Roll-to-roll fabrication of high surface area mesoporous carbon with process-tunable pore texture for optimization of adsorption capacity of bulky organic dyes

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Abstract

Large-scale (multigram-to-kilogram) fabrication of soft-templated ordered mesoporous carbons (OMC) is enabled by roll-to-roll (R2R) processing via evaporation induced self assembly of Pluronic F127, oligomeric phenolic resin (resol), and tetraorthosilicate (TEOS) from ethanolic solution. The solution concentration, TEOS loading (etchable for microporous framework), and crosslinking temperature impact the pore structure. Here we demonstrate that mesoporous carbons with surface areas up to 2455 m²/g can be obtained under the proper processing conditions. Transmission electron microscopy (TEM), small-angle X-ray scattering (SAXS) and nitrogen adsorption-desorption isotherms reveal (i) suppressed framework shrinkage with increasing solution concentration during casting, (ii) improved long range order and higher surface area with increasing TEOS content up to 3:1 TEOS:resol, and (iii) enhanced porosity with crosslinking at 100 °C. These differences can be

explained on the basis of block copolymer thermodynamics and mechanical reinforcement by silica. This family of OMCs are effective adsorbents for bulky aqueous organic dyes, such as methylene green (MG) and methyl blue (MB), with high adsorption capacities of 0.436 g MG/g OMC and 0.378 g MB/g OMC obtained. This R2R method provides a facile method to generate significant quantities of OMCs with tunable pore textures.

Keywords: *ordered mesoporous carbon; FDU-15; soft templating; evaporation-induced self assembly*

1. Introduction

Ordered mesoporous carbon (OMC) [1, 2] offers tremendous promise in a host of applications, such as energy storage as battery [3] or supercapacitor [4] electrodes, chemical separations as membranes [5] or absorbents [6], and electrodes in solar cells [7]. An efficient synthesis route for these OMCs is the “soft-templating” method that employs cooperative assembly of carbonizable precursors with amphiphilic block copolymers (BCPs) to generate the templated nanostructures [8, 9]. Pyrolysis of the BCP-crosslinked precursor removes the template and provides a high carbon yield to generate a stable porous carbon . There are some advantages in terms of control of the pore structure using hard templating [10], such as colloidal silica templates [11]. However in both methods, small batch

syntheses, which limits scale up potential, are typically utilized for the fabrication of templated ordered mesoporous carbons. For the scale-up of OMCs, Stein and coworkers demonstrated the use of a sucrose or KCl sacrificial layer significantly improves the carbon yield [12], but this method still tends to yield sub-gram quantities. To extend this idea, Zhao and coworkers demonstrated that a sacrificial polyurethane (PU) foam scaffold [13] can generate kilograms of OMCs. Although successful, this method has several limitations associated with the evaporation of the templating solution and degradation by-products of the PU scaffold during pyrolysis. In particular, slow evaporation prevents rapid synthesis and can lead to phase separation for multicomponent coassembly, such as in the tri-constituent co-assembly approach to fabricate OMC-silica nanocomposites [14]. The etching of silica from these composites introduces the micropores in the carbon wall, which significantly increases the surface area of the OMC [15]. These high surface area OMCs could have high utility in a number of applications, such as catalysis and batteries [16, 17]. Therefore, the development of a scalable fabrication method would improve the commercial viability of these high surface area mesoporous OMCs.

Roll-to-roll (R2R) processing is an enabler of low-cost continuous fabrication of functional materials, including flexible electronics [18], electrode materials [19], organic photovoltaics [20], and nanoimprinted lithographic devices [21, 22]. Recently, we have extended the fabrication of mesoporous materials (carbon, silica, metal oxides) to the R2R

process [23]. This processing involves (1) a polyethylene terephthalate (PET) substrate for the support, (2) doctor blade casting station to generate a thick film, (3) a temperature-controlled evaporation zone to remove residual solvent, and (4) a heated zone to crosslink the precursors. The crosslinked film is easily peeled from the PET substrate to provide a free standing film for calcination / carbonization to yield the mesoporous material. However, it is unclear how the synthetic details and process conditions impact the pore architecture (surface area, pore size and porosity) in this scalable R2R process.

