Emerging carbon nanotechnology. Advances and thoughts from a young perspective[†]

Nanotecnología emergente del carbono. Avances y reflexiones desde una perspectiva joven[†]

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Abstract

The carbon element is probably the most versatile in the periodic table, giving rise (amongst other) to a diversity of high-performance materials, thereby posing one of the most studied venues towards nanoscience and nanotechnology. In this review, the past, present and future of carbon-based nanotechnology is highlighted, also focusing on emergent nanomaterials based on carbon, with new properties and processing schemes. In essence, a critical viewpoint is presented from the youngest researchers in the G-CNN group at the Instituto de Carboquímica in Zaragoza (Spain).

1. Introduction

The world is full of carbon. Carbon is the 15th most abundant element on Earth's crust, and the fourth most abundant element in the Universe (as sorted by mass content), right after hydrogen, helium and oxygen. In combination with other atoms, carbon enables life. It takes part in the most intriguing kinds of chemical bonds, molecules and materials, and its potential is known to us since the most ancient times. We can burn carbon to obtain energy and light, we feed on carbon sources, and we exhale carbon species. It was not until recent decades that the scientific community realized the true potential of carbon, together with the rise of nanoscience and nanotechnology, being the building blocks of exciting (nano)materials. Even if carbon nanotechnology grew steep in the late '80s – early '90s with the discovery and structural applications of fullerenes and nanotubes, the excitement caused by science and technology has sparkled in unanticipated materials, also constituted by carbon, with impressive properties and novel fields of application.

The research group to whom all the authors of the present contribution belong to (G-CNN), has been devoted since the mid '90s to the synthesis, deep study and specific applications of carbon-based nanomaterials, ranging from nanotubes or graphene derivatives, until today, in which we also extend our research towards other emerging nanomaterials such as graphene/carbon/polymer dots or nanocellulose, also based on carbon. These new family members provide new facets to the carbon nanotechnology, such as intrinsically full compatibility with aqueous media or a sustainable and environmentally friendly profile. In this review, a journey throughout carbon nanotechnology is presented, gathering past, present and future of the most representative carbon nanotechnology landmarks, from the point of view of the youngest cohort within the G-CNN, from Master's to PhD students, and a recently incorporated young tenured scientist. A young and fresh perspective on young and promising scientific and technological advances.

2. Carbon nanotubes and graphene derivatives. Old acquaintances with new horizons

Carbon-based nanomaterials are gaining more and more attention over the last few years because they exhibit unusual properties that allow their use in different fields [1]. Particularly, carbon nanotubes (CNTs) and graphene (G) are the most astonishing carbonaceous nanomaterials, as these can be potentially applied in new structures and devices due to their unique electronic, mechanical, optical and chemical properties [2]. In this section, a short review of CNTs and G is described, highlighting their properties and potential applications. Processing of such carbon nanostructures is also discussed, taking into account the drawbacks and possible solutions to overcome the encountered problems. Furthermore, CNTs, G and its derivatives can be assembled into thin films, thus opening the way to their use in electrodes and electrochemical applications. The assembly of G derivatives into hydrogels and aerogels used for energy management is as well reviewed.

2.1. Brief introduction and description

CNTs are considered as one of the nanostructured allotropes of carbon, made of rolled-up G sheets in a cylindrical shape (1D material). These carbon nanostructures can be classified according to the number of layers they are made of, therefore having single-walled CNTs (SWCNTs) or multi-walled CNTs (MWCNTs). In the case of MWCNTs, these were accidentally observed in 1991 by Sumio Iijima [3], while the existence of SWCNTs was pursued and demonstrated a few years later, in 1993 by the same author [4]. The outstanding potential of CNTs and particularly of SWCNTs, has motivated their study in different fields. Due to the SWCNTs excellent

electrical conductivity, they could find their place in the microelectronic industry because of the ever-growing trend of miniaturizing electronic devices, and also in electrochemical applications, as a substitute for conductive materials like copper, steel and fluorine-doped tin oxide (FTO).

As in CNTs, G is a carbon nanomaterial ideally composed of a single layer of sp^2 carbon atoms, setting a hexagonal honeycomb crystal framework (2D material), although the few-layered equivalent is also commonly considered as such. G was first studied in-depth in 2004 by Novoselov and Geim [5], to whom the physics Nobel prize in 2010 was awarded. In spite of all its outstanding chemical and physical properties, impressive stability, electrical and heat conductivity [6], it presents some drawbacks like its strong stacking and difficulty to disperse in water, and this is where graphene oxide (GO) comes in. Its excellent processability and hydrophilicity make it an interesting option for a wide range of applications, at the expense of the electrical and thermal conductivities to a certain extent. However, more efforts are needed in the optimization of the reaction procedures and in developing new environmentally friendly routes for their synthesis, in order to better industrialize the production of G and GO.

