

Effect of nitrogen doping on the pore texture of carbon xerogels based on resorcinol-melamine-formaldehyde precursors

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Abstract

N-doped carbon xerogels (CXs) were synthesized from melamine-resorcinol-formaldehyde aqueous gels by evaporative drying and pyrolysis at 800 °C. The pore texture of these N-doped CXs ranged from micro-mesoporous to micro-macroporous depending on the initial pH of the precursors solution. For different pH values, while the specific surface area varied slightly from 500 to 600 m² g⁻¹, the total void volume changed from 0.6 to 1.6 cm³ g⁻¹. Furthermore, N-doped CXs showed a wide interval of average pore diameters ranging from 19 to 1200 nm. The nitrogen amount in N-doped CXs varied from 4 to 11 wt % and XPS analysis showed that nitrogen was mainly incorporated into the carbon network as pyridine or quaternary nitrogen groups. These results indicate that this doping approach is suitable to tune the pore texture, pore size and chemical composition by adjusting the initial pH value or the amount of nitrogen precursor. Taking into account the properties mentioned above, N-doped CXs can be tailored to find applications as adsorbents, catalyst supports, materials for energy generation and storage.

Keywords: Carbon xerogels, porous carbon, texture, melamine, nitrogen doping.

1. Introduction

Porous carbon materials are versatile materials which have been extensively used in many different applications requiring different chemical, structural and pore texture properties [1–7]. Carbon materials not only encompass a wide range of properties but also present different macroscopic morphologies such as powder, monoliths, fabrics, films or spheres. This variety of morphologies plays a pivotal role in the manufacturing and process engineering to be used in multiple specific applications. Both the morphology and physicochemical properties must be taken into account before selecting a carbon material, depending on the desired application.

Carbon xerogels (CXs) have attracted great attention because their pore texture can be easily tailored by means of slight changes in the synthesis conditions, ranging from exclusively microporous to micro-macroporous structures [8]. The gelation of resorcinol-formaldehyde (RF) aqueous mixtures is one of the most used methods to synthesize CXs. This synthesis consists in the reaction between resorcinol and formaldehyde in the presence of a base, such as Na_2CO_3 , NaOH or NaHCO_3 [8–10]. This reaction leads to the formation of hydroxymethyl derivatives of resorcinol that react among them to generate branched compounds. After curing and drying, gels are pyrolysed under inert atmosphere, which leads to CXs that exhibit high apparent surface area and high pore volume. The obtained material is constituted of microporous spherical-like nodules connected together as a 3-dimensional network. In the case of RF-based materials, while the specific surface area, mainly due to the micropores located in the nodules, does not evolve significantly as the initial pH of the precursors solution is modified, the pore volume and the size of the meso/macropores,

corresponding to the voids between the nodules, varies drastically due to the modification of the size of the nodules [11,12]. Note that the pH is not the only factor that affects the structural properties: other variables such as the precursor amount, time/temperature of curing stage or drying method might influence, to a lower extent, the final characteristics of the dried gels [8,13]. Besides the above-mentioned properties, CXs also show good electrical conductivity and good thermal and mechanical properties, which also depend on the synthesis conditions.

Intensive efforts are being directed to further improving the CXs properties with application-targeted modifications. In this regard, it should be pointed out that heteroatom-doping has become an important tool to modify the wettability, basicity, electrical conductivity, catalytic performance or electrochemical behavior of carbon materials [14–17].

The replacement of a sp^2 carbon atom or an edge site with a foreign atom was shown to result in a local breaking of the electroneutrality. Nitrogen is by far the most studied element used as a modifier of the carbon network and many strategies have been developed to embed nitrogen into carbon structures. In the case of CXs, one can distinguish between *in situ* and post-doping processes. Within the most common post-treatments, N-doped CXs (N-CXs), were achieved by nitriding processes at high temperature in a nitrogen-containing reactive atmosphere (NH_3 , N_2/NH_3 , etc.) [18–20]. *In situ* doping generally involves the copolymerisation of resorcinol and formaldehyde in the presence of nitrogen-containing precursors such as melamine, urea or N-aldehyde derivatives [21–23]. The addition of N-containing precursors during polymerisation directly affects the nitrogen content as well as the pore texture because the mass ratio between monomers is different compared to a conventional synthesis involving resorcinol and formaldehyde (RF) only. In other words, the

modification of the mass percentage of nitrogen precursor causes variation in the dilution factor, leading to different distribution of particles in the sol; this in turn leads to dried polymers with a wide range of particles size and pore volumes [24].

As aforementioned, the initial pH of the precursor solution plays a key role in the structural and textural properties of RF xerogels. Since the addition of N-containing precursors also affects the pH of the precursor solution because of their different acid-base behavior compared to resorcinol or formaldehyde, deep textural changes are expected in the final N-containing carbons.

This work aims at analyzing how the pore texture of CXs is affected by N-doping when melamine is used as N-containing precursor for an *in situ* doping process. Previous studies already showed different pore textures for nitrogen-doped carbon xerogels (N-CXs) derived from melamine-RF gels [9,23]. In some of these previous works, N-CXs exhibited N₂ adsorption isotherms of Type I corresponding to microporous carbons [9]. However, microporous-mesoporous N-CXs were also obtained from melamine-RF gels [23]. These discrepancies are due to several factors such as the amount of melamine added, the curing or drying temperature and conditions, etc. Systematic studies are thus needed to draw global tendencies: in the present work, two series of N-CXs derived from melamine-resorcinol-formaldehyde dried gels were synthesized using two different amounts of melamine, keeping constant the R'/C molar ratio, where C is the Na₂CO₃ amount and R' is the sum of resorcinol and melamine amounts in the precursor solution. In this manner, the effect of N doping on the pore texture was studied in both series of N-CXs in order to understand how the amount of nitrogen precursor affects the final pore texture of N-CXs.

2. Experimental

2.1. Synthesis of melamine-resorcinol-formaldehyde (MRF) carbon xerogels

Organic xerogels were prepared by polycondensation of resorcinol (R) and melamine (M) with formaldehyde (F). This reaction was carried out in aqueous medium using Na_2CO_3 , which allowed us to modify the pH of the resorcinol-melamine-formaldehyde (RMF) aqueous solution.

To synthesize organic gels, two key parameters were fixed with regard to previous works [8]: the R'/F molar ratio (where $\text{R}' = \text{R} + \text{M}$, i.e. the sum of resorcinol and melamine amounts) was fixed at 0.5 (stoichiometric ratio) while the dilution ratio ($\text{D} = \text{total solvents/reactants}$) was fixed to 5.7. The purpose of keeping these values constant is to study the effect of the melamine amount on the pore texture as the R'/C molar ratio is modified for two different R/M molar ratios. The R'/C molar ratios used were 150, 175, 200, 225 and 250 and the two different R/M molar ratios selected were 3 (lowest melamine content) and 1 (highest melamine content). Additionally, a pair of samples were synthesized using two different R'/C molar ratio (150 and 175) and a R/M molar ratio of 7 for comparison purposes.

First, resorcinol and Na_2CO_3 were solubilised in deionised water at room temperature in a sealable flask under magnetic stirring; melamine was then added. Considering the chosen melamine amount and conditions (room temperature, mainly), melamine is not soluble in the mixture. Thus, formaldehyde was added, and the resulting mixture was heated up to 70 °C under magnetic stirring. Finally, the gelation was performed at 85 °C in an oven. After 72 h, the colour of the samples varied from dark brown at low R'/C ratio to light brown at high R'/C ratio in the case of R/M equal to 3 whereas, for a R/M ratio of 1, the appearance did not change appreciably and all samples showed a light brown colour. Then, the aqueous gels

were dried by vacuum evaporation at 60 °C for 24 h. The pressure was gradually reduced from 1.01×10^5 to 1.50×10^3 Pa. Finally, all samples were heated up to 150 °C at 1.50×10^3 Pa for 24 h.

Carbon xerogels were synthesised from dried gels by pyrolysis at 800 °C under inert atmosphere (N_2 , 4.5 mmol min⁻¹) in a tubular oven. The pyrolysis process consisted in 4 steps: (i) heating rate of 1.7 °C min⁻¹ up to 150 °C and hold for 15 min; (ii) heating rate of 5 °C min⁻¹ up to 400 °C and hold for 1 h; (iii) heating rate of 5 °C min⁻¹ up to 800 °C and hold for 2 h and (iv) cool down slowly to room temperature.

