One-pot synthesis of biomass-based hierarchical porous carbons with a large porosity development

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Abstract

A sustainable one-pot scheme for the synthesis of hierarchical porous carbons formed from biomass is developed herein. It is based on the carbonization of biomass-derived products (glucose, glucosamine, soya flour and microalgae) in the presence of an activating agent (potassium oxalate) and calcium carbonate nanoparticles that form a hard template. During carbonization, double carbonates are formed in-situ, which results in modifications in the morphology and size of the template nanoparticles, giving rise to a carbon material with an open macroporous foam-like structure rich in micro-/mesopores, the latter developing *via* a redox reaction between the carbon and potassium carbonate and also as a result of the reaction between the carbon and the evolved CO₂. The porosity can be tailored by selecting an appropriate precursor. Thus, the carbon materials are basically micro-/macroporous in the case of glucose and glucosamine, and micro-/meso-/macroporous when soya flour and microalgae are used. A direct relationship is observed between the amount of nitrogen present in the precursor and mesopore development. Hence, the addition of urea to the mixture of glucose and potassium oxalate and CaCO₃ nanoparticles also yields micro-/meso-/macroporous carbons. The materials synthesized at 800 °C have large surface areas in the ~1800-3100 m²/g range. At 750 °C, the materials synthesized from N-rich biomass combine ultra-large surface areas of 2400-3050 m²/g and a remarkable N-doping (2-3 wt % N). This combination of textural and chemical properties is highly appealing for many energy-related applications and also for adsorption-based processes.

Introduction

Porous carbon materials that have high surface areas, tunable pore structures, a high chemical/thermal stability and a good electronic conductivity are attractive candidates for many applications in the fields of catalysis,¹⁻³ gas storage/capture,^{4, 5} and energy storage^{4, 6, 7} and production.⁸⁻¹⁰ In particular, hierarchical porous carbons (HPCs) with a multimodal pore size distribution in the micro-/meso-/macropore range provide enhanced performance owing to the combination of interconnected pores at different scales serving distinctive functions: micropores for large adsorption capacity and surface area, mesopores and macropores for rapid mass transport, and macropores for acting as reservoirs or host pores.¹¹⁻¹⁴ For example, HPCs with a large pore volume are highly desirable for Li-S batteries to serve as hosts for a large amount of sulfur without blocking access of the electrolyte solution to the pores and leaving sufficient void space to allow the volume expansion of the active material.^{15, 16} Similarly, HPCs with large surface areas are good candidates for high power supercapacitors.¹⁷

HPCs have usually been synthesized by templating methods or a combination of templating and activation procedures. Thus, by using a combination of two hard or soft templates, HPCs with a bimodal pore size distribution can be obtained.¹⁸⁻²⁰ Similarly, a combination of soft and hard templates can be used to synthesize HPCs.²¹ More recently, templating approaches based on the use of polymeric precursors (e.g. polycarbosilane) have been shown to be suitable for fabricating HPCs.^{11, 14, 15} On the other hand, the physical or chemical activation of templated mesoporous/macroporous carbons is a very efficient route for developing micropores.^{22, 23} However, most

of those methodologies involve expensive chemicals, multiple steps and are therefore complicated and time-consuming. More straightforward approaches are highly desirable. We have recently shown that by selecting an appropriate organic salt (*i.e.* sodium gluconate), a hierarchical micro-/mesoporous carbon can be obtained ($S_{\text{BET}} = 1300\text{-}1900 \text{ m}^2 \text{ g}^{-1}$, $V_p \sim 0.9\text{-}1.4 \text{ cm}^3 \text{ g}^{-1}$).²⁴ Yu *et al.* employed a less straightforward approach by combining two organic salts, *i.e.* magnesium and potassium citrates, to produce carbons with different pore scales and hierarchical porous carbon nanosheets ($S_{\text{BET}} \sim 1735 \text{ m}^2 \text{ g}^{-1}$ and $V_p \sim 1.7 \text{ cm}^3 \text{ g}^{-1}$).²⁵ Similarly, Zu *et al.* by combining multi-scale inorganic salts and by controlling their crystallization and assembly through a freeze-drying process, were able to produce 3D porous carbon networks from glucose ($S_{\text{BET}} \leq 1100 \text{ m}^2 \text{ g}^{-1}$ and $V_p \leq 1.3 \text{ cm}^3 \text{ g}^{-1}$).²⁶ More recently, Deng *et al.* followed a green “leavening” strategy, whereby potassium bicarbonate -which includes a foaming agent (CO_2) and an activating agent (K_2CO_3) in its structure- was used to directly produce materials with a 3D hierarchical pore structure from monosaccharides, polysaccharides and biomass (S_{BET} up to $\sim 1900 \text{ m}^2 \text{ g}^{-1}$ and V_p up to $1.4 \text{ cm}^3 \text{ g}^{-1}$).²⁷ Zhao *et al.* applied a similar approach to a cation exchange resin with analogous results.²⁸ Strubel *et al.* synthesized HPCs with a much greater porosity development ($S_{\text{BET}} > 2600 \text{ m}^2 \text{ g}^{-1}$) from sucrose by using ZnO nanoparticles as template, either previously synthesized¹⁶ or generated in-situ using zinc citrate.²⁹

