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# Carbon Science Perspective in 2020: Current Research and Future Challenges

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### 1. Introduction

In 2016 the *Carbon* Editors decided to open the first issue of the new year with an editorial contribution to address the future challenges in carbon science. We are now conducting this exercise every two years [1,2], and the present article is the third such perspective. A number of current *Carbon* Editors and members of the Editorial Board have contributed to different sections on the state of carbon research aiming to highlight where selected research fields are moving in the near future.

Last year we celebrate the 150<sup>th</sup> anniversary of the Periodic Table that has revolutionized not only the world of chemistry, but also that of other fundamental disciplines including physics, biology, medicine, and materials science [3]. The carbon element ( ${}_{12}^{6}\text{C}$ ) occupies the second period and it is the first element of the IV group (carbon group) according to the Mendeleev Table of Chemical Elements (1869) [4]. Carbon is one of the most stable and abundant elements on Earth and it is the fourth most abundant in the Universe. It is known since ancient times but it was recognized as an atom only in the second half of the 18<sup>th</sup> century by Antoine Lavoisier [5].

Carbon is present in different allotropic forms that go from 0-dimensional to 3-dimensional structures [6], all covered by the articles published in *Carbon*. While some of the forms like graphene and their derivatives are gaining more and more popularity, we emphasize that our journal continues to also consider traditional forms of carbon, especially when new properties are discovered and exploited in the development of new functional materials, applications, or devices. In addition, our Editorial team strongly supports the publication of results that utilize less popular carbon allotropes provided that the studies are not limited to the use of new precursors and report properties that are very similar to those already described in the literature. We encourage instead the carbon scientific community to go beyond incremental works and to revisit old forms of carbon in new disruptive technologies and applications.

On these premises, we have combined our ideas and perspectives, producing a series of editorial sections based on individual subfields. First, Nikhil Koratkar presents the new findings on the partial transparency and epitaxy of graphene, which have important

implications in the field of surface engineering, Next, Vincent Meunier and Mauricio Terrones address the emerging domain of material informatics that has tremendous impact on artificial intelligence (AI) applications. The same authors cover the use of carbon materials in quantum computing. Yuan Chen then describes the important role of carbon materials in catalysis, without which most industrial processes would not be sustainable. Juan Tascon highlights the recent trends to reduce the amounts of CO<sub>2</sub> by its electroreduction to solid carbons. Elzbieta Frackowiak covers the effects of doping carbon materials with nitrogen and oxygen to achieve high electrochemical performance for applications in energy storage. Michael Holzinger provides an overview of carbon forms to enhance the sensitivity of biosensors. Sergey Mikhailovsky presents the state of the art of activated carbon and its millennial use in the biomedical field. Finally, Michael Strano covers new directions on the use of carbon nanotubes in plant biotechnology. We hope our readers will find these personal opinions and viewpoints helpful.

## **2. Partial van der Waals transparency and remote epitaxy through graphene**

Graphene is the thinnest material known to humankind [7]. As a result of its 2D structure and ultra-strong  $sp^2$ -hybridized carbon network, graphene offers an exciting blend of mechanical, electrical, thermal, and optical properties that open the door to a variety of possible applications [8–12]. One recently discovered and less widely reported property of graphene concerns its partial transparency to van der Waals interactions between various media [13–15]. Such partial transparency stems from its ultra-small thickness (~0.34 nm), which enables atoms or molecules present on either side of the graphene sheet to “sense or feel” each other via van der Waals interactions. It should be noted that van der Waals forces are extremely short range and hence any typical barrier or coating material is usually thick enough to completely screen out these interactions. However, graphene being exquisitely thin enables partial transmission of these interactions through “cross-talk” between the media present on the opposite side of the layer. This effect is based on two basic types of interactions that have important practical relevance: (i) a liquid interacting with a solid through a graphene layer, and (ii) a solid interacting with another solid material through an intermediate graphene layer.

### *2.1 Liquid-solid interaction through an intermediate graphene layer*

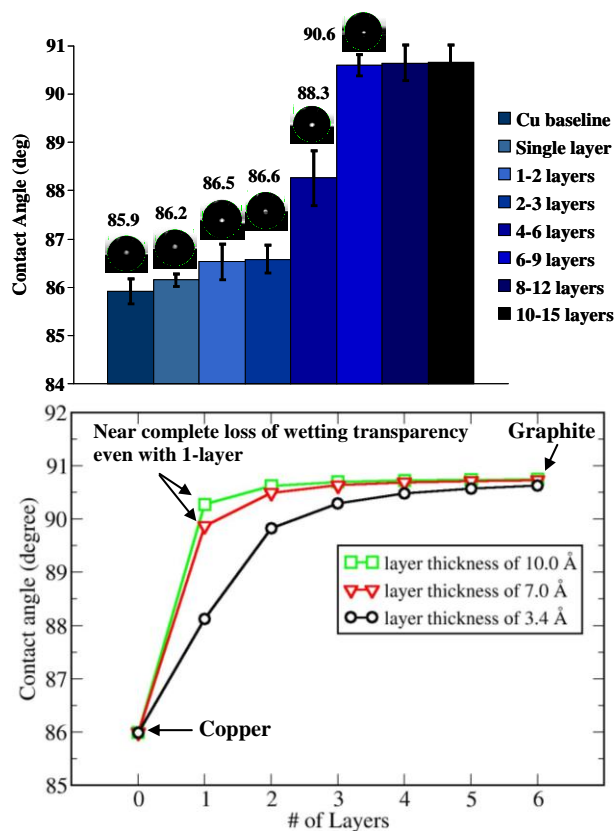
For the liquid medium, let's consider water. Figure 1 (top) shows water contact angle measurements on copper substrates with different numbers of graphene layers sandwiched between them [13]. Monolayer graphene exhibits partial wetting transparency since the graphene/copper contact angle is only slightly larger than that of bare (uncoated) copper. With increasing number of graphene layers, the contact-angle of water on copper gradually reaches the bulk graphite value, after about 6 layers. A similar partial transparency effect has also been observed on gold and silicon substrates, but not on glass [13].

Such partial wetting transparency of graphene can be understood from continuum models using the effective interface potential approach [16,17]. The predictive model indicates that the partial wetting transparency of graphene is attributable to its extreme thinness. However, it should be noted that with even only one graphene sheet there is an increase in the water contact angle with respect to bare copper, indicating that the transparency

effect is “partial” and not total – this is to be expected since the graphene layer has a finite non-zero thickness.

As compared to other thin-film coatings, graphene has an unparalleled ability to provide partial transparency to van der Waals interactions. This is illustrated in Figure 1 (bottom) where the water contact angle transition from copper to graphite is shown for carbon film coatings on copper with thicknesses of 0.34 nm, 0.7 nm, and 1 nm. It is clear that even ultrathin 0.7 nm or 1 nm coatings fail to provide any significant wetting transparency. The transparency effect starts to become significant only when the carbon coating thickness is reduced to the level of ~0.34 nm (i.e., the thickness of graphene). Sputtered oxide or polymer films cannot rival with such extreme levels of thinness. Hexagonal boron nitride (h-BN) is the only known material system that could match graphene’s thinness. However, it is significantly more challenging to deposit monolayer h-BN on large area substrates. By contrast roll-to-roll deposition methods have been successfully developed to deposit monolayer graphene films several tens of inches in dimensions for applications such as flexible electronics [18].

Similar partial transparency results have also been reported for wetting of liquid metals (e.g., gold at 1373K) on silicon carbide [19]. A similar gradual change in contact angle was observed from SiC to bulk graphite with increase in number of graphene layers, indicating that graphene is a partially transparent barrier that allows interactions between SiC and liquid gold.



**Figure 1:** (Top) Water contact angle measurements on copper with different number of graphene layers placed on copper. (Bottom) Continuum model predictions using the classical effective interface potential approach for water contact angle transition from copper to graphite with carbon coating layers of thickness 0.34 nm, 0.7 nm and 1 nm. Adapted from [13] with permission. Copyright 2012, Springer Nature.

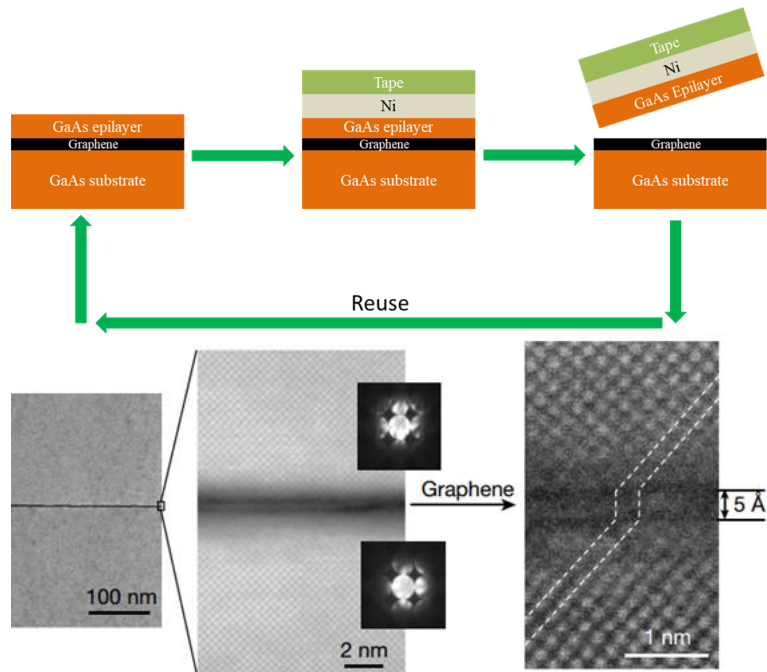
## *2.2 Breakdown in the transparency effect*

The wetting transparency of graphene is not associated to all types of surfaces. Indeed, this property completely breaks down with glass [13]. In spite of its atomic thinness, the presence of graphene at the water/glass interface disrupts the short-range chemical interactions (hydrogen bonding networks), which dictate the water/glass contact angle. Therefore, for surfaces where chemistry plays the dominant role, graphene coatings do not provide any significant wetting transparency. Graphene's transparency to van der Waals interactions also breaks down on surfaces that are much more hydrophobic than graphene [14,15,20]. This is because the interfacial energy is now dominated by the water-graphene interaction rather than the water-substrate interaction. A classic example of such a situation is for a graphene sheet transferred onto a super-hydrophobic (rough) substrate with trapped air pockets [12]. The graphene sheet essentially sits on top of these air pockets and the wetting of the graphene-coated surface is dictated by the wetting of the graphene layer rather than the underlying surface [14]. However, the partial transparency effect can be restored if the graphene layer can be made to “conform” to the surface roughness features of the substrate [15].

The literature also reports large variability in wetting data on graphene coated surfaces. A major cause for this behavior is due to hydrocarbon contamination on the graphene coating from ambient air that is unavoidable, leading to results that can vary depending on the extent and thickness of the hydrocarbon coating [21]. Liu and co-workers found that a pristine (e.g., perfectly clean) graphene sheet is hydrophilic as opposed to graphene with hydrocarbon contamination, which is hydrophobic. Such perfectly clean (hydrophilic) graphene also exhibits partial wetting transparency with respect to water, similar to what has been reported with hydrophobic (hydrocarbon coated) graphene [21].

