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Editorial review

# Carbon science in 2016: Status, challenges and perspectives

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## 1. Introduction

This year we enjoyed the 30th anniversary of the discovery of $C_{60}$: Buckminsterfullerene. This discovery in 1985 began a unique period in carbon science that saw the rise of carbon nanotube research, the isolation and characterization of graphene, and the exponential growth of international nanotechnology research that has arguably been the largest movement within the physical sciences over the last several decades. Carbon materials have led this general science movement, serving as models of structural perfection that have inspired synthesis of other materials with similar structures and symmetries.

We are fortunate in *Carbon* to be at the center of a very exciting field. Recent research on carbon materials has led to two Nobel Prizes (for fullerenes and graphene), and two Kavli Prizes in Nanoscience (to M. Dresselhaus and S. Iijima for work on carbon nanotubes). Carbon nanomaterials research has transformed the journal in many ways, and is responsible for much of its recent growth and success. As we approach 2016, however, nanoscience is maturing as a field and the graphene discovery is ten years old. Having discovered the archetypical low-dimensional carbon forms - 0D fullerenes, 1D nanotubes, and 2D graphene, what will be the next “big thing” in carbon? One is reminded of Francis Fukuyama's 1989 essay, *The End of History*, which explored whether the end of the Cold War meant the end of political struggles over the final preferred form of government. Have we reached a similar point in 2016 that would cause us to declare the “End of Carbon Science”?

Our editorial team firmly believes the answer is “no” and that many exciting challenges remain. There are various new allotropes to be synthesized, and there are major challenges in combining our basic low-dimensional forms into more complex 3D architectures. Much work is needed to develop and optimize applications of nanotubes and graphene, and concerns about the global environment are causing a resurgence of interest in carbon fibres for lightweight transportation technologies and porous carbons for energy storage and environmental protection.

We decided to try a new editorial form by combining our ideas and perspectives, each of us drawing from our individual subfields, to produce this group editorial. We leave the readers to judge the usefulness of the outcome, which is represented by the individual sections below. First, Mauricio Terrones and Yongsheng Chen begin with their thoughts on “Covalently bonded nanocarbon-based materials”. Toshiaki Enoki follows with a section entitled “From aromatic molecules to infinite graphene - bridging chemistry and physics”. Yuan Chen, the newest Carbon editor, writes about “High-purity single-walled carbon nanotubes: growth, sorting, and applications”. Alberto Bianco and Robert Hurt provide their perspectives on the “Biological behavior and safety of carbon nanomaterials – ongoing research needs” and Nikhil Koratkar with guest Rahul Mukherjee discuss “The importance of volumetric performance parameters in energy storage systems”. Also in the important area of energy applications, our new editor Elzbieta Frackowiak discusses the “Role of carbon textural properties in energy storage systems”. Marc Monthioux and Chong Rae Park describe the history and current research directions in “Carbon fibres”, and Jin Zhang writes about “Graphynes as new carbon allotropes”. Finally, Chong Rae Park and guest Yern Seung Kim write about “Nanocomposites”, and we end with a section by Robert Hurt on the various aspects of the connection between “Carbon materials and the global environment”. We hope our readers will find these personal opinions and subjective outlooks valuable.

## 2. Covalently bonded nanocarbon-based materials

During the last 25 years, new allotropic forms of pure carbon, mostly $sp^2$ bonded with nanoscale dimensions (e.g. fullerenes, nanotubes, graphene, see Fig. 1), exhibiting novel physico-chemical properties, appeared thus triggering intense research in the area of carbon nanoscience [1–5]. These unique structures have been at the forefront of nanotechnology and have had their impact as the most important building blocks in future nanotechnology applications [6–10]. However, Carbon researchers should now start

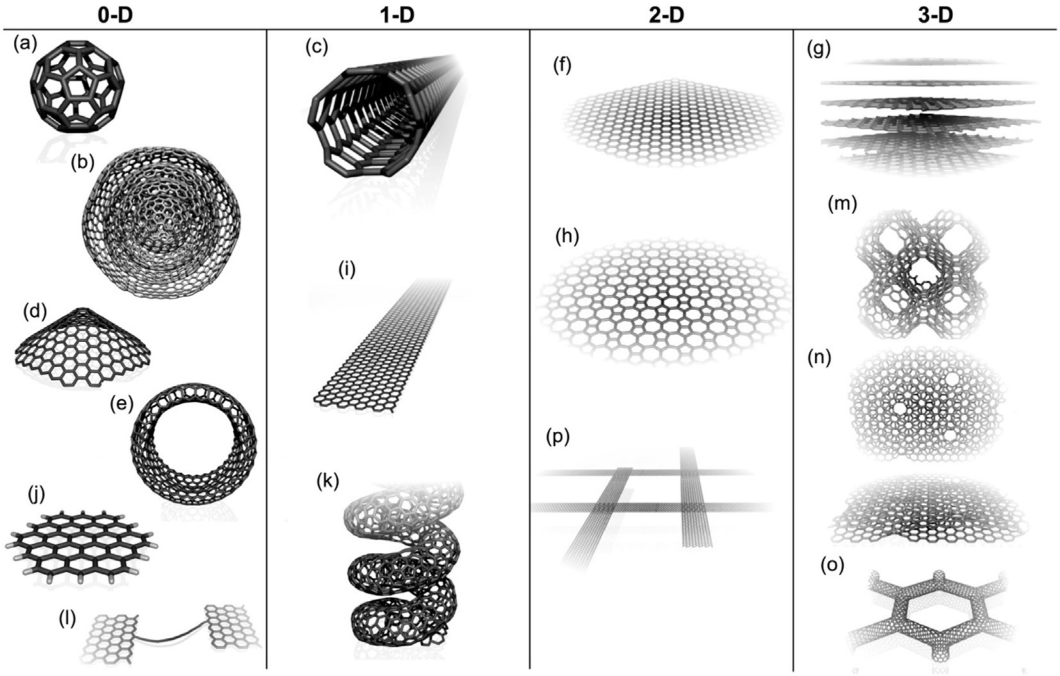

**Fig. 1.** Molecular models showing different types of carbon nanomaterials categorized by their dimensionality. It includes fullerenes, nanotubes, nanoribbons, graphene, nanotube networks, etc. that could be used as building blocks (units) to synthesize real 3D carbon materials with controlled structures and properties. Image from Terrones et al. [26].

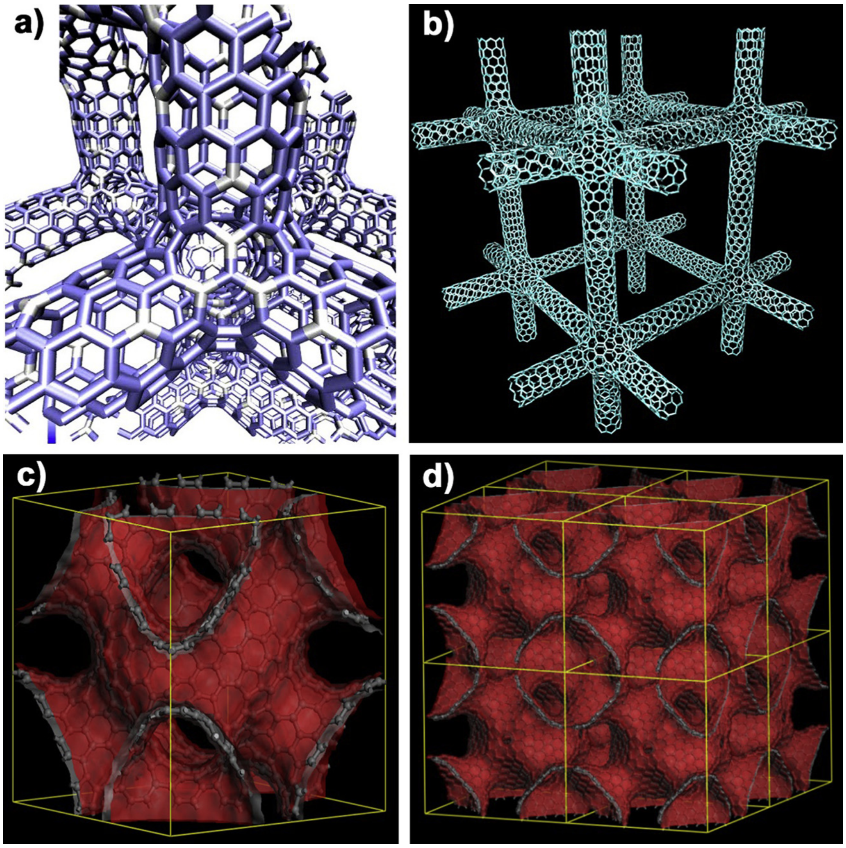

**Fig. 2.** Molecular models of different carbon nanotube and graphene 3D networks containing hexagonal, heptagonal, pentagonal and octagonal carbon rings: (a) carbon nanotube 3D covalent network following a tetragonal (or diamond-like) array; (b) a cubic carbon nanotube covalent 3D network; (c) and (d) periodic negatively curved graphene 3D structure (or foams) generated by covalently interconnecting graphene fragments with non-hexagonal rings (heptagons, pentagons, or octagons; models courtesy of J.M. Romo-Herrera and H. Terrones). (A color version of this figure can be viewed online)

developing the ability to scalably build well-ordered three-dimensional (3D) bulk materials using these nanoscale building blocks of carbon, using systematic and efficient approaches [11–19]. The implications of this are tremendous: 1) no such defined material at bulk state has been reported even though many heterostructures have been observed at the micro scale [7,12]; 2) it may be equally important for the truly scalable/bulk applications even at the bulk state of these structures, particularly for CNT and graphene, since stacking/aggregation of CNT and graphene has been hampering their bulk applications [13,16–19]; 3) some new and unprecedented properties or phenomenon, otherwise not achievable for carbon solids today, may be produced or observed with these heterostructure based materials [20–25]. The challenge would be to create such engineered 3D nanostructured carbon materials with controlled (and repeatable) structure units at bulk state.

There have been several theoretical predictions for such 3D carbon solids (e.g. Schwartzites, graphene networks, nanotube networks; see Fig. 2), but experimental results are still very scarce. The interfaces between the carbon nanoscale building blocks such as nanotubes [27–29] and graphene [30,31] need to be constructed via strong covalent bonding so that the resulting 3D structures are robust and stable. If such structures could indeed be designed and synthesized, it would lead to transformative 3D carbon materials [32–40], that will hugely impact technologies where carbon materials had been used traditionally but also in other areas of applications where the new nanocarbons hold so much promise [41].

More recently, researchers have been able to generate nanotube foams by interconnecting carbon nanotubes, graphene (or graphene oxide) sheets, graphene-nanotube systems and found that these materials are extremely light with densities of 1–50 mg/cm$^3$, and exhibit unique oil adsorption properties (able to soak up oil up to 1000 times its weight), mechanical properties (cork-like behavior with zero Poisson ratios) [42], catalytic properties, thermal properties, electromagnetic properties, etc. [43] 3D chemically bonded bulk graphene material (Fig. 3) has also been made recently with extremely high surface area and conductivity and this material has shown great performance in the energy storage application [41,44].

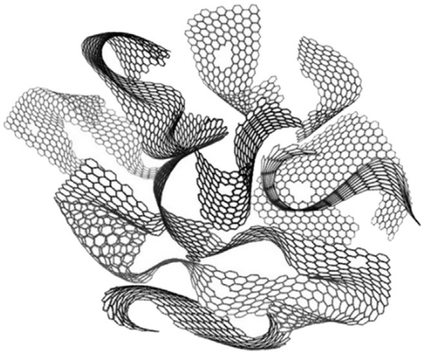

**Fig. 3.** Alternative 3D model depicting the structure of porous graphene-based material, in which the units consist of twisted sp$^2$ hybridized carbon layers (graphene domains) with sizes ranging from 4 to 6 nm (reprinted by permission from Refs. [44], copyright 2013, Nature Publishing Group).

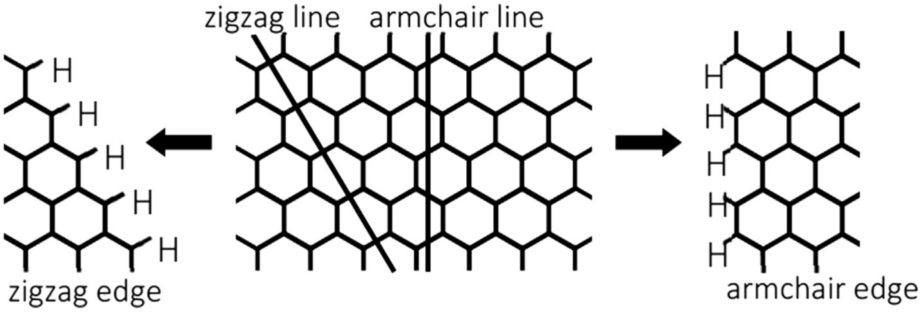

**Fig. 4.** Edge geometry; zigzag and armchair edges.

In addition to chemical vapor deposition (CVD) and hydro-solvo/thermal processes, alternative innovative growth techniques of these hypothetical 3D solids should now be a focus for carbon researchers. Recently, it has been demonstrated that graphene nanoribbons with specific diameters and nanotubes with desired helicity could be synthesized by careful polymerization of aromatic molecules [45–50]. Is it possible to follow similar approaches using negatively curved aromatic molecules such as seven-circulene and conranulene? Can we use $C_{60}$ crystals as a template for synthesizing some of these novel 3-D structures? Can

