth of laser penetration around 800 μm. Reproduced from ref. 67. (i,j) SEM and TEM images of 3D turbostratic graphene network via infrared-laser irradiation into the pre-thermolyzed mixture of citric acid and urea. Reproduced from ref. 68.

The last mechanism of making RGO foams is to treat GO as colloidal particles in the suspension, following the similar principle of Pickering emulsion. When bubbling the GO-water system, GO showed amphiphilic characteristics, stabilizing the gas-liquid interface of bubbles. After drying and reducing the GO-carried bubbles, RGO bubbles were generated. Commercial polymeric foams were also used to make RGO foams, resembling the sponge-based slurry-coating method for ceramic foams. GO flakes in suspension assembled on the backbone of polyurethane foams. After annealing, 3D hierarchical carbon-RGO was got for utilization in supercapacitors and capacitive deionization.

3.3.4) Theoretical design of 3D graphene foams.

In spite of the progresses of 3D graphene materials, neither the truly ordered nor the fully covalent 3D graphenes are realized. Current 3D graphene networks still use nitrogen, oxygen, topological defects, or exotic linkers at junction positions. In theory, it is possible to connect graphene sheets with 100% sp² hybridization, e.g. the models of honeycomb and Schwartzites (Figure 14). Schwartzite is triply periodic minimal surface (TPMS). 3D graphenes via placing four- to eight-membered carbon rings on Schwarz minimal surfaces, also called as Mackay-Terrones crystals, have negative Gaussian curvatures. Their energy was calculated to be more stable than fullerene, because heptagonal or octagonal rings can preserve the nature of 120° adjoining angles. In addition, sp³ hybridization can establish sp²-sp³ bonding at buckling positions for constructing 3D graphenes. It is meaningful considering the wide existence of sp³ hybridization in realistic carbon materials.
The foaming process relates closely to the minimal surface in mathematics. The minimal surface has zero mean curvature locally at every point. In actual foaming, there is non-zero pressure, so the structure of liquid foams isn't the type of minimal surfaces, yet it still tends to minimize the surface area relating with the minimal surface problem. Nevertheless, it is noteworthy that the blowing strategy should be a part of the future technique for manufacturing 3D graphenes structured with minimal surfaces. With updating synthesis strategy, the "crystalline" 3D graphene will be achieved for unusual electronic and mechanical properties.

3.4. Doped 3D graphenes/carbons.

The blowing approach is naturally convenient for doping 3D carbons via heteroatom incorporation in polymerization and condensation stages. The foaming process for doped 3D carbons looks similar to the previous, except purposely increasing heteroatom feedstock to alleviate the loss of heteroatom at high temperatures. The original ammonium-assisted chemical blowing of sugars actually underwent a series of doped phases: nitrogen and oxygen constituents were 18 and 6 at% at 300 °C, and became 0.4 and 1.4 at% at 1400 °C, respectively. N-doped porous carbons were obtained by heating the mixture of glucose, NH₄Cl, and melamine, where melamine supplied additional nitrogen. The nitrogen fraction was 8.36 at% after carbonization at 1100 °C. N-doped carbon foams were also generated from feedstock of (NH₄)₂CO₃, citric acid, and glucose. The nitrogen fraction was ~20 at% after foaming at 450 °C in air and carbonizing at 900 °C in argon. The urea-assisted chemical blowing of starch yielded the similar product, where urea acted as both dopant and blowing agent. The nitrogen fraction was 3.67% after carbonization at 800 °C. N-P-co-doped carbon foams were produced via pyrolyzing polyvinyl alcohol, polystyrene, cyanamide, and phosphoric acid. The fractions of nitrogen and phosphorus were 2–5 at%.

