Functional Carbon-Based Nanomaterials for Energy Storage: Towards Smart Textile Supercapacitors

Nanomateriales basados en carbones funcionalizados para almacenamiento de energía. Hacia supercapacitadores de tejidos inteligentes

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Abstract

Hybrid supercapacitors emerged as an eco-friendly technology to address the grand challenge of sustainable and efficient energy storage. Functional carbon-based nanomaterials are promising building blocks for the design of advanced electrodes for this type of supercapacitors. The boost on wearable electronics opened new market opportunities for hybrid supercapacitors integrated in textiles using carbon-based electrodes.

In this work, we will start by providing a brief introduction to the main principles of supercapacitors, followed by the importance of carbon (nano)materials as electrodes for the design of high-performance supercapacitors for energy storage. Subsequently, the progress achieved by our team in the field of hybrid carbon–metal oxide nanomaterials and smart textile supercapacitors will be highlighted.

Resumen

Los supercapacitadores híbridos surgieron como una tecnología respetuosa con el medio ambiente para dar respuesta al gran objetivo de conseguir un almacenamiento de energía eficiente y sostenible. Los nanomateriales de carbón funcionalizados presentan un gran potencial para el diseño de electrodos avanzados para este tipo de supercapacitadores. El impulso de los productos electrónicos en el vestido abre nuevas oportunidades de mercado para supercapacitadores híbridos integrados en los tejidos usando electrodos de carbón.

En este trabajo se presenta una breve introducción a los principios generales de los supercapacitadores, y la importancia de los nanomateriales de carbón como electrodos para el diseño de supercapacitadores de altas prestaciones en el almacenamiento de energía. Se resaltan los progresos de nuestro equipo en el campo de los nanomateriales híbridos carbón–óxido metálico y los supercapacitadores de tejidos inteligentes.

Keywords: carbon nanomaterials, hybrid compounds, supercapacitors, smart textile supercapacitors

Palabras clave: Nanomateriales de carbon, compuestos híbridos, supercapacitadores, supercapacitadores de tejidos inteligentes.

1. Introduction

In the era of high-tech, the development of wearable energy storage devices has been a great challenge for Society, motivated by the escalating growth of the market of portable electronics and smart technologies [1,2]. In particular, the integration of flexible supercapacitors in textiles has been a major milestone in order to produce wearable energy storage clothing for the power supply of sensors, flexible displays, among others. In Portugal, the Textile Industry is one of the core engines for the economic growth. In 2014, the Portuguese Textile and Clothing Industry represented 10% of the total national exports, which corresponds to ~4600 M€[1]. Therefore, the investment in high-tech textiles with novel functionalities is of paramount importance for this sector.

With the advances in Nanotechnology, nanomaterials emerged as potential building blocks for the design of high-performance textiles with novel functionalities (*eg.* super-hydrophobicity/oleophobicity, photochromism, thermochromism, antimicrobial properties), while providing improved comfort to the user [3,4]. In particular, carbon–metal oxide nanomaterials are promising electrode materials for the design of lightweight and flexible textile supercapacitors [1].

2. Supercapacitors: A General Overview

Supercapacitors (SCs) represent a versatile energy storage solution for a sustainable energy storage supply that bridges the gap between conventional capacitors and rechargeable batteries. As can be seen in the Ragone plot presented in Figure 1, SCs present higher power density than batteries but lower than that of traditional capacitors [5,6]. This ability allows fast charge, which is a key advantage when compared with batteries. Moreover, they present excellent cycling stability and a significantly longer cycle life (up to 10^6 cycles) than traditional batteries (up to 500 times) [6]. On the other hand, when compared with conventional capacitors, SCs present higher energy density, which is one of their fingerprint features since they can power supply the devices for longer operation time.

The current challenge for SCs nowadays is to improve their energy density and lower their fabrication costs without sacrificing their high power capability. For that purpose, new electrode materials and electrolytes are being developed.

