Preparation and CO₂ Adsorption Properties of Soft-Templated Mesoporous Carbons Derived from Chestnut Tannin Precursors

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ABSTRACT

This work presents a soft templating approach for mesoporous carbon using the polyphenolic heterogeneous biomass, chestnut tannin, as the carbon precursor. By varying synthesis parameters such as tannin:surfactant ratio, cross-linker, reaction time and acid catalyst, the pore structure could be controllably modulated from lamellar to a more ordered hexagonal array. Carbonization at 600 °C under nitrogen produced a bimodal micro-mesoporous carbonaceous material exhibiting enhanced hydrogen bonding with the soft template, similar to that shown by soft-templating of phenolic-formaldehyde resins, allowing for a tailorable pore size. By utilizing the acidic nature of chestnut tannin (i.e. gallic and ellagic acid), hexagonal-type mesostructures were formed without the use of an acid catalyst. The porous carbon materials were activated with ammonia to increase the available surface area and incorporate nitrogen-containing functionality which led to a maximum CO₂ adsorption capacity at 1 bar of 3.44 mmol/g and 2.27 mmol/g at 0 °C and 25 °C, respectively. The ammonia-activated carbon exhibited multiple peaks in the adsorption energy distribution which indicates heterogeneity of adsorption sites for CO₂ capture.

1. Introduction

Growing concern over anthropogenic carbon dioxide emissions from fossil fuel combustion as a major contributor to global climate change has increased research efforts into remediation and alternative energy sources. Combustion of fossil fuels for power generation accounts for 62 % of greenhouse gas emissions.[1] Despite an increased focus on renewable technologies for electricity generation and storage, the development of cost effective materials for the separation of carbon dioxide (CO₂) from exhaust gases remain a high priority during the current transitional gap until an effective shift to cleaner energy can be realized. This requires new materials for carbon capture and sequestration (CCS) that are effective and environmentally benign.

Porous carbon materials have been studied as CO₂ adsorbents because of their high chemical stability, high surface area, and low cost.[2-5] Though a variety of methods have been explored to synthesize carbon, one popular approach is via carbonization of natural substances (i.e. corn cobs, sawdust, fruit shells, coal tar pitch, etc.) and activation to increase the surface area for adsorption.[6-9] However, the porosity of carbon derived from these natural sources tends to be dominated by disordered micropores (diameter < 2 nm), which have slower gas diffusion rates. The presence of larger mesopores (2 - 50 nm in diameter) can better facilitate gas transport and diffusion into micropores by reducing the resistance to mass transfer and pathway distance. Thus, a hierarchical carbon that contains both microporosity and mesoporosity with uniform pore size distributions would be ideal for systematic CO₂ adsorption.

Uniform mesoporosity is typically obtained via templating of synthetic precursors, such as phenolic resins, furfuryl alcohol, sucrose, polyacrylonitrile, and polydivinylbenzene.[10] In particular, the mild conditions for condensation-polymerization of phenolic-aldehyde resins and the high char yield upon carbonization have made this a practical precursor for both soft and hard

templating techniques.[11-12] Templating methods can produce hierarchically porous carbon materials, which have proven valuable in part because the tunable pore structures are important for increased mass transport.[11, 13-14] However, synthetic precursors are often expensive which can increase the cost and energy consumption due to extensive processing and purification, offsetting the benefits of enhanced CO₂ adsorption. Using a naturally occurring biomass *in lieu* of synthetic precursors provides a means to reduce the energy consuming steps, thereby decreasing environmental impact as well as decreasing cost. For example, the naturally occurring poly phenolic material, tannin, has proven to be a suitable replacement for traditional synthetic phenolic species in adhesives.[15] Using tannins as the naturally occurring biomass for ordered carbon materials provides a cost effective alternative that uses a raw material that is readily available, resulting in a greener approach for synthesizing an efficient CO₂ adsorbent. Recent reports have also explored the use of tannins in the synthesis of porous carbon materials.[16-17]