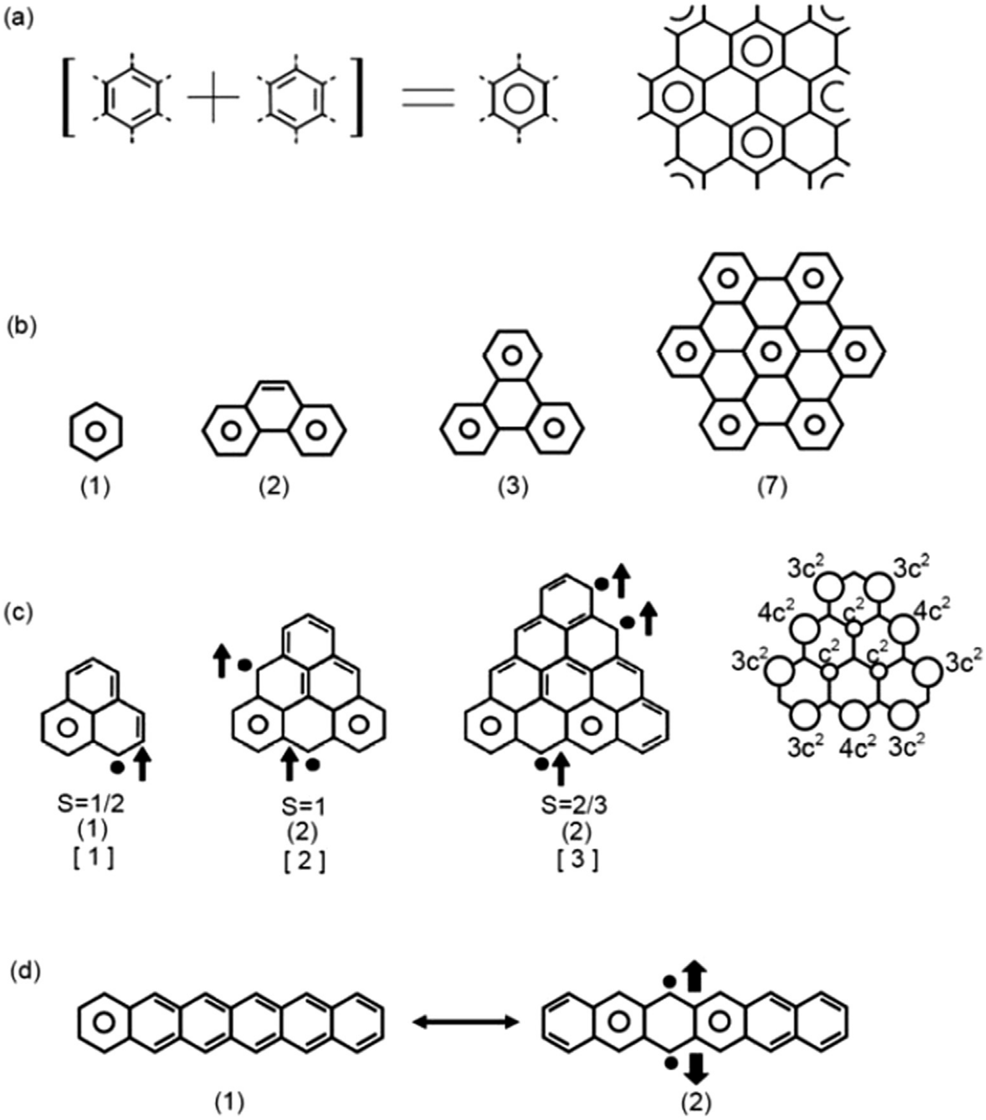

**Fig. 5.** Clar's aromatic sextet rule and two types of graphene nanostructures (polycyclic aromatic molecules) having armchair and zigzag edges. (a) Aromatic sextet (benzene ring in the resonance state) and Clar's representation of infinite graphene. (b) Armchair edged graphene nanostructures. Zigzag edged graphene nanostructures; triangular (c) and linear (d) systems. In (c) and (d), nonbonding edge states having unpaired electron (dot) with a spin (arrow) are present. The spatial distribution of the local density of states in the edge state is shown in the right of (c).

high pressures be used to produce such novel 3D solids? [51] Many questions are still open and various challenges are on the way, but someday periodic and covalently bonded 3D $sp^2$ hybridized materials will be successfully produced.

## 3. From aromatic molecules to infinite graphene - bridging chemistry and physics

Most of the materials that have interested carbon science researchers to date are built with the benzene ring, which consists of an $sp^2$-bonded hexagon, as the primary building block. Fusing an infinite number of benzene rings in two-dimensional manner gives graphene. Stacking graphene sheets gives graphite. A carbon nanotube is made by rolling up a semi-infinite graphene sheet to a hollow cylinder, while adding pentagon rings into a graphene nanofragment in building a sphere brings about a fullerene (Fig. 1). By cutting a graphene sheet into nanofragments, nanographenes such as graphene nanoribbons are created. Here a large variety of nanographenes are obtained depending on their sizes and geometrical shape, and importantly nanographenes are changed into polycyclic aromatic hydrocarbon molecules such as anthracene and naphthalene, and finally benzene when the size decreases to the molecular dimension. Accordingly, the properties of the benzene-based $sp^2$ carbon materials can be understood in terms of aromatic rule in chemistry, as carbon researchers pointed out in the early stage of research history [52,53]. In the meantime, the properties of graphite and graphene have been understood prevalently on the basis of band theory in physics after the work by P. R. Wallace [54]. Here the electronic structure of graphene is described effectively in terms of two dimensional massless Dirac fermion, having a feature of zero-gap semiconductor, and that of graphite is given as semi-metal [55]. The reason why carbon researchers have employed the band theory traditionally in understanding the properties of the carbon materials is that the materials were enough large to effectively apply the band theory. However, recently, graphene nanostructures have been one of the central issues in carbon science, for which the band theory cannot allow us necessarily to grasp the gist of a matter [56–58]. The problem here consists in the smallness in size and the edge effect due to the presence of open edges. Actually, the electronic structures depend not only on the size but also edge geometries (zigzag and armchair edges (Figs. 4 and 5)). Moreover, most importantly, the edge carbon atoms are bonded to foreign functional groups such as −H, −C=O, −COOH, −F. Depending on the size, edge geometries, and edge chemistry details, we have a huge variety of properties and functionalities (electronic, chemical, magnetic, optical, etc.) in graphene nanostructures [58] (Fig. 6). Consequently, the physics tool is not powerful enough, and instead the chemistry aspect becomes

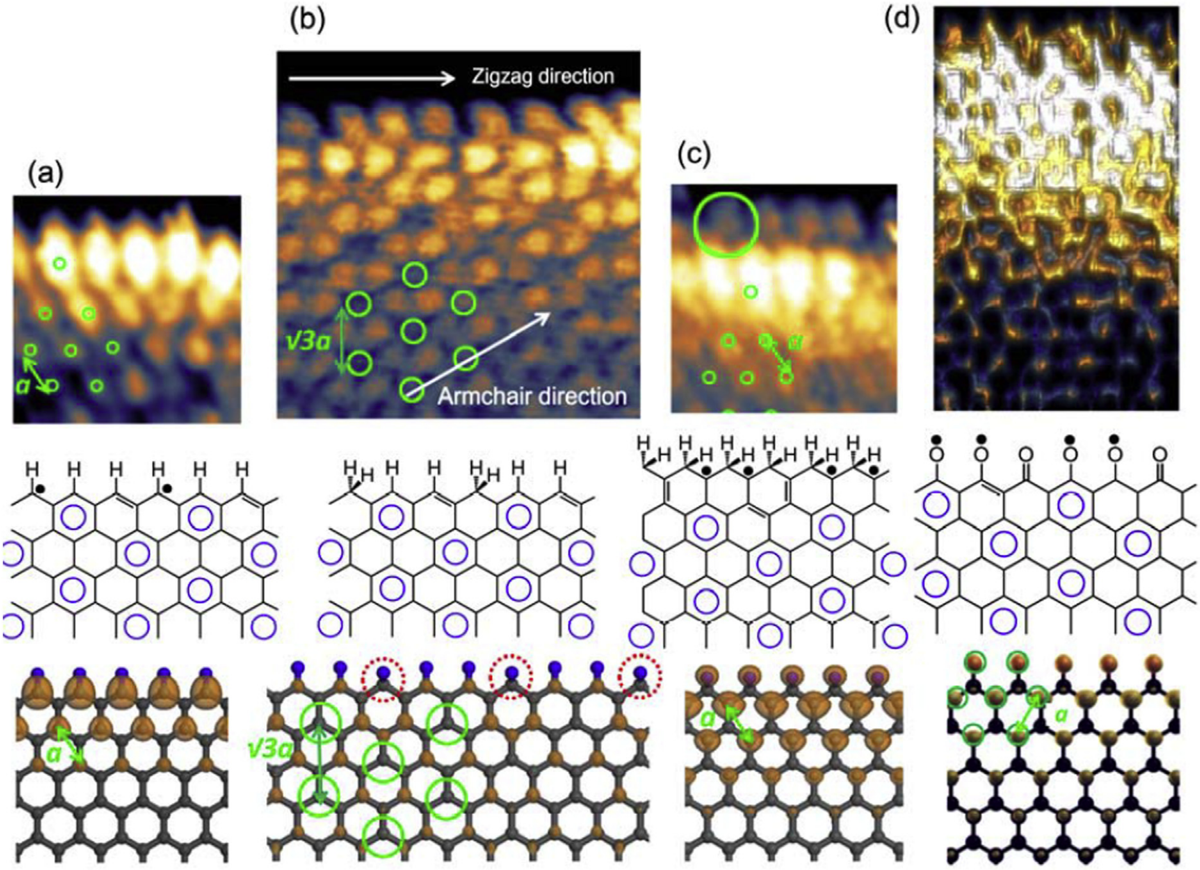

Fig. 6. A variety of zigzag edges depending on how edge carbon atoms are bonded to foreign functional groups, shown with STM images (upper), Clar's representations (middle) and local density of states (LDOS) calculated by DFT (lower). (a) mono-hydrogenated, (b) a combination of two mono-hydrogenated and one di-hydrogenated, (c) di-hydrogenated, and carbonylated zigzag edges. The dot in the Clar's representation denotes an unpaired electron of the edge state. LDOS of the edge state shown in the DFT results is localized in the zigzag edge in (a), no edge state is present in (b), LDOS is extended to H2 due to hyperconjugation in (c), and LDOS is populated to the O atoms in carbonyl due to charge transfer in (d). (A color version of this figure can be viewed online)

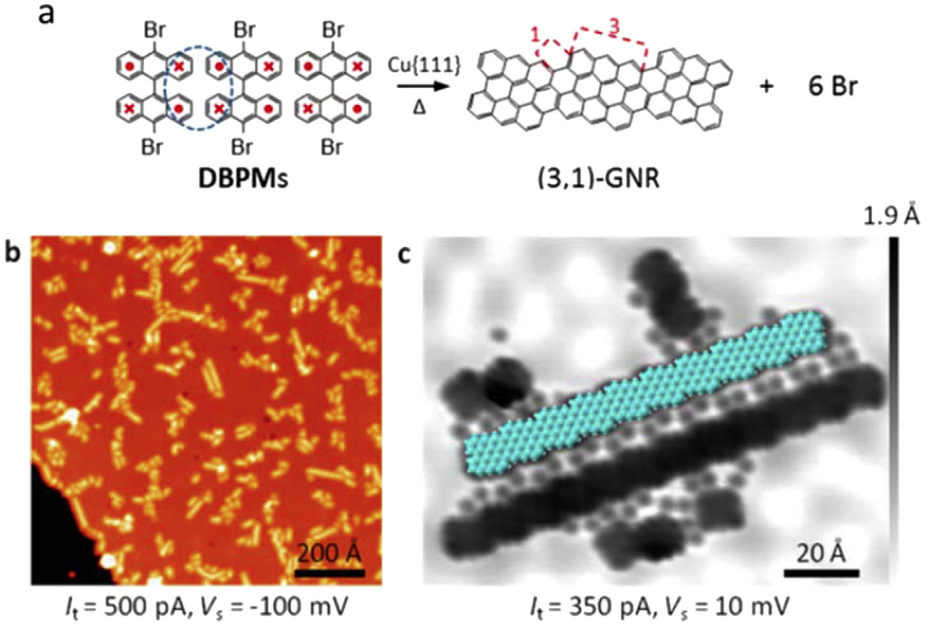

**Fig. 7.** Bottom-up synthesis of atomically precise chiral graphene nanoribbon on Cu(111) substrate. (a) Heat-induced polymerization of 10,10'-dibromo-9,9'-bianthryl precursor monomers (DBPM) under the catalyst of Cu(111) gives [3,1] graphene nanoribbons. (b) STM image of [3,1] graphene nanoribbons. (c) STM image of a graphene nanoribbon. A space-filling model is superimposed over a 10-monomer-long graphene nanoribbon. The circular features in (c) were determined to be Br atoms. Reprinted with permission from Ref. [46]. Copyright 2014 American Chemical Society. (A color version of this figure can be viewed online)

important, which is more intuitive in understanding their properties and predictable for investigating functionalities. In addition, bottom-up synthesis of graphene nanostructures, such as polymerization of monomer molecules [45–48], can give atomically precise nanostructure products (Fig. 7), which are the requisite for future molecular electronics device applications, in contrast to top-down techniques, such as lithography and unzipping of carbon nanotubes [59–61]. Graphene nanostructures are currently considered to be not only an important target in basic science due to their unconventional properties, but also important and future promising materials for applications to electronic/spintronic devices [62–65], batteries, fuel cells, catalysts [66,67], and so on. The combination of top-down and bottom-up approaches, in the former and the latter of which physics and chemistry tools are utilized, in working with graphene nanostructures allows us to step forward to interdisciplinary carbon science and technology.

