Bio-sourced mesoporous carbon doped with heteroatoms (N,S) synthesised using one-step hydrothermal process for water remediation

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Mesoporous carbon monoliths doped with nitrogen, sulphur or both have been prepared in one step hydrothermal carbonization from bio-based precursors. Glucose and pyrrole carboxaldehyde or glucose and thiophene carboxaldehyde aqueous solutions have been used as precursors for nitrogen and sulphur doped carbon materials, respectively. In the same hydrothermal process, a salt-templating approach was used to endow the material with mesoporosity. Additionally, the materials were also pyrolysed in N2 at 973 K. The average mesopore size of resulting xerogels is tuned by the used dopant. Both the doping and mesoporosity enhanced substantially the adsorption of large dye molecules. Accordingly, these metal-free, cost-effective and sustainable materials are excellent candidates for liquid phase environmental and energy applications where the dopant may play a role as catalytic active phase or electronic modulator.

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1. Introduction

The rational design of high performance and cheap nano-materials for multiple sustainable energy and environmental applications is extremely urgent but remains challenging. Carbons doped with heteroatoms (N, S) with tailored chemical composition are required for some applications in which the incorporation of heteroatoms showed some benefits such as metal-free catalysis or electrocatalysis. The doping element affects conductivity, active sites and wettability of the carbon material which is worth to explore. Top–down processes typically used for the synthesis of porous carbons (such as physical or chemical activation) does not allow a well-defined doping with heteroatoms. Hydrothermal carbonization (HTC) of carbohydrates is a bottom–up process that allows the preparation of carbon materials with tailored heteroatom content [1]. Nitrogen doped HTC [2] and Nitrogen and Sulphur co-doped HTC [3,4] were prepared in one step using glucose plus a building block containing the heteroatom. These materials have been used in several applications such as electrocatalyst for oxygen reduction reaction [2–4] or for capacitive deionization [5]. Other important aspect is the development of porosity, especially mesoporosity, which is crucial for the adsorption or catalytic application in liquid phase involving large molecules (high weight compounds, dyes or biomolecules) [6–8]. Sometimes a sacrificial template such silica nanoparticles has been used to create mesoporosity, but this approach requires multiple steps and the use of hazardous reagents [9–16]. It is beneficial if mesoporosity can be generated in one-pot during hydrothermal carbonization. The use of a special precursor (ovoalbumina) led to a mesoporous material [3] but the surface area is not very high (below 300 m²g⁻¹) even for the pyrolyzed material. Borax was used to prepare N-doped HTC with mesoporosity [4] and after pyrolysis at 1173 K the maximum surface area was 427 m²g⁻¹ formed by pores between 4 and 24 nm. A similar approach is the so-called “salt templating” method using ionic liquids or eutectic salt mixtures as porogen [17]. Using this approach, Fechler et al. prepared aerogel-like mesoporous bodies by using hypersaline conditions [18]. The basic concept behind is that the hypersaline conditions stabilize the surface of the as-formed primary small nanoparticles (<50 nm) to avoid Ostwald ripening or excessive particle growth. These primary particles at sufficiently high concentration then turn collectively unstable, undergoing spinodal phase separation and cross-linking toward the final porous carbon gels. The more salt is added, the smaller the primary particles are and hence the higher the surface area is. Thus, this method allows structural control by varying the salt concentration.
concentration and salt type. Recycling of the reaction medium in all these cases is very simple: the salt is washed away with water, filtered, and can be reused after evaporation of the water. This procedure creates a mesoporous monolithic bodies in one single step. A variant of this approach is when ZnCl₂ is not washed after hydrothermal carbonization and the material is pyrolyzed. During pyrolysis, the remaining ZnCl₂ has a second role as an activating agent to develop further microporosity [19]. Following this later approach, other authors prepared mesoporous carbon materials introducing ZnCl₂ during hydrothermal carbonization of coconut shell in a 2:1 weight ratio [20,21]. In that case, the solid was not washed after hydrothermal synthesis but pyrolysed at 1073 K.

As far as we know, salt templating approach has not been used to generate mesoporosity in heteroatom doped carbons. Herein, we explored how this approach allows tuning the dopant content and mesopore size in one pot. The prepared materials have showed enhanced performance in the adsorption of dyes even without the need of an activation step. It is foreseen that these materials will exhibit enhanced performance in liquid phase reactions of energy and environmental interest.

2. Experimental

For the prepaarations, anhydrous Glucose (panreact), Pyrrole-2-carboxaldehyde (Sigma–Aldrich), 2-Thiophenecarboxaldehyde (Sigma–Aldrich) were used.

For the synthesis of N-doped carbon materials, 3 g of anhydrous Glucose, 4.5 g of ZnCl₂, 0.50 g (5.3 mmol) of Pyrrole-2-carboxaldehyde and 1.5 mL of H₂O were thoroughly mixed and treated in the autoclave in the same conditions mentioned above.

For the synthesis of S-doped carbon materials, 3 g of anhydrous Glucose, 4.5 g of ZnCl₂, 0.59 g (5.3 mmol) of 2-Thiophenecarboxaldehyde and 1.5 mL of H₂O were thoroughly mixed and treated in the autoclave in the same conditions mentioned above.