2.2. Processing of carbon nanostructures in water: advantages and bottlenecks

The extraordinary properties of carbon nanostructures have been materialized in several applications using the dispersion technique. Due to the native hydrophobicity of these nanomaterials, the most common way to process them includes the use of organic solvents and surfactants [7], and also ultra-centrifugation techniques which increase the dispersion purity, separating amorphous carbon and metal impurities [8]. Despite the good results achieved by using all the above mentioned, the emerging technologies based on water processing with a more environmentally friendly character are on demand, reason why some new approaches need to be taken into account. Beyond the use of toxic surfactants or polymer wrapping, the covalent functionalization approach, which involves the functional groups attachment to the carbon nanostructures, has led to an enhancement in the dispersing properties [9]. However, the chemical modification of the carbon framework implies a decrease in the electrical conductivity of the nanomaterial. Since 2018, the G-CNN group has been devoted to the use of biopolymers, such as nanocellulose, as dispersing agents of carbon nanostructures [10]. When cellulose nanocrystals are combined with SWCNTs, its crystalline plane with higher hydrophobicity is adsorbed onto the CNT framework, creating hybrid nanomaterials with high colloidal stability [11]. In general, the advantages of biopolymers as dispersing agents ensure an efficient processing of carbon nanostructures in water within an environmentally friendly scenario, opening a wide range of applications, especially in biological sciences, also bringing a good opportunity to implement these materials in electronic devices by using non-toxic methodologies.

2.3. Assembly of carbon nanostructures into thin films: electrodes and electrochemical applications

CNTs and G derivatives are potentially applied in the development of electronic devices [12,13], and for the fabrication of functional transparent conducting films (TCFs) [14]. One of the key aspects that must be taken into account is that a good adhesion with the substrate is required to maximize all the above-mentioned applications. In this context, in our research group, new methodologies to improve the adhesion of SWCNTs on flexible plastic substrates have been developed, by using immersion techniques with nitric acid and *N*-methyl pyrrolidone [15]. For any envisioned electrochemical application with CNTs, it is mandatory to avoid charge transfer processes, which are detrimental for the efficiency, selectivity and lifetime of the device. A pretty interesting solution consists of adding a synthetic additive to a CNT water-based dispersion, which is also compatible with the fabrication of conductive CNT films [16]. As a matter of example, in our research group it has been demonstrated that the addition of a chemically modified acrylic latex allows the fabrication of flexible electrodes on plastic substrates, which also efficiently block faradaic transfer reactions across the electrode-electrolyte interface [17].

Other potential fields in which CNTs could be used are photocatalysis and energy devices [18], intensively studied with hybrid composites made of SWCNTs and metal oxide semiconductors (e.g. TiO_2). In particular, in our research group the electrochemical response of SWCNTs/TiO_2 hybrids has been well studied, together with their related optoelectronic properties, opening new ways to implement these inorganic composites in macroscopic systems, taking advantage of their nanoscale properties [19]. Related to photocatalysis and production of clean energy, a promising technology of growing interest in which SWCNTs are potential candidates is the photoelectrochemical water splitting, which uses both luminous (ideally, sunlight) and electric energies to carry out the oxidation of water molecules. Consequently, this reaction will also generate hydrogen, considered as one of the best sustainable alternatives to fossil fuels. Therefore, SWCNTs could be employed as conductive substrates for electrode manufacturing, towards clean energy generation.

In this context, hybrid film electrodes made of TiO_2 filled with different percentages of SWCNTs have been developed. As shown in reference [20], if methanol is added to the electrolyte, a huge increase in the potentiostatic photocurrent is detected for the 0.02% SWCNT/TiO_2 electrode at pH = 2 if compared with the same measurement in the absence of such alcohol. This demonstrates that SWCNTs improve the photocatalytic activity of TiO_2 under well established and controlled conditions [20]. TiO_2

can also be combined with G derivatives such as electrochemically reduced GO (ECrGO) for improving its photoactivity by depositing a very thin film on top of nanostructured TiO_2 electrodes. It has been confirmed that ECrGO acts as hole acceptor, and its functionality depends on the resulting space charge region. As a consequence, it can behave as a hole transport layer (HTL) enhancing the photoactivity, or as a hole blocking layer (HBL) inducing a decrease in such property, depending on if the thickness of the ECrGO layer is below or above the one of the space charge region [21]. However, TiO_2 is not the only photocatalyst known in such scenario. Other inorganic semiconductors such as ZnO have also excellent properties making it suitable for these purposes. It has been demonstrated that ZnO can be combined with GO and related materials to improve and enhance its photoactivity (**Figure 1**) [22].
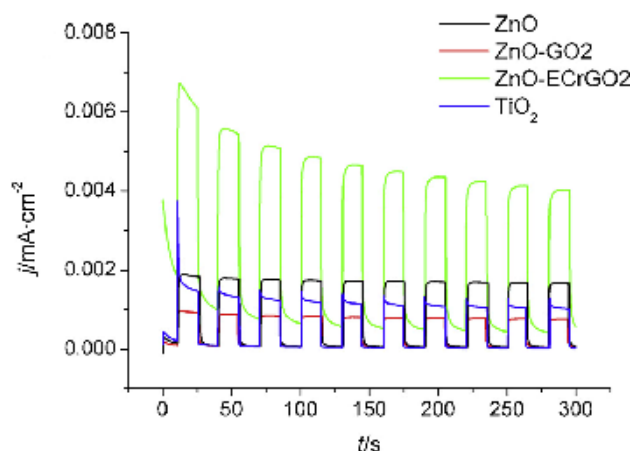
Figure 1. Potentiostatic on-off measurements in which water oxidation is carried out. Reproduced from reference [22] with permission from Elsevier © 2020.

All these potentiostatic measurements were performed at 0.4 V (Ag/AgCl, 3M NaCl), showing that the photocurrent values of the ZnO-ECrGO2 hybrid were the highest ones if compared with the other electrodes, resulting in a composite with an impressive photocatalytic performance.

