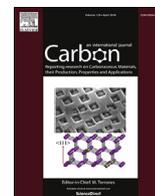




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Perspectives

A carbon science perspective in 2018: Current achievements and future challenges

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1. Introduction

This article aims to provide a perspective on a number of new challenges and current trends in carbon science. A number of *Carbon* editors have contributed sections to this article in the spirit of motivating carbon scientists to discover new materials, exciting new properties, and to fabricate new functional devices. This document is crafted as part of a recent tradition of the editorial *Carbon* team, to provide a broad perspective of the state of carbon research [1].

The readers will agree that carbon is a fascinating element that can adopt different hybridizations: sp , sp^2 and sp^3 (Fig. 1). Different carbon allotropes result from controlling these hybridizations.

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Diamond (consisting of a three-dimensional sp^3 -hybridized carbon network), and graphite (made of stacked layers of sp^2 -hybridized carbon atoms) are two examples of bulk realizations. However, at the nanoscale, other carbon allotropes, such as fullerenes, carbon nanotubes and graphene appear, and *Carbon* has published thousands of articles related to these forms. What is next? Is it possible to still predict and synthesize novel forms of carbon by controlling carbon hybridization at the nanoscale? While the most often explored systems today remain sp^2 hybridized forms of carbon (Fig. 1), we note that sp and sp^3 should now be explored more intensively at the nanoscale. In the following sections, we will summarize recent achievements and current challenges regarding the following carbon allotropes: 1) sp linear carbon chains, 2) sp^2 graphene nanoribbons, 3) sp^3 low-dimensional systems (flexible diamonds), and 4) three-dimensional (3D) graphene-based structures (Fig. 1). Although the physicochemical properties of pure carbon materials continue to surprise us with their diversity and novelty, the synthesis of hybrid structures containing carbon and other compounds have recently re-emerged with the appearance of a broad array of 2D materials. In this context, we will also describe novel photo-catalytic effects of graphene-chalcogenide systems, and how carbon-based materials will be key elements in the fabrication of wearable electronic devices. Finally, we will describe current challenges in the design of biocompatible carbon

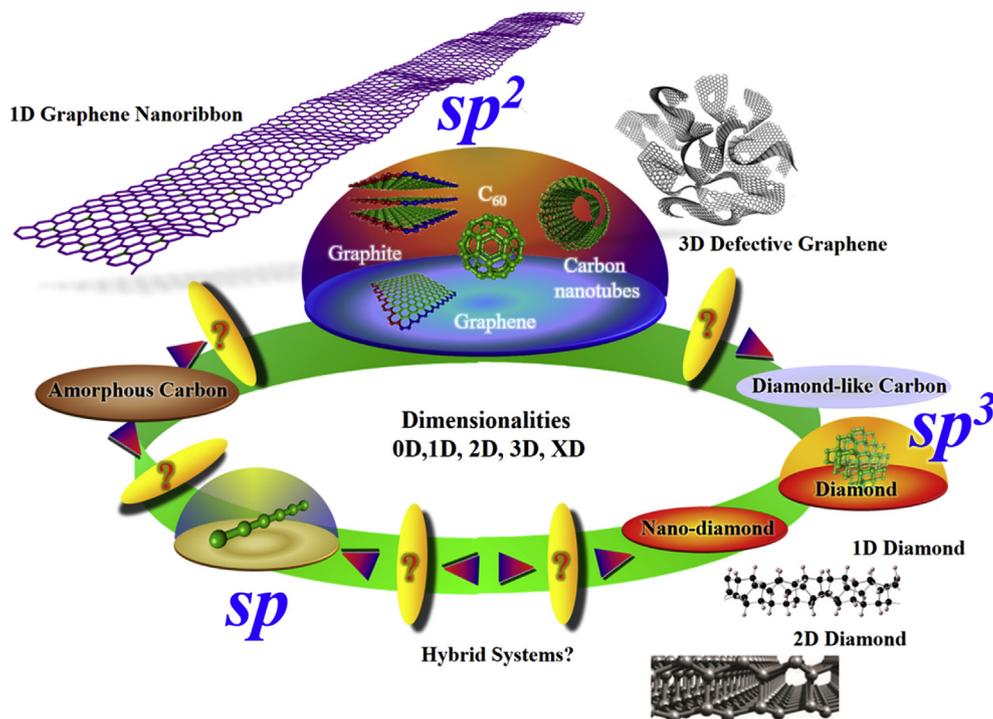


Fig. 1. Diversity of carbon materials based on their hybridization. It is noteworthy that sp^2 hybridized carbon is currently the most explored subject while sp and sp^3 hybrids await exciting discoveries in the coming years. (A colour version of this figure can be viewed online.)

nanomaterials, where research efforts are focused on developing safer carbon materials to eventually become part of consumer products. We hope the readers will find this perspective article valuable and that some of the ideas and challenges presented will motivate the emergence of new research areas.

2. Linear carbon chains

Although substantial progress on the applications of carbon nanotubes (CNTs) and graphene electronic devices has been made, the complex process of separating high purity semiconducting CNTs and the limited ability of tuning the bandgap of graphene, have delayed some electronic applications. Due to their exciting properties, alternatives such as sp -based linear carbon chains have recently attracted the attention of scientists. However, these linear carbon chains are chemically active, are unstable in ambient conditions, and their intrinsic physical and chemical properties have received less attention by researchers [2]. For example, theoretical studies reveal that linear carbon chains possess higher modulus and stiffness than graphene, CNTs and diamond and that their mobility is extremely high based on their intrinsic one-dimensional structure, and their bandgap can be tuned upon strain [3,4]. In addition, linear carbon chains are important for understanding fundamental solid state physics, such as quantum conductivity. Furthermore, their cohesive energy is *ca.* 7.0 eV/atom, which is higher than that of unsaturated carbon atoms at graphene edges. In this section, we describe the current research status of the synthesis and characterization of linear carbon chains, with emphasis on infinite (or long) linear carbon chains. We also expect to see more papers on this subject submitted to *Carbon* in the following years.

Linear carbon chains are considered ideal one-dimensional (1D) carbon materials and they can adopt two different configurations: polyynes and cumulenes. Polyynes consist of carbon atoms with alternating triple and single bonds and are semiconducting due to

localized π -electrons on the triple bonds, while cumulenes with all double bonds are metallic due to the presence of delocalized π -electrons.

Linear carbon chains can be stabilized by trapping them between graphene layers using *in situ* TEM [5,6]. It is interesting to note that linear carbon chains under strain are semiconducting and follow the polyynic structure, whereas metallic chains under no strain exhibit the ohmic behavior of metallic cumulenes [6,7].

The second way of stabilizing linear carbon chains is to encase them in the hollow core of CNTs. The experimental evidence of the presence of linear carbon chains inside multi-walled carbon nanotubes (MWCNTs) came from high-resolution transmission electron micrographs (HRTEM) and Raman spectroscopy studies [8]. However, several questions are yet to be answered: (1) how do these molecules grow inside CNTs in the arc apparatus? (2) How much are they structurally and thermally stable? and (3) How do they contribute to the electronic properties of carbon nanotubes? Recently, a large portion of long linear carbon chains were introduced inside MWCNTs via atmospheric arc discharge in the presence of boron, specifically without using a metal catalyst [9]. The closed-end growth mechanism of MWCNTs in the arc process is very suitable for growing these chemically active linear carbon chains inside MWCNTs. Linear carbon chains are found to be stabilized when the innermost tube diameter is in the range of 0.6–0.8 nm and the residual carbon atoms are present inside the innermost tube (Fig. 2 (a)). The Raman map of linear carbon chains are shown in Fig. 2 (b), and each color has its corresponding Raman spectra in Fig. 2 (c). Strong Raman peaks coming from linear carbon chains around 1850 cm^{-1} indicate that the linear chains are spatially distributed homogeneously throughout the MWCNT with a high filling ratio (*ca.* 80%). Furthermore, when the linear carbon chains are first subjected to high pressure (up to 10 GPa), red shifts of vibrational modes occur after the release of the pressure. This indicates certain irreversible structural changes in the linear carbon chains such as the coalescence of different linear carbon chains [10].

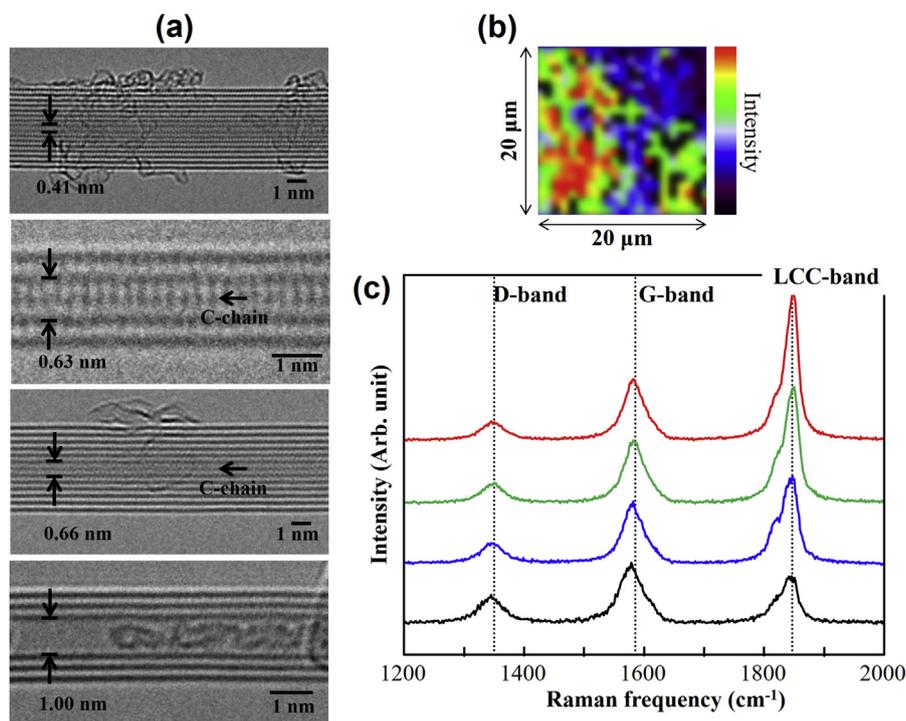


Fig. 2. (a) TEM images of pristine MWCNTs synthesized via arc discharge. A MWCNT with an innermost tube diameter of 0.41 nm does not have any carbon species inside the hollow core (top), two MWCNTs with innermost tube diameters of 0.63 and 0.66 nm exhibit black dotted line along the centerline (middle) and a MWCNT with an innermost tube diameter of 1.0 nm contains amorphous like carbons (bottom). (b) Raman map image of linear carbon chains-derived bands obtained from MWCNT tape using a 532 nm laser line. Each color in (b) exhibits its typical Raman spectrum in (c). Note that linear carbon chains-derived Raman peaks around 1850 cm^{-1} , are observed throughout the whole sample. (A colour version of this figure can be viewed online.)