Herein, we demonstrate how the casting solution concentration, TEOS loading and crosslinking temperature impact the pore structures of soft templated, FDU-15-like OMCs fabricated by the R2R process. For a single template and without using a swelling agent, the pore size of resultant OMCs can be effectively tuned between 3.6 nm and 5.2 nm. Moreover, very large surface areas, maximum obtained is 2455 m²/g, are achievable with hundred grams of material produced in a single batch. With the facile synthesis and widely tunable pore properties, these OMCs are evaluated as adsorbents for water purification with methylene green and methyl blue examined as model organic dyes. Intriguingly, the dye capacity is not significantly impacted when the surface area of the OMC is greater than 1500 m²/g. These studies demonstrate the capability to generate large quantities of high surface area OMCs by R2R processing with pore characteristics easily tunable by synthetic and processing conditions to match application requirements.

2. Experimental

2.1. Materials

Phenol (>99%), formaldehyde (ACS reagent, 37 w% in H₂O, contains 10-15% methanol as stabilizer), tetraethyl orthosilicate (TEOS) (>98%), Pluronic F127, ethanol (>99%), potassium hydroxide (KOH, >85%) and sodium hydroxide (NaOH, >97%) were purchased from Sigma-Aldrich and used as received. Thermally-stabilized polyethylene terephthalate (PET) sheet (125 μm) was purchased from Terphane Inc. A low-molecular weight phenolic resin was synthesized following the synthetic procedures reported previously for the fabrication of OMCs [8, 24].

2.2. Fabrication of Ordered Mesoporous Carbon (OMC)

The mesoporous carbons were synthesized following the initial tri-constituent assembly method as reported previously by Zhao and coworkers [25]. Briefly, 4.8 g Pluronic F127 was dissolved in 4 g of H₂O and 9-21 g of ethanol (EtOH). The solution was gently stirred for 2 h to ensure complete dissolution of the Pluronic F127. 6 g of resol solution (50 wt % in ethanol) and 6-9 g of TEOS were added to this solution and heated to 40 °C. Note that this results in an additional 3 g of ethanol from the resol solution and 4 mols of ethanol from each mol of TEOS after hydrolysis. The additional ethanol from TEOS on hydrolysis is

significant: 5.31 g, 6.63 g, and 7.96 g of ethanol can be evolved from 6 g, 7.5 g, 9 g of TEOS, respectively. After stirring this solution for 2 h at 40 °C, the solution was cast on the PET substrate by doctor blade coating at 50 cm/min as shown in Fig. 1A. The gap of the doctor blade was set to produce a wet film thickness of 400 μm (Note: we have found that film thickness does not impact the pore texture for a variety of wet thicknesses examined between 300 μm and 500 μm). The residual solvent was removed by heating the film at 50 °C for 1 h in the first thermal zone as shown in Fig. 1B, then a second thermal zone was used to crosslink the phenolic resin at 90, 100, 120 or 140 °C for 3 h. The crosslinked film was peeled from PET substrate and carbonized in a tube furnace (SentroTech Inc.) in N_2 . The furnace temperature was first increased to 600 °C at 1 °C/min, then to 800 °C at 5 °C/min with the temperature held at 800 °C for 3 h, followed by slow cooling to ambient temperature. The silica within the carbon-silica framework was subsequently etched with 3M KOH in ethanol:deionized water (1:1 v:v) solution for 3 days. The powder was washed with deionized water 10 times and then dried under vacuum at 80 °C for 24 h prior to characterization. In this work, we use a standard nomenclature for the OMC powders of OMC-x-y-z, where x is the mass ratio of TEOS/resol in the casting solution, y is the mass ratio of ethanol/resol excluding the ethanol developed on hydrolysis of TEOS, and z is the crosslinking temperature in °C. The solid concentration for the casting solutions is calculated as $(\text{solids}/(\text{solids}+\text{water}+\text{ethanol}))$, where solids constitute the added mass of

TEOS, F127 and resol. As a control, FDU-15 was fabricated using the previously reported P123:resol ratio and processing conditions [24, 26].

