

Materiales de carbono @LCM: una actualización

Carbon materials @ LCM: an update

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Abstract

LCM's main achievements towards the development of carbons for catalysis, energy and environmental applications were previously reviewed in *Boletín* n° 39 (March 2016). In the present report, we will provide an update, focusing only on our most recent work.

Resumen

Los logros más relevantes del LCM sobre el desarrollo de materiales de carbono para aplicaciones catalíticas, energéticas y medioambientales, fueron publicados en el *Boletín* n° 39 (marzo 2016). Por lo que la presente publicación se centra solamente en las actividades más recientes.

1. Introduction

The Laboratory of Catalysis and Materials (LCM) has been focusing its research activities on the fields of Carbon and Catalysis since 1994. In 2004, LCM together with LSRE (Laboratory of Separation and Reaction Engineering) received the status of *Associate Laboratory*. Nowadays, the former LCM team is Research Group 4, "Catalysis and Carbon Materials", and represents approximately 40% of the Associate Laboratory LSRE-LCM (<https://lsre-lcm.fe.up.pt>). The current research activities are divided into three scientific areas, each one of them subdivided into projects and subprojects, as shown in Figure 1: 1) Nanostructured carbon materials; 2) Environmental catalysis and technologies; 3) Energy, fuels and chemicals.

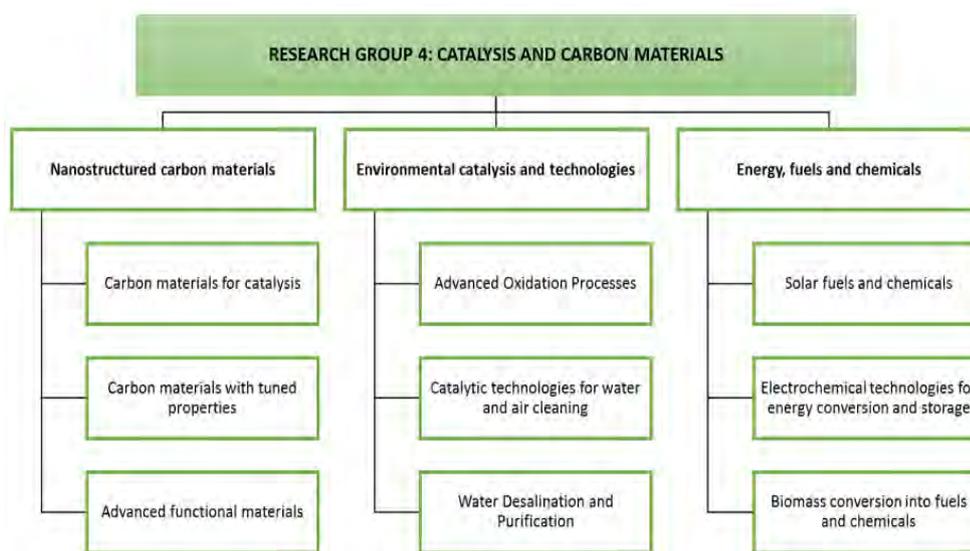


Figure 1: Scientific areas and current research projects at LCM.

Figura 1: Áreas científicas y proyectos de investigación actuales del LCM.

LCM's most relevant achievements towards the development of carbon materials for catalysis, energy and environmental applications were described three years ago in *Boletín del GEC* [1]; thus, in the present report, we will just provide an update focusing on our most recent work in each one of those research areas.

2. Nanostructured carbon materials

2.1 Carbon materials for catalysis

The application of carbon nanomaterials ("nanocarbons") either as catalyst supports or as catalysts on their own ("carbocatalysis") was recently reviewed [2], highlighting the important role of the surface chemical properties. The broad definition of *nanocarbons* includes both *nanosized* materials (carbon nanotubes/nanofibers; graphene-derived materials; nanodiamonds) and *nanostructured*

materials (carbon gels and ordered mesoporous carbons).

In collaboration with the Group of Professor Armando Pombeiro, at IST (*Instituto Superior Técnico, Univ. Lisboa*), we have used carbon-supported gold nanoparticles to catalyze the carboxylation of C_n alkanes to C_{n+1} carboxylic acids, using CO , as indicated in Figure 2. The reaction is quite difficult, since C–H activation is very hard to achieve for the least reactive lower alkanes (1–6 carbon atoms). The results showed that the catalysts prepared on a properly functionalized support (oxidation with HNO_3 followed by treatment with $NaOH$) were stable and reusable, maintaining their initial activity and selectivity up to seven consecutive cycles [3,4]. Among the different supports tested (activated carbon, carbon nanotubes and carbon xerogels), the Au catalyst supported on carbon nanotubes (CNT) exhibited the best performance (yield > 88%) [4].

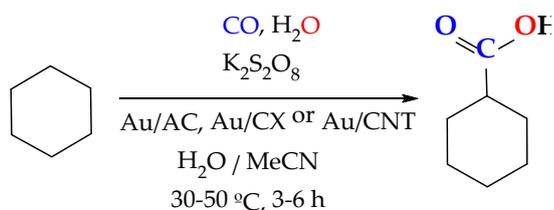


Figure 2: One-pot hydrocarboxylation of cyclohexane

Figura 2: Hidrocarboxilación de ciclohexano mediante método *one-pot*

We have also used surface functionalized carbon nanomaterials as supports for anchoring various types of C-scorpionate complexes (Au, Fe, V, Cu, Co). Figure 3 shows the immobilization protocol, using CNT as an example. These “heterogenized” complexes were efficient and recyclable catalysts for the oxidation of hydrocarbons and alcohols [5-8].



Figure 3: Immobilization of C-scorpionate complexes onto carbon nanotubes (R = H; CH₂OH).

Figura 3: Inmovilización de complejos C-escorpionato sobre CNT (R=H; CH₂OH).