For the synthesis of dual N/S-doped carbon materials, 3 g of anhydrous Glucose, 4.5 g of ZnCl₂, 0.50 g of Pyrrole-2-carboxaldehyde, 0.59 g of 2-Thiophenecarboxaldehyde and 1.5 mL of H₂O were thoroughly mixed and treated in the autoclave as mentioned above.

After hydrothermal synthesis, the solid was introduced in 500 mL of water and kept overnight. Subsequently, it was filtered, washed with abundant water and dried at 383 K in an oven.

Surface areas were determined by N₂ adsorption at 77 K (BET) using a Micromeritics ASAP 2020 apparatus, after outgassing for 4 h at 423 K. From the physisorption measurements with N₂, the specific surface area has been calculated by the BET (Brunauer, Emmet, and Teller) theory in the relative pressure range 0.01–0.10 following standard ASTM-4365, which is applicable to microporous materials. Total pore volume (VT) was calculated from the amount of N₂ adsorbed at a relative pressure of 0.99. Pore-size distribution was obtained from the desorption branch of the N₂ isotherm according to the BJH method (Barrett–Joyner–Halenda) using the DataMaster V4.0 software and assuming slit pore geometry. BJH model developed in 1951 which is based on the Kelvin equation and corrected for multilayer adsorption, is most widely used for calculations of the pore size distribution in the mesoporous and part of the macroporous range [22]; Microporous volume (Vₚ) was estimated by Density Functional Theory (DFT method), which is applicable to materials with both micro and mesopores [23]. The model fitted quite well to the isotherm with a standard deviation of ~0.05 cm³ g⁻¹ STP. Alternatively, it was also determined by CO₂ adsorption (Dubinin–Radushkevich) at 273 K in the same apparatus, after outgassing under the same conditions.

CHS analyses were carried out by combustion in a ThermoFlash 1112 elemental analyser equipped with a TCD detector. Oxygen analysis was done by direct assay which involves pyrolysis of the sample at 1343 K in a nickel/carbon bed under a known He flow. The outlet flow, after passing through a separation column, ends in a TCD detector. The oxygen content of sample is quantified on the basis of CO analysis.

SEM analysis was carried out with a microscope SEM EDX Hitachi S-3400 N with variable pressure up to 270 Pa and with an analyzer EDX Rönntec XFlash of Si(Li). The samples were sputtered with gold previously to measurements. The images were obtained from the secondary electron signal.

HRTEM of was carried out using a FEI Tecnai F30 electron microscope equipped with Gatan Energy Filter and cold field emission gun (FEG) operated at 300 kV with 1.5 Å lattice resolution. TEM specimens were prepared by ultrasonic dispersion in ethanol and a drop of the suspension was applied to a holey carbon support grid.

Ex-situ XPS spectra were recorded with an ESCA+– (Omicron) system equipped with Al/Mg radiation source to excite the sample. Calibration of the instrument was done with Ag 3d5/2 line at 368.27 eV. All measurements were performed under UHV, better than 10⁻¹⁰ Torr. Internal referencing of spectrometer energies was made using the dominating C 1s peak of the support at 284.6 eV. The program used to do curve fitting of the spectra was CasaXPS after baseline Shirley method.

For the adsorption tests, two dyes with different molecular sizes were employed, namely, methylene blue and Rhodamine B. To this end, 2 mg of the porous xerogels was immersed into 12 mL of a 0.05 mg mL⁻¹ aqueous solution of the dye, which was then gently shaken in an incubator at 20 °C for 72 h to ensure that the adsorption equilibrium is reached. The adsorbed amounts were then calculated from the difference between the initial and equilibrium concentration of the dye, as determined with UV–vis absorption spectroscopy.

3. Results and discussion

The hydrothermal carbonisation produced xerogel bodies which adopt the form of the mould in which they are synthesised (Fig. S1 supplementary material). The microscopy inspection of the materials (Fig. 1) revealed that the prepared materials have similar morphology, irrespective if they are undoped, N-doped or S-doped. They are formed by the aggregation of primary particles of size smaller than 20 nm (Fig. 2a,b) and the high magnification shows that they have an onion-like morphology. When the material is pyrolyzed at 973 K, it is possible to see small nanodomains leaving pores between them (Fig. 2c, d) although the morphology of the particles transforms slightly from rounded to flake-like.

Table 1 compiles the textural parameters of different samples. HTC sample, which was prepared without salt templating, showed negligible surface area measured by N₂ physisorption (Fig. 3). For HTC calcined at 973 K (HTC–973), the surface area is not negligible and the isotherm is of type I indicative of microporous material. Thus, the pyrolysis of HTC develops microporosity accessible to N₂.

To get further insight about microporosity, HTC and other selected samples were also characterized by CO₂ adsorption (Fig. 4 and Table 2) showing a non-negligible surface area of 142 m² g⁻¹. In samples HTC and HTC–973, SCO₂ > SCO₂ and VC0₂ > VT, indicating the presence of ultramicroporosity. This is due to kinetic restrictions to N₂ diffusion in micropores of dimensions similar to those of the adsorbate [24,25]. The Pore size distribution estimated by application of DFT method to CO₂ adsorption isotherm determine a mean pore size of 0.55 nm. On the other hand, in HTC–Zn and HTC–