Hydrothermal synthesis of ordered mesoporous carbons from a biomass-derived precursor for electrochemical capacitors †

Shanshan Feng, Wei Li, Jinxiu Wang, Yanfang Song, Ahmed A. Elzatahry, Yongyao Xia and Dongyuan Zhao

Here, we report the reproducible synthesis of highly ordered mesoporous carbons (OMCs) with a 2D hexagonal mesostructure via a facile hydrothermal method employing β-cyclodextrin as a renewable and environmentally-friendly carbon precursor, which gives the OMCs a high surface area and micropore surface areas, as well as an oxygenated surface. As a supercapacitor electrode, these OMCs exhibit a high specific capacitance and a high electrochemical stability.

Ordered mesoporous materials have attracted tremendous attention because of their fascinating properties including regular, uniform and interpenetrating mesopores, tunable pore sizes, high surface areas, large pore volumes as well as abundant framework compositions. 1–6 As a remarkable category of ordered mesoporous materials, mesoporous carbons are of great interest due to their important and particular merits such as good electric conductivity, easy functionalization, high chemical inertness, and excellent mechanical stability; as a result, they manifest promising applications in adsorption, catalysis, gas storage, energy storage and conversion, etc. 7–18

So far, enormous research activities have been dedicated to the synthesis of ordered mesoporous carbons with diverse morphologies, pore symmetries, pore sizes and functionalities. 7–10 One of the most popular methodologies is the hard-templating process, in which ordered mesoporous silicas are often used as the hard templates. 19–22 However, the use of mesoporous silica as a sacrificial scaffold makes the process complicated, high-cost and time-consuming, and in turn, unsuitable for the large-scale production and industrial applications. 9,10 Another effective method is the soft-templating approach, which relies on the self-assembly of copolymer soft-templates and carbon precursors followed by the carbonization of mesoporous polymer frameworks and the removal of surfactant templates. 23,24 It has been well demonstrated that phenolic resins derived from base-catalyzed polymerization of phenols and aldehydes are the most useful and effective carbon precursors for ordered mesoporous polymers and the corresponding carbon materials. 25–33 Although great progress has been achieved over the past decade, the industrial implementation is hampered by the utilization or release of hazardous substances during their preparation or uses. Indeed, these mesostructured phenolic resins are all based on formaldehyde (direct use or in situ formed by hexamethylenetetramine decomposition) as a cross-linking agent, which is known to be carcinogenic and should now be removed from all industrial processes. 34 Therefore, it is of much interest and greatly desired to fabricate ordered mesoporous carbon materials from environmentally-benign carbon precursors.

Recently, there has been a trend to synthesize carbon-based materials from biomass-derived materials by a facile hydrothermal carbonization route, as these are inexpensive, worldwide available, renewable and nontoxic, among other properties. 35–40 Herein, we demonstrate a simple and reproducible synthesis of ordered mesoporous carbons (OMCs) based on the soft-templating strategy via a typical hydrothermal carbonization route (Fig. 1). We chose β-cyclodextrin (denoted as β-CD) as an environmentally friendly carbon precursor, which is a cyclic oligosaccharide consisting of a porous-shaped structure with a hydrophobic cavity and hydrophilic rims made of hydroxyl groups. Mixed triblock poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) (PEO–PPO–PEO) copolymers of Pluronic F127 and P123 were employed as templates. The resulting mesoporous carbons show a highly ordered mesostructure with a two-dimensional (2D) hexagonal p6mm symmetry, a high specific surface area (~781 m² g⁻¹) and a large pore size of ~4.5 nm, as well as exhibit a considerable performance as an electrochemical capacitor electrode with a...
long cyclic life, excellent rate capabilities, and a high specific capacitance of \( \sim 157 \) F g\(^{-1} \) at a current density of 0.5 A g\(^{-1} \) in a 6.0 M KOH aqueous solution.