The simplified structure of a SC is composed by two electrodes (positive and negative), an electrolyte, two current collectors and a separator membrane [7]. The electrodes are constituted by conductive

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[1] Data estimated by Associação Têxtil e Vestuário de Portugal (ATP) based on the indicators from Instituto Nacional de Estatística.

materials with a large specific surface area and/or by electrochemically active materials. The electrolyte is an ionically conducting medium that exists between both electrodes and has the main function of transporting ions until the surface of the electrodes. The separator is an ion-permeable electron-insulating membrane, *i.e.* it allows the migration of electrolyte ions and electrically isolates the two electrodes. The current trend in textile SCs is to replace liquid electrolytes by solid-gel ones that act both as electrolyte and separator. Finally, the current collectors are connected to the electrodes and are responsible for the electrons transport.
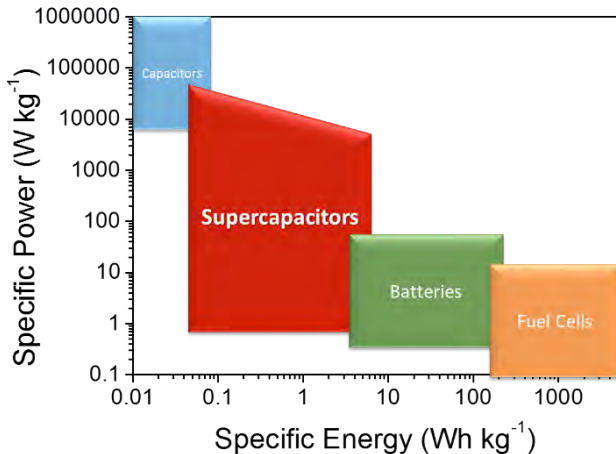
Figure 1. Ragone Plot comparing different energy storage technologies (adapted from ref. 6).

SCs taxonomy divides them in different categories depending on the electrodes type/function as well as on the energy storage mechanism. They can be classified into three large groups: *electric double-layer capacitors* (EDLCs), *pseudocapacitors* and *hybrid capacitors* (Figure 2) [7].

In **EDLCs**, the capacitive charging occurs in the electrode/electrolyte interfaces and charge is stored electrostatically by a non-Faradaic mechanism [7]. There is no charge transfer between the electrodes and the electrolyte which enables a longer cycle life. Therefore, EDLCs usually have higher power density when compared to batteries of similar dimensions. Carbon (nano)materials have been the most widely used electrode materials in EDLCs [8].

On the other hand, in **pseudocapacitors** the energy storage process involves charge transfer between the electrode and the electrolyte by means of reduction-oxidation reactions, ion intercalation/deintercalation and electrosorption (Faradaic mechanisms) [9]. The charge transfer process is similar to that of a battery, but the transfer rates are higher since in pseudocapacitors

electrochemical reactions occur at the surface and in the bulk near the surface of the electrodes instead of propagating into the bulk material [5]. Due to the nature of the storage mechanism, pseudocapacitors present higher capacitance than EDLCs, albeit their lower power density. Both cycle life and storage capability thus fall between those of batteries and EDLCs. The pseudocapacitive electrode materials most commonly used are transition metal oxides/hydroxides and electrically conducting polymers [7,9].

Hybrid capacitors emerged as a novel solution to overcome the limitations of EDLCs and pseudocapacitors, combining both abovementioned charge storage mechanisms in a single device [7]. This can be accomplished through the use of composite or hybrid materials composed by an EDLC-type and a pseudocapacitor-type component as electrodes, the so-called *composite* or *symmetric hybrids*. Hybrid capacitors can also be classified as *asymmetric hybrids* when they couple two electrodes with different storage mechanisms: in one of the electrodes, only an electrostatic process occurs, whereas in the other electrode redox reactions or a combination of non-Faradaic and Faradaic processes occur. Finally, the third type of hybrid capacitors are *battery-type hybrid capacitors*, where one of the electrodes is a material containing Li^+ ions to enable Li^+ intercalation/deintercalation similarly to battery mechanism.

