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 centraremos 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 ºC) 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, CO_2 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 ^{13}C-enriched samples were prepared [12]. ^{13}C 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 sp^2 and sp^3 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 ^{13}C–^{13}C 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 sp^2- or sp^3-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 ºC), 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.
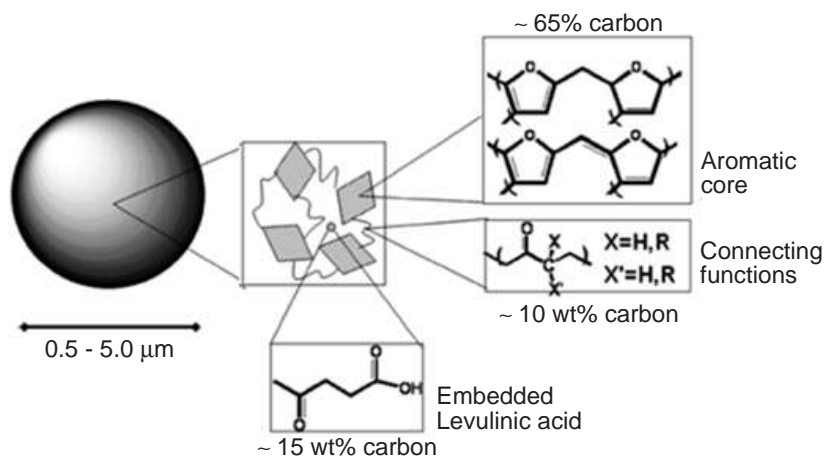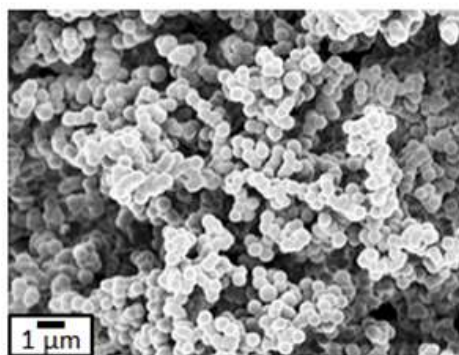
3. Porous HTC

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 m^2/g, and pore volumes in the 0.6-1.4 cm^3/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 (600-850ºC) 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 ºC 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 ºC) generate ACs with a lower porosity development and narrower PSDs, while the ones produced at 180–240 ºC 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 1. SEM micrograph of HTC material obtained from glucose at 180 ºC 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 ºC 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).

HYDROTHERMAL CARBON
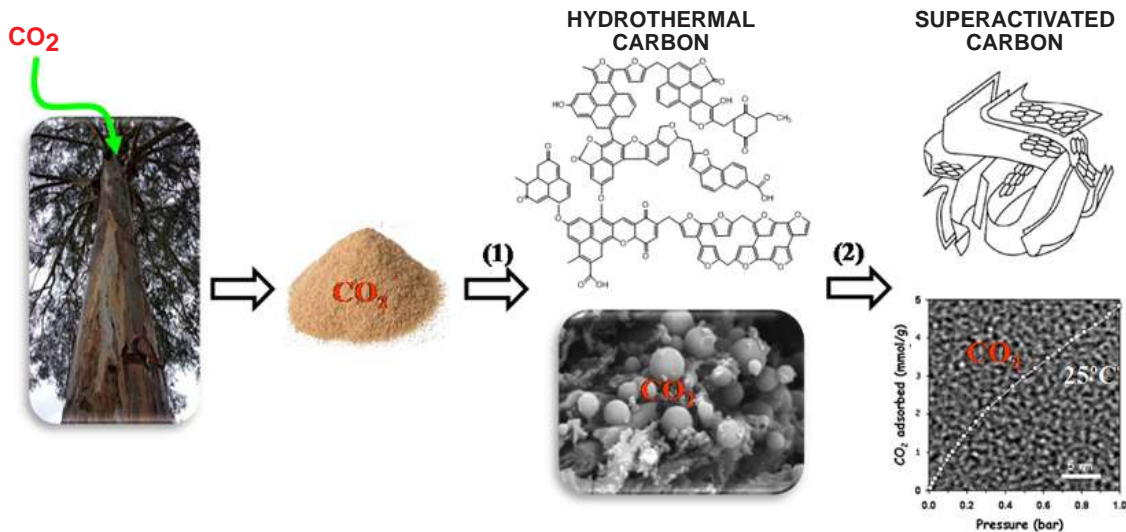
SUPERACTIVATED CARBON

CO_2

(1)

(2)