## *2.3 Solid-solid interaction through an intermediate graphene layer*

Recent work indicates that graphene is not only partially transparent to liquid-solid interactions, but this principle also applies to solid-solid interactions. This was demonstrated by carrying out epitaxial growth of thin film materials on graphene coated substrates [22–25]. The “copying and pasting” of the substrate registry through graphene enables the use of this technique as an economically inexpensive approach (Figure 2, top) for the fabrication of high-quality single crystals of semiconducting materials. Initial studies achieved homoepitaxial growth of GaAs on graphene coated GaAs (Figure 2, bottom) [22]. Such homoepitaxy studies were successfully extended to InP and GaP. The next major milestone was the successful demonstration of remote epitaxy for heteroepitaxial systems such as growth of copper on sapphire through a graphene buffer layer [23]. This demonstrated the generality of the concept and proved that graphene is partially transparent to solid-solid interactions and permits the transmission of information regarding the registry of the atoms forming the substrate.



**Figure 2:** (Top) Schematic for remote epitaxy process allowing reuse of the host substrate. (Bottom) High-magnification scanning transmission electron microscopy image at the GaAs/Graphene/GaAs interface showing epitaxy. Adapted from [22] with permission. Copyright 2017, Springer Nature.

A key question is whether other ultrathin 2D materials (e.g., h-BN) can perform equally well as graphene in terms of allowing solid-solid interactions. Studies indicate that while monolayer hBN is transparent to a certain degree, it tends to significantly interfere with the epitaxial process due to its polar nature [24]. By contrast, graphene being less polar is much less intrusive to the epitaxial process. This demonstrates that polar (electrostatic) interactions play a key role in epitaxial processes at solid/graphene/solid interfaces. It also shows that depth of penetration of the potential field from the substrate depends on the polarity of the 2D material positioned on top of it. While highly polar 2D materials (with inherent dipole in their structure) screen the potentials from the substrate, non-polar ones like pristine graphene allow the atomic potentials to pass through due to the non-polar nature of carbon-carbon bonds and lack of inherent dipole in its structure.

It was also shown that solid-solid interactions through 2D layers depend not only on the polarity of the 2D material, but also on the polarity of the substrate itself [24,25]. In general, it was demonstrated that more ionic substrates (e.g., GaN and LiF) exert a much greater influence on the epilayer growth and thus are more suited for remote epitaxy through the graphene layer. This can be explained based on the longer range of electrostatic interactions for highly polar (ionic) substrates when compared to less polar (covalent) substrates.

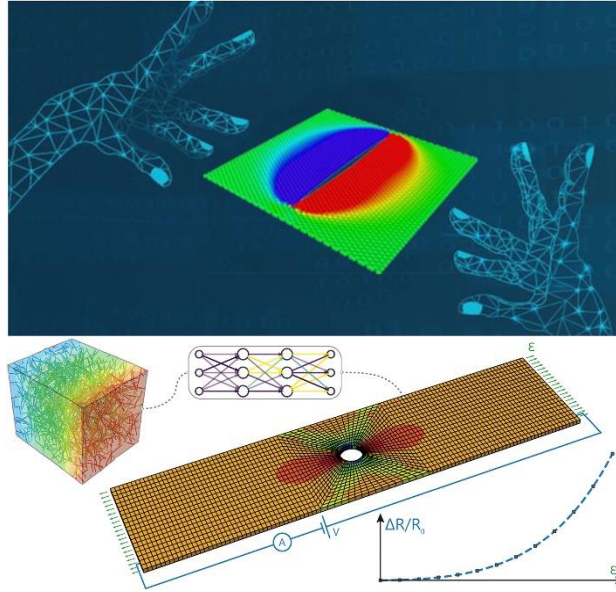
While very limited work has been performed on liquid-liquid or gas-gas systems, it appears that graphene could indeed be partially transparent to such interactions. These

fundamental investigations are of great practical significance in surface coatings, helping to solve surface engineering problems that require wetting tunability.

### **3. Machine learning in carbon materials**

Recent years have seen a tremendous increase in the development of materials informatics for the characterization and discovery of new materials. This field includes the use and management of big data [26], high-throughput computational materials techniques [27], and, more recently, the application of artificial intelligence (AI) methods to materials-relevant problems [28]. Reasons explaining the fast growth in this field range from the development of increasingly accurate theoretical descriptions of electronic behavior in reduced dimensionality systems to the availability of supercomputing power accessible to a growing number of research groups. Machine learning (ML) is an example of AI methods. It is based on the application of statistical algorithms where performance improves with training (in a typical ML process, learning is performed on a portion of the data available – the training set – while testing is performed on the rest of the data). In addition, the resources and tools now available to facilitate the application of ML techniques have lowered the barrier to scientific discovery to a point where the combination of big data and AI has been referred by some authors as “the fourth paradigm of science” [29]. While ML methods have been applied to a broad range of materials, they have proven particularly useful for emerging materials, including nanostructured and low-dimensional structures (e.g., layered materials). For instance, carbon-based materials have recently been the subject of many studies driven by ML techniques. In this context, it is not surprising that the Editors of *Carbon* are now receiving a growing number of original article submissions on this subject and it is expected that the journal will handle more and more studies where the path to discovery involves in one way or another ML and its applications.

The applications of ML in Carbon cover a wide spectrum of subfields. For example, Matos *et al.* used predictive multiscale models of the multiaxial strain-sensing response of conductive carbon nanotube-polymer composites to develop a training dataset used, in turn, to predict the electro-mechanical response of components of arbitrary shape subject to a non-uniform, multiaxial strain field [30]. In another study, Gernand *et al.*, employed machine learning techniques to assess carbon nanotube pulmonary toxicity based on previously published studies, in a quest to guide future development with minimized risk [31]. In a recent paper published in *Carbon*, different ML algorithms and artificial neural network structures were used to predict the mechanical properties of single-layer graphene under various conditions such as system temperature, strain rate, vacancy defect, and chirality, in order to predict fracture stress/strain and Young’s modulus [32] (Figure 3). In that study, high-throughput computations were combined with classical molecular dynamics (MD) simulation to generate the training dataset. The authors of the study explored the use of a number of conventional ML algorithms (e.g., the stochastic gradient descent, the k-nearest neighbors method, the decision tree, and support vector machine), thereby providing a broad assessment of the usefulness of each technique for predicting the mechanical properties of graphene [32].



**Figure 3:** (Top) An artist's view of the digital manipulation of graphene's mechanical properties. Reproduced from [32] with permission. Copyright 2019, Elsevier. (Bottom) Schematics of the optimized artificial neural network to convert raw data into resistivity plots. Reproduced from [30] with permission. Copyright 2019, Elsevier.

In another study, high-throughput classical MD computations were used to construct the learning dataset, supervised ML and artificial neural network models to predict the interfacial thermal resistance between graphene and hBN using only information on the system's temperature, the coupling strength between the layers, and in-plane tensile strains. The authors established that among all tested algorithms, a deep neural network method provides the best prediction results when compared to the ML models [33]. ML can also be used to understand the properties of graphene containing foreign atoms. Heteroatom doping has endowed graphene with many desirable properties and boosted its applications. To address this potential, Dieb *et al.* combined atomistic simulations with ML methods to search for the most stable structures of doped boron atoms in graphene [34]. In another paper published in this journal, Fernandez *et al.* use ML methods to correlate the electronic properties (e.g. electron affinity, energy of the Fermi level, electronic band gap, and ionization potential) of 622 optimized graphene structures with their structural features [35]. Using 30% of the available data as test set, the authors showed to be very accurate with a strong correlation of  $R^2 \sim 0.9$ . In a different application of ML, Yang *et al.* developed a method to predict the specific sequence of single-stranded DNA for its ability of dispersing and sorting a given single-walled carbon nanotube (SWCNT) described by its chirality and handedness [36]. Another increasingly popular application of ML in material science is in the development of improved interatomic potentials. For instance, Fujikake *et al.* adopted that approach to model the physics of the interaction of lithium atoms with graphene, graphite, and disordered carbon nanostructures. Here, the interatomic potentials were obtained using data collected using density functional theory [37].

Overall, the few ML studies on carbon materials published over the past few years already demonstrate the promise these new numerical techniques will have in the field. For example, ML algorithms could be used to predict the most stable  $sp^2$  hybridized forms of three-dimensional (3D) carbon with specific surface areas, and mechanical/electronic properties. ML approaches could also be linked to the experimental synthesis of carbon nanotubes (CNTs) with specific chiralities and electronic properties. In this case, synthesis conditions (e.g., temperature, precursor, catalytic substrate, pressure, etc.) can be correlated to *in situ* Raman spectra output indicating the type of tubes (metallic or semiconducting) that are synthesized. These data could be then fed to a robot able to learn how to synthesize carbon tubules of specific conducting properties [38,39]. We expect that further developments have the potential to revolutionize the way we treat and exploit experimental data. It will also allow development of predictive theories and is even poised to allow discovery of new behaviors and materials with optimized properties. However, much work is needed to realize the potential of ML and the use of large datasets. This includes, but not limited to, proper archiving and data availability across fields and techniques.

#### **4. Carbon and quantum computing**

Quantum computing technology is based on the exploitation of quantum entanglement. Entanglement is a unique resource for quantum information processing and communication where classical bits (that can only store values “0” or “1”) are replaced by quantum bits (qubits), where any superposition of the “0” and “1” states is possible. Entanglement is typically done between spin states or single photons.

In practice, a robust scalable quantum technology requires meeting two antagonistic demands [40]. First, a well-isolated system is needed to allow high-precision control. Second, the quantum system needs to be scalable. For this latter point, solid-state technology is very attractive, as it can benefit from all the knowledge developed in nanofabrication techniques established for the semiconductor industry. One very promising quantum technology system is diamond with nitrogen-vacancy (NV) centers. The NV center in diamond is a defect consisting of one substitutional nitrogen atom and an adjacent vacancy and whose electronic ground state is a spin triplet that can be controlled coherently at room temperature. Thus, this system exhibits atom-like properties in a well-controlled and robust solid-state device, thus meeting both requirements listed above [40]. Many fundamental studies have been devoted to demonstrate the use of NV centers for quantum computing applications. For example, researchers have exploited the quantum physics of NV centers to experimentally demonstrate a violation of Bell’s inequality, thus showing the manifestation of nonclassical correlations between entangled qubits [41]. Furthermore, experimental studies of spin-photon entanglement and two-photon quantum interference have demonstrated the possibility of generating entanglement between NV spins with a spatial separation of three meters [42].

In addition to allowing control, one desirable characteristics of qubits is their long coherence times with respect to time scales needed for their manipulation (e.g., computation). To meet this requirement, graphene nanoribbons and quantum dots have been proposed as ideal candidate materials. Long coherence times in graphene spin

qubits are due to carbon's very weak spin–orbit coupling and hyperfine interaction, thus presenting desirable properties for fault tolerant quantum computing [43].

Another application of carbon materials in quantum computing and quantum cryptography is the possibility of using SWCNTs as electrically triggered, single-photon sources at room temperature at desirable wavelengths. This property stems from SWCNTs' strong excitonic binding energy and the possibility to broadly tune their band gap (and thus the range of wavelength of the emitted photons) as a function of tube diameter. One drawback of SWCNTs as single-photon-sources is their low quantum yield and a high sensitivity to spectral diffusion. A number of advances have been recently reported addressing this issue, notably by chemical functionalization and by optimizing electrical contacting and resonator coupling [44].

