

## **N-containing carbons from styrene-divinylbenzene copolymer by urea treatment**

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N-containing synthetic carbons with narrow porosity were prepared from a chlorinated styrene and divinylbenzene copolymer by a multistep method with a yield of 34 wt.%. Surface chemical treatment and thermal carbonization of the starting copolymer was monitored by urea impregnation. Steam activation, oxidation and an additional heat treatment gave the final product. The synthesis route was designed in a cost-effective way. The porosity and the concentration of the introduced nitrogen atoms were determined at each step. The final product has a surface area of 1135 m<sup>2</sup>/g. More than 70 % of the pore volume comes from micropores with an average width of 0.7 nm. The 2.3 atomic % surface nitrogen atoms are distributed among five detectable species, of which about 44 % is quaternary nitrogen.

**Keywords:** nanoporous carbon, surface chemistry, surface N-group, pore structure, XPS

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## 1. Introduction

Activated carbons (ACs) are multifunctional materials with a broad range of applications, e.g., sorption, ion exchange, coordination, reduction and catalytic properties.

The presence of various elements (O, S, N, P, B, Si, etc.) as heteroatoms in the carbon matrix, or as surface functional groups, fundamentally influences the performance of AC in sorption-related processes, such as electrochemical and catalyzed reactions [1-3] or gas separation [4]. Introduction of nitrogen atoms into AC enhances the activity of the surface in processes accompanied by electron transfer, such as reduction of molecular oxygen or electropositive metal ions, oxidation of hydrides and organic substances, etc. [1, 2, 5-8]. It is therefore an urgent task to develop technologies to obtain ACs that contain N-atoms with various chemical states.

Nitrogen-containing carbons can be prepared in several ways:

1) Carbonization and activation of N-containing (co)polymers and resins: matrices of acrylonitrile, vinylpyridine, etc. [5, 9, 10];

2) Heat treatment of ACs in N-containing atmosphere, e.g., in  $(CN)_2$ ,  $NH_3$ , etc. [11-13];

3) Heat treatment of oxidized ACs after impregnation with N-containing compounds, e.g., urea, cyanotriamide, etc. [14-16].

Nitrogen containing carbon obtained from synthetic carbon from styrene matrix (SCS) by the first method has a unique well developed pore structure, a chemically reactive surface and high mechanical strength. However, it is not environment-friendly, as it is prepared from hazardous vinylpyridine (grade VP-1Ap) based ion-exchange resin. Moreover, owing to their high cost, the use of N-containing copolymers and resins as initial material for AC production is not reasonable from an economic point of view.

As for the second method, ammonia is the most suitable modifier, being a relatively low cost chemical product. However, its use involves complex concerns due to its high toxicity, low reactive capacity and the need for high-pressure equipment.

For the third method, we propose here a route that is based on an SCS type AC, which can be routinely obtained from a chloromethylated copolymer (CMC) of styrene and divinylbenzene in a multistep synthesis (Scheme 1 [9]).

For an economically feasible technology the favoured process should be simple, non-hazardous with respect both to the hardware and the chemicals, and of reasonable cost for both chemical agents and energy. With up-scaling in mind, a realistic approach to prepare AC with nitrogen content is by introducing nitrogen in the carbonization stage in the form of a high nitrogen-content compound, such as urea (46.6 % nitrogen). Urea or the other nitrogen sources can be introduced at any stage of the technological chain in Scheme 1. However, in practice it is convenient to add urea only in the CMCS stage, as this sample has already a sufficiently developed pore structure and a reasonably high specific surface area (40-60 m<sup>2</sup>/g) [9]. It possesses sulphonate, carboxyl and phenol functional groups to react with urea. Furthermore, in this case, the carbonization and heat treatment stages of the impregnated material can be combined, which is very important for industrial scale production. The potential routes of nitrogen atom introduction into the SCS-type AC are considered in Scheme 2. It can be assumed that the NH<sub>2</sub> groups of the urea establish chemical bonds with the surface functional groups of CMCS to form intermediate heterocycles (Scheme 3).