Tannins are categorized in two broad classes: the condensed and the hydrolysable tannins. Condensed tannins, generally recognized by their oligomeric flavonoid structures, are a class of catechol or flavanols which are highly reactive and have been shown to self-polymerize.[18] The hydrolysable tannins are comprised of polyphenolic substituted glucose molecules that are cleaved upon the introduction of weak acids or bases yielding gallic and ellagic acids (**Fig. 1**). [19-20] The gallic acid moieties found primarily in hydrolysable tannins exhibit a directing effect that is similar to that of resorcinol, a phenolic carbon precursor often used in templated mesoporous carbons.[13, 21] While the two classes of tannins occur independently and are typical of a given species, both classes have a high char yield and are microporous upon

carbonization without templating but the acidic nature of hydrolysable tannins can be utilized in the novolac synthesis as a polymerization catalyst.[19, 22-24]

In this work, we report the use of hydrolysable chestnut tannin (*Castanea sativa*) in a novolac type phenolic resin for the soft-templating synthesis of porous carbon with uniform porosity using a copolymer surfactant. In essence, chestnut tannin was explored as a suitable replacement for the phenolic resins because of its similar properties, including hydrogen bonding with the triblock copolymer template. By varying the synthesis parameters such as tannin:surfactant ratio, cross-linker, reaction time and presence of an acid catalyst, the pore structure could be tailored with a range of pore sizes and surface areas. The tannin-based porous carbon was then exposed to ammonia activation at high temperature to increase the surface area and micropore volume while incorporating nitrogen functionality into the framework. These activated carbons showed high CO₂ adsorption up to 3.44 mmol/g at 0 °C at 1 bar. The interaction of CO₂ with the porous carbon was examined by measuring the heats of adsorption and calculating adsorption energy distributions to show the presence of multiple adsorption sites.

2. Experimental

2.1. Chemicals

The triblock copolymer, Pluronic F127 (EO₁₀₆PO₇₀EO₁₀₆ 12600 kDa), formaldehyde solution (37 wt. % in H₂O, 10-15% methanol stabilized), and glyoxal solution (40 wt. % in H₂O) were purchased from Sigma-Aldrich Chemical Inc. Ethanol (EtOH, 200 proof) and hydrochloric acid (HCl, 37 % aq.) were purchased from Fisher Scientific. Chestnut tannin extract was purchased from Traditional Tanners Supply. All reagents supplied were used without further purification.

2.2. Synthesis

Mesoporous carbons were synthesized by *in-situ* self-assembly of chestnut tannin extract (CT) and Pluronic F127, the structure-directing agent, in acidic ethanol. Typically 2.52 g of Pluronic F127 dissolved in 18 g of a stock acidic solution prepared with 100 g EtOH, 90 g H₂O, and 2 g HCl. After dissolution, 6 g of CT was added with 2.6 g of 37 wt. % formaldehyde and stirred for a specified period of time. The solution was then cast on a petri dish to evaporate the solvent overnight and subsequently transferred to an oven for curing at 80 °C for 24 h. The samples were then carbonized at 600 °C for 2 h with a ramp rate of 5 °C/min. The CT is a heterogeneous mix of polysubstituted glucose as shown in Fig. 1 without a defined composition. For this reason, the mass ratio of the raw CT to F127 template was varied from 0.5 to 3 to study the effect on the morphology of the carbon product. Typically, the above synthesis is performed under acidic conditions to catalyze the polymerization of the phenolic with an aldehyde and increase hydrogen bonding between the carbon source (CT) and the template (Pluronic F127) thereby eliminating the need to pre-polymerize the phenolic polymer as a resol prior to inclusion within the template. Because of the acidic nature of the CT, however, one series of samples was synthesized without the HCl catalyst, instead using a solution consisting of 52.6 wt.% ethanol. Formaldehyde or glyoxal was added as 1:1.6 and 1:2.3 by weight, respectively, in relation to CT. The reaction time was measured from the time the aldehyde cross-linker was added, or when no cross-linker was present to study the effect of the cross-linker on morphology, to when chestnut tannin was added. The reaction time was varied from 40 min to up to 6 h to determine the effect of cross-linking on morphology.

Samples are designated by their CT: F127 wt. ratio, solution conditions (A-acidic or N-neutral), reaction time (in minutes), cross-linker designation (F - formaldehyde, G - glyoxal, or X - none), and reaction temperature (in °C). A description of each sample is given in Table 1.

Table 1. Description of the experimental synthesis parameters for each sample.