Small-angle X-ray scattering (SAXS) patterns (Fig. 2a) of the as-made OMCs reveal five well-resolved scattering peaks with a \( d \)-spacing ratio of \( 1/\sqrt{3} / \sqrt{4} / \sqrt{7} / \sqrt{9} \), which can be well indexed as the 10, 11, 20, 21 and 30 reflections of 2D hexagonal symmetries (a space group of \( p6mm \))\(^{25,26} \), indicating a highly ordered regularity of the surfactant/carbohydrate mesophases. The intense 10 scattering peak reflects a \( d \)-spacing of 15.7 nm, which corresponds to a large unit-cell parameter \( (a_0 = 18.1 \) nm). After a carbonization-treatment at 700 °C, the resulting OMCs also show three resolved SAXS peaks (Fig. 2b), thus suggesting that an ordered 2D hexagonal mesostructure can be well retained. The 10 reflection peak slightly shifts to a larger \( q \) value, which reflects a unit cell parameter \( (a) \) of 11.3 nm for OMCs, implying that the framework shrinkage is as large as 37% upon carbonization. The decreased diffraction intensity and less resolved SAXS patterns are probably due to the low polymerization degree and soft nature of the hydrothermally-produced carbohydrate networks, which cannot stabilize the pore frameworks at some domain during the high-temperature thermal treatment.

The field-emission scanning electron microscopy (FESEM) image (Fig. S1†) shows that the resulting OMCs, after carbonization at 700 °C, are irregular cross-linking nanoblocks. High-resolution FESEM images (Fig. 3A and 3B) clearly reveal that the OMCs consist of long-range stripe-like hexagonal arrays with open windows, indicating a highly ordered regularity. Transmission electron microscopy (TEM) images (Fig. 3C and 3D) of the OMCs also show well-ordered hexagonal arrays of mesopores with 1D channels that are similar to those for FDU-15\(^{25,26} \), further confirming a 2D ordered hexagonal mesostructure. The cell parameter \( (a) \) estimated from the TEM images is approximately 11.0 nm, which is in agreement with the value calculated from SAXS data. The mesopore size is roughly evaluated to be about 4.0 nm for the OMCs after carbonization at 700 °C. The wide-angle XRD pattern (Fig. S2A†) for the OMCs displays two broad diffraction peaks at \( 2\theta \) values of 25° and 44°, which are characteristic of amorphous carbon frameworks,\(^{14} \) well consistent with the Raman spectra (Fig. S2B†).

\( \text{N}_2 \) adsorption–desorption isotherms (Fig. 4a) of the OMCs prepared from \( \beta \)-CD as a carbon precursor after carbonization at 700 °C show a typical type-IV curve with a H1 hysteresis loop, which is typical of mesoporous materials with cylindrical channels. For comparison, ordered mesoporous carbons (FDU-15) derived from phenolic resins have been prepared and studied, which possess a similar 2D highly ordered hexagonal mesostructure (Fig. S3†). The specific Brunauer–Emmett–Teller (BET) surface area was calculated to be \( \sim 781 \) m\(^2\) g\(^{-1} \), which is higher than FDU-15 (\( \sim 661 \) m\(^2\) g\(^{-1} \)) carbonized at 700 °C (Fig. S4†). This mostly results from the big difference of micropore surface areas calculated from the \( V_t \) plot method of the OMCs (\( \sim 579 \) m\(^2\) g\(^{-1} \)) and FDU-15 (\( \sim 372 \) m\(^2\) g\(^{-1} \)). Moreover, the textural properties comparison of the ordered

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**Fig. 1** Schematic illustration of the formation process of ordered mesoporous carbons derived from \( \beta \)-CD as a carbon source via a hydrothermal process at 140 °C and carbonization-treatment at 700 °C.

**Fig. 2** SAXS patterns of the as-made ordered mesoporous carbonaceous frameworks prepared from \( \beta \)-CD as a carbon source via hydrothermal treatment at 140 °C (a) and calcined mesoporous carbons at 700 °C (b).