## 4. High-purity single-walled carbon nanotubes: growth, sorting, and applications

The single walled carbon nanotube (SWCNT) is a carbon allotrope that has a unique 1D tubule structure formed by wrapping a single graphene sheet. The twist angle of the graphene sheet and the diameter of tube defines the SWCNT's chirality, which controls its electronic, optical, thermal, mechanical and magnetic properties [68]. Since the first report of SWCNT synthesis in 1993 [69,70], SWCNTs have always been produced as a mixture of different chiralities, and thus obtaining high-purity SWCNTs has been a key hurdle for realizing their wide potential applications. In the last three years, research efforts from different fronts have reached a point where high-purity SWCNTs are on the horizon (Fig. 8). In 2014, two different approaches were reported to grow a single type of SWCNT with high-purity [49,50]. One approach attempts to achieve nanotube structure control by controlling metal catalyst structure [49,71], while the other tries to amplify nanotubes from carbon seeds with defined structures [50,72,73]. Selective growth of high-density semiconducting SWCNT arrays on flat surfaces has also made significant processes [74–80]. New theoretical studies using the nanotube/catalyst interface thermodynamics and the kinetic growth theories have widened the understanding of chirality selectivity towards near-armchair tubes [81] and the slow growth rate of zigzag tubes [82]. In 2013, a novel method based on aqueous-two polymer phase separation has emerged as an easily accessible and versatile approach for sorting nanotubes [83–85], which is promising for low-cost scalable production of high-purity SWCNTs. Gel chromatograph based separation methods have also yielded high-purity single chirality optical isomers [86–88]. Recent studies in miniaturized electronic circuits [89–92], solar cells [93,94], biological imaging and medicinal therapy [95,96] also consistently highlight that the performance of SWCNTs in such applications depends on their chiral purity (Fig. 8).

In our view, the following research areas will be of great importance for driving the SWCNT research field forward. First, new catalysts/seeds and growth processes are needed to selectively synthesize SWCNTs of different chiralities. It is essential not only to achieve selectivity towards specific chiralities, but also to increase SWCNT yield. Sufficient quantity of high-purity SWCNTs is required for further sorting and applications, which still cannot be successfully achieved by existing methods [49,50,71–73,97]. Second, the purity of SWCNTs has to be significantly increased using more efficient and scalable sorting methods [98]. For example, semiconducting purity of parts-per-billion (ppb) level may be necessary for digital logic technology, which is not yet attainable [91]. Third, faster and more accurate characterization techniques are necessary to determine the abundance of SWCNTs with different chiralities, as well as to evaluate SWCNT semiconducting purity at ppb level. All current characterization techniques, such as transition electron microscope, diffraction, photoluminance, absorption and Raman spectroscopy, need improvement in order to meet these goals. Fourth, novel assembly techniques are needed to integrate structure-controlled (chirality, length and alignment) SWCNTs into various functional systems, for example 2D thin films or 3D

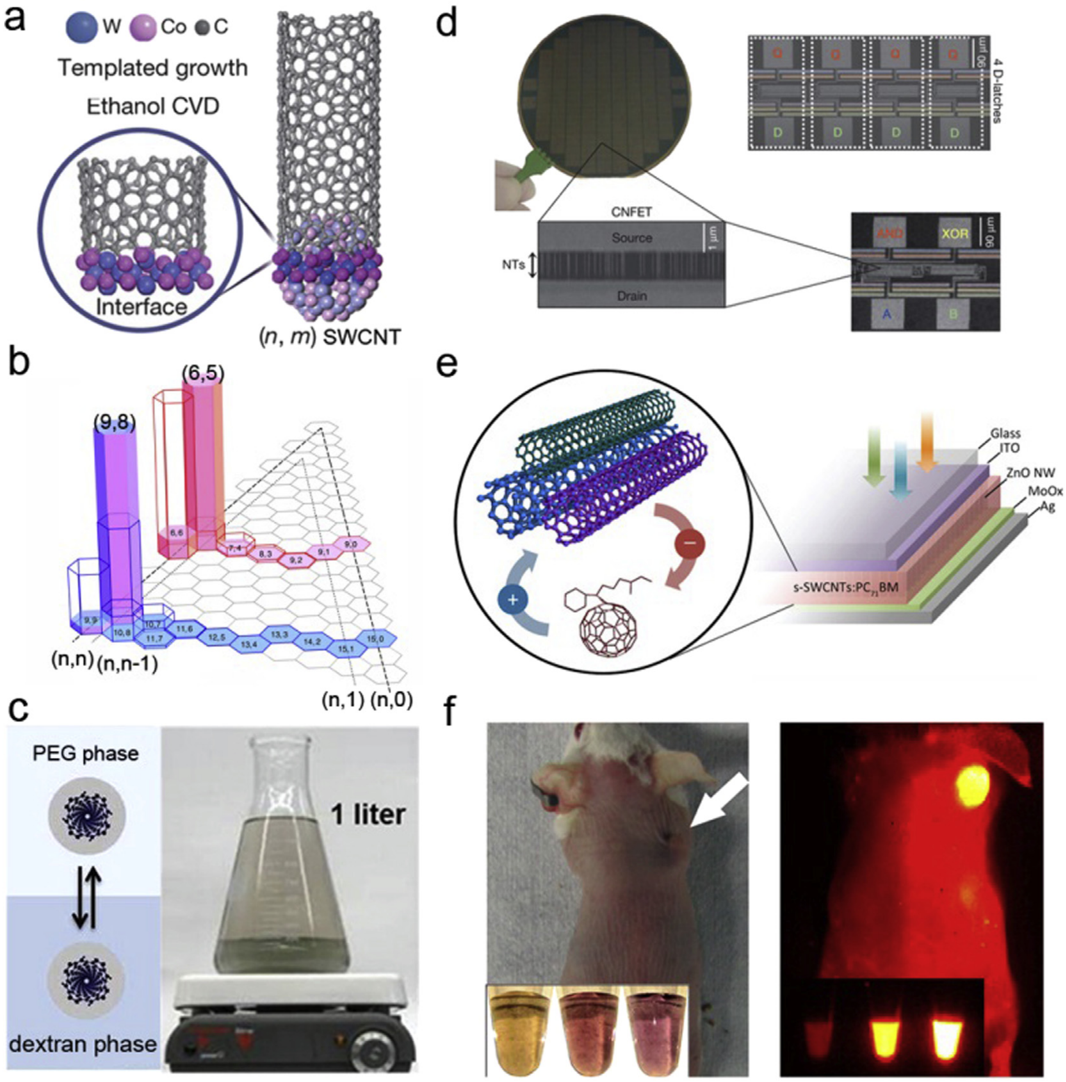

**Fig. 8.** Examples of recent progress from different fronts of SWCNT research. (a) Selective growth of (16,2) nanotubes from Co–W catalyst, reprinted by permission from Macmillan Publishers Ltd: Nature [49], copyright 2014. (b) Theoretical calculation predicts the (n,m) distribution of nanotubes at 0.8 and 1.2 nm, reprinted by permission from Macmillan Publishers Ltd: Nature Communications [81], copyright 2014. (c) Scalable sorting of SWCNTs using polyethylene glycol (PEG) and dextran two phase separation. Reprinted with permission from Refs. [83], copyright 2013 American Chemical Society. (d) Scanning electron microscope images of the first carbon nanotube computer, reprinted by permission from Macmillan Publishers Ltd: Nature [90], copyright 2013. (e) Polychiral semiconducting nanotube-fullerene solar cells. Reprinted with permission from Refs. [94], copyright 2014 American Chemical Society. (f) Sorted (6,5) nanotubes for simultaneous tumor imaging and photothermal therapy. Reprinted with permission from Refs. [95], copyright 2013 American Chemical Society. (A color version of this figure can be viewed online)

composites for transistors, solar cells and sensors. Hybrid materials comprised of SWCNTs and other components, such as fullerene, graphene-based materials, and other nanoparticles, may provide innovative solutions for some applications (see Fig. 1 and also Section 1). Fifth, high density aligned semiconducting SWCNT arrays are desired for transistor applications [89]. This challenge is currently being addressed by either assembling sorted high-purity SWCNTs [99–104] or direct selective growth of SWCNTs [74–80]. Continuous efforts are still needed to achieve the desired targets [89]. Sixth, there was certainly hype in the world of SWCNT research over the last two decades [105]. Therefore, it is the time now to demonstrate the applicability of high-purity SWCNTs in electronics, energy, environmental and medical industries [106]. Last but not least, more theoretical studies in understanding SWCNT growth and their chirality-dependent properties will help refine the SWCNT research targets. CARBON publishes many recent advances in SWCNT research, which range from synthesis [107,108], sorting [109,110], characterization [111], assembly [112], applications [113], to theoretical calculation [114,115]. We are hoping to publish more exciting and cutting-edge works in the coming year.

## 5. Biological behavior and safety of carbon nanomaterials – ongoing research needs

Carbon nanotubes, first observed in the decades of the 1950's and 60's, and 70's [2,116] and studied at the atomic level in 1991 by Sumio Iijima [3], have been at the forefront in the nanotechnology movement. Only a few years after Iijima's report, concerns were raised about possible human health risks, and carbon nanotube toxicology was the subject of a special issue in *Carbon* in 2006 [117]. Indeed, some multi-walled carbon nanotubes have geometric similarity to some types of asbestos fibres, and in 2008 their carcinogenic potential in mouse models was reported [118,119]. Concerns about toxicity quickly spread to all types of carbon nanotubes, and the issue came to the attention of the media and of

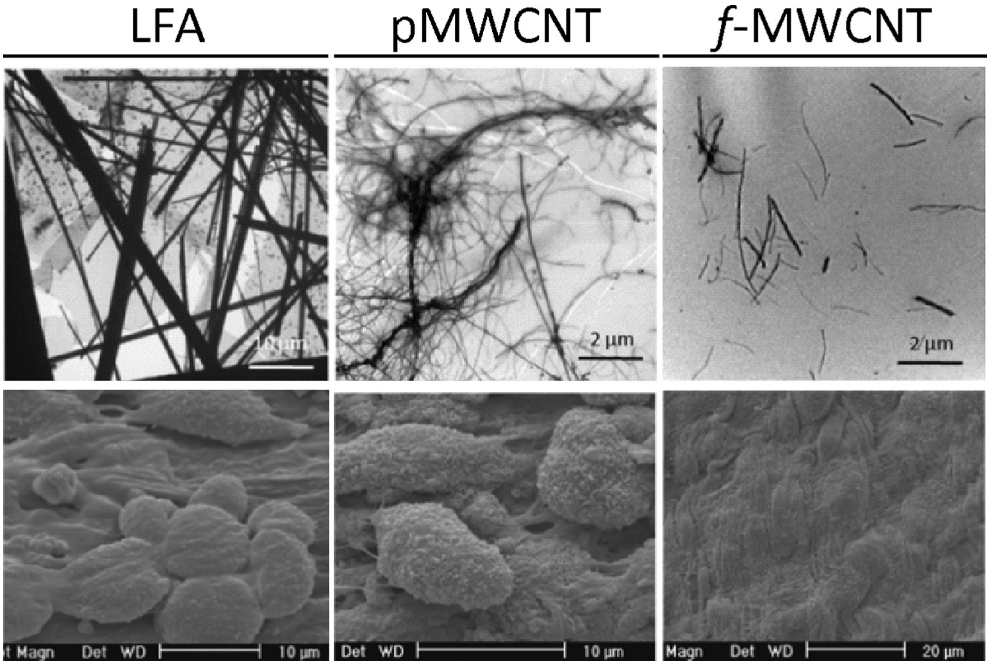

**Fig. 9.** Transmission electron microscopy images of the different carbon nanotubes: (Top line) LFA, long fibre amosite (asbestos fibres); pMWCNT, long pristine nanotubes; *f*-MWCNT, functionalized nanotubes. (Bottom line) Diaphragms of mice sacrificed after 7 days: SEM images of the diaphragm surface showing the presence of granulomatous inflammation with LFA, pMWCNT, but not with *f*-MWCNT. Adapted with permission from Ref. [121]. Copyright 2013, Wiley-VCH Verlag GmbH & Co.

agencies responsible for assessing the occupational and environmental health risks of new chemical substances.

Recently, one particular type of commercially available multiwalled carbon nanotubes, identified as MWCNT-7, has been formally classified as “possibly carcinogenic to humans” by the International Agency for Research on Cancer (IARC).[1] Their report cites sufficient evidence from toxicological studies to certify this level of risk classification and is important information for guiding the introduction of such materials into the market in a responsible manner that avoids significant human exposures. This is an important finding, but should not be interpreted as evidence for human health risks for other types of CNTs. In fact, the IARC working group acknowledged that the other types of carbon nanotubes, besides MWCNT-7, cannot be classified at this time, as there is not sufficient evidence, particularly concerning chronic endpoints.[2] IARC's decision not to rule yet on other CNT types highlights the ongoing importance for researchers to identify the underlying physicochemical properties that govern the biological response to all 1D carbon forms. This wide variability in the 1D nanocarbon family was clear to materials scientists early on, and was a particular point made in *Carbon's* early editorial on the topic of health risks and the potential for safe material design and selection [117].

A variety of recent studies have been addressing the role of CNT type and surface formulation on the biological response. Special concerns have been raised about long, stiff CNTs relative to deformable or “tangled” CNTs, which are typically thinner [119]. Surface functionalization to render CNTs hydrophilic has been reported to reduce bundling and aggregation [120], and thereby also reduce the *effective* length of the aggregate structure and reduce pathogenicity/cancerogenicity [121] (see Fig. 9). Wang et al. have reported that the non-covalent coating of CNTs with a non-ionic amphiphilic polymer (Pluronic F108) reduced their profibrogenic effects *in vitro* and *in vivo* [122]. The literature on biomedical applications typically provides some data on toxicity [123] and in this field it is common to modify raw CNT characteristics by shortening and functionalization strategies to promote dispersion [120], and these treatments often lead to short, hydrophilic varieties that do not show pathogenicity at the doses applied [121]. There is also published evidence that N-doping can improve CNT biocompatibility [124–126].

Nanotube type also effects *exposure*. Nakanishi et al. have recently studied six different types of nanotubes in the context of occupational exposure and combined information on exposure with data on *in vivo* biological response to propose a hazard quotient [127]. This study showed significant differences between CNT types, with SWCNTs showing the lowest risk, and suggested that the workplace risks can be limited by minimizing the airborne concentration of micron-scale aggregates ($1\ \mu m < d < 4\ \mu m$), which contain most of the respirable mass.