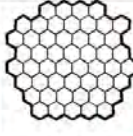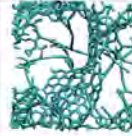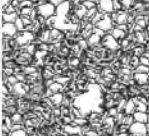## 3. Carbon (Nano)Materials as Electrodes in Supercapacitors

Carbon (nano)materials have been among the top choices as electrodes for energy storage applications owing to their versatile structures ranging from 0D to 3D and tunable surface chemistry [8]. In particular, activated carbon, graphene, carbon nanotubes, onion-like carbons and templated carbons have attracted great interest as EDLC-type electrodes for SCs owing to their high electrical conductivity, large specific surface area, easy handling, high chemical and thermal stability and excellent mechanical properties [8,10]. Due to these features, carbon-based SCs exhibit high power density, high charge-discharge rates, excellent cycling stability and long operation life. In Table 1 is presented a comparison between different types of carbon-based materials commonly used as EDLC-type electrodes.

Each type of carbon-based material has its unique structure and features [12]. For instance, 0D and 1D carbon nanomaterials, such as carbon onions and carbon nanotubes, allow achieving high power density due to the fast adsorption/desorption of the electrolyte ions on their surface. On the other hand,
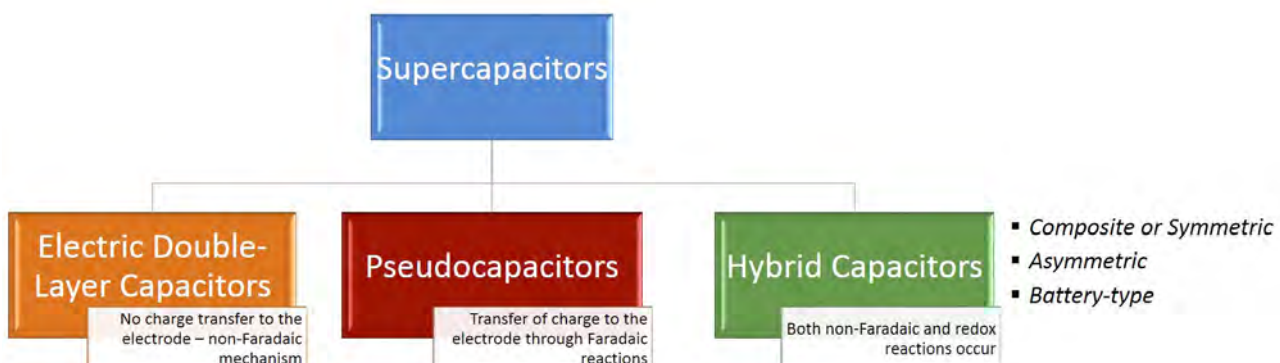
Figure 2. Flow-chart of SCs taxonomy.

Table 1. Comparison between different types of carbon-based materials used in EDLCs[a]

Material	Carbon onions	Carbon nanotubes	Graphene	Activated carbon	Carbide derived carbon	Templated carbon
Dimensionality	0-D	1-D	2-D	3-D	3-D	3-D
Conductivity	High	High	High	Low	Moderate	Low
Volumetric Capacitance	Low	Low	Moderate	High	High	Low
Cost	High	High	Moderate	Low	Moderate	High
Structure						

[a] Reproduced from ref. 11 with permission from The American Chemical Society.

graphene, a 2D carbon nanomaterial, can provide higher charge/discharge rate and volumetric energy density. Porous 3D carbon materials such as activated carbon, templated carbon and carbide-derived carbon present higher surface areas and pores in the Å or nm range, delivering higher energy densities if their pore dimensions matches the size of electrolyte ions [12]. Therefore, the selection of the proper type of carbon material will depend on the requirements of the target application.

In particular, in the case of the market of portable electronics, carbon nanotubes (CNTs), graphene, activated carbon and carbon fibers have attracted significant interest for the fabrication of flexible and wearable energy storage systems (*eg*. SC fabrics/fibers, plastic electronics, Figure 3) [10].

