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C – Carbon: an Essential Element
The Versatility of Carbon:
Custom-Made Nanostructures

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C – Carbon: an Essential Element

The Versatility of Carbon: Custom-Made Nanostructures

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ABSTRACT

In spite of being one of the simplest elements in the Periodic Table, carbon can form an enormous variety of stable structures. In fact, there is a whole branch of Chemistry dedicated to its compounds. On the other hand, there is also a branch of Materials Science dedicated to the multiple forms of the element as a material. Diamond (sp^3 hybridization) and graphite (sp^2 hybridization) are the two ordered carbon allotropes known since ancient times. The discovery of the fullerenes in 1985, followed by the observation of carbon nanotubes in the early 1990s', marks the beginning of the new era of carbon nanomaterials. These include both *nanosized* carbons, as well as *nanostructured* carbons, most of them exhibiting the graphitic structure. The edges of the graphene layers and structural defects provide reactive sites where various types of surface functional groups can be formed. *Doping* is also possible, when carbon atoms in the graphite lattice are replaced by heteroatoms, such as nitrogen or boron. Thus, in addition to controlling the texture and structure of these materials, we are also able to tune their surface chemical properties, allowing the design of *custom-made* carbons for specific applications. The methodologies used for the synthesis of these carbon nanomaterials will be reviewed, and selected applications will be discussed.

1. FROM CARBON ATOMS TO CARBON MATERIALS

Carbon is the element number 6 in the Periodic Table, and its corresponding ground state electronic configuration is $1s^2 2s^2 2p^2$. All four orbitals of the outer shell (one s- and three p- orbitals) are involved in bonding, as they form hybrid orbitals: either two sp - and two p- orbitals; three sp^2 - and one p- orbitals; or four sp^3 - orbitals. The hybrid orbitals are involved in σ -bonds, while the p-orbitals are involved in π -bonds [1].

The four sp^3 - orbitals are oriented in a tetrahedral arrangement, forming angles of 109.5° . This is the type of hybridization found in C compounds involving only single bonds, such as CH_4 . Covalent bonding between carbon atoms with this configuration leads to the diamond structure.

The three sp^2 - orbitals form angles of 120° in a planar trigonal arrangement. This type of hybridization is found in carbon compounds with double bonds, and in carbon materials with the graphitic structure. Graphite consists of stacked layers of carbon atoms covalently bonded in a hexagonal lattice (graphene layers), the layers being held together by weak van der Waals forces.

The two sp - orbitals are opposed (angle of 180°) leading to a linear molecular geometry, as found in compounds with triple bonds, such as acetylene. The corresponding carbon allotrope (carbyne) would consist of an infinite linear chain of carbon atoms, either with alternating single and triple bonds, $-C\equiv C-C\equiv C-$ (polyyne structure), or with only double bonds, $=C=C=C=C=$ (cumulene structure). These structures are the subject of intense research, but they are highly reactive and unstable, and do not exist in nature (at least in pure form).

Diamonds may be "*a girl's best friend*" (Marilyn Monroe dixit), but it is the graphitic structure that dominates the industrial applications of carbon materials. The most important carbon products, in terms of their global consumption and market value, are listed in Table 1, together with their main applications. These carbon products represent a global market value in excess of 250×10^9 US dollars per year.

Table 1

The most important products of the carbon industry

Product	Consumption (Mt/y)	Market value (10 ⁹ \$/y)	Main application
Metallurgical coke	> 350	> 200	Production of iron in the blast furnace
Prebaked anodes	> 30	> 10	Aluminium smelting
Carbon black	> 15	> 15	Filler for rubber (tires)
Graphite electrodes	> 1	> 15	Steelmaking in the electric arc furnace
Activated carbon	> 3	> 5	Adsorbent
Carbon fibers	> 0.3	> 6	Composite materials