Metal-contained salts can assist the chemical blowing approach, based on similar expectations to the second part of section 3.3. Doped 3D graphenes/carbons are obtained after acid leaching. N-doped 3D graphenes/carbons were produced via foaming glucose and Zn(CH₃COO)₂, poly-o-phenylenediamine and Ni(NO₃)₂, or polyvinyl dichloride, melamine, and ZnO. N-P-O-co-doped 3D graphenes were got by heating Artemia cyst shells with phosphorus, Ni(CH₃COO)₂, and KOH (Figure 15a-e). The metal species can be kept for certain purpose. Through heating the mixture of glucose, NH₄Cl, and Co(NO₃)₂, the carbonaceous foam with dispersed CoO was evolved (Figure 15f-i). Co₃P-loaded N-doped porous carbons were finally achieved after phosphorization, which exhibited OER activity.
The N-doped 3D carbons open up multifunctional potentials as versatile metal-free 3D electrodes. Nitrogen doping strengthens capacitive energy storage in supercapacitors: pyridinic, pyrrolic, and pyridone nitrogens supply pseudocapacitance as an electron donor to attract cations or as a catalyst for underpotential redox. Nitrogen doping facilitates electrocatalytic oxygen reduction reaction (ORR) of fuel cells: pyridinic nitrogen activates the neighbored carbons with Lewis basicity for ORR under acidic conditions; quaternary nitrogen increases carrier concentration and conductivity.\textsuperscript{90,91} Either electron-rich (nitrogen and phosphorus) or electron-deficient (boron) doping can display ORR activity.\textsuperscript{92} B-doped 3D RGO was got by physical blowing: CO\textsubscript{2} was pumped into GO-borane-tetrahydrofuran system at a pressure of 150 atm, to form porous GO and final porous RGO.\textsuperscript{93} The boron fraction was 2.9 at%, which also accelerated ORR.

3.5. C\textsubscript{3}N\textsubscript{4} foams.

The blowing strategy is worthy synthesizing the "heavy-doping" system, graphene-like carbon nitride C\textsubscript{3}N\textsubscript{4}. C\textsubscript{3}N\textsubscript{4} is a conjugated polymer with a bandgap of 2.7 eV, having excellent optoelectronic property in photocatalysis. C\textsubscript{3}N\textsubscript{4} bulk has low SSA and quick recombination of carriers against photocatalytic performances. Although C\textsubscript{3}N\textsubscript{4} is a layered material, it isn't easy to get C\textsubscript{3}N\textsubscript{4} nanosheets for increasing SSA. The blowing technology is applied to producing C\textsubscript{3}N\textsubscript{4} nanosheets via controlling the chemical release of gases and the polymerization level of cyanamides. In heating melamine and NH\textsubscript{4}Cl\textsuperscript{94} or dicyandiamide and NH\textsubscript{4}Cl,\textsuperscript{95} the released gas blew cyanamide-derived polymers into foams, which were converted into C\textsubscript{3}N\textsubscript{4} foams at 550–600 °C (Figure 16). C\textsubscript{3}N\textsubscript{4} foam networks prevented the
agglomeration of C$_3$N$_4$ nanosheets. The C$_3$N$_4$ foams possessed large surface area, high electron transport ability, and increased lifetime of photo-excited carriers. They demonstrated enhanced photocatalytic performances for H$_2$ evolution or RhB degradation.

Figure 16. (a) Scheme of synthesizing strutted C$_3$N$_4$ foam as well as C$_3$N$_4$ flakes. (b-d) TEM images of C$_3$N$_4$ foam obtained at 600 °C with marked heating rates. Reproduced from ref. 94.

3.6. BN foams and 3D BN nanosheets.

Considering the similar polymerization capacity between hydrogen-carbon and hydrogen-boron-nitrogen systems, the blowing method is available for making BN foams. Different from graphitic layers, the heteroatom bonding with partially ionic nature makes BN exhibit complementary functionalities to the graphitic counterparts. BN layers have high bandgap, electric insulation, oxidation resistance, chemical tolerance, and low dielectric constant. BN layers also have high thermal conductivity and mechanical strength owing to intralayer strong bonding, and show lubrication owing to interlayer weak van der Waals forces. BN materials are applied to deep ultraviolet illuminants, dielectric gates, insulating thermal conductors, protective coatings, neutroncapturers, and anticancer medicines.