Very recently, Shi et al. reported the synthesis of long linear carbon chains by thermally treating double-walled carbon nanotubes (DWCNTs) around $1500\text{ }^{\circ}\text{C}$ [11,12]. The DWCNTs were catalytically synthesized and thus their inner tubes, exhibiting a diameter of 0.6–1.0 nm, were optimum for stabilizing linear carbon chains inside the hollow cores. Theoretical studies revealed that DWCNT containing linear carbon chains are metallic due to charge transfer from CNTs to the linear carbon chains, even though both the CNT and linear carbon chains are semiconducting [13].

Even though a number of studies have been carried out on the structural characterization of linear carbon chains, their intrinsic properties based on their ideal one-dimensional features, such as electronic, optical, mechanical and transport properties still need to be elucidated. In addition, the growth mechanism of linear carbon chains inside DWCNTs should be understood in detail: (1) how can we explain the carbon source of linear carbon chains inside DWCNTs? (2) why are linear carbon chains not observed inside SWCNTs with diameters ranging from 0.4 to 0.8 nm? Furthermore, the fabrication of air-stable linear carbon chains without using encapsulation will be one of the biggest hurdles for their application in next-generation electronics. However, the judicious control of bonding states via sp/sp^3 and sp^2 or their combination will allow us to utilize metallic or semiconducting linear carbon chains in the future. Such approach should generate unexpected electronic and optical properties based on their unique 1D features, thus widening nanocarbon science and technology.

3. Graphene nanoribbons: towards atomically sharp low-dimensional sp^2 hybridized all-carbon heterojunctions

One-dimensional graphene nanostructures occupy a special place in Carbon science, due to their unusual properties stemming

from lateral confinement that can open a band gap – not present in extended graphene – with controlled quantum states. For example, a variety of outstanding width- and edge-related phenomena emerge from the specific geometry of graphene nanoribbons (GNRs). While the expression of these properties depends dramatically on the details of the atomic structure of the GNR [14–16], this dependence is both an opportunity and a curse. The opportunity arises from the possibility of devising radically new functionalities, depending on the specific design of the graphene nanostructures, far beyond those expected from extended graphene systems or conventional semiconductors. The challenge, on the other hand, is related to the fact that atomically precise systems must be experimentally obtained in order to harness the full potential of graphene nanosystems and exploit their properties as quantum materials for novel applications.

The challenge has eluded conventional synthesis approaches, such as chemical vapor decomposition (CVD) techniques [14,16] but it has now been solved elegantly by recently developed on-surface chemical methods, such as the surface-assisted bottom-up assembly of small precursor monomers into atomically precise GNRs, as pioneered by Fasel and Müllen in 2010 [17]. Even though proof-of-principle realization of GNR-based Field-Effect Transistors (FET) has been reported (including the difficult step of transferring GNRs from a metallic substrate to a substrate relevant to electronic applications) [18,19], creating reliable “GNR-based electronics” remains a true challenge that calls for further development of those approaches for the controlled assembly of nanocarbons at the single-atom level and the subsequent development of devices. One challenging step is the careful design of the starting monomer that can lend itself to the formation of the desired GNR, with a given edge structure and width, and in turn, with a well defined bandgap [20,21]. These efforts have allowed the expansion of the family of

GNRs, and in particular those with armchair-type edges (AGNRs). The catalog of realizations keeps growing with the well-controlled synthesis routes for atomically precise 5-AGNR [22,23], 7-AGNR [17], 9-AGNR [24], and 13-AGNR [25]. The formation of these GNRs proceeds in two steps: a polymerization of the monomer triggered by dehalogenation catalyzed by a metallic surface (Ullman coupling) that leads to the formation of a linear polymer, which then yields atomically precise graphene nanoribbons after cyclodehydrogenation at moderately higher temperature. A number of GNRs remain difficult to obtain using this method as no obvious route exists – yet – in the design of precursors amenable to the formation of some particular GNR types. Remarkably, a new monomer might not be needed to generate new types of GNRs. Indeed, cyclodehydrogenation can also occur between the sides of aligned GNRs, and the combination of elemental GNRs can result in the synthesis of their “overtone” by cross-dehydrogenative coupling (lateral fusion). Examples include 14-AGNR [26–29] and 21-AGNR [26,28,29] obtained from the fusion of two and three 7-AGNRs, respectively; 10-GNR, 15-AGNR, and 20-AGNR from 5-AGNRs [30]; and 18-AGNR from side fusion of two 9-AGNRs [29]. Note that while armchair-edged GNRs have been the subject of intense scrutiny, the formation of zigzag-edge GNRs remains an extremely challenging task, even though specifically designed precursor monomers have been shown to yield atomically precise zigzag edges [31,32] and recent development in surface-catalyzed formal [2 + 2] and [2 + 2+2] cycloadditions of *ortho*-activated tetracene species on a Ag (111) substrate has enabled the possibility of creating zigzag-edged GNR segments [33].

Going back to the formation of GNRs with armchair edges, studies have also shown that appropriately doped precursors can yield site-specific doped GNRs, such as nitrogen-doped GNR chevrons [34,35], sulfur doped 13-AGNR [36], or boron-doped AGNRs [37,38]. We note that while the cited research exploits on-surface chemistry, these methods have also been extended to solution synthesis [39], but with the additional difficulty that surface characterization techniques are more difficult to apply in this case.

Moving beyond the formation of individual GNRs and doped-GNRs, the on-surface bottom-up synthesis approach has been successfully extended to the fabrication of graphene nanoribbon heterojunctions and heterostructures, thereby opening a range of opportunities for exploiting GNR-based structures in multifunctional electronic circuits. Fig. 3 provides examples of the state-of-the-art in this field. For example, by combining pristine hydrocarbon precursors with their nitrogen-substituted equivalents, the Fasel's group created heterostructures consisting of seamlessly assembled segments of pristine (undoped) graphene nanoribbons and site-specific nitrogen-doped graphene nanoribbons [35]. This type of heterostructure between chemically distinct components has been demonstrated in other structures as well [40,41], and usually yields type-II, “staggered gap” heterostructures. Alternatively, covalent junctions between GNRs of different width by mixing different monomers [42,43] or by cross-dehydrogenative side-fusion [26,27] can yield the formation of type-I “straddling gap” heterostructures, owing to the strong dependence of AGNR's bandgap with the structure's width [21]. Progress in this field has been significant. For example, in the most recent example shown in Fig. 3c, Crommie and co-workers demonstrated that heterostructures can be made from a single precursor monomer resulting in an initially uniform fluorenone-doped GNR that is then excited to lead to the cleavage of specific sacrificial carbonyl groups to form sharp interface between electronically distinct segments [41].

Clearly, the possibility of creating atomically precise heterojunctions and of building FETs using GNRs as active channels [18,19] promises the development of a new class of carbon quantum materials where the intricacies of quantum mechanics, including the

emergence of topological states [44] can be exploited for the development of new carbon-based electronic components, sensors, and optoelectronic systems. In the following months we expect to see more papers published in *Carbon* related to the bulk synthesis of GNRs and the fabrication of electronic quantum devices with unprecedented performance. In addition, we expect to see more papers using similar assembly processes able to grow graphene nanoplatelets with specific dimensions and edge morphologies. Traditionally, the journal *Carbon* has not published many reports related to carbon nanoribbons. However, over the past three to five years, the number of articles about carbon nanoribbons have increased, be it regarding their synthesis, characterization, processing, or theoretical description. As this particular field is witnessing an unprecedented growth thanks in part to the development of highly controlled chemical routes for their assembly, we expect to consider more and more papers for publication on this topic in the months and years to come.

4. Low-dimensional diamonds: 1D and 2D sp^3 hybridized carbons

Recent theoretical [45–48] and experimental [49–52] works have demonstrated that bilayer graphene (sp^2 hybridized carbon) could be transformed into a diamond monolayer (sp^3 hybridized carbon), also known as diamane [46]. Since the structure of graphane, a hydrogenated graphene monolayer [53] is predicted to be more stable than diamane, the latter could be further stabilized if sandwiched between a capping inert layer and a substrate. However, further theoretical possibilities for its stability should be carried out in the near future.