Sample Designation	Mass ratio CT: F127 ^a	pH adjustment	Reaction time [min]	Cross-linking agent	Reaction temperature [°C]
1N40G30	1 : 1	None	40	Glyoxal	30
1N40F30	1 : 1	None	40	Formaldehyde	30
1N40X30	1 : 1	None	40	None	30
1N40X50	1 : 1	None	40	None	50
2.38N80F50	2.38 : 1	None	80	Formaldehyde	50
2.38N120F30	2.38 : 1	None	120	Formaldehyde	30
2.38N240F30	2.38 : 1	None	240	Formaldehyde	30
2.38N360F30	2.38 : 1	None	360	Formaldehyde	30
0A145F65	3.2 : 0	Acidic	145	Formaldehyde	65
0.8A80F50	0.8 : 1	Acidic	80	Formaldehyde	50
2.38A70G30	2.38 : 1	Acidic	70	Glyoxal	30
2.38A60F30	2.38 : 1	Acidic	60	Formaldehyde	30
2.38A100F30	2.38 : 1	Acidic	100	Formaldehyde	30
2.38A240F30	2.38 : 1	Acidic	240	Formaldehyde	30
2.38A360F30	2.38 : 1	Acidic	360	Formaldehyde	30

^a Mass ratio of chestnut tannin extract relative to Pluronic F127

2.3 Activation

Activation was performed on carbonized samples with flowing anhydrous ammonia NH₃ at 800 °C with a ramp rate of 20 °C /min to 800 °C and held for 20 min. Thermal cycling occurred under Ar flow. Ammonia activated samples were designated with a leading ‘N’ i.e. “N2.38A70X50”.

2.3. Characterization

Nitrogen (N₂) sorption analysis was performed using a Micromeritics Tristar 3000 at -196 °C. Prior to measurement, samples were degassed under flowing nitrogen at 170 °C for 180 min. The specific surface area was calculated using the Brunauer-Emmett-Teller (BET) equation utilizing the adsorption branch.[25] The microporous surface area was determined from the t-plot in the low-pressure adsorption of P/P₀ from 0.1 to 0.2 with a carbon black standard. The pore size distribution plot was derived from the adsorption branch using the Kruk-Jaroniec-Sayari (KJS) method with carbon black STSA.[26] For micropore analysis, density functional theory (DFT) was used with adsorption isotherms acquired by a Quantachrome AS-1 using N₂ adsorption at -196 °C after degassing the sample under vacuum at 170 °C. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images were obtained using a Hitachi HD 2000 STEM microscope operating at 200 kV.

XPS analysis was performed using a PHI 3056 XPS spectrometer with an Al K_α source (1486.6 eV) at a measurement pressure below 10⁻⁸ Torr. High-resolution scans were acquired at 350 W with 23.5 eV pass energy and 0.05 eV energy step. Survey scans were measured at 350 W with 93.9 eV pass energy and 0.3 eV energy step. The binding energies were shifted to account for charging by setting the main carbon signal to 284.8 eV.

2.4. Adsorption studies

CO₂ and N₂ adsorption isotherms were measured gravimetrically with an Intelligent Gravimetric Analyzer, Hiden IGA, using 99.995% purity CO₂ and >99% purity N₂. The uptake measurements were corrected for buoyancy of the system and samples. Samples were first degassed under vacuum at 150 °C until a stable weight was achieved.

The CO₂ adsorption isotherms at 0 °C and 25 °C were fit using the Langmuir, Sips, and Toth models.[27-28] The fits from the Toth model equation were used to determine the CO₂ isosteric heat of adsorption. Details of the fitting procedure and the Langmuir and Sips fitted CO₂ isotherms can be found in the Supporting Information.

3. Results and Discussion

3.1. Synthesis of Chestnut Tannin derived Mesoporous Carbon

Soft templating of phenolic-based resins to synthesize ordered mesoporous carbon is based on the removal of a triblock copolymer template during the carbonization process leaving a phenolic-based carbon inverse replica of the template structure[2]. While the template additive, i.e. the carbon source, can alter the phase behavior of the triblock copolymer,[29] it can also facilitate changes to unique structures that are retained after pyrolysis. In this respect, hydrogen-bonding between the phenolic carbon precursor and the triblock copolymer can be considered essential for obtaining ordered pores via self-assembly of the micelles.[14, 30-31] The potential of the hydrolysable tannin as a precursor in porous carbon synthesis is attributed to the presence of gallic acid, which has been shown to react similarly to resorcinol.[14, 21, 32]

