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Convenient design of porous and heteroatom self-doped carbons for CO₂ capture

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Abstract:

Porous and heteroatoms self-doped carbon (PHCs) materials are synthesized for the first time by employing carbonization of casein with $ZnCl_2$ at a temperature of 800 °C. The synthesis involves a one-step solid state carbonization cum activation to synthesize PHCs with high specific surface areas and surface functionalization with nitrogen and oxygen. The textural properties of PHCs including specific surface area, pore volume and pore size can easily be controlled by adjusting the activation amounts of $ZnCl_2$. The optimized material (PHC4) is synthesized with $ZnCl_2$ /casein impregnation ratio of 4 and it shows a high specific surface area (1080 m² g⁻¹) and an appreciable amount of heteroatoms, nitrogen (4.4%) and oxygen (4.7%). PHC4 exhibits a high CO₂ adsorption capacity at 0 °C/1 bar (3.5 mmol g⁻¹) and 0 °C/30 bar (15.8 mmol g⁻¹). Additionally, the presence of heteroatoms on the surface results in enhancement of interactions between CO₂ and the adsorbents which are evident from a high value of isosteric heat of adsorption (~35 kJ mol⁻¹) calculated using Clausius Clapeyron's equation. The reported activation synthesis strategy could be explored further to devise advanced functional nanomaterials for specific adsorption applications.

1. Introduction

In recent decades, the major human influence on global warming is the increasing emissions of carbon dioxide into the atmosphere [1, 2]. Therefore, this problem needs to be addressed on an urgent basis using technologies such as carbon capture and storage (CCS) [3]. Typically, absorption using aqueous amine solutions is a widely employed method for CO₂ capture [4]. However, the porous materials such as nanoporous carbons, nanoporous carbon nitrides, mesoporous silicas and metallosilicates, metal-organic frameworks (MOFs), zeolites and ionic liquids which are widely used in many applications including adsorption and separation, catalysis, and energy storage and conversion, are considered as alternative candidates to amines for CO2 capture [5-11]. In the past, several research groups have extensively documented the abovementioned materials for CO_2 capture [12-15]. However, these methods suffer from either of the constraints such as moisture sensitivity, complicated synthesis, low CO₂ uptakes, low selectivity and lastly, the overall costs of the energy consumption for materials regeneration [16]. Compared to these methods, CO₂ adsorption using porous carbon materials is gaining significant attention owing to their high recyclability, fast sorption kinetics, easier and cheaper synthesis approaches and comparative benchmark working capacities for CO₂ adsorption [17]. This promising behaviour of porous carbons for high CO₂ adsorption is a result of their decisive characteristics such as high specific surface area, tunable porosity and functionalized surface chemistry. More importantly, the physisorption nature of the process offers the biggest advantage in terms of lower energy consumption for material regeneration [18].

It is now firmly established in the existing literature that CO₂ adsorption in porous carbons is mainly dependent on the amount of microporous content and the specific surface area [19]. Additionally, the inclusion of lightweight heteroatoms such as nitrogen and/or oxygen into the skeletal carbon structure has been shown to improve the interactions between adsorbate and adsorbent [20, 21]. Nitrogen and oxygen-containing functional groups tend to impart polar character to the carbon surface which elevates the quadrupole-diploe interactions between the adsorbate and the adsorbent [22]. Several instances on the enhanced CO₂ capture performance of activated carbons doped with heteroatoms have been reported [23, 24]. In general, the heteroatoms such as nitrogen and/or oxygen could be introduced into the carbon skeleton by treatment of carbon precursors with nitrogen/oxygen containing agents or by direct carbonization of nitrogen and/or oxygen rich carbon precursors. Casein is a biologically functional protein which contains a significant amount of carbon (~53%) and high amounts of nitrogen (~16%) and oxygen (~ 26%) [25]. As such, it presents an attractive and feasible starting material for the synthesis of efficient adsorption materials pending that a substantial number of heteroatoms could be retained in the carbon structure during the process of carbonization. Casein has been studied extensively in the past for its use in cosmetics, drug and food sectors [26].