High-pressure experiments have recently revealed that bilayer graphene could be reversibly transformed into diamond [49–52]. Theoretical calculations by Barboza et al. [45] also predicted that a hydroxylated diamond monolayer (also known as diamondol), formed by merging two graphene layers via sp^3 hybridized carbon atoms (Fig. 4a), would behave as a 2D semiconducting ferromagnet with a 0.6eV energy gap. The same group, together with experimentalists, reported *in situ* high-pressure Raman experiments of bilayer graphene using water as the pressure transmission medium [51]. This work showed that pressure values above 7.5 GPa would result in the formation of sp^3 -hybridized carbon, as determined by observing the splitting of the G-band; the process was found irreversible [51].

More recently, nano-indentation experiments on epitaxial bilayer graphene, consisting of two layers of graphene on a SiC (0001) surface, revealed the reversible formation of an ultra-stiff and ultra-hard phase of a diamond-like phase (Fig. 4b) [52]. Interestingly, this ultra-hard phase was only observed in bilayer graphene and not in mono- or few-layer graphene. In this context, Kvashnin, et al. [48] predicted the phase diagram vs. multi-layer graphene and their findings reveal pressure values that could result in the formation of 2D diamond as a function of the graphene layers [48].

There are still many open questions regarding the stability and the isolation of this novel 2D flexible diamond. Additional theoretical work should also be carried out in order to predict the properties of 2D diamonds and hetero-structures of 2D diamonds and graphene. These sp^2 - sp^3 carbon van der Waals solids would be transparent and would exhibit exciting thermal, magnetic and electronic properties. We expect readers get motivated and submit such papers to *Carbon*.

One experimental challenge that remains is the development of a bulk synthesis method for these flexible 2D diamonds. High-pressure experiments constitute an alternative; unfortunately, this route is not scalable and still very costly. A real breakthrough

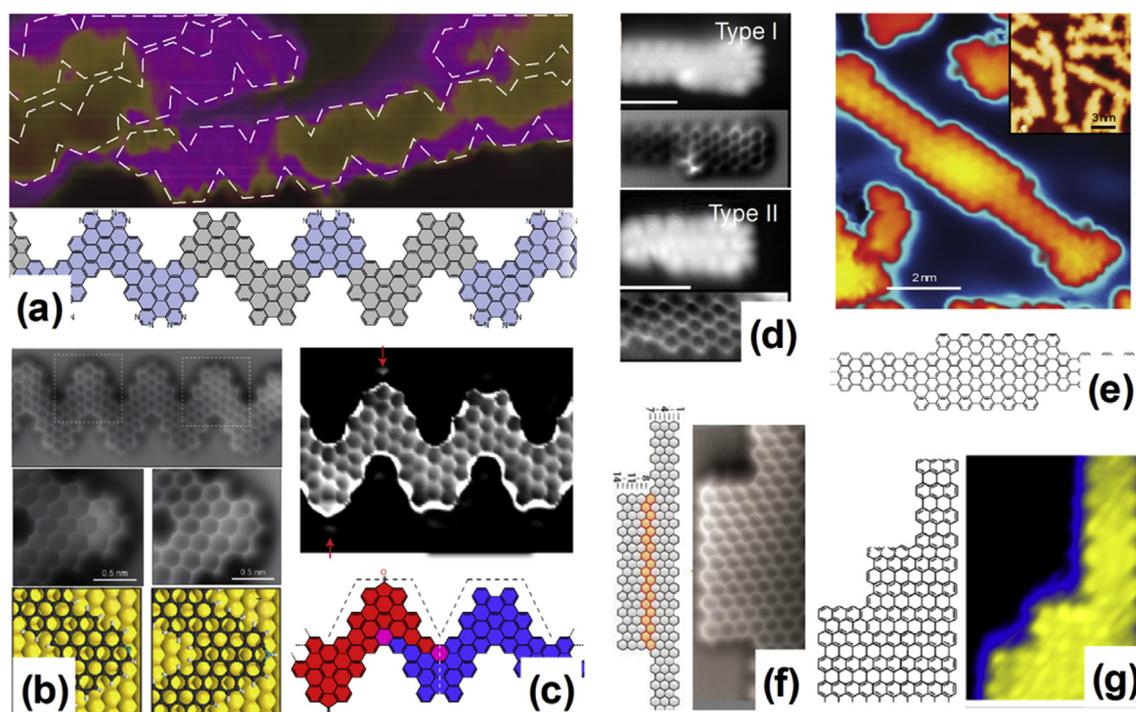


Fig. 3. Examples of experimental realizations of atomically precise junctions between GNRs. Types (a)–(c) correspond to junctions between chemically distinct components. These systems usually yield type-II, “staggered gap” heterostructures. Panels (d)–(g) are examples of covalent junctions between GNRs of different width. In this case, the GNR segments display significantly different band gaps, leading to the formation of type-I “straddling gap” heterostructures. (a) Junction between GNR chevrons composed of pristine and N-doped individual components [35]; (b) Junction between discrete segments of fused phenanthridine and carbazole groups [40]; (c) Junctions between a fluorenone and a non-functionalized chevron [41]; (d) Heterostructure between a 7-AGNR and a 5-AGNR [42]; (e) Heterojunction between a 7-AGNR and a 13-AGNR [43]; (f) Quantum dot formed by a small bandgap 14-AGNR sandwiched between two 7-AGNR segments [27]; (g) Double junction between a 7-AGNR, a 14-AGNR, and a 21-AGNR of decreasing bandgap [26]. Examples (a), (b), (d), and (e) correspond to junctions involving two distinct monomers, while examples (f) and (g) involve the same initial monomer where intermediate structures are side-fused by an additional cyclodehydrogenation, explaining why the junctions develop between N-AGNR, 2N-AGNR, 3N-AGNR, etc. Note that the heterostructures shown in (c) also only involve a single initial monomer with heterojunctions made by an initially uniform fluorenone GNR that is excited to lead to the cleavage of specific sacrificial carbonyl groups. Reprinted (adapted) with permission from Ref. [35]; Copyright (2014) Springer Nature (panel a); with permission from Ref. [35]; Copyright (2016) John Wiley and Sons (panel b); with permission from Ref. [35]; Copyright (2016) Springer Nature (panel c); with permission from Ref. [35]; Copyright (2016) American Chemical Society (panel f); with permission from Ref. [35]; Copyright (2016) American Chemical Society (panel g). (A colour version of this figure can be viewed online.)

would be to use CVD processes such as hot filament CVD in the presence of H_2 and CH_4 , to yield scalable synthesis of 2D or 1D diamonds. We expect some readers would get motivated and carry out experiments along these lines.

Regarding the synthesis of 1D diamond nanowires (the narrowest 1D diamond crystal; Fig. 5), Badding, et al. reported that solid-state reactions of frozen molecules of benzene at high pressures (e.g. 20 GPa), result in the formation of 1D diamond structures [54,55]. These 1D structures are usually packed in bundles (Fig. 5) and exhibit characteristic Raman modes (radial breathing and flexural modes) [54]. This method could use other template units to form N-doped 1D diamond nanowires [55]. Theoretical calculations indicate that there are many stable possibilities of combining sp^3 and sp^3/sp^2 hybridized carbon atoms and their behavior could have tunable electronic properties including superconductivity due to novel π electron overlap [56]. The challenge is to devise a practical route to produce large amounts of these 1D nanodiamonds and more importantly, to establish if synthetic pressures could be reduced so that scalable processes can be developed. Additionally, CVD processes should be explored in order to produce such fascinating 1D flexible diamonds.

5. Three-dimensional graphenes

Another challenging issue regarding graphene is the large-scale synthesis of bulk 3D graphene, while maintaining the 2D sheet

structure and properties. This is not trivial to achieve as graphene sheets tend to re-stack due to their strong π – π interactions. Therefore, 3D cross-linked graphene structures have become an alternative, where the graphene sheets must be separated along the c -axis direction (out of plane), perpendicularly to the graphene basal plane, and become “locked” so that π – π interactions are minimized. In this context, two types of materials can be made, one results from the interconnection of three dimensional rolled graphene sheets (CNTs), so they become the building units of a 3D cross-linked graphene monolithic network (3DGraphene) [57]. The other possibility is to have a hybrid material in which graphene sheets are separated by an additive in order to form graphene composites.

An effective, yet not perfect, way consists of engineering a graphene material in which individual graphene sheets are bonded (or stitched) together to construct a 3D monolithic network via edge reactivity using C, O, S, and even metal atoms as linkers. Because of the chemical linkages at the edges, graphene sheets are kept separated along the c axis and locked to avoid adopting a layered graphitic structure [58]. Therefore, these bulk materials should exhibit graphene's intrinsic properties at the macroscopic scale. In the literature, many 3D graphene-based materials are actually graphene composites, consisting of graphene sheets randomly placed with other components. Although these systems may show incremental properties, their performance is not maximized as the graphene sheets are not covalently interconnected.