2.4. Assembling of graphene derivatives into 3D structures: hydrogels and aerogels

Translating the properties of 2D materials to 3D is not an easy task. Although G aerogels stand out because of their high porosity and high specific surface area, they also display other interesting properties such as super flexibility, compressibility, low density, good mechanical strength and a conductive structure. Re-stacking of the G nanosheets is one of the main issues during the synthesis of 3D structures. Although templates are commonly used in order to avoid this problem, a post-synthesis treatment is required to remove them [23]. However, GO can be used as precursor because the abundance and nature of functional groups may contribute to the nanosheets self-assembly. Nevertheless, in order to obtain similar properties to G, a reduction step must be carried out. A hydrothermal process in an autoclave can be

used as a one-pot synthetic method to obtain rGO hydrogels. During this process the functional groups are removed leading to an increase of hydrophobicity and a loss of surface charges which induces the linkages between graphene nanosheets and phase separation [24]. Particularly, the G-CNN group has deeply studied the pH influence on the final hydrogel structure [25], concluding that, at an acidic pH value, a greater number of oxygenated groups remains, inducing a flatter morphology. However, at a basic pH the stacking via hydrogen bonds is minimized and the reduced rGO nanosheets, which are more twisted and bent, connect through the borders creating structures with higher porosity. Furthermore, it is possible to orientate the porosity of graphene aerogels. The G-CNN group has applied a widely used technique, unidirectional freeze casting, to rGO hydrogels with a certain cross-linking degree in order to obtain aligned and continuous microchannels [26]. The as obtained aerogels have been demonstrated to be suitable for their use as supercapacitors [27]. Supercapacitors are only one of the multiple applications of G-based aerogels. Their structure and high porosity give them exceptional properties for catalysis, batteries, sensors, liquid separation or biomedicine, among others.

3. Advanced hybrid materials based on carbon nanostructures for energy applications

Carbon nanostructures have dominated the material science field since its first apparition in the 20th century, when some new structures like fullerenes and CNTs were described. This interest rose up when G emerged in early 2000s. Although carbon nanostructures have demonstrated to be highly reliable materials, only in a few cases the raw ones were good enough to be useful by themselves. In order to improve their properties and processability, multiple composite materials have been developed, giving carbon nanostructures different roles depending on the desired result. Carbon nanostructures-based hybrids have excelled in many applications. This section focuses in energy applications, as one of the most prominent fields for carbon nanomaterials due to the pressing needs of developing new electric generation sources and storage devices.

3.1. Energy storage devices

Batteries have been largely studied for more than a century and they are nowadays one of the most employed tools in contemporary electrical mechanics. Traditionally, the batteries field has been dominated by the use of metallic oxides [28] but their low availability and the increasing need for more efficiency have pushed the research out of the long-standing limits. Following the first examples of carbon nanostructures working in batteries, an increasing number of research groups have developed different functional hybrids with a promising future [29]. Despite of alkali-ion-based batteries being still the best performing materials, the progressive incorporation of carbon

nanostructures offers a new bunch of possibilities to improve the state-of-the-art in a short term. Another closely related branch of batteries research is the development of supercapacitors. This technology has rapidly emerged as one of the most studied energy applications [30] due to its complementary functionality with batteries. Originally studied with metallic oxides and bulk carbon electrodes, carbon nanostructures have outperformed most of the known systems, boosting the interest for applying this newer materials family to this particular field. Therefore, a wide variety of carbon nanostructures have been implemented successfully as supercapacitors [31] due to their ability for remaining stable after thousands of charge-discharge cycles and the possibility of being integrated in flexible substrates [32]. Moreover, combining carbon nanomaterials with others to build functional hybrids paves the way to improving their performance [33]. It remains clear that new energy storage systems are needed for increasing efficiency and sustainability, in order to cope with current applications. In this field, carbon nanostructures have played a crucial role during the latest years and their interest is growing day by day. Although the future applicability of these nanomaterials on batteries is still unclear, due to the dominancy of alkali-ions-based ones, supercapacitors seem to be the most promising way to apply this whole family of materials.

3.2. Energy generation sources

With an increasing necessity of deploying greener energy sources, due to the worsening issues associated to climate change, carbon nanostructures have revealed themselves as a crucial part of the new energy generation devices. One of the most important fields in energy generation, in order to substitute fossil fuels for less contaminant ones, is the hydrogen generation by water splitting [34]. Typical semiconducting metals or metal oxides have been used for many years as single photoelectrodes, but the combination of these materials with other carbon nanostructures leads to some synergetic effects that can be exploited to boost the material efficiency (**Figure 2**) [35,36]. In this way, the G-CNN group has reported some advances in hybrid photoelectrodes, where the addition of carbon nanostructures to the TiO_2 layers improved their performance drastically [19,21]. Moreover, carbon nanostructures can act as a highly porous surface able to host metallic nanoparticles, thereby increasing their efficiency in water splitting reactions [37]. These structures have gained significant importance since aerogels based on graphene and GO have been described. Our group has been actively working in this area and some important advances have been reported, controlling the internal structure of the aerogels by easily modifying the reaction conditions [25,26].