Herein, we have synthesized a series of porous and heteroatom self-doped carbons (PHCs) using casein through solid state activation with ZnCl₂. The drawbacks such as high material cost, equipment degradation and toxicity associated with the use of conventional potassium salts for activation such as potassium hydroxide for the production of activated carbons could be avoided by employing mild activating agent $ZnCl_2$ [27]. The effect of synthesis conditions on the amount of heteroatom content and carbon structure was analysed. A high temperature of 800 °C was used for carbonization to achieve best results for specific surface area and surprisingly a considerable amount of nitrogen and oxygen was retained in the carbon skeleton at this temperature which indicates high thermal stability of heteroatoms in the structure of synthesized materials. The materials were applied for CO₂ adsorption at different conditions of temperature (0 °C, 10 °C and 25 °C) and pressure (0 - 30 bar). The optimized material, PHC4, showed a high CO₂ adsorption capacity of 3.5 mmol g⁻¹ at 0 °C/1 bar and 15.8 mmol g⁻¹ at 0 °C/30 bar and a high value of isosteric heat of adsorption (~35 kJ mol⁻¹). The insufficient amount of literature on activation of casein and the promising nature of the porous heteroatom doped carbons (PHCs) developed in this study for high-pressure CO₂ capture signifies the forthcoming popularity of casein as a substrate for synthesizing functional nanoporous materials for various other adsorption applications as well.

2. Experimental section

2.1 Synthesis of porous and heteroatom self-doped carbons (PHCs)

PHCs were synthesized using a one-step solid-state activation procedure. Casein from bovine milk (Sigma Aldrich) was used as the starting precursor without any modifications. A given weight (1 g) of solid casein was mixed with different amounts (1 - 5 g) of solid zinc chloride to make five combination mixtures. The individual combinations were uniformly mixed using a pestle and mortar. This was followed by the carbonization of the individual mixtures in a tubular furnace at a temperature of 800 °C achieved using a heating rate of 5 °C min⁻¹. A constant supply of N₂ gas

through an inlet ensured that the inert atmosphere is maintained inside the tubular furnace during carbonization. The mixtures were kept at the target temperature for two hours to maximize the effect of temperature. Afterwards, the cooled carbon products were washed with 2M HCl and distilled water. The washed products were dried in an oven at 100 °C. The obtained final materials were denoted as PHCn, where n denotes the impregnation ratio of ZnCl₂/casein used for carbonization. For example, PHC4 was prepared by mixing 1 g casein with 4 g ZnCl₂ followed by carbonization at 800°C. For comparison, a non-activated sample PHC0 was also synthesized by direct carbonization of casein under similar conditions.

2.2 Characterization of PHCs

Nitrogen sorption isotherms were obtained at -196°C using a Micromeritics ASAP 2420 instrument. Prior to analysis, all samples were outgassed under vacuum for overnight at 200°C. Specific surface area (SABET) was measured using BET (Brunauer Emmett-Teller) method and total pore volume (V_t) was measured at p/po = 0.99. Total micropore area (S_{micro}) and micropore volume (V_{micro}) were determined using the t-plot method. Pore diameter was calculated using the original density functional theory (DFT) method. Crystal structure of PHCs was investigated from XRD diffraction patterns obtained with a Panlytical Empyrean XRD instrument. During analysis, the samples were irradiated with CuK α_1 and K α_2 radiation ($\lambda = 1.5406$ Å and 1.5444 Å) produced at an operating voltage and current of 40 kV and 40 mA, respectively. XRD patterns were recorded at a high angle range of $2\theta = 10 - 70^{\circ}$ under a continuous scan using a step size of 0.006°. Surface morphology of activated carbons was investigated using SEM images obtained with a Zeiss Merlin scanning electron microscope with an operating voltage of 2 kV. X-ray photoelectron spectroscopic (XPS) measurements were performed using Kratos Axis Ultra X-ray photoelectron spectrometer. A monochromatic Al Ka X-ray operating at 225 W, 15 kV and 15 mA are employed as a source of incident radiation. The parameters used for recording survey scans were as follows; pass energy (160 eV), (binding energy range - 1200 - 0 eV) and dwell time (100 ms). Pass energy was shifted to 20 eV for recording high-resolution scans. All samples were outgassed for overnight under vacuum before the actual analysis. CHN elemental composition data was collected using a Perkin Elmer instrument. Raman spectra were acquired using a Horiba LabRAM HR evolution Confocal Raman spectrometer using a 50 mW, 532 nm laser source with 10% power intensity. Each spectra represent an average of 40 acquisitions with 1 sec accumulation time.

