

Supplementary Information for

**Templated synthesis of the microparticles with carbonaceous skeletal  
structures using polymer cubosomes as templates.**

Jeongeun Song<sup>1</sup>, Subin Choi<sup>1</sup>, Jongwoo Lim<sup>1\*</sup>, and Kyoung Taek Kim<sup>1\*</sup>

<sup>1</sup>Department of Chemistry, Seoul National University, Seoul 08826, Korea

**Contents**

**Materials and Methods**  
**Supplementary Figures**

## **Materials and Methods**

**Materials.** All reagents and chemicals were used as received from Sigma Aldrich, Alfa Aesar, and TCI. Dichloromethane (MC) was distilled over CaH<sub>2</sub> under N<sub>2</sub>. Tetrahydrofuran (THF) was refluxed over a mixture of Na and benzophenone under N<sub>2</sub> and distilled before use. Unless otherwise noted, all reactions were performed under N<sub>2</sub>.

**Methods.** NMR spectra were recorded on an Agilent 400-MR DD2 magnetic resonance system and Varian/Oxford As-500 using CD<sub>2</sub>Cl<sub>2</sub> and CDCl<sub>3</sub> as solvents. Molecular weight of block copolymers was measured on an Agilent 1260 infinity gel permeation chromatography (GPC) system equipped with a PL gel 5 μm mixed D column and differential refractive index detectors. THF was used as an eluent with a flow rate of 1 mL min<sup>-1</sup> at 35 °C. A PS standard kit (Agilent Technologies) was used for calibration. Matrix-assisted laser desorption ionization time-of-flight mass spectroscopy (MALDI-TOF-MS) was performed on a Bruker Ultraflex III TOF-TOF mass spectrometer equipped with a nitrogen laser (335 nm). The analytical sample was prepared by mixing a THF solution of analyte with a THF solution of matrix (sinapinic acid). The prepared mixture was loaded on the MALDI plate and dried at room temperature before measurement.

**Scanning and transmission electron microscopy.** Scanning electron microscopy (SEM) was performed on a Hitachi S-4300 at an acceleration voltage of 15 kV. Field-Emission Scanning Electron Microscope (FE-SEM) was performed on Carl Zeiss SUPRA 55VP microscope at acceleration voltage of 2 kV. The dried polymer cubosomes were placed on a conductive carbon tape and coated with Pt with a thickness of 3 nm by using Hitachi E-1030 ion sputter (20 mA, 60 s). Transmission electron microscopy (TEM) was performed on a Hitachi 7600 operating at 100 kV and a JEOL JEM-2100 microscope at 200 kV. Field-Emission Transmission electron microscopy (FE-TEM) was performed on JEOL JEM-F200 microscope at 200kV. Sample specimens were prepared by placing a drop of the sample

solution on a carbon-coated Cu grid (200 mesh, EM science). The grid was air-dried overnight.

**Synchrotron small angle X-ray scattering.** Synchrotron small angle X-ray scattering (SAXS) data were obtained on the 6D SAXS beam line at Pohang acceleration laboratory in Korea (PLS-II, 3.0 GeV). The sample-to-detector distance (SDD) was 3.5 m. The concentrated suspension of the polymer cubosomes and the carbonaceous microparticles were dried for 24 h in a freeze-dryer. Ti-SBA-15 was used as standard sample and scattering spectra of powder samples were taken in a transmission mode at room temperature (11.6 keV).

**Powder X-ray diffractometer.** X-Ray powder diffraction patterns were recorded on Bruker New D8 Advance X-ray diffractometer using a Cu  $K_{\alpha 1}$  source ( $\lambda = 0.15406$  nm). The concentrated suspension of the polymer cubosomes and the carbonaceous microparticles were dried for 24 h in a freeze-dryer.

**Raman spectrometer.** Raman spectra were obtained on Renishaw inVia microscope equipped with 514 (5 mW) excitation lasers, a 20 $\times$  objective lens (NA = 0.40, Leica), and a standard charge-coupled device (CCD) array detector (576  $\times$  384 pixels; Peltier; cooled to -70  $^{\circ}$ C). Raman spectra were recorded with an acquisition period of 10 s and wavenumbers of 400-3200  $\text{cm}^{-1}$ .

