

Hybrid/Doped Carbon-Based (Nano)materials for Advanced Applications: Eco-Sustainable Catalysis, Biomass Valorization, Energy Technologies & Smart Devices

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Abstract

Carbon-based (nano)materials are remarkable building blocks that have been boosting innovation in a multitude of advanced applications, ranging from Catalysis and Environment to Energy and Smart Technologies.

Our research group from the Associated Laboratory for Green Chemistry REQUIMTE/LAQV, at the Chemistry and Biochemistry Department of Faculty of Sciences of Porto University, Portugal, has been developing research work within the context of R&TD projects in the areas of hybrid and doped carbon-based (nano)materials for eco-sustainable catalysis, biomass valorization, energy technologies and smart devices. In this article, the main achievements and progress in these fields are reviewed.

1. Introduction

The Associated Laboratory REQUIMTE/LAQV is the largest Chemistry Network in Portugal, being recognized as a Research Centre of Excellence, covering Chemistry, Chemical Engineering and Biotechnology areas. Among the different thematic lines of LAQV, our research group – *Catalysis and Functional and Smart (Nano)materials* – which is located at the Chemistry and Biochemistry Department of the Faculty of Sciences of Porto University (LAQV@FCUP), is integrated in the thematic line of *Functional Materials*, and in the research group of *Materials for Sustainability and Wellbeing*. It is devoted to the production of advanced multifunctional (nano)materials with unique/enhanced properties through eco-friendly routes to address the 21st Century Grand Challenges, boosting innovation on for core scientific areas: (i) Catalysis for a Sustainable Environment, (ii) Renewable Energy and Climate Change Mitigation, (iii) Environmental Protection and Remediation, and (iv) Wearable Technologies and Devices.

Among the landscape of engineered (nano)materials developed by our group and used as building blocks for the aforementioned applications, carbon (nano)materials occupy a pivotal position, owing to their remarkable physicochemical properties and wide versatility in terms of doping, functionalization and composite fabrication/hybridization with other components (e.g., transition metal complexes, noble and earth abundant metals, metal oxides, polyoxometalates, etc.).

In this article, the different R&TD activities that are being carried out at LAQV@FCUP in the field of hybrid and doped carbon-based (nano)materials for

advanced applications are reviewed, with special highlight to four key applications: eco-sustainable catalysis, biomass valorization, energy production and storage technologies & smart electrochromic devices. The article starts by reviewing the works developed in the areas of recyclable heterogeneous carbon-based catalysts for oxidation and reduction reactions, namely hybrid carbon-metal complex heterogeneous catalysts, carbon supported gold(0) catalysts and the new generations of metal-free carbocatalysts and graphene-based photo(electro) catalysts for emerging pollutants removal. Afterwards, the development of biochar-based catalysts for biomass valorization is presented. Subsequently, the fabrication of hybrid/doped carbon-based (nano)materials for energy applications, namely fuel cells and electrochemical energy storage devices, including energy storage textiles and flexible devices, is described. Finally, the last section is devoted to the development of smart electrochromic devices based on carbon-poly(nickel complex) nanocomposites.

2. Eco-Sustainable Catalytic Systems Based on Carbon (Nano)Materials

2.1 Hybrid Carbon-Metal Complex Heterogeneous Catalysts for the Epoxidation of Alkenes and Allylic Alcohols

Transition metal complexes are ubiquitous catalysts in several important chemical transformations for the synthesis of valuable fine and bulk chemicals and chemical intermediates, through oxidation, addition or reduction reactions [1,2]. The heterogenization of such metal complexes on solid supports allows the combination of the catalytic properties of the homogeneous complexes with the advantages of heterogeneous catalysts, namely the ease of separation from the reaction medium, shape selectivity and reusability [3–7]. Our group has developed several anchoring procedures to immobilize Schiff-base transition metal complexes onto activated carbons (ACs) in collaboration with Professors J. L. Figueiredo and M. F. R. Pereira from the Associate Laboratory LSRE-LCM (Laboratory of Separation and Reaction Engineering and Laboratory of Catalysis and Materials), at the Chemical Engineering Department of Faculty of Engineering of University of Porto (FEUP) [8–12].

In one of those works, oxidovanadium(IV) acetylacetonate ($[\text{VO}(\text{acac})_2]$) was anchored onto two oxidized activated carbons (ACs) previously functionalized with 3-aminopropyltriethoxysilane

or with bis(3-aminopropyl)amine (methods A and B, respectively), through Schiff-base condensation between the free amine groups covalently attached

to the AC surface and the oxygen atoms of the acetylacetonate ligand, as shown in Figure 1 [13].

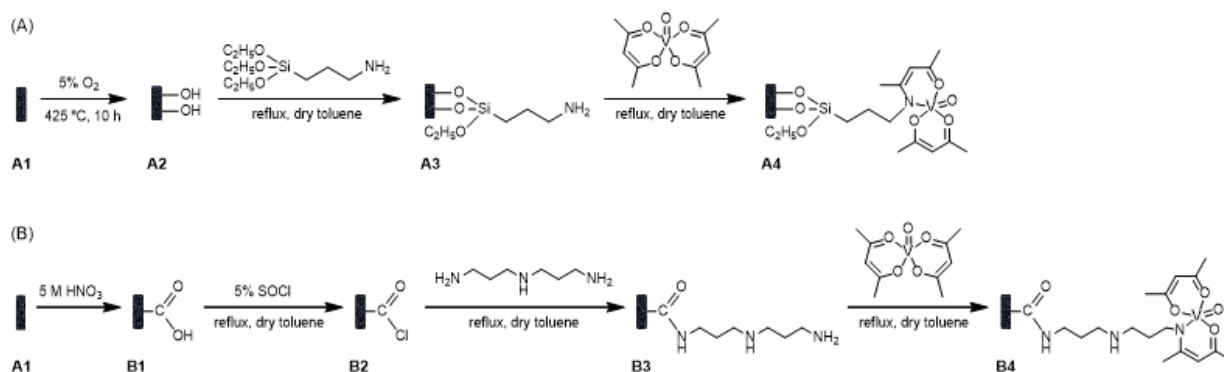


Figure 1. Proposed routes for the immobilization of $[\text{VO}(\text{acac})_2]$ onto amine-functionalized ACs by methods A and B. Reproduced from ref. [13] which possesses carboxylic surface groups, was treated with thionyl chloride to give surface acyl chloride groups (132 by permission of John Wiley and Sons).

The catalytic activity of the two novel AC-based $[\text{VO}(\text{acac})_2]$ heterogeneous catalysts, A4 and B4, was tested in the epoxidation of an allylic alcohol (3-buten-2-ol) at 0 °C in dichloromethane, using *tert*-butyl hydroperoxide as the oxygen source. Both catalysts showed high catalytic activity (A4: substrate conversion, %C = 100% after 144 h; B4: %C = 100% after 192 h), with the A4 catalyst being more active than B4 (0.4 vs 0.3 h^{-1} turnover frequencies, respectively). Moreover, both materials were reused with no significant loss of activity, indicating that the metal complexes were irreversibly anchored to the carbon surface, which prevented the leaching of the active phase and possible catalyst deactivation.

In another work, the *Jacobsen* catalyst, $[(R,R)\text{-}(1,2\text{-cyclohexanediaminomanganese(III) chloride})]$, was immobilized onto four ACs with different average pore sizes prepared by a gasification process with CO_2 during four exposure times ($X = 0, 60, 180, 300$ min) followed by thermal treatment with O_2 [14]. An increase of the specific surface area of the ACs was observed upon the increase of the gasification time, as well as of other textural parameters, such as the mesopore area, micropore volume and average pore size. Afterwards, the materials were treated with NaOH to facilitate the subsequent *Jacobsen* complex immobilization through axial coordination, as shown in Figure 2.

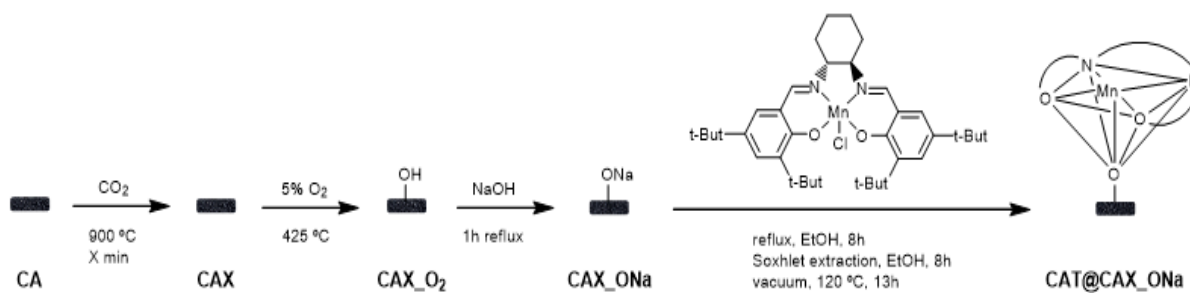


Figure 2. Anchoring procedure for the immobilization of the *Jacobsen* catalyst onto modified ACs. Reproduced from ref. [14] by permission of Elsevier.