The sample nomenclature was established as follows: DG-x-y and CX-x-y, where DG and CX stand for ‘dried gel’ and ‘carbon xerogel’, respectively, while ‘x’ gives the R/M molar ratio and ‘y’ is the R’/C molar ratio. For example, DG-3-150 would be a dried xerogel that was synthesised from a precursor solution containing 3 moles of R for each mol of M and an amount of Na_2CO_3 moles that is 150 times lower than the sum of moles of melamine and resorcinol.

2.2. Physicochemical and electrochemical characterization

The pore textures of both dried and pyrolysed samples were characterised by physical adsorption-desorption of N_2 at -196 °C, using an automatic adsorption system (Micromeritics ASAP 2420 analyzer). Pyrolysed samples were outgassed at 270 °C (133 Pa) before measurements, whereas dried gels were outgassed at 150 °C (same pressure) before analysis. The specific surface area (S_{BET}) was calculated from nitrogen adsorption data in the relative pressure range from 0.01 to 0.1 using the BET equation. The micropore volume (V_{DUB}) was determined by application of Dubinin-Radushkevich equation to the N_2 adsorption isotherm

at -196 °C up to $P/P_0 \leq 0.1$ (P_0 being the atmospheric pressure). In the case the isotherm reached a plateau at saturation, the pore volume was calculated from the adsorbed volume at saturation, V_p . Otherwise, mercury porosimetry was used to determine the total pore volume of the samples. The mercury porosimetry measurements (from 0.01 to 200 MPa) were done using ThermoScientific Pascal 140 and 240 porosimeters. The data obtained from mercury intrusion provides the pore volume (V_{Hg}) corresponding to pores larger than 7.5 nm. Moreover, the diameter of these pores (L) was determined by applying Washburn's equation for CXs series (Equation 1).

$$L = -\frac{4\gamma\cos\theta}{P} \quad \text{Eq. 1}$$

where γ is the mercury surface tension (0.48 N m^{-1}), θ corresponds to the contact angle of mercury on the solid (140°) and P is the pressure at which the mercury intrusion occurs [25]. Washburn's equation is however not applicable for samples that undergo crushing upon Hg pressure, which is the case for some of the dried gels. However, in case crushing then intrusion are observed (which is the case for some of the obtained samples), the pore diameter can be estimated using Washburn's equation at the starting point of mercury intrusion, which provides the pore size upon compression. Then, these calculated values are corrected for compression considering the ratio between the volume corresponding to the compression step and the total Hg volume detected, assuming a simple geometrical pore shape (*e.g.* sphere).

The combination of both physical adsorption-desorption of N_2 and mercury porosimetry techniques is needed to get an accurate value of the total pore volume (V_V) in the case of macroporous samples, according to the Equation 2. Indeed, nitrogen adsorption measurements do not provide an accurate pore volume value when the sample contains pores

larger than 50 nm, while the mercury porosimetry technique is not suitable for materials that display pores smaller than 7.5 nm. Therefore, provided the volume corresponding to pores between 2 and 7.5 nm is negligible, which is the case of the samples in the present study, the total pore volume V_V can be calculated by combination of both techniques:

$$V_V = V_{DUB} + V_{Hg} \quad \textbf{Eq. 2}$$

The bulk density (ρ_{bulk}) and the skeletal density (ρ_s) were measured by using mercury and helium (Accupyc 1330 pycnometer, Micromeritics) pycnometry, respectively. The weight loss and corresponding thermal effects of some non-pyrolysed samples during pyrolysis were measured by thermogravimetric analysis (SETARAM, TG-DSC111) under inert atmosphere. The thermal conditions were a heating rate of 3 °C min⁻¹ up to 700 °C and hold for 10 min. Elemental analysis of some samples was performed using a TruSpec CN LECO analyser. X-ray photoelectron spectroscopy (XPS) measurements were performed using a monochromatic Al K α X-ray beam with a spot size of 400 μm (spectrometer ESCALAB 250Xi) and the chemical analysis was performed by peak-fitting high-resolution spectra acquired in scan mode with a pass energy of 20 eV and energy step of 0.1 eV.

3. Results and discussion

3.1. Pore texture characterization

Table 1 regroups all the data calculated from N₂ adsorption-desorption, Hg porosimetry, He and Hg pycnometry. These data will be discussed below along with the raw curve analyses.

Figures 1a and 1b show the N₂ adsorption-desorption isotherms of dried gel samples (DG-3 series) as well as their pyrolysed counterparts for several R'/C ratios (CX-3 series). Both

series show different types of adsorption isotherms depending on the R'/C ratio, evolving from a micro-mesoporous solid (low R'/C ratio) to a microporous-macroporous solid (high R'/C ratio).

Like in the case of conventional resorcinol-formaldehyde gels [8], it can be clearly seen that the R'/C ratio has a strong influence on the pore texture of DGs and, as a consequence, on that of their pyrolyzed counterparts (corresponding CXs). In the case of the dried gels of series DG-3, a negligible gas uptake is detected at low relative pressures (Figure 1a), indicating a very low micropore volume for all samples ($< 0.08 \text{ cm}^3 \text{ g}^{-1}$). At high relative pressure, a large hysteresis loop can be seen for samples with low R'/C (DG-3-150 and DG-3-175), indicating the presence of mesopores (Type IV isotherm). As R'/C increases, this loop disappears due to the increase of pore size: the sample becomes macroporous, and the extra-nodular voids are not detected by N₂ adsorption anymore. This result will be confirmed below by Hg porosimetry measurements. Concerning the corresponding CXs obtained after pyrolysis (CX-3 series), a high gas uptake is measured at low relative pressures, pointing out the presence of a significant volume of micropores (Figure 1b). As expected, the pyrolysis causes the formation of micropores or the opening of ultramicropores that cannot be measured by N₂ adsorption on dried samples. The curves are all superimposed in this relative pressure region, indicating similar micropore volumes, independently of the R'/C molar ratio. This is further confirmed by the calculation of the micropore volume, with a value of $0.24 \text{ cm}^3 \text{ g}^{-1}$ (Table 1). Regarding the high relative pressure region, CXs with low R'/C ratio (CX-3-150 and CX-3-175) display again a large hysteresis loop at relative pressures between 0.70-0.95, showing a combination of Type I and IV isotherms, which is indicative of the large contribution of both micropores and mesopores in CXs. This hysteresis loop disappears for

the pyrolysed xerogels prepared with a higher R'/C ratio, again suggesting the presence of larger pores that cannot be measured by the nitrogen adsorption technique, in accordance also with the general trend usually observed for conventional carbon xerogels from R and F mixtures [8]. One can thus suspect that these CX samples in fact display a Type I + II isotherms combination, indicating that these CXs also contain macropores. For this reason, mercury porosimetry experiments were performed.

Figure 2a shows the mercury porosimetry curves of DG-3 series samples prepared using different R'/C ratios. Sample DG-3-150 is compressed without any intrusion of mercury inside the pores; this is reflected by the smooth volume increase with pressure, and was checked by sample weighing after measurement (no mass change due to mercury intrusion was observed). Sample DG-3-175 shows a similar behaviour up to 40-50 MPa; however, at this pressure, mercury briskly intrudes the pores of the dried gel, leading to a sharp increase of the detected volume at constant pressure. During the depressurization process, part of this volume is retrieved (*ca.* $0.3 \text{ cm}^3 \text{ g}^{-1}$): this could be due to both mercury release from the pores or elasticity properties of the dried gel. The other curves corresponding to the samples prepared with a higher R'/C molar ratio display the same shape, with a slight compression step followed by a strong uptake of mercury in quite a narrow pressure range. This sharp increase of volume occurs when the pressure is sufficient to enter the pore constrictions between the nodules, while the sample can withstand pressure without further crushing. In that case, the Washburn equation can be applied to obtain the pore size under compression, and the approximate pore size prior to compression is calculated geometrically. Results confirm the existence of large macropores for samples DG-3-200, DG-3-225 and DG-3-250

(Table 1). This behaviour is quite classical in organic gels issued from resorcinol-formaldehyde chemistry [25].

Regarding the CX-3 series, all observed curves typically show a strong mercury uptake at a given pressure, indicating the intrusion of mercury inside the macropores, through the pore constrictions between the carbon nodules (Figure 2b). This jump occurs at lower pressures as the R'/C molar ratio of the precursor solution becomes higher, indicating, according to Washburn's equation, increased pore sizes. These measurements confirm that the N₂ adsorption-desorption isotherms corresponding to the samples with the higher R'/C ratios are a combination of Type I + II isotherms. These curves also show that the total uptake of mercury (V_{Hg}) increases along with the pore sizes and the R'/C molar ratio. Since the micropore volume is the same for all of these pyrolyzed samples, the total pore volume of the materials, obtained upon summing V_{DUB} and V_{Hg} thus logically follows the same trend, with a maximum value around 1.6 cm³ g⁻¹ for samples CX-3-225 and CX-3-250 (Table 1).