2.3 CO₂ measurements

High-pressure CO₂ adsorption experiments were performed using a Quantachrome Isorb HP1 instrument. The analysis samples were degassed for ~12 hours at 250 °C under constant vacuum to ensure the complete removal of any moisture and impurities. Three different temperature values of 0 °C, 10 °C and 25 °C and a pressure range of 0 to 30 bar was used for the CO₂ adsorption measurements. Isosteric heat of adsorption value of the optimized material PHC4 was calculated using the Clausius Clapeyron equation. The CO₂ adsorption of PHC4 at 45 °C (actual temperature stabilized at 41.65) and its recyclability experiments were performed using a Micromeritics high pressure volumetric analyzer instrument.

3. Results and discussion

3.1 X-ray diffraction (XRD) and Raman spectroscopic analysis of PHCs

The crystal structure of the synthesized PHCs was investigated with powdered XRD (X-ray diffraction). Figure 1A shows the XRD plots for PHC1-4, which reveal the absence of any sharp peak indicating that the synthesized materials are amorphous in nature and also confirms that there are no left-over inorganic residues of zinc or casein remaining in the porous carbons after acid and water washing. There are two noticeable broad peaks observed at $2\theta = 25^{\circ}$ and $2\theta = 43^{\circ}$ in all the samples, which could be attributed to the (002) and (100) reflection planes of a poorly graphitised structure which is possibly formed during the high-temperature carbonization [28]. The degree of graphitization in all samples is almost similar and there is no noticeable difference observed in the two broad peaks among all the four samples. These results can also be correlated with the content of heteroatoms in all samples, measured using XPS (X-Ray photoelectron spectroscopy). A gradual decrease in the content of nitrogen (6.8 to 4.4%) and oxygen (6.6 to 4.7%) while going from PHC1 to PHC4 indicates that the corresponding functional groups are lost due to a combined action of high heat and chemical reaction with ZnCl₂, which help in better stacking of the graphitic layers [29]. Figure S1 shows the XRD patterns for PHC5 which also confirms the amorphous nature of the PHC derived from casein. Raman spectroscopy is a highly useful tool for elucidating the structural characterization of carbon-based materials [30]. The Raman spectra of the two best samples in terms of textural features, PHC3 and PHC4 were collected (Figure 1B) and it shows

two peaks which can be attributed to the typical D and G bands. These two bands are typically associated with sp³ hybridized carbon in amorphous carbon and graphitized sp² hybridized carbon in a layered structure [31, 32]. The ratio of intensity for the D and G bands of PHC3 and PHC4 was 1.06 and 0.99 which indicates that the latter is slightly more graphitized which results from the higher amount of ZnCl₂ used for activation. These results suggest that these materials are composed of hard carbon with a disordered graphitic carbon structure.

3.2 Nitrogen adsorption-desorption analysis of PHCs

Figure 2A depicts the nitrogen sorption isotherms of the PHC materials. As per the International Union of Pure and Applied Chemistry (IUPAC) classification, nitrogen adsorption-desorption isotherms fit into the type I which applies to microporous materials [33-35]. In all the isotherms, there is a general trend of a higher amount of nitrogen being adsorbed under a low relative pressure $(P/P_0 < 0.3)$ which indicates that the synthesized materials are microporous. PHC1 and PHC2 materials show a relatively smoother adsorption and desorption curves with no apparent hysteresis loop, however, a closer look at the isotherm curves of PHC3 and PHC4 reveals the presence of a small H4 hysteresis loop at relative pressure conditions of $P/P_0 > 0.4$, which can be associated with the presence of both micropores and mesopores [36]. Therefore, the materials show a highly developed porous network of micropores together with mesopores. This is further confirmed from the quantification of the specific surface area and other porosity parameters as summarized in **Table 1**. The obtained data indicate that the amount of ZnCl₂ used for activation has a significant influence on these parameters. PHC with no ZnCl₂ activation does not produce any significant value of the specific surface area (5.1 m² g⁻¹). Lower impregnation amounts of ZnCl₂/casein (1 and 2) yields more of the microporous character whereas a large mesoporous content is generated when higher amounts of ZnCl₂/casein impregnation are used (3 and 4). This approach provides good control over tuning the porosity of the synthesized materials to the desired pore characteristics. The specific surface area of the optimized material, PHC4, as calculated using BET (Brunauer-Emmett–Teller) method was 1080 m² g⁻¹ and the total pore volume calculated at a relative pressure of 0.99 is 0.59 cm³ g⁻¹. A mixture of micropores and mesopores along with considerable amounts of doped heteroatoms in PHC4 offers attractive material qualities for high CO₂ adsorption at both low and high-pressure regimes. The material PHC5 shows a large H4 hysteresis loop which signifies the presence of large mesopores in its structure (Figure S2).

