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Editorial

Carbon-based research advances featuring young Spanish talents

Aún recuerdo con total claridad cuándo fue la primera vez que oí hablar de los nanomateriales de carbono. Fue en el verano de 2006, cuando yo me encontraba a punto de empezar mi último curso universitario, y como premio a una trayectoria académica sin fisuras "me regalé" un viaje a Benasque (en el Pirineo aragonés) para acudir al curso de verano "Fronteras de la Química" organizado por el CSIC. Por primera vez oí hablar sobre una "nanopartícula" y sobre todo aquello que poco tiempo después sería la fuerza motriz de mi desarrollo científico: "nanotubos de carbono". Fue tal el *hype* que me generó dicha ponencia, que me marqué el reto personal de dedicar mi futuro científico a estos materiales. Y así fue. Conseguí encauzar mi carrera profesional en esos materiales, lo cual me llevó a realizar mi Tesis Doctoral en el Instituto de Carboquímica en Zaragoza y, en años posteriores, a seguir investigando en otras instituciones nacionales e internacionales.

Cientos de miles de personas se dedican a diario en el mundo a investigar de un modo u otro en materiales de carbono, aunque si realizamos una búsqueda sencilla, mayormente encontraremos los mismos nombres: Iijima, Smalley, Kroto, Tour, Dresselhaus, Ajayan, Ruoff, Geim, Novoselov,… Grandes investigadores e investigadoras (much@s ya fallecid@s) que han conseguido que la ciencia y la tecnología camine a hombros de gigantes y cuya repercusión ha supuesto toda una inspiración para otras jóvenes promesas que se han formado científicamente siendo testigos de tales avances. ¿Y qué nos depara el futuro en este campo de estudio? Decía el célebre Neil Degrasse-Tyson en 2016 que "Quizás el próximo Einstein se está muriendo de hambre en Etiopía", pues salvando todas las diferencias con el contenido de esa afirmación, podríamos asimilarlo a España. Quizá el próximo Sumio Iijima o la próxima Mildred Dresselhaus puedan ser jóvenes de origen español y/o investigando en España, pasándolas canutas, pero con gran potencial para cambiar el mundo.

De tod@s es sabido que, en este país, a pesar de las circunstancias y las condiciones de trabajo, se hace buena ciencia, y en lo que respecta al carbono, no deberíamos envidiar en calidad (en otras cosas quizá sí…) a ningún otro país. Pero de entre las mil cosas que nos faltan, hay una tan importante como la que más: la VISIBILIDAD. Para l@s jóvenes la visibilidad puede significarlo todo, así que con ese objetivo se ha organizado este "especial". En él, y a lo largo de dos números consecutivos, se presentarán distintas contribuciones de jóvenes investigadores e investigadoras nacionales cuyo duro trabajo, materializado en distintas investigaciones, opiniones o divulgaciones en el ámbito del carbono, sin duda podrán llegar a hacerles referentes contemporáneos. Y cuando eso suceda, quede este número especial como testigo y sirva una célebre frase del célebre Steve Jobs: "Si miras bien de cerca, muchos éxitos sobrevenidos de la noche a la mañana requirieron muchísimo tiempo".

Así, en el presente número tenemos importantes contribuciones en materia de nanoestructuras de carbono como la de la Dra. Miriam Barrejón Araque (Hospital de Parapléjicos de Toledo), donde revisa el uso de nanoestructuras de carbono en el conformado de ensamblados multidimensionales; la reseña de Tesis Doctoral del Dr. Antonio Domínguez Alfaro (CIC BiomaGUNE, San Sebastián), que versa sobre la fabricación de materiales porosos basados en nanotubos de carbono y polímeros conductores para su aplicación en medicina regenerativa; la contribución del Dr. Alejandro Criado Fernández (Universidade da Coruña), donde revisa el uso de grafeno para biosensores implantables; o la contribución de un servidor que, junto con el "ala" joven del grupo de investigación al que pertenezco, revisamos el estado actual y perspectivas futuras de los nanomateriales de carbono, haciendo hincapié en las nuevas nanoestructuras biocompatibles y sostenibles (como la nanocelulosa) que emergen dentro de este área de estudio. Por último, y no menos importante, un artículo de opinión de la Dra. Susana García (RCCS; Heriot-Watt University, UK), donde ilustrará su visión sobre cómo abordar el futuro de la reducción de emisiones de CO$_2$.

José Miguel González
ICB-CSIC

Carbon Nanotube 3D Architectures: from Micro- to Macro-scales

Arquitecturas de Nanotubos de Carbono 3D: de la Micro- a la Macro-escala

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Abstract

Carbon nanotubes (CNTs) are currently on the cutting edge of nanotechnology and material science and their applications in our daily life have gradually increased in the past years in various fields, such as life science, energy storage, biomedical, and environmental applications. In the past decades, great achievements have been made in the development of long fibres or 2D CNT films with promising properties for commercial applications. However, CNT 3D architectures with highly porous and hierarchical structures and specific shapes and volumes are promising for a broader range of fields. This review article summarizes the most common fabrication methods used for the preparation of CNT 3D architectures and their influence on the final material properties.

1. Introduction

Since the discovery of carbon nanotubes (CNTs) in 1991 by the Japanese chemist Sumio Iijima [1], CNTs have aroused a great deal of interest due to their remarkable intrinsic mechanical, electrical, and thermal properties, which are essential features for a wide variety of potential applications [2,3]. Despite the simplicity of their chemical composition and atomic bonding configuration, obtained when a graphene sheet is rolled up into a cylinder, in the past decades, CNTs have revolutionized the fields of nanotechnology and materials science, allowing the preparation of novel materials for diverse and interesting applications. But despite its great success, further extending their potential, to a great extent, can be achieved through the assembling of CNTs into macroscopic 3D-architectures while preserving the intrinsic properties of the individual CNTs [4]. When CNTs self-assemble into lightweight, elastic, chemically stable, and highly porous 3D nanoarchitectures these are frequently known as CNT sponges (**Figure 1**). CNT sponges in general possess advantageous properties with respect to 2D CNT-based materials: their interconnected porous structure and high specific surface area are expected to provide improved electrical conduction, thermal stability, better adsorption or electrochemical properties, high storage capacity, resistance to harsh environment, and facile doping process. However, because of the small size of CNTs and the strong pi-pi interactions that cause stacking and aggregation between them, it is not a trivial task to assemble them into 3D architectures. To put these tiny cylindrical nanotubes together into a macroscopic 3D structure with a specific distribution and interconnection, while simultaneously control the porous structure has become a challenging task within the research community for building next-generation carbon-based functional materials. In this article, I review the different approaches that have been described in the literature to develop highly porous CNT-based architectures from nanoscopic CNTs.

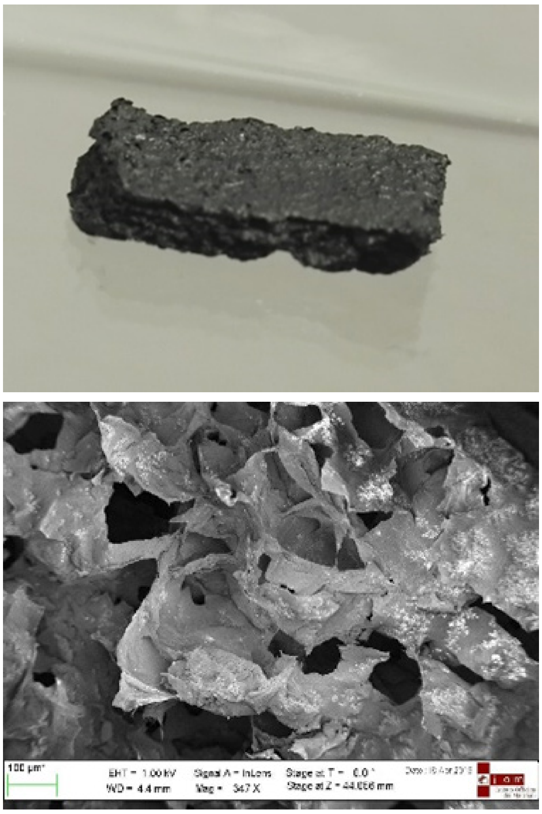

Figure 1. Photo of a CNT sponge (up) and scanning electron microscopy (SEM) image showing the porous structure (bottom).

2. Direct growth of CNT 3D architectures by chemical vapor deposition

Since the discovery of CNTs, a variety of organized nanotube architectures have been fabricated using chemical vapor deposition (CVD) [6,7]. In the late 1990s, vertically aligned CNT forests were grown on porous substrates (such as silica or glass) by CVD [8,9]. The initial challenge was to reduce the CVD temperatures, thus enabling the direct synthesis of

CNT forests onto devices [9]. However, later studies demonstrated that low-temperatures lead to CNTs with poorer crystallinity [10], not desirable in the fabrication of devices. Later approaches have developed new and advantageous methods for the catalytic growth of CNT-based 3D architectures via CVD method that allow the control of the length, quality, and density of the final structures [4]. In 2010, Gui et al. developed a slightly modified CVD process to tailor the alignment, density and porosity of the CNT 3D architectures [11]. For this purpose, the authors simply changed the carbon source (from xylene to dichlorobenzene), which resulted in a random orientation of the CNTs instead of the aligned one. Compared to other CNT-based porous materials, these structures offered additional advantages such as mechanical flexibility and robustness, electrical conductivity, and thermal stability, which are promising properties for a broad range of applications such as multifunctional structural media, sensors, high strength-to-weight ratio composites, membranes, and electrodes. The same authors reported the controlled synthesis of CNT sponges in relatively soft to hard forms with tuneable compressibility (**Figure 2**) [12]. Different densities were achieved by varying the source injection rates. The lower-density sponges showed high compressibility of up to 90% volume reduction, while the higher-density sponges recovered to 93% of original volume after compression. The authors demonstrated that these sponges could be used to work as stress sensors as well as conductive composites by direct polymer infiltration.

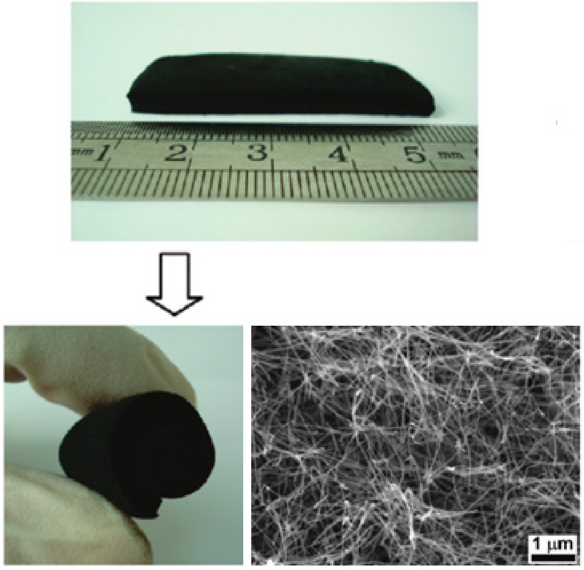

Figure 2. Soft and compressible sponge (up) and SEM image showing the random and porous network (bottom). Reprinted with permission [12]. Copyright 2010. American Chemical Society.

The introduction of heteroatoms (e.g., boron or nitrogen) during the CVD process appeared also as an effective way for creating covalent interactions between the CNTs, which significantly enhanced the mechanical properties and electrochemical performance.[14,15] Entangled CNTs fixed by elbow junctions were observed in both cases, which resulted in enhanced stability of the final material (**Figure 3**).