The heterogeneous catalysts were tested in three systems: (i) epoxidation of styrene using *m*-chloroperoxybenzoic acid as oxidant and 4-methylmorpholine *N*-oxide as co-oxidant (−5 °C, in CH_2Cl_2); (ii) epoxidation of 6-cyano-2,2-dimethylchromene using NaOCl as oxidant (0 °C, in CH_2Cl_2) and (iii) epoxidation of 6-cyano-2,2-dimethylchromene using iodosylbenzene as oxidant (at room temperature, in CH_3CN). The catalysts were found to be active and enantioselective in the three systems, as summarized in Table 1.

The activity of the heterogeneous catalysts in the epoxidation of both substrates generally increased with the increase of the porosity of the AC support. In parallel, the total Mn(III) loading in the heterogeneous catalysts increased with the AC support pore size,

as well as the metal complex distribution within the carbon porous matrix, which could account for the increased catalytic activity. Concerning the enantioselectivity, in the case of the epoxidation of styrene (system i), the increase of the AC porosity also led to an increase of the enantiomeric excess values (%ee). Moreover, when that particular reaction was catalyzed by CAT@CA180_ONa and CAT@CA300_ONa, the obtained %ee values were higher than those achieved with the homogeneous counterpart (43% vs. 40% in both cases). In the case of the epoxidation of 6-cyano-2,2-dimethylchromene, systems ii and iii, similar enantioselectivity trends were observed, except when using CAT@CA180_ONa as catalyst.

Catalyst	System	t (h)	C (%)	S (%)	ee (%)
CAT@CA_ONa	(i)	4	19	76	30
CAT@CA60_ONa		4	34	86	36
CAT@CA180_ONa		4	67	95	43
CAT@CA300_ONa		4	74	96	43
CAT@CA_ONa	(ii)	48	5	89	82
CAT@CA60_ONa		48	8	95	84
CAT@CA180_ONa		48	20	98	80
CAT@CA300_ONa		48	22	84	85
CAT@CA_ONa	(iii)	72	30	32	64
CAT@CA60_ONa		72	36	88	71
CAT@CA180_ONa		72	50	96	70
CAT@CA300_ONa		72	46	98	73

^a C – substrate conversion; S – epoxide selectivity; ee – enantiomeric excess.

Table 1. Asymmetric epoxidation of alkenes catalyzed by heterogeneous AC-supported *Jacobsen* catalysts^a

The activity of the heterogeneous catalysts in the epoxidation of both substrates generally increased with the increase of the porosity of the AC support. In parallel, the total Mn(III) loading in the heterogeneous catalysts increased with the AC support pore size, as well as the metal complex distribution within the carbon porous matrix, which could account for the increased catalytic activity. Concerning the enantioselectivity, in the case of the epoxidation of styrene (system i), the increase of the AC porosity also led to an increase of the enantiomeric excess values (%ee). Moreover, when that particular reaction was catalyzed by CAT@CA180_ONa and CAT@CA300_ONa, the obtained %ee values were higher than those achieved with the homogeneous counterpart (43% vs. 40% in both cases). In the case of the epoxidation of 6-cyano-2,2-dimethylchromene, systems ii and iii, similar enantioselectivity trends were observed, except when using CAT@CA180_ONa as catalyst.

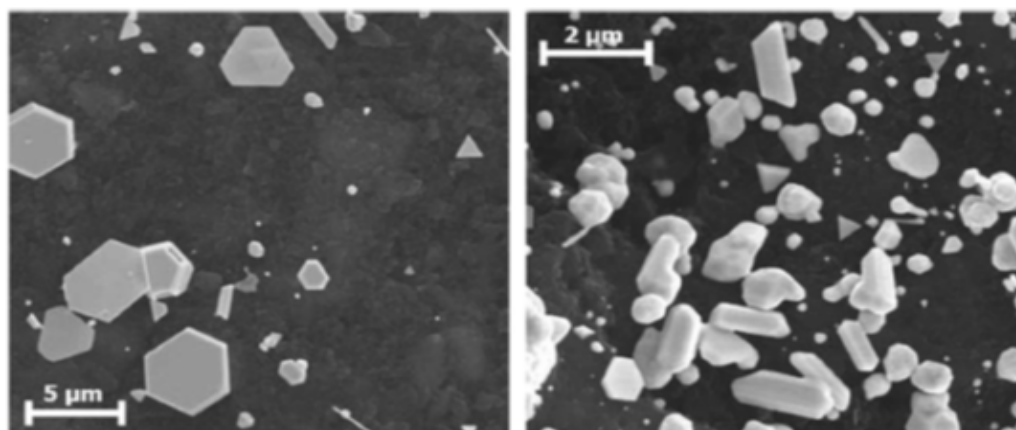
Reusability experiments revealed a general decrease of the catalytic performance of the AC-based catalysts. Nevertheless, CAT@CA180_ONa and CAT@CA300_ONa materials still led to turnover numbers (TONs) higher than those obtained in the homogeneous phase for the epoxidation of 6-cyano-

2,2-dimethylchromene with iodosylbenzene (CAT@CA180_ONa: TON = 17 vs. 16; CAT@CA300_ONa: 12 vs. 9).

2.2 Activated Carbon Supported Gold(0) Catalysts for the Oxidation of Glycerol

In the midst of our studies on the immobilization of metal complexes onto ACs, we made a serendipitous discovery. We found that these ACs could reduce Au(III) ions in solution to metallic Au(0), in the absence of any reductant. Hence, we prepared novel Au(0)-based heterogeneous catalysts by direct reduction of Au(III) ions onto different AC materials, namely a non-functionalized AC (A1, Figure 1) and an oxidized AC (A2, Figure 1), using ethanol (Au@A1, Au@A2) or water (Au@A1', Au@A2') as solvent [15]. Geometrical shaped and amorphous gold was formed at the surface of the carbon materials (Figure 3). Smaller Au particles were detected in Au@AC1 and Au@AC2 materials, as well as geometric shaped particles, while only gold aggregates could be observed in Au@A1' and Au@A2'. These results suggested that the reduction of gold in water was significantly faster than in ethanol.

Liquid-phase catalytic oxidation is a promising route



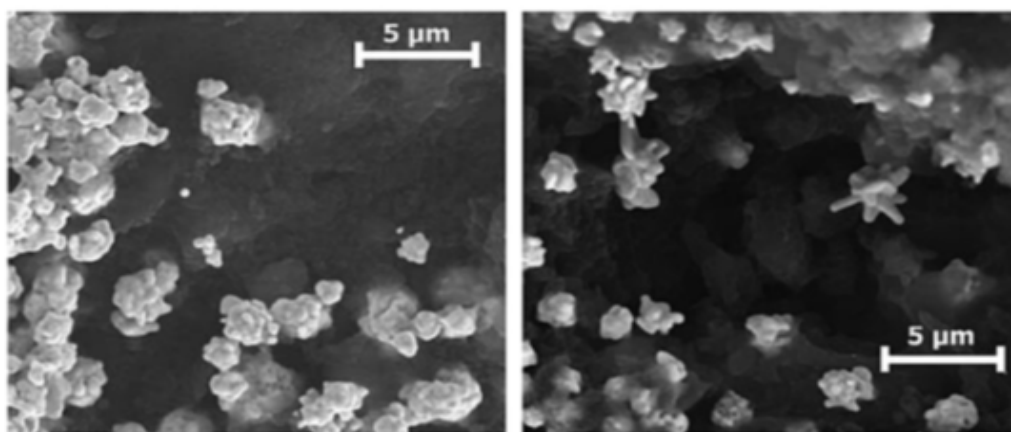


Figure 3. SEM micrographs of Au@A1 (top left), Au@A2 (top right), Au@A1' (bottom left) and Au@A2' materials (bottom right). Reproduced from ref. [15] by permission of Elsevier.

for the valorization of glycerol by conversion into useful products, provided that the used catalysts are sufficiently active and selective for the formation of compounds, such as glyceric acid. Specifically, for gold species to be active, the presence of small metallic Au(0) species is required. In this context, the new Au(0)-based heterogeneous catalysts were tested in the oxidation of glycerol (60 °C, in NaOH/glycerol, using 3 bar of O₂). Catalyst Au@A2 showed the best performance (%C = 90% after 7 h), with high and constant selectivity towards the compound of commercial interest, glyceric acid (%S = 58% after 7 h), which could be explained by the higher amount of smaller gold particles in that material.

2.3 Metal-Free Carbocatalysts

Carbon materials have been extensively used as

catalyst supports for many years. However, certain carbon materials have recently demonstrated to be promising metal-free alternatives for low-cost catalytic processes owing to their wide availability, environmental acceptability, corrosion resistance, and unique surface properties [16]. Despite the few examples of reactivity of pristine carbon materials, their catalytic activity can be greatly enhanced upon introduction of new active sites, either through functionalization with oxygen groups or through doping with heteroatoms.

In this sense, modified multi-walled carbon nanotubes (MWCNTs) and graphene flakes (GFs) were prepared by three different oxidation procedures: (i) nitric acid treatment, (ii) nitric acid followed by thermal treatment at 400 °C, and (iii) gas phase oxidation with O₂, as illustrated in Figure 4 [17].