**Fig. 3** High-resolution FESEM (A, B) and TEM (C, D) images of the ordered mesoporous carbons derived from \( \beta \)-CD as a carbon source after carbonization at 700 °C viewed from the [11] (A, C) and [10] (B, D) directions, respectively.
mesoporous carbons derived from β-CD and various OMCs derived from phenolic-resins are summarized in Table S1.† The pore diameter of the OMCs calcined at 700 °C derived from the adsorption branch of the isotherms using the Barrett–Joyner–Halenda (BJH) model is about 4.3 nm with a narrow distribution (Fig. 4b). The total pore volume is about 0.41 cm³ g⁻¹ with the contribution of 0.27 cm³ g⁻¹ from the micropores (Fig. 4c), further revealing the presence of excessive micropores in the OMCs. By using the nonlocal density functional theory (NLDFT) method, the obtained pore size distribution curve (Fig. 4c) clearly shows bimodal pores with detectable sizes of ~1.2 and 3.8 nm (Table S2†). The micropores are resulting from the removal of PEO chains trapped in the carbon precursor networks, which could offer a good charge accommodation for the supercapacitor.41,42

The thermogravimetric analysis (TGA) curve (Fig. S5†) of the as-made OMCs under a N₂ atmosphere presents a significant mass loss of about 40 wt% occurring from 250 to 350 °C, which can be mainly attributed to the decomposition of Pluronic templates.25,26 A slow weight loss of 50 wt% between 350 and 650 °C as a result of framework carbonization is observed.40 The carbonization yield is calculated on the basis of the as-made carbonaceous framework materials to be 17 wt%, which is lower than that from the phenolic resin as a carbon source (~35–43 wt%).25,26 X-ray photoelectron spectroscopy (XPS) was used to investigate the surface states of the OMCs products. The survey spectrum (Fig. S6†) shows two typical peaks of C 1s and O 1s, and the corresponding content of each element is displayed in Fig. S6A† (inset). The spectrum of C 1s in the OMCs after carbonization at 700 °C (Fig. S6B†) can be deconvoluted into several single peaks, corresponding to C–C (284.6 eV), C–O (286.2 eV), and C=O (288.2 eV) functional groups.39 Moreover, the spectra of O 1s (Fig. S6C†) further confirm these observations with three peaks at 531.8, 532.7 and 533.6 eV, which can be ascribed to the characteristic oxygen states of –C=O (carboxyl), –C=O (ester) and C–O.39

The formation process of the OMCs is depicted in Fig. 1. During the initial hydrothermal stage, the water solubility of β-cyclodextrins would increase dramatically with increasing temperature and then the precursor undergoes a hydrolysis process to produce glucose molecules with multiple hydroxyl groups under acid conditions.43,44 Then, the interaction can be generated by abundant hydroxyl groups with the PEO blocks of the copolymer PEO–PPO–PEO templates via hydrogen bonds, which favor the self-assembly of ordered mesostructures. In addition, the concentration of amphiphilic surfactants (mixed Pluronic P123 and F127) employed in this experiment was ~10 wt% much higher than the critical micelle concentration (CMC), which also facilitates the formation of ordered mesostructured micelles and stabilizes the carbohydrate/PPO–PEO–PPO-rich phase.28 With time, glucose can dehydrate to give hydroxymethyl furfural (HMF) as an active cross-linking precursor.37,38 Then, polymerization or condensation reactions do occur, forming the final continuous carbonaceous frameworks.37,38,45 Simultaneously, the highly ordered mesophases can be solidified to form the cross-linked polymer networks. After selective removal of the Pluronic copolymer templates and further carbonization of the pore frameworks, ordered mesoporous carbons can be finally obtained. A fast rate of polymerization at a high temperature would weaken the hydrogen-bonding and lead to the deformation of preformed mesostructures. Based on the consideration of the temperature dependent properties of PPO (polypropylene oxide) and PEO (polyethylene oxide) chains, a relatively low temperature (140 °C) is adopted for the hydrothermal polymerization. To ensure a “rigid” and stabilized framework, a long time (>36 h) hydrothermal treatment is utilized here.