A series of mesoporous carbon materials were synthesized in which parameters such as tannin mass ratio, solution acidity and reaction conditions were varied in order to optimize the porosity and stability of the resulting carbon. In contrast to traditional phenolic-formaldehyde (PF) resins where the mechanism for step-growth polymerization can be readily interpreted due to the well-defined precursor and ordered carbon product, biomass is often composed of a diverse mixture of compounds that can undergo multiple step-growth polymerization processes resulting in non-

uniform structure and composition. In addition, polymerization using the typical linear novolac PF resin is generally performed with an acid catalyst that increases hydrogen bonding with the polyethylene oxide (PEO) block of the template and assists in template solubility.[30, 33] The presence of acidic sugars in chestnut tannin enables minimize the need for an additional acid catalyst in the synthesis of porous carbon while the removal of the formaldehyde or substitution with a less toxic cross-linker such as glyoxal can also be implemented.[11, 34]

Fig. 2 shows microscopy images for a series of tannin-based carbons synthesized using a 1:1 ratio of tannin to pluronic under neutral conditions with a reaction time of 40 min. Samples generated without the use of the formaldehyde or glyoxal cross-linker (designated with an 'X'), and an acid catalyst resulted in a lamellar-type layered structure as seen for both samples 1N40X30 and 1N40X50. Further investigation of the N₂ adsorption isotherms indicates that the higher reaction temperature of sample 1N40X50 led to an increased surface area, pore diameter and mesopore volume as well as an increased instance of voids and defects compared to 1N40X30. Adding the cross-linker, either glyoxal (designated by 'G') or formaldehyde (designated 'F'), produced a distinct shift from a lamellar-like to a more worm-like morphology as seen for 1N40G30 and 1N40F30. Not surprisingly, both cross-linkers showed a similar effect. A series of carbon materials were next synthesized with an increased chestnut tannin ratio under neutral conditions while varying the reaction time and temperature. From the microscopy results displayed in **Fig. 3**, the higher chestnut ratio consistently produced a more ordered, hexagonal-type array regardless of the reaction time. This shift from lamellar to worm-like to a more ordered hexagonal type array is therefore governed by the degree of polymerization and interaction of the phenolic polymer with the triblock copolymer. The swelling of the hydrophilic

block upon phenolic polymerization then shifts the free-energy of mixing and leads to a change in phase morphology.

In a typical *in-situ* soft-template synthesis process with a phenolic resin, the reaction is generally performed in acidic conditions and does not require the use of a pre-polymerized resol as the carbon source.[35] **Fig. 4** shows a series of tannin-based carbons synthesized under acidic pH with a formaldehyde cross-linker at various reaction times and temperatures. In acidic conditions, the carbon consistently exhibited disordered worm-like mesostructures for all reaction times and temperatures. Acidic reaction conditions favor both polymerization and cleaving of gallic acid from poly substituted glucose. The number of “active” hydrogen bonding donors increases under acidic conditions, which swells the micelles and increases the curvature forming a disordered structure.[36] The increase in the “active” hydrogen bonding sites without compensation through the addition of more acid is most likely due to the lack of ordered hexagonal pores.

3.2. Textural Properties and Surface Chemistry

The textural data from the N₂ adsorption isotherms of the series of mesoporous carbon materials are presented in **Table S1** where the sample name indicates the tannin ratio, solution acidity and cross-linker. The surface area ranged from 242 m² g⁻¹ to 420 m² g⁻¹ for the tannin-based carbon materials which is slightly lower than values from resorcinol-formaldehyde-based carbon previously reported by Wang et al.[13] In that work, a higher carbonization temperature (800 °C) was used resulting in a higher surface area (607 m² g⁻¹) and pore volume (0.58 cm³ g⁻¹) but a lower average pore diameter (6.3 nm) compared to the tannin-based carbon reported in this work. In contrast, hexagonally ordered carbon derived from phloroglucinol-glyoxal with the F127 template (S_{BET}: 410 m² g⁻¹, average pore diameter: 7.5 nm) produced surface area and pore

size similar to the tannin-based carbon possibly due to effects resulting from the larger aldehyde in the phloroglucinol-glyoxal polymer.[11] Braghiroli et al. reported the synthesis of nitrogen-doped carbon using hydrothermally treated tannin and measured a surface area of approximately $500 \text{ m}^2 \text{ g}^{-1}$ which is slightly higher than the tannin-based carbon reported herein.[16] However, it is difficult to make a direct comparison because wattle tannin was used instead of chestnut tannin for the phenolic source, no structure directing template was present during the phenolic polymerization, and the hydrothermal carbonization in an autoclave was performed in the presence of ammonium hydroxide, effectively generating the resol instead of a novalac.