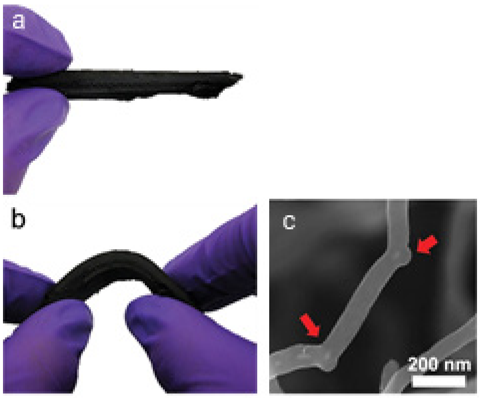

Figure 3. a) and b) Photos and c) SEM image of a boron-doped MWNT 3D architecture containing “elbow” junctions. Reprinted with permission [13]. Copyright 2012, Macmillan Publishers Limited.

CNT-based 3D macroscopic architectures can also be obtained by using a 3D catalyst template during the CVD process. He *et al.* reported a CNT sponge prepared by growing the CNTs on a 3D network consisting of conductive metal microfibers (8-mm diameter nickel fibres) [15]. This approach allowed the large-area fabrication of materials with macro-/meso-sized porosity and the combination of excellent thermal and electrical conductivity in a binderless structure with potential applications in different fields. A similar approach was employed for the fabrication of binderfree 3D sponges consisting of vertically aligned CNTs [16]. Here, the 3D architecture was fabricated through a Ni-foam templated microwave plasma chemical vapor deposition method, which yielded a graphitic microstructure with high porosity, ultralow density, reduced impedance, and enhanced cycling stability, with excellent Li-ion storage capability. In 2011, Zhao *et al.* sputtered Fe catalysts on the surface of Ni foam for the growth of 3D randomly entangled CNTs to fabricate an electrode with improved capacitive performance for supercapacitors [17].

Despite CVD approaches have been largely employed for the fabrication of CNT-based architectures with different shapes and sizes, it remains challenging to control the types of CNTs that are grown during the process (metallic vs semiconducting, or tube chirality) [18]. Furthermore, the removal of the residual catalyst is also a difficult task, since harsh conditions will affect the porous structure. Alternative methods have been also explored by different research groups in recent years.

3. Fabrication of CNT 3D architectures via Sol-Gel assembly

The preparation of CNT sponges via Sol-Gel assembly could be considered as an alternative to conventional CVD approaches to fabricate porous, ultralight, and isotropic 3D CNT architectures. The Sol-Gel assembly approach is a wet-chemical-based self-assembly process that typically consist of three different steps (**Figure 4**). First, the CNT powders are homogeneously dispersed in aqueous or organic

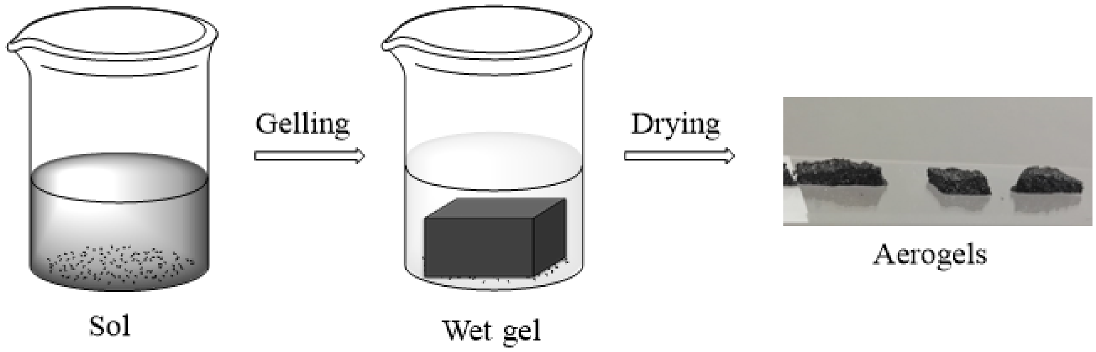

Figure 4. Schematic representation of the steps involved in the Sol-Gel process for the preparation of CNT 3D architectures via Sol-Gel assembly.

solvents to form a colloidal suspension (sol). Second, hydrolysis of the colloidal suspension takes place to form a network in a continuous liquid phase (gel). In the final step, porous CNT aerogels are obtained through the use of polymers and compression methods, freeze drying processes or cross-linking and lyophilisation [4].

The most-widely explored Sol-Gel approach has been accomplished from CNT suspensions prepared with the aid of organogelators (surfactants, polymers etc…) that allow the fabrication of freestanding CNT aerogels by freeze or supercritical CO_2 drying processes [19]. For example, Yodh *et al.* prepared different suspensions of CNTs in water with sodium dodecylbenzene sulfonate (SDBS) [20]. The suspensions were left overnight to set into elastic gels, whose structures were reinforced by small amounts of polyvinyl alcohol (PVA). Albeit at the cost of reduced conductivity, PVA-reinforced aerogels exhibited outstanding mechanical properties (for instance, they were able to hold 8000 times their weight). The as-synthesized CNT aerogels showed potential for applications such as sensors, actuators, electrodes, thermoelectric devices, as well as silica-based aerogel applications. In a later approach, the same authors used a similar strategy in which they substituted PVA by polydimethylsiloxane (PDMS), producing transparent and stretchable conducting aerogels, whose electrical conductivity was not affected under high bending strain [21]. A freestanding SWNT aerogel was fabricated by the same group through a typical sol–gel method [22]. For this purpose, the purified SWNTs were uniformly dispersed in deionized water by adding SDBS as surfactant. Thereafter, a series of treatments including ultrasonication, centrifugation, condensation, solvent-exchanging (removing SDBS), and critical-point drying, were followed and a freestanding CNT aerogel with very low density was obtained. Through this method, the aerogels were fabricated with tunable shapes such as cubes, cylinders, or cones. Using the same method, a nitrogen-doped, highly porous, SWCNT nanoarchitecture was developed via pyrolysis of polydopamine-coated 3D SWCNT aerogel [23]. The material showed high specific surface area, good wettability, and structural robustness, showing promise for application in energy storage devices and the next generation of smart textile electronic devices. In a recent study, the freeze drying technique has been employed for the preparation of a wave absorber material consisting of a CNT 3D aerogel [24]. To this end, a known volume of a CNT water dispersion was placed into a metal waveguide cavity and freeze-dried, enabling the preparation of randomly-oriented CNT aerogels (**Figure 5**). The resulting porous structure offered low surface reflections while maintaining high absorption across the band due to the highly porous surface and low conductivity. PDMS-based CNT aerogels have also been extensively employed to enhance the mechanical properties of the final materials [25]. In a recent study, a simple and easy solvent engineering method was employed to develop 3D CNT-based porous structures [26]. SWCNTs were homogeneously dispersed in cyclohexane using a micronized-milling method, and the dispersed CNT slurry was then directly transformed into the CNT aerogel in a perforated PDMS scaffold via a rapid solvent evaporation process. The porous materials exhibited low thermal conductivity and increased phonon scattering being promise for their application in flexible thermoelectric power generators.

However, adding polymers or binders during the Sol-Gel assembly process may bring impurities, increase density, and reduce porosity, leading to degradation of the intrinsic properties of CNTs. In a recent study, Luo *et al.* have reported the construction of pure CNT sponges using super aligned CNTs (SACNTs) as the starting material [27]. In this work, the authors took advantage of the strong van der Waals interactions typical of CNTs to form a continuous 3D network via a simple ultrasonication and freeze-drying procedure, without using any organic binder or template. They demonstrated that the intrinsic excellent conductive properties and thermal/chemical stability of SACNTs were preserved in the final material. Chemical bonding might be also considered as a promising method for enhancing the aerogel structure, providing a powerful way to improve the mechanical properties [4]. Zou *et al.* Reported the fabrication of an ultralight free-standing monolithic MWCNT aerogel with strong chemical bonding interactions and a honeycomb morphology [28]. Poly(3-(trimethoxysilyl) propyl methacrylate) was employed to disperse and functionalize MWCNTs, which led to a MWCNT wet gel. The MWCNT wet gel was frozen by liquid nitrogen, and

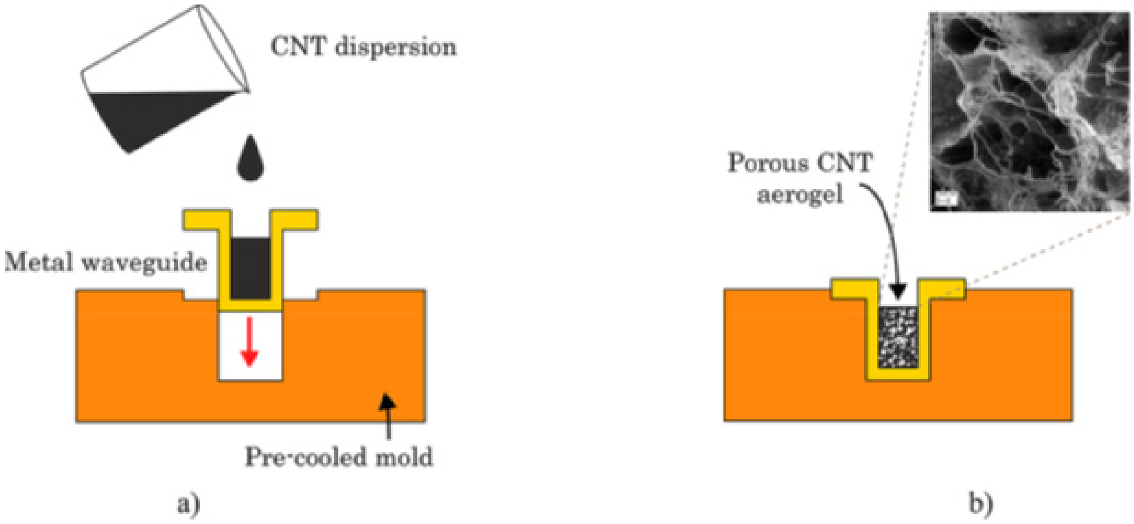

Figure 5. CNT aerogel sample preparation. A known volume of CNT dispersion is placed inside a metallic waveguide (a), prior to fast- freezing at −25 °C/−196 °C, which forms the porous aerogel (b). Reprinted with permission [24]. Copyright 2018. American Chemical Society.

the continuous growth of ice crystals generated an array of micrometer-sized polygonal ice rods parallel with the freezing direction. The as-prepared aerogel showed an excellent compression recoverable property, hierarchically porous structure, and high conductivity, showing exceptional pressure and chemical vapor sensing capabilities. More recently, carbon nanotube reinforced polyimide composite aerogels with controllable porous structures and good mechanical properties were fabricated through a freeze-drying technique and thermal imidization process [29]. It was found that the functional group content had a significant influence on the pore size and size distribution of the corresponding aerogels. Thus, the optimal polyimide/CNT aerogel displayed low density, improved compression modulus, and high thermal stability, implying its great potential as lightweight and high-performance material for aerospace applications. Even though chemical bonding can be used for enhancing the structural features of the CNT aerogels, the presence of polymers, binders, or other additives, has a negative effect on some important intrinsic properties of CNTs, such as the electrical conductivity, surface activity, and chemical stability. Therefore, the development of simple, scalable, and easy-to-control methods that decrease the costs of processing has been a pursued aim within the research community.