3.3 Pore size distribution (PSD) analysis of PHCs

The results of the nitrogen sorption are further confirmed from the pore size distribution (PSD) plots shown in **Figure 2B**. It is observed that the materials PHC1 and PHC2 are highly microporous and contain the highest volume of pores with a size range of 1.5 - 2.0 nm while samples PHC3 and PHC4 are predominantly mesoporous with the highest occurrence of pores with the size of 2.7 nm. PSD curve of PHC2 is bimodal with the size of 1.5 and 2.0 nm whereas PHC3 and PHC4 show a wide distribution of pores in the sizes of 1.6, 2.2, 2.7 and 3.4 nm.

3.4 Scanning and Transmission Electron Microscope (SEM and TEM) analysis of PHCs

Figure S3 and Figure 3 show the SEM images of non-activated PHC0 and the activated materials PHC1 to PHC4, respectively. All materials show an irregular morphology with visible bulky particles scattered throughout. The effect of ZnCl₂ could easily be inferred from a reduction in the particle size and the distortion of the surface during activation. Non-activated material PHC shows relatively large sized particles with smooth surfaces, whereas upon activation the particle size is considerably reduced, and the morphology undergoes a change to irregular lumps having pores in them. There is not much difference that could be identified between all activated samples which indicates that the varied ratio of ZnCl₂/casein impregnation produced little effect on the material morphology. These morphological changes in activated samples are attributed to the reaction of ZnCl₂ with casein during the heat treatment. It is surmised that both the reagents go to a molten state at almost the same time during carbonization as their melting points ($ZnCl_2 - 290$ °C and casein – 280 °C) are very close and their reaction causes morphological changes in the synthesized materials. The details of the porous structure of samples PHC3 and PHC4 was further explored using the TEM images which are shown in **Figure 4**. These samples show that the structure of the carbon is disordered and there is a large density of the interconnected porous structure which comprises of micropores and mesopores. The bulk of the material is darker as compared to the outside edges due to the high concentration of carbon. The sample PHC3 was further pursued for high resolution TEM which showed the presence of linearly stacked carbon sheets in the darker region that are separated with a spacing of 0.33 nm (Figure S4).

3.5 X-ray Photoelectron spectroscopy (XPS) analysis of PHCs

The surface chemistry of the activated materials PHC1-4 was investigated using XPS. The corresponding results of the elemental composition are summarized in **Table 2** and the survey

spectra are shown in **Figure 5A**. All the synthesized materials are highly carbonaceous (85.7% - 90.3%) in nature which is also indicated from their totally black colour. The carbon content is lesser in the bulk of the materials as per the CHN analysis results tabulated in **Table S1**. It also confirms that the employed one-step carbonization to convert case to porous heteroatom self-doped carbons is successful. After carbon, the other main constituents of the PHCs include nitrogen (4.4% - 6.8%) and oxygen (4.7% - 6.6%). The amount of these three elements in the PHCs could easily be controlled by varying the impregnation ratios of ZnCl₂ and case in. A gradual reduction in the number of heteroatom functional groups on the surface is observed with increasing amounts of ZnCl₂ which is attributed to a greater degree of chemical reactions. A combination of high specific surface area and the presence of heteroatoms nitrogen and oxygen on the surface of the optimized material PHCs presents a good strategy for CO₂ adsorption.