2.3. Characterization

Transmission small angle X-ray scattering (SAXS) was performed on a Rigaku MicroMax 002+ instrument with a 2D multiwire area detector and a sealed copper tube operating at 45 kV to produce CuK_α ($\lambda = 0.154 \text{ nm}$) X-rays. The scattering vector ($q = 4\pi\lambda^{-1}\sin\theta$, where θ is the scattering angle) was calibrated using silver behenate, using the primary reflection peak position at $q = 1.076 \text{ nm}^{-1}$. The 2D SAXS profiles for the OMC powders were collected in the q range from 0.12 nm^{-1} to 2 nm^{-1} . The domain spacing of the OMC powders, d , was determined from the scattering profiles as $d = 2\pi/q^*$, where q^* is the primary peak location.

A JEOL-1230 transmission electron microscopy (TEM) with an accelerating voltage of 120 kV was used to image the mesoporous carbon nanostructures using a digital CCD camera. To prepare samples for TEM, the powder was dispersed in acetone at 0.1 mg/mL and sonicated for 30 min. Two drops from the suspension were placed on 3.05 mm Cu grid (01753-F, TED PELLA, Inc.) for TEM characterization. To investigate the pore architecture, N_2 adsorption and desorption isotherms were obtained using a Micromeritics Tristar. The pore size distributions were calculated from the adsorption isotherms using the Barrett-Joyner-Halenda (BJH) model [27]. The surface areas were calculated using the Brunauer-Emmett-

Teller (BET) methodology [28].

The adsorption of methylene green (MG) and methyl blue (MB) from aqueous solution into the OMCs was determined from UV-Vis spectroscopic measurements of the solution using a variable angle UV-vis spectroscopic ellipsometry (VASE; J.A.Woollam Co., M-2000) in transmission mode. A constant initial dye concentration of 0.5 mg/mL and constant concentration of the OMC (OMC:water = 1 g:1 L) were used in all experiments. During the adsorption measurements, the suspension containing OMC, dye and water were shaken vigorously using a vortex mixer. The quantity of adsorbed dye (Q) per gram OMC (g/g) was determined from the spectroscopic measurements with the aid of a calibration curve that related solution adsorption to dye concentration, as $Q = (C_0 - C) \times V/W$, where C is the concentration of the dye in the solution after adsorption, C_0 is the initial concentration of dye in solution, V is the solution volume, and W is the mass of OMC adsorbent.

3. Results and Discussion

Ordered mesoporous carbon with high surface area are fabricated *via* roll-to-roll processing (as illustrated in Fig. 1) employing evaporation-induced self-assembly of a triconstituent polymeric solution (resol, TEOS, Pluronic F127). The governing mechanisms contributing to the formation of the ordered mesostructure are predominately: (i) evaporation of the ethanol to induce cylindrical micelles, (ii) hydrolysis and condensation of

TEOS to yield silica oligomers that promote ordering of the mesostructure, (iii) crosslinking of resol to stabilize the framework, (iv) carbonization of resol and thermal degradation of Pluronic F127 to yield mesopores and (v) removal of silica by etching to increase the surface area. Here, the impact of fabrication conditions, namely the casting solution concentration, the TEOS content, and crosslinking temperature, on the final structure of the porous carbon are investigated using the processing conditions listed in Table 1.