4. Pure CNT 3D architectures based on chemical cross-linking

The fabrication of 3D architectures through chemical functionalization and cross-linking approaches could be one of the most inexpensive, controllable, and scalable methods. Thus, the use of chemical approaches for the direct inter-tube cross-linking of CNTs has been pursued by several groups, with the common goal of fabricating 3D sponges based on pure CNTs with enhanced properties. In 2008, a CNT 3D architecture was prepared from fluorinated MWCNTs by means of compressing and heating approaches [30]. The subsequent de-fluorination of the material resulted in strong interlinking between the CNTs through covalent chemical bonding, generating a robust monolith of MWNTs with superior mechanical properties. Suzuki cross coupling chemistry has been also employed for the preparation of covalently interlinked 3D porous CNT architectures [31]. In this work, CNT powders were oxidized in HNO_3 and then converted to acid chloride. The resulting CNTs were covalently interconnected via Suzuki cross coupling reaction, and after a lyophilization (freeze drying) process, CNT aerogels made of highly porous, inter-connected structures were obtained (**Figure 6**). Leonard *et al.* used diazonium coupling chemistry for crosslinking carbon nanotubes yielding 3D CNT architectures that worked as hydrogen storage supports [32]. Ozden *et al.* prepared low-density 3D macroscopic structures made of covalently cross-linked CNTs through their functionalization with allylamine monomers followed by free-radical polymerization methods [33]. The resulting material showed higher mechanical properties, larger surface area and greater porosity showing potential for CO_2 storage applications.

Despite the great progress that has been made to control the fabrication of CNT 3D architectures, which already show promise for various potential applications, it remains challenging to achieve the improvement of several parameters, such as the synthesis of high-quality CNT sponges without catalyst or polymer impurities, or the control of the microstructure and porosity. Therefore, further research is required for the development of low-cost and large-scale approaches that allow the production of high-quality CNT 3D porous architectures, enabling industries to use them as a raw material for current applications.

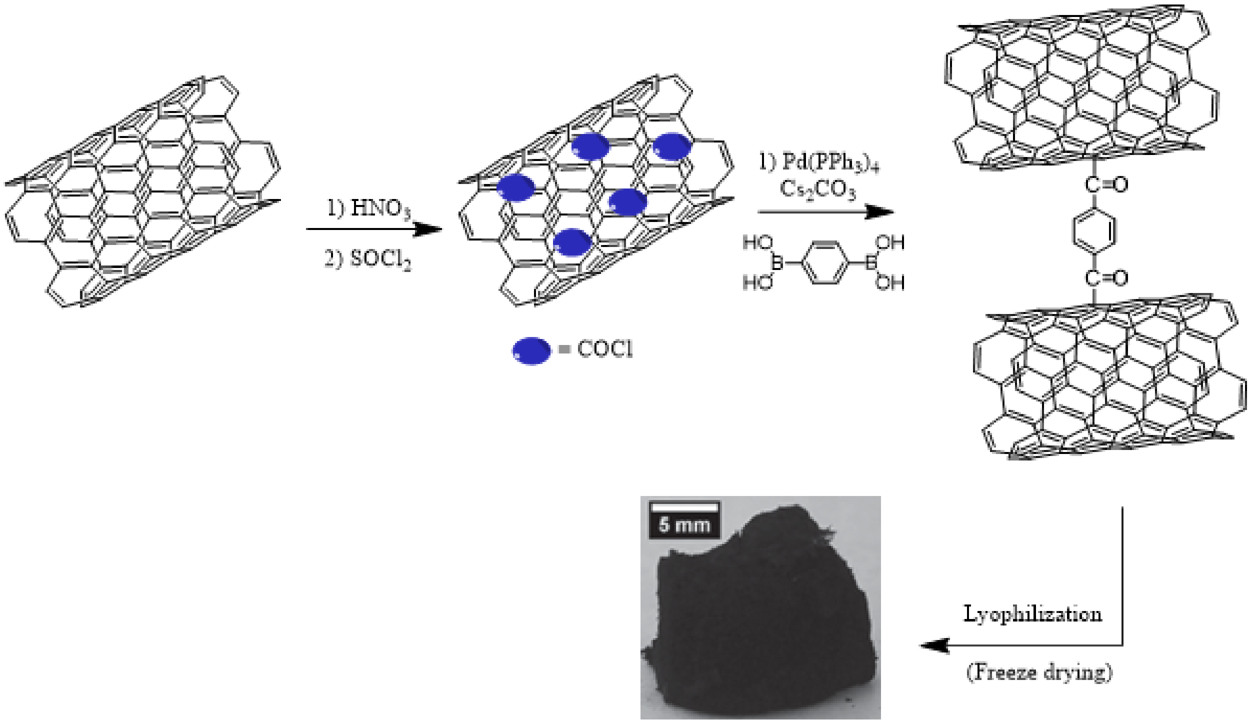

Figure 6. Schematic representation of the procedure followed for the preparation of 3D-CNT architectures from CNT powders via Suzuki cross-coupling reaction.

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Miriam Barrejón. My research career started in 2010 at the University of Castilla La-Mancha, where I carried out a Master's degree in Sustainable Chemistry. In 2011, I was awarded with a Doctoral fellowship by the Spanish Ministry of Economy and competitiveness (MICINN), which allowed me to perform my doctoral studies (2011-2015). Since I started my research career as a PhD student, I have developed a strong background and extensive experience in the field of carbon nanomaterials, developing hybrid systems for multidisciplinary application areas. Along this time, I have been involved in collaboration with several groups all around Europe, USA, and Japan. During February-June of 2014, I visited the laboratory of Professor Francis D'Souza at the University of North Texas, where I acquired wide experience in time-resolved emission and transient absorption studies. Once I finished my PhD studies, I performed a two-year postdoc (2016-2018) in one of the most important groups in the field of carbon nanomaterials, under the supervision of Professor Maurizio Prato, where I dealt with the functionalization of carbon nanomaterials for driving the growth and differentiation of neuronal stem cells. This position helped me to improve my previous acquired skills and to extend my knowledge-base in biomedical applications of carbon nanostructures. From 2019, I am a postdoctoral researcher at the National Hospital of Paraplegics in Toledo under the Sara Borrell program, and my research is focused on the chemical modification of carbon microfibers for neuronal tissue engineering.

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].

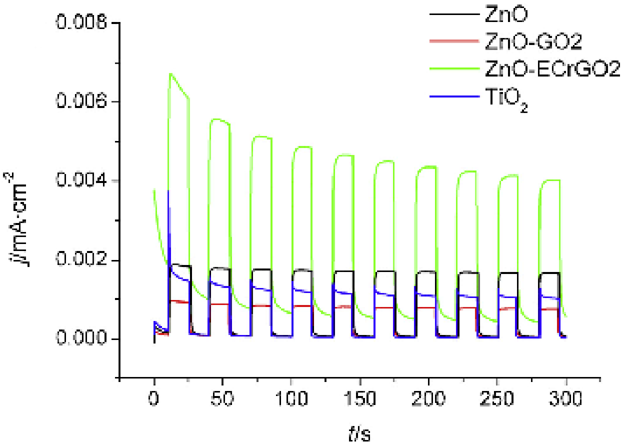

Figure 1. Potentiostatic on-off measurements in which water oxidation is carried out. Reproduced from reference [22] with permission from Elsevier © 2020.

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.

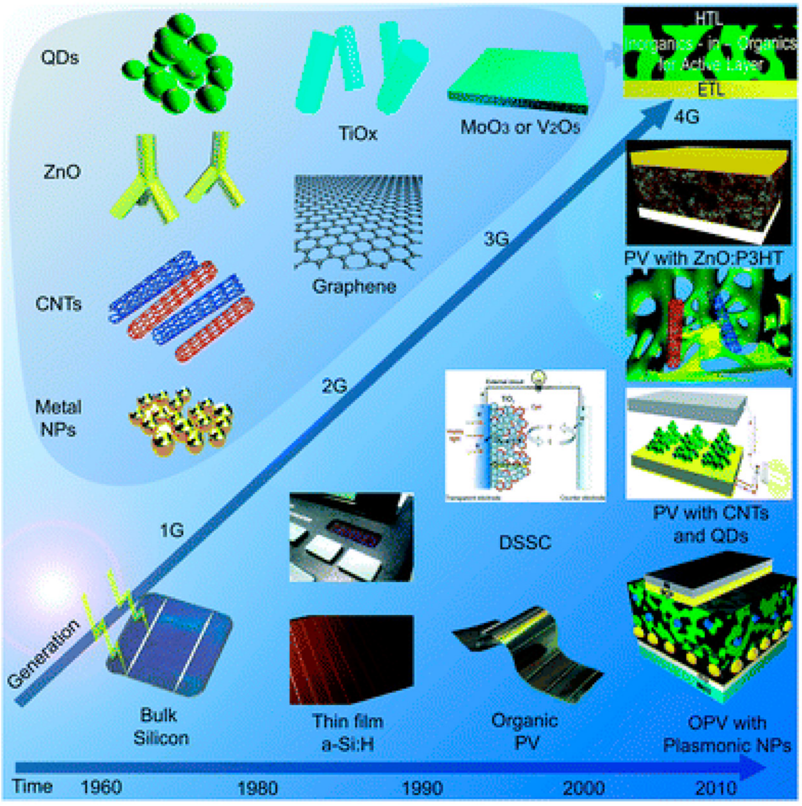

Figure 2. Overview scheme on the development of different materials for solar cells. Reproduced from reference [40] with permission from MDPI © 2019.

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

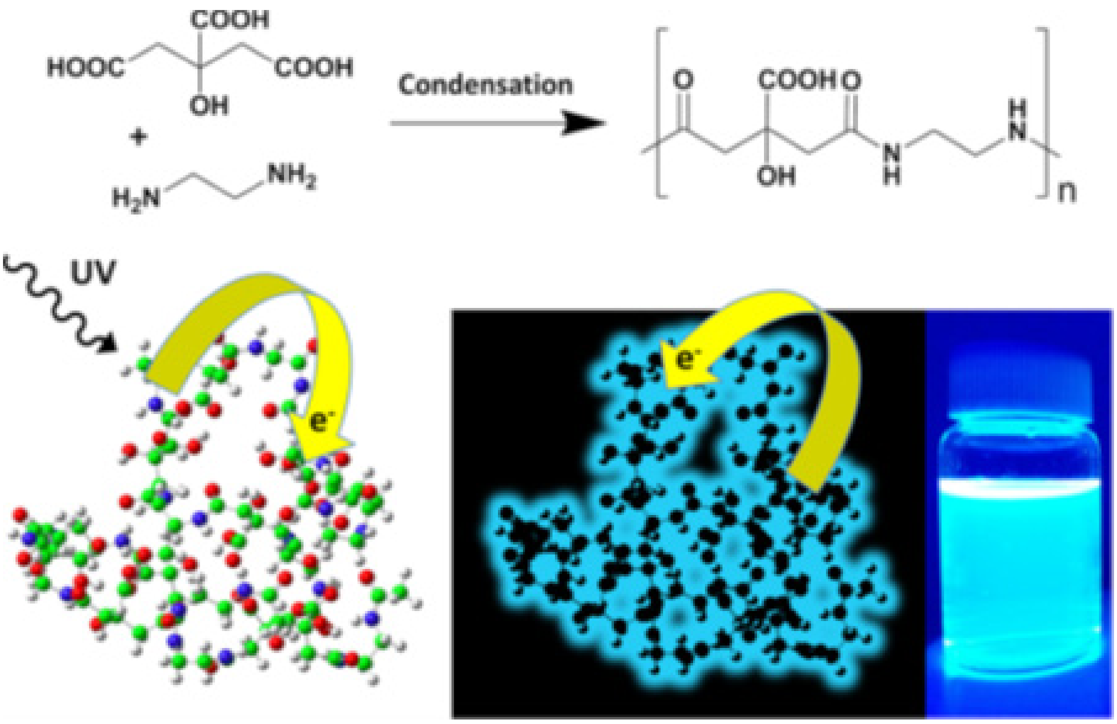

Figure 3. CDs, synthesized from citric acid and ethylenediamine showing a strong blue PL. Reproduced from reference [47] with permission of the American Chemical Society © 2018.