Figure 2. Schematic illustration of the overall synthesis procedure for HTC-based activated carbons and their application in CO_2 capture: (1) hydrothermal carbonization at 230–250 ºC (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 CO_2: (1) HTC a 230-250ºC (2 h), y (2) activación química con KOH.
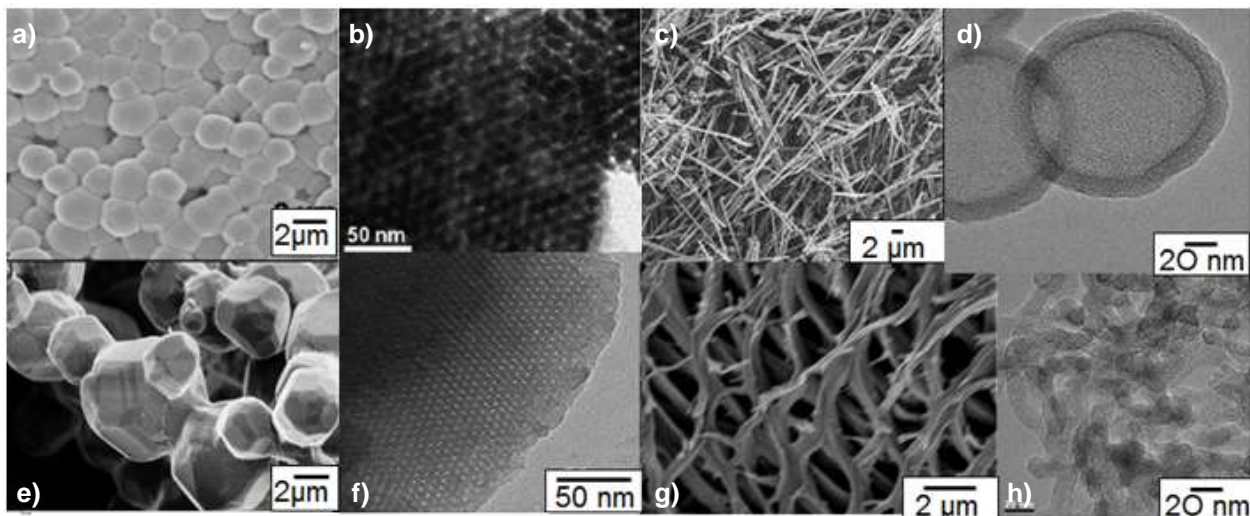

Figure 3. Porous HTCs: (a) Mesoporous HTC microspheres obtained by replication of silica using glucose (Reprinted with permission from Titirici M-M, Thomas A, Antonietti M; Adv. Funct. Mater. 2007;17(6):1010-1018; copyright © 2009, American Chemical Society). (b) Ordered mesoporous HTC obtained by replication 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. 23(22):4882-4885; copyright © 2009, American Chemical Society). (g) N-doped porous carbon obtained using shrimp/lobster food wastes after HTC and removal of $CaCO_3$ (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 membrane 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 gambas/langostas y eliminación del $CaCO_3$ (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 ºC, 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 constrains 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 $LiFePO_4$/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. Fe_2O_3 hollow spheres). In a similar fashion, HTC can also be used to incorporate pre-formed SnO_2 nanoparticles onto HTC spheres. Likewise, after the removal of carbon, mesoporous SnO_2 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
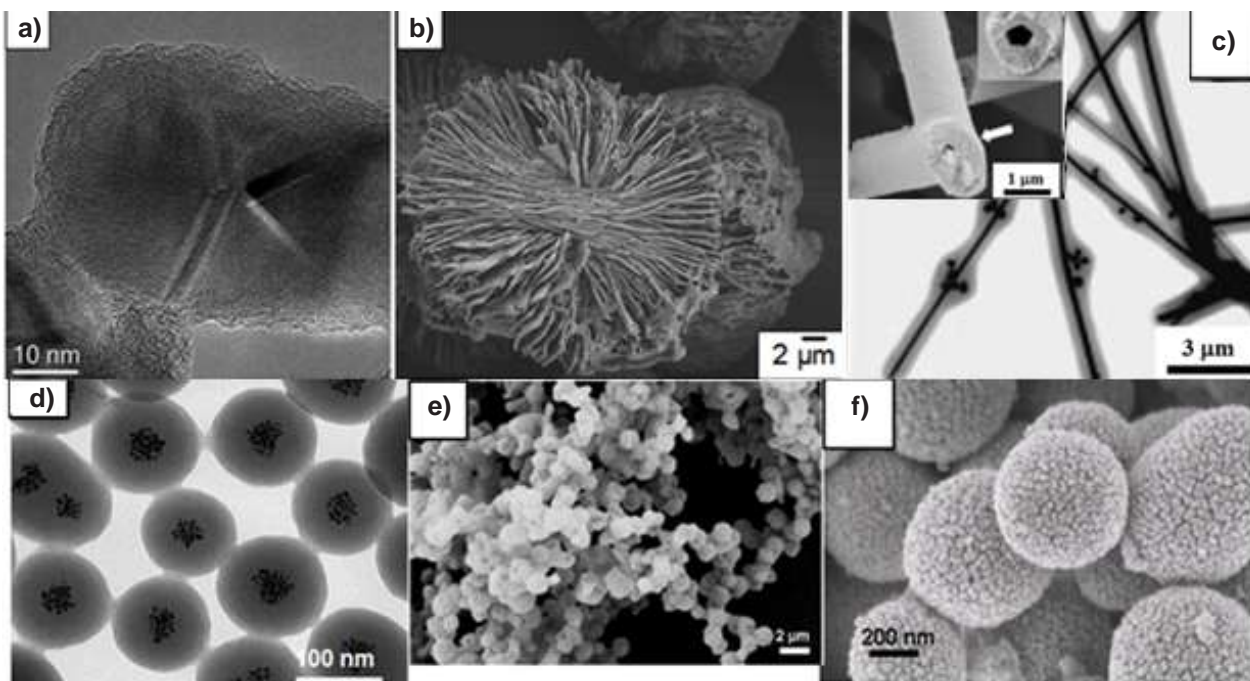