3.1. Impact of the solution concentration on structure

The solution concentration determines the viscosity and therefore the quality of the wet cast film in R2R process. Ideally, the highest initial concentration is desirable to minimize the use of unrecoverable ethanol and to maximize the areal density for the mesoporous material. A fixed TEOS/F127/resol mass ratio (2.5/1.6/1) was used to investigate the impact of solution concentration (Table 1). In this case, the amount of ethanol added to the solution is varied from 5 to 7 to 9 g per g resol, which corresponds to ethanol concentration of 45 wt% (53 wt%), 53 wt% (58 wt%), and 59 wt% (64 wt%), respectively, where the number in paranthesis includes the evolved ethanol from complete hydrolysis of TEOS. TEM micrographs (Fig. 2) show no significant differences in the ordered nanostructures of these OMCs. The SAXS patterns (Fig. 2D) of all three samples show three well-defined diffraction peaks with a ratio of $1: \sqrt{3} : 2$, consistent with a highly ordered 2-D

hexagonal cylindrical morphology ($P6mm$). However, the domain spacing determined from SAXS decreases slightly (10.8 nm to 10.2 nm to 9.2 nm) as the ethanol:resol ratio increases (5, 7, and 9).

To better probe the impact of ethanol content on the pore structure, N_2 adsorption-desorption isotherms (Fig. 3) are used. The isotherms show typical type-IV curves with a capillary condensation at $p/p_0 \approx 0.5 - 0.7$ and a H_1 hysteresis loop that is characteristic of mesoporous materials with cylindrical channels [14]. As the amount of ethanol added to the casting solution decreases, the surface area increases, up to a maximum of $2455 \text{ m}^2/\text{g}$ at an added ethanol:resol (w/w) ratio of 5. Intriguingly, the average pore size from the BJH model increases significantly for the highest surface area material with a much broader pore size distribution (Fig. 3B). The dependence of the pore size on casting solution concentration is consistent with the change in domain spacing determined from SAXS. Prior results have demonstrated a larger extent of shrinkage in thinner films [29, 30], but those films were at the scale of 10's of nm, not microns as the case of the films examined here. In this case, we attribute the larger pore size of OMC-2.5-5-100, compared to OMC-2.5-7-100 and OMC-2.5-9-100, to the limited mobility for the cooperative assembly due to the high solids concentration (45 wt%), of the initial casting solution when the least amount of ethanol is added (5 g/g resol). This limited mobility will lead to challenges in the self-assembly that kinetically traps the mesostructure. This hypothesized behavior is consistent

with the broader pore size distribution for OMC-2.5-5-100. This is somewhat unexpected as the more dilute solutions (38 and 33 wt % solids) should progress on evaporation through a similar concentration as the initial concentration (45 wt % solids) for OMC-2.5-5-100, especially since the large scale synthesis of OMCs (without TEOS) using PU foams [13] yield concentration independent mesostructures. However, solution assembly of block copolymers can be extremely process dependent [31]. We have confirmed that the larger pore size with a broader pore size distribution is reproducible with the surface area for three separate batches leading to surface areas of 2455 m²/g, 2318 m²/g, and 2372 m²/g (see Supplementary material for details). The mesostructure is dependent on the casting solution concentration when the solids content is high (e.g. 45 wt% solids) for these thick tri-constituent films.

3.2. Impact of TEOS loading on pore characteristics

The inclusion of silica in the material provides for mechanical reinforcement of the framework [25, 32] and its removal after carbonization introduces a significant micropore population. The influence of the TEOS:resol (w/w) ratio (2, 2.5, and 3) on the final OMC mesostructure was investigated at a fixed mass ratio of ethanol/F127/resol of 5/1.6/1, which correspond to 18, 22 and 25 wt% TEOS in solution. Fig. 3 illustrates that there is an optimal TEOS loading for maximizing the ordering of the mesostructure. At lower silica