**A nitrogen adsorption experiment.** The Porous structures of the samples were analyzed by a nitrogen adsorption experiment at -196  $^{\circ}$ C using a BEL BELSORP-Max system. The surface areas and pore size distributions of the samples were calculated by using the Brunauer-Emmett-Teller (BET) equation and the Barrett-Joyner-Halenda (BJH) method, respectively.

**Synthesis of branched-linear diblock copolymers.** Detailed synthetic procedures of macroinitiators were reported previously.<sup>1</sup> Before polymerization, styrene monomer was purified by basic alumina column. Using macroinitiator with the branched PEG blocks, Branched-linear diblock copolymers, PEG<sub>3</sub>-*b*-PS (PEG550<sub>3</sub>-*b*-PS<sub>148</sub> and PEG750<sub>3</sub>-*b*-PS<sub>353</sub>),

were synthesized by the atom-transfer radical polymerization(ATRP) of styrene at 100°C in the presence of the corresponding macroinitiators. Polymerization was monitored by gel permeation chromatography (GPC) over reaction time.

**Self-assembly of PEG<sub>3</sub>-*b*-PS for PCs.** A representative procedure is described. 20 mg of PEG<sub>3</sub>-*b*-PS was dissolved in 2 mL of 1,4-dioxane in a vial equipped with a magnetic stirring bar. The polymer solution in the vial capped with a rubber septum was stirred for 2 h at room temperature. 2 mL of water was added at a rate of 0.5 mL h<sup>-1</sup> to the solution via a syringe pump with stirring (800 rpm). After addition of water, the resulting suspension was dialyzed against water to remove the organic solvent by using a dialysis membrane (MW cut-off 12–14 kDa) with frequent change of water for 48 h.

**Templated synthesis of microparticles with carbonaceous reticulated networks.** PCs were collected into the tube by centrifuge. Water was removed as much as possible except for the PC submerged in the suspension. The Furfuryl alcohol (FA)/water (4:1 v/v) solution was added into the concentrated suspension of PCs and This suspension was shaken for 3 hours to penetrate the carbon precursor into the PC. After removing the precursor solution by using centrifuge and filter paper, the FA-infiltrated PCs were placed in chamber filled with HCl vapor for acid-catalyzed polymerization of FA. After 12h, the resulting particles were heated for 24h at 100°C for crosslinking of FA. Then, the particles were calcined at 450 °C under inert gas for 3 h with a temperature increase rate of 1 °C /min to obtain the porosity and decomposition of the template. Carbonization was carried out in a tubular furnace under inert gas at 900 °C for 5 h. The temperature was increased at a rate of about 5 °C /min.

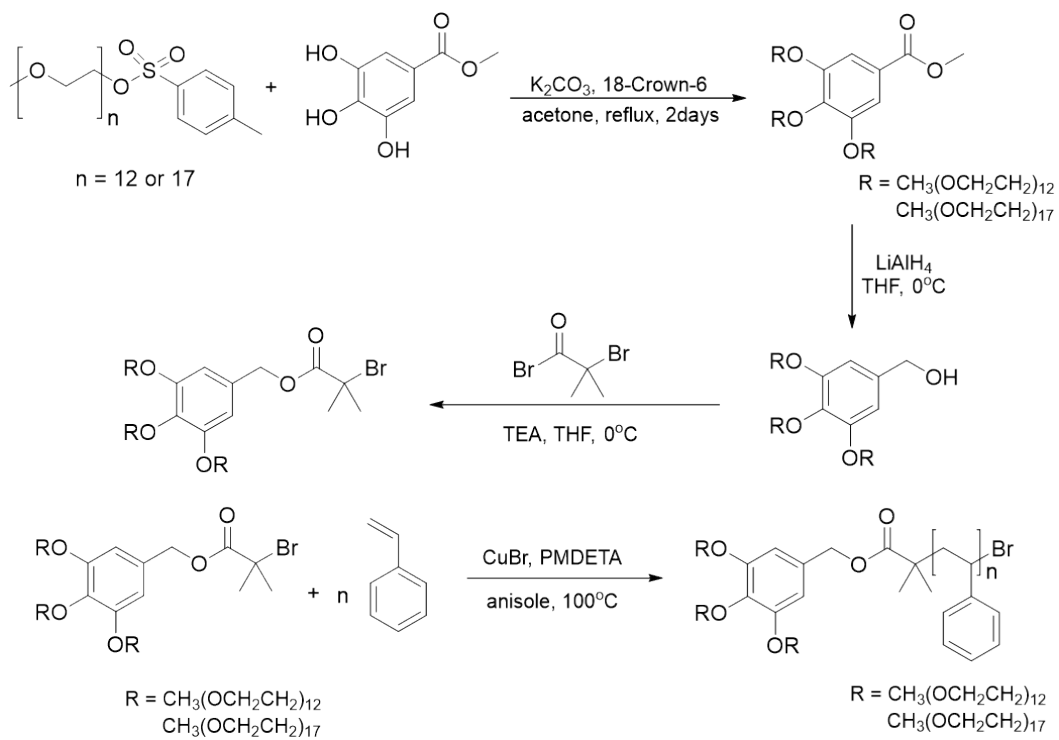
**Electrochemical measurement of cubic-ordered mesoporous carbon (cOMC) microparticles.**