Herein we propose a one-pot scheme for the synthesis of biomass-based hierarchical porous carbons (S_{BET} up to $3300 \text{ m}^2 \text{ g}^{-1}$) by carbonizing the carbon precursor in the presence of an activating agent (potassium oxalate) and a commercially available and cheap hard template, calcium carbonate

nanoparticles. By applying a simple washing step with diluted hydrochloric acid, all the inorganic species can be removed. The synthesized materials are characterized by a hierarchical porosity in the micro-/macroporous range in the case of glucose and glucosamine, and in the micro-/meso-/macroporous range when microalgae, defatted soya flour or urea+glucose are used as precursor.

Experimental section

Synthesis of hierarchical porous carbons

α -D-Glucose (96%, Aldrich), N-Acetyl-D-glucosamine (≥ 99 %, Aldrich), defatted soya flour (see reference 30 for the defatting procedure) and microalgae *Spirulina platensis* were used as carbon precursors. In a typical synthesis, the carbon precursor was thoroughly mixed in an Agatha mortar with potassium oxalate monohydrate (Alfa Aesar) and then with calcium carbonate nanoparticles (Solvay, $d \sim 67$ nm), at a weight ratio of 1:1:1. Afterwards, the mixture was heat-treated at 750-800 °C (3 °C min^{-1}) under a nitrogen gas flow and held at this temperature for 1 h. The generated inorganic impurities (*i.e.*, calcium oxide nanoparticles and potassium compounds) were removed by washing several times with diluted HCl and then with distilled water until neutral pH. Finally, the solid product was dried in an oven at 120 °C for 3 h. The product yield of the synthesis process is 4-11 % (see Table 1). The carbons thus produced were labelled X-T, where X = G (glucose), GA (glucosamine), SF (soya flour) and MA (microalgae), and T = synthesis temperature. For comparison purposes, carbon materials were prepared from glucose and defatted soya flour using only CaCO_3 nanoparticles or potassium oxalate (800 °C, ratio 1:1). These carbons were denoted X-Ca when only CaCO_3

nanoparticles were used, and X-OxK when only potassium oxalate was used as activating agent. In addition, materials were fabricated from glucose by incorporating urea to the mixture glucose/potassium oxalate monohydrate/calcium carbonate (1:1:1) using a glucose/urea ratio of 1:0.5. These samples were labelled GU-T.

Physical and chemical characterization

Scanning electron microscopy (SEM) images were recorded on a Quanta FEG650 (FEI) instrument, whereas transmission electron microscopy (TEM) images were recorded on a JEOL (JEM 2100-F) apparatus operating at 200 kV. The nitrogen sorption isotherms of the carbon samples were measured at -196°C using a Micromeritics ASAP 2020 sorptometer. The apparent surface area (S_{BET}) was calculated from the N_2 isotherms using the Brunauer-Emmett-Teller (BET) method. An appropriate relative pressure range was selected to ensure a positive line intersect of multipoint BET fitting ($C > 0$) and to ensure that $V_{\text{ads}}(1 - p/p_0)$ would increase with p/p_0 .^{31, 32} The pore size distributions were determined by applying the Quenched-Solid Density Functional Theory (QSDFT) method to the nitrogen adsorption data and assuming a slit pore model. The pore volume corresponding to micropores ($V_{<2\text{nm}}$) and mesopores below 35 nm ($V_{<35\text{nm}}$) was determined through the QSDFT method. True density was determined from Helium picnometry using a Micromeritics Accupyc 1340 and apparent density from mercury porosimetry using a Micromeritics AutoPore IV, which allowed calculating the total pore volume. Elemental analysis (C, N and O) of the samples was carried out on a LECO CHN-932 microanalyzer. Thermogravimetric analysis (TGA) curves were recorded on a TA Instruments