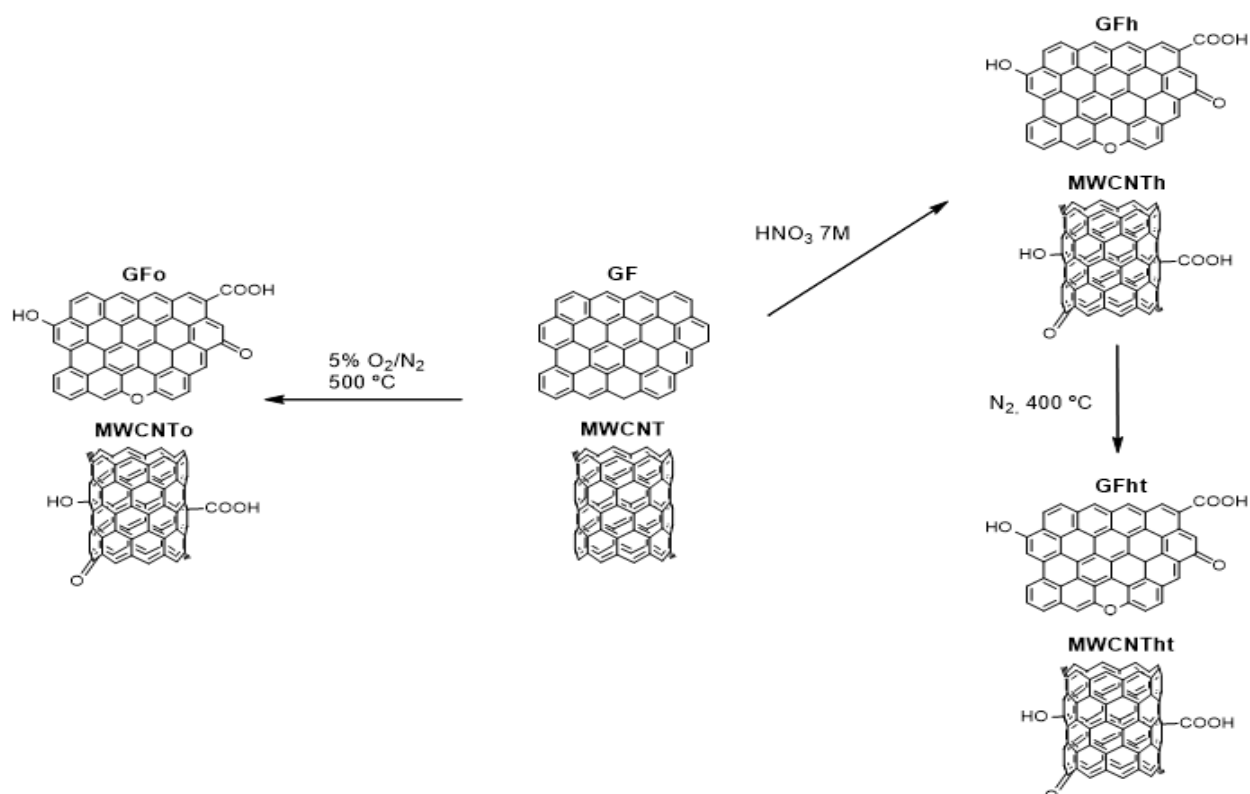
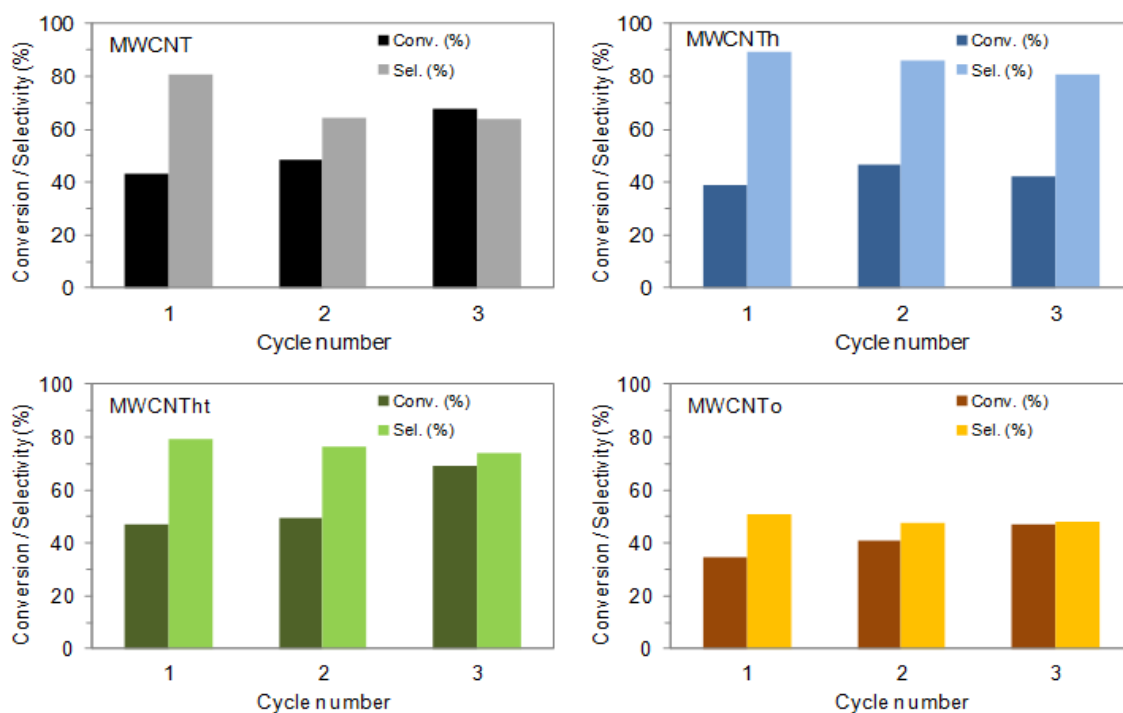


Figure 4. Schematic representation of the procedures for the oxidation of MWCNTs and GFs. Reproduced from ref. [17] by permission of The Royal Society of Chemistry (RSC) on behalf of the Centre National de la Recherche Scientifique (CNRS) and the RSC.

All the oxidized materials showed an overall increase of the oxygen content relative to the parent counterparts. Moreover, the different oxidation procedures induced different surface chemical compositions, namely: (i) nitric acid treated materials MWCNT_h and GF_h presented increased amounts of carboxylic acids, anhydrides and phenols; (ii) nitric acid followed by thermal treatment at 400 °C induced the removal of carboxylic acids and an increase of the anhydrides content; (iii) gas phase oxidation promoted the introduction of phenols, carbonyls/quinones, and lactones.

The catalytic oxidation of *cis*-cyclooctene with 30% H₂O₂ at 80 °C in acetonitrile was studied in heterogeneous phase, using the pristine and modified carbon nanomaterials as catalysts. All nanomaterials were active and selective towards epoxycyclooctane and the modifications introduced in the MWCNTs and GFs through nitric acid followed by thermal treatment at 400 °C (procedure ii), originated catalysts with superior activity and selectivity when compared with their pristine counterparts (MWCNT_h: %C = 47% vs. 43% and %S = 79% vs. 81%; GF_h: %C = 57% vs. 25 and %S = 85% vs. 76%), as shown in Figure 5.

Panel A



Panel B

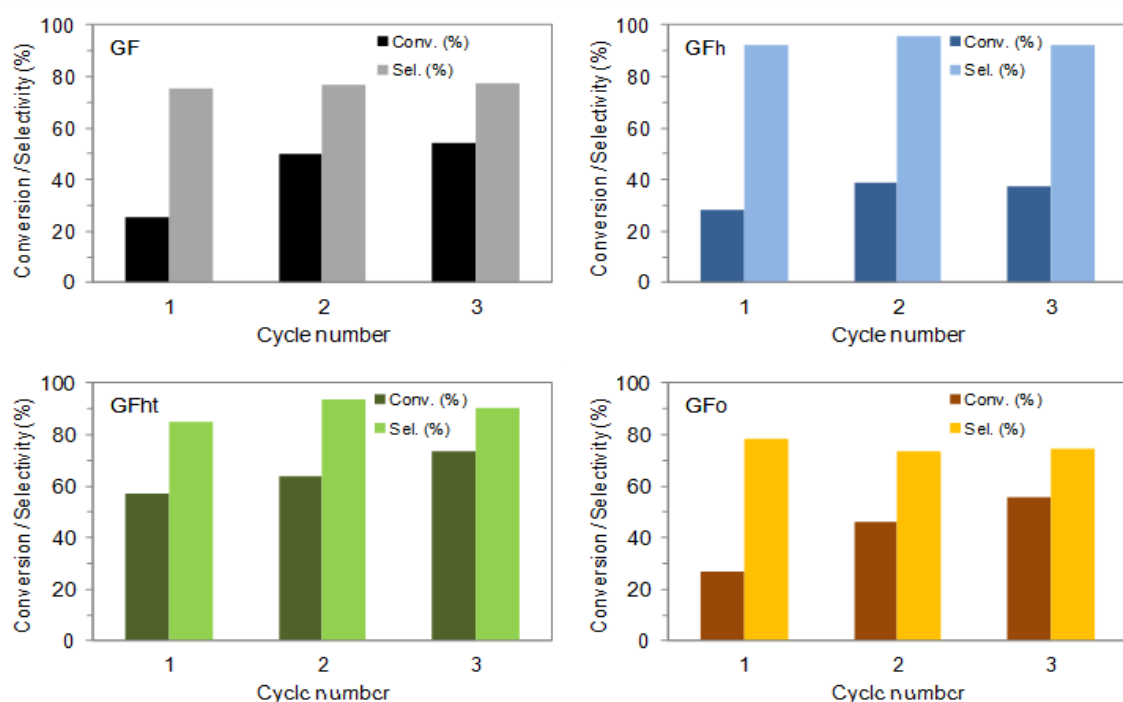


Figure 5. Substrate conversion and epoxycyclooctane selectivity evolution in the oxidation of *cis*-cyclooctene catalyzed by MWCNT-based materials (panel A) and GF-based materials (panel B) for up to three cycles. Reproduced from ref. [17] by permission of RSC on behalf of CNRS and the RSC.

