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Synthesis and properties of new nitrogen doped nanostructured carbon materials obtained by templating of mesoporous silicas with aminosugars

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Abstract

The negative templating synthesis process has been applied to prepare nanostructured carbon materials with a high nitrogen content. SBA-15 silica template was impregnated with the following carbon precursors: sucrose, glucose and amino-glucose. The structure of the materials was investigated by SAXS, WAXS and TEM. Nitrogen functions were analyzed by XPS and the textural parameters of the carbons were studied by nitrogen and CO₂ adsorption. X-ray and TEM studies confirmed that a pore nanostructure is inherited from the silica templates. XPS analysis showed that the nitrogen content of the materials can be controlled between 2 and 5 wt% and that N atoms are strongly bonded in the carbon structure in heterocycles or nitrile functions. An important result is that these nanostructured carbon materials exhibits interesting textural properties with BET surface areas ranging between 1000 and 1300 m²/g. Moreover, the study of the influence of nitrogen on the textural and structural parameters of the resulting carbon materials shows that nitrogen plays an active role during the synthesis process. This observation is also supported by the speciation of nitrogen in the nanostructured carbon materials.

Key words: A. microporous materials; B. chemical synthesis; C. photoelectron spectroscopy, X-ray diffraction

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1 Introduction.

The development of new porous carbons has become possible these last years by using a templating approach [1–7]. The method is based on the filling of the organized porous structure of a silica host by a carbon precursor in gaseous or liquid phase followed, if necessary, by a carbonization. The carbon, which is recovered after silica removal, corresponds to a negative replica of the pristine silica template. It displays an organized and interconnected porous volume including micropores and mesopores associated with high values of specific surface area and pore volume. The specificity of the templating approach is that the carbon is formed in a confined porous network (pore size < 10 nm) which confers to it structural characteristics and textural properties that cannot be obtained by conventional preparation methods [8–10].

The carbon replica prepared from sucrose as carbon precursor are especially attractive as electrode for super capacitors due to their high microporous volume and their perfectly distributed network of super-micropores and mesopores [11]. One of the challenges nowadays is to improve the super capacitor performance while keeping the advantage of the carbon replica characteristics. A solution is to introduce an hetero-element such as nitrogen in the carbon structure [12–14]. Nitrogen-containing carbon replica have been already proposed by using precursors like acetonitrile, pyrrole or polyacrylonitrile [15–20]. However, a drawback of the incorporation of nitrogen is often a significant decrease of the microporous volume as already observed for conventional or nanostructured carbons [17, 18, 21]. The most important porous volume was obtained by Kim et al. [18] who were able to polymerize polypyrrole inside the pore volume of a SBA-15 silica, and obtained an ordered mesoporous carbon material with a pore volume close to $1 \text{ cm}^3/\text{g}$ and a surface area of $940 \text{ m}^2/\text{g}$.

In this paper, we demonstrate the possibility to synthesize nanostructured carbon materials with a controlled nitrogen content and high textural properties by using aminosugars as carbon precursors. The synthesis procedure, the structural, textural and surface chemistry characteristics of the N-containing carbon replica are presented.

2 Nanostructured material synthesis

To synthesize carbon replica, a SBA-15 template was impregnated with sugar molecules. The three carbon precursors selected are presented in Figure 1. The D-glucosamine hydrochloride was used as nitrogen-containing carbon precursor. The α -D(+)-glucose and the sucrose which belong to the same family but do not contain nitrogen were used as references. The α -D(+)-glucose was

Figure 1. the three carbon precursors used for template synthesis: a) α -D(+)-glucose, b) D-glucosamine hydrochloride, c) sucrose.

selected due to its size which is comparable to the one of the aminosugar. The sucrose was chosen for comparison with previously published studies [1, 4, 6, 9].

It must be noticed that the size of sucrose is twice the ones of glucosamine and glucose. Since the size of the precursor molecule plays an important role in a confined reactional medium, the comparison between carbons obtained from both precursors is of interest. The details of the carbon preparation are given in the experimental section of the footnotes. The different carbons prepared are listed in table 1 with their associated sample name.

The synthesis of nanostructured carbon materials from silica templates includes different steps:

- the silica template was prepared according to the procedures already described in the literature [22, 23].
- The carbon precursors were introduced inside the pore volume of the silica by a liquid infiltration method [1]. In order to obtain a better filling of this pore volume, two successive infiltrations were done with the following procedure:
 - for the first infiltration, the template was mixed with a solution of sugar in water and sulfuric acid (composition: sugar/ sulfuric acid/ water = 1/0.11/4 in mass) at room temperature for 12h. The amount of solution was calculated in order to fill the pore volume of the template with the carbon and the sulfuric acid.
 - The mixture was dried 12h at 100°C, and then a pre-carbonization was done at 150°C for 6h.
 - A second infiltration was done with a more diluted sugar solution (sugar/ sulfuric acid/ water = 1/0.11/6.7 in mass). The amount of solution was calculated in order to fill the remaining pore volume of the template with

Table 1

The experimental parameters used for the synthesis of the nanostructured carbon materials.