Q6000 TGA system. X-ray diffraction (XRD) patterns were obtained on a Siemens D5000 instrument operating at 40 kV and 20 mA and using Cu K α radiation ($\lambda = 0.15406$ nm).

Results and Discussion

Structural and textural properties of the hierarchical porous carbons

The morphology of the carbon materials obtained from the different kinds of biomass-based products was examined by scanning electron microscopy (SEM). As can be seen in Figures 1 and S1, in all the cases, the carbon particles exhibit a foam-like structure. This structure is characterized by open and interconnected macrocavities with a size of around 40–400 nm, as evidenced by Figure S1. When the thermal treatment is performed solely in the presence of CaCO₃, the carbon particles show a macroporous structure (see Figures S2a, S2c and S2d) which is similar to that of the corresponding materials prepared in the presence of both K₂C₂O₄ and CaCO₃, but with a much denser structure and with fewer interconnected cavities (compare Figures S2a and S2b). On the other hand, when the thermal treatment is performed in the sole presence of K₂C₂O₄, particles with an irregular morphology are obtained (Figures S2e–f). These results suggest that chemical interaction takes place between the activating agent and the template which alters the size/morphology of the template particles, thereby modifying the final structure of the material.

A clear picture of the porosity present in these materials was obtained by N₂ physisorption. As can be seen in Figure 2a, the N₂ sorption isotherms show the presence of micropores in all the materials (sharp adsorption at relative pressures close to 0), small mesopores in the case of the materials derived

from defatted soya flour and microalgae (adsorption in the $P/P_0 \sim 0.1-0.8$ range), and large mesopores/macropores also in all the materials (pronounced N_2 uptake at relative pressures close to 1). Therefore, these N_2 sorption profiles clearly reveal that the materials derived from glucose and glucosamine possess a hierarchical micro-/macroporous structure, whereas those derived from defatted soya flour and microalgae have a micro-/meso-/macroporous structure. The presence of micro- and small mesopores is evidenced by the pore size distributions (PSDs) in Figure 2b. Regardless of the precursor used, the materials present a bimodal PSD. The smallest pore system has a similar size in all the materials, around 0.8-0.9 nm. Meanwhile, the largest pore system is centered at ~ 1.5 nm in the case of glucose and glucosamine, and around 2-2.5 nm in the case of defatted soya flour and microalgae. Interestingly, a direct relationship has been found between the percentage of nitrogen in the precursor and the development of small mesopores (2-5 nm). Thus, as can be deduced from Figure S3, glucosamine (6.3 wt % N) has the lowest volume of small mesopores, $0.27 \text{ cm}^3 \text{ g}^{-1}$ (800°C), whereas defatted soya flour (8.1 wt % N) and microalgae (11.4 wt % N) have volumes of small mesopores respectively of 0.76 and $1.18 \text{ cm}^3 \text{ g}^{-1}$ (800 °C). Table 1 presents the textural characteristics of the different porous carbons. All the materials are highly porous with BET surface areas and volume of pores < 35 nm in excess of $1800 \text{ m}^2 \text{ g}^{-1}$ and $\sim 1 \text{ cm}^3 \text{ g}^{-1}$ respectively. Especially remarkable are the BET surface areas and volume of pores < 35 nm of the materials obtained from raw biomass at 800 °C, of $\sim 2900-3100 \text{ m}^2 \text{ g}^{-1}$ and $\sim 2-3 \text{ cm}^3 \text{ g}^{-1}$ respectively. Furthermore, the total pore volume of these materials, which includes the macropores visible by SEM and not measurable by N_2