content, the ordered structure is well defined (Fig. 4A) similar to the intermediate silica content of OMC-2.5-5-100 (Fig. 1A). The long-range ordering decreases with further increase in TEOS content for OMC-3-5-100 as shown in Fig. 4B with several grains visible in the TEM micrograph. SAXS (Fig. 3C) is used to better quantify the ordering; three clear diffraction peaks are observed for OMC-2.5-5-100, whereas the scattering from OMC-2-5-100 exhibits a single sharp peak and that from OMC-3-5-100 exhibits a broad primary peak and a weak second order reflection. These attributes from the scattering indicate that OMC-2.5-5-100 is the best-ordered sample. Moreover, the primary diffraction peak in the SAXS profiles, q^* , can be quantitatively examined (Fig. 4C) to elucidate information on the long-range order. The full width at half maximum (FWHM) of the peak is inversely related to the average grain size [33]. The FWHM is most narrow for OMC-2.5-5-100 (0.09 nm^{-1}) and most broad for OMC-3-5-100 (0.14 nm^{-1}). Additionally, the domain spacing determined from SAXS is significantly smaller for OMC-3-5-100 (8.6 nm) than either OMC-2.5-5-100 (10.8 nm) or OMC-2-5-100 (10.6 nm).

The N_2 adsorption-desorption isotherms provide additional insight into the structural differences in these materials. These isotherms (Fig. 5A) show typical type-IV curves with either a H_1 or H_2 hysteresis loop, but the size of the hysteresis loop is significantly reduced for OMC-3-5-100 with the capillary condensation occurring at significantly lower partial pressure than the other two OMCs. This is consistent with the partial collapse of the

mesostructure leading to smaller pores as is best illustrated by the pore size distribution in Fig. 5B. In this case, the collapse likely occurs after removal of the silica from the framework. The carbon content is significantly smaller, which appears to be insufficient to support the structure against capillary forces associated with the evaporation of ethanol/water from the etching process. This collapse leads to an average pore size for OMC-3-5-100 that is 30 % smaller than the other two OMCs and a much smaller pore volume (Table 1). Moreover, the surface area of OMC-3-5-100 ($1269 \text{ m}^2/\text{g}$) is much less than for OMC-2.5-5-100 ($2455 \text{ m}^2/\text{g}$) or OMC-2-5-100 ($1508 \text{ m}^2/\text{g}$). As the silica was the majority phase in the wall, the micropores in the wall framework likely are also partially collapsed contributing to the decreased surface area.

3.3. Role of crosslinking temperature on porous structure

With tri-constituent self assembly, the condensation of silica oligomers drives self assembly during solvent evaporation [32], unlike the limited ordering that arises for resol-Pluronic alone [34-36]. Despite the initial development of the mesostructure on solvent evaporation, the crosslinking temperature impacts the ultimate ordered structure of the OMCs. For temperatures between 90 – 140 °C, a well defined ordered structure is clearly observed in the TEM micrographs in all cases for the OMCs (Fig. 6), although defects in the ordered structure are clearly evident for the OMC crosslinked at 140 °C (Fig. 6C). This

suggests that the mesostructure evolves during crosslinking as the resol will be more crosslinked at higher temperatures [37]. SAXS measurements provide a route to better understand these differences as shown in Fig. 6D. A primary diffraction peak is observed for all of the samples, but the primary peak position (q^*) and the breadth of this peak are both strongly dependent on the crosslinking temperature. For OMC-2.5-5-90, a complex broad scattering peak is present in the SAXS profile; there appears to be two distinct mesostructure spacings from this scattering pattern. Increasing the crosslinking temperature to 100 °C, the primary diffraction peak narrows and shifts to lower q ($q = 0.58 \text{ nm}^{-1}$); additionally, the SAXS profile contains two higher order diffraction peaks, which illustrates the highly ordered structure that is obtained at this crosslinking temperature. Further increasing the crosslinking temperature to 120 °C decreases the domain spacing from 10.8 nm to 9.7 nm and also decreases the ordering of the mesostructure as evidenced by the broadening of the primary diffraction peak position and loss of higher order reflections.