These studies were then extended to the anchoring of several mononuclear Au(I) and Au(III) complexes which are commercially available [9]. In general, the complexes supported on CNT-oxi-Na yielded the best results, possibly due to the presence of more stable phenolate and carboxylate groups. In the framework of our collaboration with IST, we are currently attempting to scale-up the procedure for the production of ketones from secondary alcohols using microwave irradiation [5,8].

2.2 Carbon materials with tuned properties

Nanostructured mesoporous carbons are widely used in catalysis, adsorption and energy storage. The mesoporosity allows processing large molecules by addressing the diffusional limitations and pore blockage that may occur in purely microporous carbon materials, such as activated carbons. The different approaches that have been reported for the synthesis of mesoporous carbons, either with a disordered mesoporosity (carbon gels) or with ordered porous systems (carbons obtained by templating) were reviewed, together with the methods used for

controlling their surface chemistry [10]. The design of both texture and surface chemistry allows tuning the properties, thus leading to materials that meet the requirements of the targeted applications.

The high toxicity of the reactants used in sol-gel and templating procedures justifies the search for alternative and more sustainable carbon precursors, such as biomass-derived compounds. However, the use of pure carbohydrates in sol-gel synthesis leads to carbon gels with poor mechanical and chemical resistance. More robust polymeric structures can be obtained by using graphene oxide (GO) or carbon nanotubes as condensation/polymerization promoters. The acidic sites on the surface of these nanocarbons promote dehydration/condensation reactions of the carbohydrates, whilst providing a scaffold for the growth of carbon xerogels, for example by hydrothermal carbonization (HTC). Based on these concepts, we obtained carbon xerogels from hydrothermally carbonized glucose-GO [11] (in collaboration with INCAR, CSIC, Oviedo, Spain) and glucose-CNT hybrids [12], subsequently activated with KOH (Figure 4).

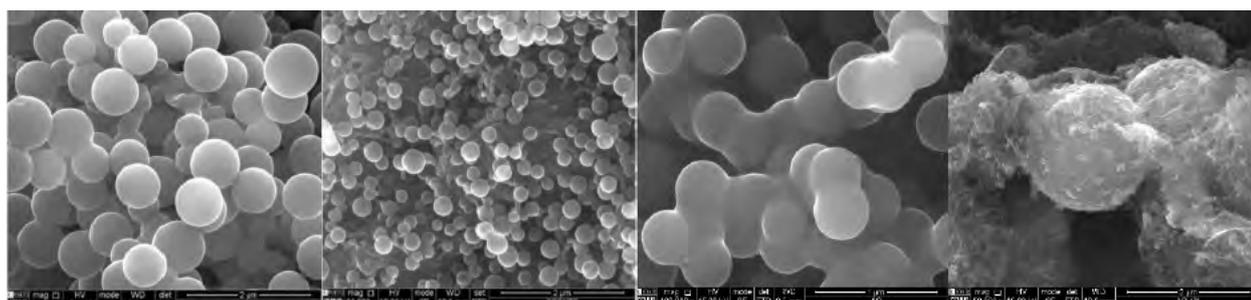


Figure 4: SEM micrographs of glucose-derived carbons: HTC Glucose; HTC Glucose-CNT_{oxid}; KOH-activated Glucose; KOH-activated Glucose-CNT (from left to right).

Figura 4: Micrografías SEM de carbones obtenidos a partir de glucosa: Glucosa carbonizada hidrotérmicamente; Glucosa-CNT_{oxid} carbonizada hidrotérmicamente; glucosa activada con KOH; glucosa-CNT activada con KOH (de izquierda a derecha).

Concerning the surface chemistry, we developed a new method for N-doping of carbon materials, which avoids the use of solvents and the production of wastes. The method consists in ball-milling the carbon material together with a suitable nitrogen precursor (such as urea or melamine), followed by thermal treatment under N_2 at 600 °C [13]. Carbon nanotubes and graphene oxide were successfully doped in this way, large amounts of nitrogen being incorporated, especially when using melamine as N-precursor. The thermal decomposition products of melamine lead to the incorporation of N-functionalities (pyridinic, N-6; pyrrolic, N-5; and quaternary nitrogen, N-Q) onto the carbon surface, as a result of the intimate mixture and the surface active sites created by ball milling (Figure 5). The method is easily scalable for practical applications, since it does not require highly specialized and expensive equipment, and has been extended to the incorporation of other heteroatoms, such as S, P and B, by using appropriate precursors [14].

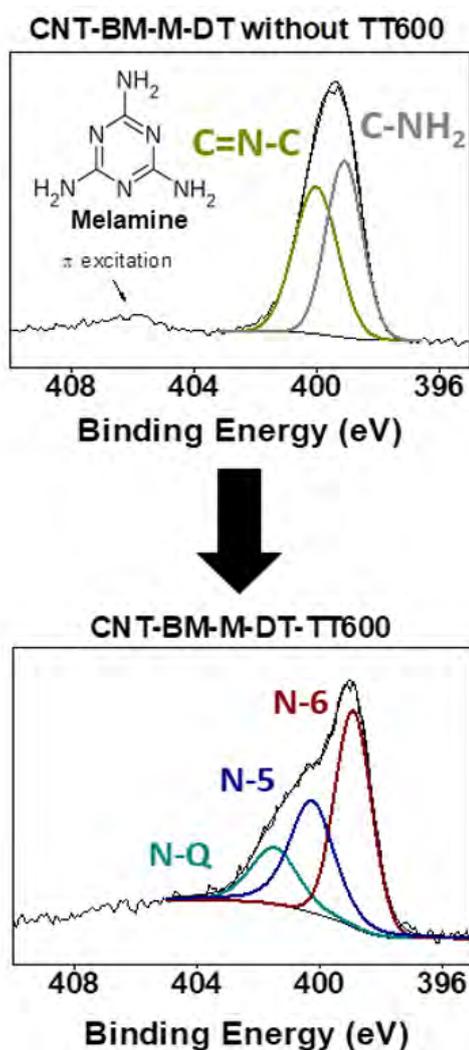


Figure 5: Changes in the N1s spectrum of ball-milled CNT with melamine upon thermal treatment (at 600 °C, under nitrogen). Adapted from reference [13].