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].

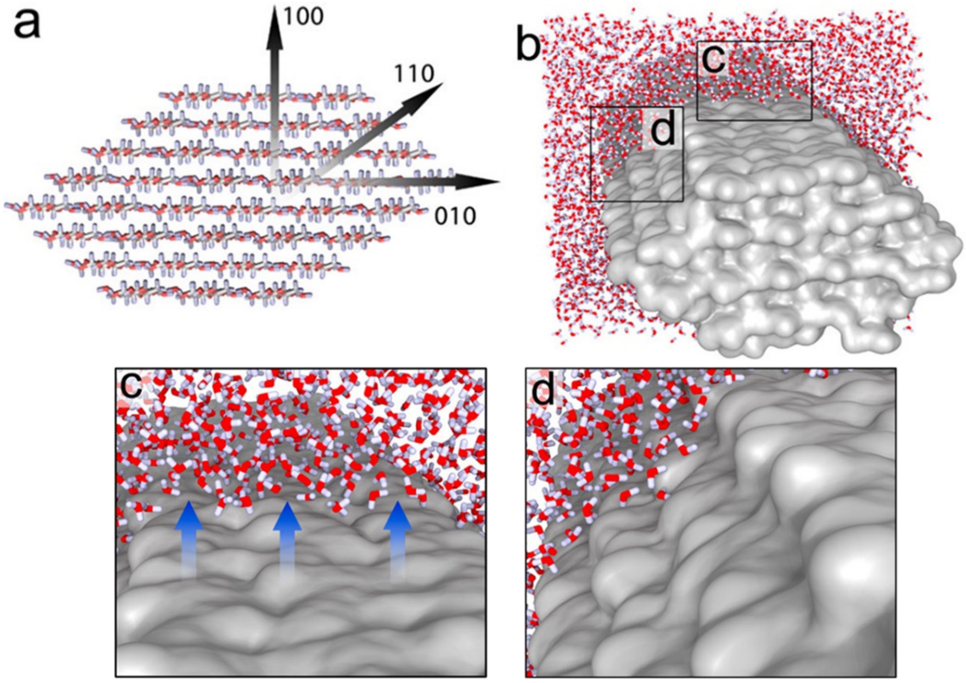

Figure 4. Simulation of the interaction of a cellulose nanocrystal with water molecules. Reproduced from reference [65] with permission from the American Chemical Society © 2020.

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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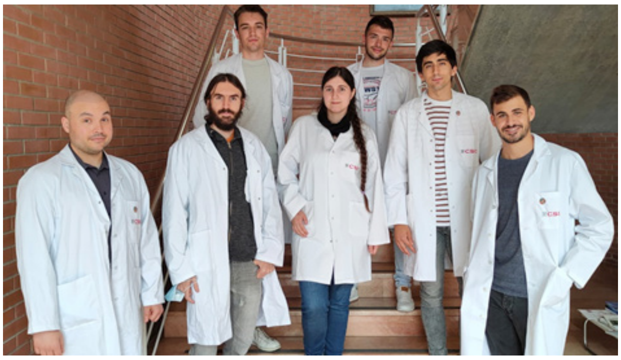

The youngest members of the Group of Carbon Nanostructures and Nanotechnology (G-CNN) at the Instituto de Carboquímica (ICB-CSIC). From left to right, lower part: Jose M. González (Tenured Scientist); Eduardo Colom (PhD student), Clara Carrera (PhD student); Victor Calvo (PhD student); Miguel Á. Álvarez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

Graphene for implantable biosensors

Grafeno para biosensores implantables

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Abstract

In this review, we will provide a comprehensive insight on the current research situations and future challenges for the graphene-based implantable biosensors. We introduce the use of graphene derivatives for *in vivo* sensing implants, discussing their synthesis and key properties for this final application. Then the most promising recent examples in the field were critically revised, with special attention to electrochemical and transistor-based biosensors. Although there are still many challenges to overcome, we can anticipate that the latest developments are paving the way for the next generation of this kind of implants. Finally, the emerging 2D materials are also presented, which are following the graphene pathway for the *in vivo* sensing field, with a broad future to explore.

Introduction

In vivo sensing is an emerging field with the potential to change health care in the coming years through personalized medicine and highly precise treatments [1]. Sensing devices implanted into patients could regularly provide appropriate health information. Continuous or periodically health monitoring can assess health conditions that can help diagnosis, treatments, or rehabilitation, increasing the survival ratio of an at-risk population, improving life quality, and reducing medical costs. Since these sensors are able to collect a large amount of data, novel data management and analysis methods, such as Big Data and machine learning, can be also applied to extract highly valuable information [2].

In vivo biosensors can specifically detect biological-related analytes or other biological parameters of interest with high sensitivity operating inside the human body or implanted into a living system. Conventional *in vivo* sensing devices present important mechanical issues, since they are metal- or silicon-based systems that are too rigid for soft biological tissues. Other general challenges need to be overcome, such as long-term biocompatibility and stability, miniaturization, reliability, and costs, to achieve an outstanding sensing performance.

New materials, such as metal nanoparticles, organic polymers and carbon-based nanomaterials, have achieved considerable progress in this field [1,3]. In particular, graphene, one of the most explored carbon-based nanomaterials, and its family can accomplish the above-mentioned requirements. Form its discovery in 2004, has captured the interest of the research community for application in many different fields, ranging from optoelectronics to composites, and supercapacitors, among others [4–6]. Thanks to the great effort spent in the last decades in graphene research field, the most promising applications to reach their final use in our society are being established. Indeed, its use in sensing is emerging as one of these fields in which graphene have gained prominence as main component of the next-generation sensors [7].

The use of graphene in implantable sensing is unquestionable, since its large surface area, remarkable optoelectronic, thermal, and mechanical properties, this carbon material can potentially dominate in all features needed: sensitivity, specificity, linear range, reversibility, response time, long-term stability, and biocompatibility. Herein, we will critically review the most promising recent sensing approaches applied *in vivo* models to be transfer to a clinical level. In addition, we will discuss the key parameters to accomplish all the analytical requirements. Finally, we will consider current limitations in translating the revised technologies into final clinical devices. We have also commented the new related two-dimensional (2D) materials recently discovered that could tackle the key challenges in the field. It is worth noting that *in vivo* graphene-based sensors that perform health monitoring includes wearable sensors, and implantable devices. However, in this review we have focused on implantable sensors *in vivo*, as their development is more challenging due to their invasiveness in living systems. In addition, comprehensive overviews of wearable sensors have previously been examined [7–11].

Production of CVD-G and GO

Many graphene derivatives have been defined, including exfoliated graphene, graphene oxide (GO), reduced GO (rGO), graphene dots, chemical vapour deposition (CVD) graphene, etc. They can be produced by two main methodologies: bottom-up and top-down approaches[12]. Particularly, the bottom-up fabrication by CVD and the top-down oxidative processes of graphite are the preferred techniques for *in vivo* sensing purposes since they are mainly based on electrodes and transistor devices.

CVD is the most used methods for industrial-scale fabrication of graphene [13,14]. This procedure allows the synthesis of graphene with reproducibility, high-quality monolayer / few-layer with low number of defects. Thus, the electronic properties of CVD graphene are exceptional to be implemented in electronic devices as we will discuss below. CVD consists in the synthesis of large-area thin layers on metal surfaces, particularly, Cu or Ni, using a carbon gas source. These metal substrates are not appropriate for *in vivo* sensing applications and graphene must be transferred to more suitable substrates, as for example soft or transparent materials (PDMS, polyimide, PET), which are part of sophisticated systems [15]. To this end, there are several methodologies, such as polymer assisted transfer, dry transfer methods or electrochemical transfer. However, the transfer process may cause damage on its surface, such as wrinkles, and contamination of the sample. To solve these drawbacks, several techniques have recently been developed. However, the complexity of the whole process is still far from an industrial large-scale production.

The top-down oxidative methodology of graphite is generally performed by its chemical or electrochemical oxidation, breaking the Van der Waals interactions between graphite layers [16]. This exfoliation allows to obtain larger quantities of GO which are highly defective but soluble in aqueous media due to the large amount of different oxygenated groups on its surface. This approach is quite adjustable, since there are several methods that permit to tune the oxidation degree, type of oxidized groups and layer dimension [17–19]. However, during this procedure, it is common to use hazard chemicals or solvents that produces oxidation residues which can produced toxic effects even at low concentrations. Although, there are not well-defined agreements to define a medical grade material, particular attention should be paid to the GO composition to be used in *in vivo* applications.

Graphene properties

The properties of graphene (mechanical, transparency, high porosity, thermal conductivity, optoelectronic, etc.) make it ideal in bioelectronics field. In addition, depending on the envisioned bioapplication, some properties are fundamental (**Figure 1**).

As mentioned above, most of the graphene-based *in vivo* implants are electronic devices (*i.e.*, electrodes and transistors); thus, the electronic properties of graphene are crucial. Graphene has unusual conductive properties [20]; it presents a zero-energy band gap with a linear energy dispersion, which permits electrons to travel faster than in other materials. Thus, it exhibits the highest electron mobility (~$2x10^5$ cm^2/Vs) and critical current density of 10^8 A/cm^2. Due to the high quality of graphene produced, CVD graphene is widely used as electrode component in electrochemical sensors [21]. This is also possible thanks to the wide electrochemical window of graphene that makes it suitable to work in biological environments. Regarding the conductivity, unlike graphene, GO shows less conductivity due to the disrupted sp^2 -hybridized carbon network produced by oxidation process and it depends on the degree of oxidation. However, the abundance of oxygen functional groups, such as epoxide, carbonyl derivatives and more groups, provides GO with an inherent redox activity in cathodic and anodic regions. This redox activity is based on the oxidation or reduction of these oxygenated groups, some at mild electrochemical potential conditions for example quinones and epoxides. This allows GO to be also exploited in electrochemical sensing [22].

Besides, CVD graphene can be implemented in field effect transistors (FETs) technology [23]. Its extraordinary charge mobility leads to FETs with a high transconductance, which generates the amplification capacity of the transistor. This fact, together with the low intrinsic noise of this CVD graphene-based FETs, leads to detect electrical signals with high signal-to-noise ratio. Indeed, it has been reported arrays of flexible FETs based on CVD graphene that can detect brain activity in *in vivo* models [24].