Figure 4. (a) Si nanoparticle coated hydrothermally with a thin layer of carbon from glucose (Reprinted with permission from Hu Y-S, Demir-Cakan R, Titirici MM, Muller JO, Schlogl R, Antonietti M, Maier J, Angew. Chem. Int. Ed. 2008;47(9):1645-1649; copyright © 2008 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim); (b) $LiFePO_4$ coated with carbon (Reprinted with permission from Popovic J, Demir-Cakan R, Tornow J, Morcrette M, Su DS, Schlögl 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 AgNO_3 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) SnO_2 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) $LiFePO_4$ recubierta con carbono (Reproducido con permiso de Popovic J, Demir-Cakan R, Tornow J, Morcrette M, Su DS, Schlögl 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 AgNO_3 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 SnO_2 (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 CO_2 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 ºC 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 300ºC was 326.1 ± 3.0 mg/g for Pb^{2+} and 150.7 ± 2.7 mg/g for Cd^{2+}, values 3 and 30 times higher than that of HTC material.

6.2.2. Gas adsorption. CO_2 capture and H_2 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 (-196ºC), 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 CO_2 capture, it was analyzed at a pressure of 1 bar and three adsorption temperatures (0, 25 and 50 ºC) [18]. The HTC-based activated carbons exhibited CO_2 capture capacities up to 6.6 mmol CO_2/g at 0 ºC, 4.8 mmol/g at 25 ºC and 3.6 mmol/g at 50 ºC. 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 CO_2 molecules. Additionally, the CO_2 adsorption is very fast, whereas N_2 adsorption is slower and much lower. In this way, the CO_2/N_2 selectivity measured under equilibrium conditions is 5.4. Furthermore, those sorbents are easily, quickly and fully regenerated by flowing a He stream at 25ºC.

Another interesting approach in relation to the use of HTC materials for CO_2 capture is based on their functionalization with amine groups, which exhibit a high affinity to CO_2. In this respect, Titirici et al. reported the CO_2 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 CO_2 capture capacities (up to 4.3 mmol CO_2/g at -20ºC). More important, these materials exhibit a very high CO_2/N_2 selectivity, up to 110 at 70 ºC.

