



Ordered mesoporous carbons obtained by soft-templating of tannin in mild conditions

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ABSTRACT

Herein, we show that soft-templating synthesis of biosourced OMCs under rather mild pH conditions is possible by controlling the reaction temperature, without using either formaldehyde or toxic phenolic reagents. Removal of the surfactant at 400 °C and subsequent carbonisation at 900 °C allows reducing the shrinkage and preserving the material mesoporosity. Self-assembly of mimosa tannin with Pluronic® F127 in mild conditions (30 °C, pH 3) leads to hierarchical OMCs with more developed porosities, more ordered mesostructures and higher nano-texture ordering than in the more acidic conditions that are commonly used in soft-templating of OMCs. Further development of the OMC porosity by physical activation with CO₂ increased the micropore volume by ~60% without significantly affecting the structural ordering. However, it decreased the mesopore volume and the oxygen content and the PSD was slightly widened in the mesopore range. The activated OMC exhibited high gravimetric capacitances of 286 F g⁻¹ (determined by cyclic voltammetry), a high capacitance retention of 50% at 12 A g⁻¹ (determined by galvanostatic charge-discharge), high energy and power densities of 5.41 W kg⁻¹ and 5.03 kW kg⁻¹, respectively, and a faster frequency response, 4.39 s, than the non-activated OMC, making it a more appropriate material for practical supercapacitors.

1. Introduction

Since their discovery, ordered mesoporous carbons (OMCs) have attracted considerable interest due to their unique properties, such as high surface areas, large pore volumes and uniform mesopores with controlled size and shape [1–3]. Their 3D nano-sized frameworks indeed produce quantum effects at the nanoscale that allow attaining unusual electrical, mechanical and optical properties [3]. Uniform mesoporous channels also facilitate the transport of ions, atoms and large molecules to active sites through the material bulk [3–5]. As a result, OMCs have been successfully applied in many fields, including catalysis [6–8], separation [9,10], environmental remediation [11,12] or energy conversion and storage [13–16].

Supercapacitors are electronic devices that can store energy at the electrode/electrolyte interface both physically, by ion accumulation forming the electric double layer, and chemically, through Faradaic reactions of the surface functional groups [17,18]. They exhibit high reversibility, long life cycle and high power density, and they are

mainly applied for providing short-term pulses in hybrid vehicles or as uninterruptible power supplies [19]. Many works have demonstrated that using electrodes based on OMCs possessing well-balanced micro/mesoporosity or hierarchical structures enhances the supercapacitor performance in terms of rate capability and cycling stability, both of them being important properties for practical devices. Thus, micropores having relevant widths provide active surface and play a key role for ion adsorption, while mesopores favour quick transport of ions towards micropores [20].

Hard-templating, also called nanocasting, is one of the most used techniques for preparing hierarchical OMCs. It indeed allows controlling shape and size of pores, as well as pore wall thickness, by selecting adequate templates, usually mesoporous silica [3,21]. However, the procedure is expensive and time-consuming, and the need to remove the silica template, generally by HF leaching, prevents its use for manufacturing OMCs at large scale.

Successful preparation of OMCs by soft-templating requires several conditions that are not easy to meet at the same time, such as micelle

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formation capability of the structure-directing copolymer, interactions between the copolymer units and the functional groups of the precursor, and crosslinking capability and thermal stability of the carbon precursor. Due to the high formation energy of C-C linkages and the limited number of precursors fulfilling the aforementioned requirements, the synthesis of OMCs by soft-templating is a complex issue [22].

Most OMCs reported in the literature have been synthesised from phenol or resorcinol as precursors, and formaldehyde as crosslinker [23,24]. Reaction of phenol with formaldehyde in acidic medium gives rise to linear polymers called novolacs, which are not appropriate to prepare OMCs because of their thermoplastic properties: they melt during carbonisation and the mesoporous structure thus collapses [25]. Some strategies thus aimed at obtaining OMCs from phenol in acidic media, such as the partial conversion of phenol into dihydroxybenzenes by catalytic hydroxylation with $\text{FeO}_x/\text{H}_2\text{O}_2$, and subsequent assembly with Pluronic® F127 and formaldehyde. However, using a metallic catalyst increased the cost of the procedure, highly acidic medium (3M HCl) was necessary to ensure the synthesis, and the resultant OMCs exhibited maximal surface areas of only $435 \text{ m}^2 \text{ g}^{-1}$ [25].

To obtain 3D interconnected, thermoset networks, reaction between phenol and formaldehyde is generally carried out in basic medium. The resultant polymers are called resoles, and have been widely used as OMC precursors in the presence of block copolymers like Pluronic® F127 [26–28]. However, resoles can only be obtained within a narrow pH interval, usually 8–9, and the assembly between resoles and PEO copolymer units takes place through H bonds and Coulombic interactions that occur at normally highly acidic pH. Thus, OMC synthesis from resoles must be normally carried out in two steps, which complicates the procedure and is time-consuming. Resorcinol has been used as substitute of phenol because there are more active –OH groups to react with formaldehyde, and it yields 3D interconnected networks both in acidic and basic media [29].

Some of these procedures include an evaporation-induced self-assembly (EISA) step to produce the mesostructure, which is not appropriate for the industrial preparation of powdered materials due to problems related to material recovery, use of large area vessels, etc. Thus, it is more appropriate to use aqueous solution routes that can be industrially implemented.