Graphene derivatives can also provide extraordinary optical properties, as high transparency, that is a crucial feature for particular *in vivo* sensing performances. For example, CVD graphene permits tissue observation with clear images in a multifunctional bioelectronic device [25].

Mechanical properties have also a fundamental role *in vivo* bioelectronics. The atomic thickness, in addition to the strong covalent bond between the C atoms of the same layer, can provide an improvement in the mechanical properties of implants and protection against stresses and damages due to mechanical perturbations. It is well known that graphene has the highest Young's modulus (1Tpa) and fracture strength. Furthermore, as mentioned before, flexibility of the implant allows to decrease the immune response during implantation, giving biomimetic features to the device. This feature allows the construction of flexible graphene-modified electrodes to recording for instance electrophysiological signals for neuronal and cardiac tissues [26].

Graphene surfaces can be chemically modified by controlled chemical functionalization using either covalent or noncovalent methods [27]. Through chemical modification, selectivity capabilities can be implemented to the graphene sensing devices that requires receptors (*e.g.*, antibodies, enzymes, nucleic acids, etc) for the specific recognition of the biological analyte.

But why, despite the large number of studies focused on graphene biomedical devices developed, only few architectures reach an *in vivo* application? Most of the times, the answer to this question resides in one key factor: biocompatibility. Although there are many publications in the literature evidencing the biocompatibility of graphene-based materials *in vitro* [11], translating them into a clinical use is not generalizable, and an extensive *ad hoc* biocompatibility evaluation needs to be performed [28]. If during the *in vitro* trials is crucial assessing the cytotoxicity of the materials employed, the *in vivo* biocompatibility estimation includes the evaluation of

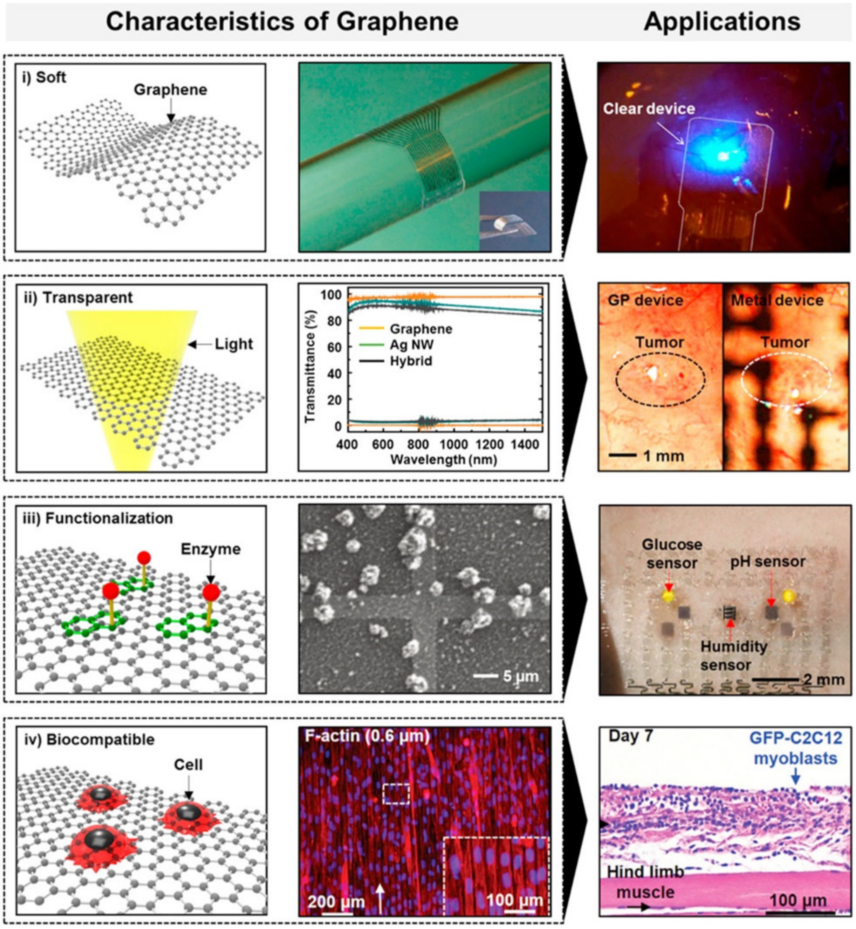

Figure 1. Properties of Graphene and bioapplications. Reproduced from ref. [10], Copyright 2019 American Chemical Society.

more complex immune responses that are not easily modelled for systematic studies. When talking about implants for sensing, the main factor to be evaluated are wound healing response to implantation, chronic inflammation, or foreign body response [29], and long-term stability and functionality of the device [30]. Although is not easy to assess the *in vivo* biocompatibility of a device, many different strategies are nowadays employed to reduce its inflammation process and promote its long-term durability [31]. Among others, tailoring the mechanical and chemical-physical properties of the device are of crucial importance for the success of an implant. As an example, the introduction of biomimetic coatings (proteins, biocompatible polymers etc.) [32,33] and the use of biocompatible flexible support materials (*e.g.*, polyimide)[34–36], are two successful strategies to reduce the immune response and ensure the implant durability.

Graphene-based *in vivo* biosensors

A biosensor could be define as device able to selectively detect and/or quantify biological-related analytes [37]. By moving from *in vitro* to *in vivo* sensing, the device must deal with complex matrix interferences, low and transient concentrations of the target analytes and immune response from the living organism [31,38,39]. Thus, just few device architectures survive to the first *in vivo* trials, and these are those which have fast response, low limit of detection, biocompatibility and operate in a point-of-care manner [1].

Considering the aforementioned properties such as electrical conductivity, biocompatibility and flexibility, graphene-related materials are promising candidates to build bioelectronic devices for *in vivo* biosensing applications [40,41].

Within the pool of the wide number of different systems, two main families of graphene-based devices were recently applied to *in vivo* biosensing: electrochemical biosensors and transistor-based biosensors. As mentioned above, it is worth clarifying that these kinds of devices can be classified also in wearable devices, considered non-invasive; and implanted devices, invasive. Herein, the discussion will be focused only on implanted devices. More information on wearable devices can be find in other reviews [7–11].

Electrochemical biosensors

In an electrochemical biosensor, the analyte recognition is transduced into an electrochemical signal [42]. These devices are usually composed of a chemically modified electrode including a biospecific receptor on its surface. Graphene-based materials were successfully applied in the development of electrochemical biosensor [22,27], as they work as transducing platform and give the opportunity of immobilizing the recognition element through different functionalization routes [43,44].

An example of real-time monitoring of analytes was shown by Taylor *et al*. who employed carbon fibre microelectrodes modified with electropolymerized PEDOT/graphene oxide composite to sense dopamine with high sensitivity and response rate [45].

To achieve high spatial and temporal resolution, the latest device architectures employ multielectrode arrays instead of single electrode probes. As an example, in the work published by Liu *at al.* a rGO/Au_2O_3 nanocomposite multielectrode array was used as a neural probe to sense H_2O_2 in hyperacute stroke model [46]. The inclusion of the graphene-based material allows to enhance both the sensitivity and the limit of detection of the sensor, while the multichannel device make it possible to simultaneously monitoring electrophysiological and chemical signal.

Multielectrode arrays were successfully applied also in electrophysiological signal monitoring, as electrical signal from neurons activation [47]. Further than only recording electrical signal from the brain, following works achieved simultaneous recording and stimulation through graphene-based electrodes [34,48,49]. As an example, the device based on porous graphene developed by Lu and co-authors allows both the recording of physiological oscillation and the electrical microstimulation of knee and ankle flexion [50]. This last application is promising in the high-resolution brain mapping and in the treatment of neurodegenerative diseases.

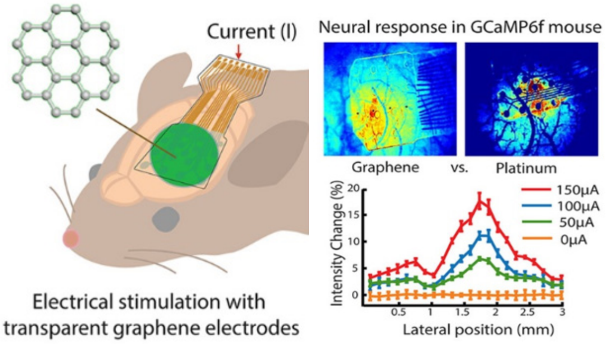

Figure 2. Transparent graphene-based electrode array for brain stimulation and recording. Reproduced from Ref. [48], Copyright 2018 American Chemical Society.

Similarly, Park *et al*. developed an innovative approach which employs a transparent graphene multielectrode arrays to perform optogenetic brain stimulation and recording [48]. In this work the benefit of working with transparent electrodes that enables light-based stimulation is emphasized, application not feasible with previous used platinum electrodes (**Figure 2**).

Transistor-based biosensors

As an alternative to the widely developed electrodes electronics, in the recent years the recording of electrophysiological and biochemical signal was performed through the FET technology [51]. This type of devices shows several advantages like amplification capability, low sensitivity to environmental interferences and ease miniaturization that coupled with the high electronic performances and flexibility of graphene represent the perfect match for *in vivo* biosensing.

In graphene-based FETs, usually solution-gated FETs (SGFETs), graphene is deposited as a channel material between two metallic conductors [41]. With this configuration, a variation of the electric field in proximity of graphene surface can be finely detected as a change in graphene electrical conductance [52]. This corresponds to the so-called field effect and these variations can be correlated with alterations in biochemical environment or electrophysiological inputs [53].

One of the first graphene transistors implanted *in vivo* was showed by Mannoor et al in 2012 [54]. Therein, the authors developed a device composed by graphene on silk transferred on a gold electrodes coil (**Figure 3**). This last component allows the wireless monitoring of graphene resistance, while the presence of water-soluble silk makes the device easily implantable. In addition, the immobilization of a bacteria selective peptides on graphene surface permits the recognition of bacteria at a single cell level in saliva through a tooth implantation of the device.

As already highlighted for microelectrodes, the trend with transistors is also to pass from single device to multidevice arrays. The work reported by Blaschke *et al*., a 16 SGFETs array based on graphene on polyimide flexible substrate was used to recording *in vivo* brain activity [55]. In a following study of the same authors, a similar microtransistor array was employed to recording of infraslow cortical brain activity, usually associated with stroke and brain injury [56]. This innovative application opens the possibility of mapping brain activity with high resolution and sensitivity, this was possible by the designed electronics and graphene biocompatibility and electrochemical stability.

Conclusions and Perspective

The advantages of graphene for implantable biosensors have been revised above. In addition, significant progress in the foreseeable future for applications in healthcare, personalized medicine, disease treatment, human and machine interfaces have been examined. In this last section, the challenges of graphene-based implantable sensors *in vivo* will be discussed.

