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Presentación

Es un placer presentar este número de nuestro Boletín que, como todos los anteriores, tiene un contenido muy atractivo y muy útil. En esta ocasión, se presentan (i) cuatro artículos científicos sobre distintos aspectos de los materiales de carbón, uno donde se revisa la carbonización hidrotermal como fuente de materiales de carbón, otro donde se presentan las últimas tendencias en investigación de materiales de carbón para dispositivos electroquímicos, un artículo donde se estudian las alteraciones electrónicas en los grafenos y su influencia en sus propiedades electrónicas finales y finalmente un trabajo sobre la química computacional como herramienta en el estudio y desarrollo de materiales carbonosos, (ii) tres reseñas de Tesis Doctorales, en este caso de gente externa al GEC pero relacionadas con nuestra actividad y (iii) una serie de reseñas de distinta índole: cabe destacar una reseña escrita por el Profesor Harry Marsh en relación con los cambios que en breve sucederán en la revista Carbon, así como la reseña del libro "Novel carbon adsorbents" que recientemente ha editado J.M.D. Tascón.

Este número se publica después de la "Carbon Conference" que ha tenido lugar en Cracovia, conferencia en la que, como viene siendo habitual, ha habido una contribución relevante de los investigadores del GEC. Además, en esta conferencia se han producido unos hechos importantes que quisiera mencionar. En primer lugar, en la reunión de los representantes de la ECA ("European Carbon Association"), se decidió que la celebración de la "Carbon Conference" europea de 2018 tenga lugar en España. Aunque falta bastante tiempo, tendremos que elegir la sede del congreso y la próxima reunión del GEC en Madrid es un buen momento para hacerlo. El segundo aspecto a destacar está relacionado con los cambios importantes que se van a producir en la revista Carbon. A partir del año próximo, el Profesor Peter Thrower dejará de ser editor jefe de la revista y el Profesor Rodríguez Reinoso también dejará de ser editor asociado. Por este motivo, se celebró durante la conferencia de Cracovia un acto para agradecer a Peter Thrower y a Rodríguez Reinoso, por todo el trabajo que han realizado en la revista. Cabe destacar que la dedicación de Peter Thrower a la revista Carbon es completa desde hace muchos años y

que gracias al cuidado e interés por mejorarla, ésta ha crecido año tras año tanto en artículos publicados como en impacto. Se puede decir sin lugar a dudas que es la revista de referencia en materiales carbonosos. El nuevo editor jefe será el Profesor Robert Hurt de la Universidad de Brown quien, con toda seguridad, seguirá elevando la calidad de la revista. También hay que señalar que desde hace poco tiempo hay un nuevo editor asociado que es miembro del GEC: el Profesor Juan Manuel Díez Tascón, lo cual es un reconocimiento a su bagaje científico y a la calidad de la investigación en materiales carbonosos que se realiza en España.

Además, quiero aprovechar para destacar que las actividades del GEC continúan en diferentes aspectos que ya se pusieron en marcha hace unos años y en otros que estamos iniciando recientemente y de los que os iremos informando a medida que vayan tomando forma. De este modo, en lo que se refiere a las actividades próximas, los compañeros de Madrid están trabajando intensamente en la organización de la próxima reunión del GEC que se celebrará en Septiembre del año próximo. En segundo lugar, se van a celebrar dos cursos, uno a finales de este año sobre materiales carbonosos y el segundo en la primera mitad del año próximo más enfocado al carbón mineral. En tercer lugar, estamos trabajando en la página web para potenciar un poco más la difusión del grupo.

Finalmente, quisiera destacar que el equipo editorial del Boletín del GEC está realizando un esfuerzo muy importante para difundir la revista, publicar artículos de interés para todos nosotros y hacer que crezca en calidad. Por todo ello, quisiera aprovechar para darles mi enhorabuena y pediros a todos vosotros que contribuyáis en la revista enviando tanto artículos de vuestra actividad científica como reseñas de las Tesis Doctorales que se derivan de dicha actividad porque, lógicamente, es una ayuda importante para el grupo y porque, además, todas las aportaciones que se publican tienen una repercusión importante como se desprende de las numerosas descargas que habitualmente tienen los números publicados.

Diego Cazorla
Presidente del GEC

Carbon materials for an efficient use of energy by electrochemical devices

Materiales de carbono para un uso eficiente de la energía en dispositivos electroquímicos

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Abstract

The efficient use of energy, in particular electricity, requires devices allowing its storage and subsequent conversion into work with a high yield. Electrochemical devices are very effective since the absence of mechanical moving parts reduces irreversibility and provides high efficient conversions. The efficiency of the device depends on the performance of the electrodes, which depends on the properties of the materials that compose them. Because most of the electrodes are made from carbons, this field of research has experienced a tremendous growth in recent years, in particular for three devices: Proton Exchange Membrane Fuel Cells, Lithium Ion Batteries and Supercapacitors. This article presents the latest research trends in this field taking as a reference the papers presented at the Carbon 2012 Conference recently held in Krakow.

Resumen

El uso eficiente de la energía, en particular de la energía eléctrica, requiere de dispositivos que permitan su almacenamiento y posterior conversión en trabajo con alto rendimiento. Los dispositivos electroquímicos son especialmente eficientes ya que la ausencia de elementos mecánicos móviles permite conversiones con una eficiencia muy elevada. El rendimiento global del dispositivo depende de las prestaciones de los electrodos, las cuales dependen de las propiedades de los materiales que los componen. La mayor parte de los electrodos están elaborados con materiales de carbono, por lo que este campo de investigación ha experimentado un enorme crecimiento en los últimos años, en particular los relacionados con Pilas de Combustible Poliméricas, Baterías de ión litio, y Supercondensadores. En este artículo, se presentan las últimas tendencias en investigación en estos dispositivos tomando como referencia los artículos presentados en la pasada Conferencia Carbon 2012 celebrada en Cracovia.

1. Introduction

Electrochemical devices are very effective for the efficient use of energy, in particular electricity, allowing its storage and subsequent conversion into work with a high yield since the absence of mechanical moving parts reduces irreversibility and provides high efficient conversions. The efficiency of the device depends on the performance of the electrodes, which, in turn, depends on the properties of the materials that compose them. Because most of the electrodes currently used for energy purposes are made from carbons, this field of research has experienced a tremendous growth in recent years, in particular for three devices: Proton Exchange Membrane Fuel Cells, PEMFC, Lithium Ion Batteries, LIB and Supercapacitors, SC. Figure 1 shows the energy and power density of the three types of devices considered. Comparing SC (Electrochemical

capacitors) with LIB, the formers show higher power density, shorter response time (1-30 s for SC vs 0.5-1 h for LIB) and longer cycle life (up to 1,000,000 cycles for SC vs up to 1,000 cycles for LIB). In contrast, SC show lower energy densities. PEMFC shows the higher energy density since this is only limited by the fuel storage capacity.

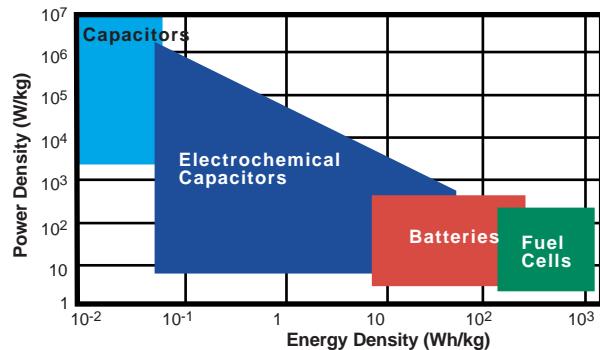


Figure 1. Energy and Power density of different electrochemical devices.

Figura 1. Energía y densidad de potencia de diferentes dispositivos electroquímicos.

2. Proton Exchange Membrane Fuel Cells, PEMFCs

H₂/air fuel cells based on proton-exchange membranes have many attractive features which make them a promising clean energy technology for powering hybrid Electric/FC vehicles. In portable applications, using direct alcohols DAFC, including bio-alcohols, is an option that is pushing the access to the market of this type of FCs. Despite the many advances made in PEMFC development, improving their performance, in particular the electrocatalyst, is still needed. In particular, reducing intolerance to CO, increasing the Oxygen Reduction Reaction kinetics and reducing cost. Efforts are being focused to reduce Pt content by alloying with cheaper metals and substituting the carbon supports by novel ones with improved performances.

CoOx-MWNTs nanocomposite as a support for Pt nanoparticles has been proposed as potential promoter for methanol electro-oxidation reaction. The results of electrochemical tests showed that the CoOx improved Pt/MWNTs performance in terms of activity and stability [1]. Non-metal Carbon alloy catalysts which acquire the catalytic activities by introducing heteroatoms, different types of chemical bonding or unique morphologies to the original carbon structures have been proposed. A catalyst prepared by ammoniation (AO) treatment of carbon nano-onions which were obtained by heat-treatment of a nanodiamond has been reported [2]. Tungsten carbides and tungsten nitrides have been proposed to substitute Pt. These materials show a very low catalytic effect for the Oxygen Reduction Reaction, but the addition of a small amount of platinum in the tungsten hemicarbide surface enhances the catalytic effect [3]. Pd based catalysts coated on MWCNTs

synthesized with Au as second metal and CeO₂ addition to prevent CO poisoning have also been reported. This type of catalyst is specially indicated for new renewable energy using direct formic acid in fuel cells [4].

Improving the performance of the support is a key to improve the catalyst activity allowing reducing the Pt content. The electrocatalyst supports should have a high surface area, electronic conductivity, a suitable pore structure and surface chemistry. Carbon blacks, in particular Vulcan XC-72® are currently used as support for electrocatalyst because they fit these properties at low cost. To improve these performances, novel carbon materials have been proposed: Carbon xerogels have been reported as catalyst supports for FC applications. The specific catalytic activity significantly increases when Vulcan is substituted by mesoporous xerogel carbons in passive DMFC configuration [5]. Pt and Pt/Ru nanoparticles supported on carbon nanofibers, CNF's have been tested and higher catalytic activity than using Vulcan has been reported. The CNF properties have shown to influence the Pt dispersion and distribution [6]. Carbon nanocoils (CNC) have recently received great attention due to the combination of their good electrical conductivity and a wide porosity. The behaviour of a Pt/CNC catalyst on the anode side of a PEM fuel cell was compared with the commercial E-TEK Pt-supported catalyst. Results showed better performance for the CNC-supported electrocatalysts [7].

Superiority of MWCNT and graphenes as catalyst support has been reported with the only drawback of high cost of these materials. Graphite Nanofibres, GNF, have been proposed as substitute for MWCNT and also as a low cost graphite source for graphene production [8]. Catalytic activity of Pt clusters can be promoted by using the interface interaction between Pt and CNT surface [9]. It has been found that graphenes and carbon nanotubes (CNTs) can act as effective metal-free electrocatalysts [10]. Improved electrocatalytic activity is due to the net of positive charged carbon atoms created in graphene site or nanotube wall. Several strategies are used to obtain graphene/CNT positively charged carbon nets. Functionalization of CNT causes enhanced electrocatalytic performance. Another approach is to put the graphene or nanotubes in highly electrophilic polymer matrix. The third way is incorporation of donor atoms into graphene/CNT site during growth. Grown of the CNTs on Si/SiO₂ by using spray pyrolysis CVD technique has been reported. Heteroatom doped carbons are receiving particular attention due to their superior performance in the ORR. N-doping is an essential factor for the catalytic efficiency of carbon-based catalysts and sulphur is receiving increasing attention as a dopant.

3. Ion Lithium Batteries, LIB

A Lithium Ion Battery is a device that storages electricity as chemical energy and then converts back this energy into electricity. Figure 2 shows the main components. There are two electrodes and an electrolyte that allows the transfer of ions between them. The interest for a LIB is the use as electrodes of materials capable of inserting Li ions, in a reversible manner, within its structure. The commercial LIB use metal oxides containing Li as cathode and different graphitic materials as anodes. Efforts in LIB development are focused in finding cheaper and sustainable graphite sources and increasing the Li intercalation capacity of electrodes.

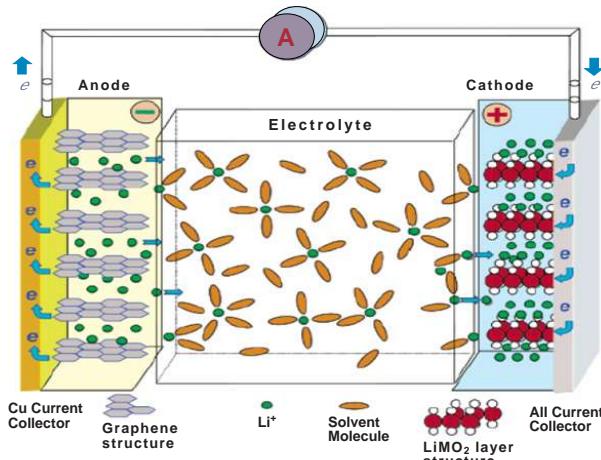


Figure 2. Main components of a Li-ion battery.
Figura 2. Principales componentes de una batería ion-Li.

3.1 Advanced 3D cathodes based on Metallic Oxides/Carbon composites

A new approach, previously used for supercapacitors, consisting of carbon nanotubes (CNTs) and conducting polymers (ECPs) with high specific power, high specific energy, and stable cycling performance through a 3D design, has been adapted to improve the power density of LIB and make it comparable with that of supercapacitors. New nanostructured cathodes based on MnO₂, supported on MWCNT have been reported [12]. The as-synthesized materials show a capacity up to 134 mAh.g⁻¹ after 100 cycles discharge and charge at 150 mA.g⁻¹.

Olivine-type LiFePO₄ is receiving attention as cathode material due to its high theoretical specific capacity (170 mAh.g⁻¹), thermal stability, safety, and potentially low cost. However, the inherent poor electronic conductivity and Li-ion diffusion coefficient at room temperature bring difficulties for high-rate battery applications. Modifications of LiFePO₄ particles by minimizing the particle size and coating them with an electron-conducting carbon layer are considered to be effective in surmounting electronic and ionic transport limitations. A Ethylene glycol (EG)-mediated solvothermal route for the large-scale synthesis of nest-like LiFePO₄ hierarchical microstructures constructed from nanoplates by using Li₂SO₄, Fe(NO₃)₃·9H₂O and P₂O₅ as raw materials, [13]. After 100 cycles, a stable capacity of 158 mAh.g⁻¹ is obtained, indicating a good electrochemical reversibility and structural stability of the material.

3.2 Anodes based on synthetic graphite and decorated nanocarbons

Natural and synthetic graphite have been extensively investigated searching for an ideal anode material in terms of capacity, cyclability, operational voltage and cost. Crystalline graphite can insert up to one Li ion for every six carbons to form the intercalation compound LiC₆ what corresponds to a theoretical reversible capacity of 372 mAh.g⁻¹. Currently, petroleum coke is used as the main precursor material in the manufacturing of synthetic graphite. However, different factors concerning cost and sustainability have prompted a research interest into other alternative precursors. Carbon Nanofibers (CNFs) obtained from natural gas and biogas have been proved to be an excellent graphite source due to their significant degree of structural order that can be significantly improved by catalytic treatment with Si at high temperature [14]. Efforts are devoted to incorporate materials with higher Li intercalation

capacity than graphite. SnO_2 and Si are the most extensively studied due to their significant higher Li capacity (781 mAh $^{-1}$ for SnO_2 and 3580 mAh $^{-1}$ for Si) low cost and low toxicity. The main drawback for their use in a real application is the low reversible capacity retention due to substantial changes in volume during the alloying/dealloying process (the so called "pulverization" problem). One of the promising methods to overcome this is to prepare Si/carbon nanocomposites by covering Si nanoparticles with carbon nanolayers by CVD. The structure of carbon-coated Si nanoparticles (nano-Si/C) is drastically changed during charge/discharge cycles in the early cycles and becomes a dendrite-like structure where Si and carbon are uniformly mixed. The dendrite-like structure has been retained over 100 cycles and nano-Si/C exhibited excellent performance (1500 mAh $^{-1}$ at 3.3C) and good cyclability (1500 mAh/g) [15].

A very effective strategy for buffering variations in volume is the use of nanoparticles of Si and SnO_2 deposited in a carbonaceous matrix, whose structure confers mechanical stability. Several carbonaceous matrixes have been used. Thanks to their amorphous structure and their individualized nanosized morphology, the Si nanoparticles deposited by Fluidized Bed CVD on the CNTs are able to be loaded with Li with excellent specific capacity on the very first charge-discharge cycles [16]. However, degradation of the electrode has been observed. This led to an irreversible capacity, added to the first discharge reversible capacity (total of 3187 mAh/g). A mean capacity loss of 2 % per cycle is observed from the 2nd to 26th cycle.

Concerning SnO_2 composites, they show a lower initial capacity but a higher cyclability. SnO_2 -carbon composites made up of tin oxide nanoparticles deposited onto the surface of a graphitic nanocarbon synthesized by a novel synthesis process based on the pyrolysis of Fe (II) gluconate exhibit very good electrochemical performance against lithium. Indeed, a capacity of 400 mAh/g for SnO_2 -nanocarbon was recorded after 50 cycles [17]. SnO_2 -Graphene composite [18] synthesized by deposition of SnO_2 nanocrystals onto the surface of graphene, presented a superior cycling stability up to 500 cycles with a capacity of 480 mAh g $^{-1}$. Such good stability could be ascribed as the strong adhesion of SnO_2 nanocrystals on the graphene support, which is of a high electronic conductivity and possesses good flexibility.

A sol-gel approach was used to synthesize LSTO/CNF anode materials by doping LTO particles with Sn $^{2+}$ and incorporation of CNFs has been reported. The LSTO/CNF composite electrodes delivered a remarkable capacity of 122 mAh g $^{-1}$ after charging/discharging at 10C for 500 cycles [19]. Graphene Nanosheet Aggregations, GNSA, analyzed under various current densities of 50 mA/g shown a first discharge and reversible charge capacities of 1647 mA h/g and 528 mA h/g respectively. And the reversible ischarge capacity remained at ca. 411 mAh/g after 50 cycles (0.5% capacity fading per cycle at 50 mA/g) [20].

4. Supercapacitors

Supercapacitors (SCs) can deliver higher power in a shorter time than batteries. However, for their use in certain applications it is first necessary to increase their energy density. Among the electrode materials used in SCs, carbons have been the most developed due to their excellent properties. Energy is stored in

a supercapacitor by two mechanisms: (i) double-layer mechanism, which consist in an accumulation of the electrolyte ions at the electrolyte/electrode interface, and (ii) pseudocapacitive mechanism, in which oxidation/reduction of the electrode is accompanied by extraction/insertion of electrolyte ions. The former mechanism works in the so called Electric Double Layer Capacitors, EDLC's. The latter has been found in transition metal oxides, and also in carbons having a high content in oxygen and/or nitrogen groups (i.e. highly functionalized carbons). Figure 3 shows the main components of both types of SC.

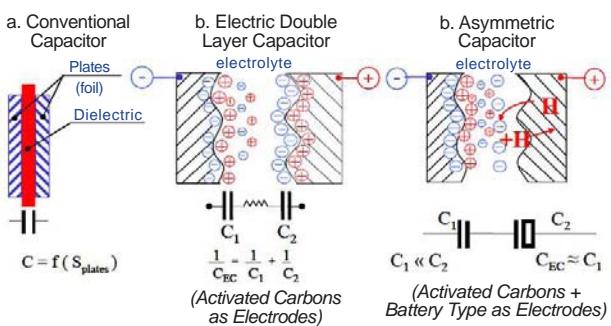


Figure 3. Main components of the different types of supercapacitors.

Figura 3. Principales componentes de los distintos tipos de supercondensadores.

Increasing energy density of carbon-based SCs (CBSCs) has been centred in two approaches: (i) Developing size-controlled porosity for EDLC's and (ii) Enhancement of capacitance through pseudocapacitive contributions provided by functional groups from physical/chemical treatments, by polymers deposition or by the insertion of transition metal oxide particles.

4.1. Carbons for Electric Double Layer Supercapacitors, EDLC's

EDLC's store energy in a polarized double layer at the interface between an ionically conducting electrolyte solution and an electronically conducting electrode. Currently efforts focus on improving the energy density of EDLC's by tuning the pore size of micro-porous carbons to increase the capacitance. The pore size leading to the maximum double layer capacitance is very close to the desolvated ion size, and the major electro-adsorption process takes place around 0.7 nm in aqueous media and 0.8 nm in organic electrolytes. Cyclic activation of non porous carbons by H_2O_2 , at 89 bars and 200 °C, followed by the decomposition of the surface functionalities, has shown to be an effective method for producing microporous carbons. After 4-5 treatment cycles, the specific surface area is between 1000-1200 m $^2\text{g}^{-1}$ and the pore entrances are adapted for the use in organic based electrochemical capacitors. The pore size can be tailored to the electrolyte ions size through one cycle by adjusting the reaction parameters i.e. pressure, temperature and time [21]. Up to now it is not clear what materials (micro- or mesoporous) are more suitable. In mesoporous carbon materials with definite well-ordered pore channels, there is unhampered in-pore ionic transit, that should show the best results in the area of supercapacitor technologies. Cyclic voltammetry of mesoporous and microporous carbon samples prepared by carbonization (600–800°C) with alkali excess showed that mesoporous carbons are more suitable candidates for SC electrodes, than the microporous ones. The origin lies in predominance

of capacitance of EDL in the case of the mesoporous samples. For the microporous samples, faradaic processes arise, which lead to slowdown of charge-discharge process and decrease in maximal number of cycles [22].

A synthesis process of carbon xerogels based on the use of microwave radiation to promote reactions between resorcinol (R) and formaldehyde (F) monomers has been reported. The carbon xerogel, AOX, was compared to commercial activated carbons and, in all the evaluated media, AOX showed a better electrochemical performance, revealing the importance of small-sized mesopores in energy storage processes. Results obtained with different asymmetric cell configuration capacitance showed values of 213 F.g⁻¹ using a maximum voltage of 1.6 V [23]. Hydrothermal carbonization has demonstrated to be an effective synthetic route for the production of functionalized carbonaceous materials from simple monosaccharides, such as glucose and xylose. The symmetric capacitors obtained from the hydrothermal treatment of the hydrolysis products of spruce and corn cobs exhibited good energy densities, with values of 6.4 and 7 W h kg⁻¹ and power densities of 0.76 and 1.08 kW kg⁻¹ in a voltage window of 0.8 V and current density of 250 mA/g, with high coulombic efficiencies [24].