The present work reports the synthesis of nitrogen-containing carbon SCS (N-SCS) from a styrene and divinylbenzene based CMC, using urea as nitrogen source. The synthesis was monitored by the development of the porosity and the overall concentration and oxidation state of the nitrogen.

## 2. Experimental

### 2.1 Materials

Porous CMC based on styrene and divinylbenzene copolymer was used as starting material. The ratio of the monomers is 90/10 and 90 % porofor (alkylbenzines) (SE "SMOLY", Dniprodzerzhinsk, Ukraine) were used. The white spherical granules have a diameter of 0.5-1.0 mm. The moisture content of the commercial product is ~22 % (w/w). The surface area is 20 m<sup>2</sup>/g and the elementary composition is the following: 91 % C, 8 % H and 1 % impurities (O and metal oxides).

Sulphuric acid (98 % v/v), nitric acid (20 % v/v) and an aqueous solution of urea saturated at room temperature were used in the reactions. All chemicals were of analytical grade.

### 2.2 Synthesis

#### 2.2.1 Nitrogen-free samples (Scheme 1)

##### 2.2.1.1 Sulphonation

100 g of CMC was stirred with sulphuric acid (200 mL, 98 %) in a glass flask (1 L) for 3 hrs at 180 °C. The evolving gases were permanently removed. The mixture was cooled to room temperature and washed with distilled water. The CMCS product was dried at 130 °C.

##### 2.2.1.2 Carbonization

50 g CMCS were carbonized in a cylindrical quartz reactor in a dry argon atmosphere (flow rate 300-400 cm<sup>3</sup>/min). The temperature was increased slowly up to 800 °C over 1.5 h and the material was kept at this temperature for another 30 min. The reactor was periodically rotated. Then the carbonized product SCSC was removed from the furnace in the reactor and cooled in an argon flow to room temperature.

### 2.2.1.3 Activation

50 g SCSC was heated to 800 °C in a cylindrical quartz reactor in a steam flow of 300-400 cm<sup>3</sup>/min and kept in these conditions for an additional period of 30 min while the reactor was periodically rotated. Then the quartz tube was removed from the furnace, and cooled first to the temperature of steam and then to room temperature before removal of the SCS sample.

### 2.2.1.4 Oxidation

30 g SCS was mixed with 150 ml 20 % nitric acid solution in a glass beaker and boiled for 4 h. After cooling the oxidized product SCSO was washed to neutral pH with distilled water, then dried at 130 °C.

### 2.2.1.5 Heat treatment

The heat treatment of SCSO was performed under the same conditions as described above in the Carbonization step.

## 2.2.2 Nitrogen-containing samples (N-SCS, Scheme 4)

For urea impregnation, 30 g CMCS was mixed with 50 ml saturated solution of urea and then kept at 150 °C until the mixture became dry to obtain CMCS-urea. The urea/copolymer ratio was 1:2 w/w. Carbonization, activation, oxidation and thermal treatment were performed as described in the previous sections. The preparation process, as well as the acronyms of the samples, are summarized in Scheme 4.

## 3. Sample characterization

### 3.1 N<sub>2</sub> adsorption/desorption analysis

Low temperature (- 196 °C) nitrogen adsorption/desorption isotherms were measured by a NOVA 2000 (Quantachrome) automatic analyzer to determine the porosity and surface area. Samples were measured after evacuation at 120 °C for 4 h. The total pore volume ( $V_{TOT}$ ) was derived from the amount of vapour adsorbed at relative pressure  $p/p_0 \rightarrow 1$ , assuming that the pores are then filled with liquid adsorbate. Data were also processed according to the multipoint BET equation to obtain the surface area  $S_{BET}$ . The Dubinin-Radushkevich (DR) approach was used to determine the micropore volume,  $W_0$  and the pore width  $w$  of the micropores assuming slit-shaped pores in this porosity range. Based on empirical studies the latter was calculated as  $w = 26 \text{ (kJ nm}^3/\text{mol)}/E_0$ , where  $E_0$  is the adsorption energy derived from the slope of the DR plot [17]. The external surface area was obtained from  $t$ -plot [18]. A Quantachrome Data Acquisition and Reduction program was used for the analysis. The bulk density was determined by measuring the mass of 10 cm<sup>3</sup> of slightly compacted material.

