

ELECTROCHEMICAL PERFORMANCES OF NITROGEN-DOPED MESOPOROUS CARBONS DERIVED FROM TANNIN

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Introduction

Supercapacitor (SC) devices store energy through the interaction of electrolyte ions with the surface of the electrode, resulting in the formation of an electric double layer (EDL). The EDL mechanism leads to high power outputs but, usually, to low energy densities in comparison with batteries. Among the strategies to improve carbon-based supercapacitors performances, the modification of the surface chemistry is frequently used. The introduction of heteroatoms in carbon materials can enhance their electrical conductivity and/or their affinity towards the electrolyte, in addition to enabling redox reactions that provide a pseudocapacitance contribution, thus further increasing the capacitance.

Materials and Methods

Ordered mesoporous carbons (OMCs) were synthesized by a surfactant- and water-assisted mechanochemical mesostructuration (SWAMM) method using mimosa tannin as carbon precursor.¹ Nitrogen doping was carried out by two routes: (i) direct physical mixing of urea and the OMC, followed by a thermal treatment; and (b) CO₂ activation of the OMC during 60 min at 900°C and then mixing the resultant activated material (AOMC) with urea, followed by a thermal treatment. For the sake of comparison, N-doping of a disordered mesoporous carbon (DMC) also synthesized by the SWAMM method, was carried out through route (i). **Table 1** shows the parameters of the doping procedure and the assigned labels for the samples. After the thermal treatment, all samples were washed in water at 70°C for 1 h and recovered by filtration.

Table 1. N-doping treatment parameters.

Sample	Carbon/Urea weight ratio	Thermal treatment		
		Duration	Temperature	Atmosphere
U1-OMC	1/1	3 h	350°C	Air flow (50 mL min ⁻¹)
U2-OMC	1/2	3 h	350°C	Air flow (50 mL min ⁻¹)
U1-OMC-N	1/1	3 h	550°C	N ₂ (50 mL min ⁻¹)
U1-OMC-Auto	1/1	3 h	550°C	Auto-generated
U1-AOMC	1/1	3 h	350°C	Air flow (50 mL min ⁻¹)
U2-AOMC	1/2	3 h	350°C	Air flow (50 mL min ⁻¹)
U1-DMC	1/1	3 h	350°C	Air flow (50 mL min ⁻¹)

The physicochemical properties of the materials were studied by N₂ and CO₂ adsorption (at -196 and 0°C, respectively), TEM imaging, XRD, XPS and elemental analysis (EA). The electrochemical performances of the assembled SCs were tested through cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS) in aqueous electrolyte (1 mol L⁻¹ H₂SO₄).

Results and Discussion

Figure 1a displays the ultramicro-, supermicro- and mesopore volume as well as the surface area of OMC, AOMC, DMC and their corresponding N-doped counterparts. **Figure 1b** shows the N and O contents measured by EA and XPS for all samples. In general, there is a decrease of pore volume and surface area as the N content increases. However, an unusual loss of porosity and consequently of surface area was observed for U1-OMC and U2-OMC. Nonetheless, TEM images of the latter samples still revealed the presence of mesopores. The latter, in addition to the considerably high N content on their surface, suggests that the porosity obstruction occurs in the narrow porosity that gives access to mesopores. For a carbon/urea weight ratio of 1, the increase of the final temperature, up to 550°C, and changed atmosphere (N₂ or air), allowed obtaining doped materials, U1-OMC-N and U1-OMC-Auto, with unblocked porosity (see **Table 1**).