Reusability experiments revealed a slight increase of the catalytic activity of the carbocatalysts for up to three cycles: this was tentatively attributed to the use of H_2O_2 as oxidant, which could be responsible for the oxidation of the nanomaterials surface, enhancing their catalytic performance. These results indicated that the fine-tuning of the morphology and surface chemistry of carbon materials, concerning the amount of defects and type and amount of oxygen

surface groups, respectively, is of high importance to pursue the fabrication of metal-free carbocatalysts with superior performance and selectivity.

In another work, MWCNTs and GFs doped with heteroatoms, namely N, P, B, and S, were prepared through a simple ball milling procedure using adequate precursors, followed by thermal treatment in an inert atmosphere, as depicted in Figure 6 [18].

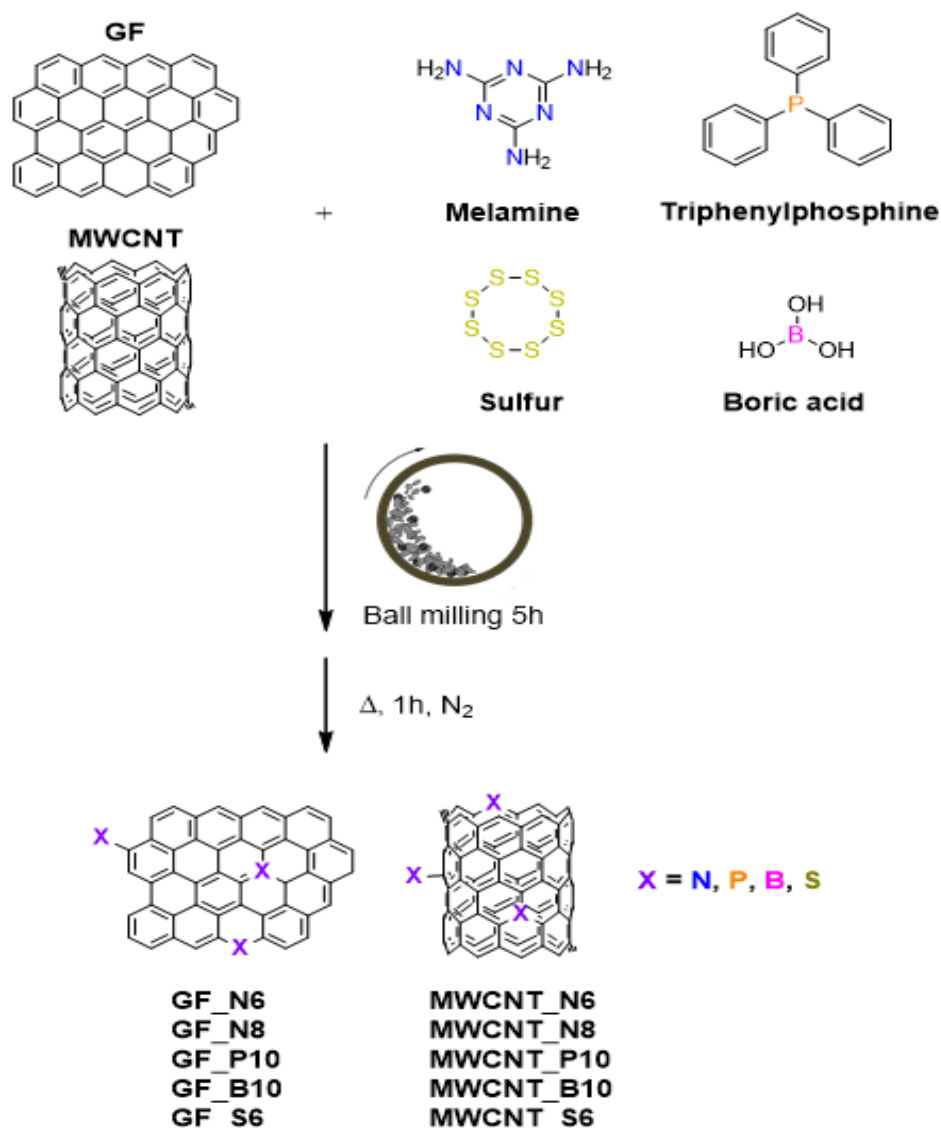


Figure 6. Schematic representation of the procedures for heteroatom doping of MWCNTs and GFs (MWCNT_XY and GF_XY, where X = doping element and Y = °C of thermal treatment/100).

The catalytic performance of the pristine and heteroatom-doped carbon nanomaterials was evaluated in the reduction of 4-nitrophenol (4-NP) in water, at room temperature, in the presence of NaBH_4 , and duly corrected for adsorption phenomena. Remarkably, the modifications introduced by doping MWCNTs and GFs with heteroatoms overall yielded catalysts with superior activity in regard to their pristine counterparts (MWCNT-based catalysts: %C = 59–80% vs. 19%; GF-based catalysts: %C = 63–84% vs. 50%), as shown in Figure 7. The only exceptions were P-doped MWCNTs and N-doped GFs, which presented inferior catalytic performance (%C = 9%

and 27%, respectively). Reusability experiments revealed no loss of catalytic activity of the doped MWCNTs for up to three catalytic cycles, whereas the GF-based materials showed some deterioration of the catalytic performance due to ineffective washing between catalytic runs. These results indicated that the doping of the carbon materials with heteroatoms (N, P, B and S) is a convenient and facile way to obtain metal-free carbocatalysts with superior performance in the reduction of 4-NP.

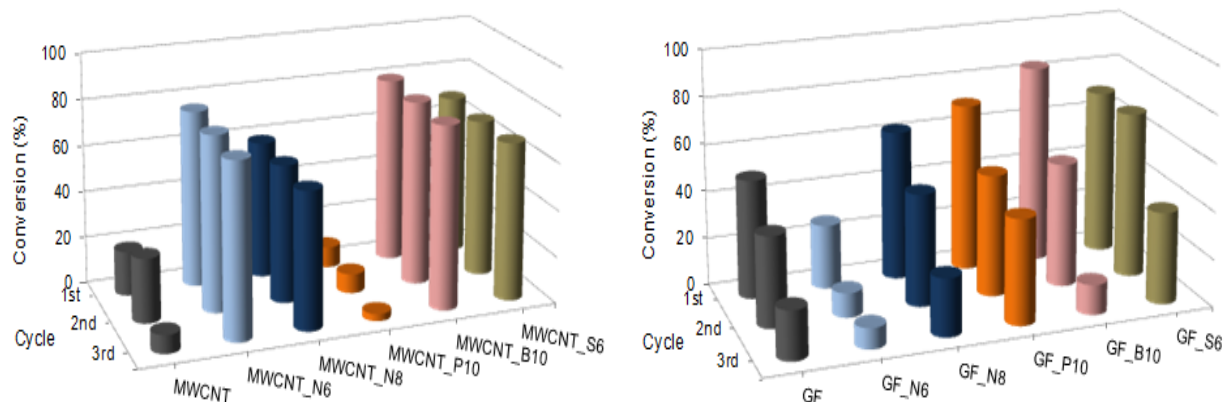


Figure 7. Catalytic results for the MWCNT and GF-based carbocatalysts in the reduction of 4-NP. Reproduced from ref. [18] by permission of John Wiley and Sons.