Certain trends are evident from the textural properties presented in Table S1 and Fig. 2 and 3. For example, the 1:1 tannin to Pluronic F127 ratio generated the largest mesopore diameters of all the carbons regardless of the presence of a cross-linker, primarily due to the interstitial spacing of lamellar-like layers. In addition, there is a clear transition in the 1N samples (1:1 ratio) from lamellar-like with large pore size in the 16 to 18 nm range to worm-like with slightly smaller pore size at 10-12 nm indicative of a change in structure during self-assembly. Increasing the tannin ratio in the 2.38N series resulted in a decreased curvature leading to hexagonal-like arrays and smaller pore size at $\sim 7.5 \text{ nm}$. [37] Throughout the tannin-based carbon series synthesized in acidic conditions where the acid catalyst may play several roles, i.e. polymerization, cleaving of the gallic acid from the polysubstituted glucose, and increased hydrogen bonding, an increased curvature was observed leading to worm-like arrays. This may be due to the steric effects resulting from the larger components of the chestnut tannin forcing a distinct conformation on the surfactant. This would be analogous to that observed by Cardoso, et al. with the photosynthetically active molecules impact on a triblock copolymer surfactant.[29]

The nitrogen sorption isotherms for the carbons obtained from both neutral and acidic conditions are shown in **Fig. 5** and **Fig. 6**, respectively. The carbon from acidic conditions (**Fig. 6**) exhibit a steeper, asymmetric hysteresis compared to the isotherms in **Fig. 5**, characteristic of interconnected spherical shaped pores found in the disordered wormlike array (shown in **Fig. 4**).[38] The opening of the hysteresis loop at lower P/P_0 ($\sim 0.88 P/P_0$) for 2.38N series compared to their acidic counterparts, 2.38A ($0.90-0.92 P/P_0$), indicates that the mesopore size distribution shifted to smaller pore diameters, which is illustrated using the BJH pore size distributions in **Fig. 5** and **Fig. 6**, respectively. The closing of the hysteresis in the 2.38A series abruptly connects to the adsorption branch at $\sim 0.45 P/P_0$, which is indicative of cavitation due to pore constrictions while, in addition to constrictions, the broad hysteresis in the 2.38N series is typical of cylindrical pores with one end closed.[39] The 2.38N series yielded similar pore diameters with increased deviation from the average pore size distribution from the ordered mesoporous carbon found by Mayes et al.,[11] which can be attributed to the heterogeneity of the carbon precursor in the formation of disordered transitional domains. Adding the acid catalyst (2.38A series) generated carbon with similar surface areas to the neutral conditions but with a larger average pore diameter.

3.3. High Temperature Ammonia Activation

For CO₂ adsorption applications, both high surface area and the presence of specific functional groups such as N-containing moieties can enhance the adsorption capacity and selectivity. A number of authors have studied the effects of thermal activation using ammonia on a variety of carbon,[10, 40-44] and ammonia activation of carbon specifically applied for CO₂ adsorption due to the basic nature of the nitrogen moiety and its behavior towards the CO₂ acid gas, in addition to increasing microporous surface area.[42-43, 45-48] Results reported by Plaza et al. indicated

that with an activation temperature of 800 °C for 2h, development of porosity in the otherwise non-porous carbonized almond shells as well as the increased nitrogen content contributed to a CO₂ uptake capacity of ~2 mmol g⁻¹ at 27 °C and 1 bar.[43] Because of these previous result, the tannin-based carbon materials which had been carbonized at 600 °C were activated at high temperature (800 °C) under flowing anhydrous NH₃ which reacts with ether-like oxygen to form imine and pyridinic nitrogen moieties on the surface and etches the carbon resulting in increased micropore surface area.[49] Moreover, surface activation of porous carbon with ammonia is initiated by the decomposition of ammonia to free radicals, such as NH₂, NH, atomic hydrogen and nitrogen, which quickly attacks the carbon leading to nitrogen-containing functionality and increased carbon burnoff.[50-51]