These changes in the pore texture as pH varies (different R'/C ratios) do not result in a substantial shift in S_{BET} values (Table 1) since the micropore volume, which is the main contribution to S_{BET} value, remains almost constant for all samples of the CX-3 series. The densities of these samples were also measured (Table 1). The skeletal density (ρ_s), which does not take into account any open porosity, remains constant, with values of 1.44 g cm⁻³ for the dried gels and 1.90 g cm⁻³ for their pyrolyzed counterparts. On the opposite, the bulk density (ρ_{bulk}), as measured by Hg pycnometry, takes into account the presence of pores. Following the trend of the increased pore volumes as measured by mercury porosimetry, the

materials prepared with the higher R'/C ratios become less dense, with values of densities decreasing from 0.70 g cm⁻³ for CX-3-150 down to 0.47 g cm⁻³ for CX-3-250.

Concerning the dried gels obtained from the DG-1 series (R'/C = 1, *i.e.* high melamine content), the N₂ adsorption-desorption isotherms (Figure 1c) show the same trend as the DG-3 series samples. One observes insignificant gas uptake at low relative pressures, and the hysteresis loop at high pressure is present, even though it appears at pressures slightly higher than those obtained from DG-3 series samples.

Regarding the pyrolysed xerogels obtained from DG-1 series, the adsorption-desorption isotherms seem to show a different trend as the R'/C ratio increased from that observed in CX-3 series samples (Figure 1d). Although all samples are characterized by the same type of adsorption isotherm with a high gas uptake at low relative pressures (Type I, corresponding to microporous solid), in this case however, the micropore volume varies from one material to the other. This was not the case for the CX-3 series. Especially CX-1-150 and CX-1-175 display much lower values of micropore volumes, 0.13 and 0.17 cm³ g⁻¹ respectively. Samples prepared from precursor solutions containing a higher R'/C ratio (CX-1-200, CX-1-225 and CX-1-250) show somewhat higher micropore volumes (and so S_{BET} values), although these values still remain lower than those calculated in the CX-3 series (~ 0.24 cm³ g⁻¹). Moreover, no hysteresis loop is observed for any of the samples, suggesting that the increase in melamine contents leads to samples without (or with very low) mesopore volume. This change of the structure can be related to the decrease of pH as the melamine amount increases. Given the fact that melamine has a pK_a value of 5.0 while resorcinol has a pK_a value of 9.0, the addition of melamine has a greater influence on the pH of the precursor solutions: the solutions are certainly more acidic than conventional RF solutions prepared in

the same conditions, which would lead to samples with much larger pores. It is however difficult to measure directly since melamine is not soluble in the medium at low temperature.

Samples prepared with high melamine content (DG-1 and CX-1 series) were also characterized by mercury intrusion porosimetry to assess the presence of large meso- or macropores. The DG-1 series shows mercury porosimetry curves similar to those obtained for the DG-3 series, with a compression stage followed by some intrusion of mercury inside the pores. This intrusion takes place at lower pressures as the R'/C ratio becomes higher, proving the formation of increased pore sizes (Figure 2c). The pyrolyzed samples (CX-1 series) again show a steep increase of intruded mercury at a given pressure (Figure 2d), indicating the presence of macropores, except for sample CX-1-150. The measurements were repeated with the same outcome, suggesting that, for this particular sample, the narrow pores become blocked or tightened after pyrolysis (Figure 2d), and that the material remains soft enough to undergo compression. The comparison of the dried and pyrolyzed samples shows that the intrusion of mercury occurs at lower pressure values than for the materials of the corresponding DG-1 series, indicating a shrinkage of the average pore size after pyrolysis. This is confirmed by the calculated results gathered in Table 1 obtained from mercury porosimetry measurements for the DG-1 series and CX-1 series. In this case, no clear trend can be drawn regarding the evolution of the pore volume (V_{Hg}). Nevertheless, it should be noted here that the pore volume decreases by around 60% after pyrolysis, much more than observed for the DG-3/CX-3 series.

The total void volume (calculated by using Equation 2) drops as the R'/C ratio is lowered; sample CX-1-150 presents however a V_V value higher than sample CX-1-175 since the former presents a small fraction of mesopores (pores lower than 50 nm). It can also be seen that V_V

values are smaller ($0.65\text{--}1.26\text{ cm}^3\text{ g}^{-1}$) than those obtained for CX-3 series samples ($0.94\text{--}1.63\text{ cm}^3\text{ g}^{-1}$). Therefore, it is possible that the structure shrinks as the quantity of melamine rises in the initial precursor solution (pH decreases) for DG-1 series, by comparison to DG-3 series. This observation is opposite to the one usually encountered for the conventional RF gels that show a higher shrinkage when pH increases. This discrepancy could be explained by an enhancement of the crosslink density when molecules of melamine are added to the polymerization reaction [26,27]. In addition, ρ_{bulk} values are higher than those attained by the CX-3 series, which is in agreement with the shrinkage mentioned above.

In order to get a better insight in how the pore texture is affected when changing the melamine contents, additional samples were synthesised by reducing the melamine amount down to a R/M ratio equal to 7 in the initial precursor solution. For that purpose, the R'/C was fixed at 150 and 175 because samples CX-3-150 and CX-3-175 were the only ones that presented a well-defined microporous-mesoporous texture. Figure 3 shows the isotherms for the samples prepared by using a ratio equal to 175 but with a different mass of melamine in the initial precursor solution (samples with R'/C = 150 are not shown because the same tendency was observed). It can be observed that the proportion of melamine added to the initial precursor solution has a significant impact on the pore texture. An initial precursor solution with a low melamine content (R'/C = 7) leads to micro-mesoporous CXs, while a high melamine concentration (R'/C = 1) leads to a Type I isotherm corresponding to microporous materials. However, it can be observed in the isotherm that CX-1-175 shows some difficulties in reaching the saturation pressure and tends towards infinity at high pressures ($P/P_0 = 1$), indicating the existence of macropores. Therefore, sample CX-1-175 displays a combination of Type I and II isotherms, which was confirmed after Hg

porosimetry. It should be mentioned that there are differences between CX-7-175 and CX-3-175 isotherms. The hysteresis on the adsorption-desorption isotherm for CX-7-175 becomes smaller and shifts to lower P/P_0 values in comparison to CX-3-175 (similar behaviour happened for CX-7-150 and CX-3-150), indicating that the increase in the initial pH of the precursors solution when melamine was reduced leads to CX with lower pore size (~ 6 nm) than CX-3-175 (~ 27 nm). Therefore, it can be concluded that the pore texture still can be tailored by adjusting the initial pH, just like in the case of carbon materials issued from conventional RF gels.

3.2. XPS analysis

XPS chemical analysis was performed on high-resolution spectra (C 1s, N 1s, O 1s). The typical N1s spectra obtained in non-pyrolyzed samples (DG) and pyrolyzed samples (CX) are shown in Figure 4. In non-pyrolysed samples (Figure 4a), the broad N 1s peak can be fitted with two chemical components: a first one (~ 398.5 eV) corresponding to pyridinic groups, and a second one (~ 400 eV) corresponding to pyrrolic-N groups [28]. After pyrolysis (Figure 4b), the N 1s spectrum clearly shows two distinguished components. The first one, centred at 397.5 eV, can be ascribed to pyridinic groups in chars; the second one, centred at 400.8 eV, is related to quaternary (i.e. graphitic) N [29].

The high resolution (HR) spectra of the C 1s for non-pyrolysed samples (Figure S1, supporting information) showed that, in DG-1 samples, the C-C=O bonding varies with the R'/C value while this is not the case in DG-3 and CX-3 samples. A lower functionalization is obtained in CX-1 samples.

Table 2 summarizes the XPS results for the DG and CX series, with the atomic percentage of the different N chemical environments shown in Figure 4. The N wt% is derived from the XPS composition assuming that the surface and bulk composition is homogeneous. For DG-3 samples (low melamine dried gels), the N wt% ranges from 5% (high R'/C) to 15% (low R'/C) while in DG-1 samples it ranges from 23 to 31%. Higher values are obtained for low R'/C values (and high pH) while lower values are obtained at high R'/C values (and low pH). The theoretical amount of N% in DG-3 and DG-1 series is ~12 and ~23 wt%, respectively. Since XPS is a surface analysis (the photoelectron escape depth is about 10 nm) the XPS-derived N wt% could underestimate or overestimate its bulk value; for instance, depending on the synthesis conditions, the sample surface could show enriched in N, as for low R'/C values - high pH, or with a loss in N due to its desorption during the drying process as for high R'/C values - low pH.