We believe that in the following years, more papers on the controlled creation of point defects in  $sp^2$ - and  $sp^3$ -hybridized carbon systems will be published, and especially those with applications related to quantum sensing and quantum single-photon emission. For example, for single photon emission, it is key to incorporate single metal atoms in carbon lattices. Regarding graphene and carbon nanotubes, it is important to develop strategies to incorporate BN domains in a controlled way, and to understand their role in quantum-related applications. Controlled strain in these carbon systems could also be evaluated, as strain in conjunction with point defects could result in the appearance of novel quantum phenomena. Proper characterization protocols of such systems need further development, as the current techniques do not necessarily identify/quantify single atomic defects. It is also important to understand the growth and properly characterize the structure of quantum dots, as they can be of  $sp^2$  or  $sp^3$  nature. In the near future, *Carbon* will put together a special issue on quantum carbon materials for quantum technology applications that include quantum sensing, quantum metrology, quantum computing, and quantum communications.

## 5. Carbon materials in catalysis

Catalysts are used in 85-90% of the current industrial chemical processes to realize selective and energy-efficient production of desirable chemicals from fossil or renewable resources [45]. Although most of the current commercial heterogeneous catalysts are based on metals supported on stable inorganic oxides, such as  $Al_2O_3$  and  $SiO_2$ , carbon materials have been used in a small fraction of commercial catalysts since the 1960s [46–48]. For example, activated carbon is used as a support material for precious metals in the synthesis of fine chemicals, such as hydrogenation of benzene and aliphatic or aromatic nitro compounds [48]. Several commercial petroleum refined catalysts use carbon materials, such as activated carbon and carbon black, for hydrodesulfurization [46]. For the platinum-based electrocatalysts used in low-temperature fuel cells, carbon black is almost exclusively used as catalyst support [49]. The production of toxic phosgene also involves *in situ* carbon catalysts [50]. In addition, carbon materials offer unique advantages in catalysis, such as high surface area, hierarchic porosity, rich surface chemistry, relatively high chemical inertness, and electrical conductivity. These properties enable carbon materials to serve as efficient supports to disperse and anchor metal atoms, or even play multifaceted roles as adsorbents or catalysts themselves.

However, most research efforts devoted to the catalysis applications of carbon materials remain confined in the research laboratories.

The apparent disconnect between basic research and commercial applications has been attributed to the difficulties in understanding and precisely controlling the physical and chemical properties of carbon materials [46,47]. The emergence of carbon nanomaterials, such as fullerene, carbon nanotubes, and graphene, with well-defined structures and unique electronic, electrical and chemical properties, offers opportunities to address the difficulties mentioned above, thus enabling the creation of high-performance catalysts [51]. Over the last three decades, significant research has been made in this area. The following six interconnected areas are the current hot topics in this field and are selected to serve as a guide for readers to explore the vast amount of published literature (Figure 4).

*Nanocarbon supports:* Carbon nanotubes and graphene-based materials are explored as supports for various metals and metal oxides [52,53]. Studies on using traditional carbon materials as catalyst supports showed that the surface area, pore size distribution, and carbon surface chemistry, actively control the stabilization of metals, thus significantly affect the resulting catalytic performance [46,54]. When compared to activated carbon and carbon black, carbon nanomaterials offer several key advantages as catalyst supports. First, they possess well-defined structures in pristine forms, which provide better tunability of the surface chemistry (e.g., oxygen contents, wettability, acidity, chemical inertness). Second, they exhibit higher electrical conductivity for longer length scales (depending on carbon nanotube length and lateral size of graphene sheets), which is crucial to enable efficient electron transfer in electrocatalysts [55]. Third, they can be used as nanoscale building blocks to assemble macroscale porous architectures, which may improve the mass transfer of reactants and reaction intermediates. Interestingly, most of the currently reported studies claim improved catalytic activities and stability for metal/metal oxide catalysts supported on carbon nanomaterials [52,53].

*Heteroatom doping:* The role of heteroatoms on carbon surfaces, especially nitrogen, has long attracted research interest. The nitrogen functionalities were considered to have the opposite effect of that of oxygen-containing groups, which endow amphoteric character to carbon surfaces [54]. In 1984, a nitrogen-doped carbon produced by high-temperature ammonia treatment was first reported to enhance the catalytic activity [56]. It took 25 years to discover that nitrogen-doped carbon nanotube arrays have a superior catalytic activity compared to platinum-based electrocatalysts for oxygen reduction reaction (ORR) in alkaline fuel cells [57]. Expensive precious-metal based electrocatalysts have been a bottleneck for large-scale application of several potentially sustainable chemical conversion devices, including hydrogen fuel cells, water electrolyzers, and metal-air batteries, all hot research topics over the past 20 years due to growing environmental concerns associated with global climate change. The 2009 findings on nitrogen-doped carbon nanotubes led to the expansion of research interests in exploring other nitrogen-doped carbon nanomaterials as catalyst supports or catalysts for ORR, oxygen evolution reaction (OER), and hydrogen evolution reaction (HER), all critical for the development of energy conversion devices. This research has also been recently expanded into doping

of carbons with different heteroatoms (e.g. boron, sulfur, phosphorous, and co-doped combinations) [58,59].

*Carbocatalysis:* The study of direct catalytic roles of different functional groups on the surface of carbon materials has a long history dated back to the 1930s [46]. Carbon nanomaterials, including carbon nanotubes, graphene (and graphene oxide), carbon quantum dots, and nanodiamonds, bring a new perspective to the field of carbocatalysis (also called carbon-based metal-free catalysts). Carbocatalysts have potential applications in industrially essential reactions, such as ORR, styrene synthesis, acrolein and cyclohexane oxidations, and benzene hydroxylation [60,61]. However, several challenges remain, as it is important to elucidate the exact catalytic role of different carbon functional groups in reaction mechanisms and achieve their control in practical carbocatalyst applications.

*g-C<sub>3</sub>N<sub>4</sub>:* Alternative to nitrogen-doping, there are various ways to incorporate nitrogen into carbon materials in order to create carbon nitride materials. A unique synthesis method is possible for the generation of graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>), which is one of the oldest synthetic conjugated polymers. An important discovery in 2009 showed that g-C<sub>3</sub>N<sub>4</sub> is chemically and thermally stable as a visible-light-active photocatalyst [62], thus opening a new field in photocatalysts. The catalytic activities of g-C<sub>3</sub>N<sub>4</sub> have been found to depend on their structural properties. Different methods have been explored to modify the electronic structure, nanostructure, crystal structure, and heterostructure of g-C<sub>3</sub>N<sub>4</sub>, leading to materials with catalytic properties applicable to a large variety of chemical reactions [63,64].

*Carbon nanoarchitectures:* Enabling efficient mass transfer of reactants and reaction intermediates is essential for the catalytic performance of porous solid catalysts. Mass transfer in carbon catalysts depends on their morphological architectures and interfacial properties. Early studies focused on the effect of pore size distribution and surface functional groups of bulk carbon materials [46]. Subsequently, various carbon molecular sieves, carbon aerogels, and carbon spheres were synthesized to control porosity at different length scales using hard or soft templating methods [65,66]. Recent studies concentrate on carbon nanomaterials as building blocks to create carbon nanoarchitectures with hierarchical pore structures; these may show superior properties when compared to their individual constituting carbon nanomaterial components [67]. It is noteworthy to mention that carbon nanomaterials often lose their desired nanoscale properties when assembled into macroscale structures. Therefore, controlling their assembly is critical to translate their unique nanoscale catalytic properties into macroscale carbon catalysts.

*Nanoconfinement:* Carbon nanomaterials, especially carbon nanotubes, offer unique confinement opportunities in their nanoscale internal channels [68]. First, the size, shape, and chemical properties of nanoparticles are influenced by this confinement. Second, the properties of reactants and solvent molecules are also modified inside nanoscale channels. Third, the mass transport behavior of molecules (e.g., water) is significantly different in nanochannels. All these phenomena have been explored in catalytic

applications. For example, confined metal or metal oxide nanoparticles exhibit different catalytic activity in reactions, such as hydrogenation, Fischer-Tropsch synthesis, and CO<sub>2</sub> reduction [69]. The concepts of ultrashort (millisecond) contact time reactors inside carbon nanotubes and of using carbon nanotube membranes to shift the equilibrium in reversible reactions are also being explored [51].

It is clear that several new areas have been quickly emerging in the last five years, and these areas will attract significant research interest in the upcoming years (Figure 4).



Figure 4: Schematic illustration of current hot research topics and emerging new research directions in the field of carbon material-based catalysts.

**MOFs/COFs:** Metal-organic frameworks (MOFs) are polymers with 1D, 2D, or porous 3D structures coordinated with metal ions or clusters using organic ligands. Building blocks in covalent organic frameworks (COFs) are linked by strong covalent bonds instead. Both MOFs and COFs contain unsaturated metal sites and active groups on their organic linkers [70]. MOFs/COFs and some other ordered organic structures can be used as self-sacrificing templates/precursors to synthesize carbon catalysts, exhibiting advantages in terms of tailorable morphologies, hierarchical porosity and facile functionalization with other heteroatoms and metal/metal oxides [71]. A critical issue in carbon catalysis is the difficulty of precisely controlling their physical and chemical structures using standard organic/inorganic templates or precursors [72]. The key challenge during the carbonization of MOFs/COFs lies in the careful control of their physical and chemical properties, which vary during pyrolysis or thermal annealing.

**Graphdiyne:** Graphdiyne is a new 2D carbon allotrope comprised of hexagonal benzene rings and diacetylenic linkages via unique sp-sp<sup>2</sup>  $\pi$ -conjugated structures. Graphdiyne offers uniform pores, high carrier mobility, high electrical conductivity, and moderate bandgap, which are attractive for photocatalysis, photoelectrocatalysis, and electrocatalysis. The exploration of graphdiyne has just started, and many questions are

waiting to be answered, including its specific role in the catalytic reactions, its competitive advantages over polymeric semiconductors, such as g-C<sub>3</sub>N<sub>4</sub>, and the feasibility of structure-controlled scalable synthesis[73,74].

*Single-atom catalysis:* The size of metal particles is a critical factor when determining their catalytic activity. Single-atom catalysts (SACs) contain isolated metal atoms homogeneously dispersed on supports, which could maximize the use of metal atoms and sometimes provide high activity and selectivity [75]. The initial studies on SACs are all based on metal oxide supports. Recently, carbon materials, such as graphene and MOF-derived carbon materials, have been used as supports to synthesize single-atom catalysts [71,76]. These catalysts have demonstrated superior catalytic performance for some reactions. More importantly, they offer alternative opportunities to understand the interactions between metal species and carbon supports. It should be kept in mind that although SACs are key components, the carbon-based supports likely contribute to the overall performance and further studies are needed in order to elucidate the reaction mechanisms.