4.2. Heteroatom Doped Carbons

To achieve high performance supercapacitors, the use of heteroatom-doped graphenes and MWCNT as electrode material has also been proposed. Boron- and nitrogen-doped graphene samples prepared by the combined plasma treatment and high-temperature thermal treatment have been used and a large increase in the specific capacitance was observed [25]. N-doped carbons from amino containing carbohydrates; macro-mesoporous N-doped carbogels from glucose and albumin; microporous N-doped materials from glucose and algae; non-porous dual sulphur-nitrogen-doped carbon microspheres from glucose and cysteine or thiethyl-cysteine; hollow spheres doped solely with nitrogen, solely with sulfur or with both nitrogen and sulfur have been proposed [11]. The N-doping of activated carbon electrode by ammonium carbamate treatment has been shown to be effective in improving the durability against the high voltage charging for electric double layer capacitor [26]. Vanadium nitride/carbon nanotube (VN/CNTs) nanocomposites obtained by sol-gel synthesis of VN in presence of CNTs has been reported. Introduction of CNTs to obtain the VN/CNTs composites leads to a significant increase of the total surface area and pore volume. The VN nanoparticles are homogeneously dispersed and their rich-oxygenated surface is accessible for redox reactions with the electrolyte ions. The electrochemical properties of supercapacitors built with these nanocomposite electrodes are improved compared to a system built with VN or VN mechanically mixed with CNTs. Capacitances of 270 F/g of VN and 171 F/g of electrode were reported [27].

4.3. Carbon doped with Re-dox systems for Pseudo-Capacitance induced Supercapacitors

The technique called "super growth method" has been developed to mass-produce highly pure SWCNTs (hereinafter, referred to as "SG-SWCNTs") containing impurities such as metals and amorphous carbons in small amounts. The method enables to synthesize a few millimeter-long SWCNTs aligned perpendicularly on the substrate in a short time. Due

to these advantages, a SG-SWCNT capacitor cell can work at 3.5V achieving an energy density of 16 Whkg⁻¹ and a power density of 10 kWkg⁻¹. A 1400F capacitor cell has been produced [28]. The direct growth of graphene/SWCNT hybrids by CVD with FeMgAl layered double hydroxides as the catalyst precursor has also been reported. The combination of graphene and SWCNTs prevented them from aggregating and the unique structure endowed the high-rate transportation of electrolyte ions and electrons throughout the electrode matrix, which gave rise to the high electrochemical performance of the hybrids. A maximum specific capacitance of 156 F/g was obtained at a scan rate of 10 mV/s. The graphene/SWCNT electrode also showed a good cycle performance, and the capacity retains 95 % of the original value after 5000 cycles at a scan rate of 100 mV/s [29].

A low cost alternative treatment based on the introduction of redox-active molecules has been studied: The incorporation of the methylene blue-redox system to an MWCNT-based EDLC led to an increase of four and a half times the original cell capacitance value provided by MWCNTs in sulfuric acid (from 5 to 23 F.g⁻¹) with no significant increase in the ESR and an excellent long-term cycling behaviour (reduction of 12% in capacitance after 6,000 galvanostatic cycles). Capacitance values of 71 F/g and 131 F/g for anode and cathode have been reported [30]. Carbon-based electrochemical capacitors operating in different aqueous solutions with various dihydroxybenzenes as source of pseudocapacitance have been reported. The highest capacitance values (283 F g⁻¹ at 5 mV.s⁻¹) were observed for 0.38 mol.L⁻¹ hydroquinone dissolved in 1 mol.L⁻¹ H₂SO₄. Similar values were obtained for alkaline electrolyte with hydroquinone (275 F g⁻¹ at 5 mV s⁻¹) being higher than for electrolytes without dihydroxybenzenes [31].

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Hydrothermal carbonization: a greener route towards the synthesis of advanced carbon materials

Carbonización hidrotermal: una ruta “verde” de síntesis de materiales de carbono avanzados

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Abstract

This review paper provides an overview of the hydrothermal carbonisation (HTC) technology, a “green” and versatile strategy for the synthesis of advanced carbon materials suitable for a wide variety of applications of high impact in the current society. We will focus on the carbon formation mechanism, chemical and structural properties of hydrothermal carbons, porosity development, nanostructuring, functionalisation and applications.

Resumen

Este artículo de revisión proporciona una visión general de la tecnología de carbonización hidrotermal (HTC), estrategia “verde” y de gran versatilidad de síntesis de materiales de carbono útiles en una gran variedad de aplicaciones de gran impacto en la sociedad actual. Nos centramos en el mecanismo de formación del material carbonoso, sus propiedades químicas y estructurales, desarrollo de porosidad, nanoestructuración, funcionalización y aplicaciones.

1. Introducción

Carbon can be found in a wide variety of allotropes from crystalline (diamond, graphite) to amorphous (carbon black, activated carbon, glassy carbon, etc). In the past decade, the nanostructured forms of crystalline carbon (fullerenes [1], carbon nanotubes [2], graphene [3]) received increasingly attention due to their remarkable properties based on their unusual physico-chemical properties. The main disadvantage of using such crystalline nanocarbons for energy and environmental related application is their high production costs. This is related to the rather expensive fossil-based precursors and catalysts utilised, as well as to the complicated apparatus used for their production, normally involving high temperatures. Taking that into account, carbon materials derived from renewable resources such as, for example, biomass will play a very powerful role in this direction in the near future. So far, excluding activated carbons [4, 5], only little research has been done on the synthesis and characterisation of the structure of carbon materials based on natural resources. This is surprising, given that carbon material synthesis has been done since the beginning of civilization on the basis of biomass (through coal formation), with the petrochemical age being only a late deviation. Therefore, an approach towards advanced carbon synthesis based on renewable resources, mimicking the natural process of coal formation, would be a significant operation, as the final products represent a significant proportion of modern materials.

Biomass is highly available and recyclable, and can be either transformed into biofuels (bioethanol [6, 7], biodiesel [8, 9]) as a replacement of the fossil-based fuels, or can be converted into highly valuable “green” carbon. Conversion of biomass into “green” carbon by different processes than classical pyrolysis

is crucial, since it allows fine tuning of the carbon chemical structure and morphology in order to meet the required applications. This is where the highly unconventional technique of hydrothermal carbonisation, denoted from here on as HTC, comes into play.

In HTC, pure carbohydrates as well as raw lignocellulosic biomass wastes are converted into valuable carbon materials using water as a carbonisation medium at mild temperatures (< 200 °C) under self-generated pressures [10]. Even though this methodology was developed almost 100 years ago [11], its full potential as a synthetic route for carbon materials having important applications in several crucial fields of 21-st century such as catalysis, energy storage, CO₂ sequestration, water purification, agriculture, has been revealed only in the past few years, with main contributions from the authors of this current review. This paper will offer an overview on the recently developed HTC technology including formation mechanism and final chemical structure, porous materials, heteroatom doping, hybrid carbon-inorganic materials and various applications.

2. Formation Mechanism

The formation of HTC-based materials is a very complex process due to the multitude of simultaneous reactions occurring in the autoclave during the hydrothermal treatment. In order to study the transformation mechanism into HTC material, glucose was selected as a good model carbon source and ¹³C-enriched samples were prepared [12]. ¹³C NMR was used to investigate the chemical composition and local structure of the hydrothermally treated materials. Several standard MAS-NMR techniques (singe pulse (SP), cross-polarization (CP) and inversion recovery cross-polarization (IRCP)) were used to identify the amount and type of sp² and sp³ carbon sites. In addition, bond filtering techniques based on J-coupling (insensitive nuclei-enhanced by polarization transfer (INEPT)) provided a clear-cut distinction between protonated and quaternary carbons. Finally, the connectivity between carbon species was identified using a 2D ¹³C-¹³C correlation experiment based on double-quantum excitation of through-space dipolar-coupled nuclei. It was found that about 60% of the carbon atoms belong to a cross-linked furan-based structure. Furan moieties are directly linked either via the R-carbon or via sp²- or sp³-type carbon groups, where cross-linking can occur. Additional cross-linking sites are located at the carbons of the furan ring (Figure 1).

HTC was proposed to form upon the dehydration of hexoses (glucose and fructose) to HMF and of pentoses (xylose) to furfural [13]. Once these compounds are formed, they then undergo a very complex chemical cascade involving a simultaneous combination of ring-opening reactions to create diketones that can further undergo aldol-type condensations with the furan ring, while Diels-Alder

reactions may lead to more aromatic features, with concurrent polycondensation reactions also occurring. In summary, a set of dehydrations, polymerization (condensation and addition), and aromatization reactions will lead to the final chemical structure of HTC, which is composed of condensed furan rings bridged by aliphatic regions with terminal hydroxyl and carbonyl functional groups (Figure 1). Upon the "polymerization" of HMF or furfural, nucleation takes place followed by growth of the particles upon further incorporation of HMF-derived monomers, leading to spherically shaped particles (Figure 1).

Recently, Titirici, Falco and Baccile embarked on a project to examine the HTC of microcrystalline cellulose as well as of real lignocellulosic biomass (i.e. rye straw) and compare the chemical structure of cellulose and rye straw HTC materials to the ones derived from glucose [14]. ^{13}C solid-state NMR was used once more for the characterization and comparison of HTC materials derived from glucose, cellulose, and rye straw. In the case of glucose, changing the processing temperature allows control of both the particle diameter and particle size distribution. The final carbon chemical structure can be switched from a carbonaceous polyfuran rich in oxygen-containing functional groups to a carbon network of extensive aromatic domains. On the other hand, in the case of cellulose and generally of lignocellulosic biomass, a fundamental difference in the HTC mechanism is observed. The polyfuranic intermediate, which is characteristic for glucose-derived HTC materials at either low processing temperatures or short reaction times, cannot be observed in cellulose derived HTC carbons. In contrast, the biomass-derived HTC materials show a well-developed aromatic nature, formed already during the early stages of HTC reaction. Thus, under mild hydrothermal operating conditions (180–250 °C), cellulose reacts according to a reaction scheme that can be more associated with the classical pyrolysis process, even if the exact chemical paths are not clear yet. This study also showed how lignin is only mildly affected by HTC process and how its presence influences the final material structuring. Therefore, converting cellulose and lignocellulosic biomasses into HTC with the same chemical structure and morphology like glucose remains a very challenging task in HTC.

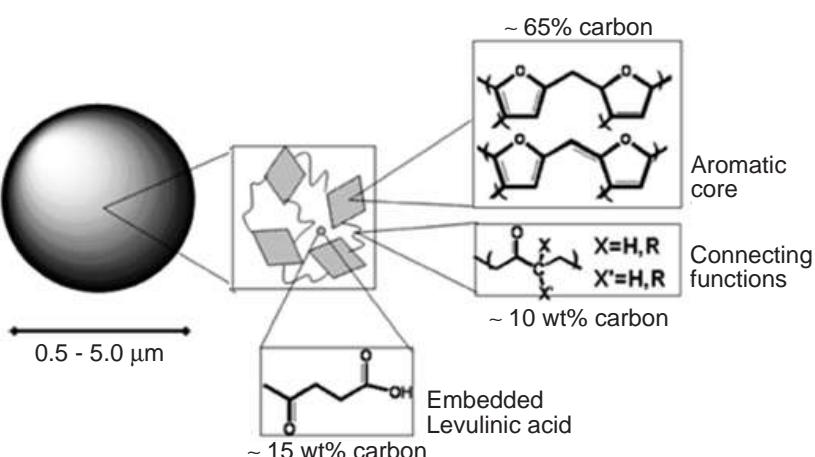
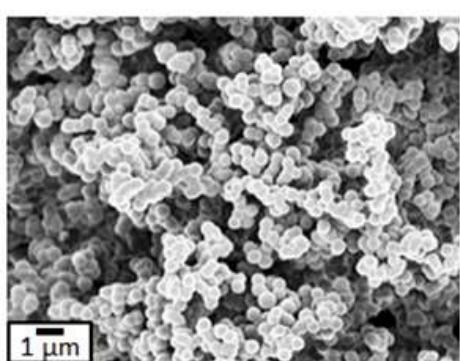


Figure 1. SEM micrograph of HTC material obtained from glucose at 180 °C after 12 h and a schematic representation of its chemical structures base on an NMR study. Adapted with permission from Baccile N, Laurent G, Babonneau F, Fayon F, Titirici MM, Antonietti M.; *J. Phys. Chem. C* 2009; 113(22):9644-9654 (copyright © 2009, American Chemical Society).

Figura 1. Imagen de SEM de un material HTC obtenido a partir de glucosa tratada a 180 °C y durante 12 h, y representación esquemática de su estructura química basándose en un estudio de RMN. Adaptado con permiso de Baccile N, Laurent G, Babonneau F, Fayon F, Titirici MM, Antonietti M.; *J. Phys. Chem. C* 2009; 113(22):9644-9654 (copyright © 2009, American Chemical Society).

3. Porous HTC

One of the main disadvantages of the HTC materials is that they present limited porosity and surface area. For certain applications, such textural nanoscale porosity is highly desirable. There are many well established technologies to produce porous carbons among which the most common ones are chemical activation [15] and templating methodologies [16].

3.1 Chemical Activation

Sevilla et al. were the first to report on the chemical activation of HTC materials as a way to generate highly porous materials [17, 18]. They applied the procedure to HTC materials derived from glucose, starch, furfural, cellulose and eucalyptus sawdust (Figure 2), achieving large apparent surface areas, up to ~ 3000 m²/g, and pore volumes in the 0.6-1.4 cm³/g range. Those materials are further characterized by narrow micropore size distributions in the supermicropore range (0.7-2 nm). Tuning of the PSD was achieved through the modification of the activation temperature (600-850 °C) and the amount of KOH used (KOH/HTC weight ratio = 2 or 4).

Afterwards, Falco and Lozano-Castelló investigated the development of porosity in HTC materials derived from glucose, cellulose and rye –straw using KOH as an activating agent at 750 °C and KOH ratio = 3 (results not published). Overall, this analysis highlights that the HTC temperature extensively affects the porosity of the derived ACs. HTC carbons synthesized at higher temperatures (e.g. 280 °C) generate ACs with a lower porosity development and narrower PSDs, while the ones produced at 180–240 °C develop a much larger porosity characterized by a greater mesopores fraction. These trends can be explained by taking into account the dependence of the chemical nature of HTC carbons upon the synthesis temperature: higher temperatures generate HTC carbons with a higher degree of aromatization resulting in enhanced chemical stability and structural order. As observed for the hydroxide activation of several coals, both features are detrimental to the reactivity of the carbon substrate leading to a reduced porosity development.

3.2 Nanocasting

In the literature there are a multitude of techniques for introducing porosity into carbon materials [19].

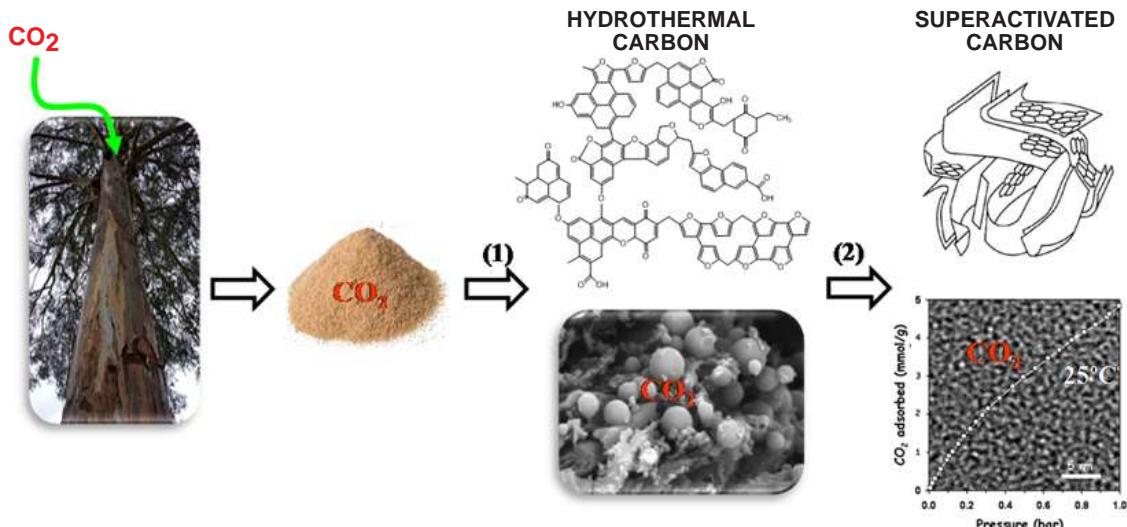


Figure 2. Schematic illustration of the overall synthesis procedure for HTC-based activated carbons and their application in CO₂ capture: (1) hydrothermal carbonization at 230–250 °C (2 h), and (2) chemical activation with KOH.

Figura 2. Ilustración esquemática del proceso de síntesis de carbones activos a partir de sustancias carbonizadas hidrotermalmente y su utilización en la captura de CO₂: (1) HTC a 230-250°C (2 h), y (2) activación química con KOH.

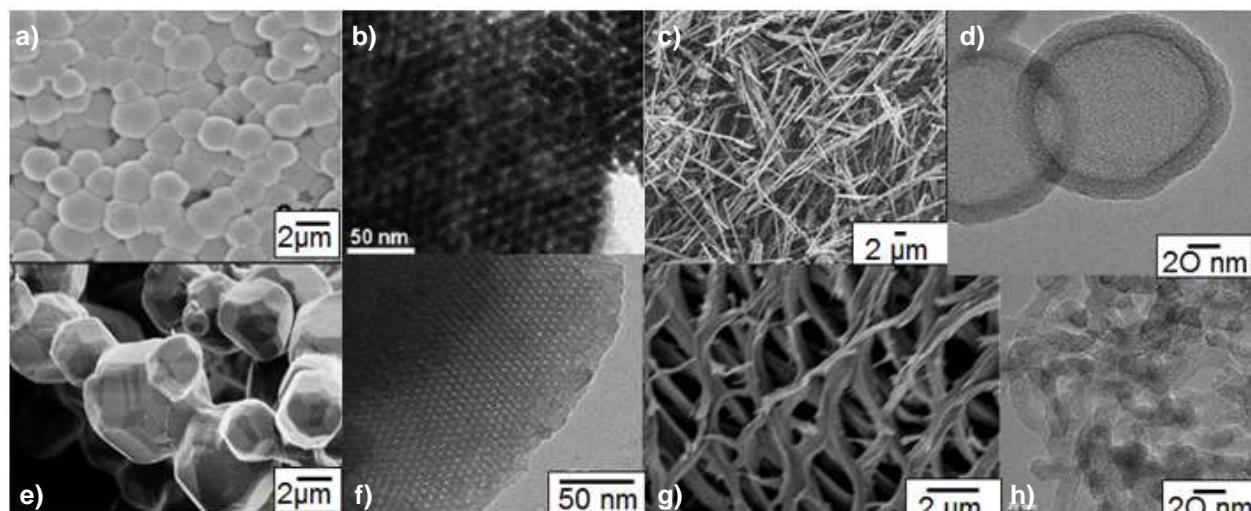


Figure 3. Porous HTCs: (a) Mesoporous HTC microspheres obtained by replication of silica using glucose (Reprinted with permission from Titirici M-M, Thomas A, Antonietti M; *Adv. Funct. Mater.* 2007;17(6):1010-1018; copyright © 2009, American Chemical Society). (b) Ordered mesoporous HTC obtained by replication of SBA-15 using furfural (Reprinted with permission from Titirici M-M, Thomas A, Antonietti M; *J. Mater. Chem.* 2007;17(32):3412-3418; copyright © 2009, American Chemical Society). (c) HTC tubular carbons obtained using a macroporous alumina membrane as template and furfural as a carbon source (Reprinted with permission from Kubo S, Tan I, White RJ, Antonietti M, Titirici MM; *Chem. Mater.* 2010;22:6590-6597; copyright © 2009, American Chemical Society). (d) HTC hollow spheres produced using latex nanoparticles as sacrificial templates and glucose as a carbon source (Reprinted with permission from White RJ, Tauer K, Antonietti M, Titirici M-M; *J. Am. Chem. Soc.* 2011;132(49):17360-17363; copyright © 2009, American Chemical Society). (e; f) Micro-mesoporous ordered HTC particles synthesized in the presence of amphiphilic block copolymers as soft templates and fructose as a carbon source (Reprinted with permission from Kubo S, White RJ, Yoshizawa N, Antonietti M, Titirici M-M; *Chem. Mater.* 2009;21(22):4882-4885; copyright © 2009, American Chemical Society). (g) N-doped porous carbon obtained using shrimp/lobster food wastes after HTC and removal of CaCO₃ (Reprinted with permission from White RJ, Antonietti M, Titirici M-M; *J. Mater. Chem.* 2009;19(45):8645-8650; copyright © 2009, American Chemical Society). (h) Porous N-doped carbon aerogel obtained using the natural interactions between carbohydrates and gelating proteins (i.e. ovalbumin) (Reproduced from White RJ, Yoshizawa N, Antonietti M, Titirici M-M; *Green Chem.* 2011;13:2428-2434, with permission from The Royal Society of Chemistry).

Figura 3. HTCs porosos: (a) Microesferas mesoporosas de HTC obtenidas mediante n de sílice usando glucosa (Reproducido con permiso de Titirici M-M, Thomas A, Antonietti M; *Adv. Funct. Mater.* 2007;17(6):1010-1018; copyright © 2009, American Chemical Society). (b) HTC con mesoporosidad ordenada obtenido mediante nanomoldeo de SBA-15 utilizando furfural (Reproducido con permiso de Titirici M-M, Thomas A, Antonietti M; *J. Mater. Chem.* 2007;17(32):3412-3418; copyright © 2009, American Chemical Society). (c) Carbones tubulares HTC obtenidos a partir del nanomoldeo de una membrana macroporosa de alúmina y furfural como fuente de carbono (Reproducido con permiso de Kubo S, Tan I, White RJ, Antonietti M, Titirici MM; *Chem. Mater.* 2010;22:6590-6597; copyright © 2009, American Chemical Society). (d) Esferas huecas de HTC preparadas mediante el empleo de nanopartículas de latex como molde y glucosa como fuente de carbono (Reproducido con permiso de White RJ, Tauer K, Antonietti M, Titirici M-M; *J. Am. Chem. Soc.* 2011;132(49):17360-17363; copyright © 2009, American Chemical Society). (e; f) Partículas de HTC con micro-mesoporosidad ordenada sintetizadas en presencia de copolímeros en bloque anfifílicos y fructosa como fuente de carbono (Reproducido con permiso de Kubo S, White RJ, Yoshizawa N, Antonietti M, Titirici M-M; *Chem. Mater.* 23(22):4882-4885; copyright © 2009, American Chemical Society). (g) Carbones porosos dopados con N preparados mediante HTC de residuos de gamba/langostas y eliminación del CaCO₃ (Reproducido con permiso de White RJ, Antonietti M, Titirici M-M; *J. Mater. Chem.* 2009;19(45):8645-8650; copyright © 2009, American Chemical Society). (h) Aerogeles porosos de carbón dopados con N sintetizados usando las interacciones naturales entre hidratos de carbono y proteínas gelatinizantes (i.e. ovoalbúmina) (Reproducido de White RJ, Yoshizawa N, Antonietti M, Titirici M-M; *Green Chem.* 2011;13:2428-2434, con permiso de The Royal Society of Chemistry).