All the Electrochemical experiments were performed using a VSP-300 potentiostats (Biologic) with a three electrode configuration in 6 M KOH aqueous solution. The working

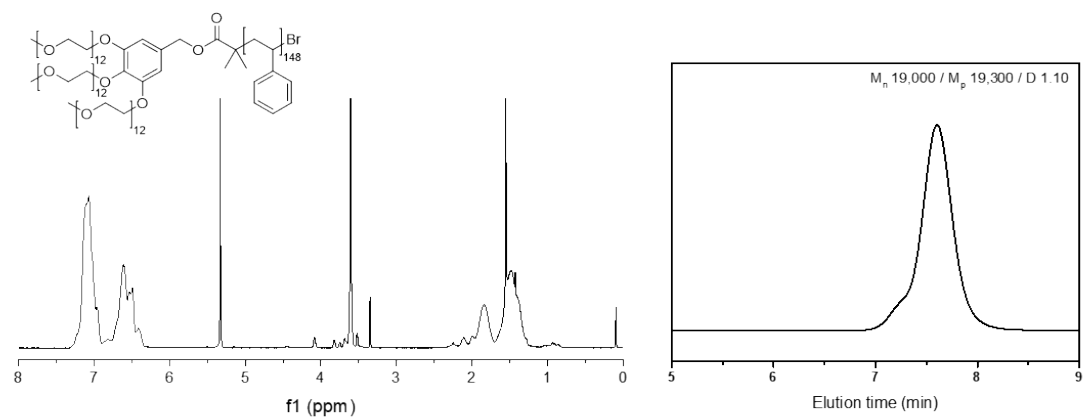
electrodes were prepared by mixing the active material (cOMC-550 and cOMC-750) with the Vulcan XC72R powder (Fuel Cell Store) as conductive materials and Nafion® D-521 (Alfa-Aesar) as a binder in a weight ratio of 20:1:5, and applying isopropylalcohol (IPA) as a solvent. The suspension was sonicated about 30 min to form a uniform mixture and subsequently loaded onto a Ni foam (1 x 1 cm<sup>2</sup> area). A Pt coil and a Hg/HgO in 1 M NaOH aqueous solution were used as the counter electrode and the reference electrode in the three-electrode system, respectively. Cyclic voltammetry (CV) was conducted within a potential range from -1.0 to 0.25 V versus Hg/HgO at various scan rates between 5 and 100 mV s<sup>-1</sup>. A gravimetric capacitance was calculated from galvanostatic charge-discharge (GCD) curves by applying the following equation.

