

Design of Three-Dimensional Porous Carbon Materials: From Static to Dynamic Skeletons**

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The design and synthesis of three-dimensional (3D) porous carbon materials with flexible characteristics have been given extensive attention owing to their potential applications under dynamic conditions, for example in flexible electronics and sensors.^[1] Historically, properties such as low density and good electrical conductivity are preferentially considered during structural design.^[2] Previously reported products are rigid and brittle, and may even break with a little deformation. Consequently, these carbon materials are not likely to be used in movable devices and arbitrary curved substrates. In this context, “flexibility”, a concept distinctly foreign to conventional rigid carbon structures, will lead to a new generation of dynamic carbon systems that are capable of substantial stretching and bending, and thus may open up substantial possibilities for their use in flexible electronics and sensors.

Like conventional, flexible paper derived from plant fibers, macroscopically two-dimensional (2D) carbon structures constructed mainly from one-dimensional (1D) carbon nanotubes (CNTs) and carbon nanofibers (CNFs) are the first carbon-based materials endowed with such flexibility. Typical products include well-assembled CNT yarns, forests, and paints, and CNF sheets, which show superelasticity.^[3] Following the rise of graphene in recent years, rapid innovations in its synthesis, characterization, and integration (sometimes with other functional linkers, stabilizers, spacers, or elastomeric polymer matrix) have resulted in bulk well-organized assemblies with extended dimensions,^[4] though some concepts have been applied directly from research on graphene’s “elder brother”, CNT. And thus, even based on earliest designs, a range of flexible graphene-based films have been successively fabricated. The flexibility is attributed to the inherent structure-directing characteristics of individual graphene sheets such as one-atom thickness, superflexibility, and easy film formation through either strong covalent bonding forces, weak π - π interactions, or even hydrogen bonding. Owing to clear advances in the design towards flexible/

stretchable 1D and 2D carbon structures based on CNTs, graphene, and their hybrids, the construction of 3D porous carbon structures that can be stretched and/or compressed has long been expected. Only recently with very recent work by Zhao, Qiu et al., Gao et al., and Yu et al.^[5] has this area broken out of its stagnation.

On the basis of extensive work regarding graphene assembly, Zhao, Qiu et al., moving one step further, devised an integrated strategy involving functionalization, lyophilization, and microwave irradiation to fabricate ultralight and highly compressible graphene aerogels.^[5a] Owing to the synergy in the proposed three-step preparation—decoration of graphene oxide (GO) with ethylenediamine, freeze-drying, and microwave reduction—these graphene aerogels display porosities as high as 99.8 % as well as outstanding compressibility. The cyclic compression test shows that such a graphene aerogel can fully recover without fracturing even after 90 % compression (Figure 1 a). The stress–strain (σ - ϵ) curves

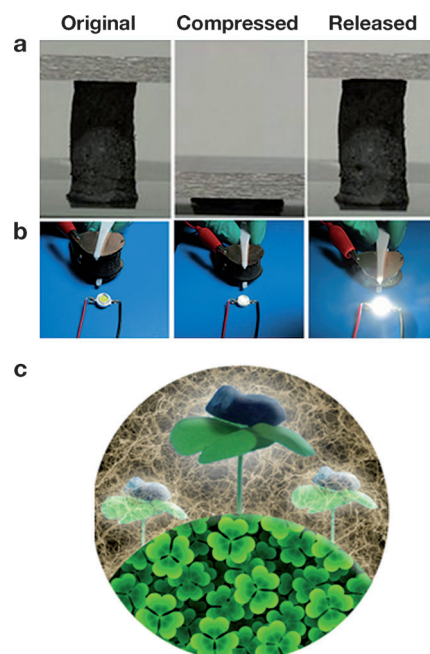


Figure 1. a) Digital photographs showing the compressibility of graphene aerogels.^[5a] b) A circuit constructed with UFA as a lightweight conductive bulk material; the brightness of the LED lamp fluctuates upon compression and release of the UFA.^[5b] c) Photograph of a CNF aerogel on top of a cloverleaf, indicating its ultralight property.^[5c]

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show three distinct regions including the elastic region ($\epsilon < 10\%$) during which the stress increases linearly, the plateau region ($10\% < \epsilon < 80\%$) in which most of the absorbed energy dissipates, and the densification region ($\epsilon > 80\%$) marked by the rapid increase of stress. Even after 1000 compressions, the product can still fully recover to its original volume and retain 70% of the maximum stress value. Such remarkable elastic stiffness may be associated with its fine microstructures: well-assembled graphene sheets that interlock with each other; tight bonding between sheets resulting from conjugation in regions of sp^2 -hybridized carbon atoms; and π - π interactions in the cross-linking sites between graphene sheets. Thanks to these unique properties, applications of advanced elastic graphene aerogels may go beyond those of their rigid counterparts, and they may play more important roles under specific dynamic conditions. Besides the above multistep synthesis, Li et al. and Qu et al. also reported the one-step preparation of well-assembled graphene aerogels showing similar mechanical features.^[6,7]

