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

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

M. Barrejón*

Nerural Repair and Biomaterials Laboratory, Hospital Nacional de Parapléjicos (SESCAM), Finca la Peraleda s/n, 45071 Toledo, Spain

* *Corresponding author: miriam.barrejon@uclm.es*

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.

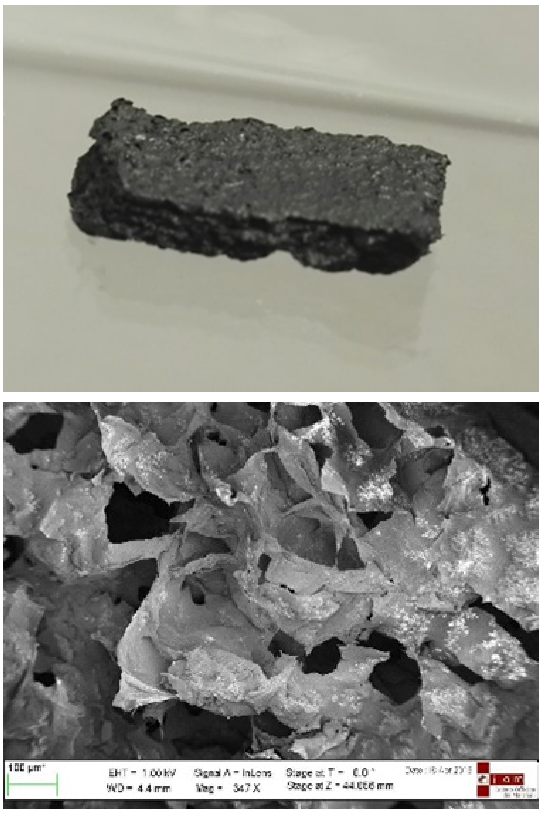

Figure 1. Photo of a CNT sponge (up) and scanning electron microscopy (SEM) image showing the porous structure (bottom).

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.

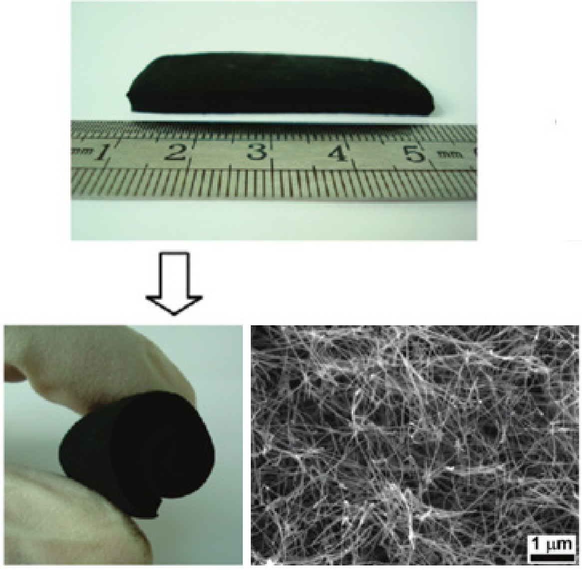

Figure 2. Soft and compressible sponge (up) and SEM image showing the random and porous network (bottom). Reprinted with permission [12]. Copyright 2010. American Chemical Society.

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**).

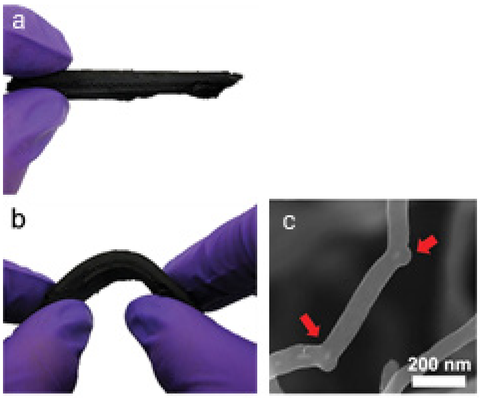

Figure 3. a) and b) Photos and c) SEM image of a boron-doped MWNT 3D architecture containing "elbow" junctions. Reprinted with permission [13]. Copyright 2012, Macmillan Publishers Limited.

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

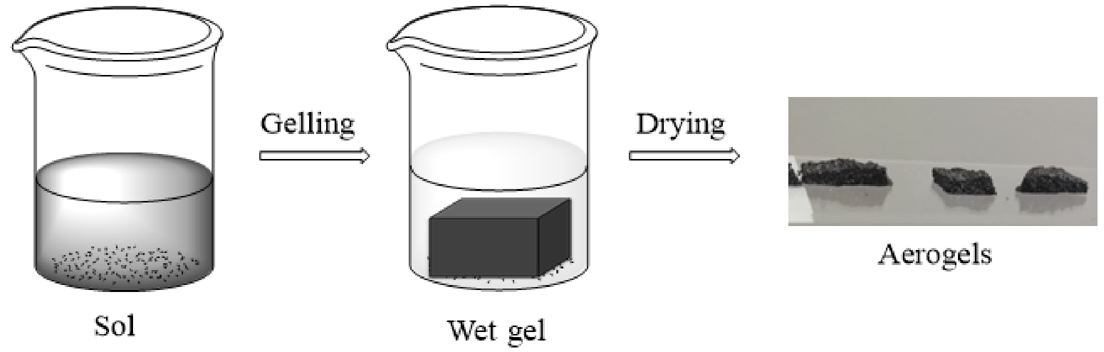

Figure 4. Schematic representation of the steps involved in the Sol-Gel process for the preparation of CNT 3D architectures via Sol-Gel assembly.