*Defects in carbon materials:* Carbon materials contain various defects, which are responsible for modifying their physicochemical properties, ranging from the surface reactivity to the surface mobility of adsorbed species, electrical conductivity, and surface hydrophilicity [51]. Changes in these properties, in turn, lead to different catalytic performance, as well as different interactions between the carbon supports and the metal/metal oxide particles. Although defects play a critical role in the catalytic behavior of carbon materials, few studies were able to elucidate their roles in detail. It is challenging to obtain well-defined defects (e.g., type, concentration, and location) and the *in situ* characterization is also challenging with respect to their dynamic changes during reaction conditions [77]. Recent studies have started to controllably introduce defects into carbon materials, examine the exact roles of specific types of defects [78], as well as exploring defect engineering as a tool to create emerging highly active carbon catalysts [77,79].

*Surface functionalization:* Functional groups can be introduced on carbon material surfaces by various methods, such as chemical oxidation, physical adsorption, covalent bonding, or noncovalent  $\pi$ - $\pi$  interactions [54,80]. As mentioned above, the catalytic roles of carbon surface functional groups have been studied for many years [46,81]. In this context, oxygen-containing functional groups covalently attach to the sp<sup>2</sup>-hybridized carbon network, such as ketonic groups that play critical catalytic roles [82]. An emerging functionalization approach is to wrap carbon materials with polymers containing polar oxygen groups to form composites, thus leading to highly active electrocatalysts [83]. Therefore, various surface functional groups need to be further explored, and hopefully, some functional groups and their processing methods can be identified to create extremely active and stable carbon catalysts.

Overall, carbon catalysts have been applied to various catalytic reactions, and some reactions have attracted the attention of scientists due to their relevance to socially relevant topics involving green chemistry, renewability, and sustainability, including ORR, OER, HER, and CO<sub>2</sub>, and N<sub>2</sub> reduction reactions. Although the spotlight reactions are

evolving with time, the fundamental challenge for carbon catalysts is to understand the correlations between physical and chemical characteristics of carbon materials and their catalytic activities, so that highly active carbon catalysts with excellent stability can be used for practical applications. Furthermore, studies revealing their long-term toxicity and health impacts, especially for carbon nanomaterials, are needed.

In recent years, catalysis research of carbon materials has become very active. *Carbon* has published many excellent studies over these years. As a forum for communicating scientific advances in the field of carbon materials, we expect that the manuscripts submitted to *Carbon* in catalysis areas focus on the roles of carbon materials and advance our understanding on how carbon materials contribute to the observed catalytic activities. Studies of composite catalysts, in which carbon materials do not play a central role, would be more suitable for many other catalysis-focused journals. However, in some cases, carbon-based supports might serve a very critical role beyond serving as inert substrates, thus making the composite system of interest to the carbon community. Considering the background explained above, we would like to encourage our community to continue contributing both research articles and reviews in the area of catalysis.

## **6. Novel carbon forms from carbon dioxide electroreduction**

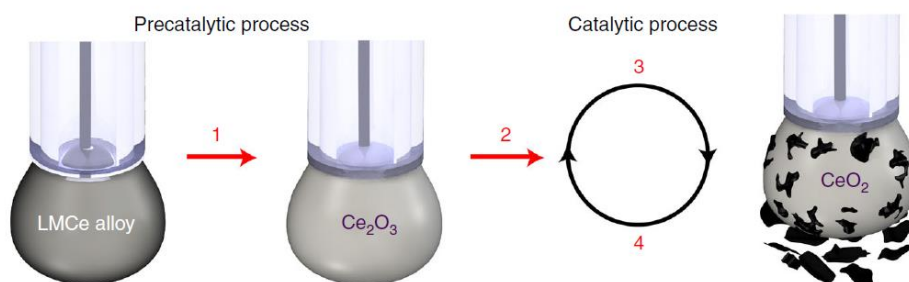
This section focuses on new carbon solids obtained by electroreduction of CO<sub>2</sub>. CO<sub>2</sub> can be considered as an “infinite” source for synthesizing new carbon forms [84]. Nowadays, burning fossil fuels in transportation and the production of electricity or heating generates large amounts of CO<sub>2</sub>, thus making it the most abundant gas produced by humans and the most notorious greenhouse gas. Besides the progressive transition of human economy to carbon-neutral energy sources (to reduce the generation of CO<sub>2</sub>), there is a pressing need to develop emerging technologies capable of capturing and storing the emitted CO<sub>2</sub>. Particularly desirable processes for CO<sub>2</sub> disposal are those transforming it into liquids or, even better, solid products with high strategic value such as fuels.

One way to transform CO<sub>2</sub> into valuable products is through its electrochemical reduction [84]. This process [85–87], leads to value-added chemicals (e.g., carbon monoxide, formic acid, acetic acid) and liquid fuels. Its advantages and challenges have been summarized by Qiao *et al.* [88], who identified an insufficient catalytic activity and stability as the main bottleneck. Therefore, intense research is under way to identify suitable catalysts, including solid carbons [85, 88–97] to develop this process.

As mentioned above, obtaining solids instead of liquids, from captured CO<sub>2</sub>, can be advantageous to minimize the risks associated with their accidental release to the environment. Nevertheless, reversing the combustion of fossil fuels by transforming CO<sub>2</sub> into carbon must be carried out with minimal energy consumption (lower temperature). Moreover, CO<sub>2</sub> is a rather inert and thermally stable molecule, and the design of CO<sub>2</sub> reduction electrocatalysts that operate at low overpotentials and at room temperature is very challenging. In this context, Esrafilzadeh *et al.* [84] have recently succeeded in transforming CO<sub>2</sub> by this method into elemental carbon. These authors used a liquid metal-based catalytic technology, with an added advantage of avoiding catalyst deactivation by coking.

Of particular interest to the *Carbon* readers are the characteristics of solid carbons appearing as black floating debris after prolonged electrolysis of CO<sub>2</sub> using cerium-containing alloys as catalyst [84]. These carbon products were collected, purified and characterized. They consisted of small agglomerated flat sheets of amorphous carbon with interatomic distances of 0.34 nm, and typical nano-flake thicknesses of 3 nm. This new type of carbonaceous material is mainly composed of C-C and C=C carbon bonds (84.5 at%), in addition to covalently bound oxygen (15.0 at%), with small quantities of Sn, likely associated with residues from the metallic catalyst.

The electrochemical process on the liquid metal electrode is capable of converting gaseous CO<sub>2</sub> into solid amorphous carbonaceous nanosheets at a low onset potential of only -310 mV vs. CO<sub>2</sub>/C. This is quite remarkable when considering the stability of the CO<sub>2</sub> molecule. The proposed catalytic mechanism, illustrated in Figure 5, includes a pre-catalytic reaction (Reaction 1,  $2 \text{ Ce} + 1.5 \text{ O}_2 \rightarrow 2 \text{ Ce}_2\text{O}_3$ ), and a catalytic cycle for the CO<sub>2</sub> reduction to amorphous carbon sheets (Reactions 2-4). The reaction leading to solid carbon can be then written as  $\text{Ce}^0 + \text{CO}_2 \rightarrow \text{CeO}_2 + \text{C}$  (Reaction 3).



**Figure 5:** Scheme of the CO<sub>2</sub> reduction process constituted by various reactions (1-4), based on Raman measurements. Reproduced from [84], with permission. Copyright 2019, Springer Nature.

The synthesized carbons were tested for possible applications. For example, as a two-electrode capacitor they exhibited a maximum capacitance of 250 F·g<sup>-1</sup> at 10 mV·s<sup>-1</sup>, which is comparable to some of the best performing carbon-based supercapacitors in aqueous electrolytes. Therefore, this new type of carbon materials can be of high interest in energy storage, while any carbon monoxide obtained as a by-product could also be used as a feedstock for further industrial processes.

One advantage of using liquid metal-based catalysts to reduce CO<sub>2</sub> to solids is to avoid catalyst deactivation by coking, a relevant topic of the *Carbon* journal. It has been known for some time that carbonaceous deposits deactivate catalysts. Therefore, we would like to clarify the definition of “coke”. In carbon science, this term is associated to a solid rich in non-graphitic carbon which has passed through a liquid or liquid-crystalline state during carbonization [98,99]. The term coined by scientists working on catalysis is rather arbitrary, as they use the term “coke” to name the material originated by decomposition (cracking) or condensation of hydrocarbons on catalysts, whereas the solid product of CO disproportionation ( $2 \text{ CO} \rightarrow \text{C} + \text{CO}_2$ ) is called “carbon” [100]. However, both types

of materials deactivate catalysts by physically covering the catalyst surface, rendering its active sites inactive by mere physical blockage. Recently, liquid metal-based catalysts [101] have been found to be remarkably resistant towards deactivation via coking [102], as their liquid nature hinders adhesion of any produced carbonaceous material to the catalyst surface by van der Waals forces. Indeed, unlike traditional heterogeneous catalysts, liquid metal-based catalysts are highly dynamic and catalysis is believed to proceed at homogeneously distributed metal atoms located at the surface of a liquid metallic phase. Therefore, in this regard, liquid metal-based catalysts are expected to be ideally suited for the continuous CO<sub>2</sub> reduction to solid carbons.

Liquid metal-based catalysts allow excluding the catalyst material and the electrolyte as potential sources of the carbonaceous materials, deriving exclusively from CO<sub>2</sub>. This process takes place at ambient conditions, making it very competitive as it operates with very low energy consumption. The process is different from higher-temperature approaches used to generate carbon materials, such as carbon nanofibers [103], carbon nanotubes [104] dissolved in molten carbonates, or multi-layer graphene on Cu-Pd alloys at 1000 °C under CVD conditions [105], from CO<sub>2</sub>. The solid carbons obtained from CO<sub>2</sub> electrochemical reduction on Ce-containing alloy catalysts at room temperature feature a highly porous superstructure as a result of an agglomerated plate-like morphology with a typical thickness of 3 nm [84]. One can assimilate this type of carbon material, containing about 15 at% oxygen, to many existing high surface area disordered carbons. Even if they do not seem to show characteristics making them unique, these carbons from CO<sub>2</sub> can have important applications in energy storage, catalysis, environmental protection and other fields where their surface plays a crucial role. At the same time, these preliminary findings can contribute to develop an interesting negative emission technology for CO<sub>2</sub> disposal.

## **7. Heteroatom doping of carbons for energy storage**

The properties of carbon materials are often modified or improved by the insertion of foreign atoms, the most exploited ones being oxygen, nitrogen, sulphur, boron, and phosphorous [106]. Heteroatom-doped carbons are among of the most beneficial families of materials used in energy related applications. They are widely utilized for energy storage/conversion, in electrochemical capacitors, fuel cells, and Li-ion batteries. Among the foreign elements, N plays a particularly important role. A small quantity of N (e.g. 1-5%) can act as a percolator improving the electrical conductivity of carbon, whereas an amount exceeding 10% can dramatically increase the resistivity, owing to rise of sp<sup>3</sup> hybridization.