2. THE DAWN OF CARBON NANOMATERIALS

The discovery of C₆₀ (Buckminsterfullerene) by Harold Kroto, Robert Curl and Richard Smalley¹¹, in 1985 [2], triggered an intense research activity in the area of carbon nanostructures. In fact, C₆₀ is one member of a whole family of fullerenes, ranging up to giant molecules such as C₅₄₀. Fullerenes are molecular solids, consisting of covalently bonded carbon atoms, forming polyhedra with hexagonal and pentagonal faces. In 1991, while synthesizing fullerenes by arc discharge, S. Iijima reported the formation of tubular structures consisting of several concentric graphene layers (multiwalled carbon nanotubes, MWCNTs) [3]; two years later, the observation of single-walled carbon nanotubes (SWCNTs) was reported almost simultaneously by two independent teams [4,5]. These findings are usually highlighted as marking the birth of carbon nanomaterials, but this is really not true. Indeed, there are several reports dating back to the 1950's showing carbon structures that can be unmistakably identified as MWCNTs, although they were not called "nanotubes" at the time [6,7]. Such materials were then described as carbon (or graphite) filaments, sometimes as carbon "whiskers". This area of research became very active in the 1970's, when various groups attempted to understand the mechanisms of carbon formation from hydrocarbons on metal surfaces and catalysts. Considerable insight into the subject was achieved when it became possible to follow the reaction continuously. L.S. Lobo used a microbalance to study carbon formation on different metals, and found that only Ni, Fe and Co were active catalysts; moreover, he observed that they were not deactivated during the process. Based on accurate kinetic measurements, Lobo proposed a mechanism that involved the diffusion of carbon through the metal, driven by a concentration gradient; thus, carbon would precipitate at the back of the metal crystallites, which would therefore be carried on top of the growing deposit, keeping their surface available for reaction and explaining the constant rates of carbon formation observed [8,9]. At about the same time, R.T.K. Baker developed a controlled atmosphere electron microscopy (CAEM) technique that allowed to observe the catalyst *in-situ* under reaction conditions. While studying the Ni catalyzed decomposition of acetylene, he recorded the growth of carbon filaments

¹¹ These three scientists received the 1996 Nobel Prize in Chemistry for the discovery of the fullerenes.

carrying the metal particles on top. He proposed basically the same mechanism as Lobo, but invoked a temperature gradient (from the exothermic acetylene decomposition) as the driving force for carbon diffusion through the metal particles [10]. This assumption is obviously wrong: a temperature gradient drives heat transfer, not mass transfer; similar growth of carbon filaments is observed when the hydrocarbon decomposition is endothermic (e.g., in the case of methane); moreover, it violates the causality principle [11].

In general, the carbon filaments observed and reported by Baker on a variety of metals and alloys are not tubular, and can be classified as fishbone (or herringbone), platelet and ribbon, according to the orientation of the graphene layers with respect to the filament axis. In the most frequent configuration (fishbone), the graphene layers are at an angle, being neither parallel nor perpendicular to the axis [12]. In its *“Recommended terminology for the description of carbon as a solid”*, IUPAC proposed the designation of “filamentous carbon” for such materials [13], but they are currently known as “carbon nanofibers” (CNFs), a designation that was introduced by Nelly Rodríguez [14].

Both CNFs and MWCNTs can be considered as different types of filamentous carbon, as they can be obtained by similar procedures from the decomposition of hydrocarbons in the presence of metal catalysts, a process known as Catalytic Chemical Vapor Deposition, CCVD [15]. Their common features were addressed in a dedicated NATO Advanced Study Institute that took place in Budapest, in June 2000 [16].

In addition, such structures can act as templates for the growth of so-called Vapor-Grown Carbon Fibers (VGCFs): in the first stage, a filament grows by CCVD; then, at higher temperatures, the filaments cease to grow and start thickening as a result of pyrolytic carbon deposition [17,18]. Figure 1 shows three different carbon materials obtained from methane by CCVD in our Laboratory. Temperature is the most important parameter determining the type of structure formed.

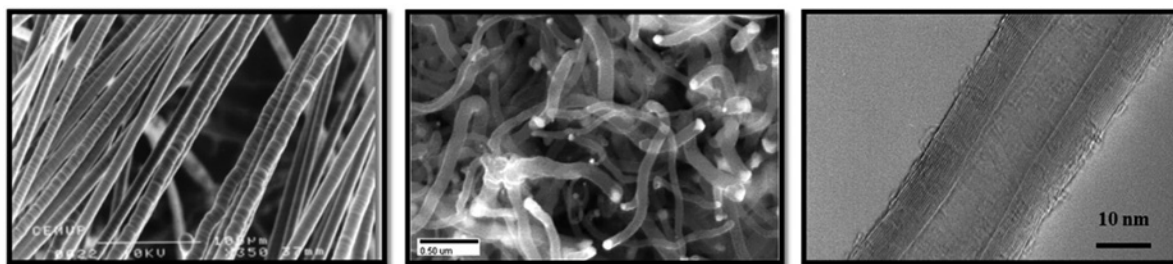


Figure 1

Carbon materials obtained from methane by CCVD. From right to left: MWCNTs (diameter \approx 25 nm); CNFs (diameter \approx 100 nm); VGCFs (diameter \approx 10 μ m).