This inhomogeneity could result from the fact that melamine and resorcinol do not react with formaldehyde at the same speed, so that melamine will preferably be located either in the core of the gel nodules or at their surface, depending on the concentration or pH. Namely, at low crosslinking conditions, i.e. for low pH values and large pores, melamine should mainly locate on the nodules surface. In this scenario, in the synthesis of RF gels, the stoichiometric R/F ratio evolves with the pH: when the pH decreases, the addition of F to R in *para* position, occurring after addition in *ortho*, decreases, leading to linear polymerized sequences that finally lead to larger polymer nodules by microphase separation [30]. The same can be stated for melamine. Therefore, a large amount of formaldehyde would not react and would therefore evaporate during the drying, leading to a decrease of the carbon content in the final structure. However, too large N content is observed in samples with low R'/C

values (DG-1-150, DG-1-175 and, to a lesser extent, sample DG-3-150); moreover, the decrease of the N content due to melamine evaporation is quite unlikely, owing to its low vapor pressure (6666 Pa at 315 °C), so, the non-homogeneous distribution of melamine in the nodules at high pH values is therefore probably the best explanation for the observed trend.

In pyrolyzed samples, the %N decreases as a consequence of the pyrolysis step. The generation of graphitic nitrogen (quaternary N) is in agreement with the evolution of nitrogen groups present in melamine structure after carbonization [29]. Other nitrogen sources or N-containing carbon materials also led to the formation of such nitrogen groups [28,31].

3.3.Elemental analysis (EA) and thermogravimetric measurements

The bulk elemental compositions of two dried gels and their pyrolyzed counterparts are reported in Table 3. Regarding the nitrogen amount (N_{EA}), values obtained for the dried materials are in line with the theoretical one (12 wt %). The N_{EA} decrease after pyrolysis (down to 4.3 and 4.2 wt % for CX-3-150 and CX-3-250, respectively) is due to the loss of volatile N-containing components together with the cracking of C-O and C-H bonds, leading to the formation of amorphous carbon (as reflected in the carbon content for pyrolyzed samples). It is worth mentioning that the nitrogen mass percentage deduced from EA does not change with the R'/C ratio. However, it was observed that the total nitrogen content (wt %) obtained from XPS shifted with R'/C ratio for both dried and pyrolysed samples of the same series. Furthermore, both N_{XPS} and N_{EA} amounts for samples DG-3-150 and CX-3-150 are close, indicating a homogeneous distribution of N in the surface and in the bulk both after drying and pyrolysis. In contrast, samples with a higher R'/C ratio (DG-3-250 and CX-3-

250), the discrepancy between EA and XPS derived N content indicate that N groups are preferentially located at the centre of the nodules, probably due to differences in melamine and resorcinol reactivity. Therefore, the formation of the nodules could occur in a heterogeneous manner. Their core could result from a preferential reaction between melamine and formaldehyde molecules, while the shell would be formed to a larger extent from the polymerisation between resorcinol and formaldehyde. This difference in reactivity that leads to phase separation has been already reported by Carrot et al. from copolymerization of monomers with different reactivity, obtaining particles with a RF core and a shell based on 2,4-dihydroxybenzoic acid [32].

TG and DSC curves reflecting the pyrolysis of DG-3-200 and DG-1-200 samples are shown in Figures 5. In agreement with the literature, during the pyrolysis of N-doped xerogels, samples show three reaction stages [33]: the first mass loss (25 - 130 °C) is attributed to the evaporation of water and possibly formaldehyde molecules that did not react, the second mass loss (130 - 300 °C) is related to the desorption of trapped water inside the deepest pores and the start of the pyrolysis of more volatile compounds accompanied by cracking of C-O bonds and the third mass loss (>350 °C) corresponds to the progressive carbonisation associated with the cracking of C-H bonds in formaldehyde and melamine. Although three endothermal signals corresponding to the mass losses were identified in each sample, the second endothermal signal in the DSC profiles of sample DG-1-200 is sharper than the one in DG-3-200. We conclude that a higher amount of melamine leads to a higher loss of volatile compounds during the pyrolysis process. Indeed, the total mass loss after the pyrolysis at 700 °C is ~60% in the DG-3 series, which is in agreement with what has been observed for conventional R-F dried gels, while it is ~73% in the DG-1 series (higher mass

of melamine) confirming the presence of a higher amount of volatile compounds which are eliminated leading to more variable final (surface) compositions and structure.

4. Conclusions

N-doped carbon xerogels based on melamine-resorcinol-formaldehyde (MRF) solutions were prepared by sol-gel synthesis followed by a simple evaporative drying and subsequent pyrolysis. These porous carbon materials were characterized to assess the effect of the melamine amount and Na_2CO_3 concentration on the pore texture properties for fixed dilution or R'/F molar ratio. The results indicate that the pore texture is mainly tailored by the pH of the solution, though this variable could not be measured directly under the present experimental conditions; indeed, the M-R-F solution needed to be heated up to 70 °C in order to solubilize melamine and get a homogeneous solution before the gelation process. Beside this, qualitative observations have shown that, as the amount of basification agent (Na_2CO_3) increases, which corresponds to a decrease of the R'/C ratio, the pore size decreases, both after drying and after pyrolysis as typically observed in RF gels. The obtained materials showed pore size ranging from mesopores to large macropores after drying; the synthesized series clearly show that the pore texture of the materials still remain controllable to some extent mainly *via* the pH. The pyrolysis induces the development of micropores and a shrinkage of the material which gets more pronounced as the amount of melamine in the solution is increased. In most cases, both the pore volume and pore size decrease upon pyrolysis. The modification of the melamine content also affects the pore texture: given the low pKa value of melamine compared to resorcinol, the introduction of melamine leads to a decrease of the pH. Thus Na_2CO_3 and melamine contents both influence the initial pH, hence

it is important to adjust these two variables accordingly. The pore texture also depends on the R'/C ratio: at low values ($R'/C = < 175$), the average pore size increases as the melamine content decreases, while the opposite occurs at higher R'/C values. These changes in pore sizes are related to the modification of the size of the nodules. Indeed, the meso-or macropores reflect the size of the voids existing between these nodules. If the size of the latter decreases, the pore size evolves in the same direction. Finally, elemental analysis showed that the N content depends from the initial melamine loading; by combining XPS measurements we could also identify the conditions leading to a homogeneous or inhomogeneous N-functionalization of the carbon network: namely, depending on the melamine content and pH, nitrogen can be either more concentrated at the outer shell of the organic nodules, or concentrated more within the core carbon nodules. The interdependency of pH and melamine content is complex and will need further dedicated studies.

In conclusion, a particular advantage of using this method to prepare N-doped CXs is to keep control on the porous texture and nitrogen doping level (with possible N doping gradient from surface to bulk), leading to carbon materials features tailored to the final application.

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Tables

Table 1. Pore texture characterisation of the dried and carbon xerogel series.

Sample	S_{BET} $\text{m}^2 \text{g}^{-1}$ ± 10	V_{DUB} $\text{cm}^3 \text{g}^{-1}$ ± 0.05	V_{Hg} $\text{cm}^3 \text{g}^{-1}$ ± 0.05	V_{V}^{a} $\text{cm}^3 \text{g}^{-1}$ ± 0.1	ρ_{bulk} g cm^{-3} ± 0.02	ρ_{s} g cm^{-3} ± 0.02	$d_{\text{p,max}}$ nm $^{\text{c,d}}$
DG-3-150	208	0.09	0.87	0.97 ^b / 0.96	0.55	1.44	- ^d
DG-3-175	134	0.06	1.42	1.05 ^b / 1.48	0.48	1.44	35 ^c
DG-3-200	77	0.03	1.53	1.56	0.44	1.44	295 ^c
DG-3-225	77	0.03	1.56	1.59	0.43	1.43	1170 ^c
DG-3-250	63	0.03	1.65	1.68	0.41	1.43	1870 ^c
CX-3-150	590	0.24	0.80	0.94 ^b / 1.04	0.70	1.86	19 ^e
CX-3-175	608	0.24	1.20	1.00 ^b / 1.44	0.55	1.90	47 ^e
CX-3-200	591	0.24	1.30	1.54	0.51	1.90	224 ^e
CX-3-225	564	0.23	1.40	1.63	0.49	1.88	696 ^e
CX-3-250	587	0.24	1.36	1.60	0.47	1.93	1210 ^e
DG-1-150	102	0.06	1.50	1.56	0.46	1.46	27 ^c
DG-1-175	45	0.03	1.73	1.76	0.40	1.45	83 ^c
DG-1-200	48	0.03	1.75	1.78	0.42	1.46	192 ^c
DG-1-225	43	0.03	1.80	1.83	0.40	1.45	712 ^c
DG-1-250	12	0.01	1.67	1.68	0.40	1.47	1500 ^c
CX-1-150	307	0.13	0.42	0.65	0.64	1.83	- ^d
CX-1-175	385	0.17	0.32	0.49	0.88	1.88	83 ^e
CX-1-200	543	0.22	0.43	0.65	0.81	1.88	142 ^e
CX-1-225	517	0.21	0.81	1.02	0.67	1.94	449 ^e
CX-1-250	485	0.19	1.07	1.26	0.57	1.89	965 ^e

^a Obtained from $V_{\text{DUB}} + V_{\text{Hg}}$ (combination of N_2 adsorption and mercury porosimetry). ^b V_{p} obtained from plateau. ^c estimated value after crushing (error ~10%), ^d not calculable (crushing only), ^e calculated by Washburn's equation (error: ± 5 nm).

