

## Ordered Carbohydrate-Derived Porous Carbons

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## Supporting Information

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Carbon materials with periodic ordered pore structuring draw extensive attention in adsorption,<sup>1</sup> separation science,<sup>2</sup> catalysis,<sup>3</sup> and more recently in areas of new energy cycles (e.g., electrochemistry,<sup>4</sup> energy storage,<sup>5</sup> and fuel cells<sup>6</sup>). Interest in ordered carbons is generated from enhanced application performance originating from the nanoscale chemical environments offered by micro and mesoporous domains. Development of organized, uniformly sized and shaped pore texture, in tandem with controlled pore wall chemistry, brings additional benefits for some selected applications. Production of ordered porous carbon materials has been previously achieved via “nanocasting”<sup>7,8</sup> replication of ordered inorganic solids such as zeolites and mesoporous silica<sup>9</sup> (e.g., SBA-15 to CMK-3<sup>10</sup>). These multistep syntheses involve carbon source impregnation (e.g., phenol-formaldehyde,<sup>11</sup> mesophase pitch,<sup>12</sup> or sucrose<sup>13–15</sup>), carbonization (e.g., > 700 °C), and inorganic hard template removal (e.g., via acid etching using HF (aq)) to yield inverse replication of the hard template pore structure. Selection of template pore structure allows access to different ordered pore structures (e.g., *p6mm*, *Ia3d*).<sup>13,16</sup>

Zhao et al. and Dai et al. have recently developed a direct route to ordered carbons via the organic–organic self-assembly of a soft block copolymer (e.g., Pluronic F127) and suitable aromatic carbon precursor(s) (e.g., phloroglucinol<sup>17</sup> or phenol/formaldehyde<sup>18–22</sup>). Hydrogen bonding interactions orientate the resulting polyaromatic network, while pore structuring is controlled by polymeric template (e.g., via concentration and structure), copolymer–precursor ratio, pH, solvent polarity, and the presence of a catalyst. Solvent extraction or thermolysis is then used to remove the template. More recently, based on this self-assembly/soft-templating approach, the preparation of single crystal mesoporous carbons was accomplished by Zhao et al., with the intention of developing these materials for future applications in nanodevices (e.g., optical devices).<sup>23,24</sup>

Carbons prepared by these strategies present rather chemically condensed (e.g., graphitic-like) pore walls/surfaces, inhibiting facile postchemical modification and limits surface hydrophobicity/polarity modification. Broadening this, the transformation of carbohydrates via the aqueous-based, mild, inexpensive and facile hydrothermal carbonization (HTC) route (e.g.,  $T \approx 180$  °C,  $P < 10$  bar) produces functional carbonaceous materials.<sup>25</sup> Under these conditions, the

carbohydrate (e.g., the hexose D-Glucose) dehydrates to give hydroxymethyl furfural (HMF) followed by co-condensation/polymerization to produce hydrophilic carbonaceous materials with ~70 wt % C content.<sup>25</sup> The micrometer-sized essentially nonporous spheres produced have surfaces decorated with hydroxyl, olefinic, lactone, carbonyl and carboxyl groups.<sup>25</sup> Further heat treatment directs surface chemistry and hydrophobicity/polarity if carbonization (e.g., at higher temperatures) is used as a control vector. We have previously reported a combined HTC/nanocasting synthesis using sacrificial inorganic templates (e.g., SBA-15) to yield inverse carbon replicas.<sup>26</sup> In this communication, the first report of the synthesis of ordered porous carbonaceous materials via a direct sustainable HTC/soft templating approach is presented.

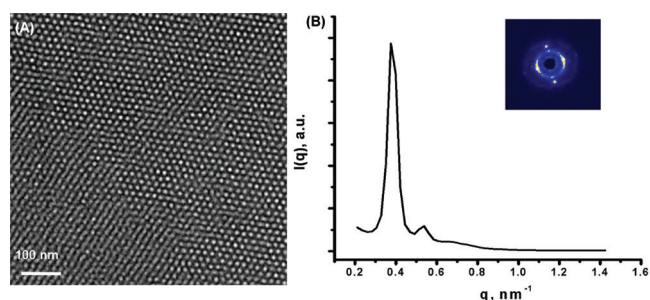
HTC of D-Fructose (Fru) occurs at a temperature as low as 130 °C; a significantly lower temperature compared to other hexoses (e.g., D-Glucose; 180 °C).<sup>27</sup> Typically, block copolymer micelles used in soft-templating are not stable at the typical HTC process temperature (i.e., 180 °C);<sup>28</sup> therefore the use of Fru allows access to micellar self-assembly enabling soft-templating. In our first attempt, the HTC of Fru was performed at 130 °C in the presence of the block copolymer surfactant Pluronic F127 yielding a precipitate of a template-carbon composite (denoted as C-MPG1-*com*). A detailed synthesis procedure can be found in the Supporting Information. The isolated composite presented a well ordered structure with an F127 micelle diameter of ~10 nm and carbon wall thickness of ~6 nm, indicating the successful self-assembly of F127 in the presence of the HTC reaction of Fru (Figure 1A). Synchrotron small-angle X-ray scattering analysis (SSAXS) demonstrated a well-resolved pattern with the *d*-spacing value of the first peak equivalent to 16.8 nm, corresponding to a unit cell parameter of 23.6 nm for a cubic *Im3m* structure (Figure 1B).<sup>29,30</sup>