Table S2 shows the textural data of the ammonia activated carbon. In general, activation with ammonia increased the surface area and, in some cases, the increase was significant. For example, the surface area of N0.8A80F50 increased from 315 m² g⁻¹ to 747 m² g⁻¹. The increased surface area can be attributed to the annealing that occurred in the 200 °C difference between the carbonization temperature and the activation temperature. As the carbonization temperature is increased, the carbons undergo an annealing process resulting in more uniformity of the pores, including pore shrinkage. This uniformity change also results in higher surface areas. In the two samples that exhibited lower surface areas, N2.38A100F30 and N2.38A240F30, the aggressiveness of the ammonia activation most likely led to pore collapse. This is evidenced by the drastic drop in the mesopore surface area and micropore volumes.

3.4. XPS Characterization

A set of ammonia-activated carbon samples representative of the various synthesis parameters (N1N40X50, N2.38N360F30, N0.8A80F50, and N2.38A360F30) was chosen for further investigation of the CO₂/adsorbent interaction using XPS, isosteric heats of adsorption, CO₂/N₂ selectivity, and micropore analysis. The increased temperature during ammonia activation destabilizes the nitrogen and only a small portion of stable nitrogen moieties remains after activation. The nature of the nitrogen species was investigated using XPS measurements (see **Fig. 7**), where the nitrogen species can be deconvoluted from the N1s spectra into pyridinic nitrogen (398.4 eV), pyrrolic nitrogen (400.5 eV), and oxidized nitrogen impurities (402.7 eV). A clear distinction between the nitrogen functional groups was found for the samples with a short reaction time (**Fig. 7a** and **7c**), which exhibit more of a mixture of pyridinic and pyrrolic nitrogen, compared to the samples reacted for 360 min (**Fig. 7b** and **7d**), which have primarily pyridinic-like nitrogen.

3.5. CO₂ Adsorption Characteristics

The set of ammonia-activated carbon samples (N1N40X50, N2.38N360F30, N0.8A80F50, and N2.38A360F30) chosen for further investigation included a 1:1 mass ratio with no cross-linker, both neutral and acidic reaction conditions, and higher mass ratio carbon. The samples were ammonia activated because the additional porosity and the presence of heteroatoms such as nitrogen can impact the adsorption capacity and CO₂ interaction with the surface of the carbon increasing the adsorption at low pressures. **Fig. 8** shows the CO₂ adsorption isotherms for the four different tannin-based carbons acquired at both 0 °C and 25 °C. The isotherms all show a rapid rise in CO₂ adsorbed at low pressure followed by a smaller increase in uptake as the pressure approached 1 bar, which is typical of adsorption on porous carbon materials. In addition, the adsorption capacity is higher at the lower temperature, which is indicative of an

exothermic adsorption process. More recently, biomass based activated porous carbons derived from acacia fruits[17], poplar anthars,[52] and pine nut shells,[53] give high CO₂ adsorption capacities of 3.748 mmol g⁻¹, 4.18 mmol g⁻¹, and 5.0 mmol g⁻¹, respectively, 25 °C and 1 bar, which can be attributed to the significantly higher surface areas (>1400 m² g⁻¹) comprised primarily of micropores formed by harsh KOH activating conditions. Furthermore, metal organic frameworks have shown CO₂ capture capacities as high as 6.4 mmol g⁻¹ under dry conditions, however, these materials are susceptible to effects from water.[54-55]

Table 2 shows results from the CO₂ adsorption capacities at 1 bar for the two different temperatures. From the capacities at 0 °C, there is a relationship between the adsorption capacity and the total surface area. For example, N0.8A80F50 had the highest CO₂ adsorption at 3.44 mmol g⁻¹ and the largest surface area of 747 m² g⁻¹ (see Supporting Information, Table S2) while N2.38A360F30 had the lowest adsorption and the lowest surface area. In contrast to typical physisorption behavior, the CO₂ capacity of N2.38A360F30 at 25 °C was only marginally higher than at 0 °C which is possibly due to pore collapse though this requires further investigation.

Table 2. CO₂ adsorption capacities, micropore surface area, CO₂ isosteric heats of adsorption and XPS analysis of porous carbons.