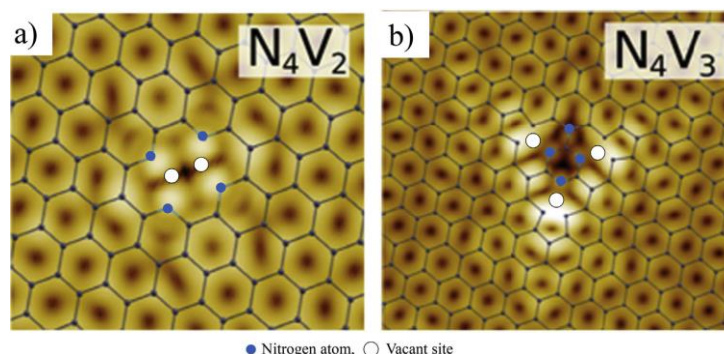
### *7.1 Nitrogen-doped carbon materials*

Doping of carbons with nitrogen atoms greatly advanced during the past decades [107–120]. Nitrogenated carbons can be obtained directly by pyrolysis of N-rich compounds such as melamine [107,108,113–115], polyacrylonitrile [116], polyvinylpyridine [116], nitrates [117], urea, or suitable biowastes. This pyrolytic process results in materials with a large amount of heteroatoms within the carbon network. Alternatively, nitrogen can be introduced by chemical vapor deposition from ammonia [118], pyrrole [119], acetonitrile [109], and pyridine [109]. Conducting polymers such as polyaniline, polypyrrole have also

been used as a N precursor [111], but unfortunately such methods cannot be scaled up. N-doped carbons can also be obtained by post thermal treatment of carbons or carbon electrodes with ammonia [112].

Nitrogen can be incorporated into a central graphitic domain in the form of quaternary nitrogen (N-Q) by replacing a carbon atom in the host lattice. Another form is the pyridinic (N-5), where N atom is placed in the six-atom-ring present at the edges. Pyrrolic N replaces carbon atom instead in five-atom rings. Another N functionality is pyridine with an oxygen atom in the close neighborhood of a nitrogen atom.

The different types of functionalities play an important role in the electrochemical performance. The analysis to identify the different N forms is not simple and not fully understood because of the lack of standard samples and the atomic rearrangements occurring during synthesis. In this context, Yamada *et al.* have simulated the XPS spectra for various types of N-functional groups within carbons, but further experimental studies are necessary to clarify the precise positions of the peaks of the different N-doped carbon materials [121]. Hence, the role of nitrogen doping in electrochemical applications is still unclear. Production of carbons with only one type of N-group is challenging. Such an attempt has been undertaken by the group of Sato [122–125]. Here, carbonization of nitrogen-containing aromatic compounds was performed at 700°C. When 1,7-phenanthroline was used as a carbon precursor, the final product contained 92% of pyridinic nitrogen. The reasons for the formation of this material with a high percentage of pyridinic nitrogen are mainly due to their reduced hydrogenation of this heteroatom [122]. Because of the decomposition of N-functional groups as the temperature increases, lowering the carbonization temperatures by selecting the appropriate precursors is another approach to solely introduce one type of functional group [124,125]. However, the precise location and the exact identification of the chemical form of N within the carbon materials are still challenging [109,126]. For example, observations by scanning tunneling microscopy (STM) confirmed the presence of only pyridinic groups with vacant sites (Figure 6), whereas XPS analysis revealed that the same material was also rich in quaternary nitrogens [126].



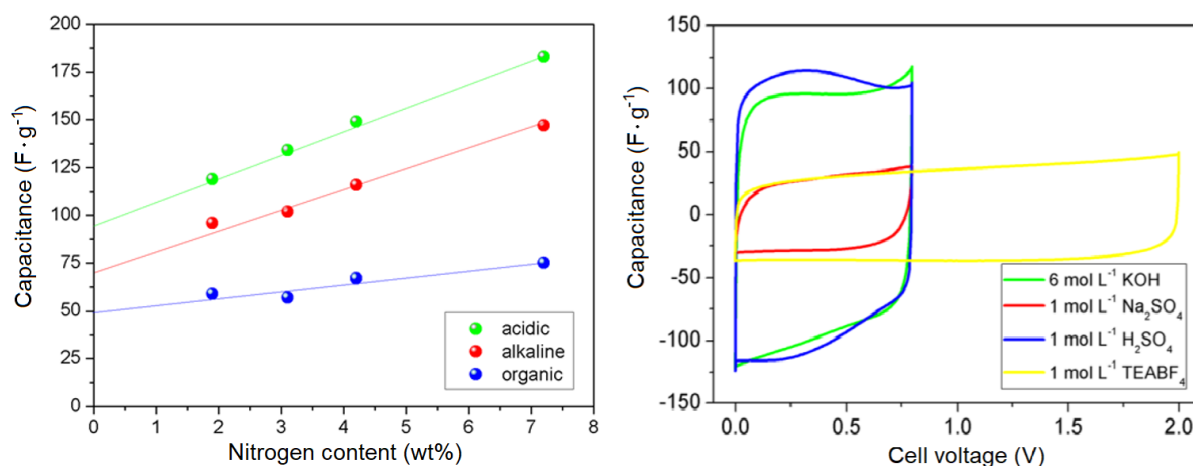
**Figure 6:** Experimental and simulated STM images of four pyridinic atoms with a) two and b) three vacancies. Reproduced from [109] with permission. Copyright 2018, Elsevier.

In summary, a complete chemical description of nitrogen groups embedded within carbon materials is complicated to achieve, and the utilization of complementary techniques together with modeling are indispensable for determining their type and quantification.

### 7.2 Nitrogen-doped carbon materials in electrochemical capacitors

Nitrogen-doped carbons are of interest for the fabrication of electrochemical capacitors. Taking into account the role of conductivity for charge propagation, the N-Q functionality plays an important role. Concerning its electronic state, N-Q is very stable. Indeed, the nitrogen introduction decreases the conduction valence band gap, *in turn*, it increases the conductivity of carbon but it also improves the wettability of the material. A good wettability is indispensable in an electrode for the proper functioning of the electrochemical system.

The increase of capacitance originates from pseudocapacitance effects. Contrary to oxygen functionalities, the increase of the capacitance is not always displayed in the form of peaks but the lack of peaks does not exclude the redox processes. Apart from faradaic reactions, a high capacitance originates from enhanced ion sorption caused by electronic heterogeneity. Voltammograms for electrodes containing N-doped carbons present regular square-like shape and higher currents appear when lowering the HOMO-LUMO gap. Generally, carbon materials enriched with nitrogen have two-fold higher capacitance than pure carbon materials. It was found that the capacitance is proportional to the N% content for carbons obtained from polyvinylpyridine, polyacrylonitrile and their blends with coal tar pitch (Figure 7, left) [116]. A sharp capacitance drop is observed when nitrogen exceeds 10 wt.%. It must be stressed that a beneficial effect of nitrogen has been observed only for acidic and alkaline electrolytes [107,115]. In neutral and organic media this effect is not so visible (Figure 7, right) [115]. Hence, the N-doping strategy of electrode materials should be strictly linked with a choice of the electrolyte.



**Figure 7:** (Left) Capacitance values versus nitrogen content of N-enriched PAN-derived carbons in 1 M H<sub>2</sub>SO<sub>4</sub>, 6 M KOH, 1 M TEA-BF<sub>4</sub> in acetonitrile (PAN, polyacrylonitrile). Reproduced from [116] with permission. Copyright 2014, John Wiley and Sons. (Right) Capacitance of N-doped carbons derived from melamine/formaldehyde blend in various electrolytic solutions. Reproduced from [115] with permission. Copyright 2011, the Royal Society of Chemistry.

Taking into account all possible nitrogen arrangements, it seems that N-Q is the most stable form affecting conductivity, capacitance values, charge retention and high regimes in nitrogenated carbons [110].

### *7.3 Oxygen-doped carbon materials*

Carbon materials always contain oxygen groups in their structure, especially if biomasses are the precursors. As a general rule, a high amount of oxygen results in a high resistivity. It is clear that for electrochemical applications the electrical conductivity is a critical parameter. Hence, carbon forms with an oxygen content over 10% are not useful for any electrochemical application. In this context, research has been devoted to synthesize carbon materials with oxygen functional groups to improve the capacitor performance. However, the reversibility of these redox processes is very moderate, with long-term cycling. Similarly, typical activated carbons rich in oxygen functionalities do not display good characteristics in time. Oxygen in the form of quinone/hydroquinone (Q/HQ) redox functional pair can supply additional capacitance with good cycling. It should be underlined that oxygen groups grafted to carbon (e.g., linked by chemical bonds), present a good long-term cyclability. In this context, Belanger and coworkers demonstrated that redox anthraquinone groups, selectively grafted on activated carbon, exhibit good capacitance performance with cycling [127]. On the basis of these results, future developments should reconsider this strategy in order to obtain carbons rich in redox active Q/HQ pair, operating in aqueous electrolytes.

In summary, heteroatoms doping can endow carbon materials with exceptional properties. The amount and type of heteroatoms and functional groups should be strictly controlled. Quite often 2-5% content already affects positively the electrochemical performance. Therefore, the preparation of very selective N-doping without oxygen is really challenging and further effort in this direction is highly desirable. This might allow the synthesis of new carbon materials with characteristics close to those of noble metals, which are still far from being paralleled. We encourage the carbon scientists to pursue efforts in the design and synthesis of novel carbon forms doped with heteroatoms with a controlled chemical structure in order to clearly understand the reasons of enhanced electrochemical performances.

## **8. Carbon nanomaterials for biosensors**

Carbon is one of the most frequently used elements in the fabrication of electrochemical biosensors. This is mainly due to its chemical inertness over a wide potential range, its surface chemistry, and its excellent electrical conductivity [128]. In macroscopic shapes, carbon already shows a rich variety of structures. Standard biosensor electrodes can be based on e.g. glassy (or vitreous) carbon, (pencil) graphite, doped diamond, carbon paste, or carbon black. Interestingly, nanosized carbons add new optical and electronic properties and thus provides more than just an enhanced specific surface [129].

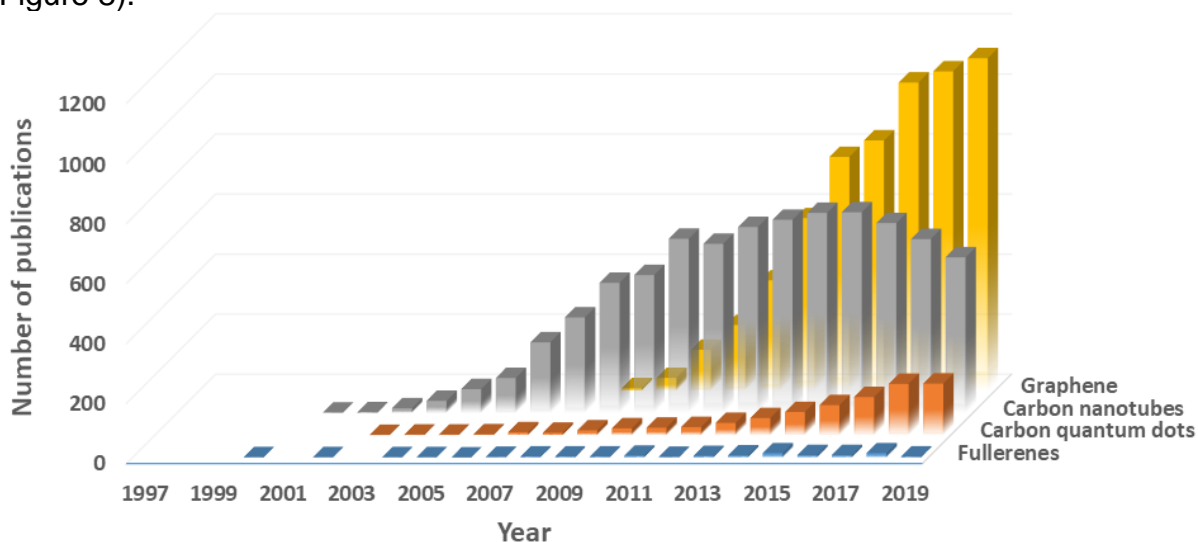
As discussed above, existing carbon materials can be functionalized using well-established reactions to attach chemical functionalities able to immobilize bioreceptors [130]. Electrochemical functionalization is appropriate since carbon materials are principally used as electrodes in electrochemical biosensors. Very efficient is the

electrogeneration of thin functional films based on polypyrrole, polyaniline, or polythiophene; their monomers can be modified with chemical functions for the immobilization of biomolecules [131]. The electrochemical reduction of diazonium salts is another widely used functionalization method for carbon materials [132]. Alternatively, the hydrophobic character and extended  $\pi$ -system of  $sp^2$  nanocarbons allow noncovalent functionalization or the simple deposition of biocomposite or bioreceptor layers, which are sufficiently stable in aqueous media [133].