These approaches underline the potential for using the tools of materials science and particle technology to manage and reduce the human health risks of carbon nanotubes and can likely be extended to other types of carbon nanomaterials [128]. In particular, graphene and its related 2D carbon forms [128] are now receiving significant interest from industry, the lessons we have learned from carbon nanotube research should be considered carefully and applied early [129,130]. In December 2014, the *Scientific Committee on Emerging and Newly Identified Health Risks* has placed graphene nanomaterials in the hazard category that recommends the urgent estimation of risks.[3] The proper assessment of the safety profile and the health impacts of a new material is a basic

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[1] http://www.psr.org/environment-and-health/environmental-health-policy-institute/responses/iarcs-review-carbon-nanotubes.html.

[2] http://www.psr.org/environment-and-health/environmental-health-policy-institute/responses/iarcs-review-carbon-nanotubes.html.

[3] http://ec.europa.eu/health/scientific_committees/emerging/docs/scenihr_s_002.pdf.

fundamental task that is needed to translate research into any type of commercial application. Based on the available results reported in the literature, some graphene materials can cause adverse biological responses [131], much work is needed to understand the behavior of the wide variety of 2D carbons of different thickness, lateral dimension, and surface chemistry. Some of the existing data on graphene materials appears to be in conflict [132], as was the case for the early data on carbon nanotubes, and only time and further research will give us a full picture of graphene's behavior in living systems.

In 2016 and beyond, we believe much more research is needed on the biological responses to the carbon nanomaterial family and the studies should carefully consider and document their physicochemical properties and how those properties determine bionano-interactions. To properly understand and manage the potential health impacts of carbon-based nanomaterials, we believe it will be necessary to: i) conduct comparative biological effects studies on well-defined material libraries with systematic variations in physicochemical properties; ii) to measure responses at different scales (cells, organs, and tissue); iii) to benchmark results across the literature to benefit from the lessons already learned in this field; and iv) to continue to establish, if required and as proposed for some nanotubes, constraints on formulation, handling, and use to manage exposure. A robust program of research, comparative analysis, and possible regulation will promote: i) safe manufacturing, development and use of nanomaterials, ii) the assessment of technological risk versus risk perception to harmonize technical and social visions; and iii) the elaboration of new forms of ethics for an easy societal acceptance of novel technologies based on nanomaterials.

At *Carbon*, we continue to welcome manuscripts on the biological response and biomedical applications of carbon nanomaterials. We are especially interested in studies that include an in-depth treatment of the material science aspects of the problem related to structure-activity relationships, molecular phenomena at the carbon-biological fluid interface, and safe design.

## 6. The importance of volumetric performance parameters in energy storage systems

As the global demand for high-end energy storage systems continues to rise, owing to the large-scale incorporation of mobile technologies in our society, there has been a significant expansion in research and development of energy storage technologies in academia and industries alike. The primary demands of next generation energy storage systems generally include higher energy densities (longer operational times on a single charge) [133–135], higher power densities (faster charging/discharging) [136,137], cycle life [138], cost [139,140] and safety [141–143].

Recently, as the target applications have been getting increasingly feature-intensive, the performance metrics of the energy storage systems required to support these new-age devices tend to become more vulnerable to misinterpretation. Further, as the need to identify a revolutionary breakthrough in the field of energy storage becomes increasingly important, it is necessary to guide researchers in the right direction in terms of analyzing new technologies for commercial viability. One of the foremost drawbacks in this regard has been in attaching greater significance to gravimetric energy density (Watt-hour/kilogram or Wh/kg) instead of the volumetric energy density (Watt-hour/liter or Wh/L). Gravimetric energy density is generally calculated by normalizing the total stored energy in the cell to the mass of the active electrode (or sometimes, the net mass of the active electrode and the counter electrode) and is very commonly used in comparing the performance of materials in batteries and capacitors. In fact this appears to now be the accepted norm in academic papers (almost universally accepted by authors and editors alike). However in our interactions with the battery industry, it has become evident to us that industry takes a very different view. From an industry perspective, gravimetric energy density does not effectively portray the true performance potential of the material. First, an electrochemical cell is comprised of various other components including a separator, electrolyte and packaging cases. The weight of the active material often accounts for as little as ~30% of the total weight of the cell [144], thereby lowering the true gravimetric energy density by a factor of 3–4. In other words, an electrode that delivers an energy density of 500 $Wh/kg_{electrode}$ (normalized by the weight of the active electrode material) will in fact deliver a total energy density of less than 200 $Wh/kg_{cell}$ (normalized by the total weight of the cell).

Second, a large majority of the class of new-age materials for energy storage incorporate nano-structures such as nano-wires [145,146], nano-pillars [147,148] and nano-scale materials such as graphene and carbon nanotubes (CNT). Such nanomaterials often have very low packing densities [149,150], typically significantly lesser than 1 $g/cm^3$. Packing density is defined as the total mass of the material occupying a given volume. Therefore, the packing density is inversely proportional to the porosity of the active material. However, as nano-scale materials increasingly rely on superior porosity for improved electrolyte wettability and ion transfer kinetics [151–153], the packing density of these materials drop significantly, often to values less than 0.1 $g/cm^3$. In contrast, the typical packing density of natural graphitic electrodes [154] is as high as 1.7 $g/cm^3$. Comparing the performance of porous nanomaterials such as graphene (or reduced graphene oxide) paper with an electrode packing density of ~0.1 $g/cm^3$ with that of natural graphite exhibiting a packing density of ~1.7 $g/cm^3$, the differences in the gravimetric and volumetric energy densities become distinctly clear. Graphite, with an energy density of ~100–200 W h/kg would provide a volumetric density of ~170–340 W h/L while graphene, with a typical energy density of 600–800 W h/kg would provide a volumetric density of only ~60–80 W h/L. Thus, a novel material that offers ultra-high gravimetric energy densities need not necessarily have significant benefit in terms of its volumetric density. This is depicted graphically in Fig. 10, which compares the performance of graphitic anodes in lithium-ion batteries with new emerging technologies such as graphene and CNT based electrodes. An overview of the industrial standard for commercial natural graphitic electrodes in lithium ion batteries is provided in Table 1.

The importance of volumetric energy density becomes significant when considering the various applications that incorporate lithium ion batteries. As consumer and wearable electronics such as smart watches, Fitbits and Google glass become slimmer and more compact, the total volume available for the battery packs powering these devices must be reduced significantly. For instance, the typical volumes of a smart phone battery (~65 $cm^3$, 6–8% of the total volume of the phone) with a rated capacity of ~2000 mAh would certainly be incompatible with the limited storage space available in wearable electronics. Consequently, wearable electronics, with a net available battery pack volume often as low as 10 $cm^3$, integrate batteries with lower capacities and therefore, commonly suffer from quick discharges that necessitate frequent charging cycles. In this respect, it becomes evident that it is not only critical to analyze the volumetric performance of next generation energy storage systems but to also devise strategies to improve the volumetric densities that could then enable better batteries for the increasingly popular wearable electronics market.

The role of improved volumetric energy densities becomes even more evident when considering the electric vehicles sector. In fact, both the gravimetric and volumetric energy densities dictate the

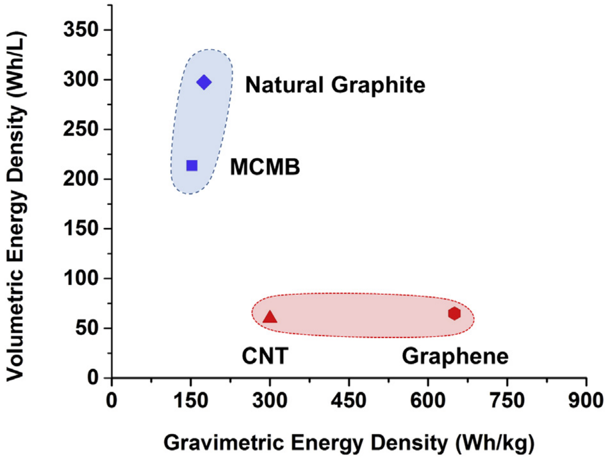

**Fig. 10.** A comparison [134,150,154,155] of the gravimetric and volumetric energy densities of commercial graphitic slurry anodes (such as natural graphite and Meso-Carbon MicroBeads- MCMB) and nano-scale carbon materials such as carbon nanotubes (CNT) and graphene paper anodes. It is evident from the figure that nano-porous carbon anodes exhibit poor packing density, thereby resulting in a significant trade-off in terms of their volumetric energy densities. In developing materials for next-generation, advanced energy storage systems it is therefore critical to analyze and improve both the gravimetric as well as the volumetric energy densities. (A color version of this figure can be viewed online)

**Table 1**
An overview of gravimetric and volumetric performance metrics of commercial graphitic anode in a half-cell configuration against lithium metal. A rate of C/10 indicates charge or discharge in 10 h.

| | Packing density (g/cm$^3$) | Achievable capacity (mAh/g, C/10) | Achievable capacity (mAh/L, C/10) | Gravimetric energy density (Wh/kg) | Volumetric energy density (Wh/L) |
|---|---|---|---|---|---|
| Natural graphite | 1.7 | 350 | 595 | 175 | 297.5 |

performance of the electric vehicle. The gravimetric energy density, if normalized by the total mass of the cells, conveys the net weight of the battery pack and hence governs the weight of the car in itself as well as the power requirements during use. A typical Tesla Model S uses ~7000 cylindrical 18650 cells, with a net weight of ~550 kg, to provide a mileage of ~300 miles. In terms of volumetric energy density, it is clear that the battery compartment in an electric vehicle, measuring an estimated 15–20 ft$^3$, will have to accommodate thousands of such cells in series and parallel configurations, thereby emphasizing the importance of improving the volumetric densities of energy storage systems.

Therefore, while next-generation energy storage systems show potential to offer superior capacities and power densities, it is still critical to assess their volumetric performance metrics as well, in order to have a detailed understanding of the commercial viability or to otherwise address short-comings in their path to commercialization. It is to be noted here that energy storage systems incorporated for stationary grid storage applications have less stringent limitations in terms of both gravimetric and volumetric densities due to factors such as the use of stationary battery systems and availability of large rooms for power storage and supply. For stationary grid storage, “Cost” seems to be the overriding performance metric that far outweighs considerations of gravimetric or volumetric energy density.

Researchers in the energy storage sector should therefore be encouraged to identify approaches to address the low packing densities and volumetric energy densities of porous nanomaterials such as graphene and CNTs, which in turn could potentially open up the path for commercial adoption of a whole new class of nanomaterials. For instance, one approach could be through the incorporation of active composite fillers such as silicon and tin oxide (lithium ion batteries) or ruthenium oxide (electrochemical capacitors) in the porous graphene matrix in order to reduce the concentration of the voids [156–160]. Another strategy could be through the use of templates during synthesis of the novel electrode materials and thereafter, through carefully controlling the porosity by means of chemical etching [161,162]. While the inclusion of porosity in electrodes is necessary to enhance electrolyte wettability and facilitate rapid ion transfer kinetics, excessive porosity leads to multiple drawbacks such as high first-cycle capacity loss in batteries and low packing densities. Another approach in addressing the volumetric densities of porous nanoscale electrodes could involve the use of compressive forces to control the thickness of the electrodes. In one such study, Ruoff and his group subjected microwave exfoliated graphene electrodes to compressive forces of 10 and 25 tons and observed a two-fold increase in the volumetric energy densities [163]. This approach is especially applicable to graphene-based electrodes synthesized via rapid reduction methods such as microwave, thermal shock and laser or photo-induced energy pulses. Such reduction approaches rely on rapid deoxygenation reactions to reduce the graphene oxide precursor material, which also leads to a significant expansion of the cross-sectional structure and hence, lower volumetric energy densities. An alternative approach in controlling the packing density of graphene electrodes was demonstrated by Kaner's group, whereby graphene oxide was gradually reduced (instead of rapid deoxygenation reactions) through repeated passes of low-intensity laser energy [164]. The group obtained impressive power densities of ~100 W/cm$^3$, ~2 orders of magnitude greater than its commercial counterparts, using laser-scribed graphene electrodes in electrochemical capacitors.

In conclusion, as new electrode materials entailing novel morphological characteristics and electrochemical properties continue to evolve in research labs across universities and industries, the specific strategy to improve the volumetric energy densities will need to be addressed and customized accordingly. In developing these next-generation materials for electrochemical energy storage systems, one should therefore consider analyzing both the gravimetric and the volumetric performance parameters in order to paint a complete picture of the feasibility of the technology. Such an approach, if followed consistently across universities and industries (and enforced by editors responsible for peer-reviewed publication), will undoubtedly help in the identification of breakthrough materials and accelerate the path to adoption of the technology in commercial energy storage systems.

## 7. Role of carbon textural properties in energy storage systems

Power sources have become more important and even irreplaceable in modern society. Can one now imagine life without mobile phones or computers? The streets are filled with a generation of young people listening to music, talking, and texting. Unfortunately, statistics show that the number of car accidents is increasing due to mobile phone use during driving. The demand for novel power sources is also driven by electric and hybrid vehicles, smart grids, electronics, and renewable energy based on non-constant sources such as wind and solar flux.

In energy storage/generation systems, carbon materials play an indispensable role [165–167]. A crucial question is: “Which type of carbon should be adapted for a specific application?”, but more important is to emphasize the relevant properties of any carbon material that determine performance. Quite often, authors try to use carbon materials because they are fashionable, but they may not be at all suited for a particular application. One of the best examples would be the application of carbon nanotubes or highly mesoporous carbons as anodes for Li-ion cells. Generally one material cannot serve all purposes. Presently graphene is very fashionable but this popularity causes it to be misapplied for many electrochemical applications [168–171]. Surely graphene can serve as a support of various active materials for capacitors and/or catalysts for fuel cells, but monolayer graphene cannot intercalate Li and thus cannot be an active material for Li-ion cells. Authors also often ignore the restacking of single layers, presence of residual oxygen in graphene and its detrimental effect on electrical parameters.