2.4 Graphene-Based Photo(Electro)Catalysts for Clean Water

In the last decades, the growth of population and worldwide industry processes is having a tremendous impact on the environment. New emerging pollutants are being detected in water and wastewater, such as pharmaceuticals, hormones and their metabolites, which can cause adverse effects on fauna, flora and human health [19–21]. In this context, the quest for new advanced technologies to ensure a safe and sustainable water supply is growing at an accelerating pace, being one of the major global challenges of the 21st century [19]. Nanotechnology-enabled photocatalytic water treatment processes are recently emerging as new opportunities to develop the next-generation of water supply and wastewater treatment systems to produce higher quality water using less energy and with lower treatment costs. Graphene-based nanosystems based on the assembly of graphene flakes and semiconductor nanoparticles stand out as new advanced photocatalytic solutions for the efficient and sustainable removal of water pollutants, with a triple role as photocatalysts, adsorbents and antimicrobial agents. In the project FOTOCATGRAF – Graphene-based semiconductor photocatalysis for a safe and sustainable water supply: an advanced technology for emerging pollutants removal (UTAP-ICDT/CTM-NAN/0025/2014), coordinated by LAQV@FCUP, and where LAQV at Instituto Superior de Engenharia of Instituto Politécnico do Porto (ISEP), CICECO at University of Aveiro, INESC-TEC@FCUP, University of Texas at Austin (UT-Austin) and the Wastewater Treatment Plant Águas do Centro Litoral teams participated as partners, the goal was the design and production of a new generation of high-performance graphene-based photocatalysts for the removal of emerging pollutants, namely pharmaceuticals from the wastewater treatment stations of the north and centre regions of Portugal (Figure 8).

To achieve that goal, LAQV@FCUP and CICECO@UA teams initially focused on the preparation of individual components: a) large-scale production of graphene flakes by cost-effective top-down approaches, (b) POMs and other metal oxides based on abundant metals and (c) metal sulphides; the UT-

Austin team participated on the advanced materials characterization. At the same time, while the LAQV@ISEP team together with **Águas do Centro Litoral** were developing analytical tools to detect and quantify the envisaged pollutants, their metabolites and transformation products in wastewaters, the INESC-TEC@FCUP team was designing and building a prototype of an electrochemical sensor capable of measuring the concentration of a specific pharmaceutical in loco.

The new generation of graphene-based nanocomposites produced were efficiently applied as electrocatalysts for the determination of several pharmaceuticals and as photocatalysts on the degradation of the envisaged emerging pollutants.

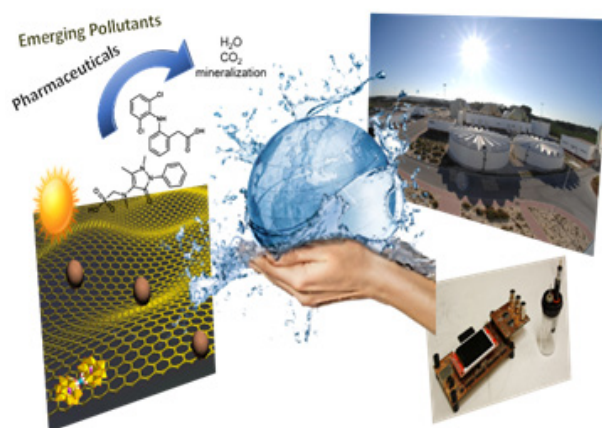


Figure 8. FOTOCATGRAF project concept.

3. Development of Biochar-Based Catalysts for Biomass Valorization

Emerging environmental concerns and declining availability of petroleum reserves have promoted worldwide interest in developing alternative technologies to convert sustainable biomass resources into value-added chemicals. Thermochemical processes have been used to obtain biomass degradation to produce biofuels, biochemicals and biomaterials, such as bio-oils, platform chemicals, biochars, etc. [22].

Biochar is a solid residual byproduct of these processes. As compared to other carbonaceous materials, biochar is an inexpensive, environmentally friendly and easily-produced charcoal [23,24]. The

properties of biochar are affected by the composition and morphology of biomass feedstock, as well as by the production process. However, the utilization of as-prepared biochar as catalyst is not ideal because of its poor physicochemical properties, including low specific surface area and poor porosity [25]. These characteristics can be improved through various activation and functionalization approaches aiming at enhancing the biochar's catalytic properties. The surface area and porosity of biochar can be increased *via* physical activation or chemical activation. The biochar surface can be functionalized by surface sulfonation, surface amination or surface oxidation. The physicochemical properties can be also finely tuned by *in situ* heteroatom doping. In addition, the preparation of composites with other materials, such as metals, metal carbides, and nanostructured carbon materials, is also a common method to make use of biochar as a catalyst material. Thus, sulfonated biochar has shown favourable activity for various acid-catalyzed chemical reactions, including esterification of organic acids in aqueous media, acylation of alcohols and amines, alkylation of aromatics and biomass hydrolysis. On the other hand, biochar-supported metal nanoparticles exhibit high performance for the catalysis of many organic

reactions, including oxygen reduction reactions in fuel cells, hydrogenation and dehydrogenation, and thermal decomposition by pyrolysis or gasification [26]. The described biochar activation/functionalization approach offers a great opportunity that can be readily incorporated into future biorefinery schemes.

Within this context, since 2018 three teams from REQUIMTE/LAQV are conducting the project *BioreVinery – A biorefinery approach to valorize vineyard pruning waste using sustainable extraction and catalytic processes* (PTDC/BII-BIO/30884/2017; Figure 9), coordinated by LAQV@FCUP. The *BioreVinery* project is based on a biorefinery concept, which aims on producing bioproducts with added-value from vineyard pruning waste (VPW), an abundant lignocellulosic agriculture waste generated in winemaking industry one of the main economic agro-food activities in the world with a special incidence in Mediterranean countries. Vine shoots are generated during vine pruning process and have extremely rich chemical constituents. However, their valorization is practically unexplored and the search for innovative uses to consider them as a resource rather than a waste is mandatory in the context of circular economy.

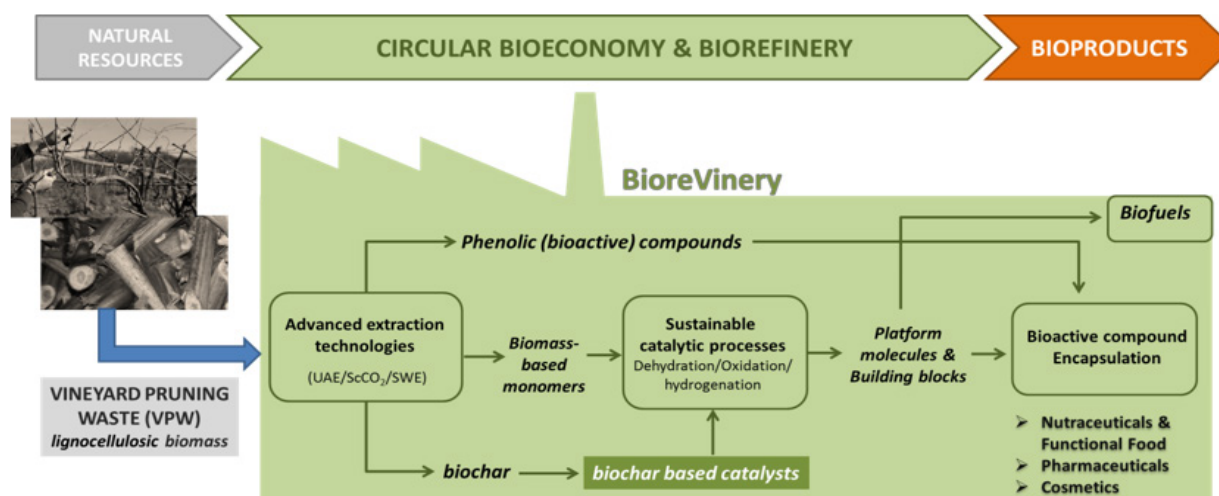


Figure 9. *BioreVinery* project representation.

The first steps of the project research work are focused on the development of advanced extraction technologies to extract phenolic compounds and to obtain biomass-derived monomers. Different extraction methodologies have been employed, including ultrasound-assisted extraction (UAE), supercritical CO₂ extraction (ScCO₂) and hydrothermal extraction under subcritical conditions (SWE). The anti-oxidant activity of the extracts obtained from these advanced extraction technologies has been also evaluated. As a byproduct of these processes, a solid fraction of biochar is obtained, which is being used for the preparation of novel catalysts to convert the produced biomass-derived monomers into the targeted bioproducts. In light of the great potential of biochar-based catalysts for catalytic biomass upgrading [27], our research is devoted to investigate their versatile applications

for the upgrading of biomass-derived VPW, including the biochar activation through different procedures (hydro treatment, CO₂ gasification) and biochar functionalization by sulfonation, incorporation of heteroatoms, metal oxides and/or metallic nanoparticles. The efficiency of the resulting catalysts will be tested in the dehydration of C₅/C₆ sugars to platform molecules (e.g., furfural, 5-hydroxymethylfurfural), and upgrading of platform molecules to valuable bioproducts by hydrogenation, oxidation and hydrogenolysis reaction pathways.

Until now, the biochar directly obtained by the SWE was used to prepared sulfonic acid functionalized catalysts using two different methodologies: a) direct sulfonation with chlorosulfonic acid and b) direct organosilylation using the 2-(4-chlorosulfonylphenyl) ethyltrimethoxysilane (CSPTMS). The as-prepared

catalysts have been efficiently used in the production of levulinate esters from levulinic acid (LA) as an excellent alternative to the homogeneous catalysts conventionally used in industry. Very promising catalytic results were obtained in LA esterification at 120 °C in butanol using the biochar-based catalysts, with almost 100% conversion and selectivity for butyl levulinate after 1 h. The evaluation of the catalysts stability revealed excellent reusability, without significant loss of activity for up to 5 cycles. Recently, and in collaboration with Professor C. A. M. Afonso [28] from Research Institute for Medicines (iMed.U LISBOA), Faculty of Pharmacy, University of Lisbon, the biochar functionalized with the CSPTMS organosilane (BIO_CSP) was used as solid catalyst on the efficient production of a biofuel additive 5-(*t*-butoxymethyl)furfural from 5-hydroxymethylfurfural at 120 °C in *t*-butanol, leading to similar yield (41%) to that obtained with MWCNTs (43 %) after long reaction times (7 h).