In addition, since formaldehyde and most synthetic phenolic molecules are highly toxic, expensive and non-renewable chemicals, their substitution by cheap, environment-friendly and renewable precursors is highly desired. Thus, hexamethylenetetramine (HMT) has been suggested as alternative crosslinker, since it is poorly volatile but still yields formaldehyde and ammonia upon hydrolysis. Mesoporous carbons exhibiting either 3D-cubic or wormlike, or 2D-hexagonal structures could indeed be prepared from HMT, resorcinol (R) and furfural (F) as carbon precursors and F127 as surfactant, by modulating the F127/RF ratio [30]. Phenolic monomers could also be successfully substituted by biosourced polymers or oligomers such as lignin or condensed tannins, respectively. For instance, Saha et al. prepared OMCs by soft-templating of lignin with Pluronic® F127, but those materials exhibited less developed porosities and wider PSDs than OMCs prepared from phenol in similar conditions [31]. As a matter of fact, lignin possesses a highly branched, complex structure and a low reactivity, both preventing its proper self-assembly with the surfactant micelles.

In contrast, condensed tannins are non-toxic and cheap bio-oligomers obtained from a variety of tree barks (chestnut, mimosa, pine, etc.), whose chemical structure consists of polycondensed flavonoid units, i.e., with 4–6 –OH groups located on two aromatic rings [32], able to undergo similar chemical reactions as phenol or resorcinol. Several methods using tannins as precursors of porous carbons have been previously reported. For instance, carbon cryogels have been prepared by sol-gel polymerisation of wattle tannin and furfural in basic media, and subsequent carbonisation. But long polymerisation times

and additional freeze drying of the organic samples, prior to carbonisation, were needed, and the resultant materials were not ordered, exhibited maximal BET areas of only $420 \text{ m}^2 \text{ g}^{-1}$ and broad pore size distributions (PSDs), between 1 and 40 nm [33]. Ordered mesoporous carbons (OMCs) have been also formerly prepared from mimosa tannin and Pluronic® F127 by a soft-templating route. However, the synthesis was carried out in highly acidic conditions (1 mol L^{-1} HCl), and the resultant OMCs exhibited maximal BET areas of $483 \text{ m}^2 \text{ g}^{-1}$ and again broad PSDs between 2 and 20 nm [34], despite using the same precursors as in the present work. OMCs exhibiting either lamellar or 2D-hexagonal structures and having various pore sizes and surface areas have thus been successfully prepared from chestnut tannin or mimosa tannin and Pluronic® F127 by modulating the experimental conditions [35,36]. Nevertheless, no control of the temperature during the oligomer-surfactant assembly, a critical step in soft-templating synthesis, was exerted, and highly acidic media were necessary to ensure the proper formation of the surfactant-oligomer supramolecular structure. Highly acidic conditions require the use of corrosion-resistant equipment and consistent security measures, which is detrimental for industrial manufacturing purposes. Thus, using milder acidic conditions to synthesise OMCs by soft-templating should be very interesting from the operational point of view.

In the present study, we synthesised hierarchical OMCs by soft-templating of mimosa tannin with Pluronic® F127 surfactant in aqueous solution. Both the pH and the temperature of the assembly step were controlled, and the soft-template was removed at moderate temperature for better preserving the ordered structure of the materials. Physical activation with CO_2 was also applied to develop further the microporosity of one of those hierarchical OMCs. The influences of the medium pH and of the assembly temperature on the development of porosity and the resultant physicochemical properties of the resultant OMCs were investigated. Finally, some of the obtained OMCs were tested as supercapacitor electrodes, and the electrochemical performances in 2 mol L^{-1} H_2SO_4 aqueous electrolyte were correlated to their physicochemical properties.

2. Experimental data

2.1. Materials

Pluronic® F127 (average molecular weight 12.6 kDa), hydrochloric acid (37% in water), sodium hydroxide (98%), and acetylene black powder (< 100 nm) were purchased from Sigma–Aldrich. Sulphuric acid solution (2 mol L^{-1}) was prepared from a concentrated sulphuric acid solution (95–98%) supplied by Sigma–Aldrich. Mimosa tannin was kindly supplied under the name FINTAN OP by the company SilvaChimica (St. Michele Mondovi, Italy). Polytetrafluoroethylene (PTFE) and glass fibre separator were provided by Aldrich and Pall Life Sciences, respectively. All the materials were used as received.

2.2. Synthesis of the ordered mesoporous carbons (OMCs)

Fig. 1 illustrates the different steps of the soft-templating route used here to obtain the OMCs:

- 1) *Mixture of tannin and surfactant aqueous solutions and auto-assembly of the mixture at controlled temperature:* the mimosa tannin solution (2 g in 16 mL of water), adjusted at a certain pH between 1 and that of tannin in water, i.e., without pH adjustment (between 4.50 and 4.65), was added to the Pluronic® F127 solution (2 g in 16 mL of water). The tannin/surfactant mixture was left for auto-assembly at controlled temperature (10, 20 or 30 °C) for 72 h. During this time, tannin molecules interacted with F127 micelles and self-organised around them, giving rise to an ordered supramolecular structure.
- 2) *Phase separation:* After 72 h, the flask was kept at room temperature (20 °C, 5 days) until complete phase separation. Next the

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