Thus, in order to choose the most efficient immobilization strategy for biomolecules it is necessary to understand the surface chemistry and defects of the carbon surface, the chemical nature of the bioreceptor, and the analyte to detect. For sensor affinity, which is defined by the specific recognition between antibodies and antigens or corresponding DNA strands, the receptor DNA or protein has to be accessible to the counterpart. For enzymatic biosensors, the analytes consist generally of small organic molecules (glucose, pesticides; etc.) or ions. Here, the entrapment of the bioreceptor in a polymer matrix, permeable to the analyte, is a well-established and efficient immobilization technique [134].

Biological receptor units can be classified in protein receptors (antibodies, antigens, enzymes) or nucleic acid-based receptors (DNA, aptamers). Proteins provide naturally amine and carboxylic acid functions, which can serve for the covalent grafting on modified carbon surfaces via peptide coupling. The phosphate backbone of polynucleotides or the  $\pi$  system of the nucleic acids already offers several possibilities to immobilize DNA. However, since the receptor DNA is in most cases synthetic, appropriate chemical functions for suitable immobilization should be considered according to the chosen signal transduction technique.

The evolution of published articles for the most attractive carbon nanomaterials (e.g., fullerenes, carbon quantum dots, carbon nanotubes, and graphene) in the context of biosensing applications reflects the interest of the scientific community for these materials (Figure 8).



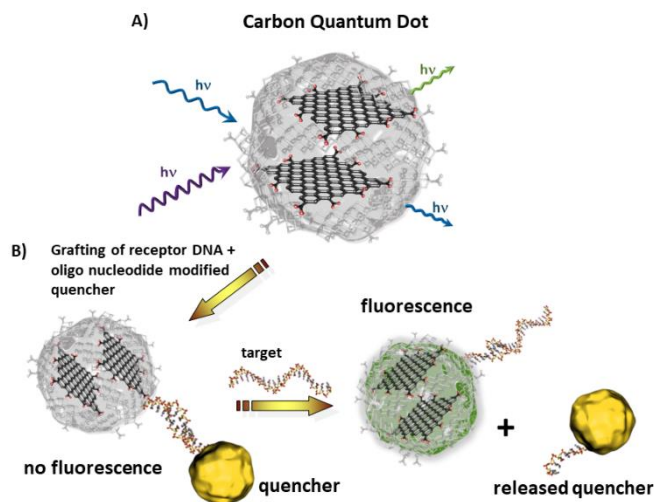
**Figure 8:** Graph of the number of published scientific articles per year since 1997 dealing with carbon nanomaterials used in biosensors (source: web of science; keywords: biosensor and fullerenes; biosensor and carbon quantum dots; biosensor and carbon nanotubes; biosensor and graphene, December 2019).

### 8.1 0D carbon: Fullerenes and carbon quantum dots

C<sub>60</sub> is considered the first discovered carbon nanomaterial and, due to the finite-size structure, it is a single molecule and not a material. It can be electrochemically reduced up to six times and this particular redox behavior motivated scientists to use it as probe for (bio)sensing applications [135]. However, the potentials of the different redox waves are not suitable for bioelectrochemical studies in buffer solutions. Therefore, C<sub>60</sub> is mainly used as nanosized scaffold and quite often in combination with other nanostructured materials to increase the surface area and thus receptor loading [136]. One major issue for C<sub>60</sub> is that it is completely insoluble in aqueous media and has very low solubility even in organic solvents. There are many possibilities to functionalize C<sub>60</sub> in order to improve its usability in the construction of bioassemblies [137]. The low yields and time-consuming isolation of these C<sub>60</sub> derivatives makes it little competitive when compared to other nanomaterials as components in biosensor setups. This explains the reduced number of publications in the biosensor field (Figure 8). Nonetheless, the optical and redox (acceptor) behaviors are still of interest for plastic solar cells or optical limiting glasses [138].

Carbon-based quantum dots (CQD) can be obtained in various contexts of carbon research. A new type of CQDs was discovered by examination of the residues obtained from the arc discharge synthesis of SWCNTs. CQDs are polydisperse fluorescent nanosized particles with isolated domains of conjugated graphene sp<sup>2</sup> carbon surrounded by diamond like sp<sup>3</sup> carbon. Contrary to their inorganic QD counterparts, which can absorb light in a large wavelength range and have a narrow emission spectrum, dependent on the particle size, the emission wavelengths of CQDs can be tuned by the excitation wavelength. Although the excitation wavelength-dependent fluorescence phenomenon is still not totally understood [139].

CQDs became in the recent years one of the emerging carbon nanomaterials for biosensing applications due to the possibility of biocompatible functionalization, low-cost synthesis, and reduced toxicity [140]. The transduction principles are similar to those of QDs where an example is illustrated in Figure 9. Last generation CQDs show even comparable quantum yields. However, the CQDs still lack of homogeneity to produce defined narrow emission spectra. The quantum efficiency and synthesis yields need to be improved [141]. The discrete evolution of the published articles using CQDs for biosensing applications reflects these issues. Considering the tremendous advances in the field of CQD development, the full potential of CQDs will be reached when the tunable photoluminescence properties will be better understood, thus allowing the development of improved scalable production methods of CQDs with controlled sizes and properties.



**Figure 9:** A) Sketch of a CQD illustrating the graphene and  $sp^3$  domains. B) Representative scheme of a standard transduction principle for DNA detection using a receptor DNA modified CQD coupled with an oligonucleotide modified quencher (e.g. gold nanoparticle). The affinity between receptor and target DNA is much stronger than with the oligonucleotide leading to the release of the quencher and the reappearance of CQD fluorescence.

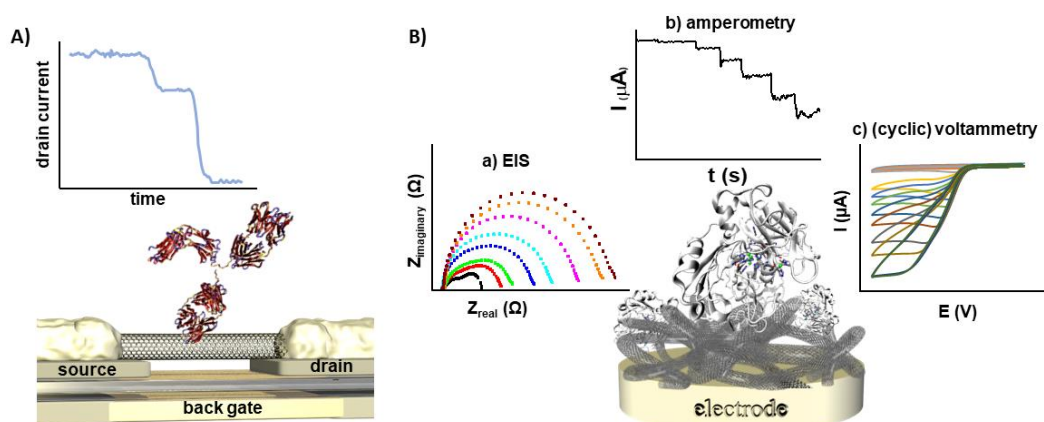
A subclass of CQDs can be obtained by upconverting carbon nanoparticles, which absorb light in the near-infrared (NIR) region and emit at shorter wavelengths. Their possible applications are envisioned as new types of biosensors, but research in this field is still at an early stage, and the upconverting properties of this carbon nanomaterial are still controversially discussed by the scientific community [142].

Carbon quantum dots are materials that the *Carbon* journal is covering not only in biosensing, but also in other fields. The use of new precursors in their synthesis is not generally considered of sufficient novelty for publication in *Carbon*, but we encourage to explore more deeply the new properties and tune the dimensions and the chemical structures and the composition of these carbon nanoparticles to achieve higher performances in the different areas of applications.

### 8.2 1D Carbon: Carbon nanotubes

For almost two decades, CNTs have been considered as the carbon nanomaterial of choice for biosensing applications [143]. These thin and long nanowires with excellent conductivity are principally used as bulk electrode material since a simple drop casting process already forms highly porous structures with low-contact resistance with the underlying macroscopic electrode. The interest in this material is also related to the developed biofunctionalization methods that allow the reliable and secure immobilization of a high amount of accessible receptor units in the porous matrix. The development of large-scale production methods [144] and the availability of low-cost CNTs with good qualities further pushed CNT biosensor research to a higher level since different batches of mass produced CNTs have almost identical properties leading to much more reproducible and uniform results. Another advantage of carbon nanotubes is that they can be processed as bulk to form coatings, sheets, or fibres as well as individual

components in transistor devices (Figure 10). There are however still some challenges in the integration of CNTs in transistors. The controlled alignment, positioning, the varying conductivity of individual CNT devices represent the major drawbacks for large scale production of identical devices [145]. These are the reasons why CNTs are mostly used as electrode material in macroscopic shapes where inhomogeneities of diameter, lengths and conductivities are averaged. CNTs are thus principally used for electrochemical biosensing.



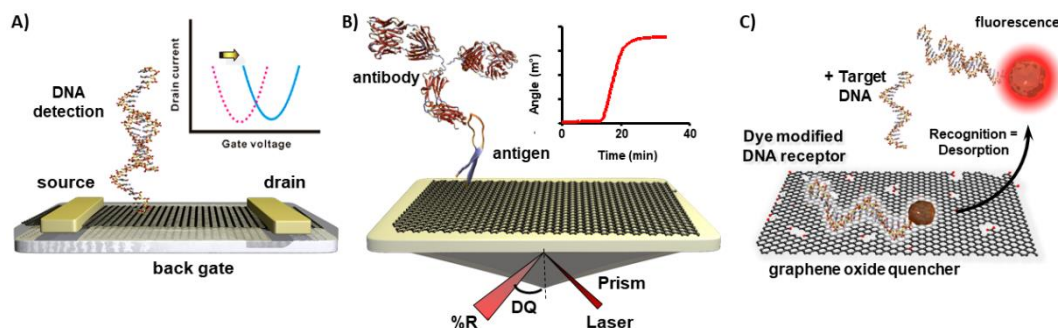
**Figure 10:** A) Illustration of a CNT biosensor in a transistor setup and the profile of signal capture. B) Electrochemical biosensor using CNTs as deposits or coatings and the different possibilities of electrochemical transduction: electrochemical impedance spectroscopy (EIS), amperometry, and voltammetry.