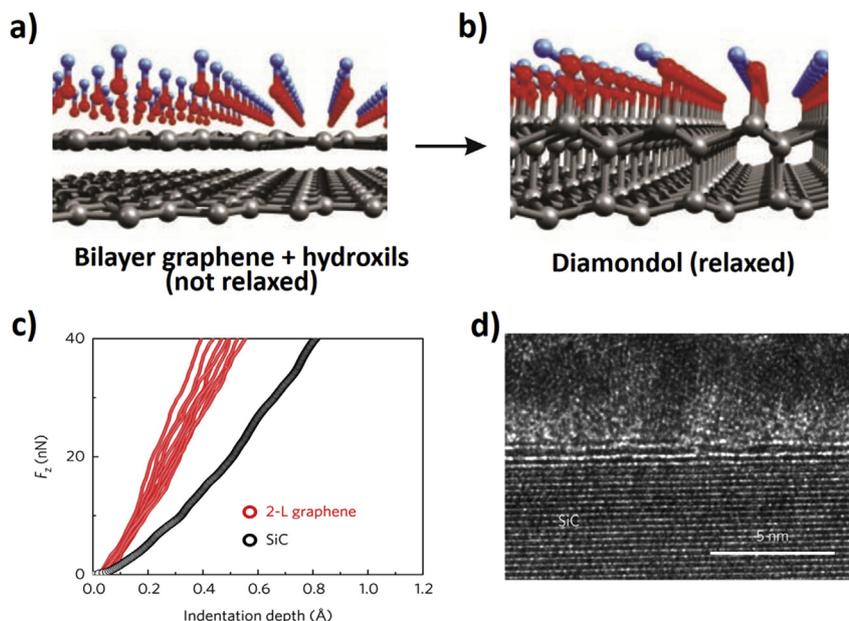


Fig. 4. (a–b) Initial and optimized geometries for two graphene layers with hydroxyl groups present on the top layer. The relaxed structure is known as diamondol [45]; (c) Experimental stiffness measurements in bilayer graphene showing an ultrastiff phase in the 2-L graphene at room temperature upon indentation [52]. The experimental indentation curves are shown for 2-L epitaxial graphene (red) and SiC (black). Curves were acquired at different positions on different samples, and (d) HRTEM image of bilayer epitaxial graphene on SiC [52]. (A colour version of this figure can be viewed online.)

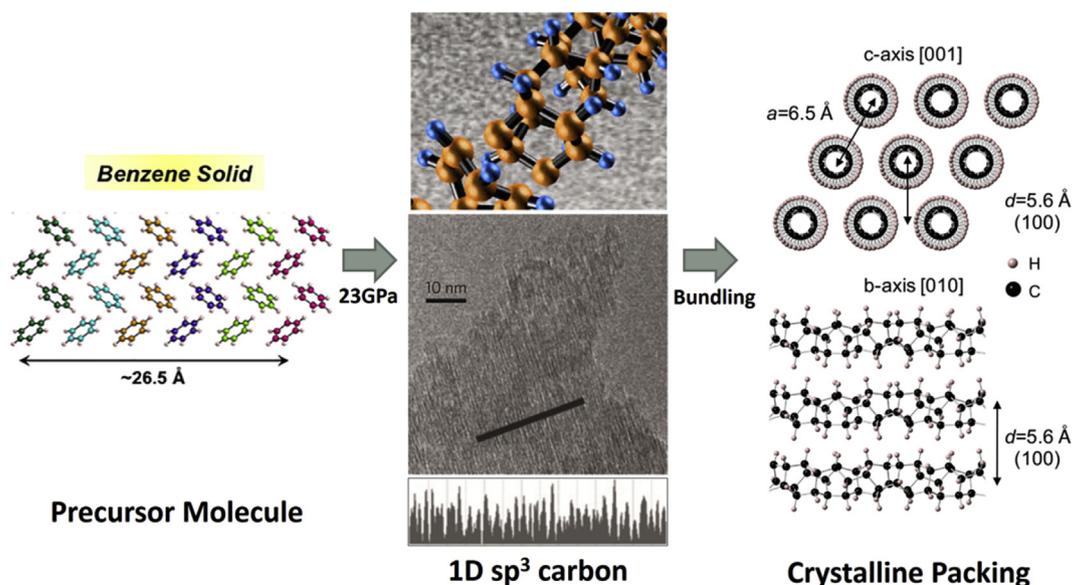


Fig. 5. Synthesis of 1D diamond nanotubes showing how solid precursors such as frozen benzene can be transformed into carbon nanotubes after applying pressures greater than 20 GPa. The middle shows a molecular model (top) and a TEM micrograph with striations spaced 6.4 Å apart extending for tens of nanometres; this spacing is consistent with that obtained from X-ray and neutron diffraction analyses and crystal structure modelling (right hand of the figure). The line profile (center bottom) along the marked path has 2 nm grid spacing [54,55]. (A colour version of this figure can be viewed online.)

Theoretical works based on triply periodic minimal surfaces (TPMs), also known as Schwartzites [59], reveal that it is possible to interconnect graphene sheets via defects adopting “Y-junctions” (GYJ) [60] (Fig. 6). Some of these 3D graphene networks have four- to eight-member carbon rings (also known as the Mackay-Terrones crystal (MTC) with all sp^2 hybridized carbon atoms (Fig. 6c) [61–63], and some have junctions established via sp^2 - sp^3 links [60,64–66]. It is noteworthy that these graphene-based networks adopt foam-like morphologies exhibiting energetic stability [65],

low mass densities and large surface areas together with unique electronic and mechanical properties [64–66]. While these crystalline structures have not been synthesized, some random graphene and CNT interconnected materials have been reported, exhibiting fascinating and unique properties [57,58,67–71]. In these theoretically proposed interpenetrating 3D graphene networks, the joined bonds are only formed by sp^2 hybridized carbon atoms. However, sp^3 carbon atoms could also be introduced and be replaced with multiple valance atoms such as O [57,58] or even

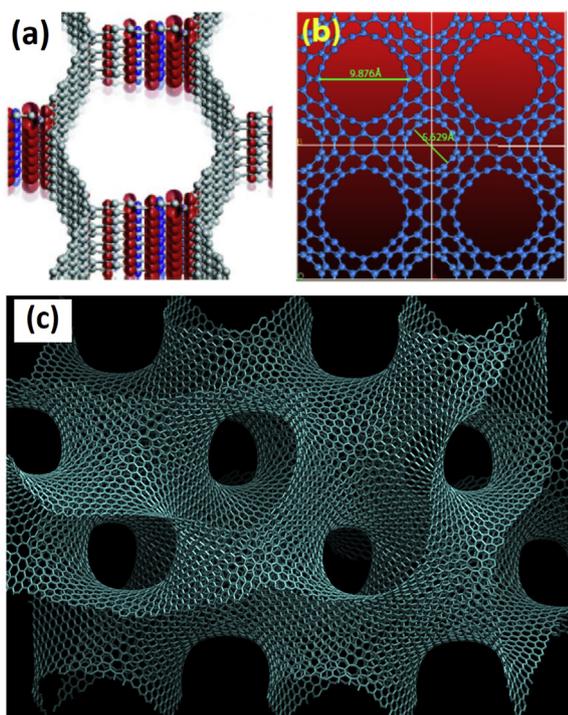


Fig. 6. Some proposed 3D carbon architectures. a) Total spin density isosurfaces of a new architecture with Y junctions formed by both sp^2 and sp^3 carbon atoms [60]; b) The top view of a 6-1-1-p MTC in a 2×2 supercell, the junctions are formed with non-six membered rings but with all atoms exhibit sp^2 hybridization [61]; c) molecular model of an extended periodic gyroid surface decorated with graphene; note the presence located at the saddles (courtesy of H. Terrones). (A colour version of this figure can be viewed online.)

multiple linking molecules [72]. Both types of junction units (e.g. with and without sp^3 hybridized carbons) may also widely exist in other carbon-based materials including amorphous carbon.

While many reports have been published about graphene composites with and/or without 3D cross-linking [72], truly cross-linked 3D graphene materials have been increasingly demonstrated. There are two main approaches to achieve such 3D graphene materials [66–68,70,73–77], one is using CVD on 3D metal templates [78–80], and the other is by reducing graphene oxide (GO) [81] and then cross-linking these units together with linking agents [82–84].

These 3D graphene materials exhibit many excellent and some unprecedented properties [60,62,63,65,85]. These include electronic [86–88], mechanical [69,89,90], energy efficiency [91–96], photo propulsion [58], catalytic [97,98], high surface areas [57,62], wide bandwidth radar/microwave and THz absorption [99–103], liquid absorption [104,105], gas adsorption [63,106,107], membrane materials [108,109], etc. More recently, these systems have been coupled with 2D layers in order to achieve novel hybrid properties (see following section) [82,110–112].

Although some progress in the synthesis of 3D graphene materials has been achieved, the synthesis of truly ordered 3D cross-linked graphene covalent networks requires intense investigation to discover their potentially interesting properties. In this context, some authors have recently demonstrated that it is possible to show the outstanding properties of 3D networks based on TPMs by 3D printing different 3D gyroidal systems with polymers (Fig. 7) [113–115]. For example, Buehler and coworkers showed that 3D periodic systems with high densities reveal exceptionally high strength but the mechanical properties decrease rapidly as density decreases [114]. Therefore, there are critical 3D graphene densities

that need to be reached if outstanding mechanical properties are desired (Fig. 7). In addition, these periodic 3D gyroids reveal novel optical properties and these can operate with different wavelengths depending on the 3D periodicity [113]. Based on these recent studies, an alternative synthesis to these materials would be nano 3D printing, however, there are obstacles that need to be overcome such as nanometer resolution, but all evidence indicates that periodic 3D graphene structures would indeed be fascinating and would open a new field in carbon science. Therefore, it would be beneficial for the community to explore the synthesis of perfect crystalline 3D graphene in the near future, but emerging methods should be used to reach to those 3D materials.