Furthermore, the prepared biochar-derived materials (functionalized by the incorporation of Ni, Co and Cu metal phases *via* incipient wetness impregnation) have been tested on the catalytic transfer hydrogenation of furfural, using a batch stirred reactor and 2-propanol as solvent and hydrogen donor. The observed remarkable activity (>70%) and selectivity (>90%) towards the formation of furfuryl alcohol (industrially-valuable biomass-derived intermediate) using these catalysts established a promising catalytic route to valorize a biomass platform molecule, such as furfural, using 3d transition metal-based catalysts and without any external hydrogen supply.

4. Hybrid/Doped Carbon-Based (Nano)materials for Energy Technologies

4.1 Unitized Regenerative Fuel Cell for Efficient Renewable Energy Supply

The current global energy crisis reflected in the depletion of fossil fuels and growth of the environmental pollution, which has stimulated the development of novel renewable energy storage and conversion technologies [29,30]. Hydrogen energy storage is a crucial issue for a fully sustainable energy paradigm. H₂ produced by water electrolysis during base load moments, stored and converted back to electricity through the inverse reaction is a promising solution. The possibility of large-scale use of H₂ as a transport fuel massively increases the potential renewables and base-load electricity supply. The Unitized Regenerative Fuel Cell (URFC), which includes in the same device an electrolyzer (EL) that converts electricity in H₂, and a Fuel Cell (FC) which produces electricity using the stored H₂, has great potential [31]. The cost, weight and volume of an URFC are potentially lower than the combination of separate FC and EL units, but the materials and the device critical function requirements are severe.

Within this context, the project *UniRCell – Unitised regenerative fuel cell for efficient renewable energy supply: from materials to device*

(SAICTPAC/0032/2015) is being developed, coordinated by CICECO@University of Aveiro, and where LAQV@FCUP participates as team member along with other institutions: LSRE-LCM@FEUP, Transport Phenomena Research Center (CEFT)@FEUP and University of Trás-os-Montes and Alto Douro. *UniRCell* aims to develop a new generation of environmentally sustainable, high-performance and cost-effective materials for application in an URFC prototype. The project is organized in several tasks ranging from electrocatalysts design to membrane electrode assemblies (MEA) fabrication. The first stages of the project research work are focused on the design and preparation of novel noble metal-free composites with enhanced electrocatalytic properties for oxygen evolution and reduction reactions (OER/ORR) and hydrogen evolution and reduction reactions (HER/HOR), through eco-sustainable protocols. Our contribution is mainly focused on the synthesis and physicochemical characterization of electrocatalysts involving polyoxometalates (POMs), metal-organic frameworks (MOFs) and carbon materials (doped or non-doped), as well as on the electrochemical characterization of electrolytes and electrocatalysts.

So far, several hybrid bi- or tri-component nanomaterials based on metal oxides, POMs, MOFs and carbon materials (doped or non-doped) have been prepared and successfully applied to one or more of the reactions mentioned above. Very promising results were obtained with POM@carbon materials for HER (overpotentials of 0.033–0.044 V vs. 0.024 V for Pt/C) and ORR (higher diffusion-limiting current densities $j_L = -168.3 \text{ mA cm}^{-2} \text{ mg}^{-1}$ vs. $-130.0 \text{ mA cm}^{-2} \text{ mg}^{-1}$ for Pt/C), showing activities comparable to that of noble metal state-of-the-art Pt/C electrocatalyst and excellent stabilities. MOF-derived carbons have been synthesized at room temperature, avoiding hard condition solvothermal processes and, contrary to the more extended pyrolysis treatments, these were carbonized at relatively lower temperature, 500 °C. Their electrocatalytic properties were evaluated towards OER, exhibiting remarkable results with overpotentials as low as 0.41 V vs. RHE.

Currently, some of these novel carbon-based electrocatalysts are being incorporated onto an electrolyte membrane for future assembly and testing of MEAs.

4.2 Smart Textiles and Flexible Devices for Energy Storage

The development of clean and sustainable energy technologies has been one of the Grand Challenges of the 21st Century. Energy storage technologies became a major target to address the ever-increasing energy demand and depletion of non-renewable energy sources [32]. The fast proliferation of wearable and smart portable electronics opened new market opportunities for energy storage systems, especially for batteries and supercapacitors, with a vast scope of applications, ranging from medicine, sports, healthcare and fashion to military and the

consumer in general (Figure 10) [33]. High efficiency, durability, safety, flexibility and lightness became key requirements on the quest for wearable and flexible energy storage technologies [32,33]. Within this framework, the self-powered smart garments and portable devices currently available in the market rely on Li-ion batteries. Although displaying high energy density, they present limitations concerning their toxicity, safety, limited cycle life and high (re)charging time. Supercapacitors (SCs) emerged as an eco-sustainable and safer technology for energy storage, due to their higher power density, faster charging, longer cycle life (up to 10⁶ cycles), stability and lower maintenance cost. Nevertheless, they still present lower energy density and faster discharging than batteries [32–34].

Nanotechnology opened new horizons in the field of smart textiles to confer new functionalities to the fabrics, while at the same time preserving their intrinsic features, namely the comfort to the user.

Carbon (nano)materials are promising building blocks for the design of high-performance flexible and wearable energy storage technologies (e.g., textile/fabric/fiber SCs, plastic electronics) [34,35] we will start by providing a brief introduction to the main principles of supercapacitors, followed by the importance of carbon (nano). In particular, carbon nanotubes and graphene are among the top choices as electrode materials for the fabrication of this type of devices due to their excellent mechanical properties, lightness, high electrical conductivity, large specific surface area and high chemical and thermal stability, leading to SCs with high power density, low charging times and high cycling stability. Typically, the intrinsic energy storage mechanism of carbon-based SCs is non-Faradaic, with the charge being stored electrostatically at the electrode/electrolyte interfaces – the so-called *electrical double-layer capacitors* (EDLCs). As a result, carbon-based SCs still possess low specific capacitance and, consequently, low energy density.

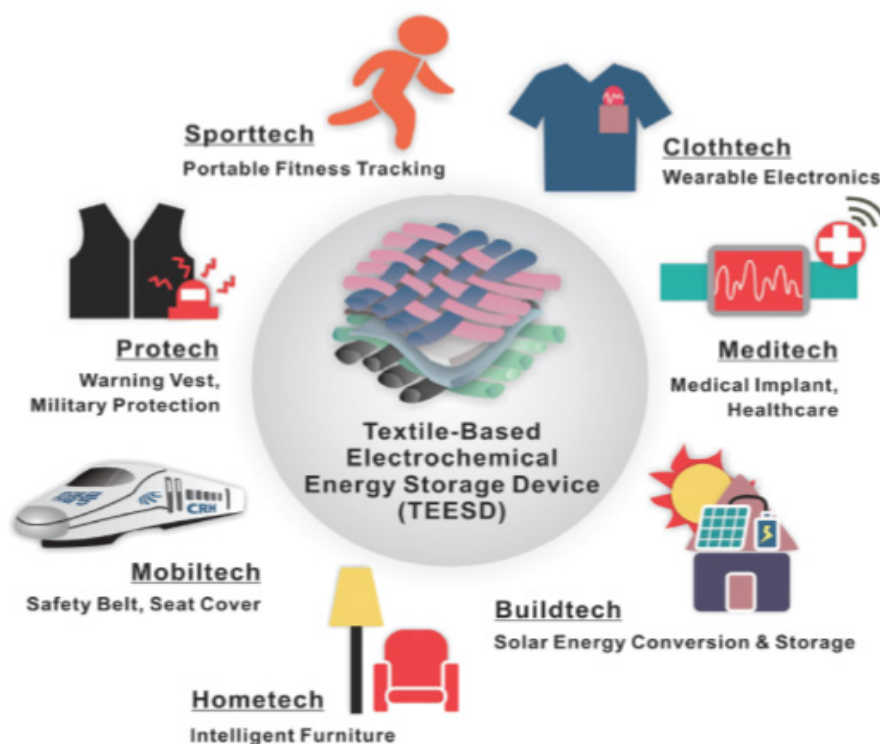


Figure 10. Applications of textile-based energy storage devices. Reproduced from ref. [33] by permission of John Wiley and Sons.