For all types of energy sources including lithium-ion batteries, supercapacitors, fuel cells or redox flow cells, any carbon material applied must have properties specific to that application. First of all, as a rule of thumb, high conductivity for all these energy applications is prerequisite. Carbon nanotubes, graphene, carbon black and onion-like carbons are perhaps the most suitable from this point of view [172,173]. Vertically aligned nanotubes often produce higher conductivity than entangled tube networks. The conducting properties of any carbon are determined by its structure, electron transport mechanism, purity, and hybridization with other components. For example, the conductivity of activated carbon is equal to 0.025 S/cm, whereas carbon black can reach 8 S/cm and carbon nanotubes more than 50 S/cm [172,173]. Interestingly, carbon nanotubes can carry the highest current density of any known materials, i.e. of the order of $10^9$ A/cm$^2$. However, in-plane *vs.* transverse direction measurements of conductivity under compression of various carbon materials [172], and in turn, electrodes, gives additional important information.

Apart from conductivity, the texture of carbon must be carefully considered. As already mentioned, mesoporous materials appear to be unsuitable for Li-ion battery electrodes [174–177]. The more mesopores in carbon, the higher the irreversible capacity [174–177]. Pores >2 nm allow penetrating of solvated lithium ions provoking formation of solid electrolyte interphase (SEI). Additionally, the mechanism of lithium storage in mesoporous carbon, proved by $^7$Li NMR [177], differs from typical intercalation taking place in graphite, where a desirable plateau is observed, whereas carbon nanotubes provide unacceptable hysteresis (i.e. the galvanostatic curve for charging and discharging forms a great loop). Apart from that, during subsequent cycles, a gradual loss of capacity is observed because of continuous SEI formation that is unacceptable for practical application [174–177]. While work on Li interactions of different forms of carbon may be scientifically interesting, high-impact papers should justify the choice of material system in terms of its potential benefit to industry and society.

In other applications, mesopores are useful and play a very beneficial role in carbon materials used as catalyst support in low temperature fuel cells, e.g. direct methanol fuel cells [178]. In this case, the diffusion of substrates to the interface and products backward to the bulk electrolyte is enhanced, in turn, improving the fuel cell performance. It is worth mentioning that mesoporous carbons, especially if nitrogenated, can serve as excellent catalysts for oxygen reduction [179].

Mesoporous carbon nanotube networks (single or multiwalled) have a limited application as supercapacitor material due to the lack of micropores. Capacitance values for pure, unfunctionalized CNTs are only moderate (20–40 F/g) [180,181]. It has been proved that they can serve as capacitor materials when grown as a forest and then pressed, to increase volumetric parameters. However, the high resiliency of nanotubes and graphene, because of exceptional mechanical properties, is extremely useful if they are applied as a

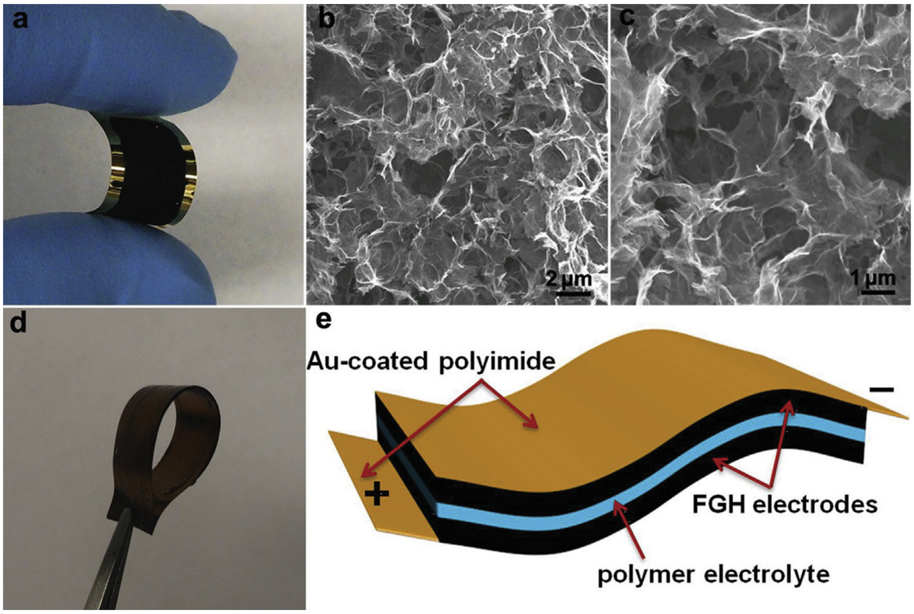

**Fig. 11.** a) Digital photograph of a flexible graphene hydrogel thin film electrode. b) Low- and c) high magnification SEM images of interior microstructures of the film. d) Digital photograph of a graphene-hydrogel-based flexible solid-state supercapacitor. e) A schematic diagram of the solid-state device with $H_2SO_4$ -PVA polymer gel as the electrolyte and separator. Reprinted with permission from Ref. [188]. Copyright 2013, Wiley-VCH Verlag GmbH & Co. (A color version of this figure can be viewed online)

support for pseudocapacitive materials such as transition metal oxides, conducting polymers or carbons rich in heteroatoms (nitrogen, oxygen, sulfur) [181–184]. Especially, if volumetric changes of the active material take place, e.g., during ion doping of conducting polymers, nanotubes allow significant prolongation of long-term cycling of electrodes without their detrimental breaking.

Much research shows that CNTs or graphene are promising composite components or building blocks for hybrid capacitor materials [181–184]. Pseudocapacitance properties from heteroatoms built into mesoporous carbon networks can be efficiently used [165–169,179–187]. Even if nanotubes or graphene alone supply very moderate capacitance values, they seem to be irreplaceable for flexible capacitors. This trend in various micro-supercapacitors and stretchable devices is growing rapidly [188–194], especially for such applications as electronics or wearable power sources [195,196]. For example, functionalized graphene hydrogel (FGH) films applied as electrodes for flexible solid-state supercapacitors are shown in Fig. 11.

Another interesting example of graphene for micro-supercapacitor application is illustrated in Fig. 12, where laser scribing was used for device fabrication [179].

A novel concept of wearable power source in the form of a smart garment (Fig. 13) has been proposed by Gogotsi and coworkers [195,196] for various military and civilian applications.

While nanocarbons receive the most attention in scientific journals, industry currently uses activated carbons for supercapacitors and graphite for Li-ion batteries as they offer excellent performance combined with cost effectiveness. Typically, most activated carbons are obtained from biomass precursors (e.g. coconut shells) and coal or polymers. Obviously, the activation process involves more or less aggressive substances (steam, carbon dioxide or KOH).

Biomass materials contain carbon as a predominant element, hence, they are perfect precursors for activated carbons but quite often authors ignore the total precursor composition. It has been shown that, apart from carbon, some precursors may contain an element playing the role of activator. Hence, simultaneous carbonization as well as activation takes place during the thermal treatment. Very attractive biomass materials containing suitable microelements are algaes [197,198] or tobacco [199]. Some types of these plants contain alkali metals (Na, K, Li), which are responsible for self-activation. In this case, the final product already has a developed surface area, quite often with a narrow pore size distribution, hence, the activation process can be omitted, which gives a great profit in total activated carbon manufacturing.

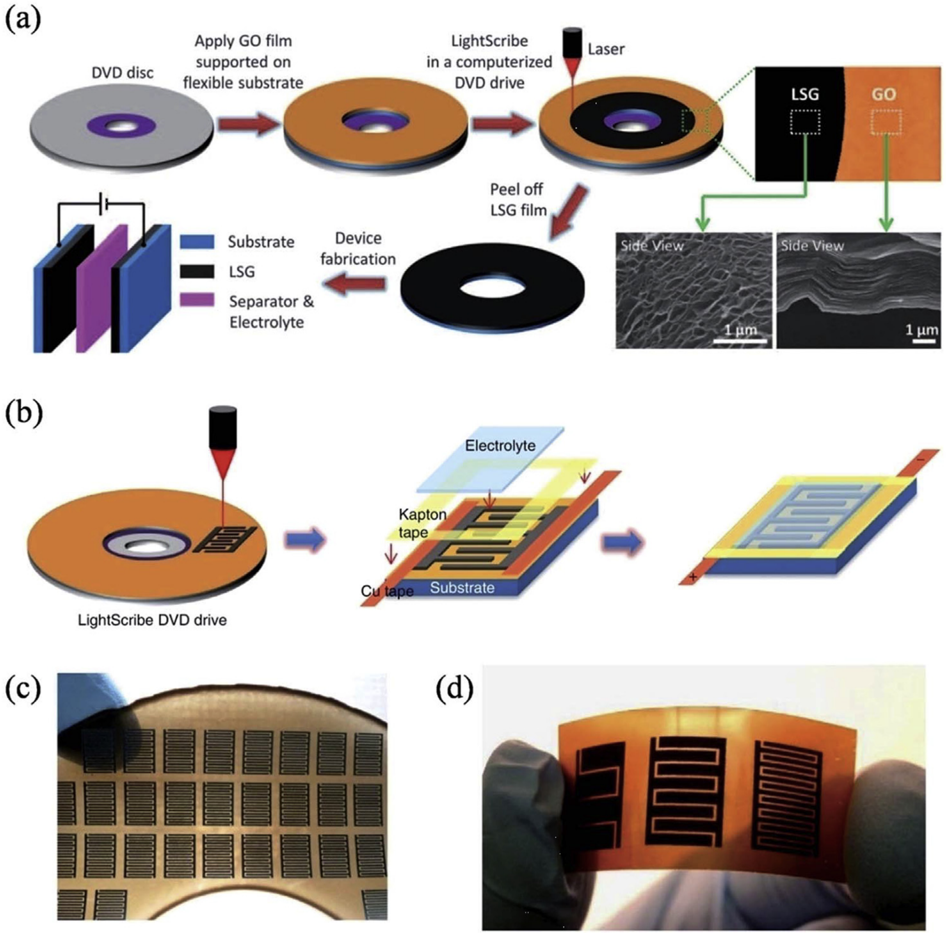

**Fig. 12.** (a) Schematic illustration of the fabrication of laser-scribed graphene-based electrochemical capacitors (reprinted by permission from Refs. [179], copyright 2015, Royal Society of Chemistry and [164], copyright 2012, The American Association for the Advancement of Science). (b) Schematic diagram showing the fabrication process for laser-scribed graphene micro-supercapacitors (reprinted by permission from Refs. [179], copyright 2015, Royal Society of Chemistry). (c) Demonstration of more than 100 micro-devices produced on a single run (reprinted by permission from Refs. [179], copyright 2015, Royal Society of Chemistry). (d) A digital photograph of the laser-scribed micro-devices with 4, 8, and 16 interdigitated electrodes (reprinted by permission from Refs. [179], copyright 2015, Royal Society of Chemistry and [192], copyright 2013, Nature Publishing Group). (A color version of this figure can be viewed online)

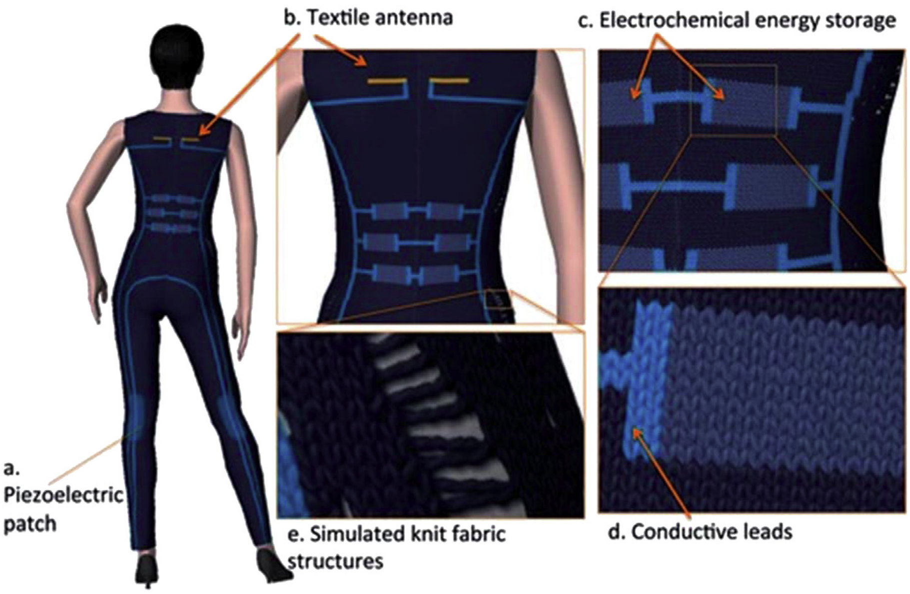

**Fig. 13.** Design concept of a porous textile supercapacitor integrated into a smart garment, demonstrating porous carbon impregnation from the weave, to the yarn, to the fibres. Reprinted with permission from Ref. [195]. Copyright 2014, Royal Society of Chemistry. (A color version of this figure can be viewed online)

In addition to the carbon material, the electrolyte is an essential second component in energy storage devices, and creates the electrode/electrolyte interface. As the expression goes, 'it takes two to tango', and these two components should match each other. Especially, in electrochemical capacitors, the textural properties of carbon, namely porosity, must be adapted to the electrolytic solution (organic, aqueous, ionic liquids or mixtures). The ion size, asymmetry, and solvation state cannot be neglected. Some novel supercapacitor concepts for capacitance enhancement and operating voltage extension have been proposed through special selection of aqueous electrolytes, e.g., neutral sulfates [200–202] and/or redox active species, e.g., iodides, bromides, hydroquinones etc. [203–207]. Additionally, it was successfully proposed to use two various electrolytes as well as two various carbon materials for positive and negative electrodes with a significant energy increase [186,187,206]. For that a suitable micro/meso ratio of porous carbons is indispensable. Obviously, a safe capacitor voltage is vital to ensure good efficiency and long cyclability.

In the realistic approach to power sources, one should not ignore cost of materials and their environmental assessment [208]. Generally, the less expensive materials, the better chance for market application. However, not only cost per 1Wh or 1W should be taken into account but also long term cyclability, i.e., cost per cycle. For this aspect, electrochemical capacitors seem to be very competitive and/or complementary to batteries, they could find a wide range of power required applications.