6. Graphene and layered semiconducting materials for photocatalysis

Two dimensional (2D) materials including graphene hold immense potential as catalysts for photocatalysis. However limited attention has been paid to their applications. For example, 2D transition metal dichalcogenides (TMDCs), such as MoS_2 and phosphorene, have been used in photocatalysis, and their performance has been restricted due to various limitations [116,117]. Single layer MoS_2 is a direct bandgap material with high absorption in the visible range; however it has limitations as a photocatalyst due to its extremely high electron-hole recombination rates and low carrier mobility [118]. At the same time, the use of phosphorene as a catalyst suffers from the lack of stability even in ambient conditions [119–121]. Therefore, the marriage of these layered semiconducting materials (LSM) with graphene, known as graphene-based layered nanocomposites (GBLC), can open up new avenues in photocatalysis. In this context, light absorbing semiconducting 2D materials can be directly grown on top of graphene by CVD thus forming vertical heterostructures [122–125]. These can also be synthesized by top down approaches and layer-by-layer stacking. A new special issue on Graphene-based heterostructures (edited by Xinliang Feng, Toshiaki Enoki and Joshua Robinson; <https://www.sciencedirect.com/science/journal/00086223/vsi/107496HK0QH>), has been recently published in *Carbon*, and we recommend the reader refer to it for further information.

Electron hole pair recombination is one of the major problems associated with photocatalysis since the recombination process competes with the catalytic process [126]. Owing to the high work function and electron affinity of graphene, GBLCs can offer a unique solution to this problem with the graphene layer acting as an effective electron trap, thereby separating them from the holes and thus minimizing the competing channel of recombination. In addition, the high carrier mobility of graphene ensures the fast and efficient transfer of electrons further increasing the efficacy of the nanocomposite as a catalyst [127,128]. One limitation of TiO_2 , which is currently one of the most popular photocatalyst materials, is the mismatch between its absorption and the solar spectrum. While TiO_2 absorbs in the UV range owing to its large bandgap (3.2 eV), UV rays constitute only ~2% of the solar spectrum, which renders these catalysts with low potential in practical applications [129,130]. With TMDCs and other layered materials as the light absorbing elements in GBLCs, this limitation can be overcome by the right choice of semiconducting material. In addition, the bandgap of many of these 2D semiconducting materials can also be tuned by strain engineering and by controlling the number of layers, thus allowing greater functionalities as catalyst [131].

While metals, in conjunction with TMDCs and other semiconductors, have also been used for promoting separation of electron-hole pairs, they face several limitations that can be overcome with the use of graphene as the charge separation layer. Since some metals have a tendency to get poisoned and deactivated

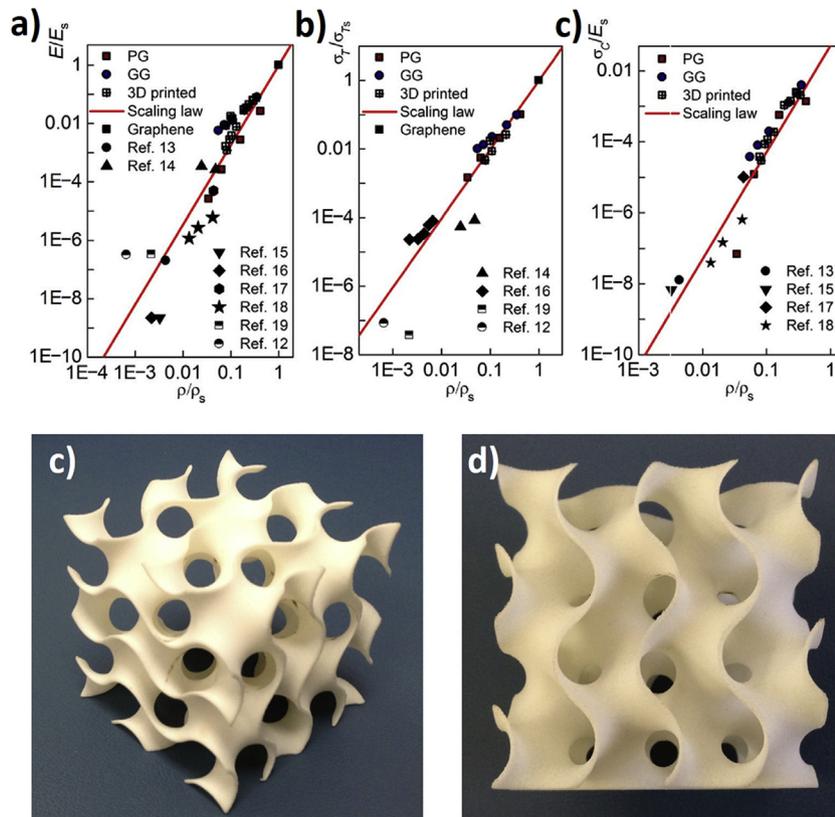


Fig. 7. The normalized Young's modulus (a), tensile strength (b), and compressive strength (c) of the 3D graphene assembly as a function of its mass density (adapted from Ref. Buehler). The data points include mechanical test results of the full atomic 3D graphene assembly (PG), the full atomic gyroid graphene (GG), and the 3D-printed polymer samples (3D-printed). The solid curves are plotted according to scaling laws obtained in the study with slopes of 2.73, 2.01, and 3.01 for (a), (b), and (c), respectively. $\rho_s = 2300 \text{ mg/cm}^3$, $E_s = 1.02 \text{ TPa}$, and $\sigma_{Ts} = 130 \text{ GPa}$ correspond to the density, Young's modulus, and tensile strength of graphene for its in-plane mechanics, used to normalize the properties of graphene materials (PG, GG, and references mentioned). $\rho_s = 1175 \text{ mg/cm}^3$, $E_s = 2.45 \text{ GPa}$, and $\sigma_{Ts} = 50 \text{ MPa}$ correspond to the density, Young's modulus, and tensile strength of the bulk material properties of polymer material for 3D printing, which are used to normalize the results of 3D-printed samples. (c–d) 3D polymer printed models of gyroid structures similar to those used by Buehler's group (models courtesy of A.L. Mackay). For references showed in (a–c) please refer to ref [114]. (A colour version of this figure can be viewed online.)

during reactions (especially if the reaction is conducted under harsh conditions), graphene, being extremely stable and inert, offers a far superior alternative. In addition, noble metals such as Pt or Au, which have been used for several catalysis-related applications, are relatively more stable but extremely expensive. Metal nanoparticles in conjunction with semiconducting materials have also been used for photocatalytic applications, but this drastically limits the interfacial area of contact.

One major limitation of using atomically thin layers for applications related to photocatalysis is their limited light absorption. This limitation can be overcome by engineering multi-heterostructures of layered systems synthesized either by layer-by-layer stacking or by direct growth. As shown in Fig. 8, an alternate arrangement of graphene and LSM can be used as a photocatalyst. The alternating layer-by-layer structure ensures efficient charge transfer and high absorption, thus overcoming the limitations associated with thin layers of 2D materials being used as catalyst. While top-down approaches (exfoliation of thin layers, transfer and stacking) are not scalable and practically relevant, recent advances in CVD techniques allowing the facile growth of large area heterostructures with high control and precision, can ensure scalable synthesis of such novel catalysts. Additionally, this layer-by-layer assembly of GBLCs allows good interfacial contact between graphene and LSM, which, in contrast, is more difficult to

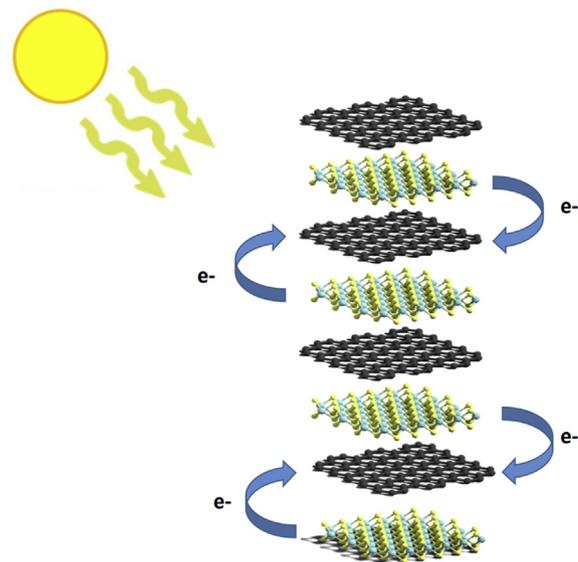


Fig. 8. An alternating arrangement of graphene and 2D layered semiconducting materials resulting in the formation of a graphene-based layered nanocomposite with enhanced absorption of light and charge transfer for photocatalytic applications. (A colour version of this figure can be viewed online.)

achieve when metals or metal nanoparticles are used as the charge transfer layer from the semiconducting material. Additionally, graphene can be used as a capping layer for protecting semiconducting materials like phosphorene, which are extremely sensitive to degradation in the environment.

In conclusion, although graphene has found limited applications in photocatalysis so far due to its zero bandgap, GBLCs can open up previously unavailable opportunities. While the LSM opens up the bandgap, preferably in the visible range (depending on the choice of semiconductor), graphene acts as an acceptor of electrons facilitating the charge transfer process. In addition, alternating layers of LSM and graphene can be formed, and these heterostructures would exhibit enhanced light absorption and enhanced charge transfer with extremely high surface-to-volume ratio. All in all, such graphene-based heterostructures have potential to surpass the current generation of photocatalysts in both functionalities and applications. Therefore, the synthesis and use of such heterostructures can open up new applications of graphene-based heterostructures beyond conventional optoelectronics. At *Carbon*, we are increasingly seeing more papers published on the synthesis and applications of these 2D systems in which graphene plays a key role, and we foresee an increase in the number of publications in this field in the near future.