The doping of carbon (nano)materials with heteroatoms (e.g., N, O, S, B, P) and/or their hybridization with transition metal oxides and/or conductive polymers constitute potential strategies to enhance the energy density properties of SCs, while preserving their power density [32,34] we review the state-of-the-art advancements in FSSCs to provide new insights on mechanisms, emerging electrode materials, flexible gel electrolytes and novel cell designs. The review begins with a brief introduction on the fundamental understanding of charge storage mechanisms based on the structural properties of electrode materials. The next sections briefly summarise the latest progress in flexible electrodes (i.e., freestanding and substrate-supported,

including textile, paper, metal foil/wire and polymer-based substrates. This improvement arises from the occurrence of an additional pseudocapacitive energy storage mechanism in the devices (Faradaic mechanism), i.e., involving the charge transfer between the electrode and the electrolyte through reduction-oxidation reactions, ion intercalation/deintercalation and electrosorption at the surface or in the bulk near the surface of the electrodes.

In this sense, a new generation of *hybrid capacitors* emerged which can be classified in three different classes, according to the nature of the electrodes [36]: (i) *composite or symmetric hybrid capacitors* – bearing two electrodes composed of hybrid or composite materials with similar composition,

both containing an EDLC-type component and a pseudocapacitive component; (ii) *asymmetric hybrid capacitors* – composed of two electrodes with different charge storage mechanisms, with an EDLC-type mechanism occurring on one electrode and a pseudocapacitive or a combination of EDLC-type and pseudocapacitive mechanisms occurring on the other electrode; (iii) *battery-type hybrid capacitors* – with one of the electrodes being a Li⁺-ion containing material to allow the occurrence of Li⁺ intercalation/deintercalation.

Another R&TD area of our research group is related with the design of high-performance all-solid-state smart textiles and flexible devices for energy storage based on hybrid carbon nanomaterials. To achieve that goal we have been fabricating novel hybrid carbon-based nanomaterials with enhanced electrochemical properties to be used as SC electrode materials through the immobilization of transition metal oxides onto oxidized/doped carbon nanomaterials. We have developed a straightforward eco-sustainable and less time-consuming one-pot coprecipitation route that promoted the controlled nucleation/growth of transition metal ferrite nanoparticles (MFe₂O₄, M(II) = Mn, Fe, Co) with sizes in the range of 3.2–5.4 nm on the surface of conductive N-doped carbon nanotubes and their subsequent immobilization

through covalent bonding (Figure 11A) [37]. The N-doped carbon nanotubes (CNT-N) were provided by the group of Prof. Antonio Guerrero-Ruiz, Instituto de Catálisis y Petroleoquímica, CSIC, Madrid, Spain. The resulting nano hybrids (CNT-N@X, where X = MnFe₂O₄, Fe₃O₄ or CoFe₂O₄) were then tested as electrode active nanomaterials in all-solid-state asymmetric paper SCs, leading to synergistically enhanced energy storage properties due to the simultaneous occurrence of EDLC-type and pseudocapacitive charge storage mechanisms. In particular, an improvement of the energy density to up to 6.0× and of the power density to up to 4.3× were achieved relatively to the symmetric CNT-N based paper SC (Figure 11B). Additionally, when compared with solid-state hybrid paper SCs based on carbon materials reported in the literature, they afforded up to 11.1× higher volumetric energy density and up to 5.2× higher volumetric power density. The paper SC that led to the highest energy density was the fully asymmetric hybrid CNT-N@Fe//CNT-N@Mn device, whereas the device that maximized the power density output was the CNT-N//CNT-N@Co system. Finally, all asymmetric SCs presented high cycling stability, preserving >90% of the initial capacitance after 1500 charge/discharge cycles.

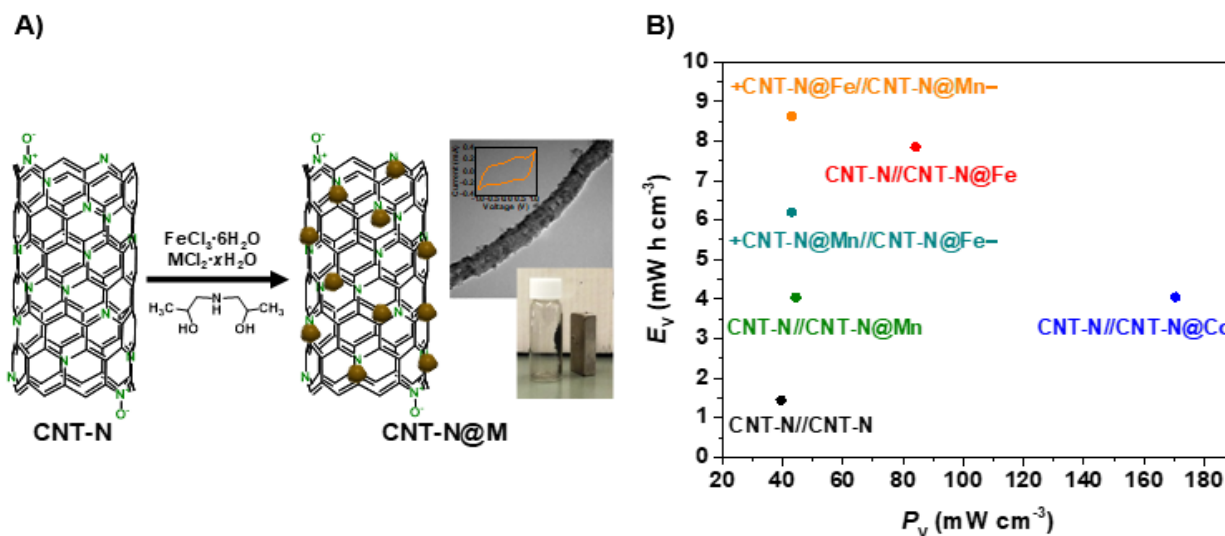


Figure 11. A) Schematic representation of the immobilization of MFe₂O₄ onto CNT-N by one-pot *in situ* coprecipitation. B) Ragone plot of energy density vs. power density of the all-solid-state CNT-N based paper SCs. Adapted from ref. [37] by permission of RSC.

Since 2018, a multidisciplinary R&TD project is being developed in this area, entitled *SmartText4EStore – Smart Textiles for Energy Storage: From New Scalable Fabrication Processes to Wearable Supercapacitor Clothing* (PTDC/CTM-TEX/31271/2017), coordinated by LAQV@FCUP, in collaboration with two research units – IFIMUP, Institute of Physics for Advanced Materials, Nanotechnology and Photonics at FCUP, and LSRE-LCM@FEUP – and the Technological Centre for the Textile and Clothing Industry of Portugal, CITEVE. *SmartText4EStore* project envisages the production of a new generation of hybrid textile SCs based on hybrid carbon nanomaterials featuring enhanced electrochemical performance, long lifetime, flexibility, lightness and safety through scalable eco-friendly

fabrication processes, to meet the energy/power density demands of wearable electronic devices.

In parallel, an entrepreneurship startup project is being developed – WESStoreOnTEX – involving members from LAQV@FCUP and IFIMUP@FCUP, aiming to boost the technological transfer of wearable energy storage technologies towards marketable products. WESStoreOnTEX is focused on the creation of innovative technological solutions for energy storage on garments or accessories to power portable devices and sensors integrated on clothes. Textile SCs with small dimensions (14 cm²) were directly integrated on clothing and, when charged for 5 min, were able to power sensor devices and lightning systems during up to 50 min (Figure 12).

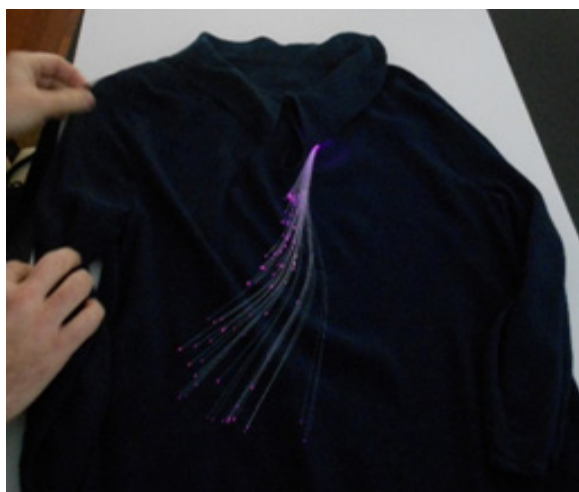


Figure 12. Digital thermometer/hygrometer sensor and LED lightning system powered by textile SCs produced by WEStoreOnTEX.

4.3 Development of Cobalt Oxide Nanofoam-Based Electrocatalysts for Energy Storage

Electrochemical energy storage devices have become key players on the development of efficient solutions for energy management [38]. Asymmetric SCs pave the way to boost electrical mobility and efficiency of storage systems, combining the “best of a battery” with the “best of a SC” to deliver enhanced energy and high power density. However, they still require important electrode material developments to increase charge storage capacity and long-term stability [39]. Zn-air batteries have raised interest due to their low price and high energy density, but face important challenges that prevent their widespread application and require more efficient air electrode electrocatalysts, namely bifunctional electrodes for both oxygen reduction (ORR) and oxygen evolution (OER) reactions. Novel functional materials are the key to enable these two storage technologies.