Despite the advantages of carbon-based SCs, they still exhibit limited specific capacitance owing to the non-Faradaic charge storage mechanism; consequently, they present lower energy density
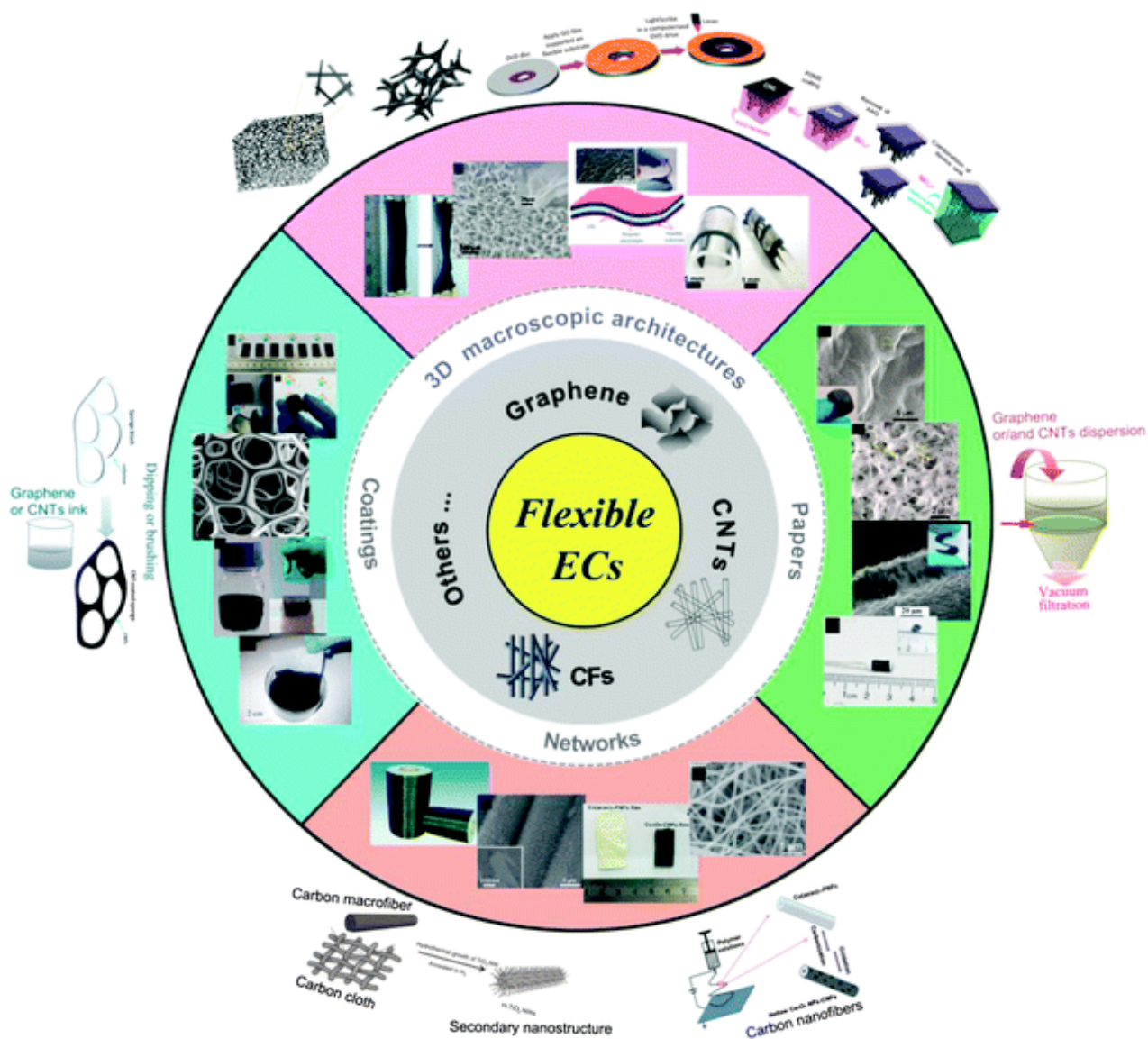
Figure 3. Fabrication of carbon-based electrode materials for flexible SCs. Reproduced from ref. 10 by permission of The Royal Society of Chemistry.

than pseudocapacitors (typically ~5 Wh/kg^{-1}) [10]. To overcome these limitations, the performance of carbon-based electrode materials has been improved by tailoring their specific surface area, pore structure, electrical conductivity and surface chemistry [13]. To achieve this goal, several strategies have been developed, namely: (i) Design of carbon materials with hierarchical porous structure, (ii) Doping of carbon (nano)materials with heteroatoms (N, O, S, B, P) and (iii) Design of hybrids/composites combining conductive carbon (nano)materials with transition metal oxides and/or conducting polymers [13–15].