7. Carbon materials for wearable devices

Wearable devices (WDs), such as smart watches, wristbands, belts, and head-mounted displays (like Google Glass), have attracted an increasing interest in recent years. Great application potential of WDs, particularly in the fields of health and medicine, education, transportation, finance, and entertainment, has already started to make significant economic, social and cultural impact. Compared to conventional electronic devices, WDs provide augmented access to electronic/computer interfaces, and hence offer smart functions such as real-time monitoring of the physiological conditions of users, or tracking and responding to various environmental stimuli [132–134]. The new generation of WDs demand enhanced wearability. For example, they might be directly worn on a large area of soft, curved, and stretchable skin [135–137]. Some types of new WDs, on the other hand, are 'invasive', being deployed as smart tattoos inserted into the dermis layer of the skin or as body implants directly embedded inside the wearer's body [138,139].

The fast emergence of novel WDs brings unique challenges in material selection. Conventional electronic devices are often constructed using bulky and heavy materials because their applications can tolerate the volume and weight. In contrast, WDs require lightweight materials, which can be packed in a smaller volume to enable comfortable integration to the human body. Second, the conventional electronic devices rely on mechanically rigid and non-deformable materials as electrical conductors, semiconductors, and insulators to realize various functions. In contrast, new WDs require soft and flexible materials, which are deformable or stretchable under external forces induced by three-dimensional body movements, including stretching, twisting, bending, or shearing. Third, although soft and flexible materials are desired, these materials should also have outstanding fatigue resistance or damage tolerance to maintain their structural integrity since WDs undergo repeated wearing or washing cycles during their lifetime. Fourth, some WDs may cover a large area of the body, making breathability an essential feature for maintaining the users' comfort. Therefore, we need materials that allow the escape of hot air and water vapor from the body. Lastly, the materials' biocompatibility is critical for WDs, especially for those that will be in direct contact with the skin or embedded inside the body. Unfortunately, the materials

commonly used in conventional electronic devices, such as bulk metal (e.g. Cu, Al, Au, Fe, Ag, Pd, etc.) films or wires, silicon wafers, acrylonitrile butadiene styrene, polyamide, and polycarbonate, cannot fully meet these requirements [140,141].

Because of their desirable mechanical, electrical, chemical, and biological properties, conventional carbon materials, carbon nanomaterials, and their composites stand out as ideal candidates for new WDs. Carbon fibers and filaments, graphite, porous carbons, CNTs, and graphene hold a great promise to address different aspects of the challenges described above. In this context, several key application areas attracted great research interest in recent years, which are briefly discussed below and also illustrated in Fig. 9.

- (i) Conducting textiles: Carbon materials, such as carbon fibers, CNTs, and graphene, exhibit good electrical conductivity comparable to that of metals, and much higher than polymeric materials. Besides, the mechanical flexibility of carbon materials is much higher than metals, showing polymer-like values. Thus, these carbon materials and their composites have been used to construct conductive yarns, fabrics or films, which are the basic components of many WDs [142–145]. Some carbon fabrics or films with particular electrical conductivity and 3D structures have been explored as electromagnetic interference shielding materials in WDs [146,147], while some other carbon fabrics with appropriate electrical resistances are applied as flexible heaters for thermal management [148–150].
- (ii) Electronics and photonics: SWCNTs and functionalized graphene can serve as flexible semiconductors with high carrier mobility [151], and carbon quantum dots and nanodiamonds are potential light emitting materials [152]. They are being used as semiconducting components for building novel flexible electronics and photonics [153,154], including flexible light-emitting devices and photodetectors [155,156]. The main competitors are conducting polymer-based flexible and stretchable semiconductors, however, carbon materials hold significant advantages in carrier mobility and material stability.
- (iii) Sensors: The electrical conductivity, band gaps, and carrier mobility of CNTs, graphene, nanodiamonds, and carbon quantum dots are highly sensitive to surface functionalization and environmental stimuli, which is a desirable characteristic for sensors. Thus, these carbon materials have been intensively tested for different types of wearable sensors, including strain, pressure, and electrochemical sensors [157–161]. While material characteristics are critical in developing wearable sensors, other challenges, such as sample preparation, powering devices, signal communication, and data analysis, should be addressed simultaneously to transform conventional sensor platforms into wearable formats.
- (iv) Energy storage: Various carbon materials exhibit large specific surface areas in combination with good electrical conductivity and mechanical flexibility. Such appealing properties of carbon materials have led to many studies on the design of novel flexible electrodes for wearable energy storage devices, such as supercapacitors and batteries [162–173]. Although various unconventional functionalities, such as flexibility, stretchability, self-healability, and color-tunability, have been introduced, the primary target in this area is still to create energy storage devices with gravimetric or volumetric energy storage capacity at least comparable to conventional energy storage devices. It is important that research efforts be devoted to finding the right balance

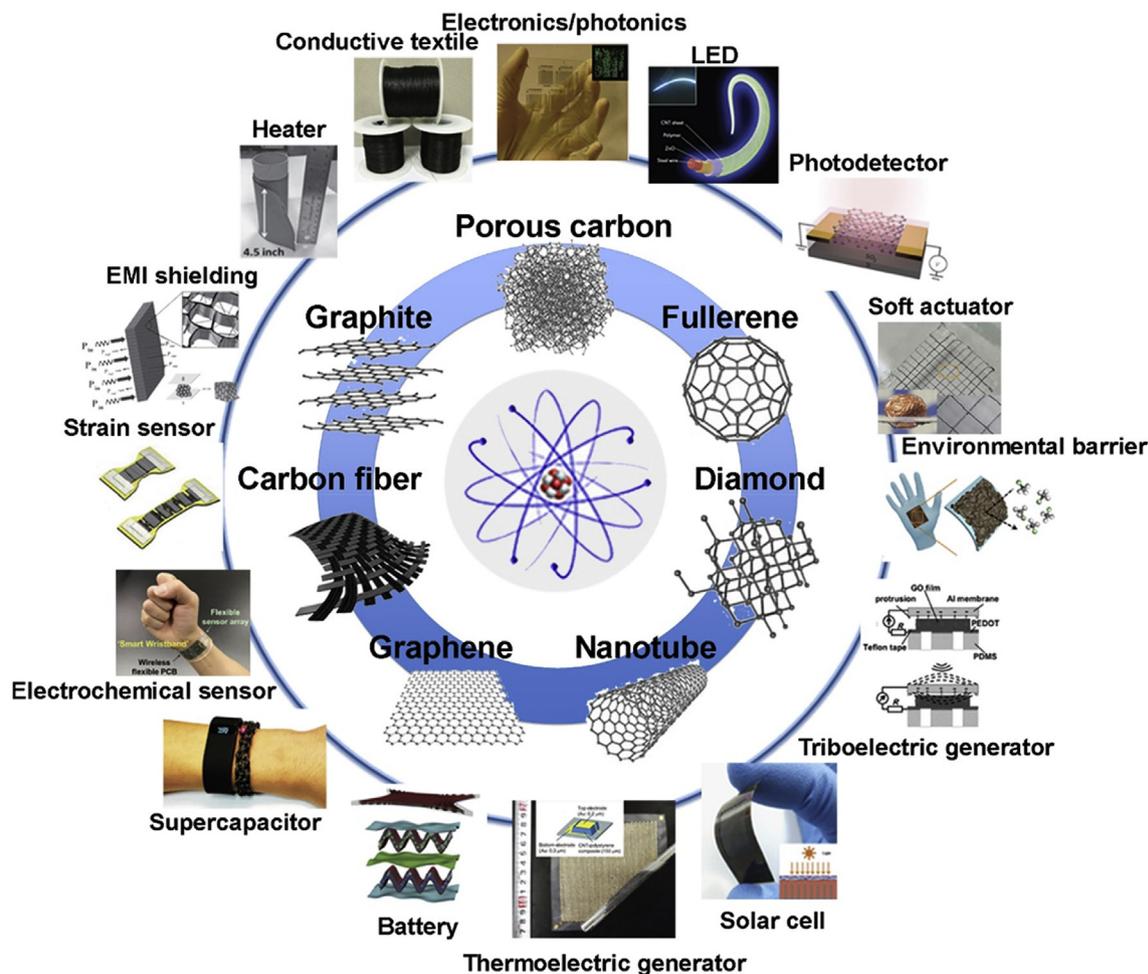


Fig. 9. Example applications of carbon materials and carbon nanomaterials in wearable devices. Conductive textile [145]. Reprinted by permission from Wiley-VCH Verlag GmbH & Co., copyright 2016. EMI shielding [147]. Reprinted by permission from Wiley-VCH Verlag GmbH & Co., copyright 2015. Heater [150]. Reprinted by permission from Wiley-VCH Verlag GmbH & Co., copyright 2014. Electronics/photronics [154]. Reprinted by permission from Springer, copyright 2017. LED [156]. Reprinted by permission from Macmillan Publishers Ltd: Nature Photonics copyright 2015. Photodetectors [155]. Reprinted by permission from Macmillan Publishers Ltd: Nature Nanotechnology, copyright 2014. Strain sensor [160]. Reprinted by permission from Wiley-VCH Verlag GmbH & Co., copyright 2016. Electrochemical sensor [139]. Reprinted with permission from American Chemical Society, copyright 2016. Supercapacitor [170]. Reprinted by permission from Elsevier, copyright 2016. Battery [172]. Reprinted by permission from Elsevier, copyright 2017. Thermoelectric generator [177]. Reprinted by permission from Wiley-VCH Verlag GmbH & Co., copyright 2016. Solar cell [175]. Reprinted by permission from Elsevier, copyright 2015. Triboelectric generator [174]. Reprinted by permission from Wiley-VCH Verlag GmbH & Co., copyright 2015. Environmental barrier [183]. Reprinted with permission from American Chemical Society, copyright 2017. Soft actuator [187]. Reprinted with permission from Macmillan Publishers Ltd: Nature Nanotechnology, copyright 2015. (A color version of this figure can be viewed online.)

between the energy storage functionality and the added extra functionalities.