### 3.2 Chemical composition

The *total nitrogen content* was measured by a "Vario MicroCUBE CHNS Elemental Analyser" (Elementar Analysensysteme GmbH).

The surface concentration and the energetic states of the nitrogen atoms were estimated from XPS. These measurements were made in a SPECS spectrometer with a Phoibos 100 hemispherical analyser. The base pressure in the UHV chamber was below  $1.0 \times 10^{-7}$  Pa. The X-ray radiation source was monochromatic Al  $K_{\alpha}$  (1486.74 eV) at 100 W X-ray power and anode voltage of 14.00 kV. The photo-excited electrons were analysed in constant pass energy mode, using pass energy of 50 eV for the survey spectra and 10 eV for the high resolution core level spectra. Spectra were recorded at angle 90°. No binding energy correction was made because the samples, mounted on conducting double-sided adhesive tape, exhibited no charging effects. CasaXPS software was used for data processing. Core level curve fitting in

different components was performed using a Shirley background and a standard least squares algorithm. The N1s region was fitted to a convolution of a Gaussian and a Lorentzian function (80:20).

#### **4. Results and discussion**

Four nitrogen-free and four nitrogen-containing carbon materials were obtained according to Schemes 1 and 4, respectively. The yields and the bulk densities are compared in Table 1.

The addition of the urea practically does not influence the bulk density of the samples, as can be concluded by comparing the corresponding values in Table 1. The yield, however, is more sensitive to urea. The N-samples always exhibit a cumulative yield that is 4-6 % higher than the parallel nitrogen-free carbons. This is valid also for the individual steps, except that of carbonization, where an opposite trend was observed.

##### *4.1 Porosity of the carbon samples*

Figure 1 compares the low temperature nitrogen adsorption/desorption isotherms of the synthesized carbon samples obtained without and with urea treatment. The derived data are listed in Table 2. As all the available models have their specific limitations, the most general standard methods were chosen.

The shapes of the isotherms are very similar, all of them showing a shape intermediate between Types 1 and 2, reflecting the mainly microporous character of the samples. Indeed, the contribution of the wider pores to either the pore volume or the surface area is limited. The adsorption is relatively high already at the very beginning of the isotherms and no hysteresis loop was detected. The only exception is the N-SCSC carbon, which exhibits limited initial adsorption and low pressure hysteresis. We should bear in mind that to produce this sample the carbonization and the chemical reaction with urea are combined in one step

and that the pore structure may not be fully consolidated. After the activation this discrepancy disappears completely and the trend of the isotherms is identical in the two sample sets. Oxidation reduces the porosity in both lines by ca. 10 %, which remains and is even exceeded after the final heat treatment.

The nitrogen-containing samples always exhibit a lower total porosity, but higher BET area, than the corresponding samples from Scheme 1. After activation, the surface area increases significantly, as expected. Both final products have a surface area in excess of 1100 m<sup>2</sup>/g. The ratio of the micropore volume to the total pore volume is also higher in the urea-treated samples and, interestingly enough, it is not really influenced by the different synthesis steps following the activation (0.75, 0.75, 0.73, for N-SCS, N-SCSO and N-SCSH, respectively). The nitrogen-free samples are less resistant, changing the microporosity from 0.60 to 0.68 and back to 0.65 in the oxidation and heat treatment processes, respectively. Due to their well developed porosity and high apparent surface area, all the samples coming through activation are good potential adsorbents for small molecules.