Strategy (i) allows optimizing the pore sizes and pore size distribution and simultaneously increasing the specific surface area, without compromising the electrical conductivity [14]. The high specific surface area increases the number of accessible active sites, contributing to enhanced capacitance, while the pore structure regulates the electrolyte ions diffusion and, consequently, the performance of the SC (power density and charge-discharge rate) [13].

On the other hand, the tuning of the surface chemistry of the carbon material can be achieved by strategies (ii) or (iii), which introduce an additional pseudocapacitive component to the device (Faradaic reactions) [13,14]. Furthermore, in the case of strategy (ii), the introduction of surface functionalities can improve the wettability of the carbon surface (hydrophilicity/lipophilicity), facilitating the electrolyte ions adsorption and ensuring their fast transport within the carbon material pores [13,15].

3.1 Heteroatom-Doped Carbon Nanomaterials

Heteroatom doping is an efficient method to fine-tune the structural and electronic properties of carbon electrode materials [14,15]. The presence of heteroatoms such as O, N, S and P on the surface of the carbon support may induce surface faradaic redox reactions and/or a local modification of its electronic structure besides improving the electrode-electrolyte interactions, due to a decrease of the gap between the conduction and valence bands and an increase of the number of local free electrons [7,14,15]. Among various types of heteroatoms, O-doping and N-doping have been the most extensively investigated for SC applications [16].

Oxygen-enriched carbon materials namely containing quinone groups are typically prepared by carbonization/activation of an oxygen rich precursor, liquid-phase or gas-phase post-treatment oxidation (in HNO_3, O_2, etc.), electrochemical oxidation and oxygen plasma treatment [14]. The oxygen-containing functional groups are usually acidic, introducing electron-acceptor properties into the carbon surface.

Nitrogen-doping can be performed by *in-situ* and post-treatment processes [14,16]. The *in-situ* route consists on the carbonization of a nitrogen-rich carbon precursor (melamine, cyanamide, polyacrylonitrile, polyaniline, etc.) followed by steam activation. The post-treatment can be performed by impregnation of porous carbon (nano)materials with N-containing reagents (NH_3, urea, amines) followed by thermal treatment, by nitrogen plasma treatment, among others. The *in-situ* approach leads to a higher amount of nitrogen-based functional groups, while the post-treatment routes can only introduce N-functional

groups on the surface of the carbon materials. N-containing functionalities such as pyridinic N, pyrrolic N, quaternary N and N-oxide present electron-donor properties which can tailor the electrodes wettability, electrical conductivity and capacitance performance [14,16]. In this context, they contribute with additional electrons and fast electron transfer, inducing negative charges on adjacent carbon atoms and widening the electrode capacitance [17].

More recently, simultaneous co-doping of two distinct heteroatoms into carbons, namely N-/P-, B-/N-, B-/P-, emerged as a promising strategy to improve the SC performance owing to the synergistic effect between both functionalities [14]. Nevertheless, special care should be taken during heteroatom doping to avoid conductivity and structural deterioration [15]. The excessive doping may increase the number of defects on the surface of carbon materials; furthermore, the formation of multiple functional groups may lead to higher leakage current and lower cycle life (fast degradation) [14–16].

3.2 Hybrid Carbon–Metal Oxide Nanomaterials

A distinct route to improve the performance of carbon-based electrodes and overall performance of the resulting SCs consists on combining the carbon material with other components that exhibit a complementary charge storage mechanism, namely pseudocapacitive transition metal oxide/hydroxide nanoparticles (NPs) and/or conducting polymers.

In particular, hybrid carbon–metal oxide/hydroxide nanomaterials constitute a breakthrough on the design of high-performance electrodes and flexible SCs [10,18]. Through the conjugation of two distinct components with complementary physicochemical characteristics in a single electrode, a synergistical improvement of the properties of the resulting hybrid electrode can be achieved when compared with those of the individual components. The conductive carbon material is used as backbone support and conductive path for electron transport, imparting EDL capacitance. Furthermore, due to the large specific surface area and porous structure, it improves the electrolyte accessibility and contact between the electrolyte and the supported pseudocapacitive component [10]. On the other hand, the grafted metal oxide/hydroxide NPs can increase the performance of the hybrid electrode material by allowing the occurrence of reversible redox reactions upon SC charging/discharging. The most commonly used metal oxide/hydroxide nanomaterials have been RuO_2, MnO_x, Co_3O_4, $NiO/Ni(OH)_2$, Fe_xO_y, $NiCo_2O_4$, etc. [1].