From the discussion above, it may be concluded that research on carbon nanostructures started some 40 years before the advent of fullerenes and nanotubes. A different terminology was used at the time, which may explain why these earlier reports are frequently overlooked in the recent literature.

3. NANOSIZED CARBON MATERIALS

After the discovery of fullerenes and carbon nanotubes, several other morphologies of nanometer-sized carbon materials have been described, such as nano-onions [19], nano-cones [20], and nano-horns [21]. A major breakthrough occurred in 2004, when Geim and Novoselov¹² were able to isolate graphene [22], which quickly became a hot topic of research with many promising technological applications. More recently, some hybrid structures were also reported, such as “nano-buds”, consisting of SWCNTs with covalently attached fullerenes [23], and N-doped graphene/SWCNT hybrids [24]. These nano-carbons are schematically shown in Figure 2.

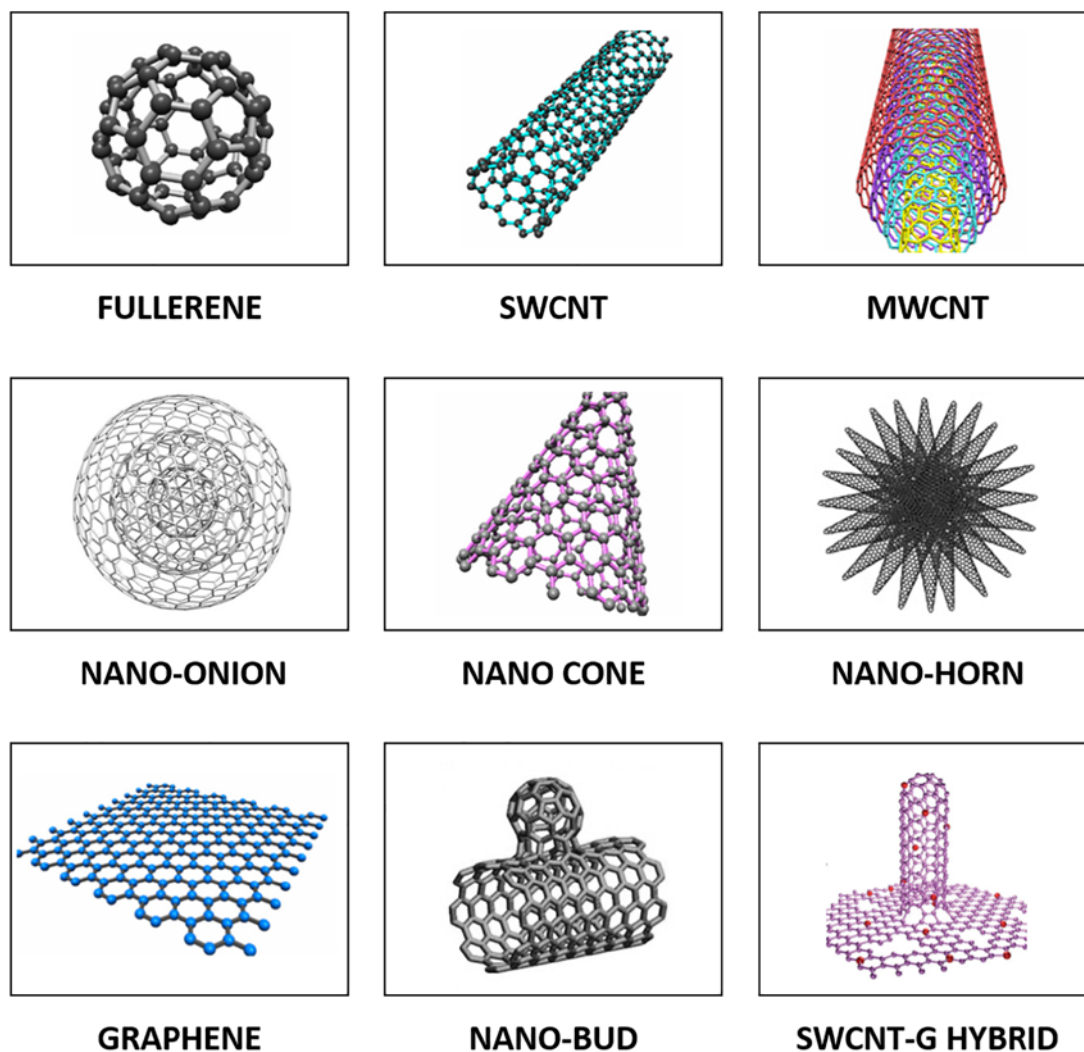


Figure 2

Schematic illustration of some nanosized carbons. Adapted from references [19-25].