Table 2. Atomic percentage derived from the fitting of N 1s, C1s, O1s XPS spectra (HR).

Sample	N (Pyridinic) at. %	N (Graphitic) at. % ± 0.2	N (Pyridone) at. %	N _{tot} at. % ± 0.6	C at. %	O at. %	N wt %
DG-3-150	7.2	/	7.0	14	65	21	14.9
DG-3-175	6.0	/	6.2	12.2	68.5	19.3	13.1
DG-3-200	3.6	/	6.5	10.1	70.7	19.2	10.9
DG-3-225	2.6	/	6.6	9.2	72.1	18.7	10.0
DG-3-250	1.5	/	3.0	4.5	74	21.5	4.9
CX-3-150	1.5	2	/	3.5	94	2.5	4.0
CX-3-175	1.7	2.3	/	4	94	2	4.6
CX-3-200	1.2	2	/	3.2	92.8	4	3.7
CX-3-225	0.4	0.7	/	1.1	83	15.9	1.2
CX-3-250	0.6	1.2	/	1.8	85	13.2	2.0
DG-1-150	15.5	/	13.5	29	58	13	31.0
DG-1-175	11.8	/	14.8	26.6	60.5	12.9	28.5
DG-1-200	8.4	/	14.2	22.6	66.2	11.2	24.5
DG-1-225	8.3	/	12.2	30.5	66	13.5	33.5
DG-1-250	9.5	/	11.6	21.1	66	12.8	22.9
CX-1-150	1.6	2.9	/	4.5	86.7	8.8	5.1
CX-1-175	3	3.4	/	6.4	90.7	2.9	7.3
CX-1-200	2.7	2.7	/	5.4	91.4	3.2	6.2
CX-1-225	2.5	2.9	/	5.4	91.2	3.4	6.2
CX-1-250	2.4	2.7	/	5.3	91.2	3.5	6.1

Table 3. Comparison between C and N wt % obtained from elemental and XPS analyses.

Sample	C _{EA} wt % ± 0.1	N _{EA} wt % ± 0.1	N _{XPS} wt % ± 0.1
DG-3-150	55.1	11.5	14.9
DG-3-250	55.5	11.1	4.9
CX-3-150	86.5	4.3	4.0
CX-3-250	86.3	4.2	2.0

Figure captions

Figure 1. Nitrogen adsorption-desorption isotherms at -196 °C. (a) DG-3 series, (b) CX-3 series, (c) DG-1 series and (d) CX-1 series.

Figure 2. Mercury porosimetry curves: (a) DG-3 series, (b) CX-3 series, (c) DG-1 series and (d) CX-1 series.

Figure 3. Nitrogen adsorption-desorption isotherms at -196 °C of samples prepared with various amounts of melamine and $R'/C = 150$.

Figure 4. Typical XPS N1s spectra of (a) non-pyrolyzed (DG) and (b) pyrolyzed (CX) samples showing the different chemical components. Chosen samples are DG-1-200 and CX-1-200.

Figure 5: Thermogravimetric analysis of dried gels: (a) DG-3-200, (b) DG-1-200.

Figure 1a.

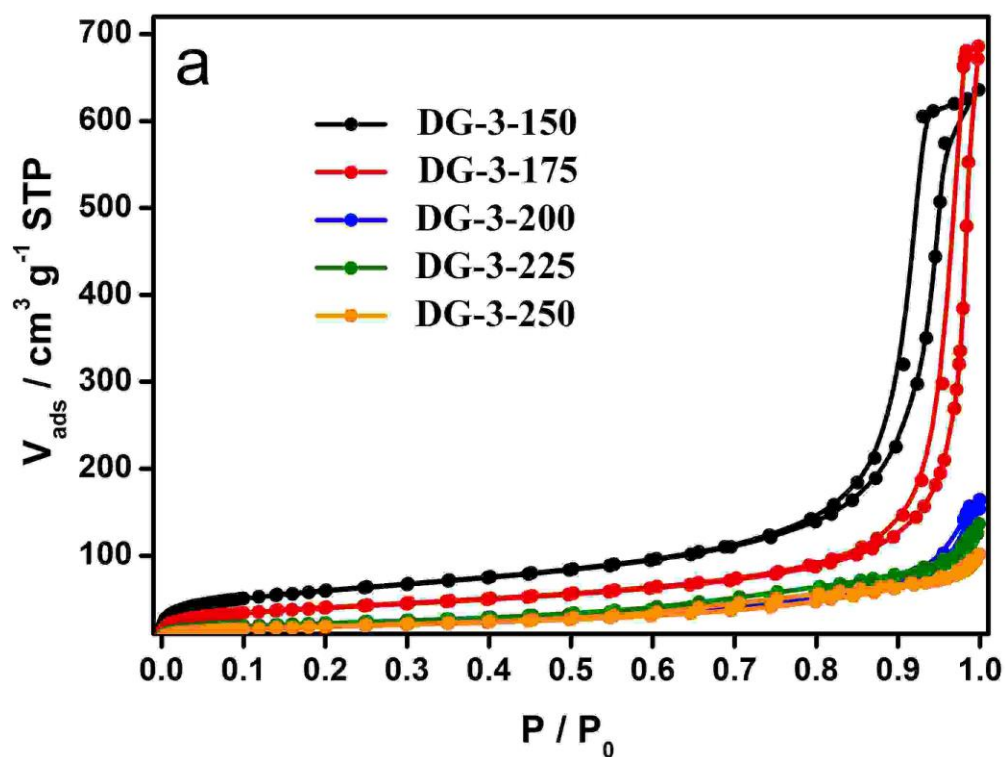


Figure 1b.

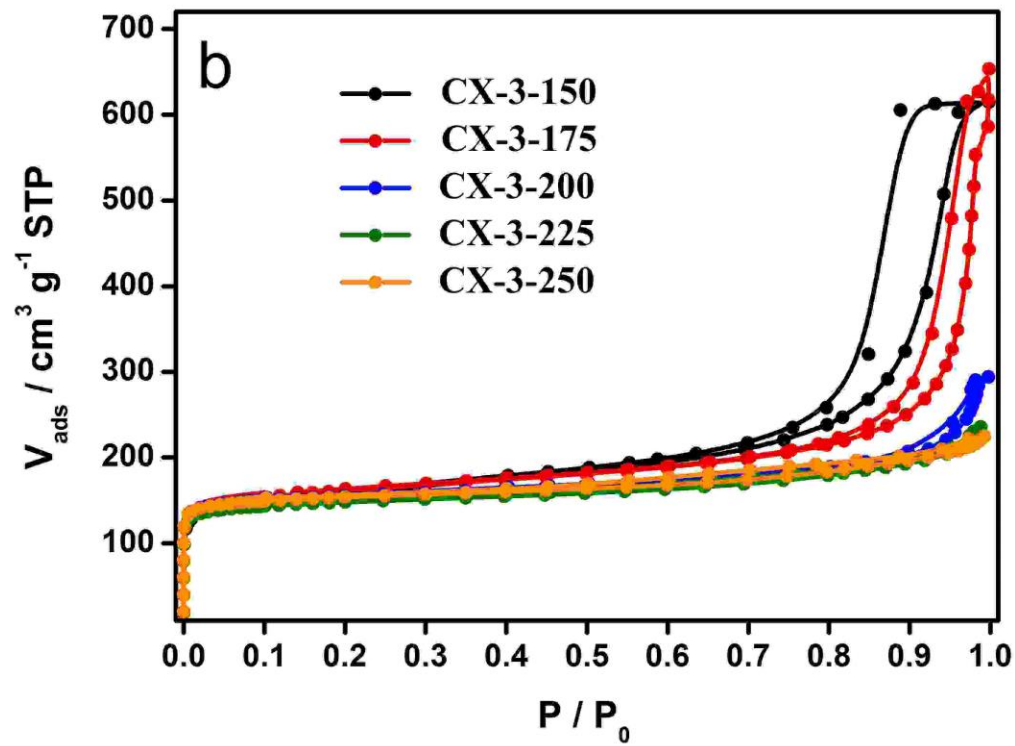


Figure 1c.