Hybrid carbon–metal oxide nanomaterials can be prepared by several methods including coprecipitation, hydrothermal, electrodeposition, among others [14]. Regardless of the process, it should ensure a uniform distribution of the metal oxide NPs throughout the support surface. The presence of surface functional groups on the carbon support that act as anchoring sites is required to ensure the robust anchorage of the NPs upon their nucleation and growth and prevent particle leaching.

Nevertheless, the design of hybrid carbon–metal oxide nanomaterials with fine-tuned physicochemical properties by controllable and easily scalable routes continues to be a challenging milestone to achieve
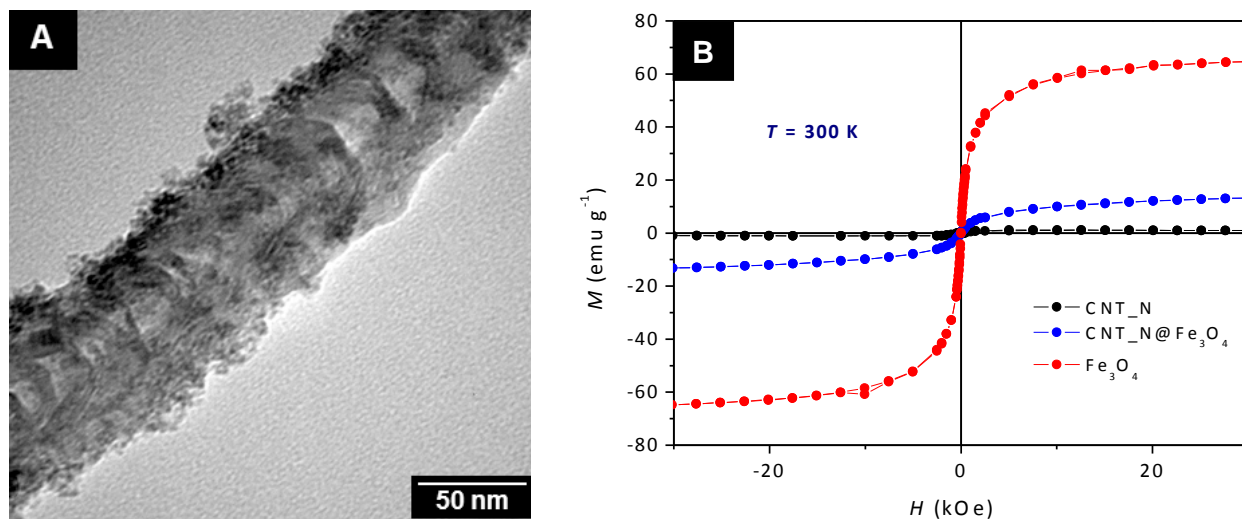
Figure 4. (A) TEM image of CNT_N@Fe$_3$O$_4$ and (B) Magnetization as a function of applied magnetic field at 300 K for CNT_N, Fe$_3$O$_4$ and CNT_N@Fe$_3$O$_4$.

high-performance SCs [18].

Our team has been fabricating novel hybrid carbon-based nanomaterials to be used as electrode materials for SCs through the immobilization of superparamagnetic transition metal ferrite NPs (MFe$_2$O$_4$ with M(II) = d-block transition metal cation) onto N-doped CNTs. To accomplish this goal, we have developed a one-pot in-$situ$ coprecipitation process that ensures the controlled formation of NPs with reduced particle size and high crystallinity throughout the support surface [19–21]. The N-doped carbon nanotubes (CNT_N) used in this work have been prepared by the group of Prof. Dr. Antonio Guerrero-Ruiz, Instituto de Catálisis y Petroleoquímica, CSIC, Madrid, Spain through acetonitrile vapor decomposition [22].