#### *4.2 Concentration and energy state of surface nitrogen species*

X-ray photoelectron spectroscopy (XPS) is one of the few methods available to get information on the local bonding environment of nitrogen in carbon materials [19] and, consequently, XPS alone [19-21] or in combination with other techniques [2, 12, 22-24] has been extensively used with this purpose.

The different chemical environments of the nitrogen atoms identified in activated carbon matrices [19, 22, 25] are shown in Scheme 5.

Based on the C1s, N1s, O1s and S2p regions of the XPS spectra, carbon, oxygen, nitrogen and traces of sulphur atoms were detected on the surface of carbon samples from Scheme 4 (Table 3). After carbonization of the CMCS–urea sample 1.9 atomic % of nitrogen was found on the



surface of the N-SCSC sample, which decreased to 1.2% during the steam activation. 2.7% was detected in the N-SCSO carbon, i.e., the N-containing groups showed some chemical resistance to the oxidative treatment. The final N-SCSH contained 2.3 atomic % of nitrogen, which increases the catalytic potential of this carbon. XPS analysis of the same material after carbonization, activation, oxidation by nitric acid and heat treatment in inert atmosphere yielded only 0.4 atomic % of N. That shows that the urea treatment is more efficient at introducing nitrogen functionalities than nitric acid. Comparison with the nitrogen content from elemental analysis, when available, shows that the distribution of the nitrogen is not homogeneous. In both cases the total nitrogen content exceeds the nitrogen content on the surface.

In order to distinguish the various oxidation states of the nitrogen in an acceptable way by curve fitting, all the high resolution N1s spectra were deconvoluted into five bands (Figure 2). The following components were structurally assigned as follows: i)  $398.2 \pm 0.1$  eV, related to pyridinic N in non-functionalised heterocycles; ii)  $399.6 \pm 0.1$  eV, pyrrolic and pyridonic N; iii)  $400.9 \pm 0.1$  eV, substitutional N in condensed polyaromatic systems where N substitutes C; iv)  $402.9 \pm 0.3$  eV, pyridine-N-oxides and v)  $405.3 \pm 0.3$  eV, nitrogen oxides (NO<sub>x</sub>). The corresponding distribution is given in Table 4.

The XPS spectra show that nitrogen atoms have been incorporated into the carbon matrix in various oxidation states (N-SCSC). Quaternary nitrogen groups are the most typical after carbonization together with urea. This group however has the highest surface concentration in all samples. After steam activation at 800 °C nitrogen forms belonging to group ii) are not detected (i.e., in sample N-SCS). The oxidation significantly increased the concentration of the oxidized forms, particularly that of NO<sub>x</sub> groups (N-SCSO). The latter proved to be the most vulnerable in the final heat treatment step (N-SCSH), where a shift toward the lower binding energy species is observed.

#### **4. Conclusions**

Urea modification of sulphonated styrene-divinylbenzene copolymer, followed by carbonization, activation and/or oxidation and heat treatment, yields a nitrogen-containing nanoporous AC. The carbons possess a developed pore structure (the BET surface area exceeds 1100 m<sup>2</sup>/g), which is similar to that of synthetic carbons obtained from styrene - divinylbenzene copolymers, but they contain up to 1.2 – 2.7 % of surface nitrogen atoms in various energetic states. The oxidation state of the nitrogen can be monitored during the synthesis. The proposed method is suitable for an up-scaled production of nitrogen-containing mesoporous and microporous carbon materials. Owing to their high surface area and nitrogen content, they can be used as adsorbents and catalysts.