¹² Andre Geim and Konstantin Novoselov were awarded the Nobel Prize in Physics in 2010 “for groundbreaking experiments regarding the two-dimensional material graphene.”

All carbons shown in Figure 2 share the graphitic structure. But there are also nanosized carbon materials with sp^3 - hybridization, namely nanodiamonds, which are produced by detonation of explosives in the absence of oxygen, a process that was discovered in 1963 [26]. The materials obtained in this way consist of a diamond core coated with a graphene shell [27], a feature that is useful for functionalization, as will be described subsequently. And, quite recently, researchers succeeded in synthesizing a “donut”-shaped sp -hybridized molecular carbon allotrope, namely cyclo[18]carbon, a ring of 18 carbon atoms with alternating single and triple bonds [28].

The global carbon nanotubes market reached 4×10^9 US dollars in 2017, a value that is expected to double by 2023 [29].

4. NANOSTRUCTURED CARBON MATERIALS

Porous carbon materials with their structure and texture controlled at the nanometer scale are included in the broad definition of nanocarbons (or carbon nanomaterials) proposed by Inagaki and Radovic [30]. These nanostructured carbons can be synthesized either by sol-gel or by templating procedures, as recently reviewed [31].

Carbon gels are obtained by carbonization of organic gels prepared by polycondensation of hydroxybenzenes with aldehydes, as first described by Pekala [32]. Figure 3 shows the steps involved in the synthesis of a carbon gel from resorcinol and formaldehyde under alkaline conditions. According to the drying method used, the materials obtained are called aerogels (supercritical drying), xerogels (conventional drying) or cryogels (freeze drying). They consist of microporous nodules which are aggregated into a network, the voids between nodule chains being the large pores (meso/macropores).

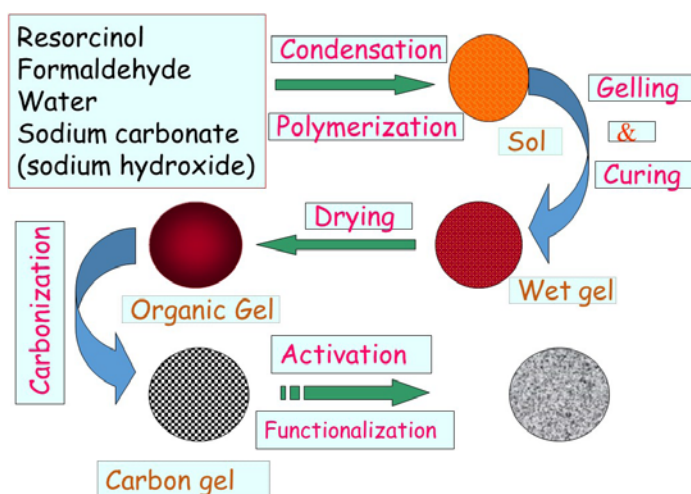


Figure 3
Steps in the synthesis of carbon gels.

The textural properties of carbon gels can be controlled by adjusting the synthesis conditions, such as the pH and the dilution ratio (molar ratio between solvents and reactants) [33,34]. Thus, it is

possible to prepare customized carbon gels, ranging from purely microporous materials to micro-mesoporous materials with well-defined mesopore sizes, and to micro-macroporous materials.

The templating methods go a step further, as they offer the possibility to control both the pore size and the tridimensional structure, yielding materials with ordered and uniform pores. In *exotemplating* (also known as *nanocasting* or *hard templating*) a porous solid is used as a mould, which is impregnated with the carbon precursor. In the case of *endotemplating* (or *soft templating*) the carbon precursors aggregate by self-assembly around the template, which consists of supramolecular structures such as micelles. In both cases, ordered mesoporous carbons (OMCs) are obtained after carbonization and removal of the template [31]. Ordered mesoporous silicas (such as MCM-48 and SBA-15) are often used as templates for nanocasting, originating mesoporous carbons with cubic or hexagonal structures, high specific surface areas and large pore volumes, their pore sizes being determined by the pore size of the template [35]. A more versatile route is provided by soft templating. As in the case of carbon gels, hydroxybenzenes and aldehydes are used as carbon precursors, while triblock copolymers (such as Pluronic® F127) are the preferred structure-directing agents [36]. The textural properties of the OMCs obtained by this method are determined by the synthesis conditions, in particular by the hydroxybenzene/template ratio [31].