Our main goal is to modulate the dielectric properties of CNT_N through the incorporation of MFe$_2$O$_4$ NPs with different types of M(II) cations, thus combining the high electrical conductivity arising from the CNTs support with the high specific capacitance imparted by the metal oxide NPs. As example, we have prepared a hybrid CNT_N@Fe$_3$O$_4$ nanomaterial by in-$situ$ coprecipitation of iron(II) and iron(III) salt precursors in the presence of the CNT_N support induced by an alkanolamine base.

The transmission electron microscopy (TEM) images (Figure 4A) revealed the presence of ultrasmall particles with average particle size of 3.2±0.6 nm throughout the bamboo-like CNTs surface.

When it comes to hybrid nanomaterials it is vital to quantify the amount of each component. When the hybrid material has a strong magnetic component and the other constituent is magnetically weak or is non-magnetic, the measurement of the magnetic properties by magnetometry is a powerful technique to determine their loadings. In our case, the hybrid is constituted by Fe$_3$O$_4$ NPs that exhibit superparamagnetic behavior at room temperature and by CNTs that can be diamagnetic but in some cases can present weak ferromagnetic or paramagnetic properties depending on the synthesis route arising from the precursors [23].

In Figure 4B are presented the isothermal magnetization curves (T = 300 K) as a function of applied magnetic field for the parent CNT_N, the unsupported superparamagnetic Fe$_3$O$_4$ NPs and the hybrid nanomaterial containing both components (CNT_N@Fe$_3$O$_4$). From Figure 4B it can be observed that the magnetization contribution arising from the CNT_N support is almost negligible when compared with that of the Fe$_3$O$_4$ magnetic nanoparticles (MNPs). On the other hand, the hybrid nanomaterial presents a similar trend to that of Fe$_3$O$_4$, albeit the lower saturation magnetization, thus confirming the presence of both CTNs and MNPs. From these curves the amount of Fe$_3$O$_4$ MNPs in the hybrid nanomaterial can be extracted with respect to that of the CNT_N support: CNT_N@Fe$_3$O$_4$ is composed by 24.5 wt% of Fe$_3$O$_4$ and 75.5 wt% of CNT_N. Moreover, the absence of magnetic hysteresis indicates that the hybrid nanomaterial is in the superparamagnetic state at room temperature, similarly to the unsupported Fe$_3$O$_4$ MNPs [19].

For the design of SCs with high performance, it is important to evaluate the electrical resistivity of the electrode since it is one of the crucial parameters to increase the SC power density P ($P = \dfrac{V^2}{4R}$, where V is the applied voltage and R is the circuit equivalent resistance) [7]. Therefore, in order to maximize the power density, the ideal electrodes should have low electrical resistivity. Another important parameter is the electrode capacitance (C), that should be high to achieve high energy density E ($E = \dfrac{1}{2} C_T V^2$, where the total capacitance C_T is half of C) [7].

To determine these properties, impedance measurements in the frequency range 20 Hz – 3 MHz were performed for CNT_N, Fe$_3$O$_4$ MNPs and CNT_N@Fe$_3$O$_4$ hybrid. The electrical conductivity values as a function of frequency, presented in Figure 5, were extracted from the impedance curves by using $\sigma = \dfrac{Z' t}{(Z'^2 + Z''^2) A}$, where Z' is the real part of the impedance and Z'' is the imaginary part, A is the effective section area and t is the thickness.

Among all nanomaterials, the parent CNT_N presents the highest electrical conductivity ($\sigma \sim 0.130$ S m^{-1} within all frequency range), with a very small Z''

Figure 6. Flexible cotton-based SC prototype (left) and LED powered by three cotton-based prototypes connected in series (right).

(not shown), which is characteristic of a conductive material. In the case of the Fe_3O_4 MNPs, it can be observed that σ is proportional to the frequency, increasing from ~10^{-8} to 10^{-5} S m^{-1}, showing that the material has a very small conductivity and presents an insulator behavior. Important to point out is that in the case of the CNT_N@Fe_3O_4 hybrid nanomaterial an intermediate electrical conductivity value was achieved of σ ~ 0.043 S m^{-1} within all frequency range.