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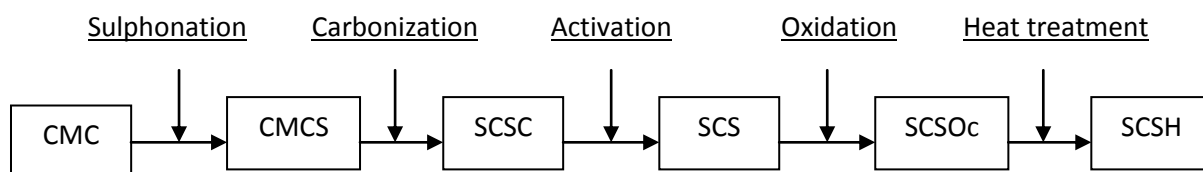
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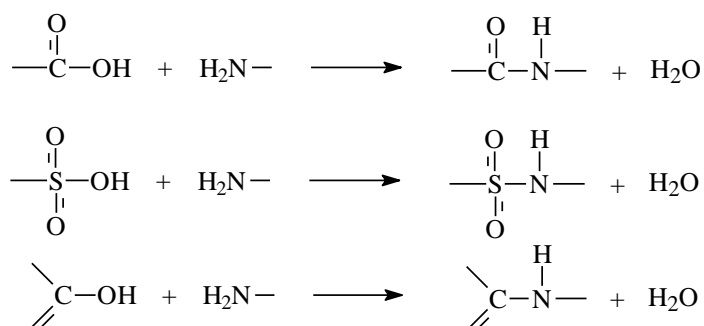
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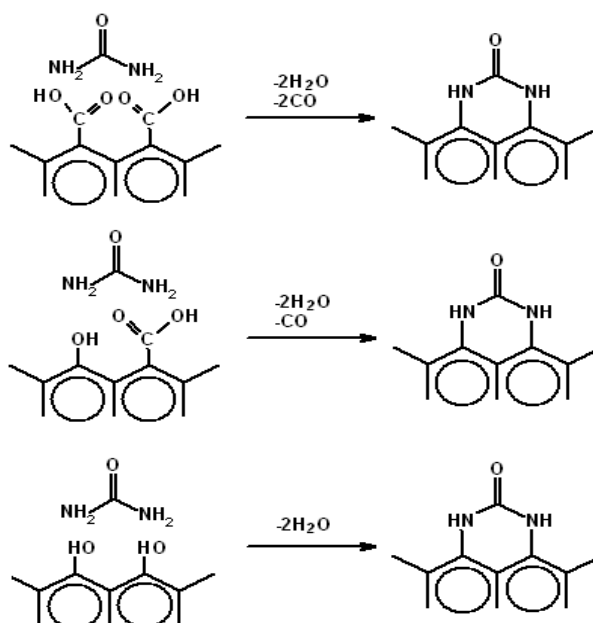
## Figures and tables



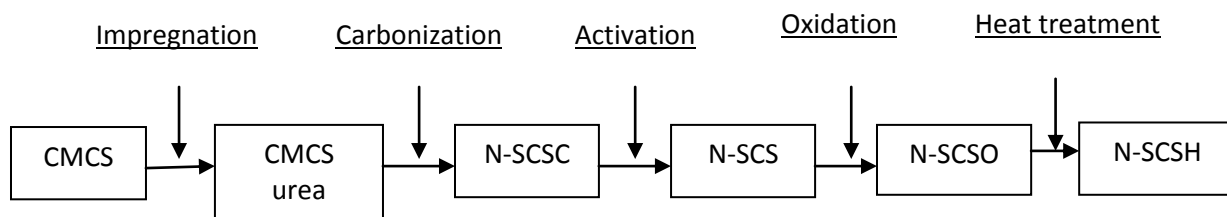
Scheme 1 Preparation of SCS type AC



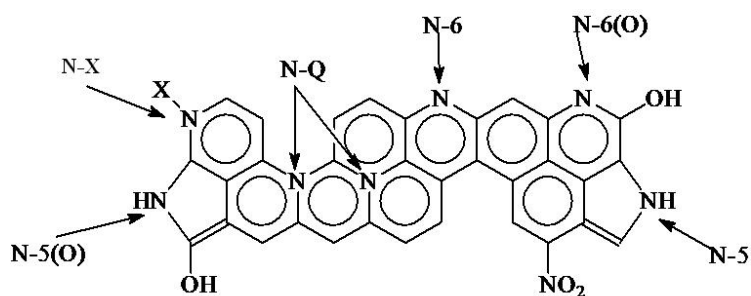
Scheme 2 Potential reactions between the carbamide and the surface functional groups



