Supporting Information

Solution Self-Assembly of an Alternating Copolymer towards Hollow Carbon Nanospheres with Uniform Micropores

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1. Experimental Section

1.1 Materials

9,9’-bis(4-glycidyloxyphenyl)fluorine and 1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD) was purchased from TCI Reagent Co. Ltd. Dimethyl formamide (DMF) and 1,4-dithiothreitol was purchased from Admas Reagent Co. Ltd. Ruthenium oxide (RuO₄, 0.5% in water) was purchased from Acros Organics Reagent Co. Ltd. Anhydrous aluminum trichloride was purchased from Sigma-Aldrich Reagent Co. Ltd. Deionized water was used throughout all experiments. Dialysis bags with a molecular weight cut off of 7 KDa were purchased from Shanghai Green Bird Science & Technology Co. Ltd. All reagents were used as received.

1.2 Instruments and measurements

Liquid-phase nuclear magnetic resonance (¹H NMR and ¹³C NMR) measurements were performed using a Varian Mercury Plus 400 MHz spectrometer with dimethylsulfoxide-d₆ (DMSO-d₆) as solvent at room temperature. The internal
standard used was tetramethylsilane (TMS). **Fourier transform infrared (FTIR)** measurements were carried out on a PerkinElmer Spectrum 100 FTIR Spectrometer at room temperature. Samples were coated onto KBr crystal wafers and then carefully dried before measurements. **Gel permeation chromatography (GPC)** curve was recorded on a HLC-8320GPC (TOSOH, EcoSEC GPC System) system at 40 °C using DMF as an eluent at a flow rate of 0.6 mL min⁻¹. **Thermal gravimetric analysis (TGA)** curve was recorded using a PerkinElmer Q5000IR thermobalance with nitrogen as the purging gas at a heating rate of 20 °C min⁻¹. **Differential scanning calorimeter (DSC)** curve was recorded on a Thermal Advantage DSC Q2000 (TA Instruments, USA) equipped with a refrigerator cooling system (RCS). 7mg polymers were placed in an aluminum pan (non-hermetic, 30 μL) and then scanned at a heating rate of 10 °C min⁻¹ from 0 to 230 °C under dry nitrogen atmosphere. The data were collected using TA Instruments Universal Analysis 2000 V 4.3A software. **Dynamic light scattering (DLS)** measurement was performed in aqueous solution at room temperature using Malvern Zetasizer Nano S apparatus which was equipped with a 4.0 mW laser. The measurement was operated at λ = 633 nm with a scattering angle of 90°. **Scanning electron microscope (SEM)** measurements were performed on a Nova NanoSEM 450 (FEI, USA) with an accelerating voltage of 5 kV. One drop of sample solution with a given concentration was dropped onto a silica wafer and dried at room temperature overnight. A thin layer of gold was coated onto the surface of samples before measurements. **Transmission electron microscopy (TEM)** measurements were performed with an FEI Tecnai G2 Spirit Biotwin instrument at a
voltage of 120 kV. One drop of the sample solution with a given concentration was dropped onto a carbon-coated copper grid. Then the copper grid was dried in the air at room temperature overnight before measurements. **High resolution transmission electron microscopy (HR-TEM)** measurements were performed with an field emission TEM (FEI, Talos F200X/TALOS F200X) with an accelerating voltage of 200 kV. **Raman spectroscopy** was conducted using a DXR Raman spectrometer (Thermo Fisher, USA) equipped with a 532 nm exciting laser radiation. **Ultramicrotome** was conducted using a cryo-ultramicrotome (Leica, UC7, Germany). To prepare the epoxy embedding ultrathin slices of HPSs, the freeze-dried powders of HPSs were first buried in liquid epoxy resin. After the curing of the epoxy resin, the sample was cut into thin slices with a thickness of about 100 nm by using a diamond knife of the cryo-ultramicrotome at room temperature. **Powder X-ray diffraction (XRD)** was carried out on a D8 Advance X-Ray Diffractometer (Bruker, Germany) with Cu Kα as the X-ray source. The energy dispersive X-ray spectrum (EDX) was recorded using SEM. The specific surface area, pore volume and pore size distribution were quantified by measuring the N₂ physisorption at 77 K in a 3H-2000PM2 specific surface and pore size analysis instrument (Beishide, China). All samples were degassed at 150 °C under vacuum for 6 h before measurements. The \( S_{\text{BET}} \) were calculated using Brunauer–Emmett–Teller equation employing adsorption data within the partial pressure \( (P/P_0) \) range of 0.04–0.32. The \( V_{\text{tot}} \) was determined from the amount of N₂ adsorbed at \( P/P_0 \sim 0.99 \). The micropore specific surface area \( (S_{t-\text{plot}}) \) and volume \( (V_{\text{micro}}) \) were estimated by the t-plot method. The pore size distribution and
cumulative pore volume were calculated by a nonlocal density functional theory (NLDFT) method.

1.3 Synthesis of the P(BGF-\(a\)-DHBDT) alternating copolymer

Typically, 2.31 g (5 mmol) 9,9’-bis(4-glycidyloxyphenyl)fluorine, 0.771 g (5 mmol) 1,4-dithiothreitol and 0.696 g (5 mmol) TBD were dissolved in 40 mL DMF in a 250 mL flask, then 40 mL ethanol was added. The obtained mixture was stirred by a magnetic stirrer at room temperature for 12 h. Afterwards, the mixture was transferred into a dialysis bag with a molecular weight cut off of 7 KDa and dialyzed against DMF and water for 2 days, respectively. After freeze-drying, the desired alternating copolymer P(BGF-\(a\)-DHBDT) was obtained as white powders. Yield: 1.97 g (64.0%).