In hard templating, a preformed porous solid is infiltrated with the carbon precursor and the carbonization occurs inside the pores, followed by original scaffold removal, yielding a carbon porous replica. This technique was intensively used for the replication of ordered silica materials (e.g. SBA-15 [20]) into the corresponding ordered porous materials CMK-3 and CMK-5 [21]. More recently, a soft-templating approach in carbon was developed by Zhao et al. [22] and Dai et al. [19] who demonstrated a direct route to ordered carbons via organic–organic block copolymer self-assembly (e.g. Pluronic: F127) and suitable aromatic carbon precursor (e.g. phloroglucinol or resorcinol).

From a sustainable and economic footing, it would be advantageous if renewable precursors could be employed in a simple, scalable (potentially carbon neutral) process (i.e. HTC) in the direct synthesis of such ordered porous carbonaceous materials. This has been demonstrated by combining the HTC of glucose with hard templates for the production of mesoporous spheres (Figure 3a) [23], ordered carbon materials (HTC-CMK-3, -5) (Figure 3b) [24], tubular carbon (Figure 3c) [25], and hollow carbon spheres (Figure 3d) [26]. However, the hard templating route using silica is tedious because of problematic infiltration procedures as well as template removal, which normally involves harsh and non-environmentally friendly conditions. In this respect, soft templating was also successfully implemented in HTC. The use of Pluronic amphiphilic block copolymers as structure-directing agents and fructose as a carbon source enabled the production of HTC materials with well-defined ordered micro- or mesopores (Figure 3e, f) [27].

A porous nitrogen-doped carbon was originally prepared taking advantage of the crustacean shells of shrimps and lobsters as natural templates. Here, the CaCO_3 nanoparticles served as removable hard templates, while chitin as a N-doped carbon source (Figure 3g) [28]. Another unique procedure to produce porous N-doped carbons was based on the natural interactions between carbohydrates (glucose) and gelating proteins. Depending on the applied conditions, either nitrogen-doped carbon nanoparticles [29] or monolithic hierarchically porous N-doped carbons were obtained in the absence of sacrificial templates (Figure 3h) [30].

4. Heteroatoms Doped HTCs

The introduction of dopants into carbon materials is a useful method of altering their physical and chemical properties. Successful work so far includes the superior performance of doped carbons in applications such as electrode materials for catalysis [31] or energy storage [32], stationary phases [33], and chemoselective adsorption [34].

The majority of research in this field has focused on N doping, which is known to induce favorable changes in the carbon material, e.g. increased conductivity [35] and high activity in the Oxygen Reduction Reaction (ORR) in fuel cells [36]. The synthesis of N-doped carbons has been achieved via a variety of pathways, such as post treatment of carbon with ammonia [37], amines or urea [38], and also more direct approaches using acetonitrile [39], pyrrole [40], polyacetonitrile [32] or polyaniline [41] as starting products.

Concerning sustainability, most of the aforementioned synthesis methods for heteroatom doped carbon materials show drawbacks in terms of the often harsh reaction conditions used. In order to avoid these

aspects a HTC route was chosen to produce materials with similar properties in a sustainable fashion. Thus, N-doped carbon microspheres were obtained by hydrothermally treating naturally occurring and nitrogen containing compounds, such as glycine [12], N-acetyl glucosamine [42] or chitosan [43]. Albumin, a glycoprotein, was also used as structure directing additive in the HTC of glucose to produce nitrogen doped carbon aerogels [30]. Nitrogen is covalently incorporated into HTC via Maillard chemistry (i.e. group of reactions occurring between reducing sugars and amino containing molecules [44]). As previously stated, HTC is formed via HMF, which can interact with amino acids/proteins and with Maillard reaction intermediates in countless possible combinations of reactants and reaction cascades. Either aliphatic nitrogen (i.e amines) or nitrogen already incorporated into a heterocycle (i.e pyrrole) can be formed under the employed hydrothermal conditions. Upon further calcination under an inert atmosphere (to increase the conductivity, i.e. for electrochemical applications), the same amount of dopant will be maintained in the resulting carbons. This is not the case for the direct pyrolysis of N-containing precursors or reagents where most of the N is lost as volatile gas. Therefore, HTC represents a powerful modality to introduce large amounts of N, as well as to mediate the type of N at low temperatures. We also need to mention that upon further pyrolysis, all the N groups are in an aromatic environment, either as pyridinic, pyridonic or quaternary N groups. Such N-doped HTCs already showed improved electric and thermal conductivities as compared with the non-doped materials [45].

Complementing nitrogen as a dopant, sulfur is receiving increasing attention in current carbon materials research. Due to its large size, S has been used more for applications where its easily polarizable lone pairs (and thus chemical reactivity) are of importance. The synthesis of these S-doped materials generally involves the pyrolysis of S-containing polymer based carbons [34, 36], but also arc vaporization in the presence of S-containing compounds such as thiophenes [36]. Concerning the combined incorporation of S and N within the same material, only a few reports exist in the literature [47, 48]. Here again HTC appears as a “greener” route towards the synthesis of S- or N- and S-doped carbon materials. For the S-doped materials, 2-thiophene carboxaldehyde (TCA) has been used, while the dual S- and N-doping has been done using cysteine (C) or S-(2-thienyl)-L-cysteine (TC) as additive during the HTC of glucose [49]. S can be incorporated either into the final HTC structure via nucleophilic or electrophilic substitutions. Addition of cysteine gave rise to a material with more pending functional groups such as thiols, amides and sulfonates. Addition of thienyl-cysteine, on the other hand, resulted in more structurally bound S, such as in thiophenes. After pyrolysis at 900 °C, the resulting materials showed almost three times higher specific conductivity than a corresponding undoped sample made from pure glucose.

5. HTC-inorganic hybrids

Controlled synthesis of carbonaceous nanocomposites has become a hot research area and led to many important results due to their combined and improved properties, with highly potential values in many fields. Two main methodologies can be distinguished for the production of hydrothermal carbon nanocomposites: post-modification and *in situ* synthesis.

Many carbon-inorganic materials have been prepared using the hydrothermal technology and due to space constraints we cannot mention all these examples. We will limit instead to a few examples. Regarding coating of pre-formed inorganic nanoparticles, silicon/carbon (Figure 4a) as well as LiFePO₄/carbon (Figure 4b) materials have been reported. Both of these composites were successfully applied respectively as anode [50] and cathode [51] in Li Ion Batteries (*vide infra*).

The important advantage of HTC materials is, as previously mentioned, their rich surface functional groups, such as hydroxyl, aldehyde, and carboxyl groups. These surface functional groups have shown remarkable reactivity toward various inorganic precursors. For example, based on the redox reaction, they could *in situ* reduce and stabilize noble-metal ions forming very fine noble-metal nanostructures, such as Ag, Au, Pt, and Pd [52-56]. The advantages of this one-step HTC process include the following: i) the carbonization process and the reduction and growth of noble metal ions proceed simultaneously, ii) the noble-metal ions can catalyze the carbonization process, and iii) it is the one-step process which can potentially be up scaled. One example is the synthesis of silver-carbonaceous nanocables (Figure 4c). These nanocables contain

pentagonal-shaped silver nanowire cores and tend to branch or fuse with each other. Pd@C core-shell nanoparticles have also been successfully synthesized by the one-step HTC process and shown selective catalytic capability for the batch partial hydrogenation of hydroxyl aromatic derivatives (Figure 4d) [56].

Titirici et al. have also reported a generalized method to produce metal oxide hollow spheres using various inorganic salts during the hydrothermal carbonization of glucose [57]. After the synthesis, the carbon is burned off while the metal ions agglomerate around into hollow carbon nanoparticles (Figure 4e, i.e. Fe₂O₃ hollow spheres). In a similar fashion, HTC can also be used to incorporate pre-formed SnO₂ nanoparticles onto HTC spheres. Likewise, after the removal of carbon, mesoporous SnO₂ spheres can be obtained (Figure 4f) [58].

6. Applications of HTC materials

The most appealing feature of HTC is the fact that it represents an easy, green and kg-scalable process allowing the production of various carbon and hybrid nanostructures with practical applications on a price base which is comparatively lower than corresponding petrochemical processes. Even though relatively in their infancy, HTC materials have already found

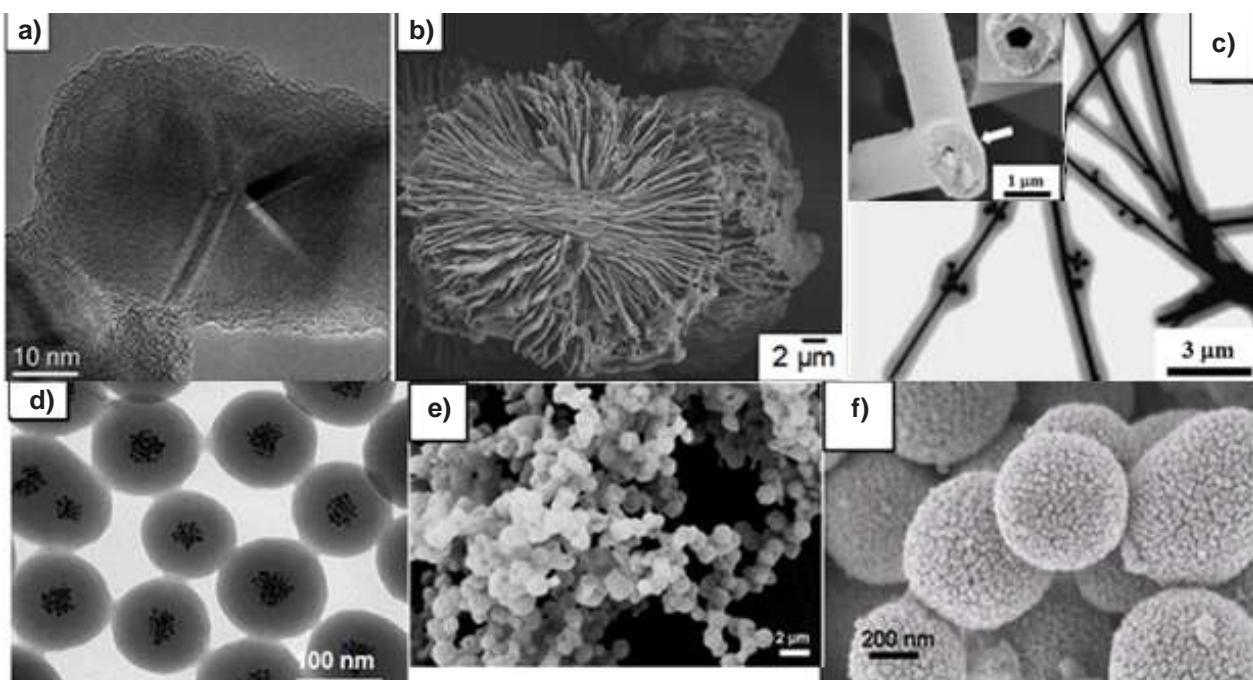


Figure 4. (a) Si nanoparticle coated hydrothermally with a thin layer of carbon from glucose (Reprinted with permission from Hu Y-S, Demir-Cakan R, Titirici MM, Muller JO, Schlogl R, Antonietti M, Maier J, Angew. Chem. Int. Ed. 2008;47(9):1645-1649; copyright © 2008 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim); (b) LiFePO₄ coated with carbon (Reprinted with permission from Popovic J, Demir-Cakan R, Tornow J, Morcrette M, Su DS, Schlogl R, Antonietti M, Titirici MM. Small 2011;8:1127-35; copyright © 2011 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim); (c) TEM micrograph of Ag/HTC nanocables obtained from starch and AgNO₃ at 160°C for 12 h (Adapted from Yu SH, Cui XJ, Li LL, Li K, Yu B, Antonietti M, Cölfen H; Adv. Mater. 2004;16:1636-1640); (d) Pd@HTC core/shell particles (Taken with permission from Makowski P, Cakan RD, Antonietti M, Goettmann F, Titirici M-M; Chem. Comm. 2008(8):999-1001; copyright © 2008, Royal Society of Chemistry); (e) SEM picture of the iron oxide hollow spheres (Reprinted with permission from Titirici M-M, Antonietti M, Thomas A; Chem. Mater. 2006;18(16):3808-3812; copyright © 2006, American Chemical Society); (f) SnO₂ mesoporous spheres (Reprinted with permission from Demir-Cakan R, Hu Y-S, Antonietti M, Maier J, Titirici M-M; Chem. Mater. 2008;20(4):1227-9; copyright © 2008, American Chemical Society).

Figura 4. (a) Nanopartículas de Si recubiertas hidrotermalmente con una fina capa de carbono obtenida a partir de glucosa (Reproducido con permiso de Hu Y-S, Demir-Cakan R, Titirici MM, Muller JO, Schlogl R, Antonietti M, Maier J, Angew. Chem. Int. Ed. 2008;47(9):1645-1649; copyright © 2008 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim); (b) LiFePO₄ recubierto con carbono (Reproducido con permiso de Popovic J, Demir-Cakan R, Tornow J, Morcrette M, Su DS, Schlogl R, Antonietti M, Titirici MM. Small 2011;8:1127-35; copyright © 2011 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim); (c) fotografía de TEM de nanocables de Ag/HTC obtenidos a partir de almidón y AgNO₃ a 160 °C durante 12 h (Adaptado de Yu SH, Cui XJ, Li LL, Li K, Yu B, Antonietti M, Cölfen H; Adv. Mater. 2004;16:1636-1640); (d) partículas con estructura tipo core/shell Pd@HTC (Reproducido con permiso de Makowski P, Cakan RD, Antonietti M, Goettmann F, Titirici M-M; Chem. Comm. 2008(8):999-1001; copyright © 2008, Royal Society of Chemistry); (e) imagen de SEM de esferas huecas de óxido de hierro (Reproducido con permiso de Titirici M-M, Antonietti M, Thomas A; Chem. Mater. 2006;18(16):3808-12; copyright © 2006, American Chemical Society); (f) Esferas mesoporosas de SnO₂ (Reproducido con permiso de Demir-Cakan R, Hu Y-S, Antonietti M, Maier J, Titirici M-M; Chem. Mater. 2008;20(4):1227-9; copyright © 2008, American Chemical Society).

numerous applications including soil enrichment, catalysis, water purification, energy storage, and CO₂ sequestration. In the following paragraphs, examples where HTC based materials have proved to be not only sustainable, but to possess extraordinary properties which in some cases surpass those of current "golden standards" will be summarized.

6.1. Agricultural applications

Much attention is currently focused on obtaining charcoal from slow-pyrolysis processes with the final aim of adding it to soils as a carbon sink and as a means of improving soil productivity. In this context, the charred material is denoted "biochar" [59, 60]. By analogy, the charred product obtained via the HTC process can be called "hydrochar". The advantage of converting biomass into hydrochar via the HTC process is that it can transform wet input material into carbonaceous solids at relatively high yields without the need for an energy-intensive drying step before or during the process. This opens up the feedstock choice to a variety of non-traditional sources: wet animal manures, human waste, sewage sludge, municipal solid waste, as well as aquaculture and algal residues. These feedstocks represent large, continuously generated, renewable streams that require some degree of management, treatment and/or processing to ensure protection to the environment.

In order to predict the behaviour of different hydrochars in soil it is very important to understand the final chemical structure of the employed biomass-derived carbon. In this regard, several groups have compared the chemical and physical properties of the materials obtained using the same precursor by pyrolysis or HTC: swine manure [61], corn stover [62] or carbohydrates and cellulose in general [63]. Those works show that pyrolysis provides arene-rich chars, whereas HTC gives rise to furan-rich chars, which contain as well abundant oxygen groups. Although there are many reports on the effect of the addition of biochar to soils, only Steinbeiss et al. [64] and Rillig et al. [65] have investigated the impact of hydrochar. Their results evidence that hydrochar should be carefully tested and optimised before applications in the field are undertaken.

6.2. Adsorption

6.2.1. Liquid phase. Adsorption is by far the most frequent application of activated carbons. Contrary to activated carbons, hydrothermal carbons produced at T = 180 °C do not have any microporosity unless further thermally treated or chemically activated. This is however counterbalanced by the high number of oxygenated groups located at their surface which can promote adsorption. Furthermore, these functionalities can be easily tuned by further surface modifications. Thus, as shown by Demir-Cakan et al., the addition of small amounts of vinyl organic monomers into the HTC of D-glucose leads to the production of carbon materials rich in carboxyl functionalities [66]. The synthesised materials were investigated in adsorption experiments for the removal of heavy metals from aqueous solutions. The adsorption capacity was as high as 351.4 mg per g for Pb (II) and 88.8 mg per g for Cd (II), which is well beyond ordinary sorption capacities, proving the efficiency of the materials to bind and buffer ions, or more specifically to remove heavy metal pollutants. Afterwards, Chen et al. followed a different approach for the introduction of carboxylic groups into the HTC products, consisting of their post-treatment in air

[67]. In this way, the adsorption capacity of the sample treated in air at 300°C was 326.1 ± 3.0 mg/g for Pb²⁺ and 150.7 ± 2.7 mg/g for Cd²⁺, values 3 and 30 times higher than that of HTC material.

6.2.2. Gas adsorption. CO₂ capture and H₂ storage are two of the current hot topics in energy and environmental science. Their physisorption in porous solids have attracted keen interest and is one of the most promising alternatives. As previously mentioned, HTC materials lack porosity development, which hinders their application in such porosity/surface area-sensitive applications. As also mentioned, Sevilla et al. circumvented that inconvenient by applying a chemical activation process with KOH (Figure 2), proving that such process is a powerful tool for the creation of porosity in HTC materials. When tested as hydrogen storage media in cryogenic conditions (-196°C), those materials exhibited capacities of ~2.5 wt% at 1 bar and in the 5.3-5.6 wt% range at 20 bar [17]. These hydrogen uptakes are in most cases superior to those obtained for other activated carbons with larger surface area under similar conditions. With regards to CO₂ capture, it was analyzed at a pressure of 1 bar and three adsorption temperatures (0, 25 and 50 °C) [18]. The HTC-based activated carbons exhibited CO₂ capture capacities up to 6.6 mmol CO₂/g at 0 °C, 4.8 mmol/g at 25 °C and 3.6 mmol/g at 50 °C. The outstanding adsorption uptakes are ascribed to the fact that a large fraction of the porosity corresponds to narrow micropores, which have strong adsorption potentials that enhance their filling by the CO₂ molecules. Additionally, the CO₂ adsorption is very fast, whereas N₂ adsorption is slower and much lower. In this way, the CO₂/N₂ selectivity measured under equilibrium conditions is 5.4. Furthermore, those sorbents are easily, quickly and fully regenerated by flowing a He stream at 25°C.

Another interesting approach in relation to the use of HTC materials for CO₂ capture is based on their functionalization with amine groups, which exhibit a high affinity to CO₂. In this respect, Titirici et al. reported the CO₂ capture by means of an amine-rich HTC product [68]. This material was prepared by a two-step process: a) hydrothermal carbonization of glucose in presence of small amounts of acrylic acid and b) functionalization of carboxylic-rich HTC products with triethylamine. This aminated HTC material shows high CO₂ capture capacities (up to 4.3 mmol CO₂/g at -20°C). More important, these materials exhibit a very high CO₂/N₂ selectivity, up to 110 at 70 °C.

6.3. Energy storage

Energy storage is necessary to i) make viable the use of renewable sources, such as wind or solar, as their supply is not continuous, ii) for increasing the efficiency of the use of energy (power levelling), iii) protection against power loss and iv) use of mobile equipments. Supercapacitors and Li-ion batteries are the two "star" energy storage devices. Whereas supercapacitors are of great interest as high power electrochemical energy storage devices, Li-ion batteries stand out for long-term energy supply.

6.3.1. Supercapacitors. This is another surface area-dependent application. Therefore, works related to the use of HTC materials as supercapacitors electrodes are based on a chemical activation process following the HTC treatment. Thus, Wei et al. analyzed the supercapacitor performance in organic electrolyte (1 M TEABF₄ in acetonitrile) of HTC cellulose (C), starch (S) and sawdust (W)

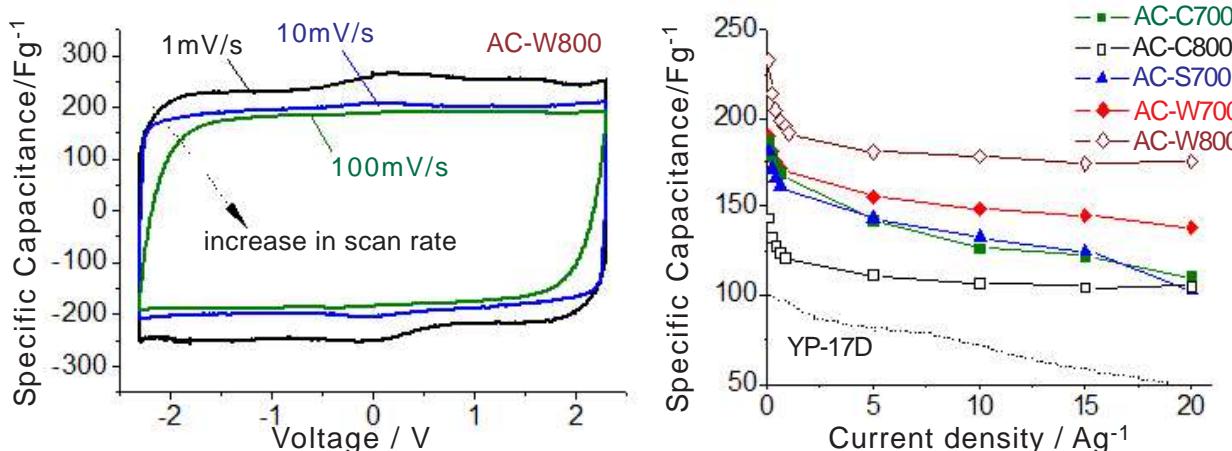


Figure 5. Electrochemical characterization of HTC-derived activated carbons in 1 M TEABF₄ solution in acetonitrile at room temperature: a) cyclic voltammograms (CV) of the activated carbon obtained from sawdust at 800°C (AC-W800) and b) capacitance retention with current density in comparison with that of commercially available YP-17D activated carbon (Reprinted with permission from Wei L, Sevilla M, Fuertes AB, Mokaya R, Yushin G; Adv. Energy Mater. 2011;356-61; copyright © 2011 WILEY-VCH Verlag GmbH& Co. KGaA, Weinheim).