Hence, through the incorporation of Fe_3O_4 MNPs onto the CNT_N support, it was possible to graft ~24.5 wt% of MNPs, while preserving the typical properties of conductive materials. This is a promising achievement since the CNT_N@Fe_3O_4 hybrid possesses metal oxide NPs that enable the occurrence of Faradaic reactions within the SC and low resistivity arising from the support for the simultaneous occurrence of an EDLC-type mechanism. Therefore, the prepared CNT_N@Fe_3O_4 hybrid is a promising electrode candidate for the design of textile-based hybrid capacitors.
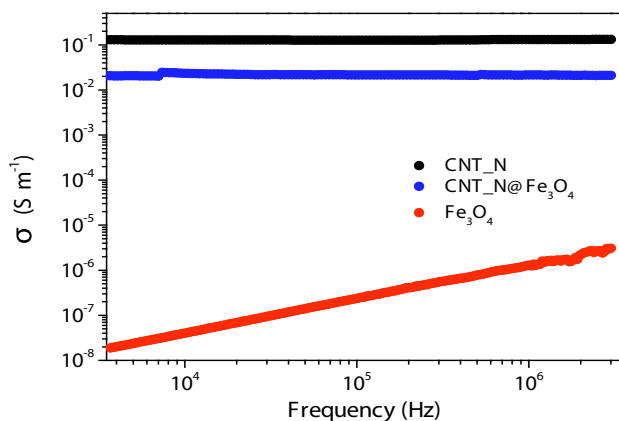
Figure 5. Electrical conductivity at room temperature as a function of frequency for CNT_N, Fe_3O_4 and CNT_N@Fe_3O_4.

4. Smart Textile Supercapacitors for Energy Storage

Textiles supercapacitors can be produced by different routes: (i) coating of pre-existing textile substrates, (ii) building-up fibers and yarns and (iii) designing custom woven or knitted architectures that incorporate the SC into the textile structure [2]. In strategy (i), the fabric is firstly coated with the electrode nanomaterials followed by the assembly of the resulting textile electrodes and the electrolyte/separator into the final SC textile. In this type of SC design, both electrodes

and electrolyte can be assembled in a multilayer configuration or side-by-side in a planar configuration. In route (ii), the electrode materials are incorporated during the fabrication of the fibers/yarns giving rise to electrode fibers/yarns that can then be knitted/woven directly into a garment; the fibers can be processed in different configurations and contain different coatings/multilayers or components [2].

The selected strategy should always take in mind production costs and scalability in order to become a viable solution. In this sense, our team has been developing textile SCs based on carbon–metal oxide nanomaterials through processes that can be easily scalable and implemented in Textile Industry using the available infrastructures.

We have started by fabricating novel solid-state and flexible textile SCs using composite electrodes constituted by carbon black and $MnFe_2O_4$ MNPs and a solid-gel electrolyte. Woven cotton substrates were dip-coated with carbon black and $MnFe_2O_4$ inks in order to produce the textile-based electrodes. The cotton-based SC prototype, which presented high flexibility (see Figure 6), was produced through the assembly of the textile electrodes and electrolyte in a multi-layered configuration.

The performance of the resulting SC fabric was evaluated by performing cyclic voltammetry, galvanostatic charge/discharge and electrochemical impedance spectroscopy (EIS). From the obtained current-voltage cycles, the determined specific capacitance of the SC prototype was 307 F/kg, leading to an energy density of 474 Wh/kg (per active mass loading). Furthermore, from the EIS measurements, an equivalent series resistance of 1.25 kΩ was obtained, leading to a power density of 117 W/kg. Although the energy density and capacitance of the SC fabric were promising, the equivalent series resistance was responsible for a small power density. Nevertheless, by connecting three SC fabrics with 1×1 cm^2 in series, we were able to light a green LED for up to eight minutes (Figure 6).

Finally, the results obtained in this work demonstrated the feasibility of combining nanomaterials dispersions with dyeing processes used in the Textile Industry to design lightweight and flexible textile SCs. New processes are currently being developed by our team to fabricate high-performance textile SCs using different types of fabric substrates and hybrid carbon–metal oxide nanomaterials as electrodes.

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