Solar cells stand out as energy generation devices, which could substitute non-renewable sources in a nearby future. In this way, carbon nanomaterials have worked remarkably as electrodes or active layers in different types of solar cells. For example, P3HT:PCBM (a hybrid made by a polythiophene derivative and a functionalized fullerene) has been broadly implemented in organic solar cells and is one of the most employed hybrids [38]. Moreover, some hybrid composites have been developed in order to outperform the classic materials used in these devices.
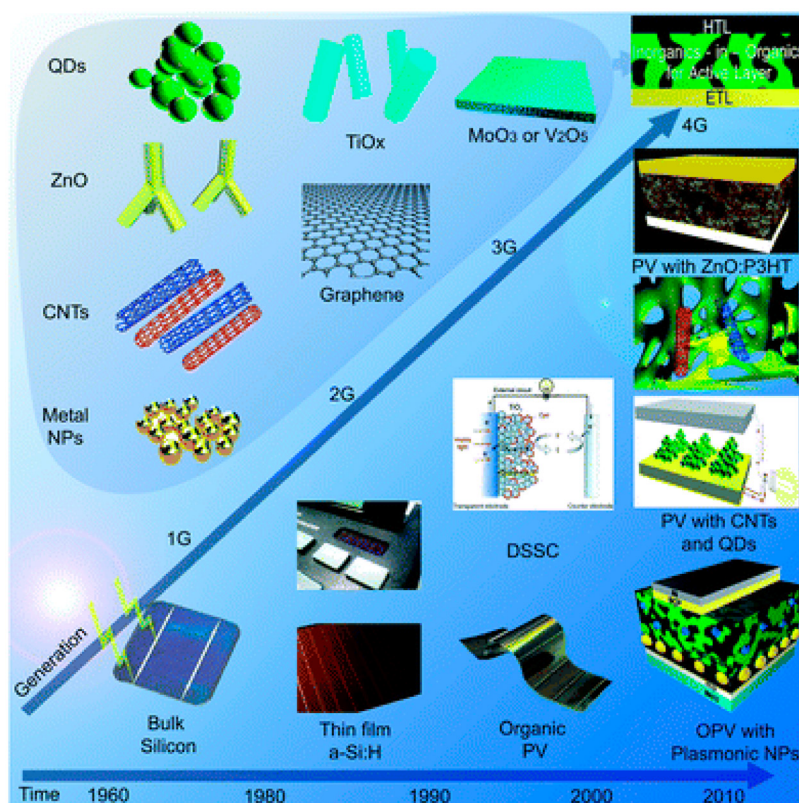
Figure 2. Overview scheme on the development of different materials for solar cells. Reproduced from reference [40] with permission from MDPI © 2019.

Therefore, carbon hybrids have been implemented successfully in substitution of HTL materials in perovskite solar cells [39] or combined with conductive polymers and metallic nanoparticles in the so-called "4GEN solar cells" [40]. The G-CNN research group is currently working in developing and understanding the behavior of new nanostructured hybrid systems for higher photocurrent generation in solar cells [41,42]. In essence, carbon nanostructures open new possibilities in energy generation sources. The implementation of such hybrids to these largely studied devices allows to improve their efficiency, stability or even permitting to develop new features due to synergetic interactions between carbon nanostructures and classic materials. The urgent requirements for finding greener and renewable energy sources have recently boosted the interest in both fields and they will become even more important in the upcoming years.

4. Luminescent carbon nanostructures: carbon and graphene quantum dots

4.1. Framework and context. Synthetic approaches

Since their early discovery during the purification of SWCNTs by electrophoresis [43], the carbon dots (CDs) have caught the attention of the scientific community. They can be defined as quasi-spherical carbon nanoparticles within a range of 1 to 10 nm, whose more remarkable feature is the photoluminescence (PL), but also a low-cost synthesis methodology, water solubility and excellent biocompatibility. CDs can be classified into three main groups: graphene quantum dots (GQDs), consisting of 1-10 graphene few layers with several functional groups on the edges; carbon nanodots (CNDs), which are spherical carbon nanoparticles with a sp^2 core that also can be dived in carbon nanoparticles (absence of crystal lattice) or carbon quantum dots (presence of crystal lattice); and finally polymer dots (PDs), which are nanosized entangled polymer chains, prepared from linear polymers or monomers [44]. In the same way as other carbon-based nanomaterials, CDs synthetic methods can be divided into two approaches: top-down and bottom-up. The top-down approach involves the physical or chemical breakdown of a carbonaceous source (CNTs, G, graphite, carbon black, biomass…). Although specific techniques are used depending on the starting material, the most common ones are electrochemistry [45], solvothermal reactions, ultrasound synthesis, biomass pyrolysis [46] or chemical oxidation [45] among others. Bottom-up synthetic methods are based on the reaction or polymerization of small molecules, usually rich in functional groups such as amides, amines, aldehydes or carboxylic acids [46]. These reactions can be microwave-induced, template-assisted or carried out in an autoclave.