The C1s, N1s and O1s XPD peaks were further deconvoluted into high-resolution peaks to explore the nature of bonding of these atoms on the surface of PHCs. Figure 5 (B-D) shows a highresolution C1s, N1s and O1s spectrum for the optimized sample PHC4 whereas the Figure S5 depicts a high-resolution plot for PHC (1-3) samples. In PHC4, C1s is deconvoluted into four peaks which correspond to sp² C=C (284.2 eV), sp³ C-C (285.1 eV), C-O/C-N (286.6 eV) and O-C=O (290.1 eV), respectively [37]. N1s spectra is resolved into four peaks centred at binding energy positions of 397.9 eV (pyridinic-N), 399.1 eV (pyrrolic/pyridonic-N), 400.4 eV (quaternary-N) and 402 eV (oxidized-N) [38]. The O1s splits into a pair of peaks corresponding to C=O (531 eV) and C-OH/ O-C=O (532.7 eV) functional groups [39]. It is surmised that the high-temperature chemical activation of casein leads to condensation of the structure resulting in the formation of interconnected cyclic carbon and nitrogen-containing structures such as cyclohexane, benzene, pyridine and pyrroles occupied by heteroatom functional groups on the surface. A considerable amount of nitrogen and oxygen species is found in the carbon structure even after the activation and carbonization at 800 °C, indicating that these functional groups are thermally stable. The high-resolution C1s, N1s and O1s spectra of other samples (PHC1-3) also show the presence of carbon as the main element and contain nitrogen and oxygen functional groups on their surface as shown in Figure S4.

3.6 Carbon dioxide (CO₂) adsorption analysis of PHCs

The main factor determining the CO₂ uptake by porous materials is the specific surface area whereas the existence of nitrogen-containing groups is also believed to be an influential aspect for enhancing the interactions between CO₂ and adsorbent [40]. Additionally, as per the recent reports, the contribution of oxygen moieties cannot be ignored for CO₂ adsorption as their presence impacts the surface polarity of the adsorbent materials [41]. As such, a combination of these factors is considered to be highly desirable in a porous carbon structure, which, however, is exceedingly challenging to achieve in practical terms. In our investigation, we successfully demonstrated the synthesis of PHCs with this unique triple combination of casein which itself acts as a source of carbon, nitrogen and oxygen without any added source from outside. The existence of nitrogen and oxygen-containing functional groups in the carbon structure was confirmed from the XPS measurements. **Table 1** summarizes the results of CO₂ adsorption under different conditions of pressure and temperature for the synthesized materials. The high-pressure CO₂ adsorption isotherms obtained at a temperature and pressure of 0 °C and 30 bar, respectively, were compared for PHC (1-4) and are presented in **Figure 6**.

Among all the materials, the non-activated sample is highly non-porous and shows a very low specific surface area of 5.1 m² g⁻¹ and therefore the CO₂ adsorption was not carried out for it. The specific surface area and pore volume of PHC1-4 increases with the increasing amount of zinc chloride used for activation. For example, the material PHC1 which is synthesized with the lowest ZnCl₂/casein impregnation amount of 1 shows a specific surface area of 540 m² g⁻¹ and pore volume of 0.22 cm³ g⁻¹. However, the specific surface area and specific pore volume of sample synthesized with a high impregnation amount of ZnCl₂/casein (4) are 1080 m² g⁻¹ and 0.59 cm³ g⁻¹. This is attributed to a higher degree of chemical reactions between the substrate and the activating agent. As specific surface area is the decisive factor for CO₂ adsorption, hence the CO₂ adsorption of the materials at high pressure of 30 bar follows in the order PHC4 (15.8 mmol g⁻¹) > PHC3 (13.4 mmol g⁻¹) > PHC2 (10.2 mmol g⁻¹) > PHC1 (6.7 mmol g⁻¹). The same is true for CO₂ adsorption of these materials at pressures < 30 bar. Therefore, it is crucial to carefully select right amount of impregnation of the activating agent when designing such adsorbents for CO₂ capture. The relationship between specific surface area and CO₂ adsorption capacity has been previously reported in the existing literature [42]. The role of heteroatoms in CO₂ adsorption is

particularly important at low pressures and could be deduced from the values of CO₂ adsorption per unit surface area.