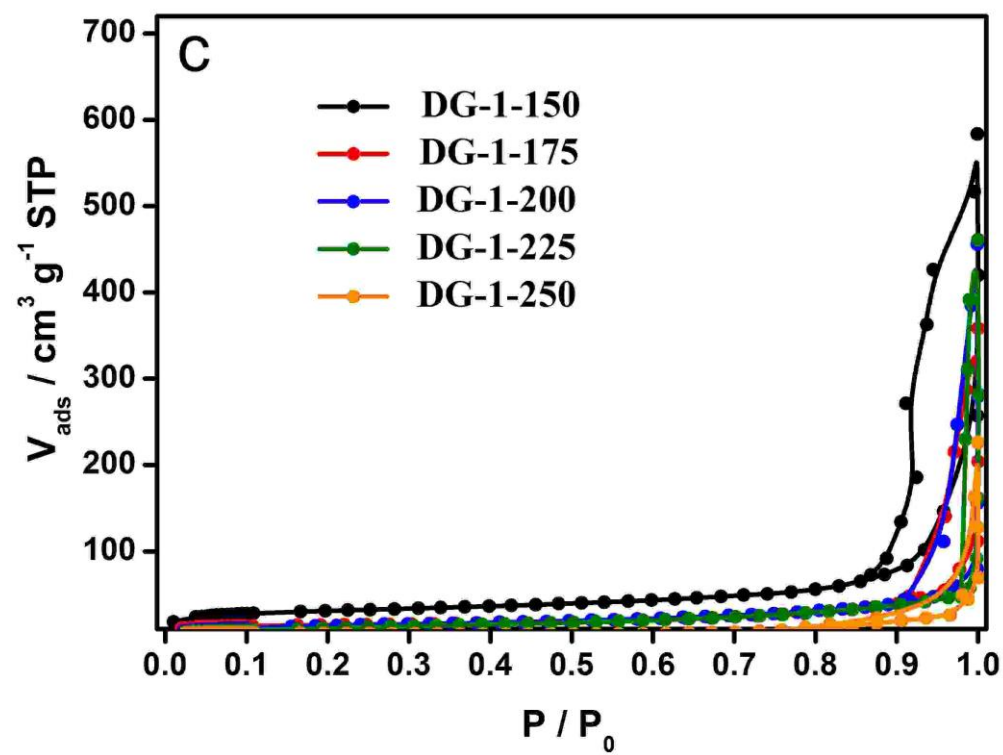


Figure 1d.

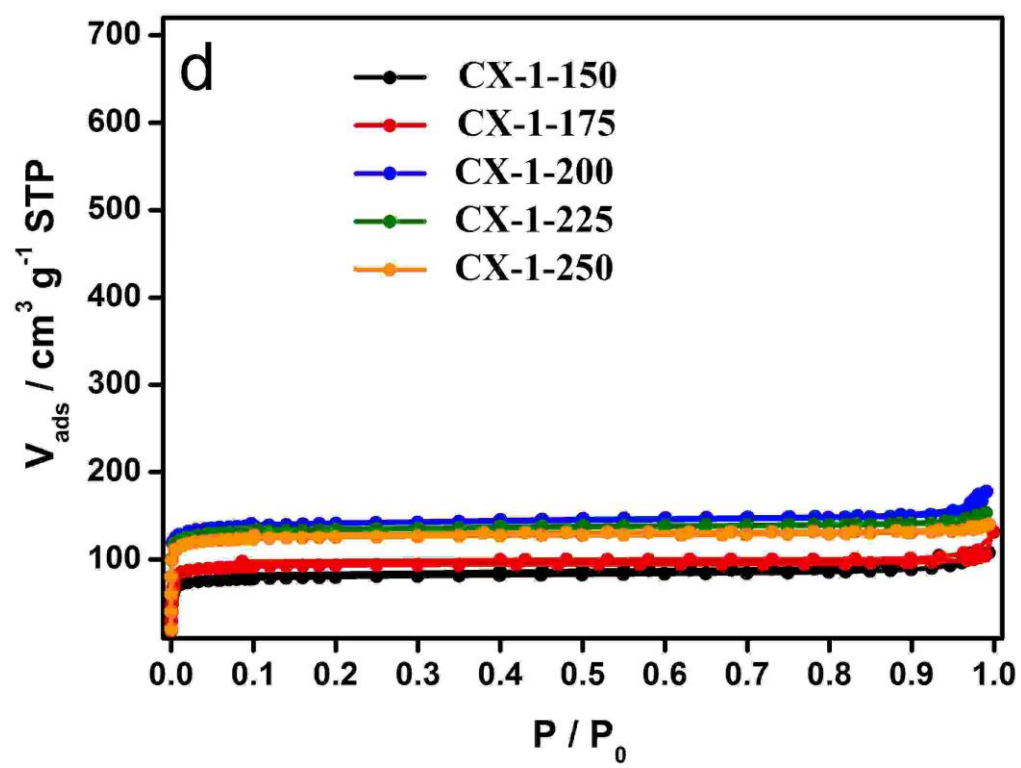


Figure 2a.

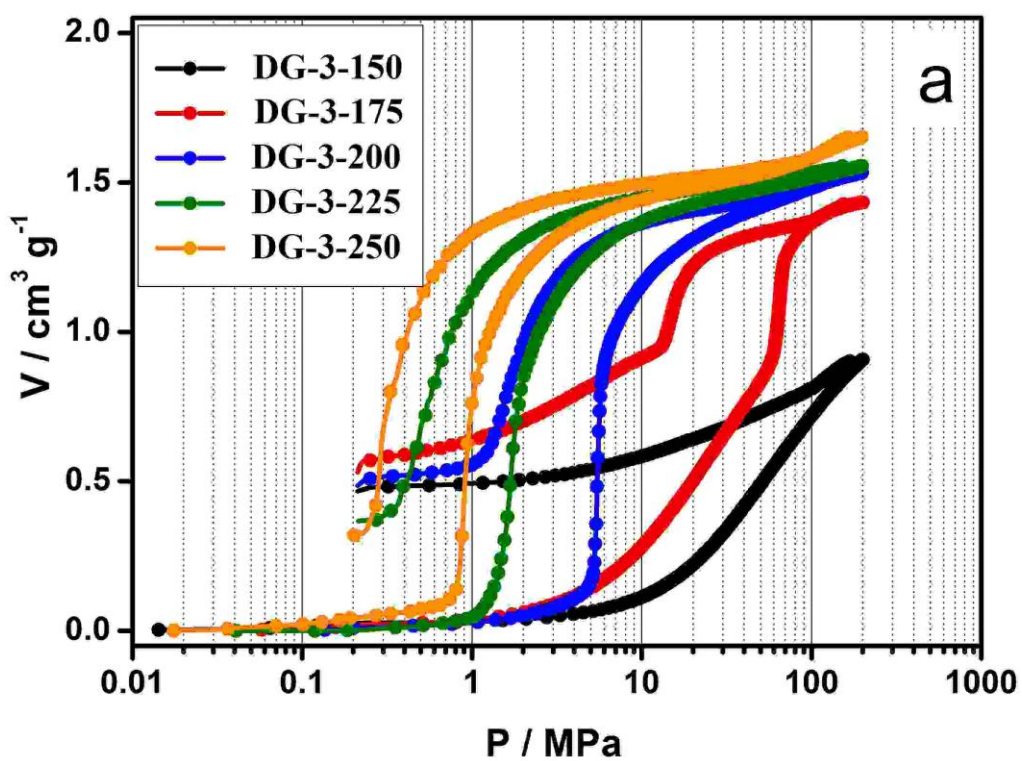


Figure 2b.