The electrochemical capacitive performances of the OMCs prepared by the hydrothermal carbonization route and the control sample FDU-15 after carbonization at 700 °C were evaluated by cyclic voltammetry (CV) and galvanostatic charge/discharge techniques. CV curves of the OMCs and FDU-15 (Fig. 5A) at a low scan rate of 5 mV s⁻¹ in a 6.0 M KOH aqueous electrolyte both present a quasi-rectangular voltammogram shape, exhibiting a typical double-layer capacitance behavior. When the scan rate increases from 5 to 200 mV s⁻¹, a similar rectangular shape is well retained (Fig. S7†), indicating the highly capacitive nature and the small equivalent series resistance (ESR) with a rapid charging-discharging
characteristic. The charge/discharge cycling tests of the OMCs were conducted at current densities from 0.5 to 20 A g\(^{-1}\). Charge/discharge cycling tests at different current densities (Fig. 5B) all show isosceles triangular shape, suggesting an excellent Coulombic efficiency and an ideal capacitor behavior. The specific capacitance of the OMCs is calculated from the charge/discharge curve at a current density of 0.5 A g\(^{-1}\) to be \(\sim 157\) F g\(^{-1}\), which is much higher than 112 F g\(^{-1}\) for FDU-15 and many ordered mesoporous carbons derived from other carbon precursors (Fig. S8 and Table S3†). As shown in Fig. 5C, even at a current rate of 20 A g\(^{-1}\), the OMCs can still deliver \(-127\) F g\(^{-1}\), which is about 81\% of the initial capacitance at 0.5 A g\(^{-1}\). Moreover, cyclic tests show that 97\% of its initial capacity can be retained even after 2000 cycles at a current density of 2 A g\(^{-1}\) (Fig. 5D). The electrochemical behaviors of the electrodes could be clearly understood by electrochemical impedance spectroscopy (EIS) measurements. In the low frequency region, the impedance plot increases with a nearly vertical line (almost 90° phase angle), indicating a very good double-layer capacitive performance.\(^{46,47}\) At high frequencies, small arcs are observed (Fig. S9† inset), indicating that the charge-transfer resistance between the OMCs and the electrolyte is small, which is superior to that for FDU-15. The excellent performances should be attributed to the unique properties of the OMCs. Firstly, the uniform opened mesoporous channels not only promote the accessibility of surface sites, but also facilitate the transport of electrolytes. Secondly, the high surface area offers a good charge accommodation.\(^{48}\) In addition, the well-defined oxygen functionalities not only enhance the surface wettability, but also afford pseudo-capacitance.\(^{44}\) All these results demonstrate that the ordered mesoporous carbons derived from the \(\beta\)-CD via hydrothermal carbonization route are very promising as an advanced electrode for a supercapacitor, compared with those derived from toxic phenolic resins.

**Conclusions**

In summary, we have reported a simple and reproducible soft-templating synthesis of ordered mesoporous carbons via a facile hydrothermal method employing \(\beta\)-cyclodextrin as a new, renewable and environmentally-friendly carbon precursor. The resulting OMCs exhibit a 2D ordered hexagonal mesostructure and possess a high surface area of \(\sim 781\) m\(^2\) g\(^{-1}\), a uniform pore size (\(\sim 4.5\) nm), and finely developed oxygenated surface functionalities, which favour the electrolyte transport and ion adsorption/desorption. When used as supercapacitor electrode materials, the OMCs show a high specific capacitance of \(\sim 157\) F g\(^{-1}\) at a current density of 0.5 A g\(^{-1}\), an excellent rate capability, and a high electrochemical stability by repeating galvanostatic charge/discharge at a current density of 2 A g\(^{-1}\) for up to 2000 cycles in a 6.0 M KOH aqueous solution. This approach paves a new, scalable and green way for the synthesis of functional ordered mesoporous carbon materials using environmentally-benign biomass and biomass derivatives as carbon precursors, which will find many applications in sorption, biomedicine, and energy storage and conversion.

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**Notes and references**