Thermal treatment under N<sub>2</sub> at 550 °C removed the template to yield an aromatic, functional carbonaceous product (denoted as C-MPG1-*micro*), composed of 82.6 wt % C, 14.2 wt % O, and 3.2 wt % H, respectively (Table 1). Scanning electron microscopy (SEM) images of C-MPG1-*micro*

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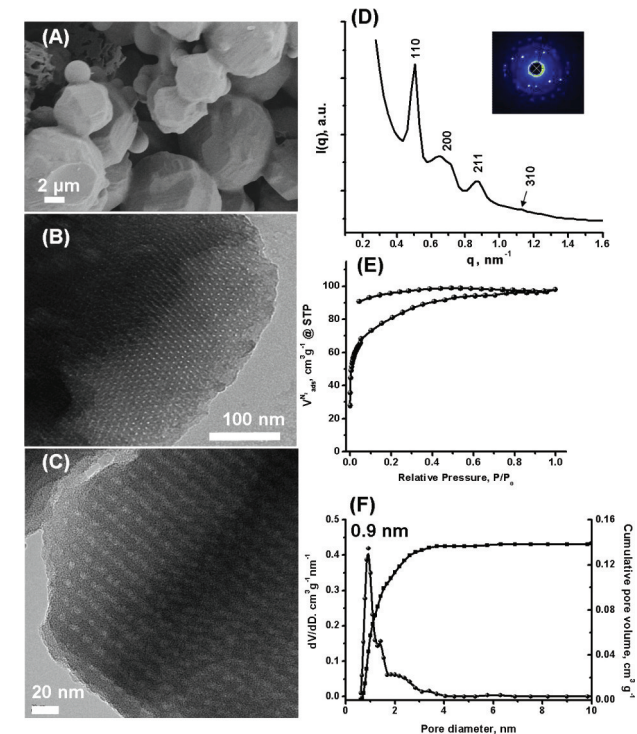
**Figure 1.** (A) TEM micrograph and (B) Synchrotron SAXS pattern of C-MPG1-com (inset; 2D scattering pattern).

**Table 1.** N<sub>2</sub> Sorption Characteristics and Elemental Analysis Data for Presented Carbonaceous Materials

sample	$S_{\text{BET}}$ ( $\text{m}^2\text{g}^{-1}$ ) <sup>a</sup>	$V_{\text{micro}}$ ( $\text{cm}^3\text{g}^{-1}$ ) <sup>b</sup>	$V_{\text{meso}}$ ( $\text{cm}^3\text{g}^{-1}$ ) <sup>b</sup>	$V_{\text{total}}$ ( $\text{cm}^3\text{g}^{-1}$ ) <sup>b</sup>	PS (nm) <sup>c</sup>	C (wt %) <sup>d</sup>
C-MPG 1-com	3.4	0	0.01	0.01		60
C-MPG 1-micro	257	0.11	0.03 (22%)	0.14	0.9	83
C-MPG 1-meso	116	0.04	0.06 (60%)	0.10	1.0, 4.0	79

<sup>a</sup>BET surface area. <sup>b</sup>Microporous, mesoporous, and total pore volume from QSDFT method, with the % ratio of mesopore to total pore volume in parentheses. <sup>c</sup>Pore size calculated from QSDFT method. <sup>d</sup>Elemental analysis data.

indicated a layer-by-layer growth mode to form relatively uniform cuboctahedron-like particles of 1–10  $\mu\text{m}$  diameter (Figure 2). Although of similar size to previously reported