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

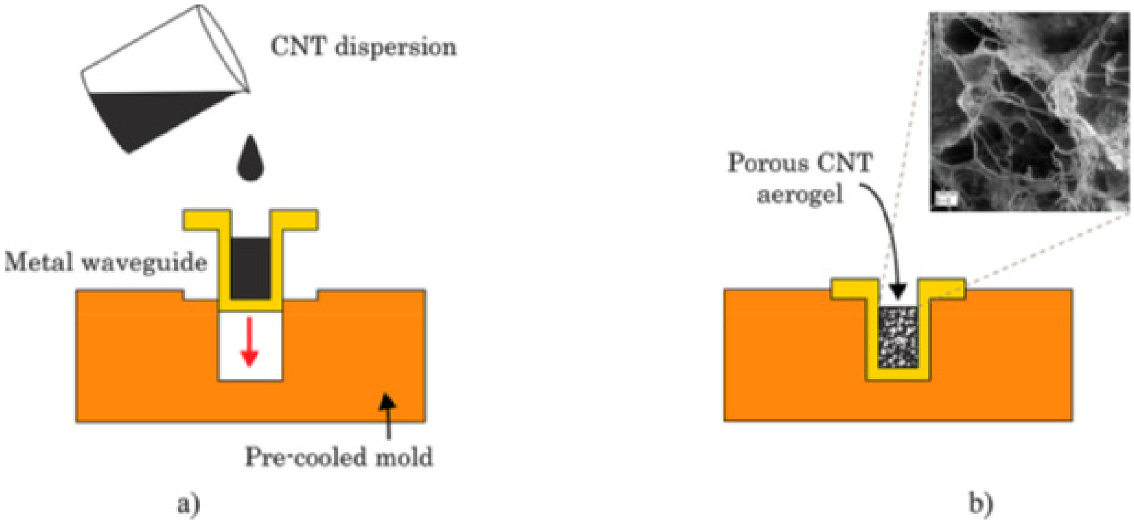

Figure 5. CNT aerogel sample preparation. A known volume of CNT dispersion is placed inside a metallic waveguide (a), prior to fast- freezing at −25 °C/−196 °C, which forms the porous aerogel (b). Reprinted with permission [24]. Copyright 2018. American Chemical Society.

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.

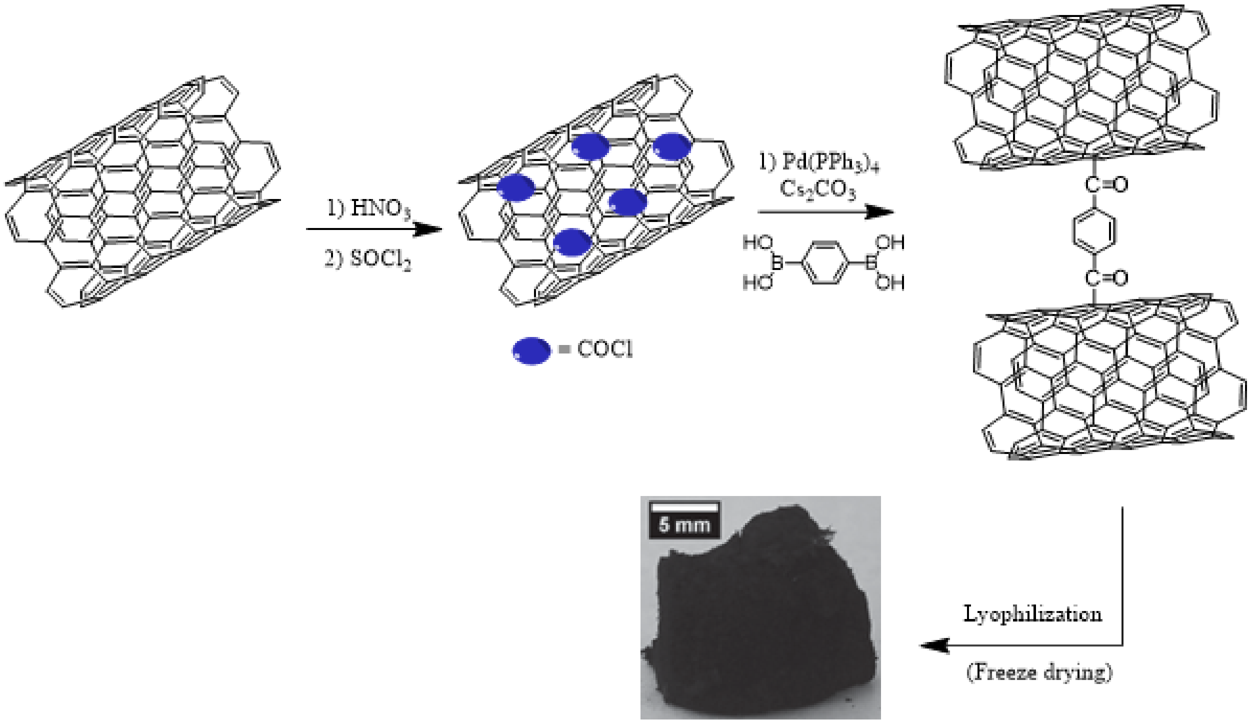

Figure 6. Schematic representation of the procedure followed for the preparation of 3D-CNT architectures from CNT powders via Suzuki cross-coupling reaction.

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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.