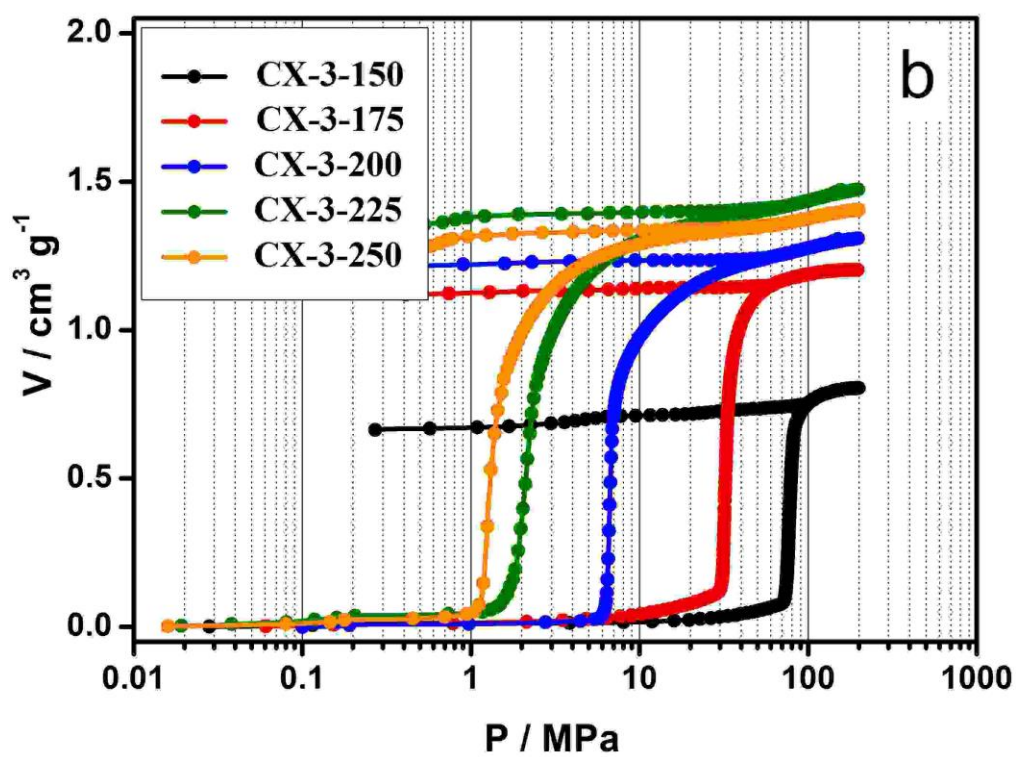


Figure 2c.

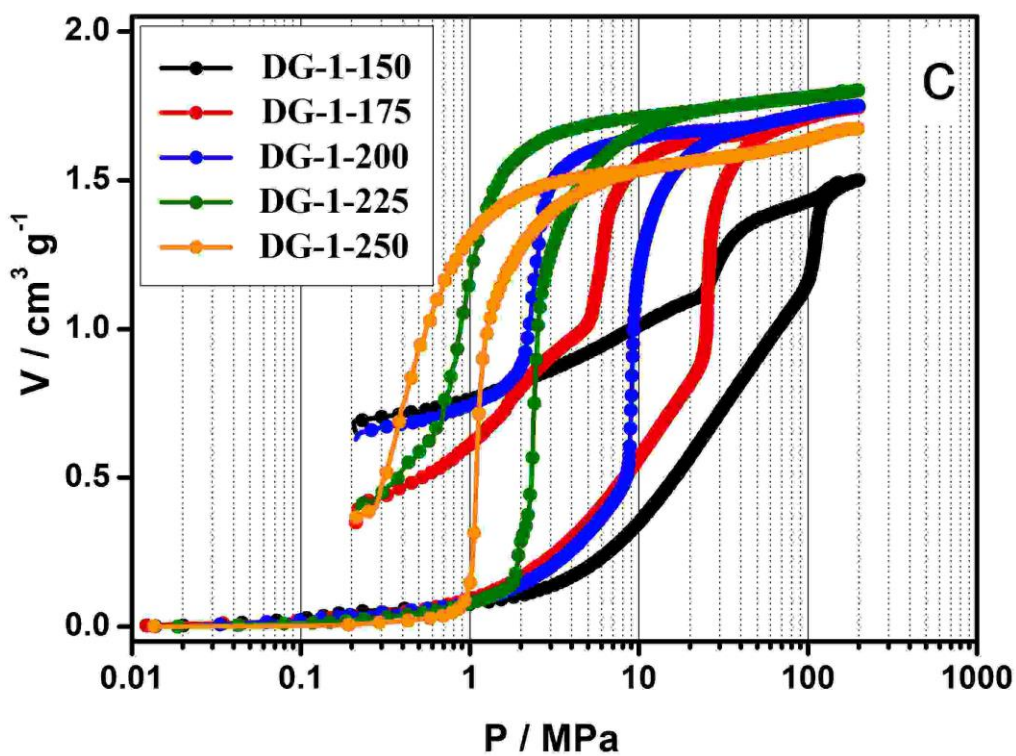


Figure 2d.

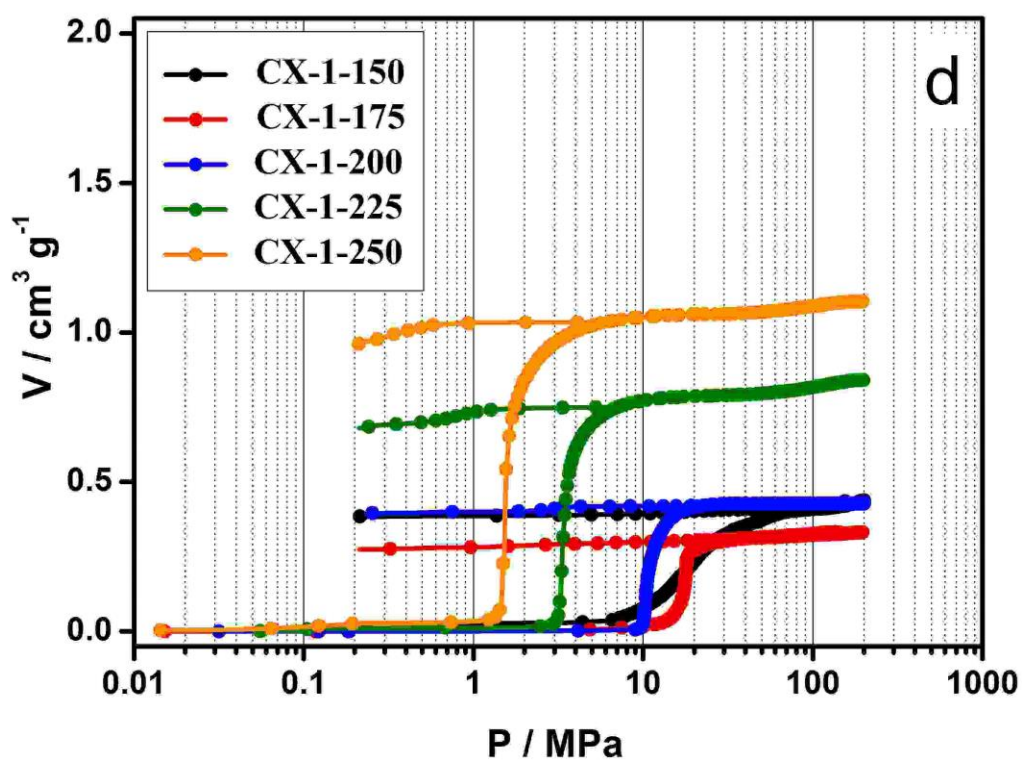


Figure 3.

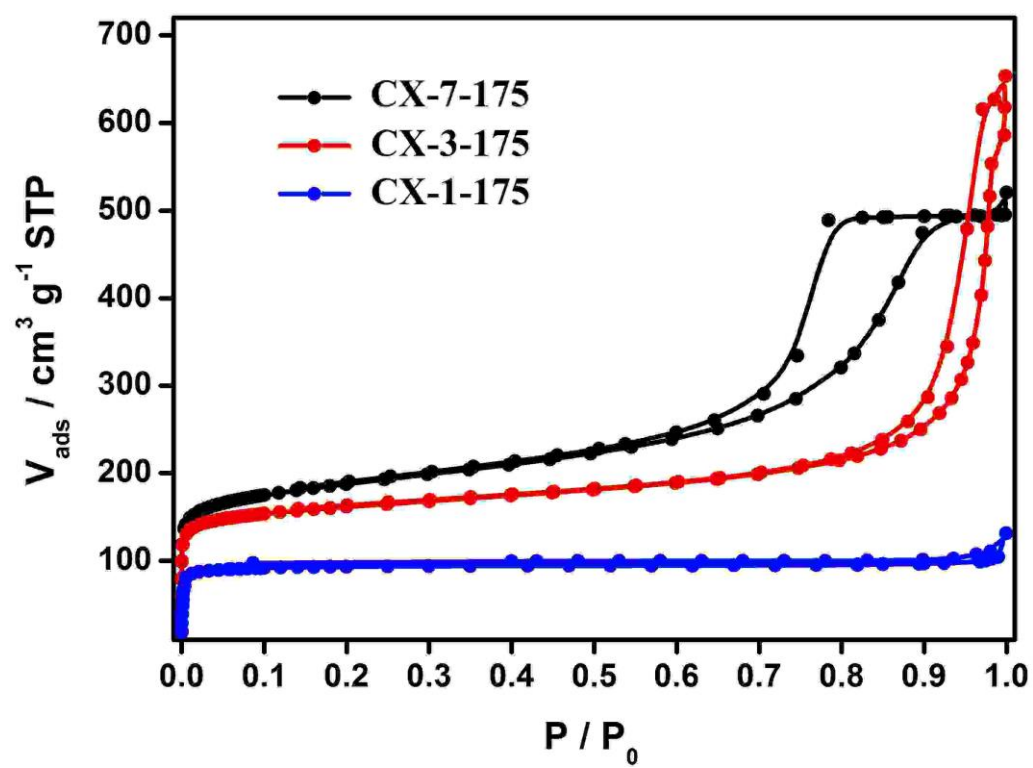


Figure 4a.