In the last decade, researchers have widely explored the use of graphene for analytical and *in vitro* sensors [27,57]. Although several promising works could revolutionize the medicine field in the next years, the contribution of the research community to implantable sensing is more limited since it must satisfy the highly strict regulations for medical devices [58]. Indeed, the

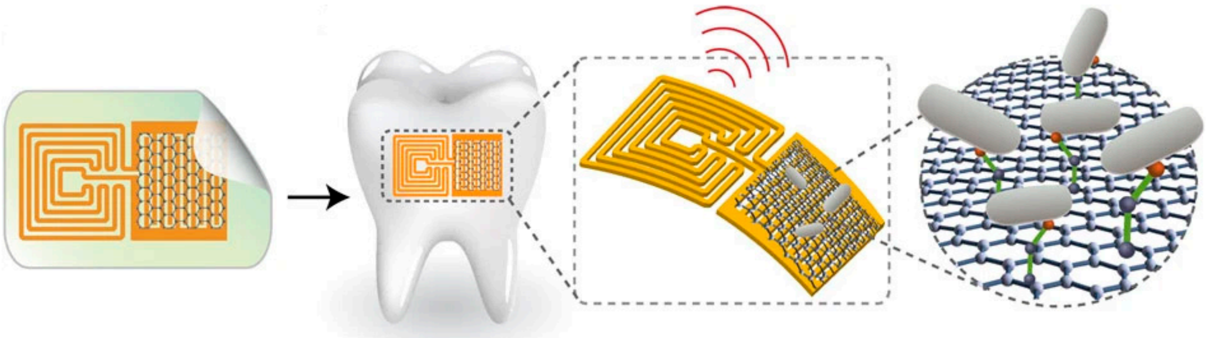

Figure 3. Schematic representation of peptide–graphene nanosensor. Reproduced from ref. [26], Copyright 2017 American Chemical Society.

most challenging issue is related to human health risks. The biocompatibility and biological toxicity, of graphene must be further assessed, especially in long-term *in vivo* studies. In addition, graphene *in vivo* sensors, must satisfy the strict regulations on sterilization to avoid the inflammatory response after implantation because are invasive. Long-term stability and mechanical durability are also necessary since implantation can require tedious surgical interventions and then the device can be stressed in some tissues.

One of the main current issues is related to the synthesis of graphene. CVD graphene is the most used derivative for in *vivo* sensing. CVD is a promising method to prepare high quality, homogeneous, reproducible graphene at industrial level. However, uniform large areas of monolayer graphene are harsh to be synthesized. In addition, the mandatory transfer process can decrease the quality of the material obtained and thus the proper function of the final device. Therefore, new developments in CVD technology are necessary. The direct growth of high-quality graphene on flexible and biocompatible surfaces at large scale should be the optimum solution.

Another main challenge in most biosensors is to implement specificity to the target analyte. As mentioned above, this is achieved by a controlled chemical modification of graphene to link specific receptors. But the lack of selectivity is still burdening *in vivo* sensors in some types of tissues. For example, the development of graphene implants in the nervous system with real time detection of biomarkers, such as neurotransmitters, neuromodulators, etc. are yet to be achieved [23]. Furthermore, integrated multifunctional sensors that are able to monitor different biological parameters using different receptors are highly desirable for disease treatments.

Although exciting implantable sensors have been developed, the scenario to produce fully integrated implantable sensors that can replace the current technology under the same performance conditions are still far. In addition to outstanding sensors, it also requires the development of other components, such as graphene compatible integrated circuits, miniaturized wireless hardware, and efficient power sources. Hence, although graphene provides a variety of distinctive characteristics to *in vivo* sensing, limitations are also present.

In recent years, other 2D materials have been demonstrated to be promising sensing device components [40]. Beyond graphene, within the world of 2D materials, it is possible to find different families according to their composition and electronic properties (**Figure 4**): as a typical 2D insulator, h-BN is a graphene-like layered material which has great resistance to charge transport and a great in-plane thermal conductivity. Examples of semiconducting 2D materials can be black phosphorus and transition metal dichalcogenides. An interesting feature of these semiconductor materials is that their electronic properties can be tuned with different approaches, for instance number of layers or changing their composition. This wide range of band gaps and carrier mobilities make them suitable candidates for FETs. Finally, as typical 2D metals, MXenes have been recognized as a good promising biosensing platform due to the high metallic conductivity and excellent electrical properties. But, to the best of our knowledge, there are just a few reported examples of *in vivo* sensing with such new 2D materials [59].

Similar to the current graphene "infancy", despite the number of publications about newer 2D materials has been increasing in recent years, there are still many issues to address. The first challenge is related to their large-scale synthesis with desirable size and thickness. To this regard, it is usual to use toxic reagents and solvents in the preparation process. Another main challenge is their long-term stability in *in vivo* experiments. A firm understanding of their toxicology / biocompatibility will be necessary for each material depending on the synthesis procedure. During *in vivo* experiments, 2D materials encounter complex biological environments and these conditions could degrade the device over a short time depending on the material. Cheng *et al.* have reported MoS_2-based bioresorbable and multi-functional sensor for intracranial monitoring of pressure, temperature, strain, and motion in animal models [59]. Preliminary studies suggest that monolayer MoS_2 is a biocompatible semiconductor, which can be completely dissolve in biofluids after more than 2 months. However, more exhaustive studies of their biocompatibility, degradation process and environmental stability are need it. At this point, this field of *in vivo* researching on 2D materials is by now following the footsteps left by graphene during the last decade.

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3D Structures based on carbon materials and conducting polymers for electroresponsive cell cultures

Estructuras 3D basadas en materiales de carbono y polímeros conductores para cultivos de células electroresponsivas

Antonio Dominguez-Alfaro

Thesis defended in 2021 at the University of Basque Country (UPV/EHU) in Donosti, País Vasco, Spain

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Objectives and Novelty

The next generation of therapies for cancer or neural diseases require the development of structures that mimic cellular scenarios ruled by interconnectivity, three-dimensionality, porosity, stiffness, biocompatibility and, in the case of electroactive cells: conductivity. These structures, known as scaffolds, can simulate conditions and environments that occur in living organisms, allowing the study of specific mechanisms. However, most of the scaffolds reported in the literature do not match all those requirements simultaneously. Carbon nanotubes (CNTs) possess outstanding properties as their high electrical conductivity or tunable biocompatibility that have rocked them as excellent interface nanomaterial with biological tissue. However, their main limitation stems from the formation of 3D structures without incorporating other additives. Conducting polymers (CPs), confers three-dimensionality similar than conventional insulator polymers at the same time that maintain the inherent properties of the CNTs. The present work summarizes three innovative methods tailored to manufacture scaffolds composed of CNTs and the conducting polymer poly(3,4 ethylenedioxythiophene) (PEDOT) for electroactive cellular culturing. All the methods are based on the principle of polymerizing the PEDOT polymer, *i.e* chemical oxidative and electrochemical polymerizations. The aim of this PhD thesis is the development of conductive and porous materials and their correlation with maturation and proliferation of electroactive cells as astrocytes C8-D1A, neuroblastome SH-SY5Y and primary cardiomyocytes.

Results

Vapour phase polymerization (VPP) is the first technique that was developed to manufacture porous scaffolds. The reaction is a chemical oxidative polymerization that take place in presence of carbon nanotubes thanks to iron (III) catalyst, forming the PEDOT polymer around the tubes (see **Figure 1a**). The reaction take place in a vapour phase within a Schlenk sealed tube, placing the EDOT monomer at the bottom and using crystal sugar grains as porous generator (see **Figure 1**). The polymerization occurs within the interstices of the sugar grains, doping the CNTs with the conducting polymer. Subsequently, after the cleaning process, the scaffold presents a controlled porosity with porous size below 250 μm and above 45% of emptiness, corroborated by scanning electron microscopy (SEM) and micro-computer tomography analysis (see **Figure 1c**). The formation of this 3D structures represents a huge improvement in the methodology since PEDOT, in absence of CNT, collapses by itself when forming the 3D macrostructure. This methodology allows the modulation of time and temperature, having a remarkable impact in the compositions and correlatively on the mechanical properties. Moreover, PEDOT/CNT materials presents very high conductivity, improving previous insulator polymer/CNT scaffolds. Finally, the scaffold biocompatibility was evaluated using C8-D1A astrocytes culture. Astrocytes are involved in neurogenesis and commonly studied in neural models. The scaffolds present excellent attachment of the cells and growth corroborated by immunofluorescence assay, LDH and SEM (see **Figure 1c**). VPP represents a very powerful and versatile methodology that allows its use with other conducting polymers such as polypyrrole (PPy). This method has also been expanded to PPy/CNT scaffold and their interactions, properties and formation of these porous three-dimensional structures were also studied.

In the second methodology, the reaction is carried out in a three-electrodes chamber throughout a chronoamperometry reaction where the scaffold template is used as a working electrode (**Figure 1**). This methodology is known as the electropolymerization (EP) and avoids the use of oxidants or strong reaction conditions. Compared to the previous work, EP possesses an additional step of nucleation on the electrode surface. The role of CNTs as nucleation agent of the conducting polymer was deeply studied. The presence of CNTs assists the three-dimensional polymerization and helps the formation of larger macrostructures (>1 μm). While PEDOT scaffolds present a smooth surface and do not present three-dimensionality, PEDOT/CNT scaffolds possess internally connected pores and a rough surface topography. Moreover, the presence of brush-like structures along the topography confirms their compositional differences (**Figure 1d**). Besides the morphology, the presence of CNTs improves the conductivity of the device, confirmed by impedance analysis and four-point probe measurements. These PEDOT/CNT scaffolds were used as supporting materials for endogenous differentiation of neuroblastoma SH-SY5Y cell line without the addition of any chemical, confirmed by the use of different immunoassay labelings and SEM morphology evaluation. Apart from the PEDOT polymer, this methodology allows the manufacturing of PEDOT derivative scaffolds, that are not very well reported in literature. We also explored scaffolds formed with PEDOT copolymerized with a bis malonyl functional EDOT monomer (bisPEDOT) in the presence and absence of the CNTs, forming mixed 3D structures.