Figura 5. Caracterización electroquímica de carbones activos obtenidos a partir de materiales HTC en una disolución 1M de TEABF₄ en acetonitrilo a temperatura ambiente: a) voltametría cíclica del carbón activo obtenido a partir de serrín a 800°C (AC-W800) y b) evolución de la capacidad específica con la densidad de corriente en comparación con el carbón activo comercial YP-17D (Reproducido con permiso de Wei L, Sevilla M, Fuertes AB, Mokaya R, Yushin G; Adv. Energy Mater. 2011;356-61; copyright © 2011 WILEY-VCH Verlag GmbH& Co. KGaA, Weinheim).

activated at 700 and 800°C with a KOH/sample weight ratio = 4 [69]. The performance of those materials was spectacular, recording the highest capacitance ever reported for porous carbons in a symmetric two-electrode configuration using such electrolyte, i.e. 236 F/g (100 F/cm³) at 1 mV/s (Figure 5a). It exceeded the specific capacitance of commercial activated carbons optimized for EDLC applications, such as YP-17D, by 100 %. What is more, the samples were capable of retaining 64 to 85% of the capacitance when the current density was increased from 0.6 to 20 A/g (Figure 5b).

Zhao et al. have analyzed the capacitance behaviour of N-containing HTC carbons activated with KOH (weight ratio of KOH to hydrothermal carbons = 1 to 4, and T = 600°C) [42]. Those materials exhibited excellent electrochemical performance in KOH 6 M and H₂SO₄ 1 M, achieving specific capacitances up to 220 and 300 F/g at a current density of 0.1 A/g in the basic and acidic electrolyte respectively. This superior capacitance is due to the combination of EDLC capacitance and pseudocapacitance arising from redox reactions of the nitrogen functionalities. Thus, humps were detected at around 0.5 V vs. SCE. Additionally, good capacitance retention at high current density (4 A/g) was observed, which proves good conductivity and quick charge propagation in both electrolytes.

6.3.2. Li-ion batteries. Carbon is the most used negative electrode material in Li-ion batteries. In this regard, HTC materials have also been used as electrodes in Li-ion batteries. The first study performed by Wang et al. demonstrated that the reversible lithium insertion/extraction capacity of this kind of material is much higher than the theoretical capacity of graphitised carbonaceous materials [70]. The performance of hollow HTC nanospheres as anodes in Li⁺ as well as Na⁺ ion batteries has also been studied [71]. The reversible capacity at a 1C rate could reach up to 370 mA h/g. Even at the very high rate of 50C (18.6 A/g), a capacity of ~100 mA h/g is still maintained. This value is much higher than traditional graphite electrode (almost negligible at such a high rate).

Besides the use of pure HTC materials as electrodes in Li-ion batteries, great importance has been given to the utilisation of HTC/inorganic composites as electrode materials. In this regard, Hu et al. successfully in situ coated commercially available Si nanoparticles with a thin layer (10 nm) of HTC material via the conversion of D-glucose [50]. The resulting composite was further carbonised to increase the conductivity of the carbon layer resulting in a Si/SiO_x/C composite with a markedly improved cyclability compared with pure Si. The reversible capacity was as high as 1100 mA h/g at a current density of 150 mA/g. Similarly, mesoporous SnO₂ microspheres were synthesized using HTC of furfural in the presence of SnO₂ nanoparticle sols (Figure 4f) [58]. The stable reversible capacities were ~370 and 200 mA h/g at the current densities of 1 and 2 A/g.

The development of improved cathode materials is recognised as even more challenging than anode materials. In this respect, olivine LiFePO₄ is considered one of the most promising cathode materials for Li-ion batteries. Urchin-like hierarchical mesocrystals of pristine LiFePO₄, as well as carbon coated LiFePO₄ composites, have been synthesized by Popovic et al. using a simple one-step solvothermal method (Figure 4b) [51]. The lithium storage performance of the pure LiFePO₄ was compared with that of its carbon-coated counterparts, proving to be superior.

6.4. Energy production

Fuel cells have received increasing attention over the last decade for their potential to be a key component of a future green energy system. Among the different types, polymer electrolyte and direct methanol fuel cells (PEMFC and DMFC respectively) are very promising candidates for vehicle and other portable applications due to their quick start-up, compactness and light weight, high power density and simplicity. However, the main barriers for the commercial utilization of these devices are the high cost and short durability of the catalyst (Pt), which is used to initiate the reactions both in the anode and cathode. Intensive research is therefore being

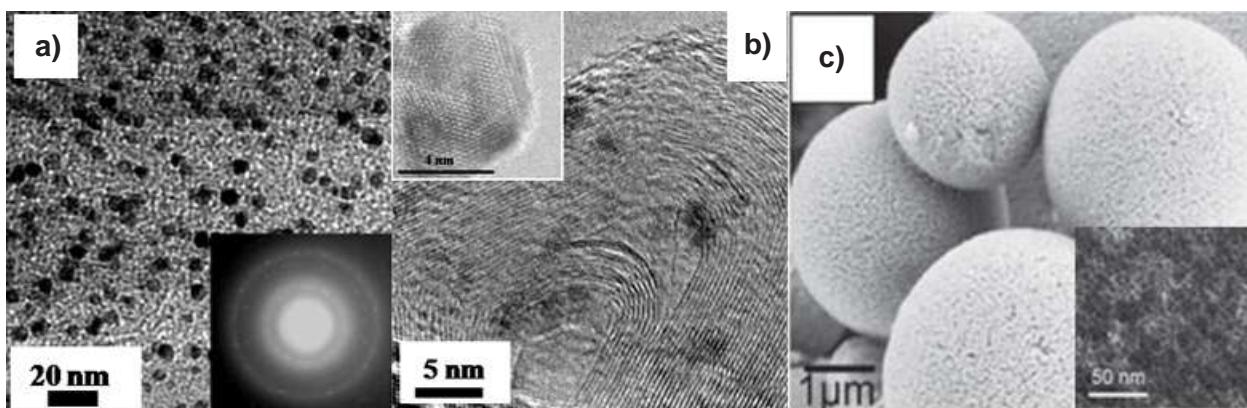


Figure 6. a) HRTEM image of Pt nanoparticles deposited over HTC hard carbon spherules (inset: selected area electron diffraction pattern of Pt nanoparticles) (Reprinted with permission from Yang R, Qiu X, Zhang H, Li J, Zhu W, Wang Z, Huang X, Chen L; Carbon 2005;43(1):11-6.; copyright © 2005, with permission from Elsevier), b) HRTEM image of PtRu nanoparticles deposited over carbon nanocoils obtained from HTC sucrose (inset: detail of a PtRu nanoparticle showing the cubic structure) (Reprinted with permission from Elsevier from Sevilla M, Lota G, Fuertes AB, J; Power Sources 2007;171(2):546-51; copyright © 2007), and c) SEM and TEM images of the C@TiO₂ "dyade"-type network (Reprinted with permission from Zhao L, Chen X, Wang X, Zhang Y, Wei W, Sun Y, Antonietti M, Titirici M M; Adv. Mater. 2010;22(30):3317-21; copyright © 2010 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim).

Figura 6. a) Imagen de HRTEM de nanopartículas de Pt depositadas sobre esferas HTC (inset: SAED de las nanopartículas de Pt) (Reproducido con permiso de Yang R, Qiu X, Zhang H, Li J, Zhu W, Wang Z, Huang X, Chen L; Carbon 2005;43(1):11-6), b) imagen de HRTEM de nanopartículas de PtRu depositadas sobre nanoespirales de carbono obtenidas mediante HTC de sacarosa (inset: detalle de una nanopartícula de PtRu que muestra su estructura cúbica) (Reproducido con permiso de Elsevier de Sevilla M, Lota G, Fuertes AB; J. Power Sources 2007;171(2):546-51; copyright © 2007), y c) imágenes de SEM y TEM de la estructura tipo diada C@TiO₂ (Reproducido con permiso de Zhao L, Chen X, Wang X, Zhang Y, Wei W, Sun Y, Antonietti M, Titirici M M.; Adv. Mater. 2010;22(30):3317-21; copyright © 2010 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim).

conducted to develop a suitable carbon support which can provide high dispersions of Pt nanoparticles and a good stability against corrosion (oxidation).

The first to explore the use of a HTC-based carbon as support for the anode electrocatalyst in fuel cells was Yang et al. [72]. They deposited 10 wt% Pt nanoparticles over carbon spherules obtained by HTC of sucrose at 190°C and post-treatment at 1000°C (Figure 6a). Those catalysts had a better performance than Pt/Vulcan in methanol electro-oxidation due to the higher utilization of Pt particles as a result of higher accessibility. Other authors have applied a catalytic graphitization step to increase the crystallinity of HTC carbon, as electrical conductivity is one of the key properties of a carbon electrocatalyst support. Most of those electrocatalysts outperformed Pt/Vulcan or PtRu/Vulcan electrocatalysts in the electro-oxidation of methanol (Figure 6b) [73-76].

The major limit in the performance of PEMFC and DMFC is the cathodic oxygen reduction reaction (ORR). However, to date, only one report concerning the use of HTC carbon as cathode electrocatalyst has been published. It consists of dual N- and S-doped carbon aerogels obtained by HTC of S-(2-thienyl)-L-cysteine or 2-thienyl carboxaldehyde in the presence of ovalbumin and glucose [78]. Those materials exhibited impressive electro-catalytic activity for the ORR reaction in fuel cells. In acidic conditions, all doped aerogels showed very good stability compared to a platinum based catalyst, as well as an activity which is still much better than ordinary carbon supports, but not competitive to the noble metal systems.

6.5. Photocatalysis

In the past decade, much research effort has focused on extending the photoresponse of the TiO₂ to the visible region. Among these attempts, TiO₂ doping, either with main group elements or transition metals, has been the most important approach for improving the photocatalytic performance of the catalyst. In

this regard, HTC has been used to produce carbon doped TiO₂ with visible light activity [77]. It was shown that the surface of nanometre sized carbon materials can also show collective polarization modes and therefore, these optical absorption transitions are feasible to sensitize TiO₂ which then acts as a novel "dyade"-type structure, with an improved TiO₂ hole reactivity, while the electron is taken up by the carbon component (Figure 6c). This results in an improved photocatalytic activity over the complete spectral range.

Other applications of HTC materials that have already been explored include heterogeneous catalysis (hydrogenation of hydroxy aromatic derivatives [56], dry methane reforming and partial oxidation of methane [79], Fisher-Tropsch reaction [80] or biodiesel production [81], among other reactions), magnetic applications (magnetic separation [82], contrast agents in MIR [83]) and bioapplications (bioimaging [84] and drug delivery [83,85]).

7. Conclusions

The underlying motivation for doing research on HTC materials is the ever-growing need to reduce the dependence on fossil fuels and move towards more sustainable technologies. The aim of this review was to give an overview of a "palette" of functional nanomaterials suitable for a wide range of essential and sustainable applications.

We strongly hope that throughout this review we could convince the reader that HTC, a simple and sustainable technique for carbon material formation, is a viable and powerful addition to the toolbox of carbon-based technologies. Although future optimization of the herein presented materials and detailed deconvolution of the complex HTC mechanism, as well as learning how to rely entirely on raw biomass for the production of the same quality materials are needed, we do believe that it is highly likely that HTC-derived carbon based materials will ultimately overcome current favored fossil-based materials and in that way contribute to more sustainable technologies.

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Electronic inhomogeneities in graphene: the role of the substrate interaction and chemical doping

Inhomogeneidades electrónicas en grafeno: el rol de la interacción con el substrato y el dopaje químico

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Abstract

We probe the local inhomogeneities of the electronic properties of graphene at the nanoscale using scanning probe microscopy techniques. First, we focus on the study of the electronic inhomogeneities caused by the graphene-substrate interaction in graphene samples exfoliated on silicon oxide. We find that charged impurities, present in the graphene-substrate interface, perturb the carrier density significantly and alter the electronic properties of graphene. This finding helps to understand the observed device-to-device variation typically observed in graphene-based electronic devices. Second, we probe the effect of chemical modification in the electronic properties of graphene, grown by chemical vapour deposition on nickel. We find that both the chemisorption of hydrogen and the physisorption of porphyrin molecules strongly depress the conductance at low bias indicating the opening of a bandgap in graphene, paving the way towards the chemical engineering of the electronic properties of graphene.

Resumen

Hemos estudiado las inhomogeneidades locales de las propiedades electrónicas del grafeno a escala nanométrica utilizando técnicas de microscopía de sonda próxima. En primer lugar, nos centramos en el estudio de las inhomogeneidades electrónicas causadas por la interacción del grafeno con el sustrato en muestras de grafeno exfoliado sobre óxido de silicio. Encontramos que las impurezas cargadas, presentes en la interfaz entre el grafeno y el sustrato, perturban considerablemente la densidad de portadores y alteran las propiedades electrónicas del grafeno. Este hallazgo ayuda a comprender la gran variabilidad entre distintos dispositivos que se observa típicamente en dispositivos electrónicos basados en grafeno. En segundo lugar, investigamos el efecto de la modificación química de las propiedades electrónicas de grafeno, crecido sobre níquel por depósito por vapor químico. Encontramos que tanto la quimisorción de hidrógeno como la fisisorción de moléculas de porfirina logran reducir fuertemente la conductancia a bajo voltaje, lo que indica la apertura de un *gap* en el grafeno, allanando el camino hacia el diseño químico de las propiedades electrónicas de grafeno.

1. Introduction

Since the first experimental realization of graphene [1], its unique properties [2-4] have boosted the research in this novel material. Due to the high sensitivity of graphene to external electric fields, it can be used for sensing applications or as the channel in field effect transistors. This high sensitivity,

however, makes graphene very vulnerable to charged impurities in the surroundings and to chemical doping [5, 6], leading to a large device-to-device variation in the electronic performance [6]. This effect is especially critical because graphene is all surface and thus when it lays on a surface or it is covered by a layer of adsorbates almost every single carbon atom of the graphene layer can be altered by the graphene-substrate interaction or the chemical doping.

In this work we review experimental results on the local electronic properties of graphene, focused first on the study of the electronic inhomogeneities caused by the graphene-substrate interaction (based on Ref. [7]) and second on the variation of the local electronic properties of graphene by chemical modification of the surface (based on Ref. [8]).

2. Graphene-substrate interaction: exfoliated graphene on SiO₂

When graphene is exfoliated on insulating substrates, the presence of charged impurities typically generates electric fields strong enough to change the doping level of the graphene layer at the nanoscale [9, 10]. As a consequence, graphene-based electronic devices show a large device-to-device variation in electrical performance and reproducibility [5, 6]. We have developed a combined scanning tunnelling and atomic force microscope (STM/AFM) to characterize the electronic properties of graphene layers even when they are deposited on top of insulating substrates. This scanning probe microscopy (SPM) tool can operate as an AFM, without the need of a conductive substrate, to locate the graphene flake. The microscope relies on an STM which has been supplemented with a piezoelectric quartz tuning fork force sensor [11, 12] in the so-called *qPlus* configuration [13] (spring constant $k \sim 12500$ N/m, resonance frequency $f_0 \sim 32.1$ kHz and quality factor $Q \sim 4200$). The use of a carbon fiber tip has found to optimize the performance of this type of combined STM/AFM microscopes [14-16].

The measurement starts by positioning the carbon fiber tip on top of a graphene flake (prepared by cleavage of highly oriented pyrolytic graphite on a SiO₂/Si substrate using silicone stamps [17]) with the help of a long working distance optical microscope (see Figure 1a). Then the AFM capability of our combined STM/AFM is used to scan the region under study (see Figure 1b) and thus to determine thickness of the different areas of the flake. Before starting the STM measurements the tip is positioned onto the flake, which is electrically contacted by a gold electrode (deposited by shadow mask evaporation), and the scan range is reduced (dashed square in Figure 1b) in order to avoid the tip reaching the insulator substrate which would result in a tip crash

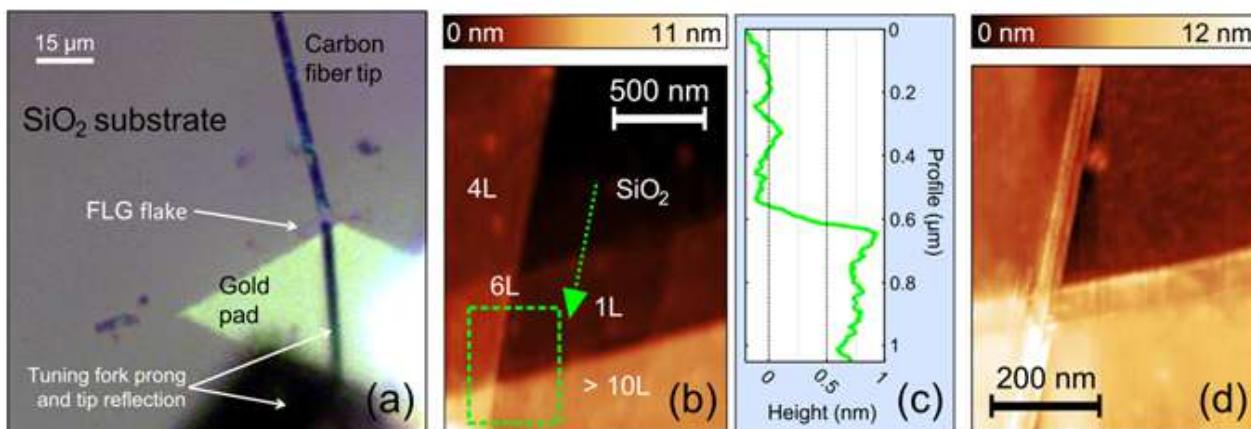


Figure 1. (a) Optical image of the coarse tip positioning on a few-layers graphene flake. (b) AFM topography image of the interface between the few-layers graphene flake and the SiO₂ substrate. Areas with different number of layers (labelled as >10L, 6L, 4L and 1L) are found. (c) Topographic line profile acquired along the dotted line in (b), showing the interface between the SiO₂ substrate and a monolayer graphene region. (d) STM topography image of the region marked by the dashed rectangle in (b). Adapted from Ref. [7].

Figura 1. (a) Imagen óptica del posicionamiento grueso de la punta del microscopio sobre un copo de pocas capas de grafeno. (b) Imagen de topografía AFM imagen de la interfaz entre el copo de pocas capas de grafeno y el sustrato SiO₂. Se distinguen áreas con diferente número de capas (etiquetadas como >10L, 6L, 4L y 1L). (c) Perfil topográfico adquirido a lo largo de la línea de puntos en (b), mostrando la interfaz entre el sustrato SiO₂ y una región monocapa de grafeno. (d) Imagen topográfica STM de la región marcada por el rectángulo de trazos en (b). Adaptada de Ref. [7].

that degrades the sample and/or tip irreversibly. Figure 1c shows the topography of a mechanically exfoliated graphene flake deposited on a 285 nm SiO₂/Si substrate obtained in the constant current STM mode. All STM measurements were acquired under ambient conditions.

In order to gain a deeper insight in the role of charged impurities on the electronic properties of graphene, we have also measured (simultaneously with the topography) the variations of the tunnelling barrier height (see the supplementary information of Ref. [7] for technical details) because the tunnelling current decay constant (β) is strongly influenced by the presence of subsurface charges [18, 19]. In fact, the presence of negatively (positively) charged impurities causes an electric field which effectively shifts upwards (downwards) the energy of the bottom of the band by an amount ΔE . This effect reduces (increases) the apparent tunnelling barrier height, Φ_{app} . This barrier height change can be modeled as $\Phi_{app} = (\Phi_{graphene} - \Phi_{tip} \pm \Delta E)$ where $\Phi_{graphene}$ and Φ_{tip} are the graphene and the tip work function respectively. The associated tunnelling decay constant then changes according to $\beta = 2\sqrt{2m \cdot \Phi_{app}} / \hbar$ (m is the electron mass and \hbar is the reduced Planck constant).

Figure 2a shows the spatial variation of β for a multilayer graphene simultaneously measured with the STM topography (Figure 1d). The β image for a multilayer shows an almost constant value ($5.3 \pm 0.5 \text{ nm}^{-1}$), typical of STM operation in air [20]. The spatial variation of β for single-layer graphene, on the other hand, shows strongly localized inhomogeneities (identified as dips in the β image) caused by local doping induced by negative charged impurities in the substrate (Figure 2b). These inhomogeneities in the tunnelling decay constant can be also observed by measuring tunnelling vs. distance traces at different positions in the single layer graphene region (Figure 2d).

Considering that each dip in the β image (Figure 2b) is due to the presence of one individual negative charge we can estimate the density of charged impurities by tentatively counting the number of depressions in a given area, resulting in an impurity density $\sigma = (2.9 \pm 0.6) \cdot 10^{11} \text{ cm}^{-2}$. A more objective procedure to statistically analyse the short-range ordering [21] and spatial variation of β is to obtain the radially-averaged autocorrelation function $g(r)$, shown in Figure 5c. The typical radius r_{FWHM} at half minimum of the localized inhomogeneities is obtained from the radial distance at which the value of $g(r)$ is

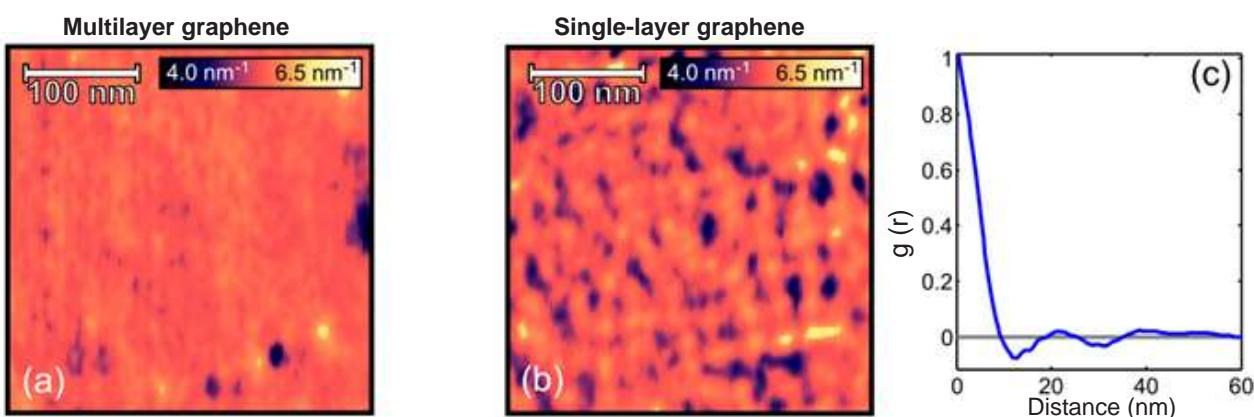


Figure 2. (a) and (b) show the local tunnelling decay constant maps measured on a multilayer and a single-layer region, respectively. (c) Radial autocorrelation function of the local tunnelling decay image in (b). Adapted from Ref. [7].