It was difficult to massively produce BN nanosheets, because of difficult intercalation into BN parent bulk, in sharp contrast with graphenes. BN foams or 3D BN nanosheets were initiated by a chemical self-blowing method in 2011 via controlled heating of ammonia borane (Figure 17). Ammonia borane was dehydrogenated into polymeric aminoborane at 120 °C, then polyiminoborane at 160 °C, and finally BN at 1200 °C (Figure 17a-b). During the pyrolysis, the release of hydrogen effectively foamed the polymers over 100 °C (Figure 17c-e), which polymeric foams became BN foams at 1200 °C (Figure 17f). The cell size of BN foams was over 100 μm. The walls of BN foams were further purified into pure BN nanosheets with thickness of 1-5 nm and lateral dimension up to 100 μm (Figure 17g-h). The yield of BN nanosheets was 25 wt%, better than those in chemical vapor deposition or solution exfoliation. An improved chemical self-blowing route involved a pre-heating and a moderate heating rate of 8 °C min$^{-1}$ in pyrolysis of ammonia borane. They helped the gas-capture and foaming, yielding BN foams with higher SSA of 130 m$^2$ g$^{-1}$. The further preceding heating of ammonia borane at 70 °C for 32 h resulted in BN foams with SSA up to 560 m$^2$ g$^{-1}$. BN foams and derived BN nanosheets as fillers reinforced the mechanical strength of composites based on polycarbonate or polymethyl methacrylate, and they displayed oxygen-related ultraviolet and blue luminescence.
Adding exotic blowing agents is a more controllable way to foam ammonia borane. Thiourea or aminothiourea was selected as blowing agents.\textsuperscript{102} They assisted the foaming of hydrogen-boron-nitrogen polymers at 200-300 °C. BN foams were got at 1200 °C (Figure 18a-c). Few-layered walls as well as hierarchical pores endowed BN foams the strong adsorption to dyes and organic pollutants.

Ammonia borane is relatively expensive, although its cost is decreasing with growing hydrogen industry. Therefore, inexpensive systems were developed to produce BN foams. Using boric acid as the boron source and polyethylene oxide (PEO) as the blowing agent, a porous BN foam with SSA of 127 m\textsuperscript{2} g\textsuperscript{-1} was got in ammonia at 1100 °C (Figure 18d,e).\textsuperscript{103}

Another precursor system was boric acid dissolved in formaldehyde-dicyandiamide resin,\textsuperscript{104} which generated a porous BN monolith in ammonia at 1200 °C (Figure 18f,g). The BN monolith had SSA up to 1406 m\textsuperscript{2} g\textsuperscript{-1}. Alternative was to heat the mixture of ammonium borofluoride and sodium azide at 320 °C in an autoclave.\textsuperscript{105} The escaped gas resulted in BN hollow spheres with diameter of 50-300 nm. BN foams can uptake hydrogen,\textsuperscript{106,107} and can load titania for photocatalytic degradation of organics.\textsuperscript{103} Particularly, BN foams are highly suitable for
environmental clean-up, e.g. the removal of oil, where BN foams are easily recycled via burning based on the anti-oxidation nature of BN.\textsuperscript{104}

Figure 18. (a) Scheme of thiourea-assisted foaming of ammonia borane for producing 3D white graphene foams. (b,c) Photo and SEM image of the 3D white graphene foam. Reproduced from ref. 102. (d) Scheme of producing BN foams using boric acid and PEO. PEO decomposed and bubbled during heating, and was finally removed at 1000 °C. (e) SEM image and photo of the BN foam derived from boric acid and PEO. Reproduced from ref. 103. (f,g) Photo and SEM image of BN cellular monoliths made by heating boric acid and formaldehyde-dicyandiamide in ammonia atmosphere. Reproduced from ref. 104.