Figura 5: Cambios en el espectro de nitrógeno N1s de nanotubos de carbono tratados a 600 °C en atmósfera de nitrógeno tras ser molidos en un molino de bolas en presencia de melamina. Figura adaptada de la referencia [13].

2.3 Advanced Functional Materials

Among the various activities pursued in this topic, the design and development of smart and functional textiles has been highly successful. One such example is the project “Cork-a-Tex Yarn” (textile yarn with high incorporation of cork) which recently received the “*Tehtextil Innovation Award 2019*” in the category of “new material”, one of the most important world prizes for innovation in technical textiles. The successful modification of the surface properties of cork in order to provide enhanced interaction with textile fibers and fabrics was based on our *know-how* on the surface functionalization of carbon materials. This was the subject of national and international patent applications [15]. We were also able to develop visible-light-induced self-cleaning functional textiles by coating graphene oxide and polymeric carbon nitride ($g-C_3N_4$) onto a cotton fabric. The coatings were efficient for the photocatalytic degradation of caffeine and rhodamine-B under LED visible light irradiation [16].

Another project concerned the development of magnetic carbon nanostructures for biomedical applications. In particular, we synthesized hydrophilic graphene-based yolk-shell magnetic nanoparticles functionalized with Pluronic F-127, for application in combined hyperthermia and dual stimuli-responsive drug delivery [17].

3. Environmental catalysis and technologies

This is a consolidated research area within the LCM Group, focusing on the development of improved technologies for the removal of pollutants from gaseous and liquid effluents and for the treatment and purification of water. Advanced oxidation processes (AOPs) are a major topic in this context, involving the development of catalysts based on nanostructured carbon materials, alone or in combination with semiconducting oxides.

In the case of water treatment, the synergies obtained by the integration of different technologies allowed the group to address the degradation of selected emergent organic micropollutants and biological contaminants. In particular, photocatalytic ozonation, photocatalysis assisted by H_2O_2 , and the use of catalytic membranes, were successful approaches. Figure 6 shows the reactor used for the treatment of contaminated water by photocatalytic ozonation in continuous mode [18].

Excellent performances were achieved with nitrogen-doped carbon materials as catalysts for AOPs [19-22], and with composites of semiconducting oxides (TiO_2 , ZnO) and nanosized carbons (carbon nanotubes, graphene-derived carbons, nanodiamonds) in photocatalysis [23-27]. Graphitic carbon nitride was another efficient photocatalyst for the degradation of organic pollutants [28-30].



Figure 6: Flow reactor fitted with LEDs for photocatalytic ozonation of contaminated water. The reactor is packed with glass rings coated with the TiO_2 photocatalyst

Figura 6: Reactor de flujo equipado con LEDs para la ozonización fotocatalítica de agua contaminada. El reactor funciona con un relleno de anillos de vidrio recubiertos con TiO_2 .

A SolarNETmix® reactor configuration for heterogeneous Fenton/photo-Fenton processes was set-up in collaboration with Research Group 2 of LSRE-LCM [31-32].

Magnetically recoverable hybrid carbon catalysts, as well as amphiphilic carbon nanotubes for catalytic wet peroxide oxidation of aqueous solutions and oily wastewaters were developed at the LSRE-LCM branch in Bragança [33-36].

The preparation of innovative carbon-based membranes for water desalination and purification applications, eventually combined with AOPs, is a recent project with promising results [37].

4. Energy, fuels and chemicals

4.1 Solar fuels and chemicals

The use of solar light to produce renewable, sustainable and carbon-neutral fuels and chemicals, has recently emerged as an attractive alternative to traditional technologies. The concept of Solar Fuels refers mainly to the generation of hydrogen from water and products derived from CO_2 such as methanol, methane, formic acid and other chemicals. Hydrogen can be produced from water using renewable solar energy through a wide range of processes, namely, electrolysis, photo-electrochemical, photocatalytic and thermochemical water splitting. Solar fuels derived from CO_2 , water (a cheap, abundant and environmentally benign solvent) and sunlight (renewable energy source) are sustainable, produce no net CO_2 emissions and offer the advantage of leading to easily transportable liquid products, such as methanol. In addition, selective photocatalysis can provide a sustainable route to the synthesis of

fine chemicals. Efficient photocatalysts are being developed in order to attain these objectives.

The photochemical generation of H_2 from water requires three components: a photosensitizer for light harvesting and electron transfer, an electron donor for the regeneration of the dye, and a catalyst for hydrogen evolution (HER). Hybrid photocatalysts consisting of $\text{g-C}_3\text{N}_4$ sensitized with free-base porphyrin dyes were prepared by impregnation through non-covalent interactions, and combined with Pt as co-catalyst for HER, EDTA being used as a sacrificial electron donor. With the best system, an amount of 326 mmol of H_2 was evolved in 6 hours under UV-vis light irradiation [38]. The synthesis of holey C-doped $\text{g-C}_3\text{N}_4$ with higher surface area and enhanced visible light absorption was also reported [39].

In the photo-reduction of CO_2 in aqueous phase, with formation of methanol and ethanol, graphene oxide-modified TiO_2 materials and derived composites loaded with Cu led to increased absorption in the visible spectral range and high photocatalytic activity [40].