CNTs seem to progressively lose their academic interest for biosensing applications (Figure 8). Although we believe that there is still room for improving the performances of such devices, the challenges should address the controlled synthesis of tubes with unique chirality, precise diameter and length.

### 8.3 2D carbon: Graphene

The reasons for the growing success of graphene in the biosensing field comprise its excellent electronic and optical properties, the inexpensive availability at lab scale, and many established functionalization methods developed for CNTs that can be easily transferred to graphene [146]. The first reports using graphene for biosensing applications are quite similar to those using CNTs [147], but the beneficial effect of these two carbon materials for different types of biosensing principles could be clearly identified after the first graphene hype [148]. While CNTs are particularly appropriate for electrochemical biosensing, monolayer graphene has its advantages as sensing elements in transistor devices thanks to a well-controlled deposition and transfer techniques. Graphene has also particular plasmonic properties which enhance the signal capture in a surface plasmon resonance (SPR) setup. Graphene and graphene-based materials like (reduced) graphene oxide have demonstrated to possess some interesting properties for DNA sensing devices (Figure 11). Contrary to CNTs, DNA, aptamers, or oligonucleotide receptors can adsorb reversibly on graphene transducer surfaces [149]. When the receptors are modified with a fluorescence dye, graphene materials work as quenchers

for these dyes acting as a non-radiant energy acceptor. The recognition event with the target leads to desorption of the dye modified receptor and recovers the fluorescence of the dye giving a detectable signal.



**Figure 11:** Most promising biosensor transduction techniques using graphene as interface or amplifier. A) Transistor via observing conductivity or Dirac point voltage changes. B) SPR sensing with graphene amplified signal capture. C) Graphene oxide for reversible adsorption of DNA in optical transduction mode.

Graphene and related carbon materials are without doubt very promising for biosensing applications but it should not be considered as the ultimate system for all types of biosensors. High-quality mass-produced graphene needs to be available to assure reproducibility and better comparability of the biosensor performances [150].

Nanostructured carbons remain a privileged material for biosensing applications. The absence of standardized production method is the major drawback for carbon nanomaterials in this type of applications since precision, reliability, and reproducibility are more important factors for the health sector than sensing performances and limits of detection. However, fundamental and applied studies developing new types of biosensors are within the scope of the Carbon journal and will continue to be covered.

## 9. Activated carbon in medicine: traditional and modern trends

### 9.1 Oral adsorbents

Activated carbon (AC), often known as charcoal, has been used in medicine for at least 3.5 millennia [151]. The original practices of administering AC as an oral adsorbent to treat intestinal disorders and as a dressing for malodorous wounds remain among its modern mainstream biomedical applications. To date, the largest segment of any carbon material use in medicine is the treatment of acute poisoning. The efficiency of single-dose or multi-dose AC oral administration has been officially confirmed by several authoritative position statements on the basis of meta-analysis of numerous publications reported on the poisoned patient management, and it has been concluded that only AC provides an efficient treatment of acute poisoning [152]. The attractiveness of using AC as a universal antidote is due to its large adsorption capacity towards most organic substances, which are usually a cause of self-inflicted deliberate or inadvertent intoxication (medical drugs). In recent years, several reports, to mention but a few, on the successful use of AC as an oral adsorbent in the treatment of large numbers of patients exposed to buprenorphine (used to treat narcotic dependence) [153], antidementia drugs [154], diarrhea

management [155], mushroom poisoning [156] and paraquat (herbicide) poisoning [157] have been published. In the latter case the authors stressed that the administration of AC within the first hour of paraquat ingestion was essential since there is no specific treatment for paraquat poisoning. A retrospective study of managing paracetamol poisoning in children aged 0-6 years revealed that AC treatment was used in 87% of cases, which was even higher than the use of the paracetamol specific antidote N-acetylcysteine [158]. There have been surprisingly few clinical trials aimed at studying possible therapeutic effects of single- or multiple-dose AC administration in the poisoning treatment, and the conclusions drawn from such trials have been controversial.

The lack of controlled clinical trials in relation to the use of oral AC for poisoning management, at least partly, is due to the unique 'case of AC', which is the fact that it has been accepted as an antidote against poisoning on the basis of a single, very famous, historical case reported in 1852 when a chemist, Pierre-Fleurus Touéry swallowed a 10-fold lethal dose of strychnine along with AC and showed no negative signs of poisoning in front of the French Academy of Medicine [159]. This precedent of establishing the therapeutic effect of a drug on the basis of a single fact was accepted even in a court case [151]. The second reason is the difficulty of arranging such a trial because of the rare nature of the poisoning by the same substance of a large group of patients and ethical considerations regarding the selection of the control group if there is no known antidote against a particular poison [152]. Regardless of the conclusions of clinical trials or single case reports about the efficacy of the therapeutic use of oral AC, the authors confirmed that it is safe to use and could be even administered to pregnant women as it does not metabolize or release any substances inside the body. Since it is easy to administer and has rare side-effects [152], AC can be used by medical non-professionals, which may improve the efficiency of AC treatment being given as early as possible after poisoning prior to a hospital admission. The judgement about potential effectiveness of AC in the treatment of acute poisoning is likely to depend on the existence or rather the absence of specific antidotes, previously reported clinical results, and on their adsorption capacity towards a particular substance in question measured *in vitro* rather than on comprehensive clinical trials. Fast removal of the poison from the gastrointestinal tract is a logical requirement for the medical treatment and its elimination by adsorption with AC provides that. Administration of AC is a cost-effective treatment, and it is very likely that in the near future a number of developing countries will organize production of medical grade AC from locally available sources such as rice husk, nut shells, fruit stones and others. The poor palatability of AC and sometimes its appearance (black powder or slurry), however, remain an issue [160]. Various attempts have been made to improve AC tolerability especially by children, such as adding flavoring agents and sweeteners. It has been suggested that adding such substances may reduce the adsorption capacity of AC and hence its efficacy [161]. It is likely that the tablet or a cookie form of oral AC will be better tolerated by patients than a slurry or powder formulation [160].

Although the treatment of acute poisoning is the main medical application of oral AC, the potential of using AC for management of chronic poisoning has also drawn substantial attention. Whereas acute poisoning is caused by exogenous toxic substances or drug overdose, chronic poisoning can occur as a result of the internal organ failure, most

common being chronic kidney disease (CKD). Kidneys play the role of a filter in the body removing waste products from blood. If their functions are reduced, the waste products accumulate in the blood causing chronic self-poisoning. The global statistical data on CKD are alarming and show a 32% increase in mortality figures of patients died from the end-stage renal disease (ESRD), the final stage of CKD, between 2005 and 2015 (the latest available data) [162]. Patients who developed ESRD receive supportive dialysis treatment and a minority get a kidney transplant. The dialysis treatment poses an enormous economic burden accounting for 2-3% of healthcare budget in developed countries although the number of such patients is lesser than 0.03% of the total population [163]. Beside the economic implications, patients on dialysis have a lower quality of life. In the developing countries the situation is worse. It has been suggested that regular administration of oral charcoal to CKD patients could delay the need for dialysis thus reducing the cost of supportive treatment. Although this idea was probably first suggested and tested over 35 years ago using N-containing activated carbon made from vinylpyridine-divinyl-benzene copolymer [164], the systematic research of the efficacy of oral charcoal treatment of CKD patients has been carried out with the spherical activated carbon AST-120 produced by Kureha Co (Japan), which was approved for such use in Japan and several other countries in Asia [165]. Despite numerous studies which confirmed that oral administration of AST-120 delays the need for dialysis treatment, the latest large-scale multi-center randomized clinical trials have not been able to demonstrate convincingly the advantages of this therapy in delaying CKD progression versus the control group. Nevertheless, it has been shown that oral charcoal administration reduces accumulation of indoxyl sulphate, one of the major uremic toxins, in the blood serum of patients, and further, more comprehensive clinical trials have been suggested [165]. The ability of AC to adsorb aromatic amino acids such as tryptophan and phenylalanine is well known, and their elimination from gut could disrupt the synthetic path leading to formation of such uremic toxins as indoxyl sulphate and p-cresyl sulphate and thus have a positive effect on CKD patients, particularly taking into account that these toxins are protein-bound in the blood and the efficacy of dialysis in their removal is poor.

The range of medical applications of oral AC administration might enhance with introduction of micro/mesoporous carbon adsorbents. Whilst for the treatment of acute poisoning microporous AC have sufficient adsorption capacity towards small molecules such as medical drugs, which are the most common cause of exogenous poisoning, some severe intoxications could be attributed to bacterial toxins released by pathogenic flora. These toxins are large biomolecules and the adsorption capacity of microporous AC towards them is low. The fact that oral charcoal administration could be used for diarrhoea management, which is often caused by bacterial infection, as a supplementary treatment [155], supports the need for the development of mesoporous AC for medical applications.

## *9.2 Carbon materials in extracorporeal medical devices*

Extracorporeal blood purification by adsorption – haemoperfusion (HP) - is used less commonly than other extracorporeal techniques such as dialysis and filtration. The key aspects of extracorporeal techniques are summarized in Table 1.

**Table 1:** Efficacy of extracorporeal blood cleansing systems (adapted from [151]).

Substance removed	Haemodialysis	Haemofiltration	Haemoperfusion over AC		
			Coated	Uncoated microporous	Uncoated mesoporous
Water	High	High	Negligible		
Small MW solutes	High	High	Medium-high*	High*	High*
Ionic	Medium-high	Medium- high	Low		
Large and medium MW solutes	Low	Low-medium	Low	Low-medium	High

\* With exception of urea, adsorption of which is low.

The main reason for this is that in the commercial HP cartridges the adsorbent granules are coated with a semipermeable membrane to improve their haemocompatibility. Such a coating makes the internal carbon surface inaccessible to large molecules and slows down the adsorption rate of small molecules due to the diffusion limitation of the solute transport through the membrane [166]. Consequently, HP over coated AC is used almost exclusively for the treatment of acute poisoning with low molecular weight substances (MW usually <300 Da) when there has been a significant delay with oral AC administration after the exposure and the toxic substance has been mostly transferred into the blood stream [167]. Nevertheless, the adsorption technique has some intrinsic advantages over dialysis and filtration [168]. It does not require the use of replacement fluid to restore and buffer the blood volume; it can potentially remove substances within a wide range of MW, which cannot be achieved in dialysis or filtration even with a large nominal MW cut-off because the membrane pores are quickly blocked by adsorbed proteins; and there is no need to use large volumes of high purity water for extracorporeal treatment. However, to realise these advantages, the adsorbent should be both uncoated and sufficiently haemocompatible. This problem has been solved by manufacturing AC from synthetic porous polymer precursors such as vinyl-pyridine-divinyl-benzene copolymer (AC SCN or SKN) and phenol-formaldehyde copolymers (AC MAST) [164,169]. Extensive *in vitro* and *in vivo* studies have proven that the uncoated SCN (and its higher activated derivative, HSGD) and MAST spherical carbon microbeads have haemocompatibility comparable to the commercial coated AC [169,170].