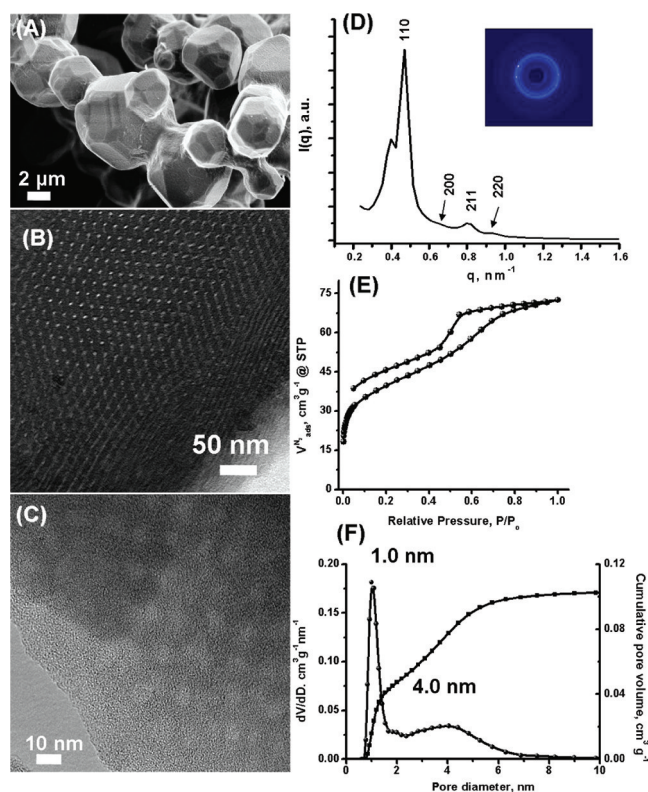
**Figure 2.** (A) SEM, (B) TEM, (C) HRTEM micrographs, (D) synchrotron SAXS pattern (inset; 2D scattering pattern), (E) N<sub>2</sub> sorption isotherm, and (F) QSDFT pore size distribution of C-MPG1-micro.

nonporous HTC materials, particles synthesized via this soft templating present a faceted edge/layered morphology, indicative of the growing direction of the carbon network by the templating phase and single crystalline particle formation (see Figure S1 in the Supporting Information).<sup>24</sup>

High-resolution transmission electron microscopy (HRTEM) images demonstrate the long-range regularly ordered pore structure (Figure 2 (B), (C) and S2 ESI). SSAXS analysis of C-MPG1-micro indicates maintenance of the near perfect cubic  $Im\bar{3}m$  symmetry from parent composite (Figure 2 (D), also see the Supporting Information). Unusually, both SSAXS and HRTEM indicate the generation of a very thick pore wall feature ( $\sim 7$ – $10$  nm) for C-MPG1-micro, whereas infrared spectroscopy (FTIR) indicated the presence of oxygenated surface functional groups (see Figure S4 in the Supporting Information). N<sub>2</sub> sorption analysis presented a nonreversible microporous type I isotherm, a product of possible structural changes in pore wall dimensions during sorption processes (Figure 2E). Specific surface area and total pore volume were calculated as  $257\text{ m}^2\text{ g}^{-1}$  and  $0.14\text{ cm}^3\text{ g}^{-1}$  respectively (Table 1). The pore size distribution was composed of a sharp peak at  $0.9\text{ nm}$  and a less discrete broader shoulder centered  $\sim 2\text{ nm}$  (Figure 2F). Comparison with C-MPG1-com indicates that pores are opened via the thermal decomposition of template. The resulting pores are smaller than before template removal believed to be in part due to structural shrinkage (e.g., carbon network condensation) or partial co-carbonization of the block copolymer.

Thermogravimetric analysis (TGA) of the F127/HTC composite presented a significant mass loss regime at  $\sim 400\text{ }^\circ\text{C}$  followed by a smaller secondary charring step at  $\sim 600\text{ }^\circ\text{C}$  (see Figure S4A in the Supporting Information). The first peak corresponds to the F127 decomposition and the second to further condensation/aromatization of the carbon structure.<sup>31</sup> After the template removal, C-MPG1-micro presents one singular mass loss event at  $\sim 600\text{ }^\circ\text{C}$ , demonstrating the near complete thermolytic removal of the copolymer template leaving a relatively stable ordered functional carbonaceous material (see Figure S4B in the Supporting Information). This treatment renders the material, as indicated by FTIR and TGA, with potentially useful functionality (e.g., phenolic hydroxyls, olefinic/lactone-type  $\text{C}=\text{O}$  and  $\text{C}=\text{C}$  groups; see Figure S4C in the Supporting Information). Further discussion of TGA and FTIR is found in the Supporting Information.