- (v) Energy harvesting: As WDs get smaller while functionality continuously increases, energy harvesting becomes the way forward to supplement energy storage devices. Several types of wearable energy harvesting devices, such as thermoelectric generators, solar cells, and triboelectric generators, have been incorporating carbon materials to realize different functions and improve their performances [174–177]. The precise performance control and seamless integration with other components need to be tackled synergistically to realize their practical applications.
- (vi) Environmental barrier: To maintain their desired operating conditions, a wide range of WDs require barrier films that impede molecular transport between their interior and surrounding. Graphene or stacked reduced GO films are virtually impermeable barriers for most molecules, including oxygen and water, which can serve as barrier coatings against rusting and environmental hazards [178,179].

Furthermore, by tuning the structure of carbon materials and the interactions among them in assembled structures [180,181], researchers are now creating breathable (for example, allowing outward perspiration while protecting the user from chemical toxicants or biochemical agents in the local environment) and stretchable carbon-based barriers for WDs [182,183].

- (vii) Soft actuator: Actuators are devices that can mechanically move or control various objects using a source of energy under a control signal. Soft actuators can easily deform and adapt to changing environments, which make them of great interest in the development of soft robots and interactive WDs [184,185]. CNTs, graphene and their assemblies are being explored in designing soft actuators due to their unique mechanical and electrical properties [186,187].

Across the different application areas discussed above, the following four common issues are critical for transferring current research efforts on carbon materials into practical WDs. First,

carbon materials have diverse physical and chemical structures. Minor changes in the structure of carbon materials often result in significant variations in their final properties. It is important to carefully tailor carbon materials to yield the desirable properties to meet the requirements of specific applications. Second, other than macroscale carbon materials, a major challenge for carbon nanomaterials is how to keep their desired nanoscale properties in assembled macroscale carbon architectures. Significant research efforts have been devoted to this aspect, and more will be required. Third, scalability is another major hurdle, which retards the application of carbon nanomaterials. The large-scale production together with good quality control and reasonable cost will determine their economic feasibility. Fourth, WDs are in more close contact with the body compared to the conventional electronic devices. Potential toxicity of new materials has to be rigorously evaluated. Proper encapsulation of certain materials will be required. Clearly, there are many exciting challenges awaiting researchers in this emerging field.

Carbon has recently published a virtual special issue entitled “Carbons for Wearable Devices” (see journal home page at: www.journals.elsevier.com/carbon) [188]. It presents 36 recent articles published in *Carbon* on how carbon materials can be tailored to realize different functions in WDs. As the journal *Carbon*, we are hoping to publish more exciting and cutting-edge work in the coming year and eventually see widespread applications of carbon materials in the development of newly emerging WDs. Providing an updated overview of our vision of this growing field in this perspective, we would like to encourage the *Carbon* community to keep up these trends and contribute with exciting research articles.

8. Perspectives on safe(r)-by-design carbon nanomaterials

New materials development often begins with a fundamental discovery followed by laboratory-scale research to improve synthesis methods and establish basic material properties. As reliable sources of test material become available, there is a significant period of laboratory research to characterize material behaviors relevant to performance in one or more proposed technological applications. Further development toward commercialization then involves integration of the material into a system, composite, or device, which undergoes further performance testing. In this paradigm of technology development, issues of safety for human health and the environment are typically addressed late, in a separate effort that is not connected to the early-stage materials R&D.

In recent years there has been a movement to replace that paradigm with a more integrated approach, in which environment, safety, and health issues are co-considered along with performance behavior in the early-stages where primary materials development takes place. By including biological response studies early, the hope is to co-optimize a new material for both performance and safety, and thus to catch and mitigate material safety issues in a phase where R&D investment is still modest, and before the operating parameters of the final system or device constrain changes to the individual material components.

This new paradigm of integrating safety and performance in the early stages of R&D is sometimes referred to as “safety-by-design” and the resulting products as “safe-by-design”. In recognition of the fact that “toxicity” and “safety” are relative terms, many researchers use the phrase “safe(r)-by-design” and focus on material modifications that reduce (if not necessarily eliminate) adverse biological responses. This new paradigm is particularly important in the case of new nanoscale materials for two reasons. First, they typically have a higher bioavailability than bulk materials, either through respiration into the human lung, ingestion into the gastrointestinal

tract, or direct injection into the bloodstream; and unlike bulk materials, nanomaterials can be internalized by living cells to access the fundamental biomolecular machinery of living organisms. In contrast, most bulk materials are poorly bioavailable, and their safety considerations revolve instead around leaching or volatilization of bioavailable species from solid surfaces into the environment, a well-known example being soluble lead ions leached from water lines, pipe fittings, or perovskite solar cells. Second, nanomaterials have properties that are sensitive to particle size, shape, and surface chemistry, so there is a real opportunity to improve their safety without full substitution, *i.e.* by reformulating the original material through intelligent modification of size and shape, or surface chemistry.

Today the concept of safe(r)-by-design is becoming accepted as an integral part of new nanomaterial development. Increasingly the government agencies that fund research are establishing specific programs to define rules for the safe design of nanomaterials. An example is the European Union's “NanoReg2”, which focuses on manufactured nanomaterials and states: “*NanoReg2 will establish safe by design as a fundamental pillar in the validation of novel manufactured nanomaterials*”. Due to the complexity of the nanomaterial landscape, it is indeed essential to establish safe(r)-by-design as a key step in the validation of any novel nanomaterial [189]. Nanomaterials based on carbon offer unique opportunities alone or when incorporated into new products, but they are not devoid of potential risks [190]. It is often possible to mitigate adverse biological responses to carbons by certain types of chemical modification of their surfaces (Fig. 10), including carbon nanotubes (CNTs), fullerenes and graphene, typically involving increases in hydrophilicity and improvements in aqueous dispersibility [190,191].

In 2010 G. Morose [192] proposed five design principles to reduce hazards and potential exposure risks to nanoparticles: 1) Alteration of size, surface, or structure; 2) Substitution by an alternative material; 3) Surface functionalization; 4) Encapsulation; and 5) Reduction in quantity [191]. Strictly associated with the concept of safe(r)-by-design are the principles of prevention-by-design aimed also at developing nanomaterials with minimum risks, exposure, hazards, and environmental and human health impact [193]. Actually, prevention-by-design is based on the same principles of the safety-by-design but expand the efforts to implement research and educational elements in an anticipatory process. A typical example concerns the case of CNT behavior that could be anticipated by considering the history of asbestos fibers, whose harmful effects were not known until workers have been exposed to the material and developed disease many years later.

The proposed principles for safer nanotechnology can be applied by product designers at various stages along the development pathway. As an example, CNT risks can be mitigated in the compositing stage by encapsulation in polymer or metal matrices [194], in which state the likelihood of direct human exposure is greatly reduced. Of course mechanical stress or chemical degradation might lead to CNT release from the matrix, and a subfield of nanosafety research is engaged in characterizing the extent and form of the debris produced from different types of composite stresses during handling, use, and end-of-life disposal. A better understanding of composite material behavior is expected to lead to recommendations for new strategies for safer design of the next generation products containing carbon nanotubes. Specific functionalization approaches (Morose's principle 1 and 3) may also allow the design of safer carbon nanotubes [195]. It has been reported that asbestos-like pathogenicity is removed when CNTs are modified by covalently linking an amino-triethylene glycol chain that disaggregates them and render them highly water dispersible [195]. An alternative possibility to modulate the toxicity of carbon

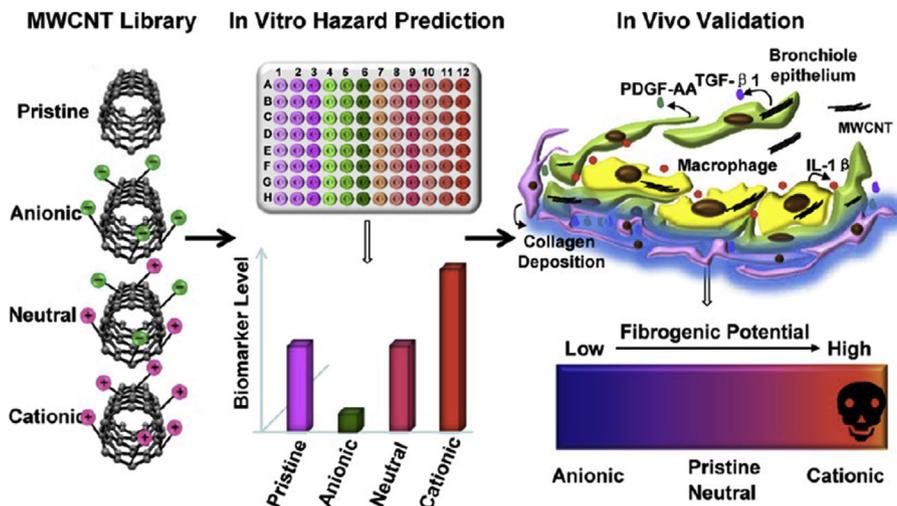


Fig. 10. Surface modification modulates the pulmonary toxicity of carbon nanotubes [191]. Copyright 2013, the American Chemical Society (used by permission). (A colour version of this figure can be viewed online.)

nanotubes is to coat their surface with biocompatible surfactants (Morose's principles 3 and 4) [196]. Encapsulation of carbon nanotubes into a pluronic copolymer makes them safer by decreasing lung fibrosis potential.