Carbohydrates can be easily converted into carbon materials by hydrothermal carbonization (HTC), but additional procedures are generally required to develop the porosity and to improve the textural properties. A recently devised strategy towards this goal consists in using nanocarbons (carbon nanotubes or graphene oxide) as condensation/polymerization promoters, simultaneously providing a scaffold for the growth of carbon gels derived from glucose [37,38].

Figure 4 shows different types of nanostructured carbons obtained in our Laboratory.

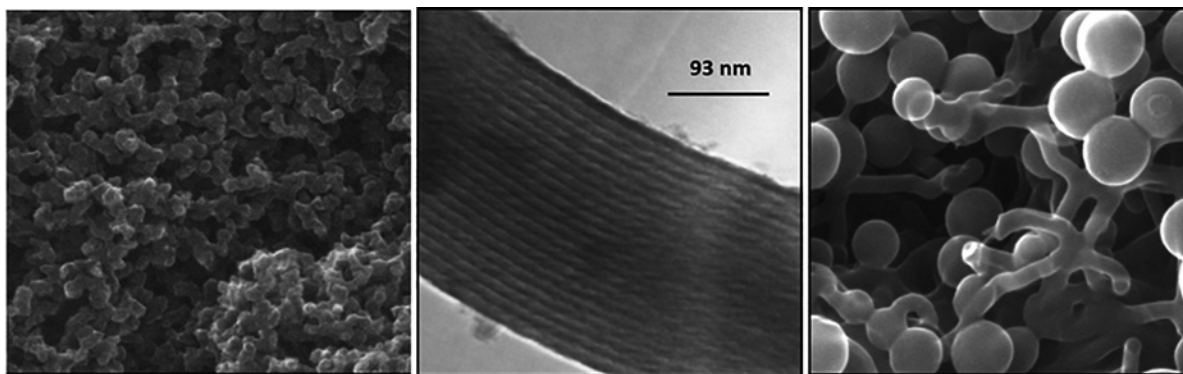


Figure 4

SEM micrograph of a carbon xerogel (left); TEM micrograph of an OMC obtained by nanocasting with an SBA-15 template (center); and SEM micrograph of a carbon gel obtained by hydrothermal carbonization of a glucose/MWCNT hybrid (right).

5. TUNING THE SURFACE CHEMISTRY

Most of the carbon nanomaterials described above are based on the graphitic structure; thus, surface functionalization is possible at the unsaturated carbon atoms at the edges of the graphene layers, and at defects of the basal planes. Oxygen functional groups are the most important; they can form spontaneously by exposure to the atmosphere, or they can be incorporated by reaction with oxidizing agents in gaseous or liquid phase. Most of these groups are acidic (carboxylic acids and anhydrides, lactone and phenol groups); ether and carbonyl groups are neutral or can form basic structures, such as quinone and pyrone groups [39].

Nitrogen-containing groups include pyridinic (N6), pyrrolic (N5), and oxidised nitrogen (NX) at the edges, and quaternary nitrogen (NQ) incorporated into the graphene structure (replacing carbon atoms). These groups increase the carbon basicity, in particular the pyridinic nitrogen [40]. Functionalization with nitrogen can be achieved by treatment with ammonia in the gas phase, by hydrothermal treatment with urea solutions, or during synthesis, by adding a suitable nitrogen precursor. A new mechanochemical method consists in ball-milling a mixture of carbon nanotubes [41] or graphene oxide [42] with a nitrogen precursor (urea or melamine), followed by thermal treatment under inert atmosphere.

Quantitative determination of the functional groups can be obtained by deconvolution of temperature-programmed desorption (TPD) profiles or X-ray photoelectron spectra (XPS), as described in detail elsewhere [39,43]. Since the different groups are stable in different temperature ranges, fine tuning of the surface chemistry can be achieved by thermal treatments at different temperatures, as shown in Figure 5 for oxygen groups, or at a given temperature for different periods of time. In this way, some undesired groups can be selectively removed, or samples can be prepared with different amounts of the required groups without significant textural changes [43,44].