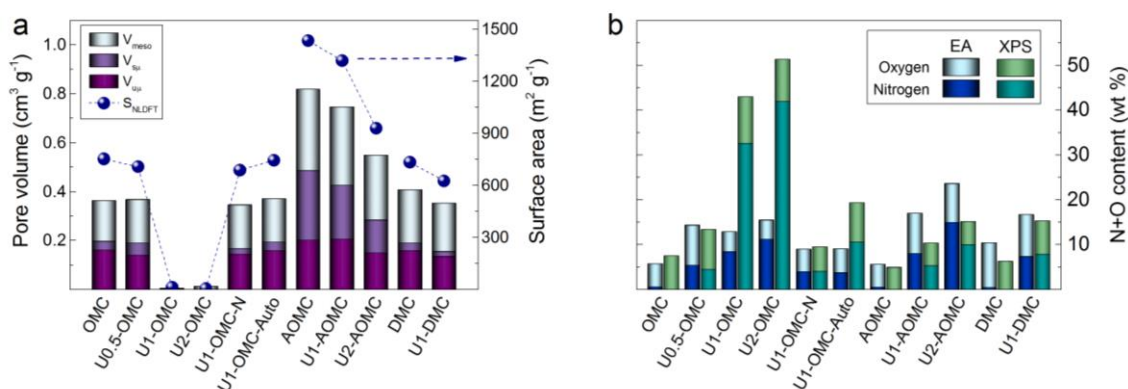


Figure 1. Physicochemical properties of the mesoporous materials and their corresponding N-doped counterparts: (a) surface area (S_{NLDFT}) and ultramicro-, supermicro and mesopore volume (V_{um} , V_{sm} and V_{meso} , respectively) calculated from the adsorption isotherms; (b) N and O contents measured by EA and XPS.

The electrochemical tests were carried out on all samples except U1-OMC and U2-OMC, having a nearly blocked porosity. CV curves at 5 mV s⁻¹, and normalized capacitances to surface area, $C_{N,S}$, as a function of current density, are shown in **Figure 2**. Tests were also carried out on non-doped materials (OMC, AOMC and DMC) used as references.

In all cases, quasi-rectangular curves were observed at low scan rate, indicating an ideal supercapacitor behaviour. In addition, it can be noticed that, except for U1-OMC-N, a general improvement of the performance due to the N-doping was observed. The low values of capacitance exhibited by U1-OMC-N (see **Figure 2a,c**) might be explained by a significantly high equivalent

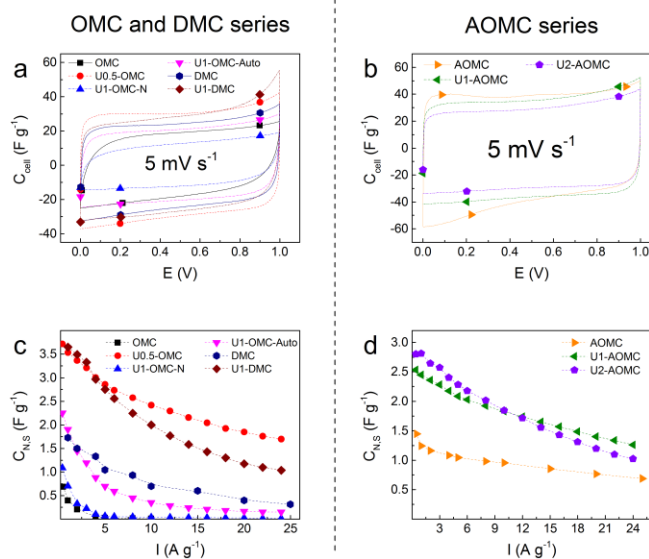


Figure 2. Electrochemical performance of N-doped and reference materials: (a, b) CV curves at 5 mV s⁻¹; (c, d) normalized capacitance to surface area, $C_{N,S}$, as a function of current density calculated from GCD tests.

distributed resistance (EDR > 100 Ω). Concerning U1-OMC-Auto, GCD tests revealed that its $C_{N,S}$ decreased drastically as the current density increased due to a high EDR ($\sim 45 \Omega$). Among the series of N-doped activated carbons, U2-AOMC exhibited the highest $C_{N,S}$ at current densities lower than $\sim 6 \text{ A g}^{-1}$ due to the pseudocapacitance contribution of the N surface functionalities. But as the current density increased, $C_{N,S}$ decreased drastically (see **Figure 2d**). This drop of capacitance values might be due to a significant change in the pore size distribution (PSD), which shifts the microporosity to narrower pores, hence hindering the diffusion of ions.

Conclusion

N-doped mesoporous carbons were obtained with a nitrogen surface content as high as 10.6 wt. %. N doping improved the electrochemical performance of DMC and AOMC materials and only improved the performances of OMC when a weight ratio of urea to OMC of 0.5 was used. As for the N-doped activated carbons, the surface modification enhanced the performance at low current densities, but the changes of textural properties (surface area, pore volume and PSD) resulted in a decreased performance at high charging rates. This study illustrates how the combined effect of N-doping, surface functionalities and textural properties accounts for supercapacitors performances. An N-doping treatment allowing a minimum modification of the textural properties would be needed.

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References

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