$$C_s = \frac{I\Delta t}{m\Delta V}$$

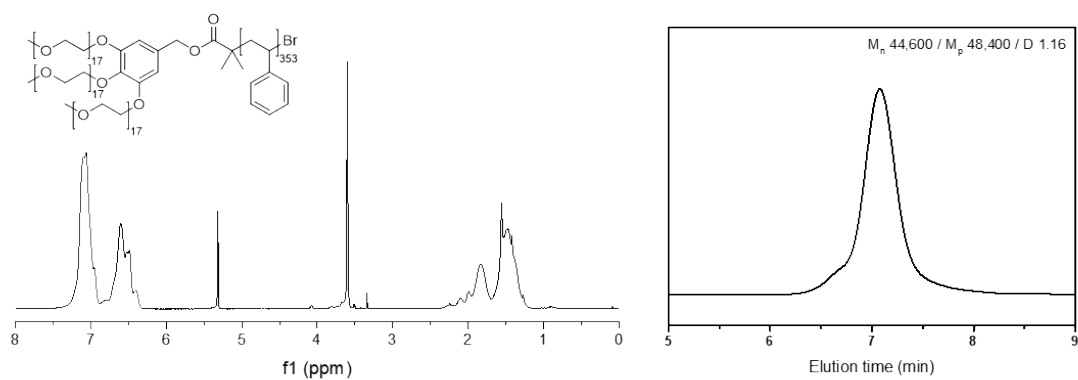
Where  $I$ ,  $\Delta t$ ,  $m$  and  $\Delta V$  are the applied current, the discharging time, the mass of active material, and the voltage change, respectively. Electrochemical impedance spectroscopy (EIS) was carried out from 100 kHz to 100 mHz with 10 mV amplitude perturbation at open circuit voltages.



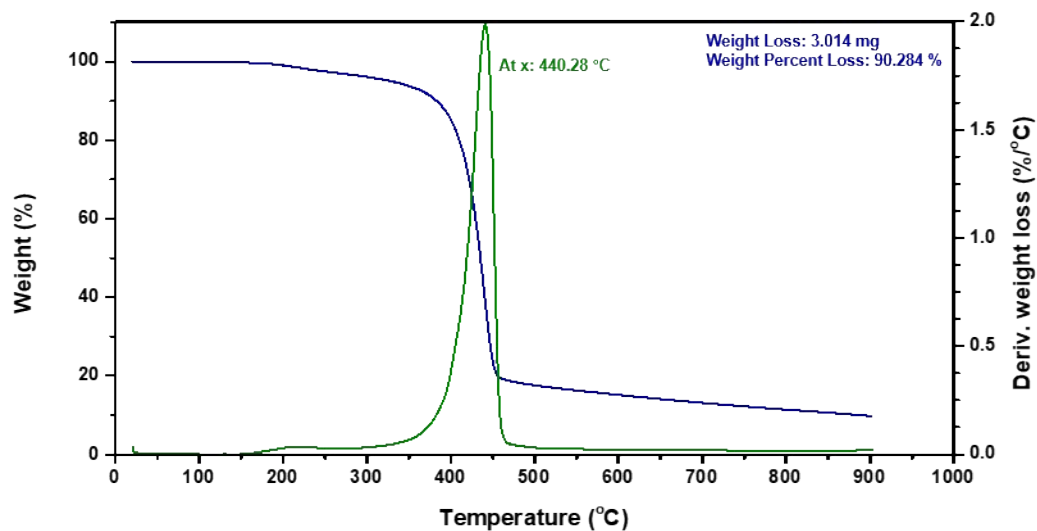
**Figure S1.** Synthesis of a branched macroinitiator and branched-linear diblock copolymers.