4.2 Photoluminescent properties. Origin, mechanisms and tuning

As mentioned above, PL is one of the most attractive properties of CDs and its origin relies on different sources, which are dependent on the method of synthesis and their structure. Three different sources have been deeply studied: i) surface states, including the surface oxidation degree or the presence of surface functional groups such as C=O or C=N, which introduce new energy levels in the CDs; ii) the quantum confinement, where the band gap and size dependence play an important role in the relaxation dynamics; and iii) the presence of molecular
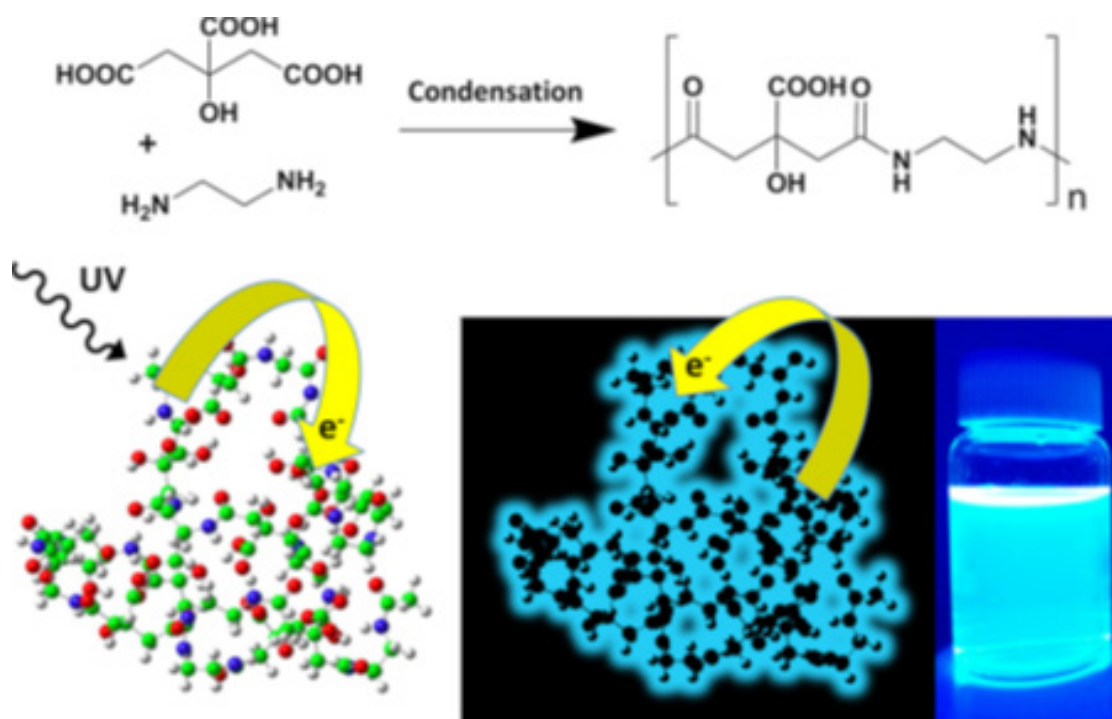
Figure 3. CDs, synthesized from citric acid and ethylenediamine showing a strong blue PL. Reproduced from reference [47] with permission of the American Chemical Society © 2018.

fluorophores in their structure. The importance and ability to exert control over these three aspects are the key to control the PL properties, thereby opening the possibility of tuning the emission wavelength [44]. The origin of the blue fluorescence in CDs was deeply studied in our research group, more specifically by Vallan et al. (**Figure 3**). Synthesizing PDs from citric acid and ethylenediamine in a microwave reactor, and reaching a high quantum yield, it was found that the origin of blue photoluminescence stemmed from the charge transfer between amide and carboxylic groups, where the H-bonds and electrostatic interactions induce rigidity in the structure, facilitating the radiative relaxation processes [47]. Despite the increase in publications dealing with CDs with different emission wavelengths, there is still a lack of consensus in a general origin of PL, where the results are mainly influenced by the synthetic method and the purification process. Generally, the PL of CDs that are purified by chromatographic column is usually discussed from a size-dependent PL approach, whereas those obtained by hydrothermal routes mainly rely on a carbon core as source of PL. On the other hand, the methods for modifying their luminescent properties depend on the characteristics of each CD.

However, certain strategies are available to all of them. As mentioned before, luminescence due to quantum confinement is dependent on the CD size: only by increasing the area of the CD it is possible to turn a blue emission into a green, yellow or red one [46]. Surface state luminescence produced by the presence of functional groups can be easily modified. In some cases, the synthesis method allows the precursors choice, as in the case of PDs [48]. Furthermore, typical organic reactions, such as condensation between carbonyl groups and amines, can be carried out as post-synthesis treatment [49]. GQDs may have tunable luminescence via doping. The heteroatom presence implies new n-π^* transitions responsible for the modification of the surface states. However, it must also be taken into account how these heteroatoms are incorporated into the structure because the π-π^* transition of C=C in the sp^2 domains is also modified. The contribution to this transition is different, for example, in the case of pyridinic N (blue shift), graphitic N (red shift), pyrrolic N (no charge doping effect) or amine N (depending on their electron-withdrawing or electron-accepting behavior) [50]. In addition, pH or the type of solvent (polar/non-polar and protic/aprotic) [50] may influence the emission by interacting with the functional groups present in the CDs, coupled to the fact that some CDs may aggregate leading to a concentration-dependent luminescence [51].