## 8. Carbon fibres

In the sixties, the need for new types of composites combining light weight and high performance (mostly demanded for aeronautic and aerospace applications) led to the development of continuous, weavable carbon fibres [209–211]. The overall process principle is to start from an organic precursor, either liquid (yet viscous) or solid but able to soften, then to spin it (i.e., to force it to go through a 30–80 μm-large hole called a spinneret), then to stabilise the resulting filament using mild oxidizing conditions to introduce cross-linking so that it keeps its morphology (instead of decomposing or melting) during the subsequent carbonisation step during which the organic fibre is transformed into a 6–15 μm diameter carbon fibre with the desired properties. A chemically-modified natural cellulose precursor patented as Rayon® was used first in the USA (Barnebey-Cheney, National Carbon), and then a new family of carbon fibres was developed starting from a synthetic organic precursor called polyacrylonitrile (PAN) [212]. A few years later, heavy molecular weight by-products from the distillation of coal tar or petroleum called "pitches" were also successfully used as carbon fibre precursors [213]. Afterwards, decades of studies and improvements have resulted, in the nineties, in the current state of carbon fibre mechanical performance as shown in Fig. 14.

Observing Fig. 14 allows stating that there are roughly two paths, one corresponding to the high strength PAN-based carbon fibres (solid, black symbols, with tensile strength culminating at ~7 GPa, yet with relatively low tensile modulus, able to culminate at ~700 GPa to the detriment of strength), the other corresponding to the high modulus pitch-based carbon fibres (open and grey-colored symbols, with tensile modulus culminating at ~930 GPa, yet with tensile strength not higher than 3–4 GPa). It is a standard observation that, correspondingly, electrical and thermal conductivities are low for the former, whereas they are high for the latter (Fig. 15). It can also be stated that (*i*) carbon fibres currently exhibit the highest mechanical performance with respect to any other non-carbon material; (*ii*) no material exists, including carbon, which would be able to generate micrometre-sized fibres able to exhibit both ultimate strength and ultimate modulus.

The reasons for the performance discrimination between the PAN and the pitch routes are understood: the specific pitches used (mesophasic, or even better, anisotropic) are graphitisable precursors and contain graphenic entities which tend to self-assemble in liquid crystalline state and align further upon spinning stresses, allowing the graphite structure (and performance) to fully develop with increasing thermal treatment. On the other hand, the PAN exhibits a nitrogen-containing ladder molecular structure, which also aligns - yet not to the extent of anisotropic pitches - upon spinning stresses, later-on transformed into folded graphene sheets. The key difference of PAN with respect to cellulose and pitches is that the nitrogen atoms, when leaving the system upon

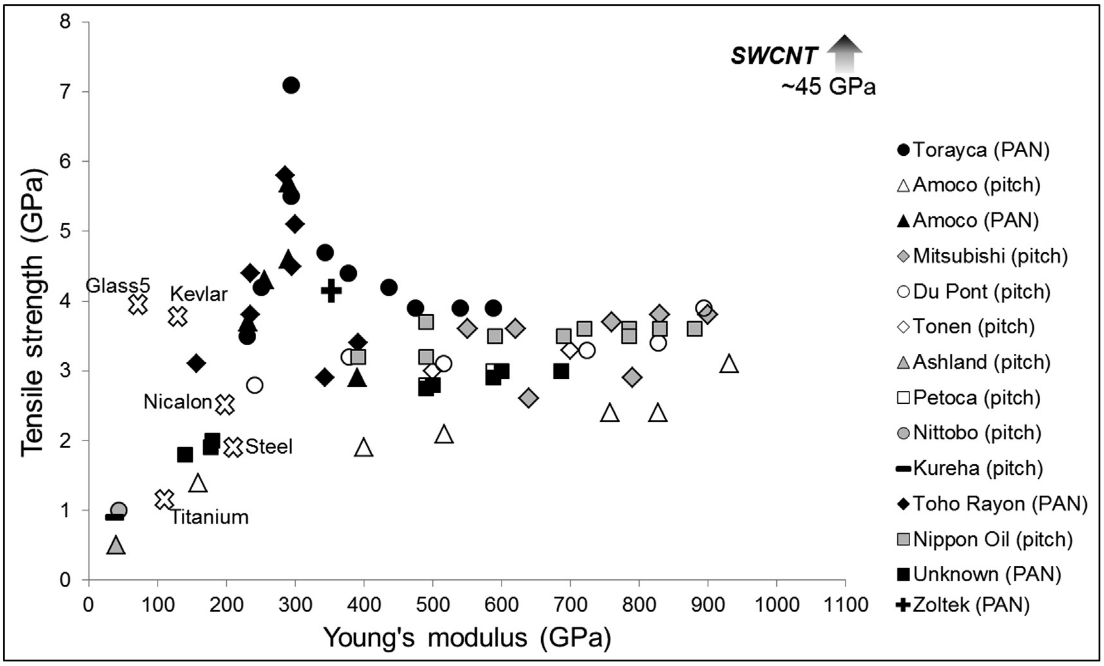

**Fig. 14.** Plot of the tensile strength versus the tensile (Young's) modulus for various fibrous materials. All solid, black symbols are PAN-based carbon fibres. All open or grey symbols are petroleum or coal-tar pitch-based carbon fibres, except for the open crosses, which are non-carbon based fibres (among the latter, "Nicalon" is a SiC-based ceramic fibre by Nippon Carbon). "SWCNT" corresponds to a single single-wall carbon nanotube. All carbon fibre data are from the manufacturers (modified and completed from Ref. [214]).

the thermal treatment, generate strong covalent bonds (the so-called "Watt mechanism" [215]) between the graphene sheets which prevent the easy gliding that otherwise affects pitch-based carbon fibres and graphite when subjected to tensile stresses. Those strong intersheet bonds are responsible for the high strength, but also for the low conductivities as they act as scattering centers and prevent the long-range development of the graphene sheets.

Hence, the two routes (PAN and pitch) are exclusive as they generate fibres with different, incompatible structural features. Based on this picture, any attempt to reach the "forbidden area" in Fig. 14 by following the PAN or pitch routes appears to be hopeless. As a matter of fact, no one has ever succeeded obtaining a carbon fibre combining both high tensile strength and high modulus (or high conductivities) so far. Correspondingly, the current efforts in the field mostly focus on addressing cost and environmental issues of the process instead. The main route currently followed for this is to look for cheaper and greener precursors, thereby aiming to reach new markets for which low or medium range performance carbon fibres are acceptable (frames and brakes for mass market automotive applications, "carbocrete" for construction). Indeed, more than half the cost of PAN-based carbon fibres comes from the precursor (PAN is a high-tech polymer, which is actually a copolymer whose detailed composition and synthesis protocols are typically proprietary) and its complex solvent-based processing. Consequently, synthetic or natural compounds such as polyolefins (e.g., polyethylene) and biopolymers (e.g., lignin and even cellulose, again) – both hopefully from recycling - are currently re-attempted as (co)precursors for their availability, and/or chemical simplicity and/or ability to be processed by the more cost-effective melt-spinning route [216–220], aiming to market prices below 5 US $/kg

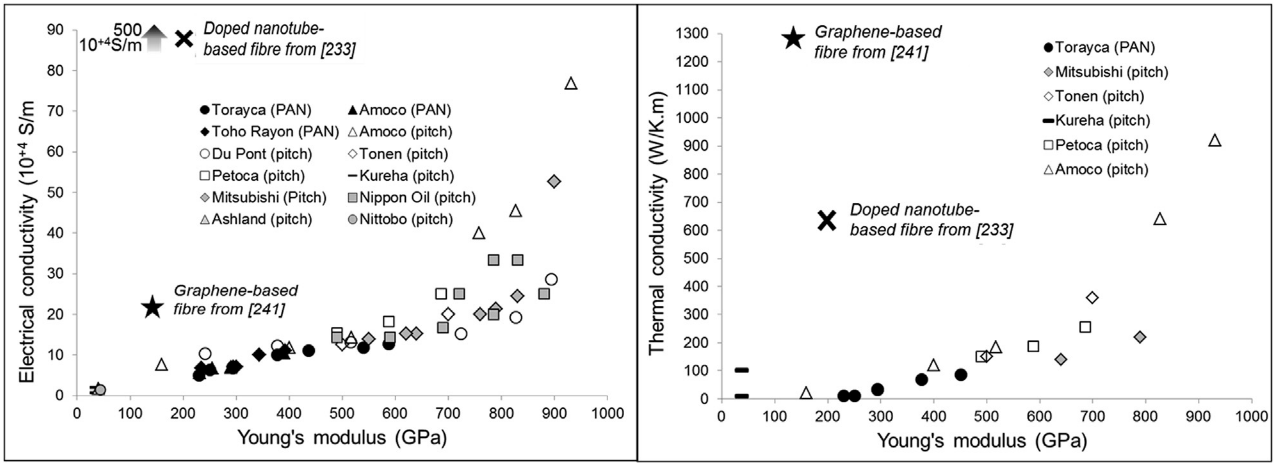

**Fig. 15.** Plots of the electrical conductivity (left) and the thermal conductivity (right) versus Young's modulus for a variety of regular carbon fibres, compared with a doped nanotube-based fibre and a graphene-based fibre from Refs. [233] and [241] respectively. All carbon fibre data are from the manufacturers.

(instead of the current 15–25 US $/kg for PAN-based fibres).

Finding alternate precursors for high modulus and high thermal and electrical conductivity carbon fibres becomes also compulsory, but is even more of an issue. Indeed, pitches are polyaromatic materials, hence are targeted as polluting and hazardous products for which a more and more severe regulation (see for instance the REACH norm in Europe) might forbid their use one day. This would result in a major industrial issue, as pitches are not only used as precursors for carbon fibres, but also are key components for carbon materials such as carbon/carbon composites (impregnating pitches) or graphite electrodes (binder pitches). Also, as they actually are by-products, it is a permanent challenge to obtain pitches with the right and constant characteristics, while the feedstock and industrial processes from which they originate are highly variable (closure of coal mines, strategy of petrochemical industries, geopolitical issues). Synthetic pitches have therefore been under development for many years (e.g., from naphthalene [221]), but have not yet succeeded in becoming economically or technically viable alternatives.

Finally, is there no hope for producing carbon fibres exhibiting the performance of both PAN-based (ultimate strength) and pitch-based (ultimate modulus) carbon fibres one day? There might be, thanks to carbon nanoforms. It is already well-known [222] that carbon nanotubes are able to combine extreme tensile strength (>40 GPa) and extreme Young's modulus (up to 1 TPa or more) (Fig. 14). Of course, those are values for a perfect, single SWCNT. Hence, based on early works dealing with reinforcing pitch [223], polymer [224], and PAN [225,226] with carbon nanotubes (CNTs) and more recently graphene-based materials [227] by adding them before the spinning step to increase the performance of the resulting carbon fibres, CNTs and graphene materials can now be used as components added to the new-precursors mentioned above [219,228–230]. Finally, more challenging but quite promising for obtaining carbon fibres with unprecedented performances are to tentatively make continuous, weavable carbon fibres solely from CNTs or graphene materials. Several routes using CNTs have been under study for about 15 years, including wet [231] or dry [232] processes, but the resulting CNT-based carbon fibres barely reach the mechanical performance of the current PAN-based and pitch-based fibres so far (in the range of 1 GPa for tensile strength, and 200 GPa for Young's modulus [233]). The main reason for this low performance is the lack of covalent bonds between nanotubes within the fibre, which can typically be fixed by promoting inter-tube interactions through an infiltration of a small amount of a specific polymer during spinning [234] or functionalization-promoted cross-linking between the tubes [235]. From the point of view of mechanical properties, however, CNT-based fibres have proven to exhibit ultimate behavior only regarding toughness, for which they can be even better than the former best ever material (spider silk) [236]. More recently, carbon fibres from graphene (or functionalised derivatives such as graphene oxide) have also been developed [237,238] using a solvent route or a dry scrolling technique [239]. Again, mechanical performance is still far below that of PAN- or pitch-based carbon fibres, with highest tensile strengths less than 1 GPa and Young's modulus below 150 GPa [240,241]. However, remarkable results are coming out. Electrical conductivities of graphene-based carbon fibres are now approaching – within a factor of ~4 – that of the best pitch-based fibres (~$2 \times 10^5$ S/m [240,241] as compared to ~$7.7 \times 10^5$ S/m for the K1100 by Amoco), while their thermal conductivity (1290 W/mK [241] even surpasses that of pitch-based fibres (920 W/mK for the K1100 fibre) (Fig. 15).

This is a remarkable result because the fact that high thermal and electrical conductivities do not come along with high Young's modulus is unprecedented in the world of regular (nanocarbon-free) carbon fibres (Fig. 15). This means that a novel inner structure has been created, different from that obtained from PAN or pitch, as a result of the original idea by Xin et al. [241] to mix both large and small graphene oxide flakes in the starting suspension. On the other hand, thanks to acid and/or iodine doping, the thermal conductivity of CNT-based fibres (~635 W/mK) can be very close to that of pitch-based fibres while their electrical conductivity (~$50 \times 10^5$ S/m) can overpass that of pitch-based fibres and reach that of metals [233]. Those two latter examples [233,241] give a clear demonstration that playing with carbon nanoforms and their derivatives (e.g., meta-nanotubes, such as functionalised or doped CNTs [242] and their graphene equivalents) could be the future of carbon fibres, regardless – so far - of the cost issue.

## 9. Graphynes as new carbon allotropes

Carbon is the element that plays the most fundamental role for life on earth. Because of its ability to form sp, $sp^2$ and $sp^3$ hybridized bonds, elemental carbon can exist in a diverse number of forms such as diamond, graphite, and carbyne. Just as Prof. Phil Walker pointed out in 1972, “the progress in the development of new carbon materials will continue to be recorded as a chapter in the over-all story of materials science.” [243] As described above, over the past two decades, many efforts have been devoted to exploring new carbon allotropes, and novel forms such as fullerene, carbon nanotube and graphene continued to be added to the family (Fig. 1). Different types of carbon allotropes can be constituted by altering the periodic building motif in networks consisting of the three forms of hybridized carbon atoms as shown in the tentative ternary carbon allotropy diagram (Fig. 16) [244].