Sample	template	1st precursor	2nd precursor	nitrogen content (wt%)	
				<i>elemental</i>	<i>XPS</i>
				<i>analysis</i>	
V15GG	SBA-15	Glucose	Glucose	0	0
V15SS	SBA-15	Sucrose	Sucrose	0	0
V15NS	SBA-15	Glucosamine	Sucrose	4	2.7
V15NN	SBA-15	Glucosamine	Glucosamine	5	4.1

the carbon and the sulfuric acid, this remaining volume was assumed to be the half of the pristine one. The mixture was then dried and pre-carbonized as described above.

- The carbonization was done at 900°C under vacuum, the heating rate was 3 K/min and the temperature was maintained for 5h.
- The mixture was then treated with fluorhydric acid (46 wt%) for 12h at room temperature to remove the silica.
- The sample was washed and dried to obtain the final carbon material.

The pristine silica is a powder with particle sizes of few microns. The carbon particles obtained at the end of the synthesis process have also this size. Whatever the precursor used, the carbon content of the carbon/silica composite is close to 33 wt%. This value is close to the maximum amount of carbon that can be formed in the pore volume of the silica with this synthesis method after two impregnations. The nitrogen content of the carbon replica indicated in Table 1 was determined by elemental analysis (CNRS Analysis Center, Vernaison, France) and by XPS (Paul Scherrer Institut, Switzerland). The X-Ray Source was Al-K α . By using aminosugars for both impregnations, a carbon with a nitrogen content as high as 5 wt% can be obtained. As expected, a lower nitrogen content is obtained when one impregnation is performed with the nitrogen-free precursor. A good agreement is found between elemental and XPS analysis showing that the nitrogen content at the surface is close to the one in the bulk material. These elemental analysis show that 37 wt% of the nitrogen contained in the pristine precursor is kept in the final material. Previous studies on the carbonization of similar nitrogen containing molecules have shown that an important fraction of the nitrogen evolve as ammonia and hydrogen cyanide [24].

Figure 2. SAXS of samples V15GG (left) and V15NN (right).

3 Characterization of the nanostructured materials

3.1 Carbon structure of synthesized materials

The structure of the materials was studied by Small-Angle X-Ray Scattering (SAXS) at the BM26 line of the European Synchrotron Facility in Grenoble (FRANCE). The SAXS spectra of the carbon replica together with the one of silica template are shown in Figure 2, and the corresponding structural parameters are reported in Table 2. Three peaks can be easily observed on the pristine SBA-15: the main one around $s=0.11 \text{ nm}^{-1}$ ((100) reflection) and two less intense peaks around $s=0.16 \text{ nm}^{-1}$ and 0.22 nm^{-1} which correspond to the (110) and (200) reflections of a hexagonal lattice. For the carbon replica, the first peak is well defined although shifted to higher value of s , indicating a decrease of the lattice parameter during the synthesis. The two other peaks are weak compared to the silica host. This can be related to the lower carbon/pores contrast compared to the silica/pores one [17]. It shows also that the carbon material is not a perfect replica of the pristine silica.

The SAXS measurements confirm that the carbon replica displays a long-range ordered porous structure and retains the hexagonal structure of the silica template. The high level of order of the pore network determined by SAXS is confirmed by the TEM observations as shown in Figure 3. From the TEM images, the unit cell size was also calculated from the mean distance between the carbon rods. This was evaluated by a Fourier Transform on selected regions of the TEM images. The values are reported in table 2 and compared to the

Table 2

Structural parameters of templates and nanostructured carbon materials. V15 is the silica template.

sample	d_{002} (nm)	a (nm) SAXS	a (nm) TEM
V15		10.8	10.3
V15GG	3.82	9.8	9.7
V15SS	3.98	10.2	9.9
V15NS	3.77	9.5	9.3
V15NN	3.66	9.5	9.3

values determined by SAXS from the position of the 100 peak and taking into account a hexagonal symmetry. A good agreement is found.