Independently, Gao and co-workers described a simple synthesis of ultra-flyweight aerogels (UFAs) with temperature-invariant (-190 – 900°C) superelasticity through the freeze-drying of aqueous solutions of CNTs and giant GO sheets, followed by chemical reduction of GO into graphene with hydrazine vapor.^[5b] Compression experiments showed a nearly complete recovery after 50–82% compression of the UFAs. The σ - ϵ curve of the 1000th cycle is identical to that of the first cycle. Remarkably, they demonstrated that the UFAs that had been compressed for 1000 cycles still retained their original thickness, macroscopic shape, and microscopic 3D porous structure, and the interactions between the cell walls remained intact. Microscopically, the building blocks consist of individual CNTs randomly pasted onto both sides of graphene sheets. In addition, this isotropic assembly of graphene and CNTs avoids the sliding and splitting of graphene sheets along a specific direction. It has been found that the synergistic effect is directly linked to the van der Waals attraction between graphene and CNTs. The graphene sheets have stronger π - π interactions between two building blocks due to the restoration of the conjugated carbon net. The uniform and tight covering of CNTs favors the load transfer from graphene to elastic CNTs, resulting in superelasticity for the whole composite aerogel. These cooperative effects between graphene and CNTs result in the following integrated properties: the ultralow density of only 0.16 mg cm^{-3} ; the ultrahigh absorption capacities for organic liquids (up to 913 times its own weight); the relatively high electrical conductivity (roughly 0.6 S m^{-1}) at the percolation threshold of as low as 0.1 vol% for a composite. As shown in Figure 1b, a light-emitting diode (LED) lamp can be illuminated under 6 V when connected with bulk UFA, and its brightness fluctuates when the aerogel is compressed and released. Indeed, in slightly earlier work, Islam et al. reported a reverse configuration of building blocks, in which the CNTs are uniformly coated by one and five layers of graphene nanoplates,^[8] which show mechanical properties similar to those of the UFAs. So, we deduce that either “graphene coating on CNT” or “CNT pasting on graphene” will reinforce the existing cross-linking points or “nodes” in the

3D networks, which may result in the expected superelasticity and complete fatigue resistance.

The building blocks, CNTs and graphene, in the above-highlighted works are well-known nanocarbons generally produced by chemical vapor deposition (CVD), and multistep exfoliation and reduction methods, respectively. As an alternative approach, Yu et al. recently reported a novel method for producing 3D CNF structures from bacterial cellulose gels, which are produced by microbial fermentation and subsequent heating.^[5c,d] The aerogel can withstand extreme heat and has sponge-like properties that allow it to absorb up to 300 times its weight in oils or organic liquids such as gasoline. Similar to the graphene aerogels fabricated by Zhao, Qiu et al., this CNF aerogel displays high flexibility; it can be compressed by more than 90% and almost recover its original volume after the compression release, thus showing that the aerogel is compliant and elastic. The robust mechanical properties of these CNF aerogels may stem from both the inherent flexibility of CNFs and the unique interconnected 3D networks of monolithic CNF aerogels. In a similar manner, the Yu group further demonstrated a highly efficient chemosynthesis for producing carbonaceous nanofiber hydrogels and aerogels^[9] through a template-directed hydrothermal carbonization process. This type of CNF aerogel retains good mechanical features and is suitable for large-scale (e.g., 12 L in volume) synthesis. In addition, the ultralow density (Figure 1c), extraordinary flexibility, and high chemical reactivity of the carbonaceous nanofiber gels give them great application potential for the removal of dye and oil pollutants and as versatile 3D templates for creating functional composite gels.

Following these major advances in the design of flexible 3D carbon structures, the next step will be to push these structures towards smarter systems with higher levels of control. At this stage, however, we must recognize that most of the unique properties of the individual nanocarbons, such as electrical conductivity for graphene and mechanical strength for CNT, still fade rapidly during their assembly into bulk 3D structures. And thus, the essential issue is to understand the nature of this phenomenon. On the road towards the ultimate goal, we may learn more from nature, in which most structures show well-defined hierarchy and marvelously smart properties.^[10] For example, future 3D carbon systems may mimic the organization of muscle tissue (more intelligent and flexible), in which individual muscle fibers can organize into larger muscle bundles. In any case, it is certain that the design of such 3D dynamic carbon materials will be at the frontier of nanotechnology in the upcoming years. And the collaboration between material scientists, chemists, and bioengineers will certainly promote advances in their design and true utility in flexible electronics, sensors, and complex mechanical structures.

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