Specifically, graphyne, which was firstly proposed by Baughman in 1987 [245], refers to a family of carbon allotropes composed of sp and $sp^2$ hybridized carbon atoms extending in a two-dimensional plane. Some structures are envisioned to have novel electronic band structure and are expected to be competitors for graphene [246]. Among various predicted structures, graphdiyne (GDY) is a certain framework containing hexagonal benzene rings connected by diacetylenic linkages in the plane.

Originally it was theoretical study that opened graphdiyne research. It is predicted that graphdiyne is the most stable carbon network containing diacetylenic linkages with a heat of formation of 18.3 kcal per g-atom C. Furthermore, electronic structure, carrier mobility and mechanical properties were also theoretically investigated. The calculation results also showed that graphdiyne is a good candidate for gas separation, Li ion battery, and $H_2$ storage because of its conjugated structure and pristine topological holes [247]. As for the experimental aspects Haley's group has done pioneering work on designing and synthesizing some large molecular segments of graphdiyne [248]. However, it was not until 2010 that graphdiyne was successfully fabricated on the surface of copper foil via an in situ Glaser coupling reaction [249]. The film with thickness of nearly 1 $\mu$m exhibited excellent semi-conducting properties. Since then, graphdiyne nanotubes and graphdiyne nanowires have been obtained [250]. Very recently, Z. F. Liu et al. reported a feasible synthetic route to graphdiyne nanowalls by employing a modified Glaser-Hay coupling reaction and confirmed the fine lattice structure of graphdiyne [251]. Achieving graphdiyne with controlled structures and distinct properties is still of great importance and a significant challenge.

After that, several follow-up studies on applications of graphdiyne have been reported. With more outstanding performance in rich electronic structure, charge separation and oxidation ability, $TiO_2$ (001)-graphdiyne nanocomposite showed excellent photocatalytic efficiency [252]. Besides, GDY-based electrodes exhibited high specific capacities, outstanding rate performances and long

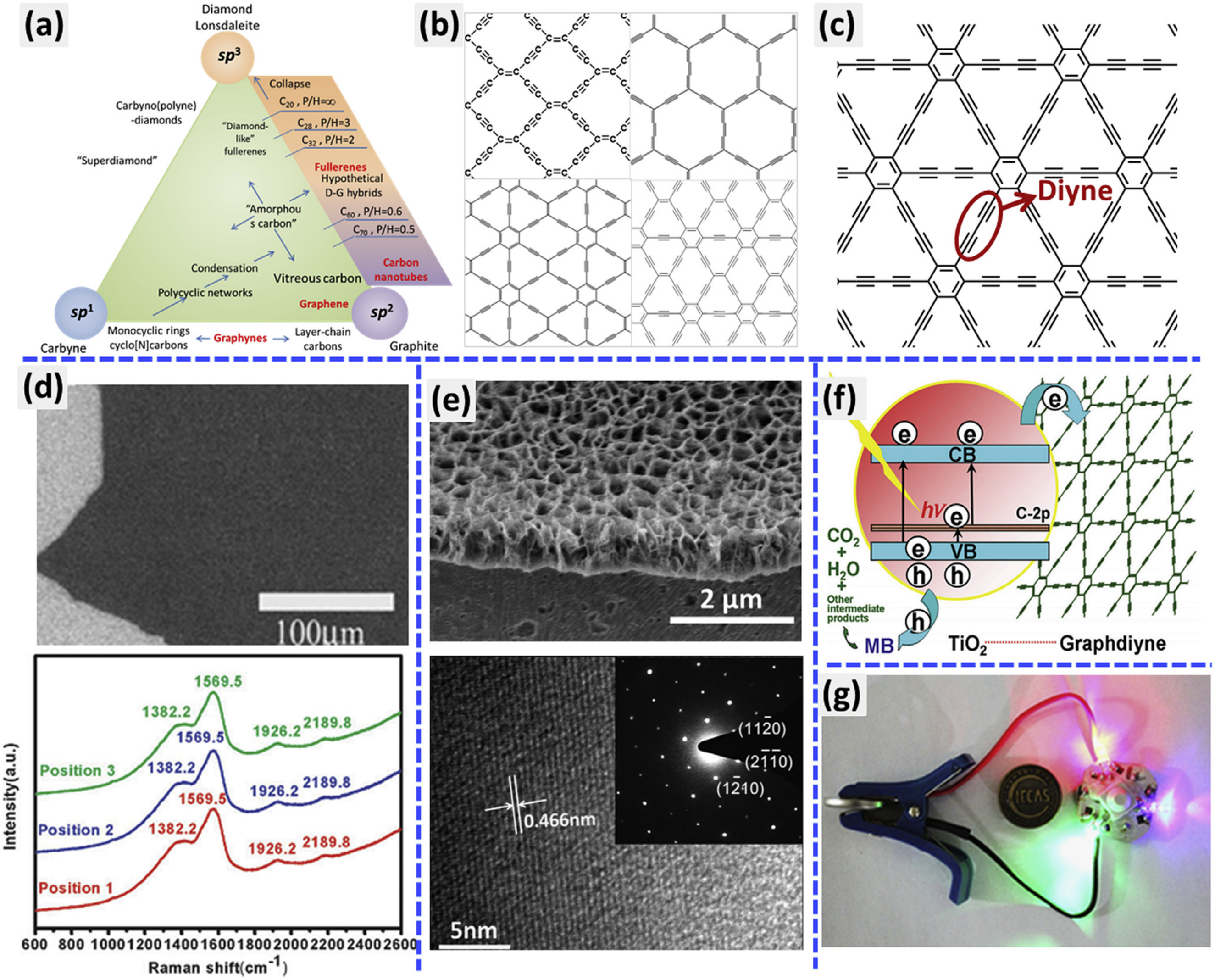

**Fig. 16.** (a) Ternary "phase" diagram of carbon allotropes. (b) Ideal atomic models of possible graphynes. (c) Structure of graphdiyne. (d) SEM image and Raman spectra of graphdiyne on Cu foil. (e) SEM image, HRTEM image and corresponding SAED pattern of graphdiyne nanowalls. (f) Schematic structure of $P_{25}$-GDY composite for photodegradation. (g) Photograph of the assembled full Li-ion battery applying discharge for lighting an LED bulb. (A color version of this figure can be viewed online)

cycle lives [253]. On the energy front, GDY was also introduced into perovskite solar cells as a dopant for hole-transporting, which was an effective strategy for enhancing device performance [254]. Furthermore, very recently graphdiyne was also employed in an ingenious design of hierarchical structure exhibiting superior super-hydrophobicity properties [255].

As for the study of graphdiyne, the general problems remaining are the enhancement of crystallization quality and the measurement of some basic properties of graphdiyne. We also need to face the challenge of developing a set of practical and standardized characterization methods. Research on graphdiyne has contributed to the expansion of the carbon material family. It is no doubt that there is still a broad space for exploring the world of carbon based on the numerous possibilities to assemble carbon atoms. The combination of experimental efforts with the development of theoretical models will be highly desired. It appears that we are entering into the next era of carbon.

## 10. Nanocomposites

Nanocarbon materials represented by carbon nanotubes and graphene-based materials are being widely explored in fabricating nanocomposites with an expectation to impart excellent mechanical/electrical/thermal properties to the composites. Indeed, numerous studies have emphasized the excellence of nanocarbon materials with respect to a variety of properties, which originates from their unique structure consisting of hexagonally arranged $sp^2$-bonded carbon sheets defined as "graphene layers" [120,256]. However, in reality, the performance of nanocomposites has not yet reached the level of expectation. For example, the mechanical performance of nanocarbon-reinforced nanocomposites is less than one third or half of that of nanocarbon materials themselves. To overcome this situation, Coleman et al. pointed out that four parameters should be carefully controlled: aspect ratio, dispersion, interfacial interaction, and alignment [257]. Even having this knowledge and the skills to control those parameters, however, many challenging issues remain if we wish to maximize the performance of nanocomposites. For example, many researchers have focused on modification of nanocarbons to improve the dispersion and the interfacial interactions with surrounding media either in the liquid or solid phase [258]. Such an effort is quite natural because poor dispersion or agglomeration of nanocarbons arises from inter-nanocarbon $\pi-\pi$ interactions that are stronger than nanocarbon–matrix interactions, and this leads to crack initiation and propagation, or causes phase separation that limits the resultant properties of the composites [259]. The poor dispersion of nanocarbons also makes it difficult to form electrical/thermal percolation networks in the composites [260]. This phenomenon becomes worse when the nanocarbon loading contents become higher (over 1–2 wt%). Further, the poor dispersibility of nanocarbons is closely related to weak interfacial interactions that in turn make the nanocarbon separate out from the matrix under applied force, implying that the nanocarbon is ineffective in its role as a reinforcing filler in structural nanocomposites [261]. With the goal of improving and/or maximizing nanocarbon dispersibility in and the interfacial interactions with the surroundings, a variety of skills to modify the surface of nanocarbons have been adopted [259,260,262–270].

It is nonetheless rather frustrating to find that the performance of the nanocomposites is still below our satisfaction despite such numerous efforts to improve the dispersibility and the interfacial interactions of nanocarbons. Further, many of the reports of improved performance are not reproducible even when strictly following the published recipe and procedures. This situation may be one of the reasons hindering the widespread commercialization of nanocomposites. It is hence a time to review our past efforts carefully and to try to find out the more appropriate and effective ways to maximize the performance of the nanocomposites. One thing to emphasize is that when adopting chemical modifications of nanocarbons it is very important, from the standpoint of quality control of the products, to provide both qualitative and quantitative data about the modification because the dispersion states of nanocarbons in the composites and hence the composite properties depends strongly on the nanocarbon/nanocarbon and nanocarbon/matrix interactions, and these vary remarkably with the degree of surface modification. For example, numerous earlier studies adopted ‘grafting-to’ or ‘grafting-from’ methods, but rarely reported data such as the degree of primary surface functionalization and subsequently the degree of grafting or secondary functionalization. In relation to this, it is also very important to develop appropriate characterization methodologies that help to obtain both qualitative and quantitative information about the surface modifications and the dispersion state of nanocarbons in the surrounding media.

As for characterizing the surface modifications, X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FT-IR), Raman spectroscopy, temperature programmed desorption/thermogravimetric analysis – mass spectroscopy (TPD/TGA-MS) and etc. have been widely adopted, but they provide only qualitative information, and cannot give a quantitative ‘degree of modification (DoM)’ of the nanocarbon surface especially when nanocarbons are grafted or further functionalized for the composite preparation. One recently developed method based on the conventional titration method may give us a possible route to obtain both qualitative information and quantitative DoM of amidation of carboxylic group functionalized nanocarbons as shown in Fig. 17a [271,272]. In this case DoM can be determined from the following equation,

$$\mathrm{DoM} = \frac{\mathrm{NF} - \mathrm{unchanged\ NF}}{\mathrm{NF}} \tag{1}$$

where NF is the number of primary functional groups (carboxylic groups for Fig. 17a). Though this method is currently limited to the covalent modification of nanocarbons, a chance still remains for the extension of the method to the cases of other covalently or non-covalently functionalized nanocarbons for determination of DoM.

On the other hand, for the determination of the dispersion status (DS) or the degree of dispersion (DD) of the nanocarbons in surrounding media studies do not typically provide quantitative information, but rather only qualitative information based on microscopic observations using scanning electron microscopy (SEM) or transmission electron microscopy (TEM) or atomic force microscopy (AFM). In some cases, a limited extent of quantitative analysis is provided using UV–visible spectroscopy, light scattering, or zeta potential measurements. There should be an appropriate characterization method through which we can determine the quantitative DS or DD. Another priority for research in this area is to find a direct correlation between the qualitative and quantitative surface modification and the DS or DD of nanocarbons in the nanocomposites. In this context one alternative approach is to monitor the changes in Hansen solubility parameters (HSP) with the surface modifications of nanocarbons and then to find a correlation between HSP and DS or DD of the nanocomposites. The HSP of CNTs, for example, can be determined with high credibility using inverse gas chromatography (IGC) and then be correlated to the dispersibility of CNTs in various solvents [273]. This kind of effort can also be extended to finding correlation between the HSP

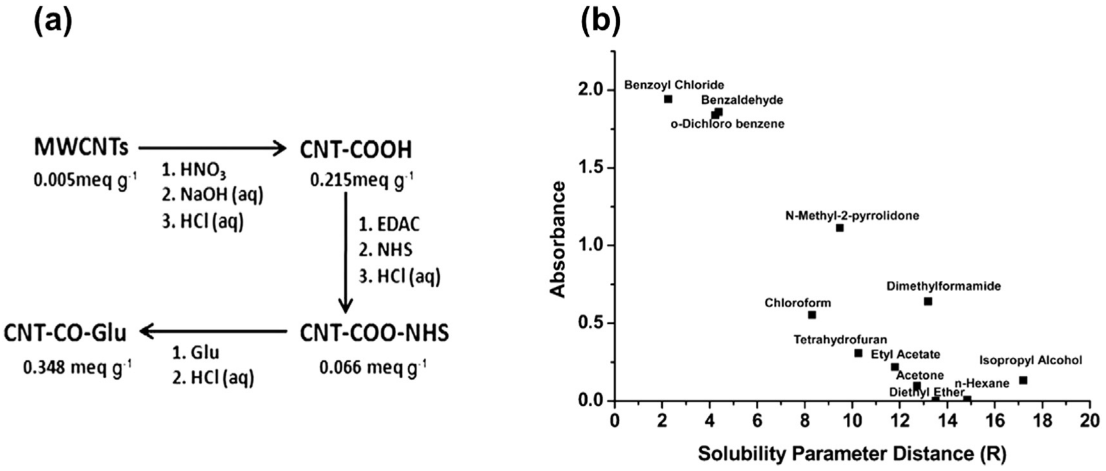

**Fig. 17.** (a) Example of determination of degree of modification (DoM) of amidation of carboxylic acid functionalized CNT with titration [272] (Reproduced from Ref. [272] with permission from Elsevier) and (b) plot of Hansen solubility parameter distance between the CNT and solvents vs. visible light absorbance for the CNT solutions showing the dispersibility of CNT [273] (Reproduced from Ref. [273] with permission from the PCCP Owner Societies).

and DD of nanocarbons in the nanocomposites.