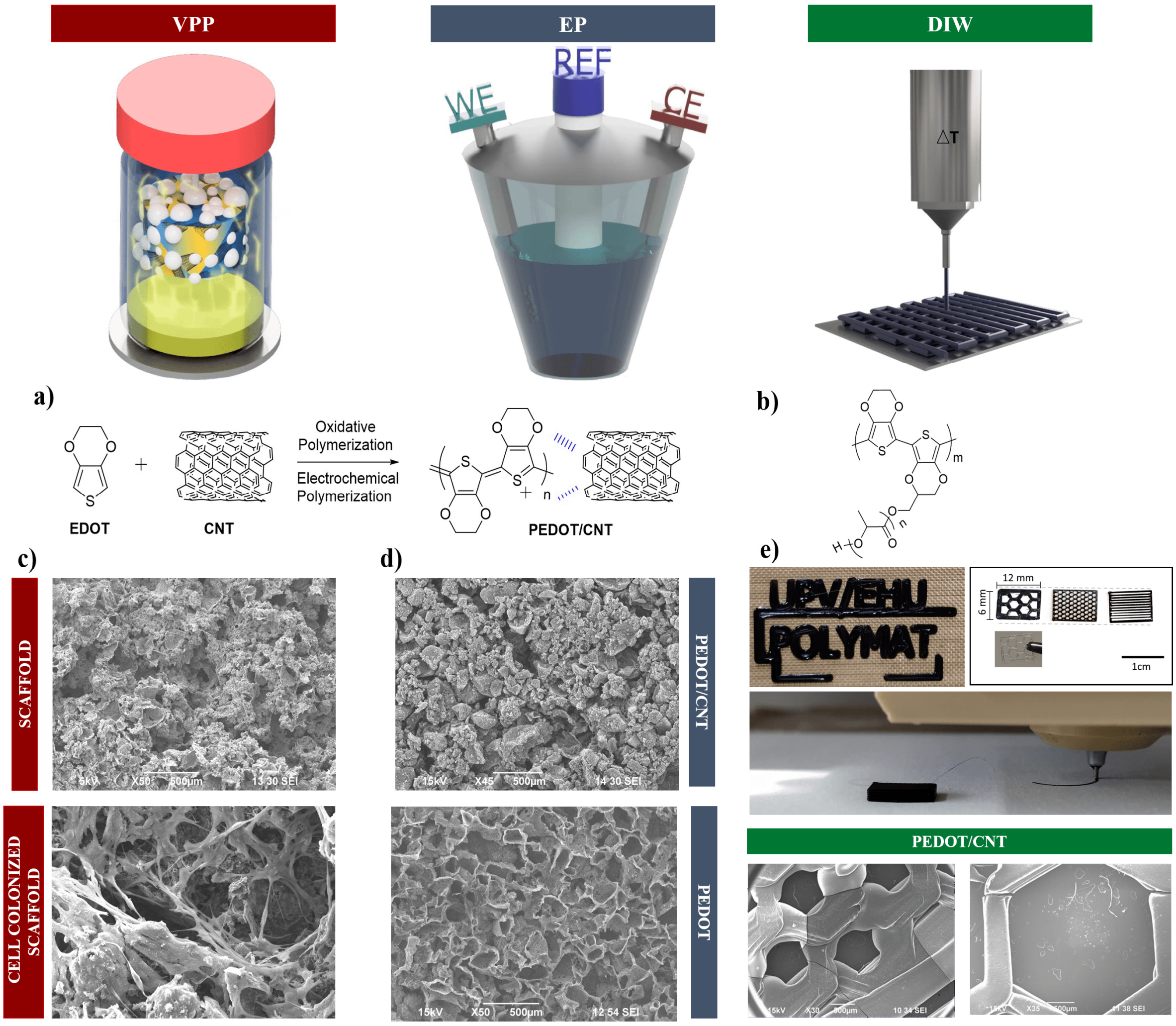

Figure 1. Schematic representation of the three methods: VPP, EP and 3D printing by DIW. a) Reaction of polymerization for VPP and EP methods, b) PEDOT-*graft*-PLA polymer designed and synthesized for 3D printing, c) SEM images of a porous scaffold (top) and the same porous scaffold colonized with C8-D1A cells (bottom), d) SEM images comparing PEDOT/CNTs (top) and PEDOT scaffolds (bottom) manufactured by EP and e) 3D printed PEDOT-*graft*-PLA structures (top) and SEM images of two different hexagonal patterns of different sizes (bottom).

Moreover, the design of a family of tailored conducting and biocompatible PEDOT-*graft*-poly(L-lactic acid) (PLA) co-polymers for direct ink writing (DIW) was also conducted. The macromonomer used was synthesized by ring opening polymerization in bulk. Copolymers synthesized with different PEDOT percentages were characterized and evaluated throughout complex viscosity for 3D printing. Finally, the most suitable composition was 3D printed, forming different shapes with high resolution (above 200-300 µm) (**Figure 1e**). Lastly, these patterns were used for cell growth and maturation of neonatal cardiac myocytes co-cultured with fibroblasts. CNTs were also incorporated within the polymer matrix, improving stability and conductivity.

Conclusions

Innovative 3D materials are required in the field of tissue engineering for addressing model diseases or body implants. The main problem observed with conductive materials is their poor processability, which restricts the manufacturing of real three-dimensional structures. Basically, in this PD thesis this main disadvantage was addressed, by developing new manufacturing methods for the formation of scaffolds composed of conductive materials as PEDOT and CNTs. The materials herein manufactured possess controlled porosity, tailored conductivity and suitable mechanical properties for implants and 3D cellular culturing of electroactive cells. In this regard, all the scaffolds presented good biocompatibility and functionality with cells throughout maturation and differentiation.

Related Publications

[1] Dominguez-Alfaro A, Alegret N, Gomez IJ, Mecerreyes D, Prato M. 2D and 3D Immobilization of Carbon Nanomaterials Throughout PEDOT Derivative Co-Polymerization. Polymers 2021; 13(3):436

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Full Thesis can be downloaded from *www.ehu.eus/es*

Antonio Dominguez-Alfaro obtained his Industrial and Chemical Engineer degree from the University of Huelva in 2015. His PhD was carried out at the research centers CIC biomaGUNE and POLYMAT in the University of Basque Country (UPV/ehu), and it was defended in 2021. He worked under the supervision of professors David Mecerreyes and Maurizio Prato. The PhD work was based on the development of porous materials composed of carbon nanotubes and conducting polymers for biomedical applications. Besides, during his PhD he carried out an internship at Rice University (Houston, Texas, in 2018). In 2021, Dominguez-Alfaro joined the Biomolecular Nanotechnology Lab led by Aitziber Cortajarena, and he is working in the development of new conducting hybrid materials.

The role of Carbon Capture, Utilization and Storage (CCUS) on the pathway to Net Zero greenhouse gas emissions: can we accelerate the transition to a low-carbon economy?

El papel de la captura, almacenamiento y usos de CO_2 en el camino hacia cero emisiones netas de gases de efecto invernadero: ¿podemos acelerar la transición hacia una economía baja en carbono?

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The world is currently facing unprecedented times due to the COVID-19 pandemic, where we are heading for a steep recession triggered by the outbreak and expected to be worse than the 2008 financial crisis. After this crisis, the time will come to rebuild our social and economic systems and we have there the opportunity to restart growth in a greener era. The current COVID-19 situation did not make the climate crisis disappear (**Figure 1**), even though in many countries the most striking and clearly visible effect of COVID-19 was a dramatic decrease of pollution levels. If we can indeed rebuild our society under a green social and economic recovery scenario, i.e., fighting climate change and promoting biodiversity, we will rebuild stronger and more sustainable economies. Furthermore, the transition to a climate-neutral economy has the potential to rapidly deliver jobs, growth, and to contribute to building more resilient societies. At the European level, calls for a Green recovery were getting louder, and in some countries COVID support to industry has been conditioned to a more sustainable operation. It seems then clear that rescue measures should advance the EU's landmark Green Deal policy package, which aims to meet the goal of getting to net zero greenhouse gas emissions by 2050.

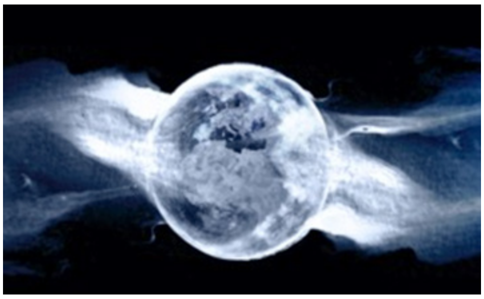


Figure 1. The world's ever-expanding CO_2 emissions (Credit: Luke Robus and Emmet Norris)

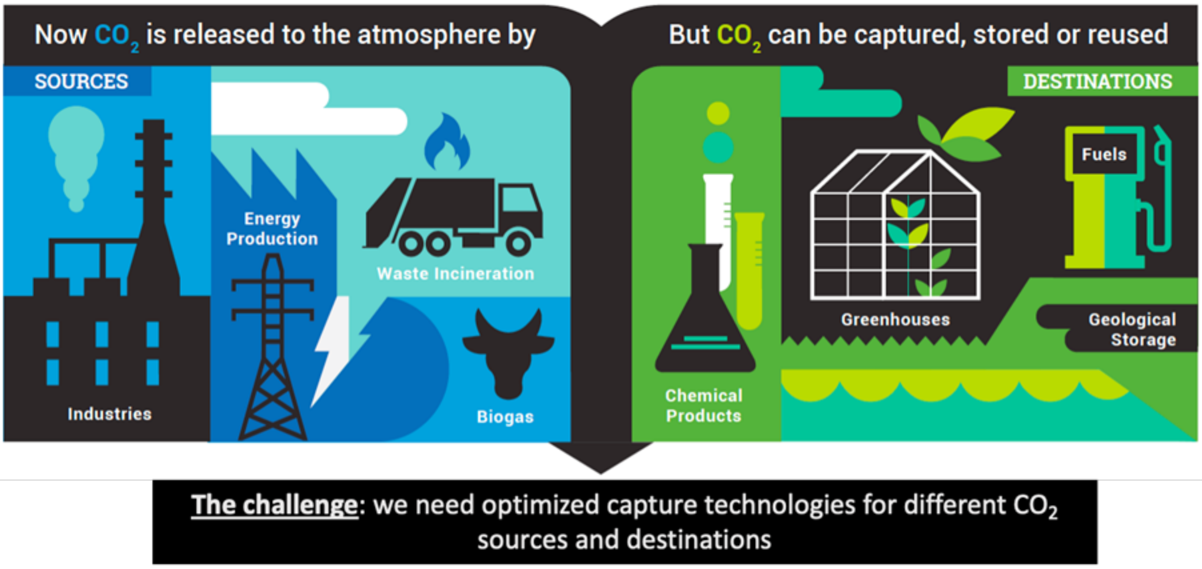
Carbon Capture, Utilization and Storage (CCUS)

Carbon Capture and Storage (CCS) is a key technology for achieving global greenhouse gas emissions reduction targets because of its role in power and industrial decarbonization. It is a proven technology that involves three steps: 1) capturing (i.e., separating) carbon dioxide, CO_2, from combustion flue gasses and gas streams produced by industrial plants; 2) the compression and transport of CO_2, and: 3) its safe storage in underground geological formations [1]. If instead of storing the CO_2 we use it as a carbon feedstock for different applications, such as the production of synthetic fuels or chemicals, then we are talking about Carbon Capture and Utilization (CCU) technologies. CCS and CCU have been often seen in the past as competing technologies and it has become evident over the past years that we need all the help we can get in order to achieve our net zero targets, hence the CCUS concept. One only needs to make sure that for every fossil fuel carbon atom we take out of the ground, we put one CO_2 molecule back, as otherwise we will never be achieving the net zero concept. CCUS technologies can reduce emissions across most existing industrial and energy facilities. But we do not need to stop here, we can also remove CO_2 from the atmosphere, either together with bioenergy or as Direct Air Capture [2]. It is widely acknowledged that the lowest cost and risk approach to achieve net zero emissions requires a broad portfolio of technologies and strategies, and not implementing CCUS would significantly increase the mitigation costs (by 29%-297%) [3] that we need to pay.

The Challenge and the Opportunity

To achieve our net zero targets, decarbonization from a variety of industrial emission sectors will be required, which highlights a marked need for capture technologies that can be optimized for different sources of CO_2 and integrated in an equally diverse range of applications of captured CO_2 as a feedstock (**Figure 2**).

At high Technology Readiness Levels (TRLs), there are substantial efforts focusing on optimizing a single particular carbon capture technology (e.g., amine-based capture) for a single typical stationary source (e.g., natural gas-fired power plants). However, significant gains in energy efficiency and other economic benefits can be obtained if we tailor make a capture technology for a particular CO_2 source



The challenge: we need optimized capture technologies for different CO_2 sources and destinations

Figure 2. Schematic with examples of CO_2 sources and destinations

(e.g., waste incineration, coal combustion, cement manufacture) and a particular CO_2 destination, such as utilization or transport via pipeline, or ship to permanent storage. This offers the opportunity for more innovative CO_2 capture technologies that are currently at low TRLs, i.e., sorbent-based ones, to breakthrough into current markets and provide the required flexibility together with reduced capital and operational costs. It is precisely this vision towards achieving zero anthropogenic CO_2 emissions, the one that drives the research of my team.