Whatever the carbon precursor, a smaller cell size is observed for the carbon compared to the silica indicating that a shrinkage of the material during the carbonization step. This decrease is usually observed when the liquid impregnation is used and it was expected for sucrose and for the other precursors [25]. The degree of shrinkage increases with the number of infiltration with the N-containing precursor. The shrinkage is also more pronounced when glucose is used instead of sucrose. These results confirm that the molecule size and the nitrogen content influence the evolution of the unit cell parameter. Such effects can be attributed to two phenomena: (i) the shrinkage of the carbon precursor during the carbonization step which induces compression strains onto the silica network (the shrinkage being dependent on the precursor type) and (ii) the alteration of the silica matrix due to the release of water during the carbonization. Therefore, an important shrinkage of the silica template is observed during the carbonization step which leads to a decrease of the lattice parameter and of the porous volume [26]. The extend of shrinkage depends on the structural and textural modifications occurring in the carbon precursor during the thermal treatment.

Wide-angle X-Ray diffraction has been conducted on the carbon replicas. It must be noticed that a small amount of carbon precursor is not able to diffuse inside the pore volume of the template, and therefore reacts on the external surface of the silica particles. As this carbon precursor is not inside a confined geometry, its carbonization leads to a higher structural order than the one of hydrocarbons which carbonize inside the pores of the silica. The differences between carbonization in a nanometer sized geometry and carbonization without any geometric limitations has already been observed for many carbon precursors [9]. Nevertheless, the values of d_{002} which are shown in table 2 give

Figure 3. TEM images of some nanostructured carbon materials: left: V15SS, center: V15GG, right: V15NN.

indications on the graphitization process of the different carbon precursors. The use of aminosugars leads to carbons with a higher level of graphitization; they remain however carbons with a low structural order. This observation support the assumption that the decrease of the cell size is directly related with the behavior of the carbon precursor during the carbonization of the Carbon/Silica composite. Because of the interest in the synthesis of nitrogen enriched carbon materials, the influence of the presence of nitrogen on the structure of the carbon material has already been pointed out [27]. Amine functional groups are labile and during carbonization, most of them are inserted in pyrrole and then pyridine rings [28, 29]. Therefore they promote the thermal annealing process and participate to the decrease of the d_{002} value. Furthermore, the increase of the structural order leads to an increase of the density of the carbon material and to the decrease of its specific volume. This observation is in agreement with the decrease of the lattice parameter which was discussed above.

3.2 Nitrogen speciation

XPS measurements were performed to obtain chemical information on C-N binding. The nitrogen functional groups present at the carbon surface were quantified by XPS from the high resolution spectra of the binding energy region around 400 eV corresponding to the N1s peak; the results are reported in table 3. As an illustration, the XPS spectra of the V15NS and V15NN samples are shown in figure 4. The N1S signal is split in five peaks [28, 30, 31].

The main three peaks centered at 398.2 eV, 400.2 eV and 400.9 eV are assigned to pyridinic nitrogen (N6), pyrrolic nitrogen and pyridinic nitrogen in

Figure 4. Decomposition of the N1S peak on the XPS spectrum of V15NN and V15NS sample.

association with an oxygen functionality (N5) (pyridone) and highly coordinated quaternary nitrogen atoms incorporated into graphene sheets (NQ), respectively. The NX peak at 402.3 eV shows the presence of nitrogen atoms included in the carbon structure and bonded to oxygen. The peak at higher energy (around 405 eV) could be attributed to nitrogen oxides. Some authors also attributed the peak between 402 and 407 eV to shake-up satellites [32]. Such a structure for the N1S region has also been observed for other products resulting from calcination of nitrogen containing compounds like Nomex fibers [33].

The increase of the nitrogen content does not modify the relative amount of each type of nitrogen as shown in Table 3. The main quantity of C-N present in the carbon corresponds to highly coordinated N atoms incorporated into graphitic sheets. It shows that nitrogen atoms which don't evolve as ammonia in the gas phase take an important part in the carbonization process. This observation confirms the conclusions of the analysis of the structural properties of nitrogen-enriched carbon materials which highlighted the role of amine groups during the carbonization. The N5 peak is also important since it contributes to c.a. 25%. Due to the high number of OH groups in the carbon precursors, the formation of pyrrolic nitrogen is rather expected. However, pyrrolic structures do not survive the high temperature treatment and are converted to pyridone-type structure [29]. The XPS results are consistent with earlier studies with coal chars and synthetic chars indicating that in high-temperature carbons (>1000K) the N1s peak can be attributed to pyridinic nitrogen located at the edges of graphene structures formed during pyrolysis (N5 and N6) and to nitrogen incorporated in these structures (NQ) [34].

Table 3

Decomposition of the N1S peak for nitrogen containing nanostructured carbon materials (percentages of the total area of the N1S peak).