4.5 Applications

The applicability fields of CDs are diverse and have been widely studied since their discovery in 2004. Regardless of the structure or the synthetic method of the CDs, energy and biomedicine are the two major fields where they are proving to be most particularly useful. Their intrinsic biocompatibility and low-toxicity are the key to their application in biomedicine. Naturally, their luminescence properties allow them to be used in bio-imaging as well [52]. Specific studies have been carried out to demonstrate their biocompatibility, as in case of GQDs which have been tested in podocytes (kidney cells). They showed a high compatibility, and demonstrated the ability to easily pass the ultrafiltration barrier [53], enabling a future application in a direct medical application in vivo as per their excellent an innocuous excretability. The biocompatibility of CDs tested in intestinal cells have also been achieved, and additionally, anticancer activity in specific human colon (Caco-2) cell lines, which make them a promising alternative to conventional cancer therapies [45]. On the other hand, special caution should always be taken in general with CDs in the same way as with all kinds of nanoparticles. It has recently been reported that irradiation during long periods (8 days) to CDs might be a possible cause of cytotoxicity [54]. Accordingly, these compounds have also emerged as an outstanding material in optoelectronic devices [55,56]. CDs can be incorporated in dye-sensitized solar cells increasing their efficiency or in perovskite solar cells as an intermediate layer improving both stability and charge transport phenomena [57]. Another studied application for these CDs is in light emission diodes, where they could be able to substitute phosphor-based white emission diodes providing more stable and ecological devices than the commercial ones [55]. Moreover, CDs have been reported to be a promising alternative to traditional semiconductors in water splitting technologies due to their low price and tunable optical properties [57].

5. Biopolymer nanostructures as cutting-edge carbon-based nanomaterials

5.1. General considerations

Biopolymers are produced by living beings from renewable resources in a sustainable biological process and they are considered the main alternative for plastics [58]. In most of them, carbon is the main component, as the core element that supports their structure. The transformation of biopolymers into nanostructures gives them enhanced properties, expanding the reach of their applications, in comparison with bulk biopolymers. Cellulose is the major biopolymer in the world, being the main structural component of plants. There are different cellulose sources and extraction procedures to synthesize different cellulose nanomaterials (CNMs). There are three different CNMs:

- Cellulose nanocrystals (CNCs): Short and needle-shaped nanosized crystals with a diameter of less than 10 nm and a length between 100 nm and 500 nm. They are mainly synthesized by selective isolation of crystalline domains of other forms of cellulose via an acid hydrolysis process to break hydrogen bonds [59].

- Cellulose nanofibres (CNFs): Long flexible nanofibres with a similar diameter than CNC, but a higher length. They are synthesized following a top-down strategy as for CNC, but in milder experimental conditions to maintain a higher length [59].
- Bacterial nanocellulose (BNC): It is produced by bacteria in a bottom-up process from a saccharide and has a similar shape to CNFs. Bacteria excrete fibres of cellulose with a nanoscale diameter, generating a 3D network in the form of hydrogels [60].

There are other examples of biopolymers nanostructures with different shapes and sizes, such as nanochitin [61], isolated from chitin by chemical or mechanical treatments to break the hydrogen bonds or nanolignin [62], derived from lignin, an aromatic biopolymer of plants.

5.2. Colloidal properties in water, drying and aggregation behavior

Considering the supramolecular structure of cellulose, in which strong hydrogen bonds between different cellulose chains are stabilized, it is readily inferred that it is insoluble in water. However, by the existence of surface hydroxyl groups, a certain hydrophilic behavior is exhibited [63]. Such hydrophilicity enables the preparation of aqueous metastable dispersions, thereby avoiding the use of additional organic reagents. Nevertheless, even though it is possible to disperse unmodified bulk cellulose in water, many procedures involve further chemical modifications to increase its hydrophilicity, and thus, the achievable concentration. For instance, (2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl (TEMPO)-mediated oxidation procedures, which result in the oxidation of specific hydroxyl groups to carboxylic acids [64]. Such treatments are not only

environmentally unfriendly but also could significantly change the original structure, so other alternatives ought to be found. Within this context, one-pot controlled sulphuric acid hydrolysis that results in the partial esterification of surface hydroxyl groups, leading to the introduction of negatively charged sulphate ester groups, could be thought as a solution [10].