Functionalization with sulfur, phosphorus and boron may also be relevant for specific applications. The subject has been addressed in recent reviews [45,46].

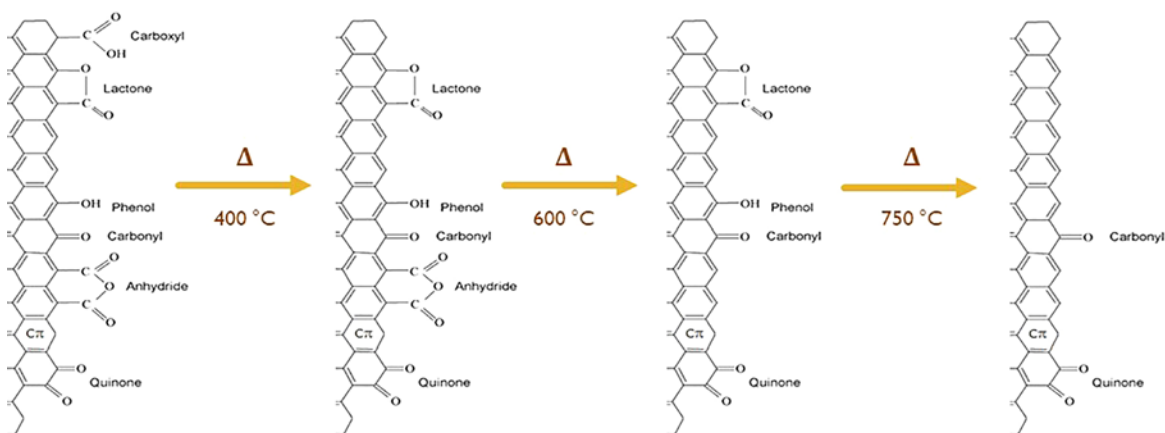


Figure 5

Schematic illustration of the changes in the surface chemistry of oxidized MWCNTs upon thermal treatments under inert atmosphere.

6. APPLICATIONS IN ENERGY CONVERSION AND STORAGE

The applications of carbon nanomaterials in catalysis were the subject of recent comprehensive reviews [25,47]. In the present communication, we will focus more specifically on the use of nanostructured carbons in electrochemical devices for energy conversion (fuel cells) and storage (supercapacitors).

The carbon electrodes for supercapacitors (or electrochemical double layer capacitors, EDLCs), should have large surface areas, hierarchical porosity, and high electrical conductivity [48,49]. Activated carbons are the standard carbon materials for this purpose. They have large micropore volumes responsible for their high adsorption capacities (micropores are defined as having width < 2 nm), which can be accessed through larger pores (mesopores with widths between 2 and 50 nm, and macropores, with width > 50 nm). These pores are organized hierarchically, larger pores subdividing into smaller ones, in a tree-like arrangement [50]. This hierarchical pattern (in series) is quite different from those of carbon gels and OMCs, where there is a parallel network of mesopores, the micropores being present in the primary nodules of carbon gels or in the mesopore walls of OMCs, as shown in Figure 6. This arrangement of the nanostructured carbons is more advantageous, facilitating the access to the micropores [51].

Hierarchical Porosity

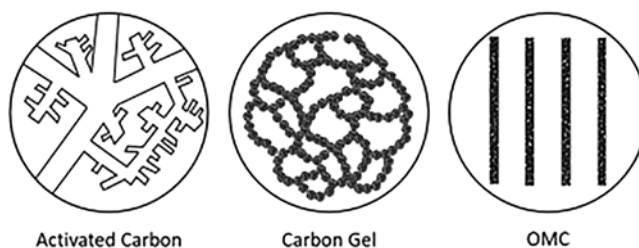


Figure 6

Comparison of the hierarchical pore systems of activated carbons, carbon gels and ordered mesoporous carbons (OMC). Adapted from references [50,51].

In addition to adequate textural properties, the surface chemistry of the carbon electrodes can also be tuned in order to enhance the capacitance, as a result of Faradaic redox reactions involving some of the oxygen and nitrogen surface functional groups (pseudo-capacitance). The presence of such groups also improves the wettability of the carbon surface [48,49].