Figura 2. (a) y (b) muestran los mapas de la constante de decaimiento túnel medidas en una región de multicapa y una región de una sola capa, respectivamente (c) Función de autocorrelación radial de la imagen de la constante de decaimiento túnel mostrada en (b). Adaptada de Ref. [7].

0.5, which yields $r_{FWHM} = 4.7 \pm 1.1$ nm. The inhomogeneities do not show long range ordering and the mean spacing between them is $d = 22 \pm 2$ nm, determined from the position of the first maximum of $g(r)$ [21], which corresponds to a charge density $\sigma = \pi^{-1}(d/2)^{-2} = (2.6 \pm 0.5) \cdot 10^{11}$ cm⁻². As the radius of the β dips presents a well-defined average value, it indicates that the charged inhomogeneities are localized at a well-defined distance from the graphene layer. If the charged impurities would be located randomly in the SiO₂ layer (300 nm thick) the distribution of radius would be much broader. Therefore, it is reasonable to assume that the charged impurities are located at the interface between the SiO₂ layer and the graphene flake.

3. Effect of chemical doping on the local electronic properties of CVD graphene

Chemical functionalization of graphene is a very promising route to achieve large scale production of semiconducting graphene for industrial applications. Indeed, the application of graphene in microelectronic devices is hampered by the lack of a bandgap which is mandatory in order to fabricate electrically switchable devices with large current on-off ratio.

Up to date several strategies have been developed to open a band gap in graphene. Here we have explored two different options. First, the exposure of the graphene surface to hydrogen plasma [22-24] that leads to the chemisorption of hydrogen atoms, which produces the sp³ hybridization of carbon network, reduces the number of delocalized sp² electrons and consequently opens a band gap. Second, the non-covalent stacking of aromatic organic molecules on graphene through π - π interaction.

3.1. Hydrogen chemisorption

The hydrogenation of CVD graphene has been done using Ar:H₂ plasma (composition of 85:15) in a reactive ion etching system with a high frequency generator operating at 13.56 MHz, capacitively coupled to the bottom electrode [25]. The gas flow is kept constant at 200 sccm and the pressure in the chamber is 0.05 mbar. We chose the lowest plasma ignition power, $P = 3$ W (power density is ~ 4 mW/cm²), and tuned the circuit impedance to reduce the built-in DC self-bias between the bottom electrode and the plasma down to zero. Each exposure is done for 40 min, which leads to moderate hydrogen coverage and is directly followed by

STM/STS measurements.

Figure 3 shows an 9×9 nm² topographic image acquired in the constant current STM mode of the surface of graphene grown on nickel by CVD.[26] Before the plasma treatment, the CVD graphene exhibits a Moiré pattern superimposed to the honeycomb lattice of graphene (Figure 3a). This is due to the lattice parameter mismatch between the graphene and the nickel surfaces and it is the characteristic of most of epitaxial graphene samples [27-29].

On the other hand, for the hydrogenated CVD graphene, the expected structural changes are twofold. First, the chemisorption of hydrogen atoms will change the sp² hybridization of carbon atoms to tetragonal sp³ hybridization, modifying the surface geometry.[30, 31] Second, the impacts of heavy Ar ions, present in the plasma, could also modify the surface by inducing geometrical displacement of carbon atoms (rippling graphene surface) or creating vacancies and other defects. Figure 3(b) shows the topography image of the surfaces CVD graphene after the extended plasma treatment. The corrugation increases after the treatment and there are brighter regions in where the atomic resolution is lost or strongly distorted.

We have also found that these bright regions present a semiconducting behaviour while the rest of the surface remains conducting (see Figure 3(c)-(d)). Although the room temperature thermal drift makes it challenging to spatially resolve the electronic properties of the samples by STS with atomic accuracy, it is possible to analyze statistically thousands of tunneling spectroscopy measurements to infer changes on the electronic properties of the graphene surface (see Ref. [8] for more details).

3.2. Porphyrin physisorption

Iron porphyrins (FePP) are deposited onto the CVD graphene surface by drop casting. The porphyrins were used without any further purification from Aldrich. A solution 1.63 mM of FePP in uvasol grade chloroform was prepared. Further, a droplet of 10 μ L of the porphyrin solution was dropcasted onto CVD-graphene surface and the solvent was left to evaporate for 3h in open air condition.

Figure 4a shows the STM topography of the CVD graphene surface after the deposition of FePP molecules. We observe six-pointed star shape protuberances with 0.26 nm in height and approximate dimension of 13 Å x 19 Å. These lateral

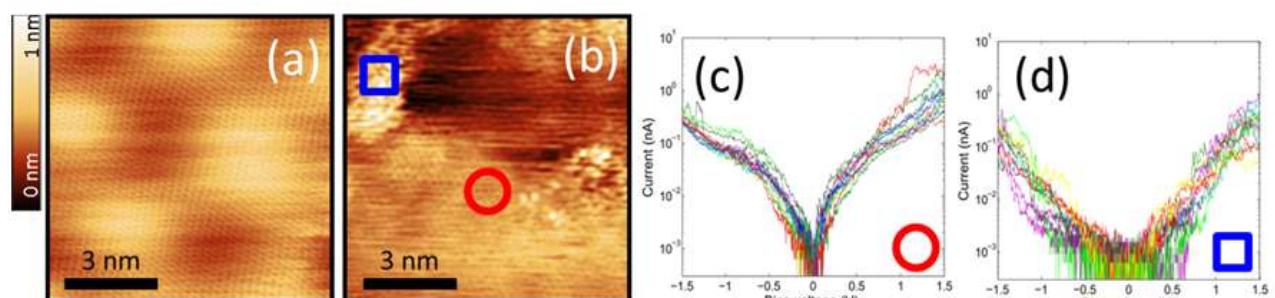


Figure 3. (a) and (b) are topography images, acquired in the constant current STM mode, of graphene grown by CVD on top of a nickel surface before and after hydrogenation. (c) Several current vs. voltage traces measured for a CVD graphene sample in regions with pristine atomic resolution like the one marked with the red circle in (b). (d) Same as (c) but measured in several bright regions, like the one marked with the blue square in (b), where the atomic resolution is distorted. Adapted from Ref. [8].

Figura 3. (a) y (b) son imágenes de topografía, adquiridas en modo de corriente constante, de grafeno crecido por CVD sobre níquel antes y después de hidrogenación. (c) Curvas corriente vs. voltaje medidas en varias regiones con resolución atómica como la marcada con el círculo rojo en (b). (d) Igual que (c) pero medidas en varias regiones brillantes, como la marcada con un cuadrado azul en (b), donde la resolución atómica está distorsionada. Adaptada de Ref. [8].

dimensions are in agreement with the dimensions of a single porphyrin molecule obtained by first principle calculations ($16 \text{ \AA} \times 16 \text{ \AA}$) (Hyperchem 6.0). The resolved six-star shape, however, does not perfectly match the expected geometrical structure of porphyrin molecules (four-star shape). The additional features in the observed star shape can be due to the splitting of the local density of the state (LDOS) of one phenyl ring. Another interesting finding is that FePP molecules are preferable physisorbed at the valleys of the rippled structure of graphene (Fig. 4a).

After the deposition of FePP onto the graphene surface, we measured the I - V traces directly on top of six porphyrin molecules (as the one indicated by the red cross in Figure 4a). The tunneling differential conductance shows a strong reduction in comparison to pristine graphene. In fact, the tunneling differential conductance traces present zero conductance (below the experimental resolution, 10 pS) for a wide range in bias, a characteristic of semiconducting behaviour while for pristine graphene the low bias differential conductance value is significantly larger than zero. Surprisingly, when this measurement is repeated on graphene several angstroms away from a single porphyrin molecule (at the topmost point of Moiré as indicated by the black cross in Fig 4a) the characteristic I - V traces (Fig. 4c) are different than that of pristine graphene (Fig. 4b). The tunnelling differential conductance at low bias is still strongly reduced. This indicates that the non-covalent modification of the graphene surface can be used to engineer its electronic properties.

4. Conclusions

We have studied the local electronic properties of graphene using scanning probe microscopy techniques. We found that when graphene is deposited on a SiO_2 surface, the charged impurities present in the graphene-substrate interface produce strong inhomogeneities of the electronic properties of graphene. On the other hand, we shown how homogeneous graphene grown by CVD can be altered by chemical modification of its surface. We found that both the chemisorption of hydrogen and the physisorption of porphyrin molecules strongly depress the local conductance at low bias indicating the opening of a bandgap in graphene.

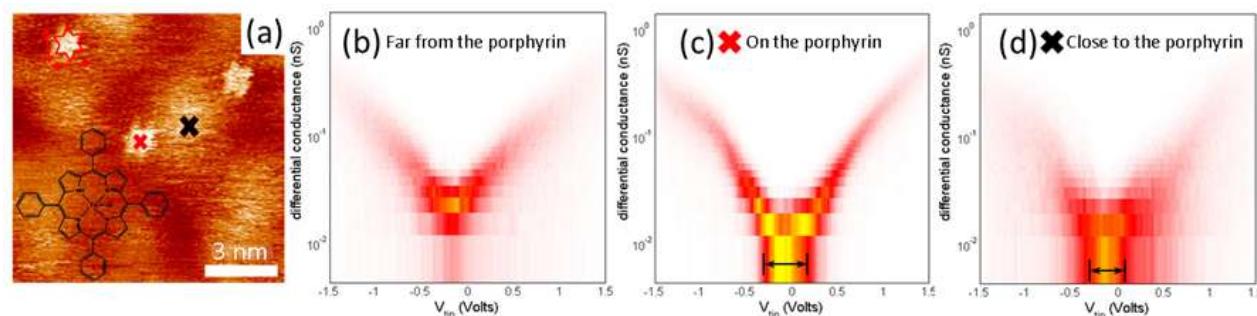


Figure 4. (a) 5,10,15,20-Tetraphenyl-21H,23H-porphine iron(III) chloride (abbreviated as FePP) molecules decorating the terraces of CVD graphene ($I_t = 0.1 \text{ nA}$; $V = 0.5 \text{ V}$). FePP can be found at the valleys of the Moiré pattern of graphene. (b)-(d) Comparison of the differential conductance measured on the graphene sample after FePP deposition. The data is presented as 2D histograms, each one built from 1000 individual STS traces. (b) STS spectra measured on top of the Moiré pattern far from the molecules. (c) dI/dV traces acquired on top of the porphyrin molecule marked with a red cross in Fig. 4a. (d) STS measured on a hill of the Moiré close to a porphyrin molecule (black cross in Fig. 4a).

Figura 4. (a) 5,10,15,20-tetrafenil-21H,23H-porfirina de cloruro de hierro (III) (abreviado como FePP), decorando las terrazas de grafeno CVD ($I_t = 0.1 \text{ nA}$; $V = 0.5 \text{ V}$). Las FePP se pueden encontrar en los valles del patrón de Moiré del grafeno. (b) - (d) Comparación de la conductancia diferencial medida en la muestra después de la deposición de FePP en grafeno. Los datos se presentan como histogramas 2D, cada uno construido a partir de 1000 trazas STS individuales. (b) espectros STS medido en la parte superior del patrón de Moiré lejos de las moléculas. (c) Curvas dI/dV adquiridas en la parte superior de la molécula de porfirina marcada con una cruz roja en la Figura 4a. (d) STS medido en la parte superior del patrón de Moiré cercano a una molécula de porfirina (cruz de color negro en la figura. 4a).

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Objetivos y características de la química computacional y su aplicación al estudio de los materiales de carbono

Goals and characteristics of computational chemistry and its application to carbon materials

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Resumen

El objetivo principal de la Química Computacional (QC) es predecir todo tipo de propiedades moleculares de sistemas químicos. Adicionalmente, la QC ofrece información útil para racionalizar o interpretar tendencias y enunciar relaciones de estructura-actividad. Para ello, la QC emplea una amplia gama de técnicas teóricas en constante desarrollo y mejora. La naturaleza del modelo molecular de interés y la del problema o propiedad a estudiar condicionan la selección del método(s) a utilizar. Muchas de las herramientas de la QC pueden ser aplicadas por todo tipo de científicos, no sólo por especialistas. Es necesario un conocimiento básico de los fundamentos de los métodos teóricos, capacidad de análisis crítico de los resultados, cierta habilidad en el manejo del software y acceso a recursos de hardware optimizados para cálculo de altas prestaciones. La caracterización de los nuevos materiales de carbono (nanotubos, grafeno, etc.) ha venido haciendo un uso intensivo de la QC. Pero la aplicación de la QC es igualmente interesante para comprender las bases moleculares del comportamiento de todo tipo de materiales de carbono.

Abstract

Computational Chemistry (CC) aims at predicting all kinds of molecular properties of chemical systems. Additionally, CC also provides useful insight for rationalizing trends in molecular properties and outlining structure-activity relationships. To this end, CC employs a wide range of theoretical techniques, which are being constantly improved by computational scientists and theoretical chemists. Both the nature of the molecular model of interest and the problem to be studied determine the choice of the computational method(s). The tools of CC can be applied by all kinds of scientists, not only by specialists. All that is needed is a basic understanding of the theoretical methods, the ability to critically analyze the results, skills in using software and hardware tools, as well as access to high performance computing resources. Concerning the role played by CC in Carbon Science, it is clear that CC, which has been intensively used to characterize the new carbon materials (nanotubes, graphene, etc.), can also be useful to unveil the molecular details of all kinds of carbon materials.

1. ¿Qué se puede obtener de la QC?

Históricamente, la QC surge como una evolución de la Química Teórica con el objetivo de investigar el comportamiento de la materia a nivel molecular mediante ordenadores; en otras palabras, la QC es sinónimo de modelización molecular.[1] Más concretamente, la implementación y aplicación de las técnicas de la QC nos permite investigar múltiples propiedades y comportamientos moleculares como son:

- La geometría molecular en un sentido amplio: además de distancias y ángulos de enlace, es

posible caracterizar la forma y tamaños relativos de todo tipo de moléculas y macromoléculas, haciéndolo además para conjuntos de confórmeros representativos.

- La energía de todo tipo de especies químicas, incluyendo intermedios, estados de transición, estados excitados, etc. Es posible, además, estimar distintos tipos de magnitudes termodinámicas tanto en fase gas como en fases condensadas.
- La reactividad química. La reactividad de una especie es un ejemplo de propiedad genuinamente química que puede cuantificarse en forma de índices de reactividad con la ayuda de la QC. Además, la QC es capaz de determinar la geometría y estabilidad relativa de intermedios y estados de transición de reacción, es decir, caracteriza los mecanismos de reacción. Más aún, la QC dispone de herramientas sofisticadas para el cálculo de todo tipo de magnitudes cinéticas como constantes de velocidad, efectos cinéticos isotópicos, secciones eficaces de reacción, factores de efecto túnel, etc.
- Las propiedades espectroscópicas, pero también todo tipo de propiedades eléctricas y magnéticas de moléculas individuales. La QC predice de modo rutinario los espectros IR, UV y RMN, siendo en muchos casos una herramienta indispensable para la correcta interpretación/asignación de los datos experimentales.
- Las propiedades físicas de las fases condensadas y materiales. La descripción correcta de las interacciones intermoleculares es un desafío que, en muchos casos, es posible afrontar con éxito con la ayuda de varios métodos. Así, por ejemplo, la QC puede caracterizar la estructura de polímeros complejos y sus propiedades mecánicas y térmicas. Del mismo modo, la caracterización de las propiedades *bulk* o superficiales de materiales sólidos es una aplicación de la QC de gran impacto tecnológico.

2. ¿Cuáles son las principales herramientas de la QC?

La clasificación sistemática de los métodos de la QC no es tarea fácil, debido a la gran variedad de métodos existentes y a la diversidad de sus implementaciones en forma de software. Esta profusión de metodología y software se refleja en la gran cantidad de acrónimos incluidos en cualquier libro o artículo dedicado a la Química Computacional. Sin embargo, para avanzar en el conocimiento y aplicación de la QC es conveniente partir de una primera clasificación de los métodos teóricos como la que se resume en la Tabla 1.

2.1. Métodos de la Mecánica Molecular (MM)

Estos métodos estiman el cambio en la energía potencial de un sistema molecular como consecuencia de pequeñas variaciones en las distancias y ángulos de enlace y, sobre todo, de los cambios conformacionales y la formación/ruptura de interacciones intermoleculares.[2] Su formulación

Tabla 1. Cuadro resumen de las características de los principales métodos teóricos de la QC. En la mayoría de las aplicaciones se asume que la aproximación de Born-Oppenheimer para la separación del movimiento electrónico y nuclear es válida. De esta manera, los métodos de la QC se utilizan para explorar las *superficies de energía potencial* (repulsión internuclear + energía electrónica) en función de la geometría molecular.

Table 1. Main characteristics of the most important CC theoretical methods. In most applications it is assumed that the Born-Oppenheimer approximation for separating electronic from nuclear motion is valid. Thus, the CC methods are used to explore the potential energy surfaces (internuclear repulsion + electronic energy) based on the molecular geometry.

Método	Fundamento	Rango de aplicación	Ventajas	Desventajas	Ejemplos
Mecánica Molecular (MM)	Potenciales de interacción	1-10 ⁵ átomos	Gran rapidez. Muy eficientes en fases condensadas	Aplicabilidad delimitada por el potencial MM seleccionado	AMBER, REBO, ReaxFF
<i>Ab initio</i>	Ecuación de Schrödinger y Función de Onda	1-10 ² átomos (todo tipo de propiedades)	Exactitud y precisión controlable	Lentos. Los métodos más avanzados son muy complicados de usar	HF, MP2, CCSD, CCSD(T)
Teoría del Funcional de la Densidad (DFT)	Teorema de Kohn-Sham y Densidad Electrónica	1-10 ³ átomos. (todo tipo de propiedades)	En general, más rápidos que <i>ab initio</i> pero su aplicabilidad es más limitada	Exceso de métodos DFT disponibles. No hay pautas para mejorar sistemáticamente los resultados	B3LYP, BLYP, PW91, PBE
Semi-empíricos (SE)	Ecuación de Schrödinger y Función de Onda o Teorema de Kohn-Sham y Densidad Electrónica (como forma de ajuste)	1-10 ⁴ átomos. (muchas, pero no todas las propiedades moleculares)	Gran rapidez. Fáciles de usar. Bastante fiables en moléculas orgánicas	Errores no sistemáticos. Escasa fiabilidad en moléculas con metales y especies inestables	PM3, PM6, SCC-DFTB

práctica requiere la adopción *a priori* de potenciales de interacción que contienen parámetros optimizados a partir de información experimental o teórica. Su gran ventaja reside en la rapidez de los cálculos MM, lo que permite modelizar sistemas con miles y cientos de miles de átomos. Mediante la aplicación de condiciones periódicas, los métodos MM nos permiten simular exhaustivamente el comportamiento dinámico y las propiedades termodinámicas de las fases condensadas. Sus principales limitaciones son que no proporcionan ninguna información o propiedad electrónica y su ámbito de aplicación viene predeterminado por los potenciales y parámetros empleados.

Los métodos MM estándar aplicados a materiales de carbono pueden proporcionar información estructural y energética inaccesible por otros medios como, por ejemplo, sobre el confinamiento de moléculas de agua en el interior de nanotubos de carbono.[3] Además, algunas de las limitaciones de los métodos MM pueden superarse en parte empleando potenciales más sofisticados (REBO, ReaxFF, etc.), que incluyen términos que describen la polarización electrónica, la transferencia de carga y la formación/ruptura de enlaces químicos, siendo así capaces de simular materiales con distintos tipos de enlace químico y en un amplio rango de condiciones. Con este tipo de potenciales es posible estudiar el comportamiento mecánico en condiciones extremas de láminas de grafeno[4] o bien el mecanismo de formación de los nanotubos de carbono.[5]

2.2. Métodos *ab initio*

Estos métodos resuelven de modo aproximado la ecuación de Schrödinger para obtener la energía y la función de onda electrónicas del sistema de interés.[6, 7] Se denominan *ab initio* porque no emplean otra información empírica que no sea la de las constantes físicas fundamentales (\hbar , e , ...). Conceptualmente, los métodos *ab initio* están relacionados con la Química Cuántica que se expone en los cursos de Química Física. Partiendo del método variacional Hartree-Fock (HF) de cálculo de

orbitales moleculares (OM), es posible formular familias de métodos *ab initio*, como las Moller-Plesset (MP) y Coupled-Cluster (CC), que están organizadas jerárquicamente en términos de su capacidad para describir la correlación electrónica (HF → MP2 → CCSD → CCSD(T) ...) de modo que, en principio, es posible predecir cualquier propiedad molecular con una exactitud controlable. En la práctica, no sólo la implementación, sino también la aplicación de los métodos *ab initio* más exactos puede ser muy complicada, así como requerir hardware de altas prestaciones y una gran cantidad de tiempo de cálculo.

En el ámbito de los materiales de carbono, los métodos *ab initio* con una mejor relación calidad coste, MP2 y CCSD(T), van adquiriendo un mayor protagonismo gracias a la creciente potencia de los ordenadores y a las constantes innovaciones en el campo del software. Por eso, es posible realizar estudios de referencia (*benchmarks*) que proporcionan energías y otras propiedades con una gran exactitud, como en el caso de las interacciones $\pi - \pi$ [8] o la reactividad química de modelos de grafeno.[9]

2.3. Métodos de la Teoría del Funcional de la Densidad (DFT)

Los métodos más populares en la QC son los métodos DFT que formulán el problema mecanocuántico de la estructura electrónica en términos de una magnitud observable, la densidad electrónica ρ , en vez de la función de onda polielectrónica Ψ .[10] La consecuencia matemática es que la energía electrónica del sistema pasa a ser un funcional de la densidad, $E[\rho]$. La implementación de los métodos DFT conduce a las ecuaciones de Kohn-Sham (KS), muy semejantes a las ecuaciones HF porque la densidad electrónica se expresa a partir de orbitales moleculares. Por tanto, en la práctica, un cálculo DFT es muy parecido a un cálculo de OM HF. Por otro lado, el método DFT de la estructura electrónica debe distinguirse del método mecánico-estadístico del mismo nombre aplicado al estudio del fenómeno de adsorción,

teniendo en común ambas teorías que se basan en una descripción efectiva de la densidad electrónica, en un caso, y de la densidad de un fluido adsorbido, en el otro.