My research group at Heriot-Watt University ambitions to change the paradigm on how novel processes based on advanced materials are developed through the integration of process engineering and basic science. At present, there is a significant gap of knowledge, which is often referred to as the “Innovation Valley of Death”, that hinders the realization of many novel promising materials beyond lab scale testing. Our approach integrates Chemical Engineering with Data Science, Computational Chemistry, Materials Science and Chemistry to synergistically deliver that integration in Open Access platforms. An example of this approach was our breakthrough on the computational design of new materials that can capture CO_2 from wet flue gasses better than current commercial ones [4].

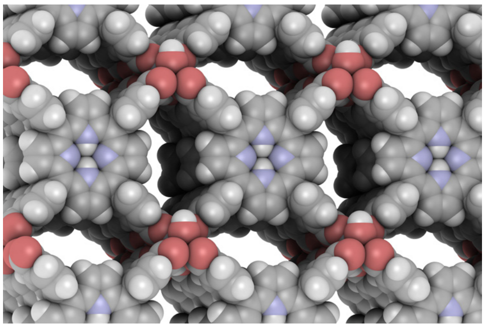


Figure 3. A molecular representation of a MOF carbon capture material (Credit: M. Moosavi and K. Jablonka; iRASPA software was used for visualisation)

This work got inspired by drug design tools used by the pharmaceutical industry, where common motifs, i.e., structural properties, are established for those molecules that bind successfully to a target protein. These common features form then the basis for designing and synthesizing actual drug molecules. By applying the same concept, we identified, out of a database of 325,000 computer-generated sorbents, those whose common motif was the ability to bind CO_2 but not water. All the materials in the database belonged to the family of Metal Organic Frameworks (MOFs) [5], which are highly versatile porous crystals that are made from combining metal nodes with organic linkers (**Figure 3**). Selected identified top-performing materials (**Figure 4**) were further synthesized, characterized and tested under mimicked real industrial operation, and results showed that our predictions were correct.

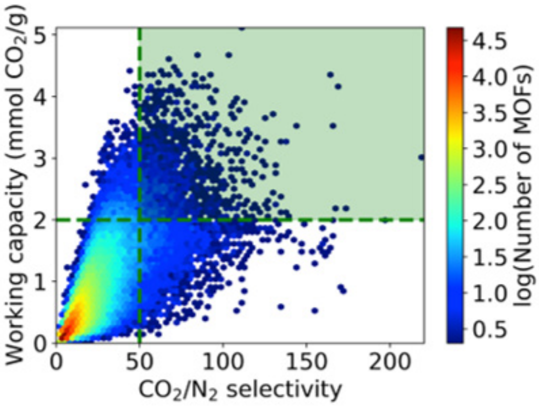


Figure 4. Computational screening of MOFs for strong CO_2 adsorption and selectivity

International collaboration as a key factor for accelerating CCUS technologies

Our current research builds up on the abovementioned efforts and aims to accelerate the transition of energy and industrial sectors to a low-carbon economy by developing a technology platform to tailor make cost-efficient carbon capture solutions for a range of different CO_2 sources and CO_2 use/destinations.

To achieve this aim, we have secured support from the European Union's highly competitive ERA-NET Accelerating CCS Technologies (ACT) Program to lead an innovative and ambitious three-year project, as part of a joint bid with academic and industrial partners from across Europe and the USA. The ambition of ACT is to facilitate the emergence of CCUS via transnational funding aimed at accelerating and maturing CCUS technology through targeted innovation and research activities.

The awarded ACT-funded PrISMa project (Process-Informed design of tailor-made Sorbent Materials for energy efficient carbon capture) received a total funding of €3.3M, and it unites the efforts of world-leading research teams from Heriot-Watt University (HWU) in the UK, École Polytechnique Fédérale de Lausanne (EPFL) as well as Eidgenössische Technische Hochschule Zurich (ETHZ) in Switzerland, Lawrence Berkeley National Laboratory (LBNL) in the USA, and SINTEF Energy Research (SINTEF-ER) in Norway. These teams have the expertise to bridge the gap between molecular sciences (LBNL and EPFL) and process engineering (ETHZ, SINTEF-ER and HWU). The consortium is supported by market-leading companies and non-governmental organizations, which are committed to minimize CO_2 emissions of their industrial sectors and provide case studies and maximise knowledge exchange and impact of PrISMa.

The PrISMa methodology (Fig. 5) starts with a high-level analysis, in terms of an effective carbon price, on how the performance of a separation process depends on the source of CO_2 and its use/destiny. This analysis is subsequently translated into key performance indicators (KPIs) that novel materials need to achieve in terms of their potential to reduce the effective carbon price in order to compete with state-of-the-art capture processes. A materials genomic approach [6] is used to screen libraries of millions of *in silico* predicted structures to identify materials that meet the KPIs. The most promising materials are then synthesized, characterised, and tested for their performance in a carbon capture process. For those materials that yield a significant reduction of the effective carbon price, a roadmap to bring these materials to TRL5 will be developed through case studies.

PrISMa provides the platform needed for high-throughput screening of materials to maximise their impact, to enable the design of efficient pilot-scale test facilities with improved processes under real conditions and, to decrease the time to market of affordable, cost-competitive, low environmental impact, and resource-efficient advanced capture technologies. As a similar approach can be developed for other separations, we expect the impact of PrISMa in terms of the potential to decrease the time to market for novel materials to go beyond carbon capture. In addition, PrISMa aims to initiate a systematic thinking about efficient solutions to mitigate CO_2 emissions from different local CO_2 sources that are optimal for a specific local setting. In such a setting the impact of PrISMa will be significant as the need for tailor-made solutions will be increasingly important if CO_2 mitigation at the local level becomes the norm.

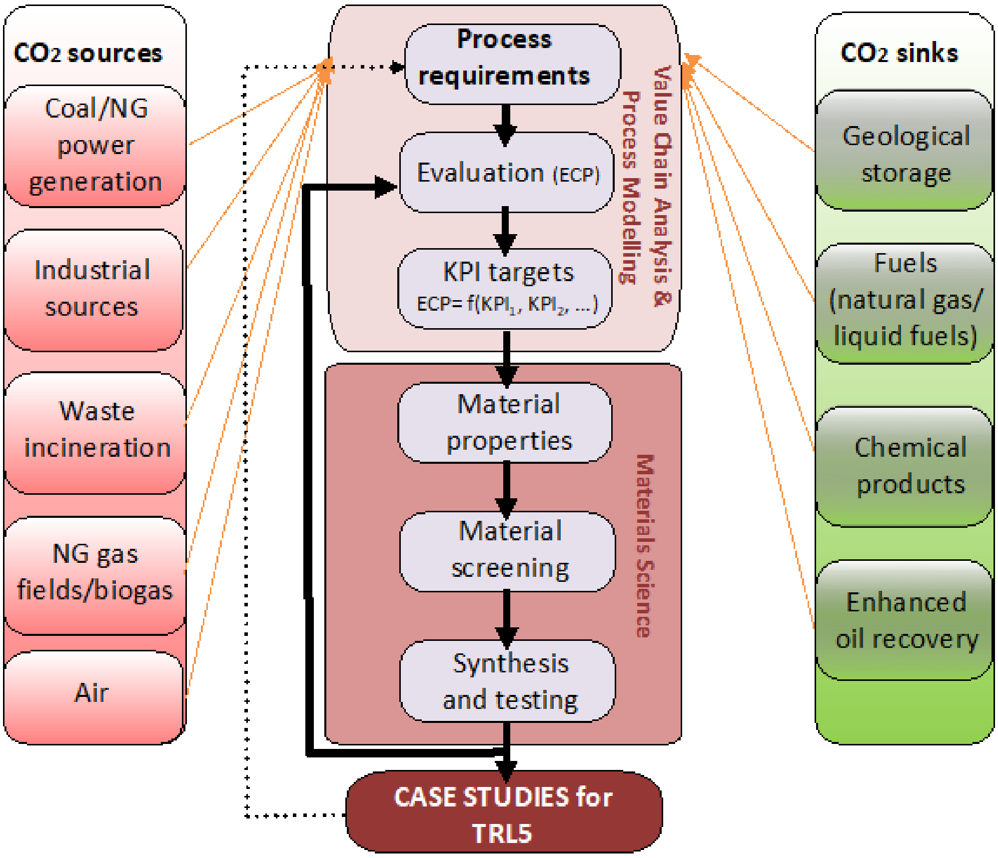


Figure 5. Illustration of PrISMa platform

Building bridges

This need for international collaboration and interdisciplinary approaches to tackle global challenges like CO_2 emissions to the atmosphere is now, more than ever, of striking evidence. Funding programmes all over the world as well as different societies and foundations are encouraging research at the global level, as well as knowledge transfer and research dissemination and outreach to the general public, as the basis for successful deployment and implementation of the required technologies to achieve net zero targets. As an example, and as the recipient of the Society of Spanish Researchers in the United Kingdom (SRUK/CERU) and Banco Santander Foundation Emerging Talent Award 2020, my goal is to create an awareness that our society needs to change into a more sustainable, equal, inclusive and diverse one.

As scientists, we are committed to drive the required research and innovation for a better society, and pushing forward the required transition to a clean sustainable energy is one of the key objectives of my research. The recognition and support from SRUK/CERU and Banco Santander Foundation provides me with the opportunity to encourage new international collaborations and strengthen the links between the Spanish and UK scientific community, to increase scientific culture in the public and act as an ambassador and inspiring reference for the role of women in Spanish science.

In a world where drastically reducing CO_2 emissions is one of our most urgent and important global challenges, we do need all the help we can get!

Acknowledgements

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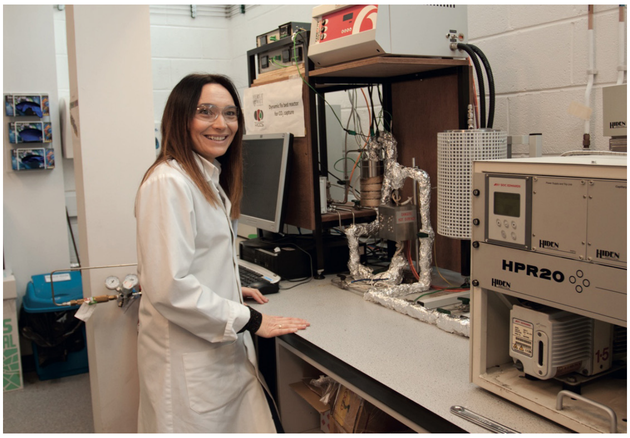

Dr. Susana Garcia is Associate Professor in Chemical Engineering and Deputy Head of the Institute of Mechanical, Process and Energy Engineering at Heriot-Watt University, which she joined in May 2014. She is also the Associate Director in Carbon Capture and Storage at the Research Centre for Carbon Solutions (RCCS), an interdisciplinary world leading engineering centre, inspiring and delivering innovation for the wider deployment of technologies needed to meet necessary carbon targets. Her overarching research theme is the design and development of processes using advanced materials for specific applications relevant to energy efficiency and environmental sustainability in different sectors. She has as ambition to change the paradigm on how novel processes based on advanced materials are developed through the integration of process engineering and basic science.

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