Sample	S _{micro} [m ² g ⁻¹]	CO ₂ uptake at 0 °C [mmol/g, 1 bar]	CO ₂ uptake at 25 °C [mmol/g, 1 bar]	Q _{st} [kJ/mol]	Total wt.% N	% N contribution to total		
						Pyridinic	Pyrrolic	Oxidized
N1N40X50	444	2.57	1.99	13.2	6.0	47.3	41.2	11.4
N2.38N360F30	510	3.14	2.14	18.5	4.3	67.5	19.9	13.6
N0.8A80F50	561	3.44	2.27	22.9	4.8	50.6	35.6	13.8
N2.38A360F30	261	2.19	2.02	10.4	3.4	93.1	4.2	2.7

To further explore the link between surface area and CO₂ adsorption capacity, DFT micropore pore size analysis (**Fig. 9**) was performed on these four samples to provide a better understanding of the adsorption capacity performance. From **Fig. 9a**, which shows the pore size distribution for the tannin-based carbon, all of the materials had visually similar distributions. However, more insight can be gained by calculating the cumulative pore volume shown in **Fig. 9b**. For example, N2.38A360F30 exhibited only a small decrease ($\sim 0.16 \text{ mmol g}^{-1}$ at 1 bar) in the CO₂ adsorption from 0 °C to 25 °C. While the micropore size distribution of this sample exhibits a high pore volume at 0.5 nm to 0.65 nm (ultramicro pore region), comparable to that of N2.38N360F30, it lacks a comparable pore volume from 0.7 nm to 2 nm (the supermicropore and micropore regions)[56] that is responsible for increased capacity, resulting in a negligible increase of uptake capacity from 25 °C to 0 °C. This anomalous behavior could also be partly due to the fact that the majority of the nitrogen in this sample is pyridinic. In addition to the very similar result for CO₂ adsorption at 25 °C and 1 bar for N1N40X50, the CO₂ capacity difference at 0 °C between N2.38N360F30 and N1N40X50 can be attributed to this increased pore volume difference between the two samples. In contrast, N0.8A80F50 exhibits the highest uptake capacity of CO₂ in the series, which can be attributed to the high pore volume of supermicropores (**Fig. 9**). The overall capacity using this material is associated with the microporous pore volume in the supermicropore region at 25 °C and 1 bar.[57-58]

3.6. Isosteric Heat and Adsorption Calculations

Increased functionalization of the surface of porous carbons can enhance the interaction between CO₂ and the adsorbent, as indicated by the isosteric heat of adsorption, resulting in enhanced capacity and a more selective approach to CO₂ capture.[59] The heats of adsorption were initially obtained by fitting the individual CO₂ adsorption isotherms acquired at 0 °C and 25

°C to the Toth model (see **Fig. 8**). Though other models were also used to fit the isotherms as shown in the Supporting Information, the Toth model provided the best fit to the experimental data. Results from the Toth model fitting were then incorporated into the Clausius-Clapeyron equation in order to calculate the heats of adsorption which ranged from 10.7 – 24.5 kJ mol⁻¹. The values are well within the range for physisorption but are lower than biomass-based porous carbons activated with ammonia (21-26 kJ mol⁻¹) and carbons that include a nitrogen-containing precursor in their synthesis (19.6-26.7 kJ mol⁻¹).[43, 60] One possible explanation could be that the complexity of the chestnut tannin precursor leads to multiple binding sites in the final carbon material each with a different interaction energy and heat of adsorption.

Though the Toth model incorporates a parameter to account for the heterogeneity of the surface, which ultimately improves the overall fit to the experimental data, little information is acquired about the nature of the heterogeneity. To obtain a greater understanding of the surface heterogeneity, we utilized the CAESAR (Computed Adsorption Energies, SVD Analysis Result) algorithm to calculate the adsorption energy distributions from the local isotherms using MatLab for the above four samples (see Supporting Information for mathematical details).[28, 61] The heterogeneity of the surface constructed as a distribution function from this data resulted in two sharp peaks for N1N40X50 and N2.38A360F30 and three distinct peaks for N2.38N360F30 and N0.8A80F50, suggesting the presence of two and three different types of adsorption sites, respectively. For all four samples, the lowest energy peak has the highest intensity. This peak ranged from 14 kJ·mol⁻¹ to 17 kJ·mol⁻¹ and is likely adsorption to active carbon sites. The next largest peak for all samples ranged from 20 kJ·mol⁻¹ to 23 kJ·mol⁻¹ and is in better agreement with nitrogen-containing carbon previously reported. Samples N2.38N360F30 and N0.8A80F50 each have an additional, higher energy peak in the 26 kJ·mol⁻¹ to 28 kJ·mol⁻¹, which is possibly