We are also investigating the selective production of aromatic aldehydes from alcohols (namely anisaldehyde, benzaldehyde and vanillin, which are used as flavouring agents), under mild conditions of pH and temperature, using a benign solvent (water). The process occurs with the simultaneous production of a valuable by-product, hydrogen. Several photocatalysts were tested, including composites of ZnO with nanocarbons (carbon nanofibers; N-doped CNTs) [41,42], and $\text{g-C}_3\text{N}_4$ [43-45]. The best performance was achieved with carbon nitride, which offers the additional advantage of being an active photocatalyst under visible light.

4.2 Biomass conversion into fuels and chemicals

Lignocellulosic biomass is an abundant and renewable raw material composed of cellulose (40-50%), lignin (15-20%) and hemicelluloses (25-35%), and each one of these fractions can be converted into valuable products. Depolymerisation of cellulose to glucose can be combined with consecutive catalytic steps leading to valuable intermediates, thus significantly reducing the cost of biomass conversion. For example, cellulose can be converted into platform chemicals using bifunctional catalysts in one-pot tandem reactions. Following this strategy, by coupling hydrolysis of cellulose to glucose and its subsequent conversion via oxidation/hydrogenation, it is possible to obtain gluconic acid, sorbitol and many other versatile building blocks for the sustainable production of chemicals and fuels (Figure 7).

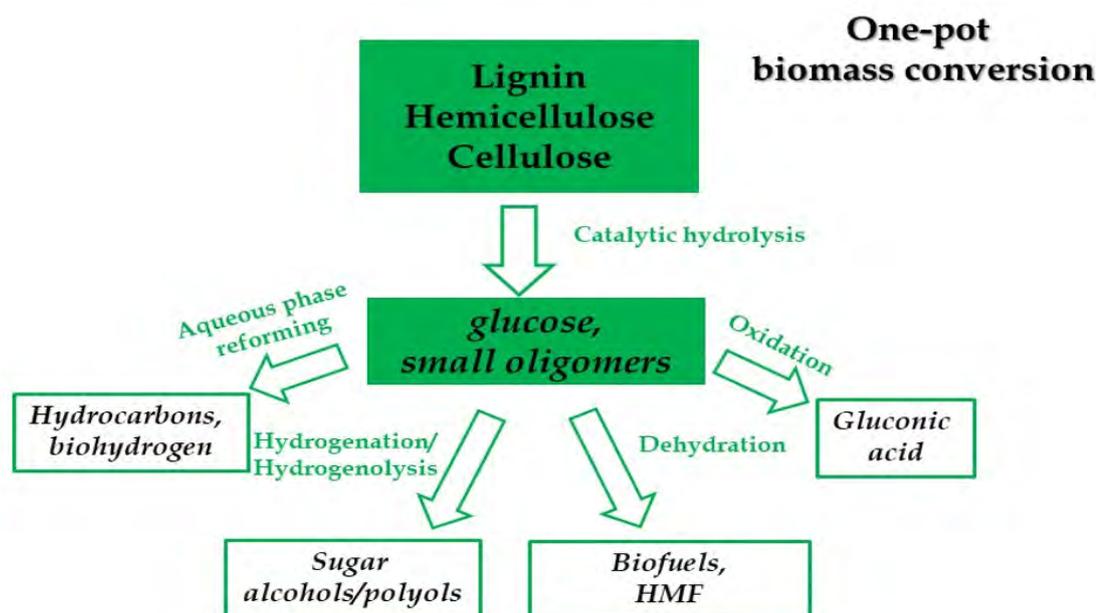


Figure 7: Alternative routes for biomass conversion.

Figura 7: Rutas alternativas para la conversión de biomasa.

Sorbitol and xylitol are two of the most important products which can be obtained from cellulose and hemicelluloses, respectively, both being in the TOP-12 biomass value-added products. We have studied the one-pot hydrolytic hydrogenation of cellulose and hemicelluloses (xylan) into these polyols using carbon-based catalysts. Ru (0.4 wt%) supported on carbon nanotubes (Ru/CNT) was found to be the most efficient of the monometallic catalysts tested for the direct conversion of cellulose [46,47]. The sorbitol yield was improved by using a Ru-Ni bimetallic catalyst [48]. The Ru/CNT catalyst was also efficient for the conversion of hemicelluloses (xylan) into xylitol. Moreover, we found that there is a synergistic effect between cellulose and xylan when converted simultaneously. Thus, yields of sorbitol and xylitol close to 80% were achieved after 6 h of reaction in the one-pot conversion of cellulose and xylan under a two-step temperature program (2 h at

170 °C + 4 h at 205 °C) [49]. Hydrolytic hydrogenation of cellulose on a CNT-supported Ru–W bimetallic catalyst produced ethylene glycol (40% yield after 3 h of reaction at 205 °C) [50].

Both the monometallic Ru and the bimetallic Ru–W catalyst were later supported on glucose derived carbons (obtained by hydrothermal carbonization followed by activation), showing enhanced performances for the production of sorbitol and ethylene glycol, respectively [51,52].

The tandem oxidation of cellulose to gluconic acid requires a bifunctional catalyst with acidic sites for the hydrolysis step and metallic sites for glucose oxidation. We developed an active and selective catalyst for this process (using cellobiose as a model for cellulose), consisting of 1 wt% Au supported on functionalized carbon xerogel (Figure 8), which achieved a remarkable selectivity to gluconic acid of 80% in only 75 minutes [53].