Suitable electrodes for EDLCs were prepared by hydrothermal carbonization of glucose in the presence of MWCNTs, followed by chemical activation with KOH. The addition of MWCNTs was found to improve the performance of these hybrid carbons, particularly the capacitance retention, as shown in Figure 7. The best results were obtained by adding just 2 wt.% of MWCNTs, the corresponding electrode (AG_2%CNT_KOH) yielding 206 F g^{-1} and 78% of capacitance retention up to 0.8 V and 20 A g^{-1} , as well as high rate cyclability (97% after 5000 cycles). This performance is much better than that of the reference activated carbon (DLC Supra 50), with a capacitance of only 150 F g^{-1} which drastically decreases above a current density of 2 A g^{-1} [38].

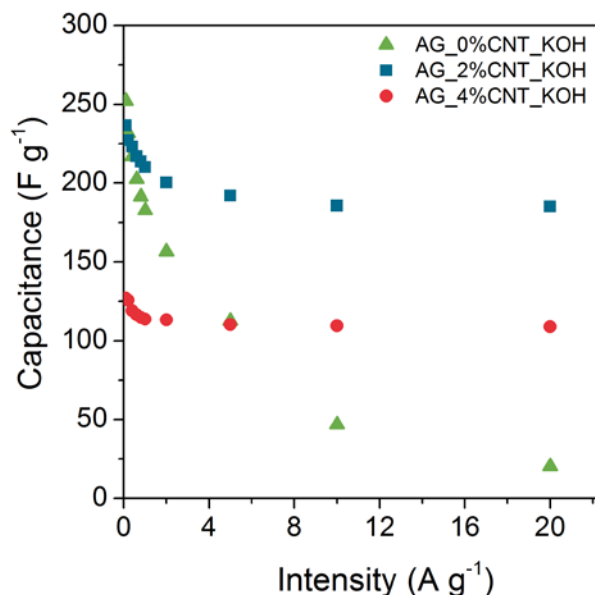


Figure 7

Capacitance retention of chemically activated glucose-MWCNT hybrid carbons with different proportions of MWCNTs (0, 2 and 4 wt.%), measured within a voltage window of 0.8 V. Adapted from reference [38].

Another set of materials was prepared following a similar procedure, but H_3PO_4 was used as a chemical activation agent instead of KOH. The carbons obtained in this way contained a large amount of both oxygen and phosphorus functional groups. The oxygen groups anchored directly to the carbon surface provided a significant contribution to the pseudocapacitance, while the phosphorus groups enhanced the electrostatic charge. The capacitance was found to increase significantly with the amount of P incorporated; moreover, higher P contents allowed to increase the current density applied. The best electrode material showed a capacitance of 110 F g^{-1} and a capacitance retention of 93% after 10 000 cycles at 10 A g^{-1} , exceeding the performance of commercial activated carbon electrodes at high current densities [52].

The situation is more complicated in the case of fuel cells (FCs). These devices generate electricity by oxidizing a fuel (e.g., hydrogen) at the anode and reducing oxygen at the cathode, the electrode surfaces being covered with a thin layer of an electrocatalyst. The currently available catalysts for the anode and cathode reactions are based on platinum supported on carbon black. The high price of Pt, its scarcity, and its sensitivity to poisons are the major hurdles that hinder the widespread application of FCs. In the quest for alternative electrocatalysts, particularly for the slow oxygen reduction reaction (ORR), two promising strategies have recently emerged, based on the use of either transition metal N_4 -macrocycle compounds, or N-containing metal-free materials, such as nitrogen-doped carbons and graphitic-carbon nitride ($\text{g-C}_3\text{N}_4$)-based hybrids [53,54].

The high electrocatalytic activity of nitrogen-doped carbon nanotubes for the ORR in alkaline media was first reported in 2009 [55]. Since then, there has been an intense activity in this area of research. In addition to carbon nanotubes, other nanosized materials have shown excellent performances. For instance, the ORR activity of the N-doped graphene/SWCNT hybrid shown in Figure 2 was found to be comparable to that of the commercial Pt catalyst [24].

Lately, we have been focusing on nanostructured carbons, in particular materials prepared by hydrothermal carbonization of glucose, since their textural and chemical properties can be tailored to enhance their electrochemical performance towards the ORR. We found that the increase of microporosity improves the limiting current density, while the incorporation of nitrogen improves the onset potential and shifts the mechanism towards a four-electron pathway. However, the type of N-groups is more important than the total amount of nitrogen. Thus, we observed that a higher N6/NQ ratio favors the onset potential, while a lower NQ/N5 ratio favors the number of electrons exchanged during ORR [56]. The addition of MWCNTs during the hydrothermal polymerization of glucose leads to further improvements in the performance of the carbon material towards the ORR, in particular as a result of higher electrical conductivity [57]. However, these materials could not match the performance of the reference Pt electrocatalyst, in spite of significant improvements.