related to nitrogen-containing functional groups within the micropores of the sample. Samples N2.38N360F30 and N0.8A80F50 with three peaks in the distribution had higher CO₂ adsorption capacities and higher total surface areas and micropore areas than samples N1N40X50 and N2.38A360F30 which had only two peaks. One explanation is that the higher surface area samples have a larger fraction of micropores which result in a higher energy adsorption and greater CO₂ adsorption capacity. The multiple adsorption sites may also be affected by the chemical state of the nitrogen-containing functionality though no clear correlation can currently be drawn with the XPS data. Furthermore, the lamellar-like morphology of N1N40X50 may influence the variety of adsorption sites formed. Thus, the CO₂ adsorption capacity using porous carbon adsorbents depends on a complex interplay between various properties including the size and morphology of micropores and the presence of functional groups such as pyridinic or pyrrolic framework nitrogen. These factors can all affect the energy distribution of adsorption and ultimately determine the selective adsorption of CO₂. The use of the CAESAR algorithm can provide additional information on the presence and heterogeneity of adsorption sites in a porous material.

4. Conclusions

A series of mesoporous carbon materials with tailored porosity were synthesized using hydrolysable chestnut tannin in a soft-templating technique by varying the synthesis conditions. Using biomass as a carbon precursor in lieu of phenolic-formaldehyde resin, disordered and ordered carbon structures with uniform porosity were synthesized over a range of morphologies even without the use of an acid precursor. The resulting porous carbon was activated with ammonia to increase the total surface area and micropore volume as well as to incorporate nitrogen functionality into the carbon framework. The activated carbon showed selective

adsorption of CO₂ with high capacity up to 3.44 mmol g⁻¹ at 0 °C and 1 bar. Using a computational algorithm, CAESAR, the activated carbon with the highest surface areas showed an additional adsorption site at high energy that likely contributed to the high adsorption capacity. Thus, hydrolysable chestnut tannin was shown to be a viable precursor to generate porous carbon with potential for carbon capture applications.

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Figure Captions

Fig. 1. Primary compounds present in hydrolysable chestnut tannin: gallic acid (I) and hexahydroxydiphenic acid (HHDP) (II) esterified as the polyol species represented here as a polysubstituted glucose (III).

Fig. 2. SEM and TEM images of 1N40G30 (a) and (b), 1N40F30 (c) and (d), 1N40X30 (e) and (f), and 1N40X50 (g) and (h), respectively.

Fig. 3. SEM and TEM images of 2.38N80F50 (a) and (b), 2.38N120F30 (c) and (d), 2.38N240F30 (e) and (f), and 2.38N360F30 (g) and (h), respectively.

Fig. 4. SEM and TEM images of 0.8A80F50 (a) and (b), 2.38A70G30 (c) and (d), 2.38A60F30 (e) and (f), 2.38A100F30 (g) and (h), 2.38A240F30 (i) and (j), and 2.38A360F30 (k) and (l), respectively.

Fig. 5. Nitrogen adsorption isotherms at 77 K (left) and corresponding pore size distributions (right) of mesoporous carbon synthesized under neutral conditions prior to activation with ammonia. Isotherms offset vertically by 30 cm³/g consecutively.

Fig. 6. a) Nitrogen adsorption isotherms at -196 °C and b) corresponding pore size distributions of mesoporous carbon synthesized under acidic conditions prior to activation with ammonia. Isotherms offset vertically by 20 cm³/g consecutively.

Fig. 7. N1s XPS spectra of (A) N1N40X50, (B) N2.38N360F30, (C) N0.8A0F50, and (D) N2.38A360F30.

Fig. 8. CO₂ and N₂ adsorption isotherms for four different tannin-based carbon with the Toth model: (a) N1N40X50, (b) N2.38N360F30, (c) N0.8A80F50, and (d) N2.38A360F30.

Fig. 9. DFT pore size distribution (left) and cumulative pore volume (right) derived from nitrogen adsorption at 77 K of mesoporous carbon after activation with ammonia.

Fig. 10. The adsorption energy distribution calculated for adsorption of CO₂ on (a) N1N40X50, (b) N2.38N360F30, (c) N0.8A80F50, and (d) N2.38A360F30.

(I)

(II)

(III)