The crosslinking temperature also impacts the pore texture as determined from N_2 adsorption-desorption isotherms shown in Fig. 7A. The hysteresis loop in these isotherms is a pronounced H_2 -type loop at the extremes of the temperatures examined and approaches an H_1 -type hysteresis loop for OMC-2.5-5-100 (intermediate temperature). The hysteresis loop of H_1 -type is a characteristic of capillary condensation and evaporation of well-defined

cylindrical pores that are open at both ends, while H_2 -type hysteresis loops are generally found in more disordered materials. This observation is consistent with the SAXS results, where the OMC-2,5-5-100 shows the best ordered mesostructure. The largest surface area and pore volume are obtained for OMC-2.5-5-100. Additionally from these adsorption-desorption isotherms, the collapse (or failure to order) of the pores for OMC-2.5-5-140 is suggested by the much lower pore volume ($0.75 \text{ cm}^3/\text{g}$) and surface area ($1093 \text{ m}^2/\text{g}$) than that found at lower crosslinking temperatures ($>1.5 \text{ cm}^3/\text{g}$ and $>1800 \text{ m}^2/\text{g}$). This is consistent with the very weak diffraction peak from SAXS for OMC-2.5-5-140. As shown in Fig. 7B, a single narrow distribution for pore size is found for all four OMCs. The average pore size for all of the OMCs is $3.7 \pm 0.1 \text{ nm}$ except for OMC-2.5-5-100 where a much larger pore size (5.2 nm) is obtained.

To explain these differences, the prior literature on the fabrication of OMCs without TEOS provides some clues. For these materials, the crosslinking temperature controls the relative rate of ordering and crosslinking [38]. At lower temperatures, the crosslinking reaction is sufficiently slow and does not impact ordering, but the crosslinking extent is lower and does not fully stabilize the mesostructure through carbonization [37]. At high temperatures, the resol crosslinks too fast for a well ordered mesostructure to develop. For OMC powders fabricated with Pluronic and resol, 120°C has been reported as the optimal crosslinking temperature [38]. However, the silica in the framework will assist in stabilizing

the structure [32], so a lower temperature may improve the ordering similar to a prior report using a two stage crosslinking process where initially 100 °C is used to promote the ordering, followed by a much higher temperature (150 °C) to crosslink the resol [37]. This competition between ordering and crosslinking likely provides the origins of the best-ordered structure for OMC-2.5-5-100. The extent of ordering impacts the mechanical properties [39], which in turn are critical to the extent of contraction of the pores during calcination. [40] These effects likely are responsible for the smaller domain spacing for OMC-2.5-5-140. Despite the large silica content, the crosslinking temperature for the resol is an important factor in determining the final structure of these OMCs.

Fig 8 schematically summarizes the influence of the three parameters examined here: Solution concentration, TEOS concentration and temperature for thermopolymerization. Increasing the concentration of added ethanol in the casting solution leads to (1) decreased average pore size, (2) decreased surface area, and (3) slightly narrowed pore size distribution. For the TEOS concentration dependence, there is an optimal concentration (22 wt %) to maximize the (1) extent of ordering, (2) surface area, and (3) d-spacing of the mesoporous carbon. Similarly, an intermediate crosslinking temperature of 100 °C leads to the best-ordered mesostructure and a larger pore size.