Scheme 3 The urea may form heterocycles with the various functional groups



Scheme 4 Preparation of N-SCS type AC



Scheme 5 Chemical forms of nitrogen identified in activated carbons

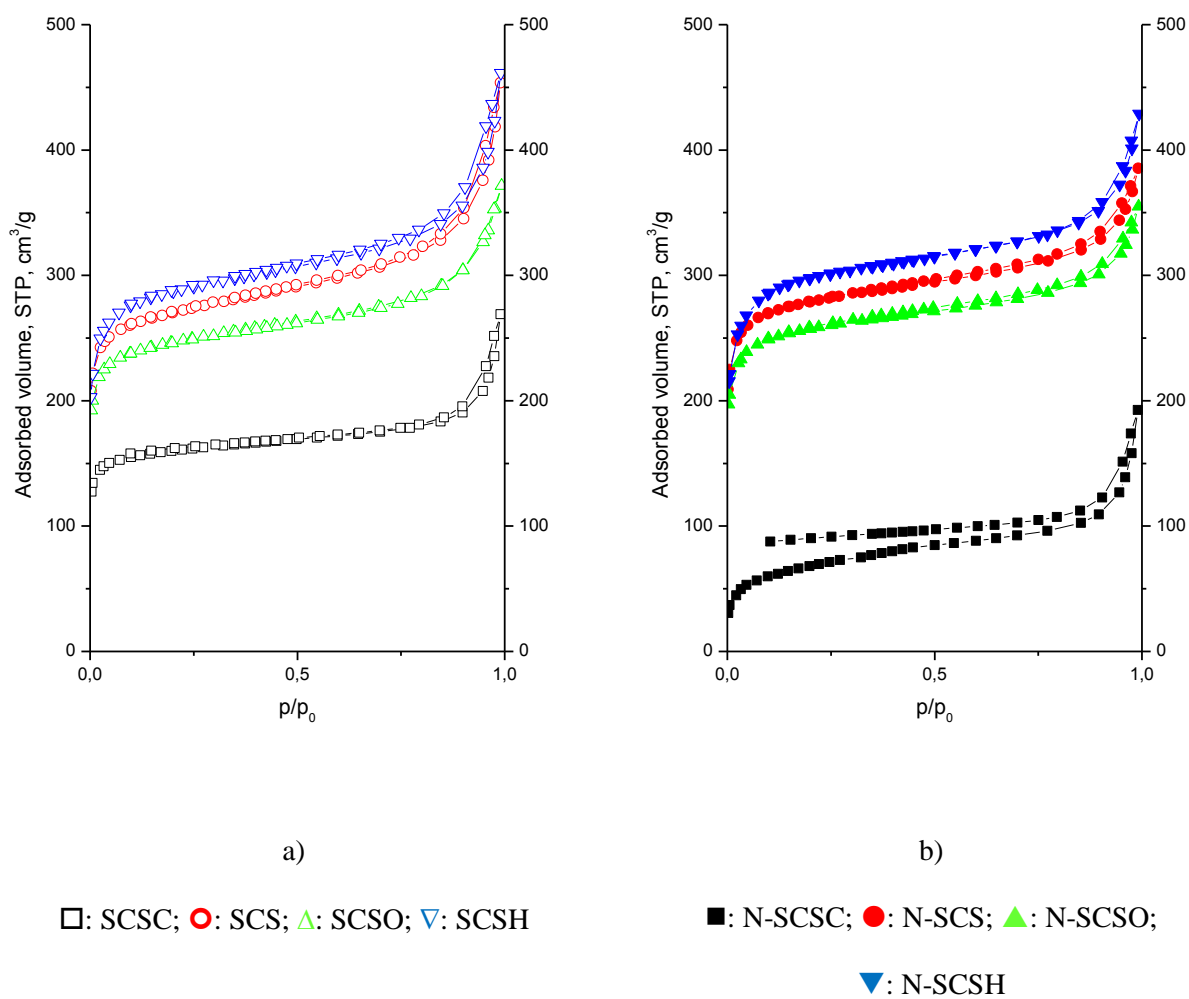
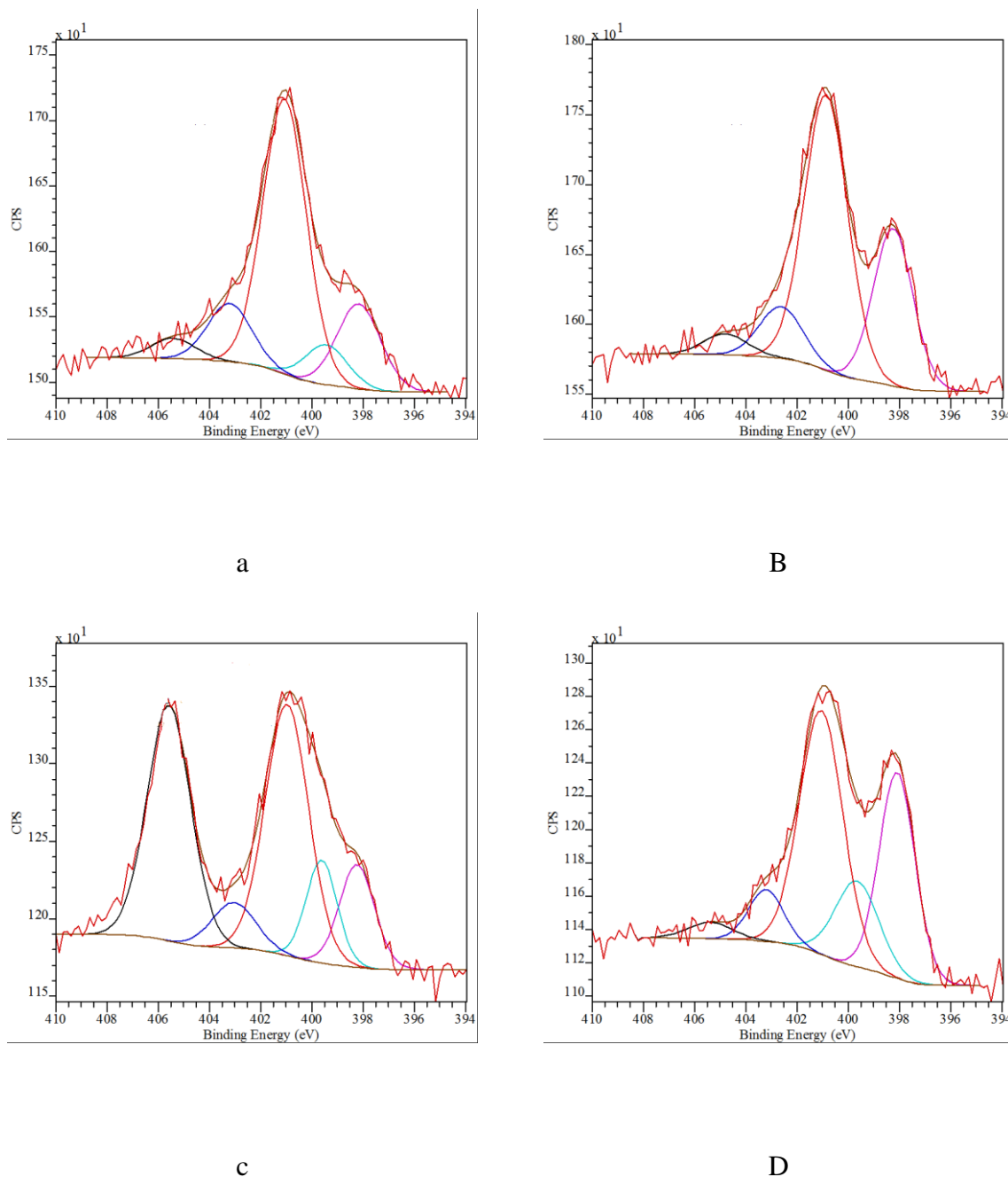