3.7. B-C-N-system hybrid foams.

The blowing method is especially worthwhile for exploring the cutting-edge three- and four-membered hybrids in B-C-N-O system. In the stage of making polymeric bubbles, hetero-elements are easily incorporated via polymerization. Merging “black” and “white” graphenes, BCN-hybrid atomic sheets have been pursued for luminescence and electronics. The blowing way was tried towards the hybrid nanosheets. Through carrying out the “chemical self-blowing” of ammonia borane in saturated ethanol atmosphere,\textsuperscript{21} C-r-BN foams as well as nanosheets were synthesized after annealing at 1200 °C. Carbon constituent was controlled via varying the quantity of ethanol (Figure 19). $x$ was 0.3~0.7. Although the C-r-BN materials were phase-separated, the C-r-BN hybridized nanosheets still showed tunable thermal bandgaps varying in 17-56 meV. Porous C-r-BN was also got via foaming the mixture of polymeric aminoborane and dimelamine borate, with the carbon fraction near 4 at% after annealing at 1050 °C.\textsuperscript{108} B-C-N-O microbelts was got via heating melamine diborate, where polar heteroatomic bonding provided effective hydrogen uptake.\textsuperscript{109} In general, it is rather difficult to get a B-C-N homogenous phase. The blowing strategy supplied inferior-but-available B-C-N hybrids for exploring adjustable compositions and functionalities in a large range.
Figure 19. (a) Photos and TEM images of C$_x$-BN foams (they were originally monoliths) as well as respective nanosheets via chemical self-blowing of ammonium borane in ethanol atmosphere. The marked constituents were calculated from X-ray photoelectron spectroscopy analysis. (b) Current-voltage characteristics of C$_x$-BN nanosheets measured by field-effect-transistor devices, showing tunable semiconductivity. Reproduced from ref. 21.

4. Emerging functionalities and applications based on advanced inorganic foams.

4.1. Structure and property of foams.

The properties of cellular solids are determined by not only the constructing matter but also the featuring cellular structure. Open-cell and closed-cell foams behave differently, and are treated differently in theory. For a realistic foam, the fraction of open cells denotes the degree of opening cells. This fraction relates to relative density, rheological behavior, and mechanical properties as a harmonic parameter, and it plays a key role for the permeability of foams to gas/liquid. The relative density is a crucial parameter of foams. It is universally used to quantify the mechanical, thermal, electrical properties of foams, in either empirical conclusions or modeling theories. The relative density can be converted into the porosity, which is useful when treating foams as porous materials.

The cell shape, size, and size distribution are important for characterizing foams. The cell shape can be inferred from the number of edges meeting at a vertex, the number of faces meeting at an edge, and the number of edges per face. The cell size is represented by the principle dimensions of cells in three orthogonal coordinates, which further determines anisotropy. The details of cells include the strut width and its distribution, as well as the wall thickness and its distribution. Besides the distributions in the whole foam, the strut is thicker near vertices in a certain cell, and the wall is thicker near Plateau borders. Optical observation, SEM visualization, or X-ray tomography give the geometrical information of foams. Considerable statistics is required upon the geometrical elements, owing to the hidden regularity of foams in geometry.

The structural factors play unique roles on the properties and functionalities of foams. For instances, pores act to blunt the tip of cracks, leading to the disruption of crack propagation and the increasing ductility. Creating pores is the basic principle for increasing SSA. Porous continuous channel is pivotal to the exchange of exotic matters. The spaces of pores can be filled by another matter for synergistic functionality. Moreover, slender struts are more bendable owing to less stress concentration, which is the mesoscopic origin of elasticity of foams. Wall thickness falls often into nanosized scales, smaller than the critical dimensions of some physical phenomena, behaving the size effect or quantum confinement effect, e.g. ballistic transport of electrons.

4.2. Structural applications of foams.

Based on the unique structures and properties of foam materials, a huge variety of applications have been practiced. The early application of foams is the lightweight structural support of loads. Special design can generate superior weight-specific mechanical properties, e.g. light-but-stiff octet-truss nanolattices to efficiently resolve stress (Figure 20). The far-ranging utilizations of foams include packaging, stuffing, and cushioning. It is particularly appropriate because of the lightness and the deformability for absorbing impacts. At last, closed-cell plastic foams are suitable for buoyancy, which are damage-tolerant.
4.3. Functional application: 3D fillers of composites based on BN foams.

Beyond the structural applications, foams are applied to a series of functional applications. The popular utilization of foams is the selective adsorption of gas molecules, organics, oils, and metal ions. Besides, the thermal insulating shell of disposable coffee cups is charged with cellular papers. The thermal insulation is performed by aluminum foams or carbon foams in aerospace, such as the heatshield of Parker Solar Probe. The application of foams is a huge topic. Below we selectively discuss two scenarios concerning 3D fillers and electrodes, respectively.