To shift pore structuring of C-MPG1-micro into the mesoporous domain, the swelling agent trimethylbenzene (TMB) was added to the F127/Fru mixture ( $\text{mol}_{\text{F127}}:\text{mol}_{\text{TMB}} = 1:0.92$ ). Thermal template removal at  $550\text{ }^\circ\text{C}$  generates carbonaceous materials (denoted as C-MPG1-meso) with faceted edge morphology similar to C-MPG1-micro (i.e., a cuboctahedron-like morphology from a layer-by-layer growth; Figure 3A). Examination of pore structuring via HRTEM images indicated maintenance of the well-ordered pore structuring upon addition of the pore swelling agent, with a pore diameter and wall thickness of  $\sim 5$  and  $\sim 10$  nm, respectively (Figure 3B, C). HRTEM images indicated also the presence of some 1D pore channels demonstrative of very localized structural inhomogeneities (see Figure S3A, B in the Supporting Information), with the corresponding SSAXS pattern indicative of an  $Im\bar{3}m$  symmetry and unit cell of  $18.9\text{ nm}$  demonstrating an increased unit regularity (Figure 3 (D), see also Supporting Information).



**Figure 3.** (A) SEM, (B) TEM, and (C) HRTEM micrographs, (D) synchrotron SAXS pattern (inset; 2D scattering pattern), (E)  $N_2$  sorption isotherm, and (F) QSDFT pore size distribution of as-synthesized C-MPG1-*meso*.

The transition from a type I (i.e., for C-MPG1-*micro*) to a type IV  $N_2$  sorption profile for C-MPG1-*meso* with associated capillary condensation feature at  $P/P_0 \approx 0.45$ , was observed indicated by a shift in pore structuring into the mesopore domain (Figure 3E). A reduction in surface area ( $S_{\text{BET}} = 116 \text{ m}^2 \text{ g}^{-1}$ ) and total pore volume resulted ( $V_{\text{total}} = 0.10 \text{ cm}^3 \text{ g}^{-1}$ ; Table 1) was also observed. A bimodal pore size distribution is generated with a new mesopore diameter maximum at  $\sim 4.0 \text{ nm}$  and a discrete micropore peak at  $1.0 \text{ nm}$  (e.g., from template removal in mesopore walls; Figure 3F). Correspondingly, mesopore volume as a proportion of the total pore volume increases from  $\sim 20\%$  in C-MPG1-*micro*, to  $\sim 60\%$  for C-MPG1-*meso*.

As a general premise, we believe that Fru is absorbed in the initial stages via H-bonding in the hydrophilic PEO moiety of F127. For a conventional micelle scenario, saccharide HTC proceeds in this area (i.e., via dehydration/polycondensation) to generate a polyfuran-like network, as discussed elsewhere,<sup>32</sup> such that the organized block copolymer micellar phase is essentially “templated”. For C-MPG1-*meso* and normal micelle phase templating, the added TMB is believed to interact with hydrophobic PPO moieties, thus swelling the spatial volume of the hydrophobic region, which in turn results in the observed pore expansion into the mesopore range, analogous to previously described classical inorganic material synthesis.<sup>33,34</sup> It is important to note that the forming furanic network is rather hydrophobic and therefore the possibility of micelle inversion throughout templating still cannot be discounted.

The growth of these carbonaceous crystals is presumably determined by the rate of hexose dehydration (i.e., production

of HMF) and subsequent polymerization reactions. Interactions (e.g., H-bonding) between HMF and the PEO segments of the F127 template favor the growth of these near-perfect single crystalline carbonaceous structures. Furthermore, the absence of stirring and a suitably slow HMF feed rate (as determined by dehydration kinetics) leads to a slow growth rate and the formation of relatively large ordered particulate structures. We are currently investigating the exact mechanism and formation of the templating phase and template-carbon composite.

In summary, an elegant combined HTC/soft-templating synthesis of both ordered microporous and mesoporous functional carbonaceous materials was presented whereby the use of a simple pore swelling agent allows fine adjustment of pore size. Carbonaceous materials were prepared from a renewable inexpensive carbohydrate feedstock (i.e., D-Fructose), whereas carbonization can be performed at relatively low temperatures to yield materials with functionally useful surface chemistry.

## ■ ASSOCIATED CONTENT

### Supporting Information

Extended synthesis details and further SEM/TEM, SSAXS, FTIR, solid-state NMR, and TGA analysis data (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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