Existe un número amplísimo de métodos DFT, muchos disponibles en los programas de cálculo más conocidos.[6] Esta sobreabundancia de métodos DFT se debe al hecho de que el funcional $E[p]$ incluye un componente denominado funcional de correlación-intercambio, $Exc[p]$, cuya forma analítica es desconocida. Por eso, existen tantos funcionales DFT como aproximaciones a $Exc[p]$ han sido propuestas. Cabe destacar que muchos métodos DFT son en cierto modo semiempíricos, pues los correspondientes funcionales Exc contienen uno o varios parámetros ajustados a datos experimentales.

La ventaja de los métodos DFT es que si el funcional $Exc[p]$ se comporta bien para el problema a estudiar, entonces son métodos eficientes y fiables, mucho más rápidos que los métodos *ab initio* más sofisticados. Por esta razón, los métodos DFT son la opción por defecto en QC para simular todo tipo de sistemas moleculares. En particular, la caracterización de las propiedades *bulk* y superficiales de los materiales cristalinos se ha beneficiado enormemente de los métodos DFT en combinación con el Teorema de Bloch que incorpora la simetría cristalina en la QC.[11] No obstante, las desventajas de los métodos DFT deben tenerse presentes a la hora de utilizarlos: (a) la dificultad en seleccionar el funcional más adecuado; (b) la imposibilidad de refinar sistemáticamente los resultados de los métodos DFT como sí que es posible con los métodos *ab initio*; y (c) los errores sistemáticos de muchos funcionales como es la carencia total o parcial de energía de dispersión (que juega un papel clave en los materiales de carbono) en un cálculo DFT.

En la práctica, tanto la experiencia computacional acumulada como la validación frente a resultados experimentales o *ab initio* son necesarias para escoger el funcional DFT más adecuado. Para la simulación de materiales de carbono, el funcional B3LYP, el cual rinde geometrías, propiedades espectroscópicas y energías termoquímicas razonablemente precisas para compuestos orgánicos, ha sido el más popular seguido de otros funcionales como PBE, M06, PW91, B97D, etc. No obstante, la tendencia más actual en cálculos DFT de materiales de carbono parece que pasa por emplear los funcionales semiempíricos de la familia M06 u otros funcionales combinados con potenciales MM que dan cuenta de la energía de dispersión.[12]

2.4. Métodos Semiempíricos

Los métodos semiempíricos (SE) son métodos químico cuánticos, es decir, obtienen la energía y orbitales moleculares, pero lo hacen simplificando los cálculos HF o DFT al remplazar valores esperados de la función de onda o de funcionales de la densidad electrónica por formas paramétricas ajustadas estadísticamente empleando grandes conjuntos de datos experimentales (geometrías moleculares y calores de formación) y/o datos teóricos generados por métodos *ab initio* o DFT.[1] De esta manera, los cálculos SE son casi tan rápidos como los cálculos MM hasta el punto que es posible realizar cálculos SE en sistemas de miles de átomos. Por su naturaleza, la fiabilidad de los métodos SE es baja si se estudian moléculas poco representativas (por ejemplo, con metales de transición) y/o propiedades moleculares que no se han tenido en

cuenta en la parametrización. Por lo tanto, el uso satisfactorio de estas técnicas está de nuevo condicionado a la experiencia computacional previa y su validación frente a métodos más exactos.

El método PM3, y su versión más moderna conocida como PM6, son formulaciones SE del método *ab initio* HF que gozan de gran aceptación para predecir geometrías y entalpias de reacción de compuestos orgánicos. Estos métodos se han utilizado con éxito para simular la ruptura de láminas de grafeno y nanotubos[13] o la respuesta estructural del óxido de grafeno frente a cambios de pH en medio acuoso.[14] Por otra parte, partiendo de las ecuaciones DFT y aplicando técnicas de teoría de perturbaciones, se ha desarrollado el método SE llamado SCC-DFTB, de gran importancia en la Ciencia de Materiales porque permite simular todo tipo de materiales sólidos (metales, materiales magnéticos, etc.) incluyendo, claro está, materiales de carbono. De este modo, la aproximación SCC-DFTB permite analizar estructuras y materiales mixtos empleando modelos de gran tamaño (nanoclusters de Fe y C, por ejemplo).[15]

2.5. Estrategias multimétodo y métodos híbridos

La gran variedad metodológica de la QC es tanto un inconveniente como una virtud. Es un inconveniente porque dificulta su aplicación, pues es necesario conocer bien los fundamentos de muchos métodos para seleccionar en cada caso el método adecuado e interpretar correctamente los resultados. Afortunadamente, se han escrito excelentes monografías sobre QC que, sin llegar a entrar en los detalles técnicos más prolíficos, explican claramente los fundamentos y dan pautas sobre la aplicación de los distintos métodos.[1, 2, 6, 7, 10, 11]. Al mismo tiempo, la disponibilidad de muchos métodos es un punto fuerte de la QC ya que permite a los usuarios avanzados aprovechar la información de distintas técnicas aplicadas a un mismo problema. Normalmente, un estudio de modelización molecular de un problema concreto implica la aplicación de varios métodos (*ab initio* y DFT, por ejemplo). Más aún, es posible formular métodos híbridos, como los métodos DFT/MM que combinan en un mismo problema una descripción MM del sistema con un tratamiento DFT electrónico para una parte del mismo.[7]

3. Algunas cuestiones prácticas sobre la aplicación de la QC

La Figura 1 resume la interrelación entre recursos hardware y software que son necesarios para un uso eficiente de la QC. Por un lado, se emplean programas de edición y visualización molecular, ya sea como aplicaciones locales instaladas en las estaciones de trabajo de los investigadores o bien en modo remoto. Por supuesto, el grueso de la producción de datos corre a cargo de los programas de cálculo y simulación. Estos últimos demandan gran cantidad de recursos computacionales por lo que es muy importante que se ejecuten en ordenadores optimizados para cálculo científico o en centros de supercomputación como los gestionados por la Red Española de Supercomputación[16] y el CESGA-CSIC.[17] Idealmente, los usuarios de la QC no deben preocuparse de la gestión de dichos programas, tan sólo de la realización de sus trabajos y de la transferencia de datos, siendo por tanto imprescindible el apoyo prestado por técnicos de sistemas para el aprovechamiento de los recursos computacionales de uso compartido. A continuación,

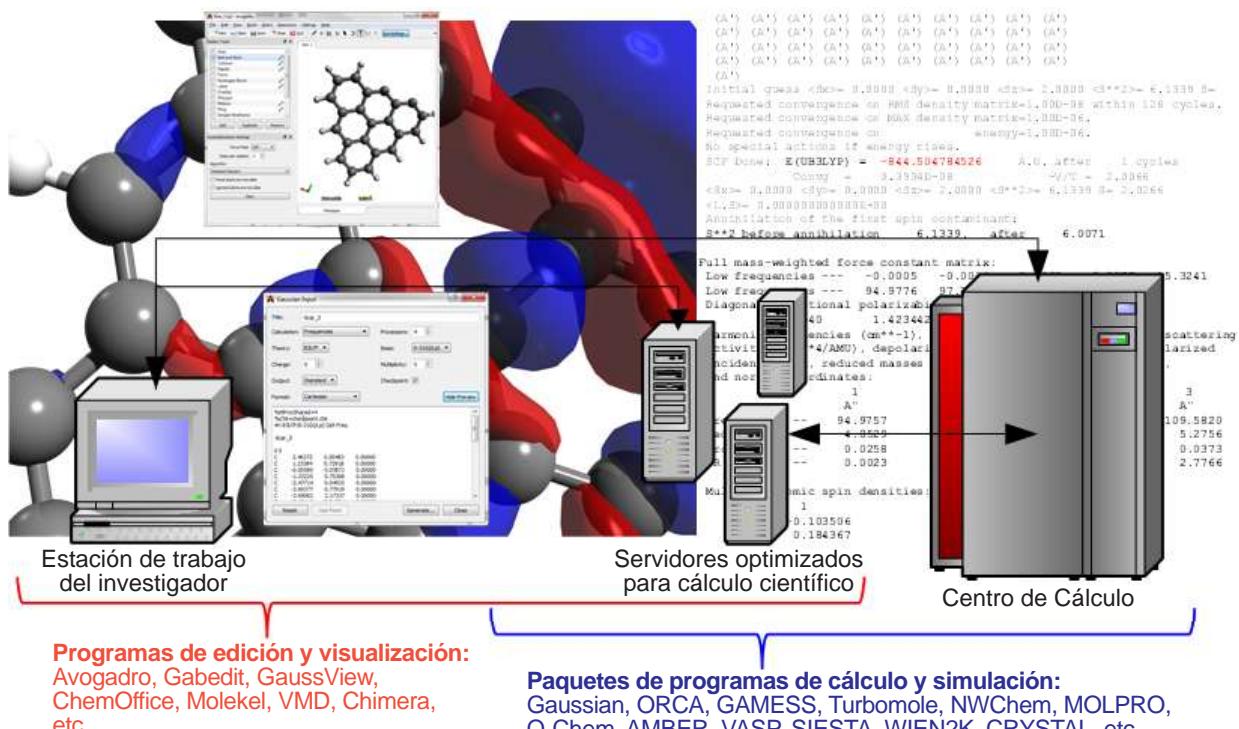


Figura 1. Representación esquemática de las tareas y herramientas software/hardware de la QC.
Figure 1. Schematic representation of the tasks and hardware/software tools of computational chemistry.

comentaremos brevemente una secuencia típica para el estudio de modelos moleculares que no requieran un muestreo exhaustivo del espacio de fases, como sería el caso más complejo de los modelos que incorporan disolventes líquidos y/o macromoléculas flexibles.

Una vez que se ha seleccionado el método(s) QC para el modelo planteado, el investigador comienza su estudio empleando alguno de los programas de edición y visualización molecular con los que se construye y/o analiza la geometría de todo tipo de sistemas moleculares. En muchos casos, estos programas ofrecen modelos preformados (*templates*) muy útiles para el modelado de materiales de carbono. Junto con la edición de geometrías y su visualización con distintas representaciones, estos programas suelen incorporar otras funciones como son la realización de cálculos MM, la visualización de OMs y superficies moleculares, la animación de modos normales de vibración y espectros basados en cálculos ab initio o DFT, etc.

Existen muchos programas de edición molecular. Muchos son comerciales e incluso licencias sin ánimo de lucro pueden tener un coste elevado. Otros son muy dependientes del sistema operativo. En otros casos, los programas son muy complicados de usar y/o están totalmente orientados a un tipo de sistemas químicos determinado (macromoléculas, materiales cristalinos, etc.). Sin embargo, se pueden destacar algunos programas como Avogadro y Gabedit: ambos son de libre distribución, relativamente fáciles de usar, están disponibles tanto para Linux como Windows e incorporan varios métodos MM ampliamente utilizados.[18, 19].

Partiendo de la geometría del modelo inicial, los programas de cálculo se encargan de minimizar su energía (optimizando su geometría molecular) y calcular las propiedades moleculares requeridas (energías libres, energías de solvatación, propiedades electrostáticas y espectroscópicas, etc.). Habitualmente, el investigador emplea varios métodos de cálculo por lo que es bastante normal

utilizar más de un programa de cálculo, ya que la implementación de algunas técnicas es más eficiente en unos programas que en otros. En la actualidad, existe un amplio catálogo[20] de programas de cálculo en QC que ofrecen todo tipo de métodos (MM, ab initio, DFT y SE). Entre todos ellos destaca el paquete Gaussian conocido por su gran sencillez de uso y su amplísimo abanico de métodos y técnicas teóricas.[21] Aunque se trata de un software comercial, Gaussian es el programa más utilizado en QC. Pero también existen muchos otros códigos distribuidos comercialmente o bajo licencia GNU que son igualmente recomendables y eficientes, entre los que merece ser destacado el paquete ORCA,[22] pues al igual que Gaussian es un software muy fácil de manejar y especialmente eficiente en el estudio de sistemas de gran tamaño. Cabe destacar que para el tratamiento con métodos DFT de sistemas cristalinos existe otra familia de programas de cálculo como VASP o WIEN2k, los cuales son en general más complicados de utilizar.

Por último, merece la pena advertir que los cálculos QC generan una gran cantidad de datos, máxime cuando muchas investigaciones se diseñan para estudiar amplias familias de moléculas o sistemas con cientos y miles de átomos. Por esta razón, el usuario avanzado de la QC debe adquirir diversas habilidades informáticas para agilizar el tratamiento y análisis de los datos. No es extraño que la fase de análisis y extracción de conclusiones sea técnicamente más laboriosa que la preparación y ejecución de los cálculos previos.

4. Química Computacional: ¿Una herramienta CAD para los materiales de carbono?

En mi opinión, la QC se va convirtiendo en una herramienta CAD (Computer-Aided-Design) que permite crear y testear en los ordenadores dispositivos moleculares innovadores, de la misma manera que los ingenieros electrónicos o mecánicos disfrutan de potentes herramientas de diseño asistido por ordenador para trasladar rápidamente sus diseños a las plantas de fabricación. Pero, ¿es

realmente la QC una herramienta de CAD molecular tan robusta y fiable como las usadas en ingeniería? ¿Lo es específicamente para el caso de los materiales de carbono?

Centrándonos primero en el campo de los materiales ordenados de carbono como son el grafeno y los nanotubos, se constata fácilmente que los métodos de la QC tienen ya un papel muy destacado en la investigación de estos nuevos materiales. En cierto modo, esta relevancia no es sorprendente, no sólo por el protagonismo de estos materiales en Nanotecnología, sino también porque se trata de estructuras químicas constituidas en su mayoría por el elemento C que no suelen plantear dificultades especiales en los estudios computacionales más allá de su tamaño (aunque hay excepciones notables a esta afirmación en el caso del grafeno[23]). Así, una búsqueda bibliográfica durante los últimos 20 años resulta en más de 2500 referencias con resultados computacionales sobre grafenos y nanotubos de carbono, alcanzando algunos trabajos un gran impacto como, por ejemplo, los cálculos DFT de gaps de energía de nanocintas de grafeno.[24] Abundan los artículos 100% computacionales, tanto para ofrecer explicaciones a nivel molecular del comportamiento singular de estos materiales,[25, 26] como para simular su reactividad química,[27] o bien ensayar nuevas propiedades y aplicaciones,[28] etc. Otros trabajos reportan observaciones experimentales,[29] generalmente espectroscópicas, que son complementadas o interpretadas con la ayuda de cálculos teóricos. Por lo tanto, no es exagerado concluir que la QC es una herramienta consolidada y necesaria para el diseño y testeo de las formas ordenadas de los materiales de carbono.

Por supuesto, la enorme diversidad de los materiales de carbono condiciona la potencial aplicabilidad de la QC. En el caso de materiales desordenados, que incluso carecen de una formulación química definida como son los carbones activos porosos, la QC se ha empleado para la caracterización de propiedades químicas de compuestos modelo, generalmente hidrocarburos policíclicos aromáticos y funcionalizados con heteroátomos o en interacción con moléculas pequeñas (adsorbatos). En otras palabras, los compuestos modelo de otros materiales carbonosos son de nuevo, grafenos, eso sí, representativos de la química superficial de los materiales más complejos. En este ámbito, encontramos aplicaciones de la QC muy variadas: la determinación de la basicidad intrínseca de grupos funcionales oxigenados,[30] la interpretación de algunas señales espectroscópicas en el IR,[31] el estudio del enlace químico y propiedades magnéticas de la estructuras de borde,[32] la interacción entre clúster metálicos y superficies de carbono,[33], los fenómenos de adsorción en carbones activos,[34] la estabilidad de compuestos de intercalación,[35] los mecanismos de reacción química y catálisis heterogénea,[36-38], etc.

Obviamente, la fiabilidad de los resultados de los cálculos QC sobre compuestos modelo depende de la relevancia del modelo, además de ser más o menos sensibles a los efectos de truncamiento. Por consiguiente, no es de extrañar que algunos autores aspiren a construir modelos moleculares realistas de los materiales de carbono desordenados empleando la técnica de *reconstrucción* con la que se genera y se crece un modelo molecular del material que sea consistente con la información experimental disponible sobre composición y

estructura (por ejemplo, de dispersión de rayos X).[39, 40] Este enfoque exige combinar algoritmos estocásticos y métodos de la QC para construir, modificar y evaluar la bondad de los sucesivos modelos. Por supuesto, el mejor modelo molecular así generado puede ser la base para investigar computacionalmente múltiples propiedades. Sin duda, la construcción de modelos moleculares *realistas* de materiales complejos sigue siendo técnicamente muy compleja, pero muy probablemente es ya una empresa viable para muchos tipos de materiales de carbono utilizando las herramientas de la QC actual. Por eso, cabe esperar que, a medio plazo, los métodos de la QC combinados con recursos de cálculo y de almacenamiento de datos faciliten la construcción de librerías de modelos moleculares para materiales de carbono desorganizados bien contrastados, a partir de los cuáles sería posible entrar en una nueva fase de diseño y estudio computacional de dichos materiales.

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Peter A. Thrower

A tribute to a half-century of dedication to carbon materials

Francisco Rodríguez Reinoso

A significant role to advance the quality of carbon journal

Harry Marsh¹

Professor Peter A Thrower

Born in 1938, and educated in Norfolk where he was described as being a strong pupil, Peter was accepted into the University of Cambridge (UK) obtaining his B.A. (1960) in Physics, his M.A. (1963) and finally his Ph.D (1969). After graduating Peter was employed as a Scientific Officer with the UK Atomic Energy Authority, Harwell leaving as Head of Carbon and Graphite Materials Section (1969). This covers his period of major interest in the use of graphite as a moderator in nuclear reactors. It was at this time that a similar interest in graphite and other carbon materials was expanding at Pennsylvania State University, in the USA, under the direction of Professor P.L. Walker. Peter was recruited as an Associate Professor of Materials Science creating a research team working with graphites (1969-1983). As an outstanding teacher and researcher, he was elected to a full Professorship in 1983, retaining this position until 1998 when he retired as an Emeritus Professor to return to the UK and his home near to Great Yarmouth.



During his working days when at Pennsylvania State University, Peter worked closely with the American Carbon Society in the promotion of its Biennial Conferences. As Chairman of three such Conferences, his organization was immaculate and contributed greatly to the creation of the world-wide community of carbon scientists as we know it today. By so doing, he became familiar with the diversity of structures, properties and applications of carbon materials. More than that, he became well-known to the carbon community undertaking further tasks to advance carbon materials.

As if this sustained and dedicated support to the international carbon community was not enough, Peter took on a further responsibility, not one to be taken lightly. It was the position of Editor-in-Chief of journal Carbon taken up in 1982. No other scientist was better qualified for this position than Peter A. Thrower.

The story of this journal goes back to 1953, the time of the genesis of the carbon community. Graphite, as a moderator of neutrons and as a major component in steel production, dominated the scene. The mastermind behind the growth and coordination of research and development into carbon materials was Professor Stach Mrozowski. In 1953, he brought together for a Conference in Buffalo, USA, 75 scientists and engineers to discuss graphitic materials. The proceedings of this Conference were published in book format. In 1955 and 1957 meetings

and publication of books of proceedings were again published the latter running into two volumes. By now it was realised that interest in carbon materials had expanded so much that the book format was totally inappropriate. Working with the American Carbon Society and Pergamon Press, Stach Mrozowski 'created' the journal Carbon and became its first Editor-in-Chief. After small beginnings the journal reached a size where Stach Mrozowski needed assistance. So in 1982, Peter was in the Editorial seat and publishing 540 pages in that year. Peter has stayed in that seat for 30 years with Volume 49 containing 5400 pages, a ten-fold increase. The years saw the transfer of publishing from Pergamon to

Elsevier and the modernisation of manuscript submission from regular mail to electronic submissions. Peter transferred his office from PSU to his home in the UK in 1998. The journal has seen interests move on from graphite dominance, to the debates of 'surface area' in porous carbons, to the stories of fullerenes, carbon fibres and nanotubes and graphene.

In 2007 the American Carbon Society recognised the massive life-time contributions, made by Peter, and still ongoing, by the special creation of the Peter A Thrower Award, the first recipient being Peter.

This year sees Peter's 30th year as Editor-in-Chief (his last year) with over 50 years of close association with carbon materials. The many capacities with which he has been associated owe their success to his tenacious attention to detail and accuracy, so characteristic of Peter. This is the hallmark which has made him such an outstanding Editor-in-Chief of the journal Carbon.

The journal Carbon, during the years of Peter's editorship has seen grown both in size, to 5400 pages in 2011 and in its Impact Factor to 5.378 in 2011. This is a magnificent achievement.

Peter is departing from the Editor's chair on the occasions of his thirtieth year of service and the fiftieth year of the journal. It is a time for celebrations. The carbon community owes Peter an immense expression of gratitude. We wish him well.

Harry Marsh is a life-long friend and associate of Peter Thrower.

¹ Emeritus Professor

Professor Francisco Rodríguez-Reinoso (Paco)

For decades Paco acted as an Editor on the Editorial Board of Elsevier's journal Carbon. This is a position which rarely, if ever, sees the limelight. It requires the careful and detailed scrutiny of manuscripts submitted to Carbon for publication following an initial assessment of the reviewers. The journal publishes papers which cover the wide range of scientific topics associated with the structure, properties and applications of carbon materials. An Editor on the Editorial Board needs to have expert knowledge of some of these topics. Paco is an international scientist, travelling to all parts of the world to lecture, to educate and to formulate research topics. At home, for about forty years in the Department of Inorganic Chemistry, University of Alicante, Spain, he was Head of a large group of international research students, studying a variety of topics, but always including studies into the



production, structure and applications of microporous carbons. As such, Paco found himself at the centre of the many controversial theories which purported to describe the adsorption of gases and liquids into the microporous networks which constitute porous carbons. It was essential that the several approaches should be published, with Paco taking care for a balanced and realistic approach. For many years, Paco has been a 'king-pin' in the organisation of The Editor-in-Chief, Professor Peter A Thrower. It has to be acknowledged that Paco played a significant role to maintain and advance the quality of publications

in the journal Carbon, a task that is without much glamour. He is standing down this year of 2012 knowing that his is a job extremely well done.