Recently, new nanocarbon based composite adsorbents have been developed for their use in haemoperfusion (Table 2). The attractiveness of such materials is their large external surface area which is easier accessible to the solutes than the surface inside AC pores. They showed good biocompatibility in the experiments *in vitro*. No release of microparticles has been reported indicating that these materials could be used uncoated in direct contact with blood. They demonstrated fast adsorption kinetics and substantial adsorption capacity for middle and large MW metabolites comparable or exceeding that of mesoporous AC.

**Table 2:** New nanocarbon materials (NCM) and composites tested *in vitro* as adsorbents for haemoperfusion

Adsorbent*	Adsorbate	Comments	Ref
CNT-chitin	Bilirubin	Spherical microbeads	[171]
CNT-PVA	Endotoxin	Microspheres, aminated CNTs	[172]
rGO-chitosan	Bilirubin	Aerogel compressed in a disc	[173]
GnP-PTFE composite	Inflammatory cytokines IL-8, IL-1 $\beta$ , IL-6, IL-10 and TNF- $\alpha$	Granulated	[174]
GO-chitin composite	Bilirubin	Aerogel beads	[175]

\*PTFE – polytetrafluoroethylene; PVA – polyvinyl alcohol

It is important to note that dialysis is not capable of removing significant amounts of such metabolites as cytokines, which are involved in the pathogenesis of some life-threatening conditions such as septic shock and multi-organ failure or bilirubin associated with liver diseases such as acute liver failure characterized by high mortality rates [176]. It is anticipated that the research on the use of haemocompatible mesoporous carbon materials in extracorporeal devices will progress to pre-clinical and clinical studies since there is sufficient evidence suggesting that removing middle and large MW metabolites is beneficial to patients. The mesoporous structure of carbon adsorbents could also facilitate removal of protein bound drugs; there are many low MW hydrophobic drugs and other metabolites, which do not circulate in blood in a free molecular state but are albumin bound. Taking into account that the MW of human serum albumin is ca. 67 kDa it means that such molecules cannot be removed from blood by dialysis [177]. The most likely application of adsorption devices is going to be in-line with dialysis to increase its efficacy rather than using HP as a replacement to dialysis. Carbon adsorbents will play an important role in a Wearable Artificial Kidney (WAK). The concept of WAK is not new and it was commercially produced for a number of years as REDY system. REDY system had a number of issues with its exploitation and eventually it was withdrawn from the market. Recently, new attempts have been reported in designing a new WAK, which is lighter and more efficient than the previous designs, and AC remains an essential component of the adsorption system used in recycling of the dialysate [178]. Mesoporous carbon adsorbents could be advantageous compared to microporous AC currently used in WAK. A novel concept of HP adsorption cartridge has been suggested [169,177]. It is based on a monolithic AC column with a honeycomb structure; preliminary assessment of its haemocompatibility showed a significant improvement on the granulated AC cartridge as it has a much lower damaging effect on red blood cells due to the laminar blood flow through the monolith transport channels rather than turbulent flow through the HP column packed with AC granules.

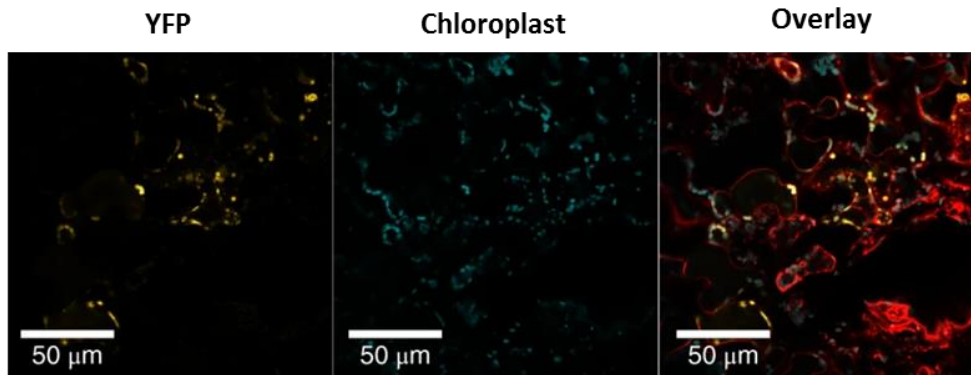
Despite the efforts aimed at discovering substance-specific antidotes and treatment modalities against particular poisons, activated carbon will continue to retain its leading position as a universal antidote administered orally or in haemoperfusion. It is certain that the research and development of medical applications of AC will continue its growth, and *Carbon* will continue to consider new forms of AC within its topics.

## 10. Nanocarbons as plant biology tools

The interface between plant organelles and non-biological nanostructures has the potential to impart organelles with new and enhanced functions. This is a new area of research with great potential. It has been recently shown that SWCNTs passively transport and irreversibly localize within the lipid envelope of extracted plant chloroplasts, promote over three times higher photosynthetic activity than that of controls, and enhance maximum electron transport rates [179]. The SWCNT–chloroplast assemblies also enable higher rates of leaf electron transport *in vivo* through a mechanism consistent with augmented photoabsorption. Nanobionics engineering of plant function may contribute to the development of biomimetic materials for light-harvesting and biochemical detection with regenerative properties and enhanced efficiency.

Plant nanobionics can be also developed to embed non-native functions to plants by interfacing them with specifically designed nanoparticles. For example, living spinach plants have been engineered to serve as self-powered pre-concentrators and autosamplers of analytes in ambient groundwater and as infrared communication platforms that could send information to a smartphone [180]. The plants employ a pair of near-infrared fluorescent nanosensors—SWCNTs conjugated to the peptide Bombolitin II to recognize nitroaromatics. The real-time monitoring of embedded SWCNT sensors also allows residence times in the roots, stems and leaves to be estimated. These results demonstrate the ability of living, wild-type plants to function as chemical monitors of groundwater and communication devices to external electronics at standoff distances.

Plant genetic engineering is another important tool used in current efforts in crop improvement, pharmaceutical product biosynthesis and sustainable agriculture. However, conventional genetic engineering techniques target the nuclear genome, prompting concerns about the proliferation of foreign genes to weedy relatives [181,182]. In two recent studies chemically-functionalized SWCNTs have been complexed with plasmid DNA and used for efficient diffusion-based delivery of the gene into chloroplasts of different plant species [181] (Figure 12), leaves and protoplasts of intact plants [182]. This nanoparticle-mediated transgene delivery tool provides practical advantages over current delivery techniques as a potential transformation method for mature plants to benefit plant bioengineering and biological studies. This technology is still in its infancy and other carbon nanomaterials able to internalize biomolecules into difficult to transfect plant cells should be explored.



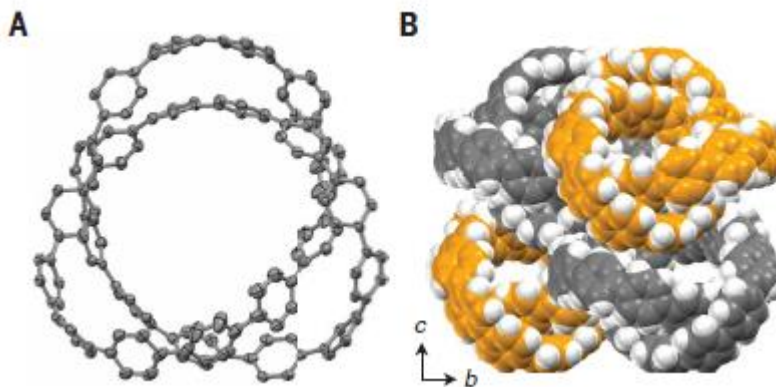
**Figure 12:** Chloroplast-selective gene delivery and transient expression, as evidenced by YFP expressions from plasmids delivered by chitosan-functionalized SWCNTs into mature 3-week arugula leaf. Confocal image was taken 2 days' post-infiltration. Adapted from [181] with permission. Copyright 2019, Springer Nature.

## 11. Concluding remarks

In this Carbon Perspective 2020 we briefly covered selected and recent developments in nanoscale graphitic carbon materials and more traditional carbons in order to highlight how they all contribute to the development of future technologies and will be continuously considered for publication in the *Carbon* journal. When making a decision to publish a paper in *Carbon*, we reiterate that the level of novelty should remain the guiding principle both for reports on fundamental carbon science and applied carbon materials. We emphasize that a precise description of the chemical structure of each new carbon material should also be the driving principle necessary to completely understand the properties of each carbon form. It is clear that it is very challenging to prepare materials with a defined chemical structure, particularly using top-down approaches. Bottom-up synthesis allows better control but suffers often of limitation in terms of scalability.

Few recent examples of bottom-up synthesis of new carbon structures might be of inspiration to design new carbon forms, particularly 3D systems. In line with our 2018 Perspective on 2D nanoribbons [2], a bottom-up strategy has been developed to move into the next generation and make this form of carbon tridimensional [183]. A multifunctional porous graphene nanoribbon has been synthesized by tuning the size of the pores with atomic precision down to 1 nm. Endowed of a highly anisotropic electronic structure, this new carbon material can be exploited as a versatile semiconductor for sieving and sensing ions and molecules in next generation FET-sensors. Another interesting contribution describes the synthesis of cyclo[n]carbons, a family of new carbon allotropes that are in practice highly reactive. Cyclo[18]carbon was prepared using atom manipulation on bilayer NaCl on Cu(111) at 5 kelvin. More precisely, cyclo[18]carbon was obtained from the elimination of carbon monoxide from its cyclocarbon oxide precursor and it is characterized by a polyynic structure with alternated triple and single bonds. Atom manipulation applied to the preparation of such new forms of carbon opens the way to the synthesis of other carbon-rich materials from the coalescence of cyclocarbon molecules [184]. In the search of new 3D structures made only of carbon atoms, a molecular trefoil knot consisting of para-connected benzene rings was recently achieved

[185] (Figure 13). Although considered rigid, the topologically chiral trefoil knot has rapid vortex-like motion in solution even at  $-95^{\circ}\text{C}$ . This characteristic dynamic behavior will certainly motivate future developments of this new type of molecular nanocarbons, for example, in the field of molecular machines as recently predicted in a report where a series of carbon nanotube knots of increasing complexity were theoretically found stable [186].



**Figure 13:** Structure of the all-benzene knot. (A) ORTEP drawing of the knot with thermal ellipsoids set to 50% probability. Hydrogen atoms and solvent molecules are omitted for clarity. (B) Packing structures of the knot; carbon: gray or orange; hydrogen: white. Solvent molecules are omitted for clarity. Adapted from [185] with permission. Copyright 2019, AAAS.

Another challenge is to combine 1D carbon nanotubes with 2D graphene in a controlled manner [187]. Theoretical work suggests that covalent bonds between these two carbon materials might have enhanced heat dissipation properties. Indeed, freestanding 3D MWCNTs on graphene have the capability of additional cooling effect. The fine control of the nanotube vertical growth on planar graphene was achieved by CVD and the covalent bonds between the two graphitic carbon forms were demonstrated microscopically and numerically. This hybrid material is able to significantly decrease the temperature at hot spots, demonstrating that the combination of 1D and 2D carbon systems has great potential for future thermal control applications.

These three examples highlight how challenges in carbon science can stimulate the creativity of chemists, physicists, biochemists, and materials scientists toward the discovery of novel all-carbon molecules with extraordinary properties. Finally, we want to emphasize the importance of assessing the impact of all carbon on health and environment. Our journal continues to cover these topics, provided that the carbon forms play the major role in the reported findings.

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