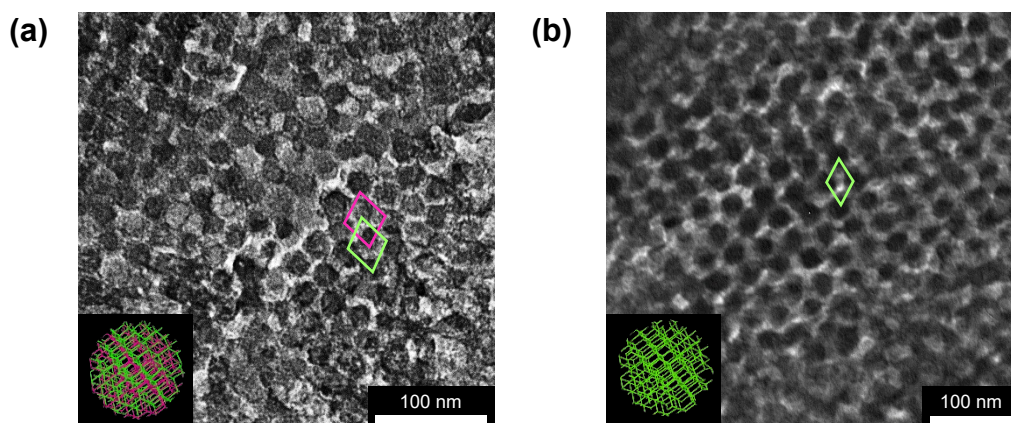
**Figure S2.**  $^1\text{H}$  NMR spectrum and GPC data of branched-linear diblock copolymers (PEG $_{550_3}$ -*b*-PS $_{148}$ ).



**Figure S3.**  $^1\text{H}$  NMR spectrum and GPC data of branched-linear diblock copolymers (PEG $_{750_3}$ -*b*-PS $_{353}$ ).