Harry Marsh is a life-long friend and associate of Paco.

Thesis Review. Sustainable biomass-derived hydrothermal carbons for energy applications

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Supervisors: Prof. Markus Antonietti (Max Planck Institute of Colloids and Interfaces) and Dr. Maria Magdalena Titirici (Max Planck Institute of Colloids and Interfaces).

Objectives and novelty

The need to reduce humankind reliance on fossil fuels by exploiting sustainably the planet renewable resources is a major driving force determining the focus of modern material research. For this reason great interest is nowadays focused on finding alternatives to fossil fuels derived products/materials. For the short term the most promising substitute is undoubtedly biomass, since it is the only renewable and sustainable alternative to fossil fuels as carbon source. As a consequence efforts, aimed at finding new synthetic approaches to convert biomass and its derivatives into carbon-based materials, are constantly increasing. In this regard, hydrothermal carbonisation (HTC) has shown to be an effective means of conversion of biomass-derived precursors into functional carbon materials. However the attempts to convert raw biomass, in particular lignocellulosic one, directly into such products have certainly been rarer. Unlocking the direct use of these raw materials as carbon precursors would definitely be beneficial in terms of HTC sustainability. For this reason, in this thesis the HTC of carbohydrate and protein-rich biomass was systematically investigated, in order to obtain more insights on the potentials of this thermochemical processing technique in relation to the production of functional carbon materials from crude biomass.

Results

First a detailed investigation on the HTC conversion mechanism of lignocellulosic biomass and its single components (i.e. cellulose, lignin) was developed based on a comparison with glucose HTC, which

was adopted as a reference model. In the glucose case it was demonstrated that varying the HTC temperature allowed tuning the chemical structure of the synthesised carbon materials from a highly cross-linked furan-based structure ($T = 180\text{ }^{\circ}\text{C}$) to a carbon framework composed of polyaromatic arene-like domains. When cellulose or lignocellulosic biomass was used as carbon precursor, the furan rich structure could not be isolated at any of the investigated processing conditions. These evidences were indicative of a different HTC conversion mechanism for cellulose, involving reactions that are commonly observed during pyrolytic processes (Fig. 1).

The evolution of glucose-derived HTC carbon chemical structure upon pyrolysis was also investigated. These studies revealed that upon heat treatment (Investigated temperatures $350 - 900\text{ }^{\circ}\text{C}$) the furan-based structure was progressively converted into highly curved aromatic pre-graphenic domains. This thermal degradation process was observed to produce an increasingly more hydrophobic surface and considerable microporosity within the HTC carbon structure.

In order to introduce porosity in the HTC carbons derived from lignocellulosic biomass, KOH chemical activation was investigated as an HTC post-synthesis functionalisation step. These studies demonstrated that HTC carbons are excellent precursors for the production of highly microporous activated carbons (ACs) and that the porosity development upon KOH chemical activation is dependent on the chemical structure of the HTC carbon, tuned by employing

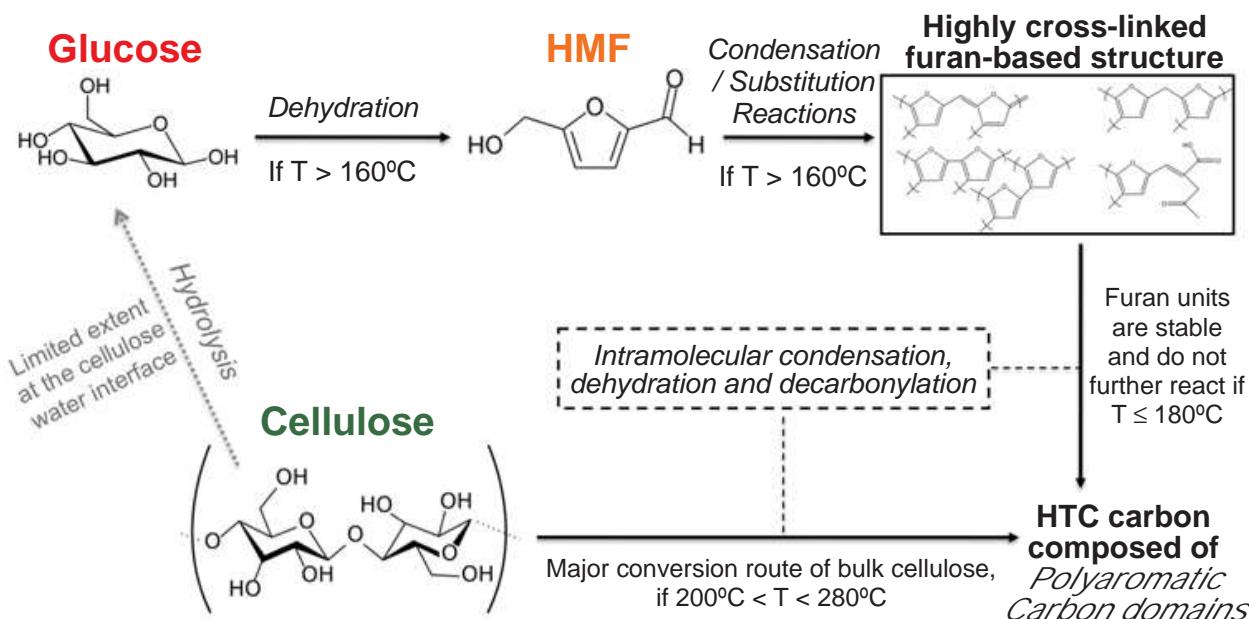


Figure 1. Proposed model for cellulose conversion during hydrothermal treatment under mild processing conditions ($180\text{ }^{\circ}\text{C} < T < 280\text{ }^{\circ}\text{C}$). [NB: Dotted lines represent minor reaction routes].

different HTC temperatures. Preliminary testing of the ACs for CO₂ capture or high pressure CH₄ storage yielded very promising results, since the measured uptakes of both adsorbates (i.e. CO₂ and CH₄) were comparable to top-performing and commercially available adsorbents, usually employed for these end-applications.

The combined use of HTC and KOH chemical activation was also employed to produce highly microporous N-doped ACs from microalgae. The hydrothermal treatment of the microalgae substrate was observed to cause the depletion of the protein and carbohydrate fractions and the near complete loss (i.e. 90%) of the microalgae N-content, as liquid hydrolysis/degradation products. The obtained carbonaceous product showed a predominantly aliphatic character indicating the presence of alkyl chains presumably derived from the lipid fractions. Addition of glucose to the initial reaction mixture was found out to be extremely beneficial, because it allowed the fixation of a higher N amount, in the algae derived HTC carbons (i.e. ≈ 60%), and the attainment of higher product yields (50%). Both positive effects were attributed to Maillard type cascade reactions taking place between the monosaccharides and the microalgae derived liquid hydrolysis/degradation products, which were in this way recovered from the liquid phase. KOH chemical activation of the microalgae/glucose mixture derived HTC carbons produced highly microporous N-doped carbons (Fig. 2).

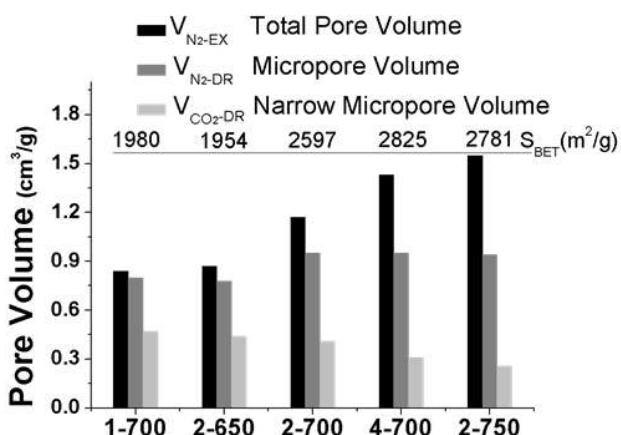


Figure 2. Porosity analysis summary. Calculated surface area (S) and pore volume (V) using different models (subscript) on either N₂ or CO₂ isotherms obtained for microalgae derived activated carbons. Name of the samples (A-B) – A corresponds to the Activation Ration and B to the activation temperature (°C)

Conclusions

In this thesis the hydrothermal carbonization (HTC) of carbohydrate-rich (i.e. lignocellulosic biomass) and protein-rich (i.e. microalgae) raw biomass has been investigated as a synthetic route towards functional carbon materials. Post-treatment processing (i.e. pyrolysis and chemical activation) has also been studied in order to improve the synthesized material properties (eg. porosity, surface chemistry). Overall the presented work in this thesis represents major progresses towards the exploitation of raw biomass for the synthesis of sustainable and functional carbon materials. It highlights the high potential of the hydrothermal method as a means of conversion of waste or cheap biomass into value added products in complete agreement with the “Biorefinery Concept”. Furthermore it represents an

important contribution to the overall HTC research field, since it proposes a new reaction mechanism for cellulose HTC conversion and it presents a detailed investigation of HTC carbon pyrolysis, which can be used as a further post-synthesis functionalization step. It also demonstrates the high suitability of HTC carbons as precursors for the synthesis of highly microporous ACs having several foreseeable applications (e.g. CO₂ capture, high pressure CH₄ storage and electrochemical double layer supercapacitors electrodes) and representing a carbon neutral/negative alternative to the fossil fuels derived high performing carbon materials.

Related publications

- 1 M.M Titirici, R. J. White, C. Falco, M. Sevilla, *Black Perspectives for a Green Future: Hydrothermal Carbons for Environment Protection and Energy Storage*, Energy and Environmental Science, 2012, 5, 6796-6822.
- 2 C. Falco, M. Sevilla, R. Rothe, R. J. White, M.M. Titirici, *Renewable Microalgae-derived Nitrogen Doped Carbonaceous Materials*, ChemSusChem, DOI: 10.1002/cssc.201200022.
- 3 C. Falco, F. Perez Caballero, F. Babonneau, C. Gervais, G. Laurent, MM. Titirici, N. Baccile, *Hydrothermal Carbon from Biomass: Structural Differences between Hydrothermal and Pyrolyzed Carbons via ¹³C Solid State NMR*, Langmuir, 2011, 27 (23), 14460-14471.
- 4 C. Falco, N. Baccile, M.M. Titirici, *Morphological and structural differences between glucose, cellulose and lignocellulosic biomass derived hydrothermal carbons*, Green Chemistry, 2011, 13 (11), 3273 - 3281.

Thesis Review. Nanostructured carbohydrate-derived carbonaceous materials

Shiori Kubo

Defended on 16.06.2011, at the department of chemistry, the university of Potsdam, Potsdam, Germany

Supervisor: Prof. Dr. Markus Antonietti

Objectives and novelty

Nanoporous carbon materials are widely used in industry as adsorbents or catalyst supports, whilst becoming increasingly critical to the developing fields of energy storage / generation or separation technologies. In this thesis, the combined use of carbohydrate hydrothermal carbonisation (HTC) and templating strategies is demonstrated as an efficient route to nanostructured carbonaceous materials. HTC is an aqueous-phase, low-temperature (e.g. 130 – 200 °C) carbonisation, which proceeds via dehydration / poly-condensation of carbon precursors (e.g. carbohydrates and their derivatives), allowing facile access to highly functional carbonaceous materials. Whilst possessing utile, modifiable surface functional groups (e.g. -OH and -C=O-containing moieties), materials synthesised via HTC typically present limited accessible surface area or pore volume. Therefore, this thesis focuses on the development of fabrication routes to HTC materials which present enhanced textural properties and well-defined porosity.

Results

In the first discussed synthesis, a combined hard templating / HTC route was investigated using a range of sacrificial inorganic templates (e.g. mesoporous silica beads and macroporous alumina membranes (AAO)). Via pore impregnation of mesoporous silica beads with a biomass-derived carbon source (e.g. 2-furaldehyde) and subsequent HTC at 180 °C, an inorganic / carbonaceous hybrid material was produced. Removal of the template component by acid etching revealed the replication of the silica into mesoporous carbonaceous spheres (particle size ~ 5 µm), representing the inverse morphological structure of the original inorganic body. Surface analysis (e.g. FTIR) indicated a material decorated with hydrophilic (oxygenated) functional groups. Further thermal treatment at increasingly elevated temperatures (e.g. at 350, 550,

750 °C) under inert atmosphere allowed manipulation of functionalities from polar hydrophilic to increasingly non-polar / hydrophobic structural motifs (e.g. extension of the aromatic / pseudo-graphitic nature), thus demonstrating a process capable of simultaneous control of nanostructure and surface / bulk chemistry.

As an extension of this approach, carbonaceous tubular nanostructures with controlled surface functionality were synthesised by the nanocasting of uniform, linear macropores of an AAO template with a diameter of 200 nm (Figure 1A and B for electron micrographs, Figure 1C for FTIR spectra). In this example, material porosity could be controlled, showing increasingly microporous tube wall features as post carbonisation temperature increased. Additionally, by taking advantage of modifiable surface groups, the introduction of useful polymeric moieties (i.e. grafting of thermoresponsive poly(N-isopropylacrylamide)) was also demonstrated, potentially enabling application of these interesting tubular structures in the fields of biotechnology (e.g. enzyme immobilization) and medicine (e.g. as drug micro-containers).

Complimentary to these hard templating routes, a combined HTC / soft templating route for the direct synthesis of ordered porous carbonaceous materials was also developed. After selection of structural directing agents and optimisation of synthesis composition, the F127 triblock copolymer (i.e. ethylene oxide (EO)₁₀₆ propylene oxide (PO)₇₀ ethylene oxide (EO)₁₀₆) / D-Fructose system was extensively studied. D-Fructose was found to be a useful carbon precursor as the HTC process could be performed at 130 °C, thus allowing access to stable micellar phase. Thermolytic template removal from the synthesised ordered copolymer / carbon composite yielded functional cuboctahedron single crystalline-like particles (~ 5 µm) with well ordered pore structure of a near perfect cubic *I*m₃*m* symmetry (Figure 1A). N₂ sorption analysis revealed a

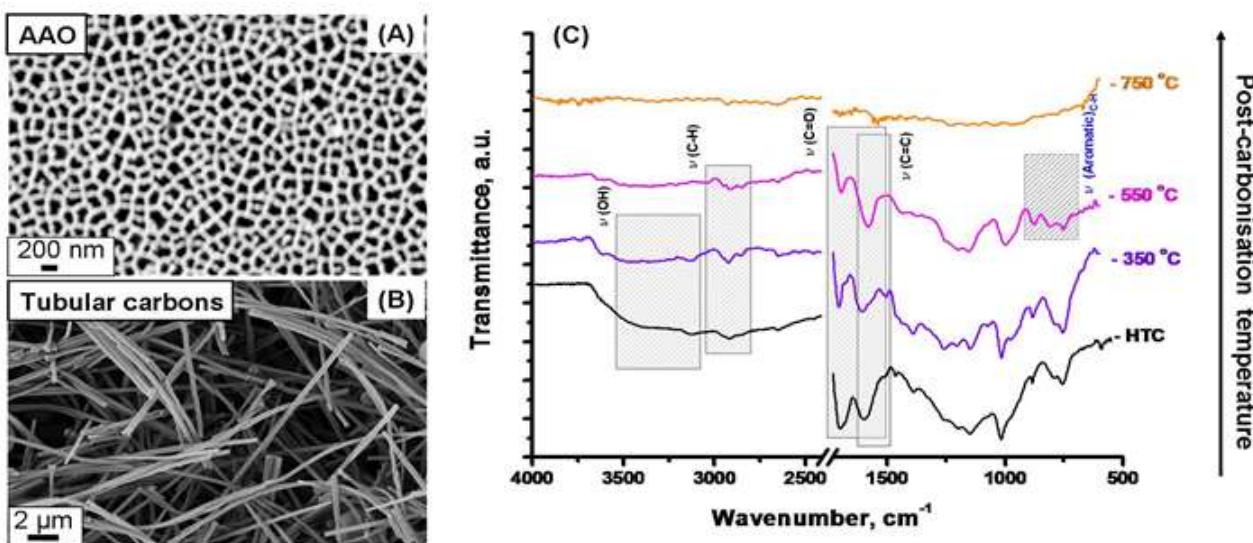


Figure 1. SEM micrographs of (A) template AAO and (B) synthesised tubular carbons. (C) FTIR spectra of tubular carbons post carbonised at different temperatures.

predominantly microporous carbonaceous material (i.e. Type I isotherm, $S_{BET} = 257 \text{ m}^2\text{g}^{-1}$, 79 % microporosity) possessing a pore size of ca. 0.9 nm (Figure 1C). The addition of a simple pore swelling additive (e.g. trimethylbenzene (TMB)) to this system was found to direct pore size into the mesopore size domain (i.e. Type IV isotherm, $S_{BET} = 116 \text{ m}^2\text{g}^{-1}$, 60 % mesoporosity) generating pore size of ca. 4 nm (Figure 1B and D). It is proposed that in both cases as HTC proceeds to generate a polyfuran-like network, the organised block copolymer micellar phase is essentially "templated", either via hydrogen bonding between hydrophilic poly(EO) moiety and the carbohydrate or via hydrophobic interaction between hydrophobic poly(PO) moiety and forming polyfuran-like network, whilst the additive TMB presumably interact with poly(PO) moieties, thus swelling the hydrophobic region expanding the micelle template size further into the mesopore range.

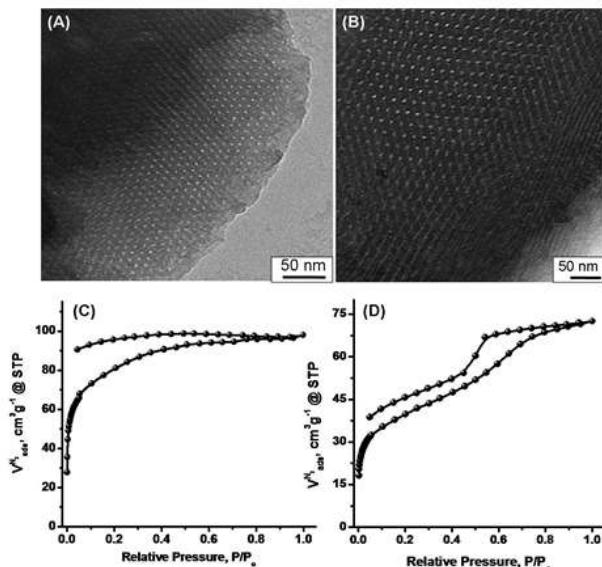


Figure 2. TEM micrographs of ordered porous carbonaceous materials synthesised (A) without and (B) with the addition of TMB. N₂ isotherms of the materials synthesised (C) without and (D) with the addition TMB.

Conclusions

The presented synthetic routes provide access to nanostructured carbonaceous materials with rich surface chemistry through a low-temperature, aqueous procedure using inexpensive and renewable carbon precursors. These carbonaceous materials are of potential interest as candidates in chromatography, electrochemistry or drug delivery. Here, ordered pore structuring potentially introduces the added properties such as linear electronic pathways desired for fast charge-discharge processes or facilitated encapsulation and release of drug molecules. This work represents an important contribution to the field of hydrothermal carbonisation demonstrating the possibility to introduce developed porosity and texture. As such the presented approaches are intended to lay the basis for the development of new high-value nanostructured carbonaceous materials with versatile applicability.

Related publications

- 1 S.Kubo, R.Demir-Cakan, L.Zhao, R.J.White, M-M.Titirici, "Porous Carbohydrate - Based Materials via Hard-Templating", ChemSusChem, 2010, 3, 188..
- 2 S.Kubo, I.Tan, R.J.White, M.Antonietti, M-M.Titirici, "Template Synthesis of Carbonaceous Tubular Nanostructures with Tunable Surface Properties", Chem. Mater., 2010, 22, 6590..
- 3 S.Kubo, R.J.White, N.Yoshizawa, M.Antonietti, M-M.Titirici, "Ordered Carbohydrate - derived Porous Materials", Chem. Mater. 2011, 23, 4882..
Full thesis can be downloaded from http://opus.kobv.de/ubp/volltexte/2011/5315/pdf/ku_bo_diss.pdf

Thesis Review. Sustainable approaches towards novel nitrogen-doped carbonaceous structures

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Presented: On 2.11.2010, Department of Chemistry, University Potsdam, 14476 Potsdam, Germany

Supervisors: Prof. Markus Antonietti (Max-Planck Institute of Colloids and Interfaces, Germany), and Dr. Maria-Magdalena Titirici (Max-Planck Institute of Colloids and Interfaces, Germany).

Objectives and novelty

Nowadays, functionalized carbonaceous materials have attracted particular interest due to their remarkable performance in industrially and environmentally important applications such as CO₂ sequestration, separation, absorption, catalysts, or in electrochemistry, etc.. However, the production methods normally rely on chemically harsh and multistep processes, typically involving high temperature treatment and often leading to the generation of significant quantities of waste, whilst in some cases the overall carbon yield of the process is rather limited. Furthermore, conventional precursors are not necessarily sustainable and relatively expensive as compared to abundant biomass-derived precursors such as the carbohydrates. Thus, this thesis will focus on novel carbonaceous materials which were produced in a sustainable fashion, using cheap starting precursors and uncomplicated synthetic approaches.

Results

The first part of this thesis presents nitrogen-doped carbons synthesized via "in-situ" and "post-functionalization" approaches. Firstly, nitrogen-doped carbons were synthesized by a one-step hydrothermal carbonization of cheap nitrogen-containing carbohydrates (e.g. chitosan and glucosamine) at a mild temperature (180 °C). These nitrogen-doped HTC materials (HC-CH and HC-GA) presented very different particle texture as compared to a reference sample prepared from pure glucose (HC-G) under the same conditions (Figure 1 a, b, c). While the resulting materials contained significant amounts of nitrogen and displayed a high degree of aromatization (Figure 1e). What's more, these N-doped carbons showed very good performance as heterogeneous base catalysts in the Knoevenagel reaction of bezaldehyde with malononitrile as well as in the cycloaddition reaction of CO₂ with propylene

oxide. Furthermore, the level of structural order of these N-doped hydrothermal carbons can be improved by further carbonization at higher temperatures, importantly, further carbonization did not result in the loss of nitrogen or the change of morphology (Figure 1 d, e). The beneficial properties of these samples were exemplified by the conductivity measurements where an increase of the conductivity was found. Since the carbonaceous materials directly synthesized via hydrothermal carbonization do not present high specific surface areas or porosity, methods were developed to increase these textural properties (e.g. chemical activation & carbonization of carbohydrate aerogels). After the chemical activation of hydrothermally treated glucosamine with KOH, the carbon particles of HC-GA were oxidized and reduced to smaller aggregated particles porous N-doped carbon materials (Figure 2), while these microporous N-doped carbons showed promising application as supercapacitors both in acid and basic electrolytes (Figure 2).