physisorption, is in the $11\text{-}16\text{ cm}^3\text{ g}^{-1}$ (see Table 1). Similar large values have been previously reported for materials with an aerogel-type structure.^{12, 33} This ultra-high internal porosity on different scales leads to low bulk densities in the $\sim 0.06\text{-}0.08\text{ g cm}^{-3}$ (Table S1), similar to that of carbon aerogels,¹² but higher than that of graphene aerogels.³⁴ On the other hand, the packing density of these materials is in the $0.2\text{-}0.4\text{ g cm}^{-3}$ range (see Table S1). At $750\text{ }^\circ\text{C}$, the materials are still highly porous, with BET surface areas in the $2400\text{-}3050\text{ m}^2\text{ g}^{-1}$ range. However, when only CaCO_3 nanoparticles are used, the materials have low surface areas of $600\text{-}900\text{ m}^2\text{ g}^{-1}$ and micropore volumes of only $0.2\text{-}0.3\text{ cm}^3\text{ g}^{-1}$, most of their porosity being made up of mesopores/macrocavities generated by the templating effect of the CaCO_3 nanoparticles. On the other hand, if only potassium oxalate is used, the carbons are highly microporous (*i.e.*, $> 80\%$ of the pore volume corresponds to micropore volume) with a surface area of $1300\text{-}2200\text{ m}^2\text{ g}^{-1}$ and total pore volume of $0.5\text{-}1.0\text{ cm}^3\text{ g}^{-1}$, which is coherent with the activating effect of $\text{K}_2\text{C}_2\text{O}_4$. These results suggest that there is a synergetic effect between both chemicals.

The incorporation of N-species during the activation process has a notable influence upon porosity development. This fact was confirmed by adding urea to the mixture of glucose/potassium oxalate /calcium carbonate. As evidenced by the N_2 sorption isotherms in Figure 2c, there is a clear increase in N_2 uptake up to a relative pressure of ~ 0.4 , indicating a notable increase in the population of small mesopores. This is confirmed by the PSDs in Figure 2d, the graph of cumulative pore volume in Figure S3 and the data in Table 1. The volume of pores in the $2\text{-}5\text{ nm}$ range is tripled compared to when glucose is used alone, with the values of BET surface area and volume of pores below 35

nm rising to above 3000 m² g⁻¹ and 2 cm³ g⁻¹, respectively. On the other hand, the use of urea does not modify the foam-like structure as can be seen from Figure S4. We have previously shown that the addition of a N-rich substance such as melamine to mixtures of KOH/hydrochar,³⁵⁻³⁷ KHCO₃/hydrochar³⁸ and K₂C₂O₄/saccharides leads to materials with a bimodal PSD in the micro-mesopore range. In the case of mixtures of K₂C₂O₄/hydrochar, melamine is somewhat less efficient in creating mesopores, the proportion of pore volume corresponding to mesopore volume increasing only up to ~ 30 %.³⁹ In the present case, it is evident that both the addition of a N-rich substance such as urea or the presence of nitrogen in the precursor leads to an increase in the population of mesopores in the synthesized carbons. However, the nitrogen already present in the biomass seems to be more efficient in creating mesopores, probably due to its more homogeneous distribution.

The degree of structural order of the synthesized materials was analyzed by XRD. As can be seen in Figure S5, all the materials exhibit broad and low intensity (002) and (10) bands at around 2θ = 22-24° and 43° respectively, indicative of their amorphous nature. Additionally, the stacking of graphene sheets decreases with the increase in temperature as a result of the creation of abundant porosity. This is particularly marked in the case of the materials obtained from defatted soya flour (HS-800) and glucose+urea (GU-750), which have a surface area ≥ 3000 m² g⁻¹ and a pore volume of ca. 3.1 cm³ g⁻¹.

Chemical characteristics of the hierarchical porous carbons

The results obtained show that both when N-rich substances are used as carbon precursor (*i.e.* glucosamine, microalgae and defatted soya flour) or

when a N-rich foreign substance (*i.e.* urea) is added, the synthesized carbons retain an appreciable amount of nitrogen under carbonization up to a temperature of 750 °C (~ 2-3 wt % N, see Table 1). The N/C weight ratios determined through XPS (0.020 for GU-750 and 0.032 for SF-750) agree with those of the elemental analysis, indicating a homogeneous distribution of nitrogen in the particles. As revealed by XPS analysis (Figure S6), the N-species present in these materials are the ones typically found in carbon materials, *i.e.* N-pyridinic (398.4 eV), N-pyrrolic/N-pyridonic (399.9 eV), N-quaternary (400.8-401.1 eV) and pyridine-N-oxide (402.5-402.9 eV).