Sample	N6	N5	NQ	NX	NA
V15NS	15 %	11 %	45 %	17 %	12 %
V15NN	15 %	9 %	47 %	17 %	12 %

3.3 Textural properties

The textural parameters of the carbon were determined with a Quantachrome A1-LP apparatus. The textural characteristics of the carbons were deduced from the adsorption isotherms of nitrogen at 77 K and of carbon dioxide at 273K. the total pore volume V_P was obtained from nitrogen isotherm at a relative pressure $P/P_0=0.95$. The volume of micropores (pores < 2 nm) V_{DRN2} was obtained by applying Dubinin-Radushkevich analysis on nitrogen adsorption isotherm at low relative pressure ($10^{-4} < P/P_0 < 10^{-2}$). The same method was used on the CO_2 isotherm to estimate the volume of ultramicro-pores (size < 0.8 nm). From these parameters, the volume of mesopores can be obtained from the difference $V_P - V_{DRCO2}$ and the volume of the so-called super-micropores is estimated by the difference $V_{DRN2} - V_{DRCO2}$.

The nitrogen adsorption/desorption isotherms of the samples are shown in Figure 5 and the textural parameters are reported in Table 4. The nitrogen isotherms of the samples are very similar. A difference can be found on the position of the mesopore hysteresis loop indicating a slight change in the size of the mesopores. This can be a consequence of the filling level of the template's pore volume by the carbon precursor which slightly differs with the nature of the precursor. Although a slight decrease is observed when the nitrogen content increases, the specific surface area of the carbon remains high for all the samples. Most interesting for the applications targeted for the carbon replicas is to check the micropores and mesopores volume.

The first observation is that the use of sucrose as a carbon precursor allow the synthesis of highly microporous nanostructured carbon materials. It has already been observed that the carbonization of sugars inside the confined geometry defined by the pore volume of a silica template leads to higher microporous volume than other precursors [35]. This was not expected since the carbonization of sucrose in a non confined geometry leads to carbon materials with very low porous volumes [9]. As shown in Table 4, the microporous volume for the samples prepared with glucose and aminosucrose is of the same order than for the carbon prepared from sucrose. Moreover, the volume of

Figure 5. nitrogen adsorption isotherms for nanostructured carbon materials obtained with SBA-15 template (the isotherms have been shifted by 300 cm³ STP/g).

secondary micropores ($V_P - V_{DRCO_2}$) and mesopores remains also very high. Therefore, the introduction of nitrogen in the carbon is not associated with a reduction of the micro- and mesoporous value as previously observed in the literature by using other nitrogen-containing precursors [17, 21]. A more precise analysis of the nitrogen adsorption isotherms shows that the small decrease of micropore volume occurs in the very low relative pressure range. The nitrogen volume adsorbed for $P/P_0 < 10^{-5}$ is similar for V15SS and V15NS (95.0 and 97.5 cm³ STP respectively) and decreases with increasing nitrogen content: 87.3 cm³ STP for V15NS and 60.0 cm³ STP for V15NN. This decrease of very small micropores can be related to the increasing structural order observed for nitrogen-enriched carbon materials. Modeling studies have shown that the presence of such very small pores is related to the bad structural order of carbon materials [36].

Table 4

Textural parameters of nanostructured carbon materials. S_{BET} : BET surface area, V_P : total pore volume measured on nitrogen isotherm at $P/P_0=0.95$, V_{DRN2} : micropore volume, V_{DRCO2} : ultra-micropore volume.

	S_{BET}	V_P	V_{DRN2}	V_{DRCO2}	$V_P - V_{DRN2}$	$V_{DRN2} - V_{DRCO2}$
	(m^2/g)	(cm^3/g)	(cm^3/g)	(cm^3/g)	(cm^3/g)	(cm^3/g)
V15GG	1270	1.12	0.48	0.31	0.63	0.17
V15SS	1100	1.19	0.47	0.29	0.72	0.18
V15NS	1200	1.15	0.47	0.29	0.67	0.18
V15NN	1070	1.19	0.40	0.27	0.69	0.13

4 Conclusions

Nitrogen-containing ordered porous carbons have been synthesized by using aminosugars as nitrogen-containing carbon precursors and SBA-15 as silica template. We were able to synthesize carbon materials with a nitrogen content as high as 5 wt% while keeping a large volume of micropores and small mesopores. The SAXS analysis showed the nanostructure of these carbon materials. A detailed study of the structural, chemical and textural properties of the nanostructured carbon materials was done. This allowed to exhibit the active role played by amine groups in the carbonization process: chemical reactions which lead to the insertion of nitrogen atom in pyridine and pyridone rings enhance the graphitization process. The result is an increase of the true density and of the structural order of the resulting carbon material, and consequently a decrease of the lattice parameter and of the volume of very small micropores is observed.

These nitrogen-enriched carbon replica display attractive characteristics to be used in super capacitors such as a significant nitrogen content to develop pseudo-capacitance effects, a high microporous volume for an efficient charging of the electrical double layer and an appropriate micro-mesoporous volume for ions diffusion. Electrochemical tests are in progress for these new carbon materials.

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