In this context, the project *Foam4Ener – Multifunctional cobalt oxide nanofoams: novel electrode materials for supercapacitors and electrocatalytic oxygen reactions* (PTDC/QUI-ELT/28299/2017) is being developed, coordinated by Associação do Instituto Superior Técnico para a Investigação e o Desenvolvimento (IST-ID), and involving LAQV@FCUP and Instituto Superior de Engenharia de Lisboa (ISEL) as team members. *Foam4Ener* project aims at designing and preparing a new generation of highly porous 3D Co-nanofoams (CoNFs) and Co-graphene nanofoams that, after functionalization with polyoxometalates (POMs) and graphene derivatives, can serve as high-performance electrodes for energy storage in asymmetric SCs and as bifunctional electrocatalysts for ORR and OER in rechargeable metal-air batteries. The IST-ID and ISEL teams have been conducting, since September 2018, work on the optimization of CoNFs preparation, while LAQV@FCUP team is focused on the production of different POM families and the preparation of doped-graphene derivatives by scalable and green synthesis routes. A set of transition metal-based POMs has already been selected for near future doping of the already optimized Co-NFs. Then, LAQV@FCUP team will be

responsible for testing the most promising candidates as ORR and OER electrocatalysts, while IST-ID team will test them on asymmetric SCs.

At the end of the project, the researchers hope to deliver novel solutions for energy storage namely, high capacity electrodes for electric mobility for asymmetric SCs, and high efficiency O₂ reaction electrocatalysts, which are crucial for the large-scale implementation of rechargeable metal-air batteries.

5. Smart Electrochromic Devices Based on Carbon-Poly(Nickel Complex) Nanocomposites

Electrochromic materials, which present reversible color changes upon the occurrence of electrochemical oxidation-reduction reactions, are a family of materials with remarkable interest for several smart applications, including energy-saving smart windows, smart optical displays and rear-view mirrors for the automotive industry [40,41]. They are typically composed of redox-active species, namely conducting polymers. The main challenge nowadays for their implementation is ensuring high optical contrast, high color switching rates, high electrochemical stability and long cycle life (reversibility of the color changes over multiple cycles) [42]. To achieve these goals, conductive polymers can be combined with nanomaterials, namely carbon-based nanomaterials, to potentiate synergistic effects [43].

Our group has been working in this field, namely through the use of graphene as electroactive nanomaterial. In particular, a new electrochromic nanocomposite based on [Ni(*salen*)] polymeric film was prepared through the incorporation of N-doped few-layered graphene (N-FLG) onto the electroactive poly[Ni(3-*Mesalen*)] film (where *Mesalen* = *N,N'*-bis(3-methylsalicylideneimine)), by *in situ* electropolymerization (Figure 13) [42]. The resulting nanocomposite exhibited multi-electrochromic properties, with the color changing from yellow (reduced state) to green/russet (oxidized state). Moreover, it presented enhanced electrochromic performance when compared with the parent poly[Ni(3-*Mesalen*)] film (Figure 13),

with 71% increase of the electrochemical stability (decrease of 2.7% of charge after 10000 switching cycles), lower switching time for oxidation and reduction (9 and 11 s, respectively), improved optical contrast (38% increase; $\Delta T = 35.9\%$) and coloration efficiency (12% increase; $\eta = 108.9 \text{ cm}^2 \text{ C}^{-1}$). More

remarkably, the electronic structure of the polymer was preserved upon the incorporation of N-FLG, with an improvement of its robustness to degradation phenomena. These achievements were assigned to morphological changes and alternative conducting pathways promoted by N-FLG.

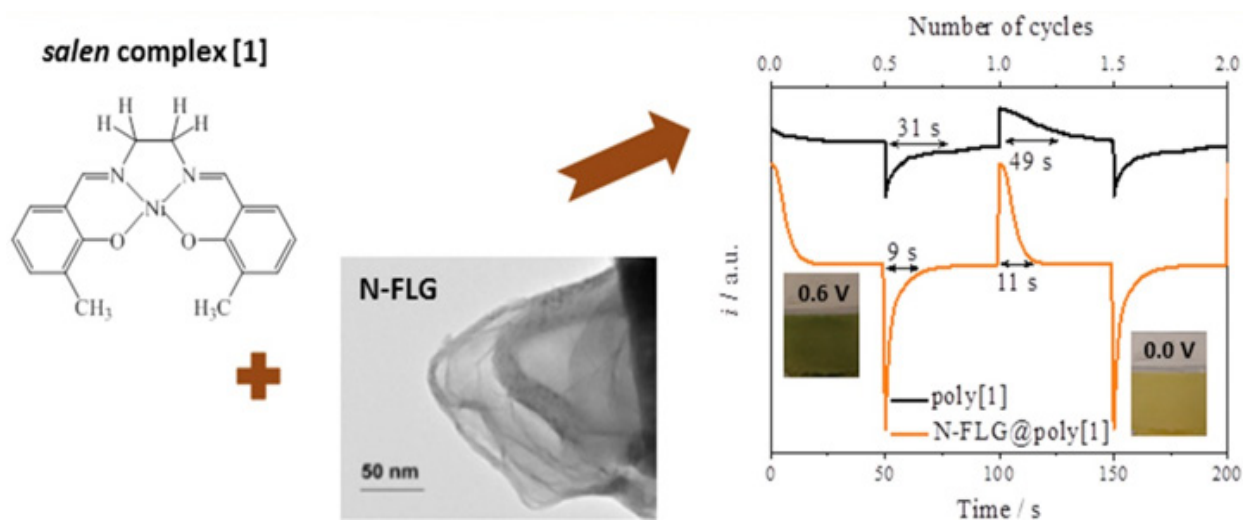


Figure 13. Chemical structure of [Ni(3-Mesalen)] complex, morphology of N-FLG and electrochemical stability of N-FLG@poly[Ni(3-Mesalen)] and pristine poly[Ni(3-Mesalen)] films evaluated by chronoamperometry. Reproduced from ref. [42] by permission of Elsevier.

In another work, graphene nanoplatelets (GFNP) were incorporated onto the same type of polymeric film [44]. The resulting GFNP@poly[Ni(3-Mesalen)] nanocomposite also presented multi-electrochromic behavior, with the color changing between yellow (reduced state) and green (oxidized state). Additionally, its switching time responses were significantly lower than those of the parent poly[Ni(3-Mesalen)] film, with 50.7% decrease in the response time for green coloration and 60.0% decrease for yellow coloration. GFNP@poly[Ni(3-Mesalen)] film also presented enhanced electrochemical stability,

with only a slight loss of charge (7%) after 10000 electrochemical cycles. Finally, a flexible solid-state electrochromic device was assembled based on GFNP@poly[Ni(3-Mesalen)] and using flexible indium tin oxide/polyethylene terephthalate (ITO/PET) as substrate (Figure 14). The device presented remarkable electrochemical stability during an extended switching test, with only 3% of charge loss after 15 days of continuous activity, highlighting the potentialities of the film for electrochromic applications, namely on optical/electronic displays and electrochromic paper.

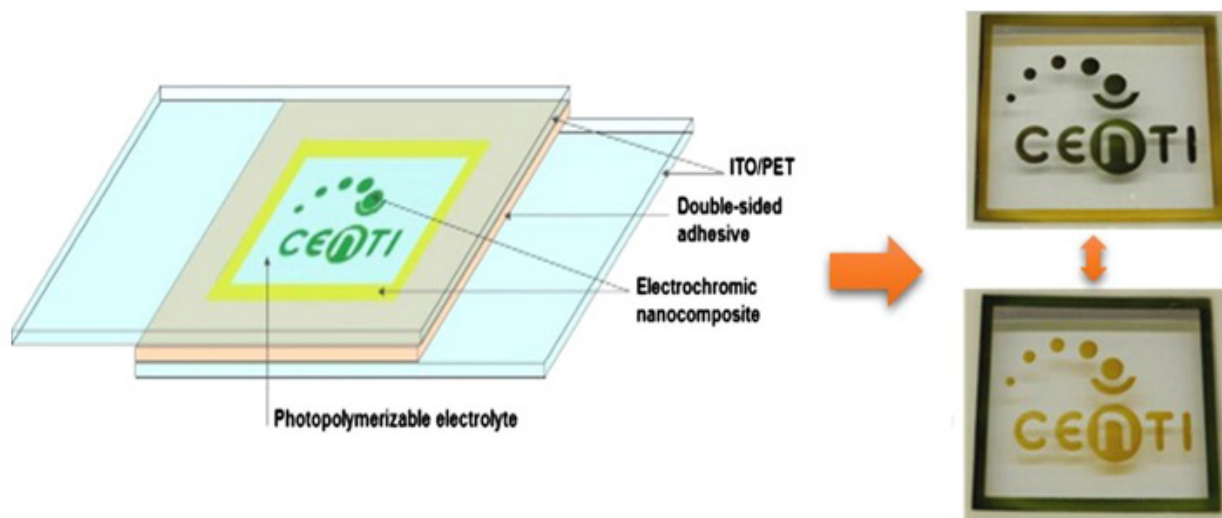


Figure 14. Schematic representation of the structure of the flexible solid-state electrochromic device based on GFNP@poly[Ni(3-Mesalen)] and pictures showing the device color change upon the application of a potential (redox process). Reproduced from ref. [44] by permission of Elsevier.

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