In contrast, at higher carbonization temperatures, nitrogen groups are almost completely removed. Thus, the materials obtained at 800 °C only contain ~ 0.6-0.9 wt % N. Comparison with the carbon materials obtained from defatted soya flour using only CaCO₃ (8.5 wt % N) or K₂C₂O₄ (~ 0.5 wt % N), suggests that potassium compounds generated by the decomposition of potassium oxalate are responsible for the preferential removal of N. This is in agreement with the appearance of potassium cyanide during activation in the presence of potassium oxalate, as observed by XRD (see next section).

Chemical and structural transformations during high temperature treatment

Further information about the chemical and structural changes that take place during the synthesis process of these materials was collected by means of XRD, TGA analysis and N₂ physisorption. The TGA curves for glucose, glucosamine and defatted soya flour mixed with K₂C₂O₄ and CaCO₃ are shown in Figure 3a and the corresponding DTGs can be seen in Figure 3b (the DTG

curve for the mixture of $K_2C_2O_4$ and $CaCO_3$ is also included for comparison). The first sharp weight loss below 100 °C in all the mixtures (including $K_2C_2O_4+CaCO_3$, as shown in Figure 3b and S7a), corresponds to that of hydration water in potassium oxalate monohydrate. Then, glucose and glucosamine show another sharp weight loss (respectively at 160 and 180 °C, as can be seen in Figure 3b) corresponding to their dehydration and the beginning of polymerization, whereas defatted soya flour shows a less pronounced weight loss associated with its pyrolysis at around 300 °C (see traces in Figure 3b). If these profiles are compared with those of the pyrolysis of the raw materials and glucose+ $K_2C_2O_4$ (Figure S7b-c), it can be seen that the presence of potassium oxalate accelerates the dehydration/polymerization of glucose, whereas it does not seem to have any effect on soya flour pyrolysis. The next sharp weight loss steps take place at 530-550 °C, 600-690 °C and above 700 °C. The weight loss above 700°C -which does not figure in the TGA/DTG curves of $K_2C_2O_4+CaCO_3$ - can be assigned to the following redox reaction: ^{40, 41}

The weight loss steps in the ~ 500-700 °C range are also observed in the mixture of $K_2C_2O_4$ and $CaCO_3$ (Figures 3a and S7a), although the maxima weight loss peaks are slightly displaced towards a higher temperature in the case of $K_2C_2O_4+CaCO_3$, as can be seen in Figure 3b, which suggests that these weight loss steps are related to chemical changes in $K_2C_2O_4$ and $CaCO_3$. In order to elucidate the processes that are taking place, XRD analysis was performed on the samples synthesized from glucose and defatted soya flour at different temperatures before acid washing. As can be seen in Figure 4a and

Figure S8, at 500 °C there is no peak corresponding to potassium oxalate, indicating its complete decomposition. However, peaks ascribable to CaCO_3 and K_2CO_3 (a very small proportion) are present, along with intense peaks corresponding to fairchildite $\text{K}_2\text{Ca}(\text{CO}_3)_2$. This double carbonate is formed by the combination of the K_2CO_3 generated in the decomposition of potassium oxalate (reaction 2) and the CaCO_3 nanoparticles used as template (reaction 3):

Indeed, it is well-known that $\text{K}_2\text{Ca}(\text{CO}_3)_2$ is generated by the K_2CO_3 - CaCO_3 system.^{42, 43} Hence, the peaks in the range of ~ 450-550 °C in the DTG curves in Figure 3b can be assigned to the decomposition of potassium oxalate and the formation of $\text{K}_2\text{Ca}(\text{CO}_3)_2$. Figure 4a shows that at 650 °C a fraction of CaCO_3 has decomposed into CaO , another fraction has reacted with a certain amount of $\text{K}_2\text{Ca}(\text{CO}_3)_2$ to form another double carbonate, $\text{K}_2\text{Ca}_2(\text{CO}_3)_3$ (reaction 4) whereas another fraction remains unchanged:

At 700 °C, the decomposition of CaCO_3 into CaO is complete (reaction 5) and $\text{K}_2\text{Ca}_2(\text{CO}_3)_3$ transforms back to $\text{K}_2\text{Ca}(\text{CO}_3)_2$ (reaction 6):

At 750 °C, $\text{K}_2\text{Ca}(\text{CO}_3)_2$ has decomposed into K_2CO_3 and CaO (reaction 7, see Figure S8), so that un-reacted K_2CO_3 and CaO are the only species persisting at 800 °C (Figure 4b):

The decomposition of $\text{K}_2\text{Ca}(\text{CO}_3)_2$ (reaction 7) seems to occur at a lower temperature in the presence of biomass/saccharides compared to the $\text{K}_2\text{C}_2\text{O}_4$ and CaCO_3 mixture (see Figure 3b), which suggests that the decomposition is promoted by the reaction of carbon with K_2CO_3 . All of these changes in the carbonate species produce modifications in the morphology and size of the template particles (for example, cubic CaO particles are observed at 800 °C, as shown in Figure S9a, in contrast to the initial sphere-like CaCO_3 nanoparticles in Figure S9b), resulting in the final foam-like structure with many interconnected macrocavities. Above 700-750 °C, the microporosity/small mesoporosity develops mainly *via* the redox reaction 1, but also by carbon gasification *via* reactions 5-7. Meanwhile, the large mesopores/macropores result from the multiple template particles derived from CaCO_3 nanoparticles (*i.e.* $\text{K}_2\text{Ca}(\text{CO}_3)_2$, $\text{K}_2\text{Ca}_2(\text{CO}_3)_3$ and CaO), resulting in a much less dense structure than that obtained in the presence of only CaCO_3 (Figure S2a). As can be deduced from the XRD patterns in Figure S8, the same carbonate species are obtained in the case of N-rich biomass or the addition of urea. Besides, in these cases, KCN is formed above 750 °C. This results in the substantial reduction of N content observed for $T \geq 750$ °C (Table S2). Thus, for $T \leq 650$ °C, the materials obtained from defatted soya flour have high N contents of the order of 7-8 wt %, compared to less than 3 wt % for $T \geq 750$ °C.

Detailed information about the gradual generation of porosity during the thermal treatment was obtained by means of N_2 physisorption analysis. As indicated by the data in Table S2 and the isotherms in Figure S10a, when glucose is the precursor, the carbons obtained at 500 and 650 °C exhibit very similar textural properties and most of their porosity consists of macropores as a

result of the templating of the calcium-based nanoparticles, as might be expected (see Figure S11). In addition, these carbons possess a small amount of narrow micropores (see Figure S10b), which is typical of carbonized glucose. Above 700 °C, due to reactions 1, 5 and 6, there is a large increase in the volume of micropores (see Table S2). In the case of defatted soya flour, the most substantial development of micro-/small mesopores also occurs above 700 °C (see Table S2 and Figure S10), in parallel with a drastic reduction in the nitrogen content (weight ratio N/C = 0.095 at 650 °C and 0.031 at 750 °C). If these results are compared with those of glucose, it can be hypothesized that the removal of CN- species is responsible for the development of small mesopores.

It should also be noted that the carbon materials developed in this work exhibit certain properties that are advantageous for energy-related applications, besides adsorption-based processes. Thus, the carbons obtained from defatted soya flour, microalgae and glucose+urea combine ultra-large pore volumes (Table 1) with relatively good electronic conductivities ($0.1\text{--}0.7\text{ S cm}^{-1}$ at 750 °C and $1.0\text{--}2.3\text{ S cm}^{-1}$ at 800 °C, see Table S1) -and even N-doping at 750 °C (2-3 wt % N)-, features which make them good candidates as hosts/supports of inorganic particles for electrochemical applications, such as metal oxides for supercapacitor electrodes, metals/metallic compounds for electrocatalysts or sulfur/selenium for Li-S/Li-Se batteries. Also, the materials obtained from glucose and glucosamine are a good option as supercapacitor electrodes with high power capability, as they combine a large specific surface area ($1800\text{--}2700\text{ m}^2\text{ g}^{-1}$) arising mainly from their micropores with macropores that act as transport pores and ion-buffering reservoirs minimizing diffusion distances.¹²