The grand challenge in the carbon nanocomposites field is to fabricate materials that achieve ultimate performance by fully utilizing the intrinsic properties of nanocarbon fillers. To meet this challenge it is very important to establish strong and firm fundamentals in the relevant aspects of carbon materials science and engineering. The issues raised in this section, such as determining quantitative degrees of modification and dispersion status, are one important step for our community toward the goal of shortening the time for the widespread commercialization of nanocomposites with economic significance. We expect that composite materials will be an topic of increasing importance in 2016 and beyond, *Carbon* is particularly interested in submissions where carbon is not just one of the components, but rather the carbon structure, properties, or behaviors are the main intellectual theme in the manuscript.

## 11. Carbon materials and the global environment

Global environmental concerns have become a major driver of research around the world. There is a proliferation of new journals and research centers on sustainability, climate change, alternative energy, and green chemistry and engineering. At the center of discussions on global environmental change is “carbon”, which appears in phrases like carbon footprint, carbon cycle, carbon emissions, and carbon credits. Of course “carbon” here refers to the element as it occurs in diverse organic substances, the most environmentally relevant of which are biomass, fossil fuels, carbon dioxide, and carbonate minerals. In contrast, our journal covers the materials science aspects of carbonaceous solid phases, the so-called “carbon materials”, such as graphene and graphite. Is the science in the *Carbon* journal relevant to the protection the global environment? The answer is definitely yes! We would like to take this opportunity to comment on three aspects of the important connection between our carbon materials and societal concerns and responses to sustainability and environmental change.

### *11.1. Engineered carbon materials for sustainable technologies*

Global climate change is driven by modern energy-intensive technologies, and a key strategy in our response is to replace those technologies with more sustainable alternatives. This research area is a major thrust in the *Carbon* journal currently, and we expect it to continue in 2016 and beyond. New carbon materials are key components in alternative energy technologies that include electrodes for batteries, supercapacitors, fuel cells, and electrolytic cells for hydrogen production from water. They are also of interest as transparent conductors in solar cells, bipolar plates in fuel cells, lightweight materials that save energy in aircraft and automotive operations, and catalysts or catalyst supports for energy transformations that include carbon dioxide reduction into fuels and commercial chemicals. Many of these applications rely on carbon's unique combination of electrical conductivity, low density, and chemical stability. Carbons can also be engineered for high surface area to enable practical high-rate processes, and much recent work in the journal has focused on ways to cast nanocarbon building blocks into active and robust 3D porous structures.

Another area of intense international activity is the development of carbon materials for the treatment or protection of air and water resources. Carbons are or may be used as sorbents for water treatment, $CO_2$ capture, and volatile chemical capture and recovery from gas streams. They are of particular importance in water treatment, where they may serve as electrodes in fresh water production by capacitive deionization (CDI), as advanced membranes, or as components in photochemical catalysts for advanced oxidation processes (AOPs). In the sorbent area, a variety of new nanostructured porous forms are being explored based on CNTs, graphene materials, or templated forms, and many show high capacities and rates in laboratory studies. The *Carbon* journal is interested in submissions in this area, but encourages authors to consider the practicality and societal benefits carefully when they choose the material system and application. Activated carbons continue to dominate in industry, where they serve as cost-effective platforms that can be flexibly tailored to specific applications through myriad chemical surface modification. For new nanostructured materials to compete in practice with activated carbons will require they find a niche where the performance advantage justifies the likely higher cost. Single-walled carbon nanotubes, for example, have very high surface areas, but their use as bulk sorbents for water treatment faces such significant economic challenges that studies in this area are necessarily of less interest to the journal and the community. We encourage authors in this area to benchmark their new materials against commercial carbons, often activated carbons, and to evaluate new sorbent technologies critically, rather than limiting their studies to basic fabrication and testing.

### *11.2. Carbon materials in the natural environment*

The second aspect of the connection is perhaps less familiar to materials scientists, because it deals with “natural” carbons – those that have not been engineered for human benefit, but rather form spontaneously through natural high-temperature processes acting on organic matter. Fig. 18 shows these natural carbon materials as byproducts or small sidestreams from the much larger global carbon cycle. Natural carbons include natural graphite and diamond, formed by geological processes acting on carbon sources such as decayed vegetable matter or carbonate minerals.

More important for the global environment are the forms of “black carbon” – a term used in atmospheric and soil and geosciences for a carbon material created by incomplete combustion of organic matter in the environment [274]. This term can cause confusion, since materials scientists do not use the term, and it is an unfortunate transposition of “carbon black”, the well-known industrial particulate carbon material manufactured by flame processes. The logic behind the term “black carbon” lies in the desire to distinguish this carbon material in complex media like soil and sediment from other forms of “carbon” – i.e. the carbon atoms found in organic compounds. Soils and sediments contain many organic compounds, but only one fraction of the total elemental carbon is chemically inert and black (strongly absorbing with an index of refraction that is approximately wavelength independent) that it deserves the name “black carbon” or “refractory black carbon.” We materials scientists can instantly recognize this “black carbon” as a member of our carbon material family, and specifically graphenic carbon – a solid material based on $sp^2$-hybridized carbon atoms and conceptualized as collections of graphene layers. In practice, black carbon is either biomass-derived char or soot formed by incomplete combustion in forest fires, and now also in fossil fuel combustion and domestic biomass combustion.

The environmental relevance of black carbon is two-fold. The soot component is important in radiative climate forcing by absorbing solar radiation either as an atmospheric aerosol, or as a coating on ice and snow deposits, and has been cited as the second most significant emission beyond carbon dioxide [275]. Aerosol black carbon particles are also active as nuclei for the seeding of clouds that can counteract global warming by scattering, rather than absorbing solar radiation, and this seeding property is influenced by carbon surface chemistry, which may undergo oxidative aging. The char forms of black carbon are sometimes referred to as

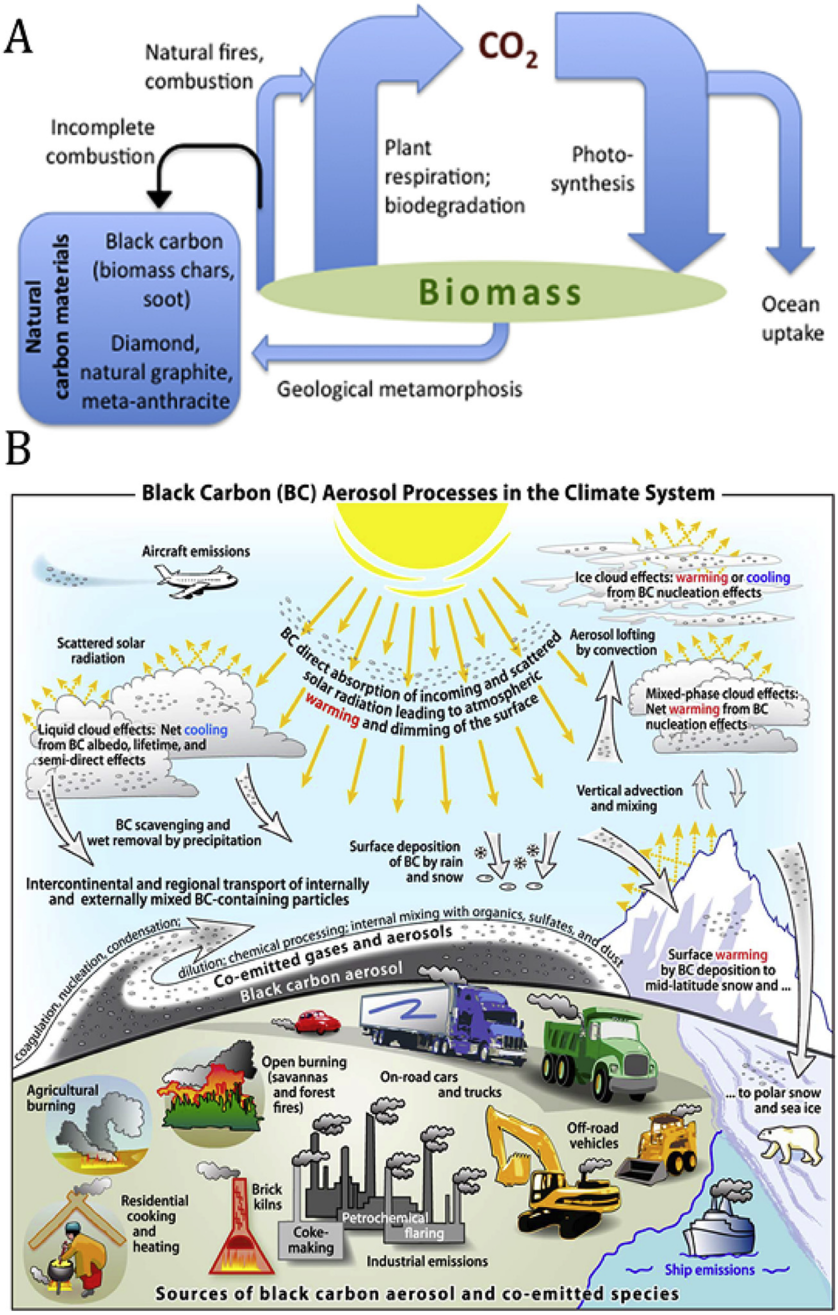

**Fig. 18.** Carbon materials in the natural environment. A. Formation routes to natural carbon materials in relation to the global carbon cycle. B. Effect of natural (black) carbon(s) on the global radiative balance, reproduced from Bond et al. (2013) [275]. (A color version of this figure can be viewed online)

"biochar", and are environmentally relevant due to their effects in soil. They offer a potential means of sequestering carbon, and also enhance soil properties such as nutrient retention, water retention, and overall soil fertility. Black carbon is the key component of the *Terra Preta*, or black earth found in Amazonia, and can be produced artificially by replacing biomass combustion with biomass pyrolysis processes, or replacing "slash and burn" agriculture with "slash and char" agriculture.

While both of these forms of black carbon or "BC" (char and soot) are very small streams in the global carbon cycle, they have a disproportionate influence on the environment as solar absorbers, soil amendments, and carbon sequestration reservoirs. While most of this work now gets published in other journals, there is an opportunity to advance this field by bringing to bear the tools of materials science to study these materials at the atomic and molecular level and relate their structures and surface chemistries to environmental behaviors.

### 11.3. Engineered carbon materials from natural or sustainable precursors

New carbon materials offer solutions to environmental challenges, but like any new technology have an environmental footprint of their own, which our community should seek to minimize. Among issues of interest to *Carbon* are the environmental and health impacts of emerging nanomaterials [117] and the design of carbon materials to reduce energy demands and chemical hazards associated with their manufacture. An area of intense activity is the development of alternative precursors and reagents for carbon synthesis. Carbon is an earth-abundant element, but many of the specific chemical feedstocks now come from finite fossil inventories, including petroleum, methane, and natural graphite. Similar to chemical technologies, there are efforts in our community to replace fossil fuel-based feedstocks with renewable ones, derived either from natural sources, waste materials, or recycled devices containing carbons (e.g. Li-ion batteries). Some feedstocks have a high local or regional significance, as a local agricultural byproduct or the waste product of a local industry. Related to this is the effort to evaluate alternative chemical reagents (e.g. for graphene oxide reduction) or earth-abundant-metal catalysts or metal-free catalysts (e.g. for CNT synthesis).

Carbon currently receives many manuscripts focused on new precursors or reagents, and in some cases the scientific innovation is hard to identify. There are thousands of potential organic substances capable of producing carbons, and evaluating them all through a routine set of synthesis and characterization steps is a formula for producing thousands of routine publications of little interest to most readers.

Carbon typically rejects papers whose main innovation is the demonstration of a new precursor when it is used to make an established carbon form that is characterized and/or used in a well-known way. Finding sustainable routes to carbon materials is important, however, so how does the journal support this effort while maintaining its commitment to publishing new and important science? This is not an easy question, but the editorial team would like to suggest a few ideas:

(a) *Structure/activity relationships*. Many manuscripts involving novel precursors would be stronger if they went beyond the basic “fabrication and testing” formula to explore the fundamental relationship between the properties of the new precursor/reagent, and the properties or activities of the resulting carbon, with special emphasis on the molecular assembly routes and surface chemistries.

(b) *Comparative analysis*. Many studies could be improved by benchmarking a new precursor or reagent against the one currently used industry, or against other proposed alternatives in the recent literature. Authors should strive for meaningful comparisons that put the value of the new material or alternative precursor in context. For example, many manuscripts offer a new nature-based substance for GO reduction, and cite the advantages over the toxic hydrazine (one of the earliest agents used), but ignore the large body of more recent work on other natural, alternative reductants, and as a result the real value of the new reductant and the importance of the finding is hard to assess.

(c) *Comprehensive evaluation of environmental impact*. Replacing a toxic or hazardous chemical with a natural and/or less hazardous alternative is a valid application of the principles of green chemistry, but at a deeper level, this substitution alone does not always ensure that the product or process is better for society. One must consider the location and magnitude of sources, transport and processing costs, energy uses, and performance implications, among others. As an example, the use of corn for fuel, for example, involves significant chemical and energy use in agriculture, and competes with its use in food production. Life cycle assessment, or LCA, is a formal tool used to examine the net impacts of a technology, by examining a much broader set of issues and impacts from product cradle to grave. While not all *Carbon* authors will be using this formal LCA tool, the principles may help guide authors toward more meaningful evaluation of new precursors, and may help raise the scientific level of these studies so they attract the interest of journals like *Carbon*.

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