3.4. Dye adsorption capacity of synthesized OMCs

To demonstrate their potential use in water purification, the fabricated OMCs with various surface area and pore structure were contacted with an aqueous solution of different dyes (methylene green and methyl blue). The equilibrium dye absorbed (Q) for the various OMC samples at 25 °C are shown in Fig. 9A. FDU-15 with 500 m²/g surface area is provided as a control for comparison [24]. For methylene green (MG), as the surface area of the OPC increases from 500 m²/g to 1269, 1508, 2058 and 2455 m²/g, Q increases from 0.3 g/g to 0.34, 0.41, 0.43 and 0.436 g/g. This is consistent with previous reports where the adsorption capacity of MG scales with the surface area [41]. The limited increase in capacity of MG at the higher surface area suggests that the increased surface area in this case is not readily accessible to MG. The maximum adsorption capacity of MG (0.436 g/g) is obtained with OMC-2.5-5-100, which is significantly higher than previous report of MCM-41 (0.1 g/g) [42]. For methyl blue (MB), the highest adsorption capacity is obtained using OMC-2.5-7-100 (0.378 g/g), which is greater than KOH-activated carbon (0.3 g/g) and similar to steam activated carbon (0.38 g/g) [43]. Interestingly, when the surface area increases from 2058 m²/g to 2455 m²/g, the average MB capacity for the OMC slightly decreases from 0.378 g/g (surface area: 2058 m²/g) to 0.372 g/g, but this is not outside of the uncertainty of the measurement. There is a significant standard deviation in the MB capacity for OMC-2.5-5-100, which suggests that the heterogeneity in this material (as evidenced by the broadened diffraction peaks from SAXS) impacts the dye capacity, likely

through the distribution of micropores.

In addition to the capacity, the adsorption kinetics are also important to consider for the utility of these OMCs for water purification. Fig. 9B shows the fractional dye removal of both MG and MB as a function of contact time for OMC-2.5-5-100. After 5 min, the OMC adsorbs 60 and 44 % of its equilibrium capacity for MG and MB, respectively. The rate of approach to equilibrium decreases for higher percentages of adsorption capacity with approximately 60 and 100 min required for the OMC to reach its adsorption capacity for MG and MB, respectively. To more quantitatively describe the adsorption kinetics of the dyes (MG and MB), a pseudo-second-order model was used to determine an effective adsorption rate, k :

$$\frac{t}{Q_t} = \frac{1}{kQ^2} + \frac{1}{Q}t,$$

where Q_t and Q are the specific mass of dye adsorbed at time t and equilibrium. As shown in the inset of Fig. 9B, t/Q_t increases linearly with time and thus the pseudo-second-order model can describe the adsorption kinetics. The effective rate constant for MG is 0.828 (min·g dye/g OMC)⁻¹, which is approximately a factor of 2 greater than for MB (0.415 (min·g dye/g OMC)⁻¹). This is consistent with the qualitative result that the equilibration takes much longer for MB (~ 100 min) than for MG (~ 60 min). Since the adsorbate is identical in this case, the difference in the rate constants is primarily due to the difference in the molecular sizes of MG and MB. The largest dimension of MB molecule (≈2.5 nm) is almost

1.6 times greater than that of MG (≈ 1.4 nm) [44]. Thus, the small pores from the removal of silica are less effective for promoting sites for adsorption of the larger dye.

4. Conclusions

The large scale synthesis of uniform mesoporous carbon with varying pore characteristics is demonstrated using process control during R2R fabrication. Tri-constituent cooperative assembly provides mesopores templated by Pluronic F127 and large micropores from etching silica from the framework. Both evaporation and thermally-induced self assembly are shown to be at play and influence the resulting pore characteristics of the OMCs. Framework shrinkage can be suppressed by increasing solid concentration in the casting solution and the fraction of TEOS in the formulation. However, the pore structure appears to collapse partially after etching of the silica for very high TEOS concentrations. An optimal crosslinking temperature range exists on the basis of insufficient crosslinking at low temperature and insufficient time to re-organize the self-assembled structure at higher temperatures. Through changes in crosslinking temperature, the pore size and the surface area are effectively controlled from 0.75 nm and 1090 m²/g at 140 °C to 2.22 nm and 2450 m²/g at 100 °C. The applicability of these OMCs to dye removal from aqueous solution is demonstrated with adsorption capacities of 0.436 g MG/g and 0.378 g MB/g. This

difference in adsorption capacities of OMCs for MG and MB appears to be determined by the molecular size of the dye. R2R processing combined with processing sensitivity provides a facile route to tune the properties of mesoporous materials, fabricated in sufficient quantity to enable through investigations of these materials in a variety of applications.