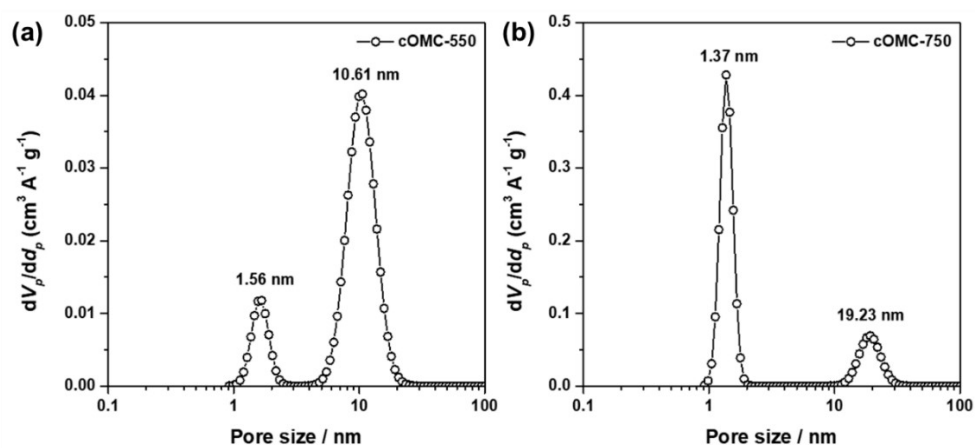


**Figure S4.** TGA data of PC-750 infiltrated with poly(furfuryl alcohol) polymerized by acid-catalyst.

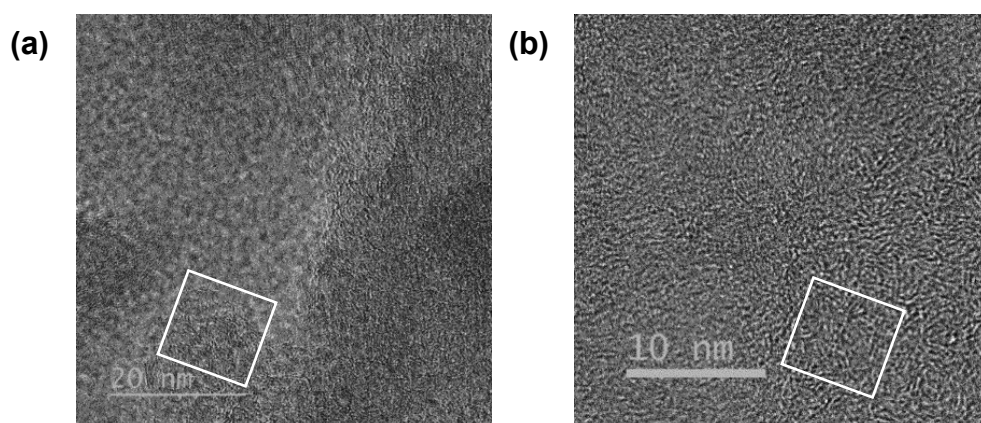


**Figure S5.** Cross-sectional TEM images of cOMC-550 (a) and cOMC-750 (b) prepared by the ultramicrotomy.

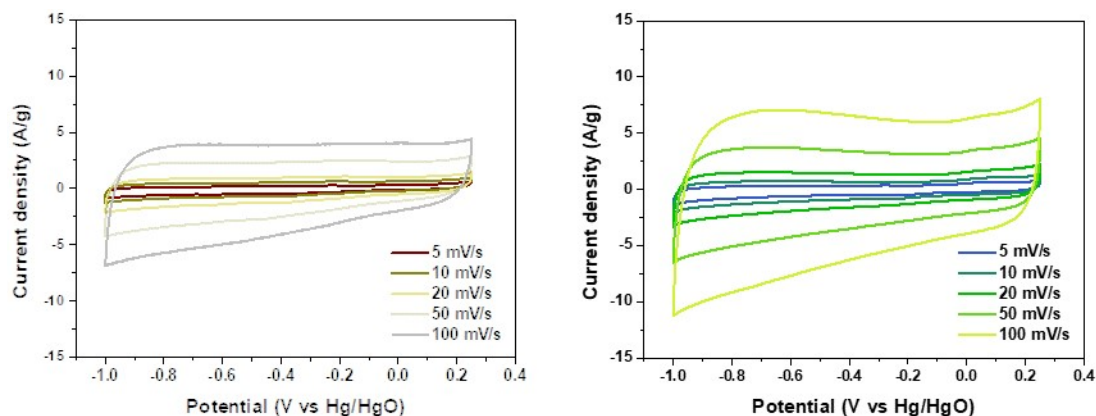




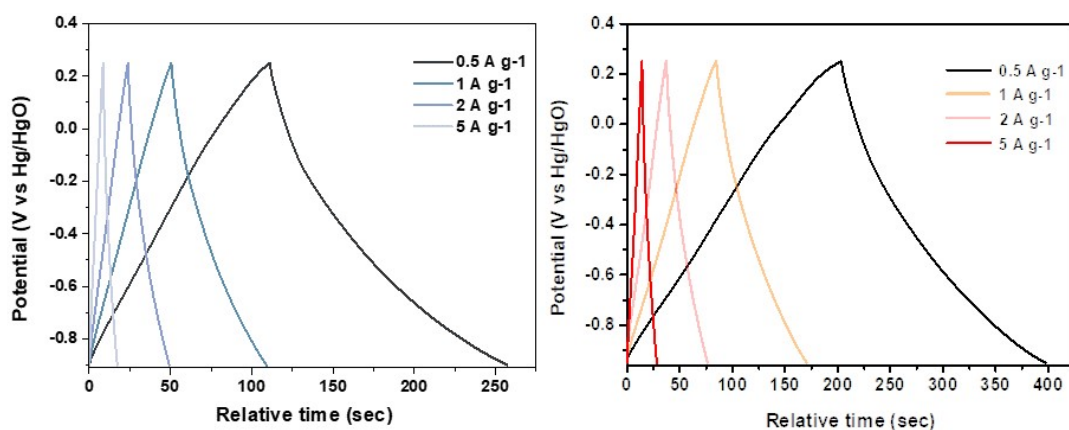
**Figure S6.** NLDFT Pore size distribution data of cOMC-550 (a) and cOMC-750 (b).



**Figure S7.** Field Emission TEM image of cOMC-550 (a) and cOMC-750 (b).



**Figure S8. (a), (b)** CV curves of cOMC-550 **(a)** and cOMC-750 **(b)** at scan rate of 5, 10, 20, 50, 100  $\text{mV s}^{-1}$ .



**Figure S9. (a), (b)** GCD profiles of cOMC-550 **(a)** and cOMC-750 **(b)** at current densities of 0.5, 1, 2, 5  $\text{A g}^{-1}$ .

## Reference

- (1) An, T. H.; La, Y.; Cho, A.; Jeong, M. G.; Shin, T. J.; Park, C.; Kim, K. T. Solution Self-Assembly of Block Copolymers Containing a Branched Hydrophilic Block into Inverse Bicontinuous Cubic Mesophases. *ACS Nano* **2015**, *9*, 3084–3096.