Conclusions

Hierarchical porous carbons with large surface areas and high pore volumes have been synthesized by means of a sustainable one-pot scheme based on biomass-based products. The strategy involves the thermal treatment of certain biomass-derived substances (*i.e.*, glucose, glucosamine, soya flour and microalgae) in the presence of a soft activating agent (potassium oxalate) and a hard template (calcium carbonate nanoparticles). During the thermal treatment, double carbonates are formed in-situ, which brings about modifications in the morphology and size of the template nanoparticles, giving rise to a final macroporous foam-like structure rich in micro- and/or mesopores. These are generated by the redox reaction of the carbonaceous products with potassium carbonate and also by carbon gasification. The carbon materials thus produced have large surface areas in the ~ 1800 - $3100 \text{ m}^2/\text{g}$ range. The porosity is tailored by selecting a suitable precursor. Thus, when glucose and glucosamine are used as carbon precursor, the resulting materials are micro-/macroporous, whereas N-rich biomass such as defatted soya flour and microalgae yield materials with a multimodal pore size distribution in the micro-/meso-/macroporous range. There is a direct relationship between the percentage of nitrogen in the precursor and the mesopore development. Therefore, by adding a N-rich substance such as urea to the mixture of glucose+potassium oxalate+ CaCO_3 nanoparticles, micro-/meso-/macroporous carbons are also obtained. The use of N-rich carbon precursors and urea allows N-doping of the final carbon material (2-3 wt % N at 750°C).

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Supporting Information

Tables including values of density and electronic conductivity, and the physico-chemical properties of the hierarchical porous carbons obtained at different carbonization temperatures; figures including SEM pictures, graph of cumulative pore volume, XRD patterns, XPS N 1s core level spectra, TGA curves, and N₂ sorption isotherms and pore size distributions.

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Table 1. Physico-chemical properties of the hierarchical porous carbons.

Carbon	Yield (%)	Textural properties				Chemical composition [wt %]		
		S_{BET} [m ² g ⁻¹]	V_{total} [cm ³ g ⁻¹]	$V_{<2\text{nm}}$ [cm ³ g ⁻¹]	$V_{<35\text{nm}}$ [cm ³ g ⁻¹]	C	O	N
G-800	9	1813	11.3	0.68	1.01	92.9	6.6	-
GA-800	11	2680	14.3	1.01	1.49	93.8	5.6	0.65
SF-800	5	2924	12.5	0.97	2.15	94.8	4.3	0.55
MA-800	4	3135	15.7	0.91	2.82	93.5	6.2	0.56
GA-750	12	2406	-	0.92	1.27	88.2	9.3	2.0
SF-750	6	2673	-	0.95	1.78	89.0	7.7	2.8
MA-750	5	3053	-	1.00	2.30	88.3	9.0	2.1
G-Ca	14	890	-	0.31	0.71	-	-	-
SF-Ca	12	620	-	0.21	0.51	79.8	10.8	8.5
G-OxK	27	1280	-	0.46	0.50	-	-	-
SF-OxK	15	2210	-	0.83	1.00	96.2	3.2	0.48
GU-750	10	3195	-	1.15	1.90	89.3	8.5	2.0
GU-800	10	3340	12.1	1.18	2.04	94.8	4.3	0.85

Figure 1. SEM pictures of the hierarchical porous carbons obtained from different precursors: a) glucose, b) glucosamine, c) microalgae and d) defatted soya flour.

Figure 2. N₂ sorption isotherms (a and c) and pore size distributions (b and d) of the hierarchical porous carbons.

Figure 3. TGA curves (a) and the corresponding DTG curves (b) for mixtures of biomass (glucose, glucosamine and defatted soya flour) + potassium oxalate + calcium carbonate. The DTG curve of the mixture potassium oxalate/calcium carbonate has been added to Figure b for comparison purposes. Atmosphere: N₂ (ramp rate = 3 °C min⁻¹).

Figure 4. XRD patterns of mixtures of glucose+potassium oxalate+calcium carbonate treated at different temperatures: a) 500-650 °C and b) 700-800 °C.

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