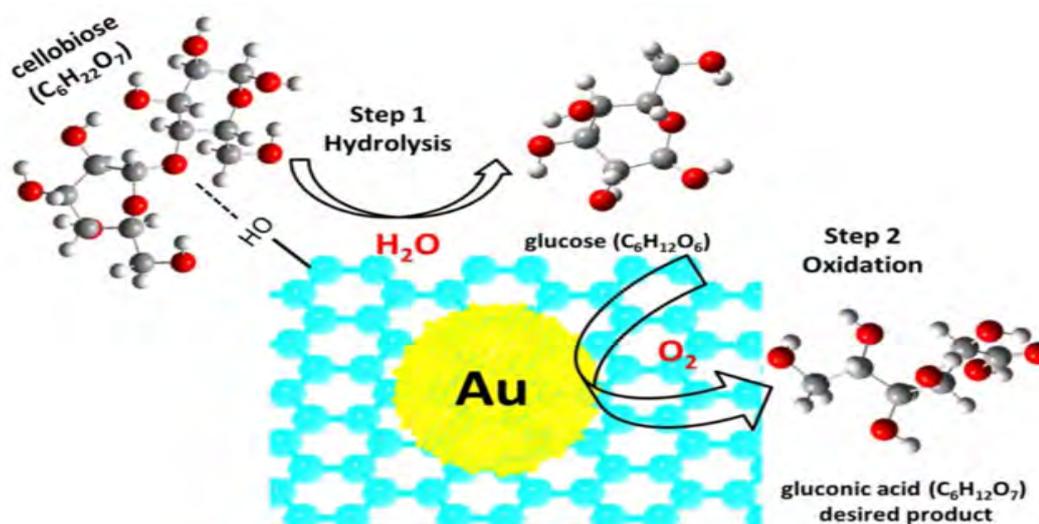


Figure 8: One-pot hydrolytic oxidation of cellobiose to gluconic acid. Reproduced from [53] with permission from Elsevier.

Figura 8: Oxidación hidrolítica de celobiosa a ácido glucónico mediante método *one-pot*. Figura reproducida de [53] con el permiso de Elsevier.

In addition, we investigated the influence of the type of surface functionalization of carbon catalysts on the hydrolysis of cellobiose. This is a key step to achieve high selectivity, since the feedstock (cellulose or cellobiose) is more stable than the product (glucose). Among the carbon xerogels (CX) prepared with different heteroatoms (S, P, N, O), CX containing 3.4 wt% of phosphorus showed the best catalytic performance, reaching 90 % cellobiose conversion with 72 % selectivity to glucose under oxidative atmosphere and in a short reaction time of only 4 h. The presence of phosphonates (-P-C-) was found to increase the selectivity to glucose up to 87 % [54].

4.3 Electrochemical energy conversion and storage

Our activities in this area include the development of hierarchical porous carbons for energy storage in supercapacitors, and carbon-based electrocatalysts for fuel cells and electrolyzers.

The intrinsic principle of charge storage in supercapacitors (or electrochemical double-layer capacitors) consists on the electrostatic adsorption of electrolyte ions on the electrode surface. The energy density can be further enhanced by promoting reversible faradaic reactions between the electrode surface and the electrolyte (pseudocapacitance). Thus, hybrid supercapacitors combining both electrostatic and electrochemical storage mechanisms can be

obtained by enriching porous carbon materials with heteroatoms (N, O, S, P or B), or by decorating their surface with transition metal oxides. The required properties for supercapacitor electrodes include a large micropore volume for ion storage, wide mesopores for enhanced ion diffusion, and good electrical conductivity [55]. We have investigated the electrochemical behavior of cerium oxide/multiwalled carbon nanotube composites prepared by sol-gel deposition of the oxide onto the carbon nanotubes. A new methodology was developed to identify the different charge storage mechanisms occurring on the surface of the composite [56]. In particular, square wave voltammetry (SWV) was used to separate the capacitive current from the pseudocapacitance. Further deconvolution of the SWV curves enabled the identification of the different faradaic processes occurring on the surface of the electrodes in acid, basic and neutral electrolytes [57].

Activated carbon xerogels obtained from hydrothermally carbonized glucose/graphene oxide hybrids were tested as supercapacitor electrodes, delivering a much higher specific capacitance than that of a commercial activated carbon (223 vs 153 F/g at 100 mA/g), as well as exhibiting a significantly improved retention of capacitance at high current densities [11]. Very good performances were also obtained with activated glucose-derived/CNT hybrid carbons [12], as shown in Figure 9 [55].

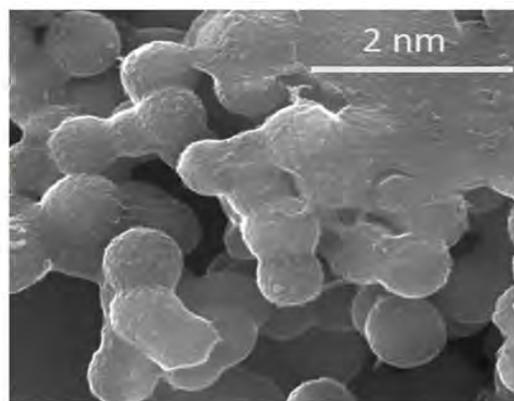
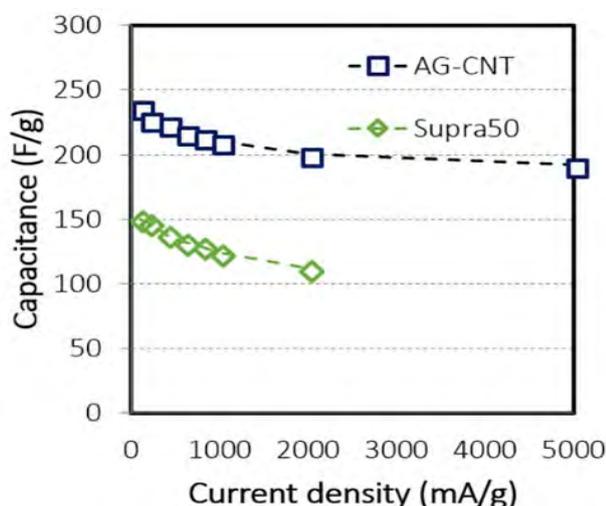


Figure 9: Electrochemical performance of a KOH activated glucose-derived/CNT hybrid carbon gel (AG-CNT), and corresponding SEM micrograph. The performance of a commercial activated carbon (Norit Supra DCL 50) is included. Reproduced from [55] with permission from Elsevier.