BN are ideal fillers for insulating thermal conductive composites, which have theoretical thermal conductivity up to 3000 W m⁻¹ K⁻¹, excellent insulation, low thermal expansion coefficient, low dielectric constant, and tremendous stability. The characteristics are fully favored by packaging materials for electronics. In thermal conduction of composites, filler-filler and filler-matrix interfaces cause most of phonon scattering, resulting in major thermal resistance. BN foams are advanced 3D fillers thanks to the elimination of heterogeneous filler-filler interfaces (Figure 21a). Some reports tried embedding the pre-fabricated BN foams into polymers by soaking or infiltration, yet the perfectly covalent 3D BN network is still lacked. Actually, even inferior 3D BN networks aren’t easy, which is worse than 3D graphene case. The BN network can also transfer mechanical forces for mechanically reinforced composites, following the similar principle of transporting phonons. A designed 3D pillared BN demonstrates the synergistic deformation mechanics based on interior tubes (Figure 21b), which might be useful for composites. 3D BN fillers maximize the continuous phonon transport and force transfer along the covalent network. They act as thermally and mechanically effective enhancers for thermal conductive composites, phase-change composites, and light-but-strong composites, useful in electronic packaging, heat storage, and engineering support, respectively.

![Figure 20](image)

Figure 20. (a,b) Property chart comparing Young’s modulus and compressive strength versus density of engineering materials, including polymeric, metallic, ceramic foams, as well as alumina ductile-like and brittle nanolattices. Reproduced from ref. 110.

4.4. Functional application: Electrochemical electrodes based on graphene foams.

The essence of porous electrodes is to utilize the dual connective networks of solid phase and void phase to transport electron and ion, respectively. The conductive solid network enables a high way for electron/phonon...
transport. The porous structure facilitates mass exchange where the continuous cavity channel benefits the diffusion of reactants and resultants, and the porous structure maximizes the electroactive interfaces between solid and electrolyte. The interface can work for ion adsorption in non-faradic processes, and for charge transfer and exchange current in faradic reactions. Conductive foams are widely employed for electrochemical electrodes, e.g. supports of enzymes or catalysts, scaffolds for microbial fuel cells, and active elements in supercapacitors or rechargeable batteries.117 Graphene foams can additionally supply high stability and SSA, which are better than nickel and titanium foams or carbon fiber papers. In appearance, the foam electrode is identified to be binder-free and free-standing.

Figure 22. (a,b) Schematic model of strutted graphene electrodes showing easy ion diffusion and minimized inner electronic contacts, as compared with milled strutted graphenes. In strutted graphenes, nearly perfect electron freeway delivers an electronic resistance of ~0. Cavities connected by breaches and open cells contribute an ionic resistance of only 0.23 Ω. Reproduced from ref. 22. (b) Trade-off chart between gravimetric maximum-power density and energy density of aqueous supercapacitors based on 3D graphene foams. Data are extracted from ref. 22,119-121. (c) Proposed volumetric energy density of an electric-double-layer symmetric supercapacitor following pore radius at three different thicknesses of pore walls. The calculation uses a unit capacitance of 21 μF cm−2 and an operated voltage of 4 V. Volumetric energy density has a local maximum at pore radius of 1~10 nm. Another maximum might appear at pore of <1 nm, resulting from desolvation of hydrated ions for entering into micropores. (d) Trade-off chart between volumetric maximum-power density and energy density of the same materials with (b).

Graphene foams have been applied as versatile electrodes for supercapacitors, solar cells, fuel cells, rechargeable batteries, water splitting, and electro-syntheses. The advantages of pristine graphene foams are most revealed in non-faradic supercapacitors (Figure 22). Activated charcoal had limited energy and power densities as a result of the block effect of narrow channels and the inner contact resistance. Graphene foams provide continuous electrolyte channels to minimize ionic resistance, and eliminate contact resistances to minimizes electronic resistance in supercapacitors (Figure 22a). They additionally provide high accessible surface area against agglomeration. Merging the three factors, graphene foams demonstrate high energy and maximum-power densities,22,118-121 e.g. 8.1 Wh kg−1 and 893 kW kg−1 for strutted graphenes operated at 1 V in 1 M H2SO4 (Figure 22b),22 and 50 Wh kg−1 and 340 kW kg−1 operated at 2.7 V in 1 M TEABF4/acetonitrile.47 On the contrary, graphene powders agglomerate easily, resulting
in sluggish kinetics and inaccessible surface. Graphene foams show thus great potentials for substituting metal foams for non-faradic and faradic electrodes.