Besides the "in situ" synthesis approach, amine-rich carbonaceous materials were synthesized via a simple two step "post-functionalization" procedure at room temperature, by grafting amine groups onto acidic hydrothermal carbons. The resulting materials showed a very high CO₂ uptake (up to 4.3 mmol g⁻¹) (Figure 3), and even more importantly indications for very high CO₂ selectivity at both low and high temperatures. The second part of this work describes a novel type of carbon/titanium dioxide nanocomposites structure synthesized at low temperature under one-step solvothermal conditions. Our results demonstrated that the surface of these nanosized carbon materials showed collective polarization modes and therefore these optical absorption transitions were feasible to sensitize TiO₂ acting as a novel "dyade" type structure, with an improved TiO₂ hole reactivity while the electron was taken up by the carbon component.

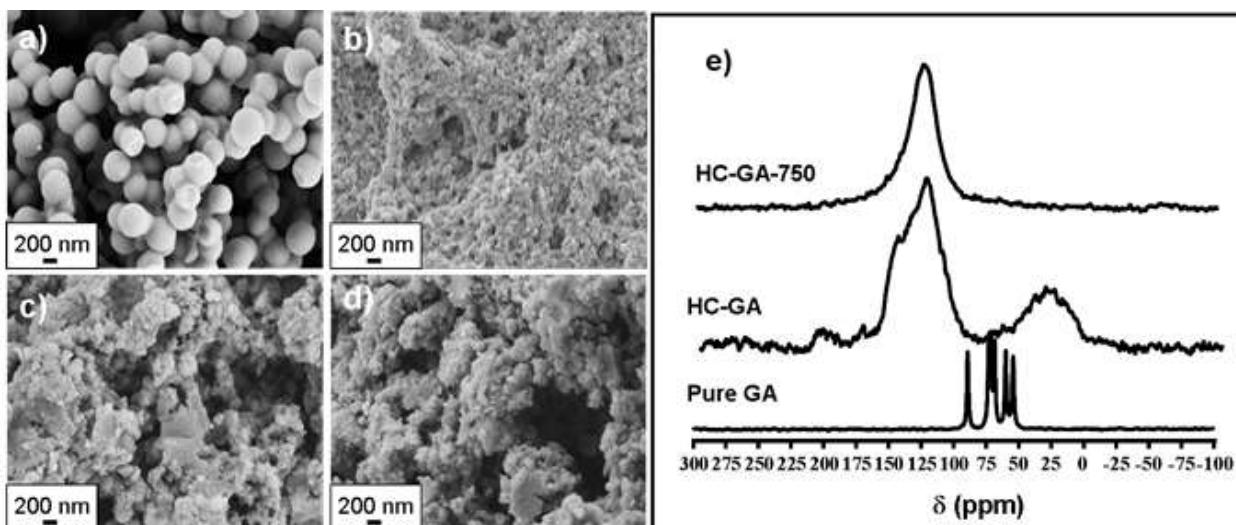


Figure 1. SEM image of the carbons obtained upon hydrothermal carbonization of a) glucose (HC-G); b) chitosan (HC-CH); c) glucosamine (HC-GA) and the sample after treatment at higher temperature (HC-GA-750). e) ¹³C CP-MAS NMR of pure glucosamine, the hydrothermally treated and further carbonized sample.

Such behavior resulted in an improved photocatalytic activity over the complete spectral range. On the basis of the C@TiO₂ "dyade" structure, nitrogen was introduced to form a novel N/C@TiO₂ structure, which has great potential applications in photocatalysis.

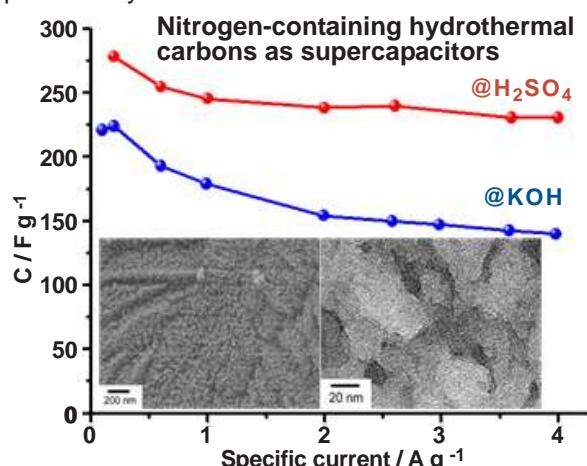


Figure 2. SEM images of microporous Nitrogen-doped materials (chemical activated HC-GA) and the specific capacitance of the resulting materials both in acid and basic electrolytes.

Conclusions

In summary, this thesis has demonstrated the application of sustainable hydrothermal carbonization material synthesis approaches for the production of novel carbonaceous structures possessing different morphologies, structures, functions as well as applications in various domains. We believe that such class of materials will play a very important role in the future, especially in fields related to energy storage or CO₂ sequestration.

Related Publications

1 L. Zhao, X. F. Chen, X. C. Wang, Y. J. Zhang, W. Wei, Y. H. Sun, M. Antonietti, M.-M. Titirici, "One-

Step Solvothermal Synthesis of a Carbon@TiO₂ Dyade Structure Effectively Promoting Visible Light Photocatalysis", *Adv. Mater.*, 2010, 22(30), 3317-3321.

2 L. Zhao, L.-Z. Fan, M.-Q. Zhou, H. Guan, S. Qiao, M. Antonietti, M.-M. Titirici, "Nitrogen-Containing Hydrothermal Carbons with Superior Performance in Supercapacitors", *Adv. Mater.*, 2010, 22(45), 5202-5206.

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4 L. Zhao, N. Baccile, S. Gross, W. Wei, Y. H. Sun, M. Antonietti, M.-M. Titirici, "Sustainable Nitrogen Doped Carbonaceous Materials from biomass derivatives", *Carbon*, 2010, 48(13), 3778-3787.

5 L. Zhao, R. Crombez, F. Pérez Caballero, M. Antonietti, J. Texter, M.-M. Titirici, "Sustainable Nitrogen-Doped Carbon Latexes with High Electrical and Thermal Conductivity", *Polymer*, 2010, 51, 4540-4546.

6 S. Kubo, R. Demir-Cakan, L. Zhao, R. J. White, M.-M. Titirici, "Porous Carbohydrate-Based Materials via Hard Templating", *ChemSusChem*, 2010, 3(2), 188-194.

7 J. Matos, A. García, L. Zhao, M.-M. Titirici, "Solvothermal Carbon-Doped TiO₂ Photocatalyst for the Enhanced Methylene Blue Degradation under Visible Light", *Appl. Catal. A: Gen.*, 2010, 390(1-2), 175-182.

8 M.-M. Titirici, R. J. White, L. Zhao, "Nitrogen-doped Hydrothermal Carbons", *Green*, 2012, 2, 25-40.

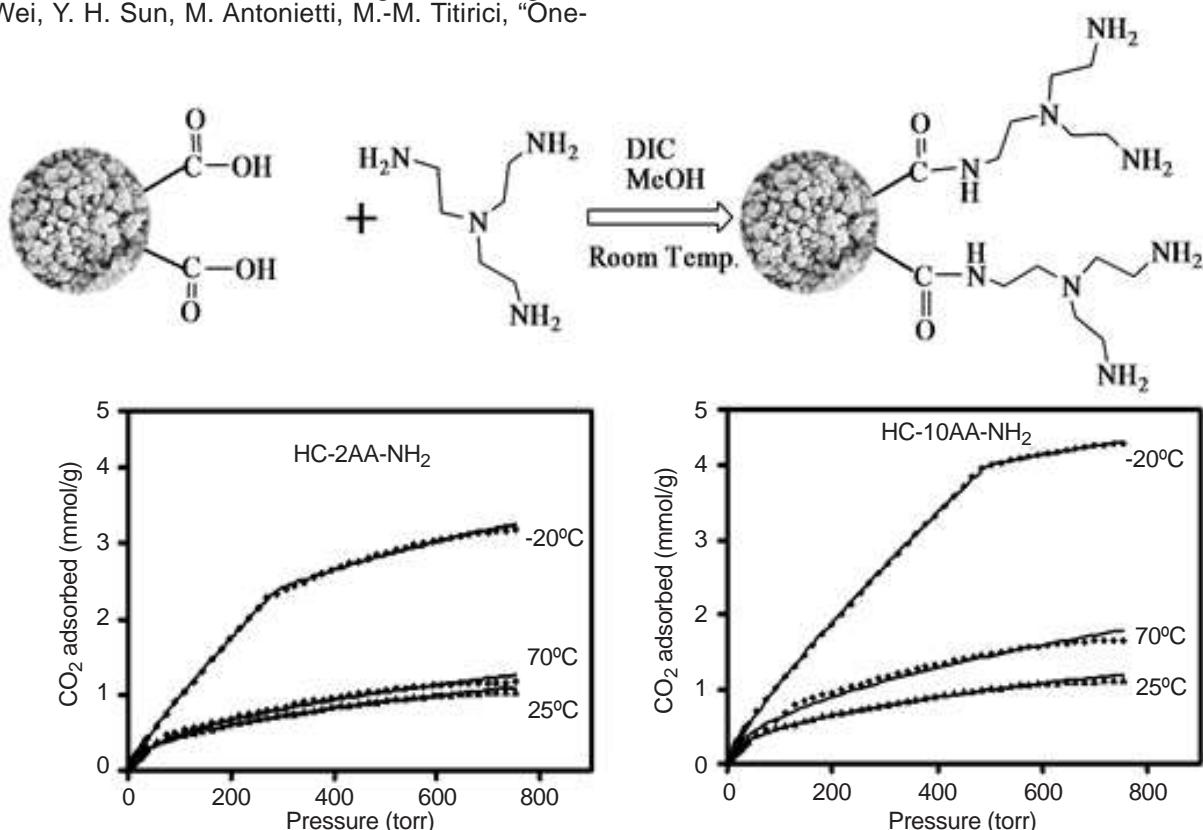
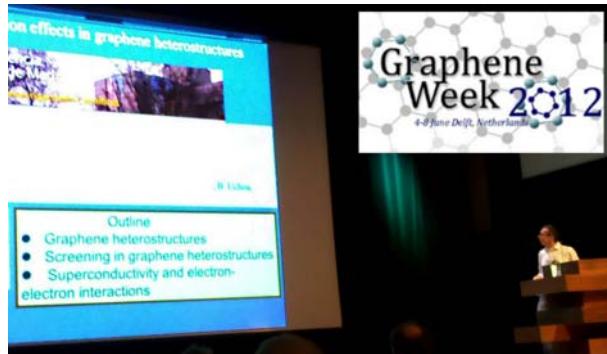


Figure 3. Synthesis scheme of amine-rich material formation from hydrothermal carbon spheres (up); and the temperature and pressure dependent uptake of CO₂ (mmol g⁻¹) on the sorbents (down).

Reseña. Sexta graphene week

Andrés Castellanos-Gómez
Delft University of Technology



La sexta Graphene Week ha tenido lugar en el centro de conferencias Aula de la Universidad Tecnológica de Delft (Países Bajos) entre los días 4 y 8 de Junio de 2012. La conferencia reunió a más de 350 expertos mundiales en grafeno.

Los temas tratados durante esta semana fueron muy variados: propiedades físicas, avances en crecimiento de grafeno, procesos químico, fabricación de dispositivos basados en grafeno y aplicaciones emergentes de este novedoso material.

La presentación oral inaugural, a cargo del laureado Nobel Kostya Novoselov, remarcó la importancia de dispositivos híbridos y heteroestructuras basadas en grafeno, las cuales no han sido muy exploradas hasta la fecha. Estos sistemas consisten en láminas de grafeno que son apiladas artificialmente, empleando una lámina atómicamente delgada de material aislante o semiconductor como separador entre las láminas de grafeno. De este modo, las propiedades electrónicas de cada lámina pueden determinarse individualmente. El interés en estos

nuevos sistemas fue patente durante la Graphene Week 2012 dado que muchos expertos mundiales mostraron resultados en sistemas híbridos basados en grafeno, incluyendo presentaciones orales invitadas de dos científicos españoles: Pablo Jarillo-Herrero (Massachusetts Institute of Technology, MIT) y Paco Guinea (Instituto de Ciencia de los Materiales de Madrid, ICMM-CSIC).

Además del contenido científico de esta conferencia, la GRAPHENE European Flagship fue uno de los temas más comentados por los asistentes. El objetivo de la acción coordinada GRAPHENE es reforzar la comunidad investigadora Europea para explotar las propiedades excepcionales del grafeno y otros materiales bidimensionales relacionados. En la cena oficial de la Graphene Week 2012, se realizaron dos presentaciones orales cortas para actualizar a los asistentes con el estatus de la GRAPHENE Flagship.

De estas presentaciones, dos mensajes me resultaron muy interesantes. Primero, el factor de impacto promedio de los grupos europeos trabajando en grafeno es de 6 (lo cual demuestra la alta calidad de la investigación Europea en un tema tan competitivo como el grafeno). Y segundo, el Consejo Superior de Investigaciones Científicas (CSIC, España) es la segunda institución más productiva a nivel mundial en el Área de grafeno (por detrás de la Academia China de Ciencias). La Graphene Week 2012 se cerró con el anuncio de la Graphene Week 2013 que tendrá lugar cerca de Bremen (Alemania), tot ziens Delft! (En holandés, ¡hasta luego Delft!) Dr. Andres Castellanos-Gomez Postdoctoral Researcher Delft University of Technology (The Netherlands) Kavli Institute of NanoScience.

Reseña. Carbon 2012

Francisco R. Morales Lara y Víctor K. Abdelkader Fernández
Universidad de Granada

El pasado mes de Junio, entre los días 17 y 22, la ciudad de Cracovia (Polonia) acogió la celebración de la conferencia internacional CARBON 2012 en su vuelta a Europa, tras su paso por la ciudad china de Shanghai.

En esta ocasión, la Polish Carbon Society fue la encargada de la organización, siendo el Auditorium Maximum, un moderno y céntrico palacio de congresos, el emplazamiento elegido para el desarrollo de la conferencia. La ciudad, capital espiritual del país, da cobijo a 760.000 habitantes (además de 1,4 millones que viven en el área metropolitana). En su interior, se ha mantenido viva la ciudad medieval con bellos ejemplos de estilos renacentista, barroco y gótico. En ella la Rynek Główny, o plaza mayor, contiene un mercado de planta rectangular en medio y numerosas iglesias como la basílica a María Santísima y otros monumentos. La plaza y sus alrededores se encuentran repletos de restaurantes y pubs. Sin duda la ciudad medieval es el corazón de Cracovia.

El segundo elemento a destacar será la colina de Wawel, que se encuentra a orillas del río Vístula. Cuenta la leyenda que tras el intento de muchos caballeros por desalojar al dragón que vivía en su interior fue un humilde campesino quien lo consiguió,

no mediante espada y escudo en mano sino a través de un cebo. Sobre esta colina se alzan el Castillo Real de Wawel (residencia de la mayoría de los reyes de Polonia) y la Catedral de San Wenceslao y Estanislao (donde están enterrados los reyes). Por último cabe reseñar el núcleo medieval de Kazimierz, el conocido barrio judío, caracterizado por sus murallas del siglo XIV y por sus casas apiñadas.

Con respecto a la organización del congreso, cada jornada quedaba inaugurada por una sesión plenaria, en las que, tanto la entidad del conferenciante como el contenido de la charla, son una muestra del alto nivel de la presente edición del congreso. Así, el primer día fue el turno de M. Sciazko (Challenges for Development of Clean Coal Technology), el martes 19 hubo doble sesión, S. Iijima (Nano-Carbon Materials: Synthesis and Application), seguido de M. Terrones (Novel Forms of Carbon: Defective Graphenes, Nanoribbons with Atomically Smooth Edges and Graphene-Nanotube Hybrid Structures), y en las siguientes jornadas K. Drechsler (The Potential of Carbon Composites for Lightweight Construction for Aerospace and Automotive Applications) y F. Béguin (Carbons for Energy Storage Solutions). Tras las plenarias, tenían lugar las charlas

cortas, las cuales se desarrollaron en cuatro salas en paralelo (lo cual siempre crea la gran duda existencial: ¿estará uno asistiendo a la charla más idónea para su campo de investigación?) y al final, para concluir la jornada, las sesiones de posters, más amenas e interactivas.

Los temas estrella, tanto en las charlas como en los posters, se centraron en esta ocasión en los diversos tipos de nanomateriales de carbono (con gran presencia del grafeno), en el almacenamiento de energía en materiales carbonosos, en la obtención y aplicaciones de novedosos nanocomposites y en los prometedores avances en los métodos de caracterización y funcionalización de los materiales de carbono.

Como viene repitiéndose en pasadas ediciones, sobre todo en las celebradas en territorio europeo, la contribución española ha sido muy importante, tanto por la calidad como la cantidad de los trabajos presentados, situándonos en una meritaria sexta posición en el ranking de países con mayor número de abstracts enviados (un nada desdeñable 7 % del total de los 749 abstracts procedentes de 51 países diferentes).

Por otro lado, durante la conferencia fueron concedidos múltiples premios entre los que cabe destacar el otorgado por la ECA (European Carbon Association) con el que se galardonó al profesor Yuri Gogotsi de la Drexel University y el premio Brian Kelly del British Carbon Group concedido al investigador postdoctoral Fei Guo de la Brown University School of Engineering.

Entre los intensos días de trabajo en las conferencias, la mayoría de los asistentes al congreso no nos pudimos resistir a realizar alguno de los tours más atractivos que se ofrecen en esta ciudad (y que se podían adquirir en la propia sede del congreso)

hacia sitios como las fantásticas minas de sal situadas a más de 300 metros bajo tierra en donde se ubica una capilla y diversas tallas, todo tallado sobre la roca salina. O a uno de los lugares donde el ser humano desarrolló al máximo su capacidad de destrucción y残酷 infinita. Se trata de uno de los campos de concentración nazis más grandes conocido como "Auschwitz-Birkenau"• y que actualmente mantiene viva la memoria de más de un millón de seres humanos (la mayoría de creencia judía) que literalmente vivieron un verdadero infierno y de los que la mayoría acabaron siendo exterminados.

Volviendo a temas más agradables, no se puede terminar sin hacer referencia a la cena de gala del congreso y en la que se dio un emotivo homenaje a Peter Throwell quien deja paso en su cargo como editor principal de la revista CARBON a Rober Hurt. Para el evento se dispuso una carpeta en el esplendido jardín del museo arqueológico de la ciudad. Todo amenizado por una banda que tocaba y cantaba muy bien "el jazz"• entre otros géneros. Ha de decirse que la carpeta se convirtió en una especie de invernadero en el que se pasaba calor, ya que, en general, fueron sorprendentes las altas temperaturas durante toda la estancia en la ciudad. El buen tiempo unido a la alta humedad de la zona fueron los culpables de ello.

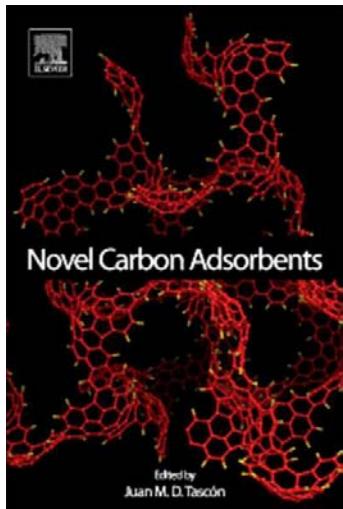
Finalmente, os recordamos que la próxima edición del congreso, CARBON 2013, tendrá lugar en la exuberante ciudad de Río de Janeiro (Brasil) en plena línea de la famosísima playa de Copacabana.

Así que sólo nos queda decir ¡Gracias a los organizadores de CARBON 2012 y la ciudad de Cracovia! Y a los miembros del GEC ¡Hasta pronto, nos vemos en Río a seguir dejando en buen lugar a la investigación española!



Reseña. Novel carbon adsorbents

M.A. Montes Morán
INCAR-CSIC



El pasado agosto Elsevier ha publicado un libro titulado "Novel Carbon Adsorbents", editado por el Prof. Juan Tascón, director del INCAR-CSIC (Oviedo) y miembro del GEC. La monografía se presenta como una posible continuación de otro libro, "Adsorption by Carbons", que había sido coeditado en el 2008 también por Tascón y el fallecido Prof. Eduardo Bottani (INIFTA, Argentina).

En esta ocasión el editor ha puesto el énfasis en los aspectos más novedosos del campo de la adsorción y los materiales de carbono. Dichos aspectos se condensan en un total de 21 contribuciones en las que se tratan temas que no fueron abordados (al menos específicamente) en el libro de 2008. "Novel Carbon Adsorbents" está dividido en 5 partes: "Introduction" (1 capítulo), "Recent Developments in Theory" (2 capítulos), "New Characterization Methodologies" (3 capítulos), "Adsorption by Novel Carbon Types" (8 capítulos) y "Emerging Applications of Adsorption by Carbons" (7 capítulos). Los títulos de las cuatro últimas secciones ponen de manifiesto la actualidad de los temas tratados en el libro, que abarcan aspectos fundamentales y aplicados de la adsorción de gases y líquidos en materiales de carbono.

A modo de ejemplo, la sección dedicada a los adsorbentes carbonosos que han despertado recientemente el interés de la comunidad científica ("Adsorption by Novel Carbon Types") incluye capítulos que tratan sobre la adsorción sobre geles de carbono, en carbonos preparados a partir de carburos, carbonos de porosidad controlada gracias a las técnicas de moldeo, carbonos preparados mediante síntesis hidrotermal, carbonos que contienen cantidades apreciables de fósforo en su superficie y, como no podía ser de otra manera, nanomateriales de carbono, con un capítulo dedicado al comportamiento del grafeno como adsorbente. 57 autores, varios de ellos miembros del GEC, han contribuido en la elaboración de este volumen de más de 600 páginas. La imagen de portada es una representación a nivel molecular de una estructura ideal de carbono que encajaría en la red porosa de la zeolita Y empleada como molde en su preparación, de acuerdo con los cálculos computacionales llevados a cabo por el Prof. Hirotomo Nishihara (Tohoku University, Japón).

Socios protectores del Grupo Español del Carbón



Industrial Química del Nalón, S.A.
NalónChem