A careful examination of the **Table 3** shows that despite having the lowest specific surface area, the sample PHC1 shows a comparatively higher value (0.39 μ mol m⁻²), which is indicative of stronger interactions between the adsorbate and adsorbent due to the presence of a material surface functionalized with higher content of heteroatoms as compared to other samples. On the other hand, PHC4 which has the highest specific surface area, but the lowest content of heteroatoms shows a CO₂ adsorption per unit surface area of 0.32 μ mol m⁻². This trend is reversed at high-pressure CO₂ adsorption at 30 bar, wherein a lower and higher CO₂ adsorption per unit surface area value for PHC1 (1.24 μ mol m⁻²) and PHC4 (1.46 μ mol m⁻²), respectively, are observed. As per these observations, it can be inferred that heteroatom plays an important role at low pressures while specific surface area is the dominant factor at high pressures. It is also observed from the shape of adsorption curves shown in **Figure 6** that all the samples did not reach complete saturation with the adsorbed CO₂ even at the recorded high pressure of 30 bar which is indicative of the mechanical stability of these carbons. As such, we believe that these materials can find a potential use for capturing CO₂ from systems such as natural gas wells, where the CO₂ comes out with very high pressure.

In pursuance of illustrating the relationship between temperature and CO₂ adsorption, the optimized sample PHC4 was subjected to CO₂ adsorption experiments at variable temperature values (0 °C, 10 °C and 25 °C) under the same pressure range (1 - 30 bar) and the obtained data is plotted in **Figure 7**. The highest amount of CO₂ adsorption is observed at 0 °C (15.8 mmol g⁻¹), which drops to 12.3 mmol g⁻¹ and 10.1 mmol g⁻¹ when the temperature is increased to 10 °C and 25 °C, respectively. This sample was further subjected to CO₂ adsorption at 45 °C and it adsorbed of 7.2 mmoles of CO2 g⁻¹ (**Figure S6**). A progressive decrease in CO₂ adsorption with an increase in temperature indicates that the process of adsorption is exothermic in nature which is a typical characteristic of the porous carbons [43]. Additionally, the recyclability of the material PHC4 was also tested using four consecutive CO₂ adsorption experiments (**Figure S7**). There is no significant change observed in the CO₂ adsorption value at 30 bar for all four cycles. All these observations indicate that the material PHC4 possess good recyclability and reusability and can be used over and over again for CO₂ adsorption.

3.7 Isosteric heat of adsorption analysis

The strength of interactions between the adsorbent carbon PHC4 and the CO₂ molecules was deduced from isosteric heat of adsorption (Q_{st}) calculated from CO₂ adsorption isotherms at 0 °C, 10 °C and 25 °C using Clausius Clapeyron's equation. The resultant curve of CO₂ adsorption vs Qst is represented in **Figure 8**. A high value of Q_{st} (~35 kJ mol⁻¹) is observed at the beginning of the adsorption process which then drops to ~26 kJ mol⁻¹ at a CO₂ adsorption value of 10 mmol g⁻¹. This indicates that the initial adsorption of the incoming CO₂ molecules occurs strongly at the freely available sites on the carbon surface and a drop in interactions is observed after these sites are occupied. It is also to be noted that the high value of Qst (~35 kJ mol⁻¹) is observed due to the enhanced interactions of CO₂ and porous carbon caused by the presence of heteroatoms on the surface. Lastly, the observed values of Qst over the whole range of CO₂ adsorption signifies that the process is physical in nature which is indicative of easier recovery of the materials for repeated use [44, 45].

