

SYNTHESIS OF NEW NANOSTRUCTURED CARBON MATERIALS BY TEMPLATING OF AMINOSUGARS

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Introduction

The synthesis by replication of ordered porous silicas has allowed the synthesis of several carbon materials. These materials exhibit a nanostructured porous network, and can have a high microporous volume^{1,2,3}. These materials have been tested for environment or energy applications such as hydrogen storage by adsorption, electrochemical hydrogen storage or supercapacitors. For this last application, the insertion of nitrogen atoms in such carbon materials could lead to significant performance improvements. For example, when carbons are used as electrodes materials in supercapacitors, it has been observed that the presence of nitrogen functional groups at the surface leads to an increase of the capacitance^{4,5}.

In this study, nanostructured carbon materials have been synthesized by templating of two ordered mesoporous silicas (SBA15 and MCM48), by using three carbon precursors: sucrose, glucose and aminoglucose. The structural and textural parameters were investigated by X-Ray diffraction (SAXS and WAXS), TEM, XPS and gas adsorption.

Synthesis of the nanostructured carbons.

The synthesis was done in four steps⁶: (1) the infiltration of the carbon precursor was done with a solution of sugar and sulfuric acid, a drying was then done at 100°C followed by a pre-calcination at 150°C during 6h; (2) in order to obtain a good carbon yield, a second infiltration was done; (3) the Carbon/Silica composite was calcined at 900°C in vacuum during 5h; (4) an etching with hydrofluoric acid was done in order to remove the silica, the carbon material was then washed and dried. The different materials used for this study are presented in table 1. We chose to use an aminosugar as carbon precursor: the D-glucosamine hydrochloride (98%, Acros Organics). Two other carbon precursors which don't contain nitrogen were used as witness: the α -D(+)-glucose (99%, Acros Organics) and the sucrose (98%, Sigma Aldrich).

The nitrogen content was obtained from XPS measurements, they were found to be in good agreement with elemental analysis: respectively 4 and 5 wt% for samples V15NS and V15NN.

Material	precursor 1 st imprégnation	precursor 2 nd imprégnation	Nitrogen wt%	S_{BET} (m^2/g)	Vp (cc/g)	V_{N_2} (cc/g)	V_{CO_2} (cc/g)	$V_p - V_{N_2}$ (cc/g)	$V_{N_2} - V_{CO_2}$ (cc/g)
V15GG	Glucose	Glucose	0	1270	1.11	0.48	0.31	0.63	0.17
V15SS	Sucrose	Sucrose	0	1100	1.13	0.40	0.25	0.73	0.15
V15NS	Glucosamine	Sucrose	2,7	1200	1.14	0.47	0.29	0.67	0.18
V15NN	Glucosamine	Glucosamine	4,1	1070	1.09	0.40	0.27	0.69	0.13

Table 1: Synthesis parameters and textural properties of nanostructured carbon materials.

TEM images of the four carbon materials are presented in figure 1, They show that we were able to obtain nanostructured materials whatever the carbon precursor used,

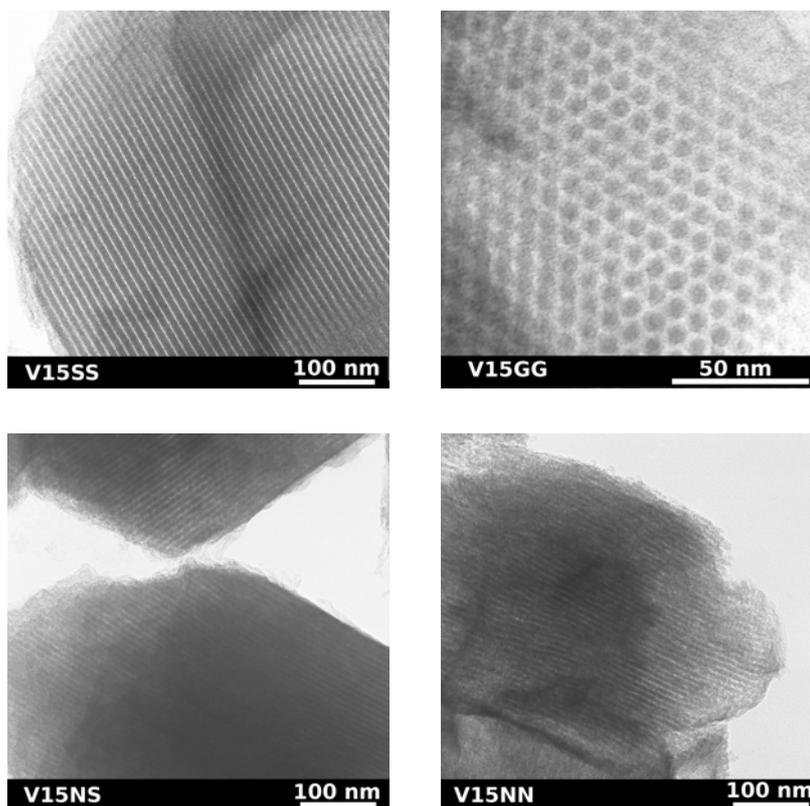


Fig 1. TEM images of ex-SBA-15 nanostructured carbon materials.

Textural characterization

The main textural parameters are also presented in table 1, and the nitrogen adsorption isotherms are shown in fig 2. We can see that all samples exhibits a significant microporous volume. It must be noted that this development of porosity from sugar precursors is related to the confined geometry in which the carbonization is done, the carbonization of sugar in a free environment leads to materials with a very low porosity^{7,8}.