Figure 1. Low temperature adsorption/desorption isotherms of the carbons obtained by Scheme 1 (a) and Scheme 4 (b)





**Figure 2.** Deconvolution of the of the high resolution N1s spectra of the nitrogen containing samples after the different synthesis steps: a) thermal carbonization in inert atmosphere (N-SCSC), b) steam activation (N-SCS), c) oxidation with nitric acid (N-SCSO), d) thermal treatment in inert atmosphere (N-SCSH)

**Table 1** Comparison of the yields and the bulk densities of the various carbon samples

Samples	$\rho_{\text{bulk}}$ , g/cm <sup>3</sup>	Yield of the step, wt. %	Cumulative yield <sup>a</sup> , wt. %
CMCS	0.49	119	119
SCSC	0.57	62	73
N-SCSC	0.61	69	82
SCS	0.41	55	40
N-SCS	0.42	54	44
SCSO	0.45	99	39
N-SCSO	0.44	102	45
SCSH	0.40	73	28
N-SCSH	0.39	75	34

<sup>a</sup>Yield relative to CMC as starting material

**Table 2** Pore structure of the resulting carbons

Samples	$V_{TOT}$ , cm <sup>3</sup> /g	$S_{BET}$ , m <sup>2</sup> /g	$W_0$ , cm <sup>3</sup> /g	$w$ , Å	$S_{ext}$ , m <sup>2</sup> /g	$W_0/V_{TOT}$	$S_{ext}/S_{BET}$
SCSC	0.41	630	0.25	7.0	60	0.61	0.10
N-SCSC	0.29	249	0.11	3.6	54	0.38	0.22
SCS	0.70	1056	0.42	7.7	139	0.60	0.13
N-SCS	0.59	1082	0.44	8.0	77	0.75	0.07
SCSO	0.57	953	0.39	9.9	93	0.68	0.10
N-SCSO	0.55	997	0.41	6.9	68	0.75	0.07
SCSH	0.71	1109	0.46	6.7	135	0.65	0.12
N-SCSH	0.66	1136	0.48	7.2	80	0.73	0.07

**Table 3** Surface composition (atomic %) of the urea-treated samples

Sample	C	O	N	S
N-SCSC*	93.0	4.5	1.9 (2.2 wt%)	0.6
N-SCS**	93.6	4.8	1.2 (1.4 wt%)	0.5
N-SCSO	86.1	10.8	2.7	0.5
N-SCSH	93.9	3.4	2.3	0.4

\*The N-content from elemental analysis is 4.2 wt%.

\*\* The N-content from elemental analysis is 2.2 wt%.

**Table 4** Distribution of the different nitrogen functionalities in the samples after deconvolution of the high resolution nitrogen spectra (%)

Sample	i) N-6	ii) N-5(O) N- 6(O), N-5	iii) N-Q	iv) N-X	v) NO <sub>x</sub>
N-SCSC	17.8	8.1	57.6	12.2	4.3
N-SCS	29.0	0	56.2	10.5	4.3
N-SCSO	12.0	10.6	36.5	6.6	34.3
N-SCSH	30.4	15.4	43.8	7.4	3.0