4. Conclusions

In summary, we have successfully demonstrated a facile and convenient one-step procedure for the synthesis of porous and heteroatom self-doped carbons (PHCs) from casein. The unique nature of the starting precursor combined with an in-situ ZnCl₂ activation allows the readymade functionalisation of the prepared carbons with heteroatoms on the surface. The synthesized materials were fully characterized for their morphology, textural properties, the degree of graphitisation, heteroatom content and their application for high-pressure CO₂ adsorption under different conditions. The amount of ZnCl₂ activation was varied to control the nature of the porosity between microporous and mesoporous domains. Through this unique approach, tunable porosity parameters such as specific surface area $(540 - 1080 \text{ m}^2 \text{ g}^{-1})$, specific pore volume $(0.22 \text{ m}^2 \text{ g}^{-1})$ - 0.59 cm³ g⁻¹), pore size (1.6 - 2.7 nm) and content of nitrogen (4.4 - 6.8%) and oxygen (4.7 - 6.8%)6.6%) were observed for the PHCs. As a result of high surface area (1080 m² g⁻¹) and considerable amount of nitrogen (4.4 %) and oxygen (4.7%) content, the optimized material PHC4 exhibited excellent CO₂ adsorption capacities at 0 °C / 1 bar (3.5 mmol g⁻¹) and 0 °C / 30bar (15.8 mmol g⁻¹) ¹). As such, this work provides a novel and versatile approach for the synthesis of porous carbons functionalized with heteroatoms with high potential for CO₂ adsorption. We believe that the presented synthesis strategy combined with the unique nature of the synthesized carbons presents

a promising platform for developing a series of next generation adsorbent systems with unique functionalities from variously functionalized biomasses which could be applied for applications ranging from adsorption to energy storage and conversion.

Conflicts of interest

There are no conflicts to declare.

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Tables and Figures

Sample	^a SA _{BET} (m ² g ⁻¹)	^b SA _{micro} (%)	^c V _{total} (cm ³ g ⁻¹)	^d V _{micro} (%)	°PW (nm)	^f CA (mmol g ⁻¹)		
						0 °C	10 °C	25 °C
PHC	5.1	-	-	-	-	-	-	-
PHC1	540	88	0.22	82	1.6	2.1 / 6.7	-	-
PHC2	777	65	0.34	59	1.6	3.0 / 10.2	-	-
PHC3	983	46	0.49	37	2.7	3.4 / 13.4	-	-
PHC4	1080	36	0.59	27	2.7	3.5 / 15.8	2.7 / 12.3	1.8 / 10.1

Table 1. Textural properties and CO₂ adsorption of PHCs

^aBET Surface Area, ^bMicropore Surface area, ^cTotal Pore Volume, ^dMicropore Volume, ^ePore width, ^fCO₂

adsorption at 1bar / 30 bar

Table 2. XPS elemental composition of casein activated with ZnCl₂

Sample	Carbon (%)	Nitrogen (%)	Oxygen (%)
PHC1	85.7	6.8	6.6
PHC2	85.5	6.6	6.2
PHC3	88.4	4.6	5.8
PHC4	90.3	4.4	4.7

Table 3. CO₂ uptake per unit surface area of casein activated with ZnCl₂

Sample	CO ₂ adsorption per unit surface area (µmolm ⁻²)			
	0 °C / 1bar	0 °C /30 bar		
PHC1	0.39	1.24		
PHC2	0.38	1.31		
РНС3	0.34	1.36		
PHC4	0.32	1.46		



Figure 1A) XRD patterns of a) PHC1, b) PHC2, c) PHC3 and d) PHC4 and **1B)** Raman spectra of a) PHC3 and b) PHC4



Figure 2 A) N₂ adsorption-desorption isotherms and B) pore size distribution curves for a) PHC1, b) PHC2, c) PHC3 and d) PHC4



Figure 3: SEM images of a) PHC1, b) PHC2, c) PHC3 and d) PHC4



Figure 4: TEM images of a) PHC3 and b) PHC4 – Note: yellow circle indicates the mesopores.



Figure 5: A) XPS survey spectra of a) PHC1, b) PHC2, c) PHC3 and d) PHC4, and B-D) C1s, N1s and O1s high-resolution spectrum of PHC4



Figure 6: Comparison of high-pressure CO_2 adsorption isotherms of a) PHC1, b) PHC2, c) PHC3 and d) PHC4 measured at 0 °C



Figure 7: High-pressure CO_2 adsorption isotherms of PHC4 measured at three different temperatures a) 0 °C, B) 10 °c and C) 25 °C



Figure 8: Isosteric heat of adsorption of PHC4 calculated at three different temperatures of 0, 10 and 25 °C