The textural characteristics depend on the type of carbon precursor. The isotherms shows that the use of aminosugars leads to a small decrease of the microporous volume of the resulting carbon material. We can see that the properties of the material obtained with infiltration of amino-glucose and sucrose are between the ones of pure ex-sucrose and the ones of pure ex-amino-glucose materials. For all materials, the decrease is observed mainly for the volume of supermicropores (above 1 nm) and small mesopores ($P/P_0 < 0.4$). The volume of ultramicropores (below 1 nm) is not influenced by the carbon precursor.

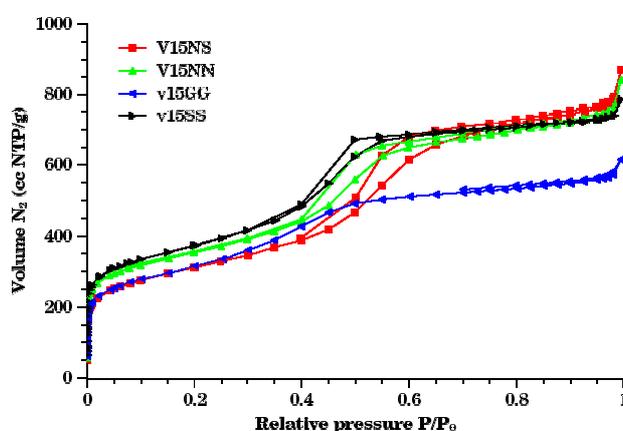


Fig 2: Nitrogen adsorption isotherms at 77 K of nanostructured carbon materials.

SAXS and XPS characterizations.

SAXS experiments were done at the European Synchrotron Facility in Grenoble (France). An example of a resulting diffractogram is presented in Fig 3. The three peaks of the hexagonal symmetry were detected on all ex-SBA15 carbons. TEM analysis confirmed the presence of this nanostructure on ex-SBA15 carbons.

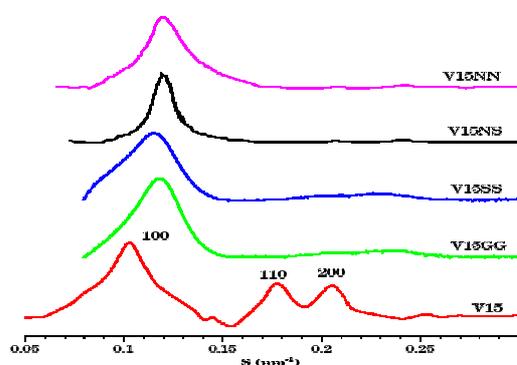


Fig 3: SAXS diffractograms of samples V15AGN

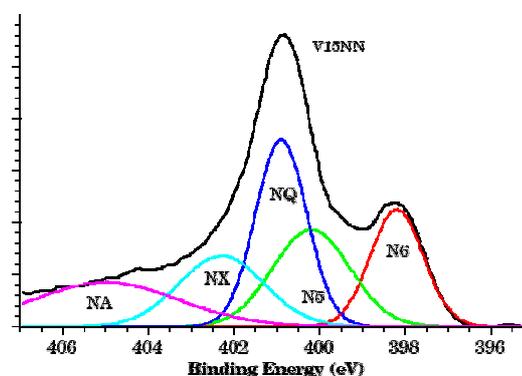


Fig 4: Decomposition of the N1S peak on the XPS spectrum of V15NS sample.

XPS analysis was done to study the nitrogen containing functional groups. The results for energies corresponding to N1s peaks are shown in Fig 4. The N1S signal was split into six peaks according to the nomenclature of Pels et al.⁹. The peaks N6 and N5 correspond to pyridinic groups, NQ to quaternary bonded nitrogen, The peak NX indicate the presence of nitrogen included in the carbon structure and bonded to oxygen while the peak NA was attributed to nitrogen oxides. This analysis shows that nitrogen is highly bonded in the carbon structure.

Sample	N6	N5	NQ	NX	NA
V15NS	16	26	30	16	12
V15NN	15	23	33	17	12

Table 2. Decomposition of the N1S peak for nitrogen containing nanostructured carbon materials.

Conclusions

By using the templating process, we were able to synthesize nanostructured carbon materials with a controlled nitrogen content. Furthermore, the textural analysis showed that these carbon materials exhibit a large volume of micropores and small mesopores. These carbon materials are attractive for applications such as supercapacitors as they have an interconnected mesopore network to allow the diffusion of species, a microporous volume which is necessary to increase the double layer capacitance and a significant nitrogen content to observe pseudo-capacitance effects.

References

- Vix-Guterl, C.; Boulard, S.; Parmentier, J.; Werckmann, J.; Patarin, J. J. Chem. Lett., 2002, 31, 1062-1063
- Vix-Guterl, C.; Saadallah, S.; Vidal, L.; Reda, M.; Parmentier, J.; Patarin, J. J. Mat. Chem., 2003, 13, 2535-2539
- Ryoo, R.; Joo, S.H.; Kruk, M.; Jaroniec, M. Adv. Mater., 2001, 13, 677-681
- Hulicova, D.; Kodama, M.; Hatori, H. Chem. Mater. 2006, 18, 2318-2326, 2006
- Frackowiak, E.; Lota, G.; Machnikowski, J.; Vix-Guterl, C.; Beguin, F. Electrochimica Acta, 51, 2006, 2209-2214
- Ryoo, R.; Joo, S. H.; Jun, S. J. Phys. Chem. B, 1999, 103, 7743-7746
- Gadiou, R.; Vix-Guterl, C. Ann. Chi. Phys., 2005, 30, 425-439
- Gadiou, R.; Didion, A.; Saadallah, S.; Couzi, M.; Rouzeaud, JN.; Delhaes, P.; Vix-Guterl, C.; Carbon, 2006, 44, 3348-3352
- Pels, J. R. ; Kapteijn, F. ; Moulijn, J. A. ; Zhu, Q. ; Thomas. K. M. Carbon, 1995, 33, 1641