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 $TEABF_4$ in acetonitrile) of HTC cellulose (C), starch (S) and sawdust (W)
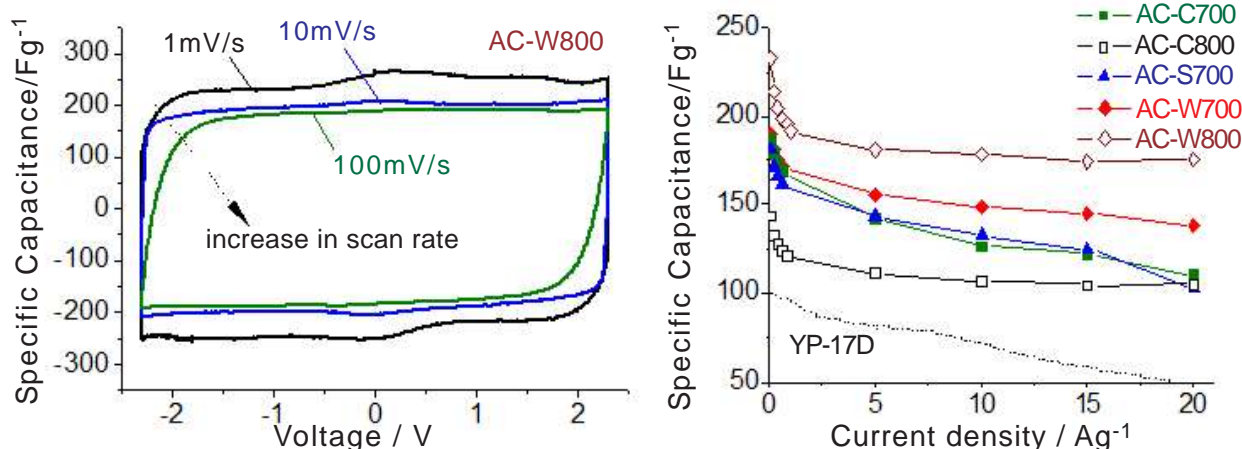
Figure 5. Electrochemical characterization of HTC-derived activated carbons in 1 M TEABF$_4$ solution in acetonitrile at room temperature: a) cyclic voltammograms (CV) of the activated carbon obtained from sawdust at 800ºC (AC-W800) and b) capacitance retention with current density in comparison with 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 TEABF$_4$ en acetonitrilo a temperatura ambiente: a) voltametría cíclica del carbón activo obtenido a partir de serrín a 800ºC (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 800ºC with a KOH/samplel 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/cm^3) 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 increase 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 = 600ºC) [42]. Those materials exhibited excellent electrochemical performance in KOH 6 M and H$_2$SO$_4$ 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/SiOx/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 SnO$_2$ microspheres were synthesized using HTC of furfural in the presence of SnO$_2$ 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 LiFePO$_4$ is considered one of the most promising cathode materials for Li-ion batteries. Urchin-like hierarchical mesocrystals of pristine LiFePO$_4$, as well as carbon coated LiFePO$_4$ 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 LiFePO$_4$ 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
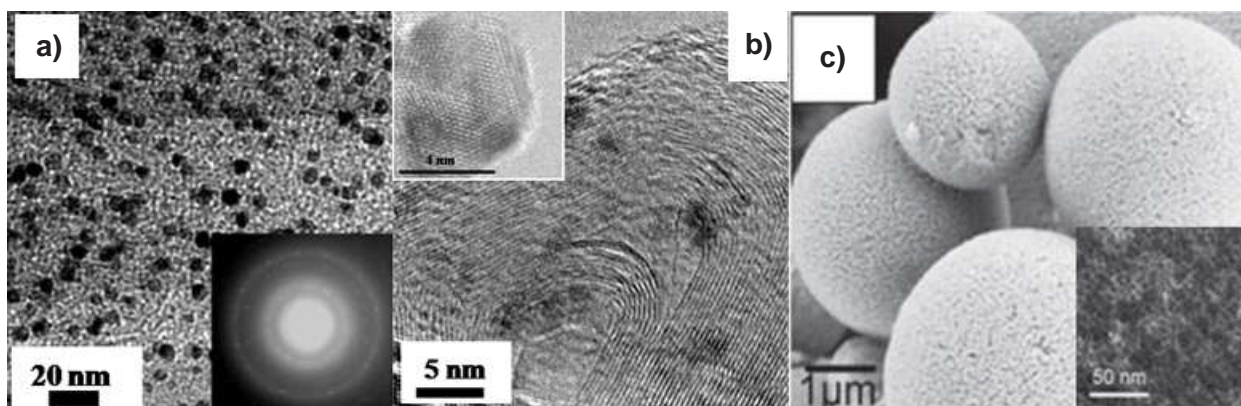
Figure 6. a) HRTEM image of Pt nanoparticles deposited over HTC hard carbon spherules (inset: selected area electron diffraction pattern of Pt nanoparticles) (Reprinted with permission from Yang R, Qiu X, Zhang H, Li J, Zhu W, Wang Z, Huang X, Chen L; Carbon 2005;43(1):11-6.; copyright © 2005, with permission 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@TiO$_2$ "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@TiO$_2$ (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 190ºC and post-treatment at 1000ºC (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 TiO$_2$ to the visible region. Among these attempts, TiO$_2$ 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 TiO$_2$ 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 TiO$_2$ which then acts as a novel "dyade"-type structure, with an improved TiO$_2$ 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 bioappliations (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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