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Table 1 Fabrication conditions for OMCs and their corresponding structural properties

Sample name	TEOS:resol (w:w)	EtOH:resol ^a w:w	Crosslink temp. (°C)	Domain spacing (nm)	Surface area (m ² /g)	Pore volume (cm ³ /g)	Pore size diameter (nm)
OMC-2.5-9-100	2.5	9	100	9.2	1823	1.41	3.7
OMC-2.5-7-100	2.5	7	100	10.2	2058	1.49	3.6
OMC-2.5-5-100	2.5	5	100	10.8	2455	2.22	5.2
OMC-3-5-100	3	5	100	8.6	1269	0.81	3.4
OMC-2-5-100	2	5	100	10.6	1508	2.28	5.1
OMC-2.5-5-90	2.5	5	90	9.9	1808	1.51	3.8
OMC-2.5-5-120	2.5	5	120	9.7	1862	1.62	3.8
OMC-2.5-5-140	2.5	5	140	8.8	1093	0.75	3.6

^a*This only includes all of the ethanol added to the casting solution. Ethanol generated by hydrolysis of TEOS is neglected in this ratio*

Figure Captions

Fig. 1 Images of components of the R2R tool used for the fabrication of the OMCs. (A) The tri-constituent solution is first cast using a doctor blade. (B) Convection heating zones are used for solvent evaporation and crosslinking of the resol.

Fig. 2 TEM images of OMCs fabricated with ethanol:resol ratio of (A) 5 , (B) 7 , and (C) 9 with fixed TEOS/F127/resol mass ratio (2.5/1.6/1). (D) SAXS patterns of these materials illustrate the highly ordered hexagonally packed mesostructure.

Fig. 3 (A) N₂ adsorption-desorption isotherms of OMCs fabricated using casting solutions with different ethanol concentration and (B) their corresponding pore size distributions. The isotherms are vertically offset by 200 and 400 cm³/g for OMC-2.5-7-100 and OMC-2.5-9-100, respectively.

Fig. 4 TEM micrographs of OMCs fabricated with TEOS:resol ratios of (A) 2 and (B) 3 with fixed mass ratio of ethanol/F127/resol of 5/1.6/1. (C) SAXS profiles of corresponding samples and an intermediate TEOS content.

Fig. 5 (A) N₂ adsorption-desorption isotherms of OMCs fabricated with different TEOS:resol ratios and (B) their corresponding pore size distribution. The isotherms are vertically offset

by 200 and 1500 cm³/g for OMC-2-5-100 and OMC-3-5-100, respectively.

Fig. 6 TEM micrographs of OMCs fabricated using crosslinking temperature of (A) 90 °C, (B) 120 °C and (C) 140 °C. (D) SAXS patterns of the corresponding samples.

Fig. 7 (A) N₂ adsorption-desorption isotherms of OMCs fabricated using different crosslinking temperatures and (B) their corresponding pore size distributions. The isotherms are vertically offset by 300, 600, and 1500 cm³/g for OMC-2.5-5-100, OMC-2.5-5-120 and OMC-2.5-5-140, respectively.

Fig. 8 Schematic summarizing the influence of the ethanol concentration, TEOS concentration, and crosslinking temperature on the characteristics of mesoporous carbons fabricated by a roll-to-roll process.

Fig. 9 (A) Dye adsorption capacity as a function of surface areas of mesoporous carbon; (B) Effect of contact time on different dye adsorption for OMC-2.5-5-100. Inset illustrates the pseudo-second-order adsorption kinetics for both MG and MB.

Fig1A

Fig1B

Fig2A

Fig2B

Fig2C

Fig3A

Fig4A

Fig4B

Fig4C

Fig5A

Fig5B

B

Fig6A

Fig6B

Fig6C

Fig6D

Fig7A

Fig7B

Fig8

Fig9A

Fig9B