Figura 9: Comportamiento electroquímico de un carbón híbrido glucosa/CNT activado con KOH y micrografía SEM correspondiente (AG-CNT). La Figura incluye el comportamiento de un carbón activado comercial (Norit Supra DCL 50). Reproducida de [55] con el permiso de Elsevier.

Concerning energy conversion, our goal is to develop a new generation of carbon-based electrocatalysts without the use of precious metals. In particular, we have been focusing on N-doped CNTs for the oxygen reduction reaction (ORR) in alkaline medium. Our results highlighted the role of pyridinic and quaternary nitrogen in determining the performance of the electrocatalyst [58]. In another report, we investigated the role of the surface oxygen functional groups of CNTs on the ORR performance. Computational

simulations showed that oxygen may adsorb on the quinone group without dissociation (leading to the indirect, or two-electron pathway), while adsorption can occur either associatively or dissociatively on the pyrone group, thus favoring the direct, four-electron pathway [59]. Interesting relationships between the nitrogen functionalities and the electroactivity towards the ORR were established in a study with glucose-derived carbons with tailored properties. It was found that a high pyridinic-N/quaternary-N ratio favors the

onset potential, while a low quaternary-N/pyrrolic-N ratio favors the number of electrons exchanged during ORR [60]. We have also prepared N-doped carbon xerogels with different micropore volumes and electrical conductivities for the ORR. By adding iron nanoparticles, we were able to achieve similar performances to the benchmark Pt electrocatalyst [61].

Our most recent research addresses an energy device that combines a fuel cell and an electrolyser, named “unitized regenerative fuel cell” (URFC). An URFC produces hydrogen in the electrolysis mode and delivers power in the fuel cell mode, thus overcoming the drawbacks related to the intermittent nature of renewable energies. The main challenge is to find active and stable bifunctional electrocatalysts for the direct and reverse reactions, namely the oxygen reduction and evolution reactions (ORR/OER) at the cathode, and the hydrogen oxidation and evolution reactions (HOR/HER) at the anode. We have been focusing on the oxygen reactions, which are the slowest. In particular, we have reported the synthesis of bifunctional electrocatalysts for ORR/OER derived from cobalt and manganese layered double hydroxides (LDH) compounded with carbon nanotubes [62], as well as Co_3O_4 supported on oxidized graphene flakes [63].

Acknowledgments

The work reviewed in this article was carried out at Associate Laboratory LSRE-LCM -UID/EQU/50020/2019 – financed by national funds through FCT/MCTES (PIDDAC). Additional support was provided by projects AIProcMat@N2020-Advanced Industrial Processes and Materials for a Sustainable Northern Region of Portugal 2020” (NORTE-01-0145-FEDER-000006) supported by Programme NORTE2020 under the Portugal 2020 Partnership Agreement, through the European Regional Development Fund (ERDF); and Project UNIRCELL (POCI-01-0145-FEDER-016422) funded by European Structural and Investment Funds (FEEI) through COMPETE2020 and by national funds through FCT. The LCM team is acknowledged for revising the manuscript and for assistance with some figures.