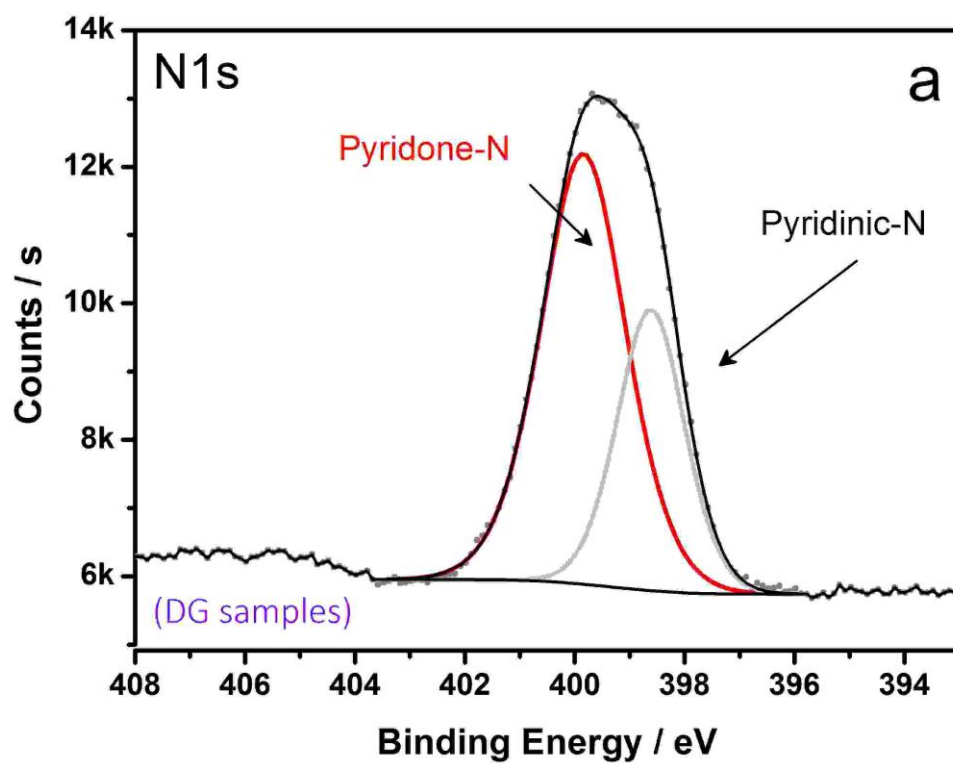


Figure 4b.

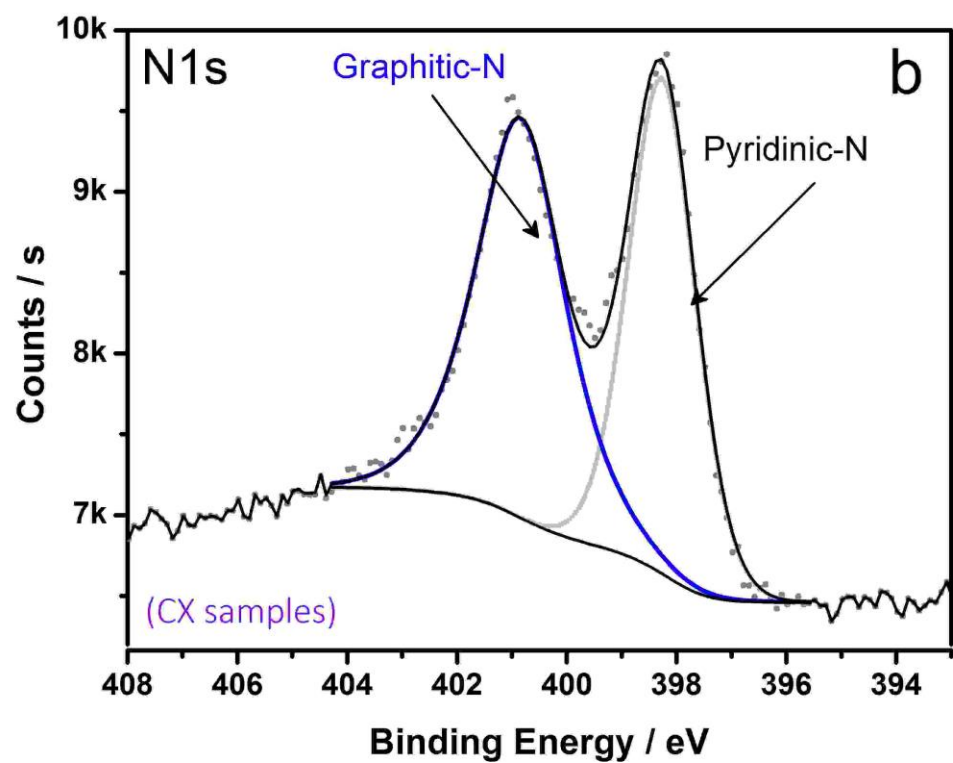


Figure 5a.

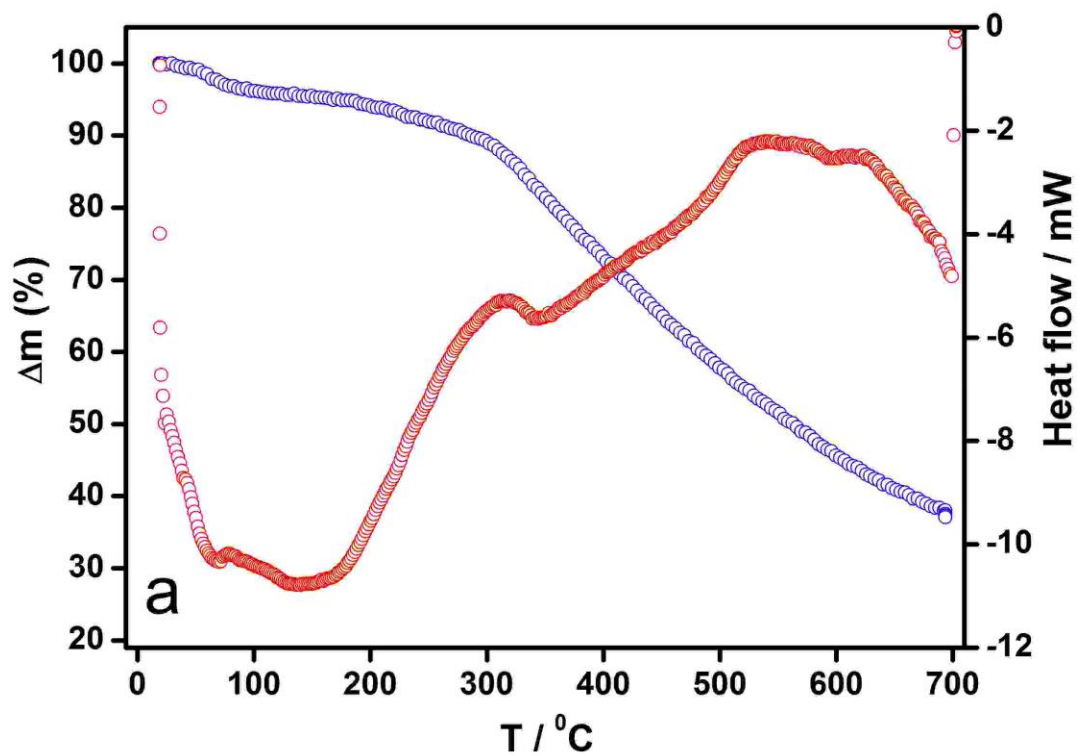


Figure 5b.