The relatively large volume of porous electrodes gets critical comments for lowering volumetric performances, which is an intrinsic problem. The interior surface area and the volume of a pore are proportional to \( r \) and \((r + t/2)^2\), respectively \((r\) is radius of a cylindrical pore and \(t\) is thickness of pore walls\). Most electrochemical performances, either electro-adsorptions or heterogeneous reactions in energy devices and electro-syntheses, are in positive correlation with surface area. Hence, there is an inevitable trade-off if calculating the volumetric performances, e.g., energy density, kinetic speed, etc. The case of electrochemical capacitance is simple, which is proportional to surface area. The upper limit of electric-double-layer energy density is estimated as \(~120 \text{ Wh} \cdot \text{L}^{-1}\), for 4 V operation in organic systems (Figure 22c). Because of the difficulty of controlling pores, the compression of low-density foams is an alternative way for increasing volumetric performances (Figure 22d).

Although porous materials have the intrinsic limitation over volumetric performances, porous electrodes remain the optimal option for supercapacitors and electrocatalyses. The volumetric energy density of electric-double-layer supercapacitors can be higher than that of lead acid battery, and the powder density is faster by the 1-3 orders of magnitude than those of batteries. The hetero-atom doping contributed additional pseudocapacitance at a cost of lowering power (owing to slower faradic charge transfer). To sum up, capacitive energy devices are still believed to be meaningful. Supercapacitors are the most promising for quick charging or output, e.g. in startup of electric vehicles and electromagnetic launching of aircrafts.

5. Conclusions and perspectives.

The blowing approach has conducted a great deal of progressive practices since its chemical industry in 1920s and since the newly developed nanosheet-based foams in 2011 and 2013. This account pictures the geometry, statics, kinetics, and dynamics in foaming, summarizes the emerging carbon foams, 3D graphene foams, carbon nitride foams, boron nitride foams, doped and hybrid foams, as well as discusses the applications of foams. There are impressive progresses and bright prospects of blown foams, yet the blowing approach for advanced foams is still a fresh field with many challenges. Properties of cellular solids depend highly on the structures. The two purposes of developing foams are to reduce density while maintaining valuable mechanics, and to supply the dual solid network and void network for functionalities. Both are incapable for dense counterparts. The blown foams tend to form covalent inner interconnection, instead of van der Waals adhesions in the case of assembly. New-structured foams are appearing for improved or specific mechanical and functional properties, e.g. auxetic foams with negative Poisson's ratio, hierarchical foams with self-similarity, foams with negatively curved surfaces, monolithic foams with all-micropores or mesopores, and microcellular solids in engineering discipline with cells of 10 nm ~ 50 \(\mu\)m.

Applications of foams have been extensively explored for lightweight structural supports. Functional applications of foams emerge recently. Foams can be used for thermal insulation because thermal flow is proportional to density. Foams can absorb sounds owing to the damping and the diffuse reflection of acoustic waves. Foams can shield electromagnetic interference via interfacial dielectric loss. Foams can gather CO2, uptake hydrogen, separate oil from water, and remove pollutions. Foams with hydrophobicity can be used as waterproof breathable waves or artificial skin, as well as electrochemical gaseous electrodes. Foams can be used as scaffolds for tissue regeneration. Open-cell foams can be used as filters, and can serve as heat exchangers in working medium. Similarly, foams can serve as thermal enhancer in heat-dissipation composites and in phase-change thermal storage. Lastly, conductive foams can be employed as electrochemical electrodes. Despite diverse applications developed, there are still a lot of blank lands. Further explorations are necessary for more possibilities in both fundamental and technological studies, particularly about the theoretical modeling, controlled production, new products, and practical applications.

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