Morose's first principle includes control of size and shape. CNTs pose an interesting case study for this first principle, in that asbestos-like pathogenicity has been associated with long, but not short CNTs, and straight, but not entangled CNTs [197]. "Entangled", however, is an aggregation state, not a fundamental material property that CNT designers can systematically target, or that governments can easily adopt for regulatory purposes. Recently,

Zhu et al. [198], proposed a "phase diagram" for carbon nanotube pathogenicity (Fig. 11) that is designed to quantitatively distinguish between straight, stiff nanotubes with asbestos-like behavior and other nanotube types that lack the length or mechanical stiffness to present themselves as rigid fibers to biological tissue. The analysis uses the Euler buckling theory to distinguish CNTs into two types: those that are "biologically stiff" and remain as straight fibers under the influence of compression forces inside the lysosome after cellular uptake; and those that are "biologically soft" and buckle to relieve the lysosomal stress [198]. This stiff/soft dichotomy is related to the casual observation of the "entangled" state, but is not dependent on processing history and is quantifiable through specification of the CNT length and diameter (Fig. 11). This phase diagram is offered as a safe design tool, and we hope that other such quantitative tools, rooted in fundamental materials science, can be developed for others materials, including graphene materials (see below), which come in a variety of lateral dimensions and thicknesses.

Another approach to safe(r)-by-design is through programmed biodegradation. Recently, Bianco and co-workers proposed a new approach to render carbon nanotubes less biopersistent by enhancing their biodegradability by endogenous peroxidases [199]. The new design is based on functionalizing carbon nanotubes with ligands able to increase the catalytic activity of oxidative enzymes leading to better biodegradability of the materials. The same strategy can be applied to graphene-based materials (Fig. 12) [200]. Again specific ligands able to enhance the interaction of peroxidases with graphene oxide render the latter better able to biodegrade and likely safer.

In this context, graphene materials with their strong commercial potential are clear targets for safe(r)-by-design approaches [201]. In terms of research priorities, most of the biological response and safety studies are focusing not on CVD graphene but on exfoliated materials (e.g., graphene oxide, few-layer graphene, graphene nanoplatelets), which can be produced as bulk powders and have significant exposure potential. One can readily calculate that a full graphene monolayer grown on a large-format Si wafer (450 mm diameter) constitutes only about 0.1 mg of mass, and is not sufficient to create hazardous doses under most circumstances. The most basic principle in environmental health is that Risk = Exposure x Hazard, and for the field to manage the risk of graphene materials clearly means to focus on exfoliated materials

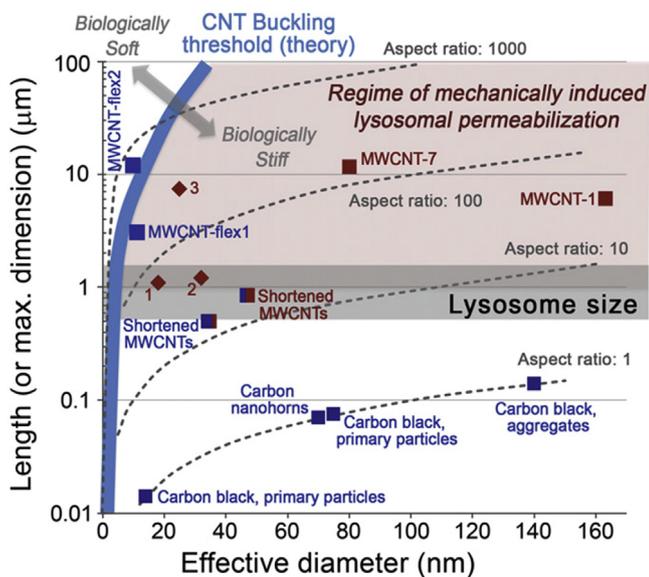


Fig. 11. Phase diagram distinguishing pathogenic from biocompatible carbon nanomaterials in the mechanical pathway to lysosomal membrane damage [198]. The Euler theory of buckling applied to CNTs encapsulated in lysosomes following uptake (thick blue curve) distinguishes biologically soft from biologically stiff varieties. CNTs that are longer than the lysosome size ($\sim 1 \mu\text{m}$) and biologically stiff fall in the red shaded region and are predicted to be pathogenic. The theory is consistent with current literature data, which is represented by red markers (for CNTs reported to be pathogenic) and blue (non-pathogenic). Note this theory is for CNTs with unmodified (pristine) surfaces. Reprinted from the Proceedings of the National Academy of Sciences [198] (with permission). (A colour version of this figure can be viewed online.)

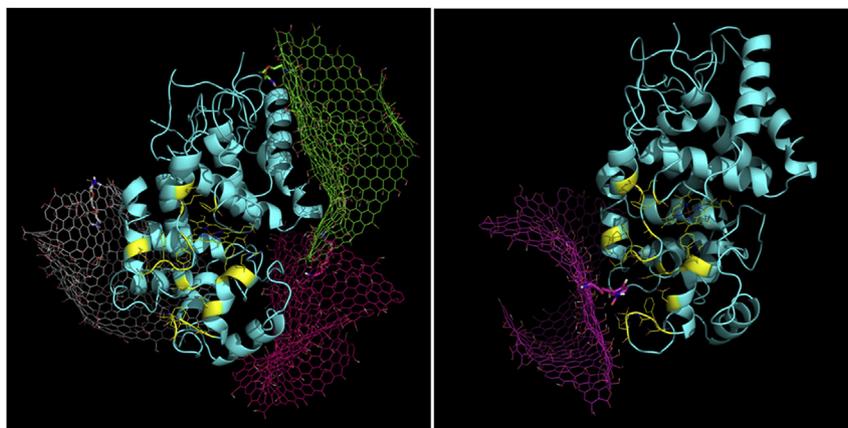


Fig. 12. Molecular models revealing the possible binding positions of horseradish peroxidase (HRP) to GO functionalized with TEG diamine (left) and with TEG-dihydroxybenzoic acid (catechol) (right). While GO functionalized with TEG alone has nonspecific binding with HRP, the presence of the catechol moiety favors the interaction of GO with the active site of the enzyme leading to an enhanced catalytic activity and a faster degradation rate. Specific functional groups are shown in bold. (A colour version of this figure can be viewed online.)

where the exposure term can be significant. Based on the available literature [202,203], Park and coworkers discuss approaches for assessing the potential hazard, exposure, and risks of graphene-based technology and ways to implement the safe(r)-by-design paradigm at various stages of the innovation process for graphene-containing products.

Finally, the design of safer nanomaterials, including the different forms of carbon, needs new test strategies to assess their toxicological impact [204]. There are only a limited number of studies describing statistical and high throughput screening models to identify the relationship between properties and hazard. Recently a model that correlates the surface charge properties of carbon nanotubes and the mortality of zebra fish embryos has been proposed [205]. This may be a good starting point for the development of guidelines to design safer carbon nanotubes and can be clearly expanded to other carbon materials. However, the research community needs to take into consideration the variety of parameters that characterize carbon materials and the descriptors of toxicity, as there is not complete agreement and convergence towards a universal model [206].

9. Final remarks

We would like to emphasize that this perspective provides our personal views. Although the challenges presented in this article mainly focus on nanoscale carbon materials, *Carbon* always welcomes papers from the traditional carbon community, with the vision of advancing carbon science and technology. Some topics along these lines include graphite intercalated compounds, nuclear graphite, carbon fibers, carbon-carbon composites, etc. However, as always, these scientific contributions should include clear scientific novelty and constitute significant advances when compared to existing literature. For example, by elucidating mechanisms that explain properties and/or performance of materials/composites, and answer fundamental questions that have not been well addressed in the literature. Reports describing materials synthesis, properties and applications without clear scientific/engineering novelty are unlikely to be considered, irrespective of whether the material in question is a new or old form of carbon. We would encourage the reader to refer to our previous perspective and editorial [1,207], in which we suggest a number of ideas to improve the quality of manuscripts submitted to *Carbon* [1], as well as recommended nomenclature of graphene and related materials [207].

We would also like to point out that *Carbon* has recently published special issues on the following subjects: Scientific Contributions of Mildred S. Dresselhaus (<http://www.sciencedirect.com/science/journal/00086223/vsi>) [208], Graphene-based heterostructures (edited by Xinliang Feng, Toshiaki Enoki and Joshua Robinson; <http://www.sciencedirect.com/science/journal/00086223/vsi/107496HK0QH> [209]) and Carbons for wearable devices (edited by Yuan Chen, Liming Dai and Yutaka Ohno; <http://www.sciencedirect.com/science/journal/00086223/vsi/106S05KMKZB> [210]). We invite the readers to read these valuable contributions and keep submitting their best work on carbon-related materials to *Carbon*.

Finally, the editorial team of *Carbon* would like to congratulate Professor Rodney S. Ruoff (UNIST, Korea) for being recognized by Chemistry & Engineering News for having the most cited paper in 2007, which was published in *Carbon* [211]. This particular paper described the reduction of graphene oxide (GO) with hydrazine into electrically conducting graphene-based sheets [212]. As a result of this recognition and in parallel with this perspective, the editor-in-chief asked Professor Ruoff to write a short perspective of carbon science for the following years. In the next contribution [213], Professor Ruoff will provide readers his own list of current carbon science challenges, some of which are also discussed above. We hope his list will also stimulate researchers to tackle such challenging topics.

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