These groundbreaking nanomaterials have their main attractive feature in an easy handling in water, opening many possibilities of sustainable processing. As such, it is imperative to know in-depth and to be able to control their interfacial interactions with water. The complex water-CNM interactions are ruled by its amphiphilic nature, being hydrogen bonds between cellulose hydroxyl surface groups and water the most dominant interaction. Besides, it is important to understand that depending on the crystalline plane and the possible surface modifications, the distribution and type of the polar surface groups will change, so as the relative hydrophilicity-hydrophobicity balance. Thus, different allomorphs, as well as CNMs obtained by varying procedures, will result in different water-CNM interactions (**Figure 4**) [65]. The above-mentioned hydroxyl groups explain also why CNMs aggregate, once dried, lead to the formation of strong hydrogen bonding between adjacent chains, resulting in an irreversible aggregation [66]. However, in order to promote commercialization and storage, it would be necessary to develop effective drying processes that could avoid irreversible agglomeration as far as possible. But this is not only mandatory to obtain a cost-effective material, but it is also required for some end-use applications. In attempt to deal with this, several procedures have been proposed encompassing different drying technologies as well as the use of additives and pre-treatments, but so far, a feasible solution does not exist yet [65].
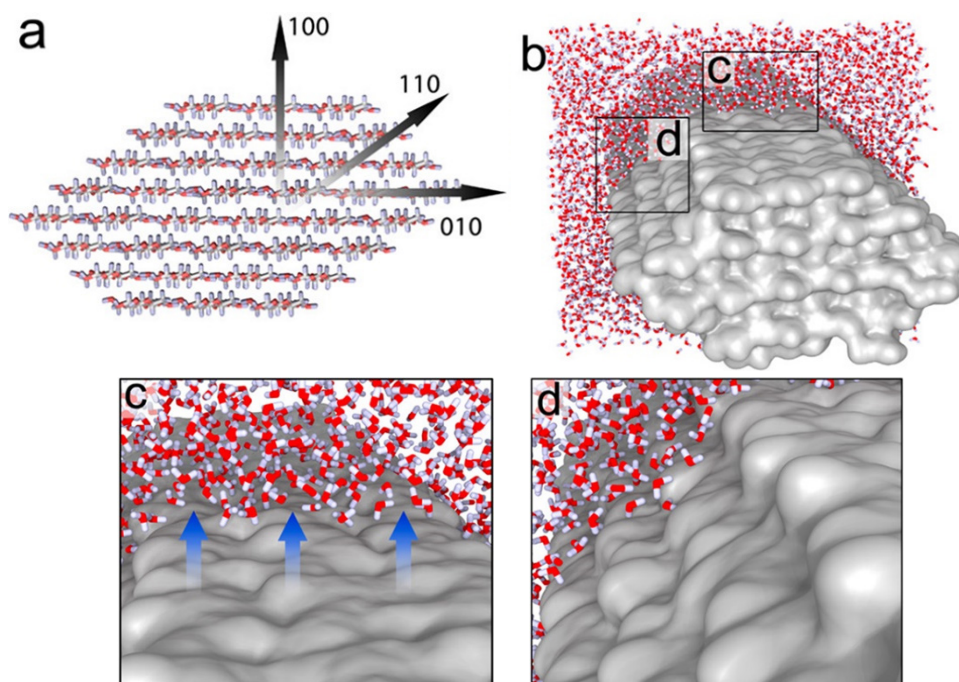
Figure 4. Simulation of the interaction of a cellulose nanocrystal with water molecules. Reproduced from reference [65] with permission from the American Chemical Society © 2020.

Aside from the uncontrolled aggregation issue, CNMs can self-assemble into 2D and 3D ensembles. Regarding CNCs, these controlled aggregation processes could be thought as a bottom-up approach in which cellulose nanocrystals act as building blocks. Different structures such as capsules, continuous fibres, films, hydrogels, aerogels, or foams, among others, can be prepared which would serve for different applications [67]. One of the most representative examples of 3D nanostructured biopolymer ensembles is the naturally-produced BNC. It is produced by an enzyme complex that is located in the inner part and along both membranes of gram-negative bacteria, the catalytic complex includes subunits to generate the glycosyl transfer in the cytoplasm and others to ensure the exportation of the fibres as they grow, first to the periplasm and then outside the outer membrane [68]. Once the BNC fibrils are extruded by bacteria and are arranged in a parallel chain of 10 to 15 fibres via hydrogen bonds. These subfibrils form microfibrils and microfibril bundles by the aggregation to generate a 3D structure of fibres with a diameter below 100 nm [69]. Concerning tailor-made CNM hydrogels, several procedures have been reported in the literature. Many of those proceedings are based on forcing attractive intermolecular interactions to be dominant, thus overcoming the repulsions that stabilize CNM suspensions [70-72]. Nevertheless, beyond physical hydrogels, it is also possible to covalently crosslink CNCs or CNFs leading to chemical hydrogels [73]. Such 3D structures can be prepared to be directly used as scaffolds for biomedical purposes or to develop drug delivery systems [74]; but there is also the prospect of obtaining highly porous aerogels, or cryogels, that would find their application in those requiring high surface areas, for example, within the heterogeneous catalysis field [75].

For such a purpose, the most common method to remove the included water is freeze-drying. This method allows to avoid the capillary forces that would arise from liquid water evaporation; therefore, the former porous structure can be fairly preserved. However, the growth of ice crystal fronts that are eventually sublimated somehow determines the pore orientation and could even modify the inner microstructure, especially, when it comes to poorly cross-linked hydrogels or weak physical gels. Regarding the freezing step before freeze-drying, apart from directly immersing in liquid nitrogen, also known as 'bulk freezing' (resulting in randomly oriented pores), it is also possible to perform the so-called 'freeze casting'. The latter approach allows driving the porous structure towards higher degrees of anisotropy, since the ice crystal fronts only grow in a single direction, and the obtained materials could take benefit from the resulting unidirectional pores [26]. However, the transition ascribed to freeze-drying has to be avoided to keep the hydrogel inner structure intact. To cope with this, supercritical drying could be performed, for instance, as it has been demonstrated that keeping chiral nematic phases

by solvent exchanging and CO_2 supercritical drying is possible, unlike when freeze-drying is conducted [76]. Nevertheless, to perform such treatment, water has to be exchanged with some solvent in which CO_2 is miscible, thus, leading to additional steps and higher reagent consumption. The drying route of BNC hydrogels also determines the properties of the dried samples, one can obtain xerogels by air-drying [77], in which the 3D network collapses, or aerogels by freeze-drying or by CO_2 supercritical drying [78].