References

- [1] J.L. Figueiredo. *BOLETIN del Grupo Español del Carbón* 2016; 39: 2-7.
- [2] J.L. Figueiredo. *In: Nanotechnology in Catalysis: Applications in the Chemical Industry, Energy Development, and Environment Protection* (Marcel Van de Voorde, Bert F. Sels, editors). Wiley-VCH Verlag GmbH & Co. KGaA, Vol.1, pp. 37-55 (2017).
- [3] A.P.C. Ribeiro, L.M.D.R.S. Martins, S.A.C. Carabineiro, J.L. Figueiredo, A.J.L. Pombeiro, *Molecules* 2017; 22: 603.
- [4] A.P.C. Ribeiro, L.M.D.R.S. Martins, S.A.C. Carabineiro, J.L. Figueiredo, A.J.L. Pombeiro, *Appl. Catal. A: Gen.* 2017; 547: 124-131.
- [5] L.M.D.R.S. Martins, A.P.C. Ribeiro, S.A.C. Carabineiro, J.L. Figueiredo, A.J.L. Pombeiro, *Dalton Trans.* 2016; 45: 6816-6819.
- [6] J. Wang, L.M.D.R.S. Martins, A.P.C. Ribeiro, S.A.C. Carabineiro, J.L. Figueiredo, A.J.L. Pombeiro, *Chem. Asian J.* 2017; 12: 1915-1919.
- [7] A.P.C. Ribeiro, L.M.D.R.S. Martins, S.A.C. Carabineiro, J.G. Buijnsters, J.L. Figueiredo, A.J.L. Pombeiro, *ChemCatChem* 2018; 10: 1821-1828.
- [8] A.J.L.O. Pombeiro, L.M.D.R. Sousa Martins, A.P.C. Ribeiro, S.A.C. Carabineiro, J.L. Figueiredo. *European Patent n° EP3397609 (B1)*, published on July 3rd, 2019.
- [9] S.A.C. Carabineiro, L.M.D.R.S. Martins, A.J.L. Pombeiro, J.L. Figueiredo. *ChemCatChem* 2018; 10: 1804-1813.
- [10] M. Enterría, J.L. Figueiredo, *Carbon* 2016; 108: 79-102.
- [11] M. Enterría, F.J. Martín-Jimeno, F. Suarez-García, J.I. Paredes, M.F.R. Pereira, J.I. Martins, A. Martínez-Alonso, J.M.D. Tascon, J.L. Figueiredo. *Carbon* 2016; 105: 474-483.
- [12] N. Rey-Raap, M. Enterría, J.I. Martins, M.F.R. Pereira, J.L. Figueiredo. *ACS Appl. Mater. Interfaces* 2019; 11: 6066-6077.
- [13] O.S.G.P. Soares, R.P. Rocha, A.G. Gonçalves, J.L. Figueiredo, J.J.M. Órfão, M.F.R. Pereira. *Carbon*, 91: 114-121 (2015).
- [14] O.S.G.P. Soares, R.P. Rocha, J.J.M. Órfão, M.F.R. Pereira, J.L. Figueiredo. *C* 2019; 5: 30.
- [15] A.F.M.F. Ramôa, M.G.C.O.B.S.M. Pizarro, J.A. Morgado, S.O. Prozil, M.F.R. Pereira, O.S.G.P. Soares, P.S.F. Ramalho, C.A.M.P. Sá, V.L.G.P. Sá, S.G.C.S. Ventura, J.S. Abreu. *International Patent Application: PCT/IB2017/050485*, Filing Date: January 2017. Portuguese Patent: 109121, Entry Date: January 2016.
- [16] M. Pedrosa, M.J. Sampaio, T. Horvat, O.C. Nunes, G. Dražić, A.E. Rodrigues, J.L. Figueiredo, C.G. Silva, A.M.T. Silva, J.L. Faria. *Appl. Surf. Sci.* 2019; 497: article 143757, in press (<https://doi.org/10.1016/j.apsusc.2019.143757>).
- [17] R.O. Rodrigues, G. Baldi, S. Doumett, L. Garcia-Hevia, J. Gallo, M. Banobre-Lopez, G. Dražić, R.C. Calheta, I.C.F.R. Ferreira, R. Lima, H.T. Gomes, A.M.T. Silva. *Mat. Sci. Eng. C-Mater.* 2018; 93: 206-217.
- [18] N.F.F. Moreira, J.M. Sousa, G. Macedo, A.R. Ribeiro, L. Barreiros, M. Pedrosa, J.L. Faria, M.F.R. Pereira, S. Castro-Silva, M.A. Segundo, C.M. Manaia, O.C. Nunes, A.M.T. Silva. *Water Res.* 2016; 94: 10-22.
- [19] O.S.G.P. Soares, R.P. Rocha, A.G. Gonçalves, J.L. Figueiredo, J.J.M. Órfão, M.F.R. Pereira. *Appl. Catal. B: Environ.* 2016; 192: 296-303.
- [20] 16. D.F.M. Santos, O.S.G.P. Soares, A.M.T. Silva, J.L. Figueiredo, M.F.R. Pereira. *Appl. Catal. B: Environ.* 2016; 199: 361-371.
- [21] M. Martín-Martínez, R.S. Ribeiro, B.F. Machado, P. Serp, S. Morales-Torres, A.M.T. Silva, J.L. Figueiredo, J.L. Faria, H.T. Gomes. *ChemCatChem* 2016; 8: 2068-2078.
- [22] R.P. Rocha, O.S.G.P. Soares, A.G. Gonçalves, J.J.M. Órfão, M.F.R. Pereira, J.L. Figueiredo. *Appl. Catal. A: Gen.* 2017; 548: 62-70.
- [23] C.A. Orge, O.S.G.P. Soares, J.L. Faria, M.F.R. Pereira. *J. Environ. Chem. Eng.* 2017; 5: 5599-5607.