Better results were achieved with a micro-macroporous activated carbon xerogel doped with nitrogen and iron [58], demonstrating the importance of tuning both the textural and surface chemical properties of the carbon material in order to optimize its electrochemical performance. The organic gel was synthesized by microwave heating, and the synthesis parameters were selected in order to obtain macropores of about 100 nm. A carbon gel was then obtained by physical activation with carbon dioxide at 1000 °C (sample AX-1000). The activation procedure yielded a material with large surface area (1460 m²g⁻¹) and micropore volume (0.5 cm³g⁻¹); moreover, the high activation temperature allowed to reach an adequate electrical conductivity (140 S m⁻¹). This sample was then functionalized with nitrogen (AX-1000N). A third sample was prepared by impregnating AX-1000N with iron(II) phthalocyanine (AX-1000NFe). Figure 8 shows the electrochemical performance of these samples, in comparison to a commercial ORR electrocatalyst (20 wt% Pt on carbon black, Pt/C). The wide macropores facilitate the access of the reactants to the micropores, where the catalytic sites are mainly located, and nitrogen-doping shifts the reaction mechanism to the four electron pathway (direct route), as shown in Fig. 8b.

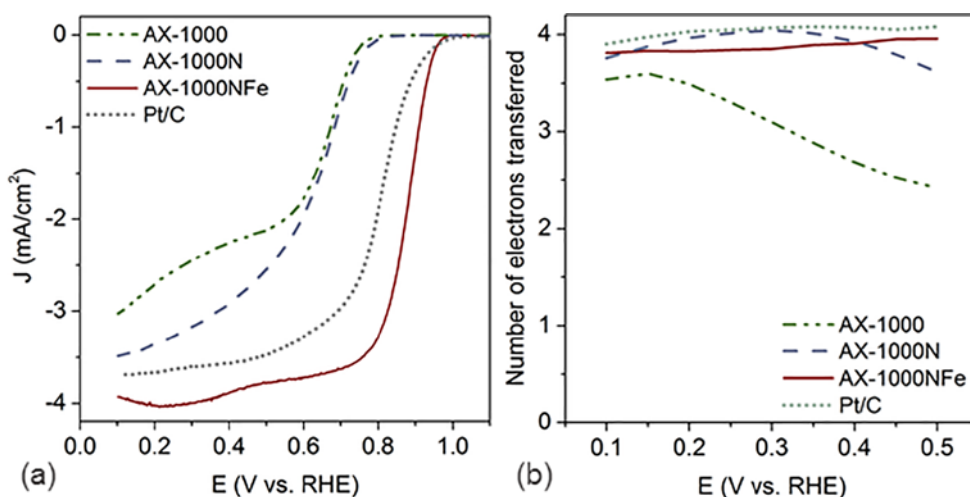


Figure 8

Effect of nitrogen and iron doping on the electrocatalytic performance of a micro-macroporous carbon xerogel: Linear sweep voltammograms (a) and number of electrons transferred during the ORR (b). The performance of a commercial Pt/C catalyst is included for comparison. Adapted from reference [58].

Further improvements were achieved after incorporation of iron, the performance of sample AX-1000NFe being comparable to that of the commercial platinum electrocatalyst [58].

7. SUMMARY AND OUTLOOK

The versatility of carbon is unmatched in the periodic table. Carbon is present in a huge variety of compounds, some of them essential to all living organisms; this is the realm of Organic Chemistry. Moreover, carbon also plays a key role in several other equally important areas. In his essay “*The four worlds of carbon*”, S.H. Friedman refers the role of carbon in converting iron into steel, in making polymers, and in providing most of the energy used by mankind (fossil fuels) [59]. But the industrial dimension of carbon must also be recognized, as the products of the carbon industry account for a sizeable market share (cf. Table 1). Carbon nanomaterials appeared only in the 1990’s, but there is already a considerable industrial production, especially in the case of MWCNTs, which are mainly used for the manufacture of polymer matrix composites. Nanostructured carbons with hierarchical porosity, obtained by sol-gel and templating procedures and functionalized or doped with heteroatoms, offer the possibility of fine-tuning their texture and surface chemistry, allowing the design of *custom-made* materials for the envisioned applications. Some examples were discussed in the field of energy conversion and storage, which is currently the focus of a considerable research effort and where major breakthroughs are foreseeable in the short term.

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