5.3. Derived materials from nanostructured biopolymers

Porous carbon materials with hierarchical structures are highly desired for catalytic and energetic applications. Many commonly used procedures involve the use of synthetic precursors as starting materials for its further conversion into highly porous carbons by pyrolysis at high temperatures [79]. However, the current context calls out the challenge of accomplishing a development compatible with sustainability, so the usage of renewable sources (such as CNMs) emerge as an appealing solution. Within this framework, any of the CNMs could be used as raw material for the production of porous carbons through a bottom-up approach. As it has been stated previously, the use of CNCs as building blocks to self-assemble into porous aerogels, could lead to porous carbon aerogels upon pyrolysis, with novel structural features. On the other hand, BNC materials can also be used as a biomass source for carbonization, due to their high carbon content in the dried form, the 3D network structure, and the possibility of functionalization through hydroxyl groups [80]. Huang et al. [81] used this material as both the cathode and the interlayer in lithium–sulphur batteries depending on the thickness with good results. Nevertheless, among CNMs, CNFs and CNCs stand out for this purpose, as explained by the possibility of employing different cellulose sources as well as different extraction procedures. Besides, the existence of different cellulose allomorphs has to be considered too. This leads to a lack of standardization within CNMs which makes it difficult to replicate further experimental processings. For instance, considering the usage of CNCs as a precursor for the preparation of 3D structures, the difference between using tunicates or cotton linters as the cellulose source would be important, since the former will result in longer nanocrystals than the latter, favouring its self-assembly. It can be as well considered that a CNC (or CNF) milder extraction procedure would lead to higher crystallinity degrees than harsher conditions, ultimately influencing their properties.

6. Conclusion and future outlook

Carbon nanotechnology has reached sufficient scientific maturity regarding the oldest members of this family, namely fullerenes and nanotubes. The former have a clear niche application in organic

solar cells (as an integral part of the P3HT:PCBM hybrid), whereas the latter are specially valued in electronic and electrochemical applications as per their easy assembling capability into thin conductive films. Something similar is applicable to the graphene family, in which the rich diversity of derivatives makes it possible to exploit their excellent physical and chemical properties and turn them into useful applications (mainly in energy and medicine) via the assembly into 3D structures. However, the same bottlenecks and drawbacks still exist, impeding their full potential development and the compliance with sustainability principles. Thus, some emerging nanomaterials made also by carbon are currently generating excellent prospects in this regard, such as nanocellulose or carbon dots, which may not only provide a better way to disperse or hybridize the older carbon nanomaterials, but also show by themselves a true potential to be the next paradigm of sustainable carbon nanotechnology. Their easy aqueous processing and their groundbreaking features (unique interactions with water, high self-assembling potential, easier functionalization, photoluminescence…) will make the translation of carbon nanotechnology into tangible applications in a near future.

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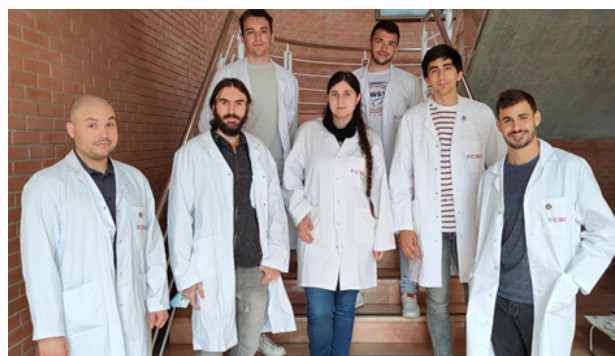
The youngest members of the Group of Carbon Nanostructures and Nanotechnology (G-CNN) at the Instituto de Carboquímica (ICB-CSIC). From left to right, lower part: Jose M. González (Tenured Scientist); Eduardo Colom (PhD student), Clara Carrera (PhD student); Victor Calvo (PhD student); Miguel Á. Álvarez (PhD student). Upper part: Lucas Güemes (Master student); Carlos Martínez (Master student).

José Miguel González-Domínguez obtained his BsC in Chemistry in 2007 from the University of Extremadura (Spain) and his PhD in Chemistry in 2012 from the University of Zaragoza (Spain), while working at the Institute of Carbon Chemistry (ICB-CSIC) under the supervision of Prof. Maria Teresa Martínez. As a postdoctoral researcher, he worked at ICB-CSIC, at the University of Trieste (Italy), in Prof. Maurizio Prato's group; and at the Faculty of Chemistry at University of Castilla-La Mancha. Very recently, he promoted to Tenured Scientist in ICB-CSIC, while being a member of the G-CNN research

group. He has been the recipient of some important research fellowships (Marie Curie, Juan de la Cierva formación and incorporación), and several young researcher's awards, including the extraordinary Doctorate award, an award from the Spanish Royal Society of Chemistry (RSEQ) in 2012 and an award from the Spanish Carbon Group (GEC) in 2013. In 2018 he was granted with the representation of the Carbon element by the IUPAC in their periodic table of younger chemists, and highlighted as one of the most representative young chemists worldwide. His main focuses are carbon nanostructures and their composites for structural, sensing and biomedical applications, with special focus on green processing approaches and industrial transference. In particular, he is now leading different research projects dealing with the use of biohybrids made of carbon nanotubes or graphene with nanostructured polysaccharides (nanocellulose, nanochitin) for the sustainable processing of functional conductive inks, anticancer therapies or highly efficient coatings for the stone-based cultural heritage. Last but not least, he also has a solid track record in scientific outreach, by which he organized some events and imparted many talks to the general public (such as in academia, industry, bars, schools…). He is a frequent writer of scientific posts, and he is developing an educational project (@incluciencia), funded by FECYT and FGCSIC, to use science for motivating teenage students in a way that empowers them to fight against academic exclusion.