- [24] M. Pedrosa, L.M. Pastrana-Martínez, M.F.R. Pereira, J.L. Faria, J.L. Figueiredo, A.M.T. Silva. *Chem. Eng. J.* 2018; 348: 888-897.
- [25] C.A. Orge, O.S.G.P. Soares, J.L. Faria, M.F.R. Pereira. *J. Environ. Chem. Eng.* 2017; 5: 5599-5607.
- [26] C.A. Orge, M.F.R. Pereira, J.L. Faria. *Chem. Eng. J.* 2017; 318: 247-253.
- [27] C.A. Orge, J.L. Faria, M.F.R. Pereira. *J. Environ. Manag.* 2017; 195: 208-215.
- [28] L. Svoboda, P. Praus, M.J. Lima, M.J. Sampaio, D. Matýšek, M. Ritz, R. Dvorský, J.L. Faria, C.G. Silva. *Mater. Res. Bull.* 2018; 100: 322-332.
- [29] N.F.F. Moreira, M.J. Sampaio, A.R. Ribeiro, C.G. Silva, J.L. Faria, A.M.T. Silva. *Appl. Catal. B: Environ.* 2019; 248: 184-192.
- [30] A. Torres-Pinto, M.J. Sampaio, C.G. Silva, J.L. Faria, A.M.T. Silva. *Appl. Catal. B: Environ.* 2019; 252: 128-137.
- [31] M.J. Lima, C.G. Silva, A.M.T. Silva, J.C.B. Lopes, M.M. Dias, J.L. Faria. *Chem. Eng. J.* 2017; 310: 342-351.
- [32] M.J. Lima, A.M.T. Silva, C.G. Silva, J.L. Faria, J.C.B. Lopes, M.M. Dias. *Chem. Eng. J.* 2016; 287: 419-424.
- [33] R.S. Ribeiro, A.M.T. Silva, J.L. Figueiredo, J.L. Faria, H.T. Gomes. *Appl. Catal. B: Environ.* 2016; 187: 428-460.
- [34] R.S. Ribeiro, A.M.T. Silva, P.B. Tavares, J.L. Figueiredo, J.L. Faria, H.T. Gomes. *Catal. Today* 2017; 280: 184-191.
- [35] R.S. Ribeiro, R.O. Rodrigues, A.M.T. Silva, P.B. Tavares, A.M.C. Carvalho, J.L. Figueiredo, J.L. Faria, H.T. Gomes. *Appl. Catal. B: Environ.* 2017; 219: 645-657.
- [36] J.L. Diaz de Tuesta, B.F. Machado, P. Serp, A.M.T. Silva, J.L. Faria, H.T. Gomes. *Catal. Today* 2019; in press (<https://doi.org/10.1016/j.cattod.2019.07.012>).
- [37] M. Pedrosa, G. Drazic, P.B. Tavares, J.L. Figueiredo, A.M.T. Silva. *Chem. Eng. J.* 2019; 369: 223-232.
- [38] E.S. da Silva, N.M.M. Moura, M.G.P.M.S. Neves, A. Coutinho, M. Prieto, C.G. Silva, J.L. Faria. *Appl. Catal. B: Environ.* 2018; 221: 56-69.
- [39] E.S. da Silva, N.M.M. Moura, A. Coutinho, G. Dražić, B.M.S. Teixeira, N.A. Sobolev, C.G. Silva, M. Graça, P.M.S. Neves, M. Prieto, J.L. Faria. *ChemSusChem* 2018; 11: 2681-2694.
- [40] L.M. Pastrana-Martínez, A.M.T. Silva, N.N.C. Fonseca, J.R. Vaz, J.L. Figueiredo, J.L. Faria. *Top. Catal.* 2016; 59: 1279-1291.
- [41] M.J. Sampaio, A. Benyounes, P. Serp, J.L. Faria, C.G. Silva. *Appl. Catal. A: Gen.* 2018; 551: 71-78.
- [42] R.A. Fernandes, M.J. Sampaio, E.S. da Silva, P. Serp, J.L. Faria, C.G. Silva. *Catal. Today* 2019; 328: 286-292.
- [43] M.J. Lima, A.M.T. Silva, C.G. Silva, J.L. Faria. *J. Catal.* 2017; 353: 44-53.
- [44] M.J. Lima, M.J. Sampaio, C.G. Silva, A.M.T. Silva, J.L. Faria. *Catal. Today* 2019; 328: 293-299.
- [45] J.C. Lopes, M.J. Sampaio, R.A. Fernandes, M.J. Lima, J.L. Faria, C.G. Silva. *Catal. Today* 2019; in press. (<https://doi.org/10.1016/j.cattod.2019.03.050>).
- [46] L.S. Ribeiro, J.J. Delgado, J.J.M. Órfão, M.F.R. Pereira. *Catal. Today* 2017; 279: 244-251.
- [47] L.S. Ribeiro, J.J. Delgado, J.J.M. Órfão, M.F.R. Pereira. *ChemCatChem* 2017; 9: 888-896.
- [48] L.S. Ribeiro, J.J. Delgado, J.J.M. Órfão, M.F.R. Pereira. *Appl. Catal. B: Environ.* 2017; 217: 265-274.
- [49] L.S. Ribeiro, J.J.M. Órfão, M.F.R. Pereira. *Bioresource Technol.* 2017; 244: 1173-1177.
- [50] L.S. Ribeiro, J. Órfão, J.J.M. Órfão, M.F.R. Pereira. *Cellulose* 2018; 25: 2259-2272.
- [51] N. Rey-Raap, L.S. Ribeiro, J.J.M. Órfão, J.L. Figueiredo, M.F.R. Pereira. *Appl. Catal. B: Environ.* 2019; 256: in press (<https://doi.org/10.1016/j.apcatb.2019.117826>).
- [52] L.S. Ribeiro, N. Rey-Raap, J.L. Figueiredo, J.J.M. Órfão, M.F.R. Pereira. *Cellulose* 2019; 26: 7337-7353.
- [53] K.M. Eblagon, M.F.R. Pereira, J.L. Figueiredo. *Appl. Catal. B: Environ.* 2016; 184: 381-396.
- [54] K.M. Eblagon, A. Malaika, M.F.R. Pereira, J.L. Figueiredo. *ChemCatChem* 2018; 10: 4934-4946.
- [55] J.L. Figueiredo. *Surface and Coatings Technology* 2018; 350: 307-312.
- [56] M. Enterría, A.G. Gonçalves, M.F.R. Pereira, J.I. Martins, J.L. Figueiredo. *Electrochim. Acta* 2016; 209: 25-35.
- [57] M. Enterría, A.G. Gonçalves, M.F.R. Pereira, J.I. Martins, J.L. Figueiredo. *J. Electroanal. Chem.* 2019; 847: in press (<https://doi.org/10.1016/j.jelechem.2019.113269>).
- [58] I.M. Rocha, O.S.G.P. Soares, I.M. Fernandes, C. Freire, J.L. Figueiredo, M.F.R. Pereira. *ChemistrySelect* 2016; 1: 2522-2530.
- [59] I.M. Rocha, O.S.G.P. Soares, J.L. Figueiredo, C. Freire, M.F.R. Pereira. *Catal. Sci. Technol.* 2017; 7: 1868-1879.
- [60] R.G. Morais, N. Rey-Raap, J.L. Figueiredo, M.F.R. Pereira. *Beilstein J. Nanotech.* 2019; 10: 1089-1102.
- [61] M. Canal-Rodríguez, N. Rey-Raap, J.A. Menéndez, M.A. Montes-Morán, J.L. Figueiredo, M.F.R. Pereira, A. Arenillas. *Micropor. Mesopor. Mat.*, in press. <https://doi.org/10.1016/j.micromeso.2019.109811>.
- [62] M.F.P. Duarte, I.M. Rocha, J.L. Figueiredo, C. Freire, M.F.R. Pereira. *Catal. Today* 2018; 301: 17-24.
- [63] M.P. Araujo, M. Nunes, I.M. Rocha, M.F.R. Pereira, C. Freire. *ChemistrySelect* 2018; 3: 10064-10076.