\(^{1}\)H NMR (400 MHz, DMSO-\(d_6\)): \(\delta\) 7.82-7.91 (br, 2 H), 7.29-7.39 (br, 4 H), 7.21-7.29 (br, 2 H), 6.93-7.02 (br, 4 H), 6.72-6.83 (br, 4 H), 5.00-5.32 (br, 2 H), 4.57-4.82 (br, 2 H), 3.75-3.97 (br, 6 H), 3.49-3.63 (br, 2 H), 2.41-2.74 (br, 8H). \(^{13}\)C NMR (400 MHz, DMSO-\(d_6\)): \(\delta\) 157.9, 151.9, 140.0, 138.3, 129.4, 128.3, 126.6, 121.1, 114.9, 72.1, 71.3, 69.4, 64.3, 36.4.

1.4 The self-assembly of P(BGF-\(a\)-DHBDT) in solution

In a typical procedure, 50.0 mg P(BGF-\(a\)-DHBDT) was dissolved in 100 mL DMF in a 500 mL flask under the magnetic stirring for 1 h at room temperature. Then 100 mL deionized water was added dropwise into the solution in 10 hrs by using a 150 mL dropping funnel. In the process of adding deionized water, light blue turbidity appeared in the solution, which indicated the formation of P(BGF-\(a\)-DHBDT) aggregates. The solution of the P(BGF-\(a\)-DHBDT) aggregates was subsequently
dialyzed against deionized water for one day to remove DMF. After freeze-drying, the self-assemblies of P(BGF-α-DHBDT) were obtained as white powders.

1.5 RuO$_4$ vapor-staining of the HPSs

RuO$_4$ staining was carried out via a vapor-staining method$^{1-4}$. In detail, a copper grid with ultrathin sections of the HPSs embedded in epoxy resin was placed in a culture dish. Then 2 drops of 0.5% solution of RuO4 in water were added to the culture dish. After 10 min of exposure to RuO$_4$ vapor at room temperature, the sample was taken out and observed under HR-TEM. One should wear safety glasses and vinyl gloves when working with the staining work and the whole staining procedure was performed in a fume hood to prevent personal exposure to the hazardous vapour of RuO$_4$.

1.6 Synthesis of CL-HPSs through the crosslinking of the BGF segments by the Scholl reaction

Typically, 200 mg HPSs and 2.2 g (15 mmol) anhydrous AlCl$_3$ were added into a 100 mL flask and evenly blended by using a vortex mixer. Subsequently, 10 mL CHCl$_3$ was added into the flask. Then the reaction mixture was stirred with magnetic stirrer at 58 °C under N$_2$ atmosphere for 3 days. Finally, the CL-HPSs were washed once with ethanol, twice with 1 M HCl-H$_2$O, thrice with ethanol, and then dried in a vacuum oven at 75°C for 24 h, giving pale brown powders. Yield: 192 mg (96.0%).

1.7 Preparation of HCSs with uniform micropores through the pyrolysis of CL-HPSs

The resulting CL-HPSs (180 mg) were placed in a porcelain boat and then carbonized
in a tube furnace under N\textsubscript{2} atmosphere at 800 °C for 2h with a heating rate of 3 °C min\textsuperscript{-1}. After thermal treatment, the resulting products were naturally cool to the room temperature. Yield: 49.6 wt.%. As a control experiment, the uncrosslinked HPSs (200 mg) were carbonized under the similar pyrolysis conditions. Yield: 20.6 wt.%. 

1.8 KOH activation

The crosslinked HPSs were activated by KOH. Typically, a 6 M KOH aqueous solution was added dropwise to the CL-HPSs until a KOH/HPSs weight ratio of 3:1 was attained. The impregnated sample was dried under vacuum at 50°C for several hours. After that, the mixture was placed in a stainless boat and then carbonized at 800 °C for 2h with a heating rate of 3 °C min\textsuperscript{-1} in a horizontal stainless tube under a N\textsubscript{2} flow. The system was allowed to cool to the room temperature and the products were washed with deionized water repeatedly until pH=7 and dried at 100 °C overnight.

1.9 Electrochemical measurement

Electrochemical performance of HCSs as electrode materials of supercapacitors was evaluated on a CHI 760E electrochemical workstation. Cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS) measurements were performed in a three-electrode system with 6 M KOH aqueous electrolyte. Platinum (Pt) wire was applied as counter electrode with Ag/AgCl electrode as reference electrode. The working electrode (2 mg) was prepared by mixing HCSs with acetylene black and poly-tetrafluoroethylene (PTFE) binder at a weight ratio of 80:10:10 and pressed on Ni foam current collector (geometric surface
area of ca. 1 cm²). The electrode was dried at 80 °C for 12 h before measurement. The range of electric potential was -1 to 0 V (Ag/AgCl) at different scan rates and different current densities at ambient temperature. Nyquist plots of the samples were recorded at open circuit potential with 5 mV ac amplitude over a frequency range of 100 kHz–0.01 Hz. Specific capacitance $C_s$ was calculated from GCD curve according to the following equation:

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

where $C_s$ is specific capacitance (F g⁻¹), I is discharge current (A), $\Delta t$ is discharge time (s), m is the mass of active materials (g) and $\Delta V$ is potential window (V).
2. Results and Discussion

2.1 Characterization of the P(BGF-a-DHBDT) alternating copolymer

**Figure S1** The $^1$H NMR spectra of two monomers DTT (a) and BGF (b) and the resulting alternating copolymer P(BGF-a-DHBDT) (c) in DMSO-$d_6$.

The successful synthesis of the alternating copolymer is demonstrated by $^1$H NMR spectroscopy (Figure S1). After polymerization, the proton signal at 2.14 ppm, which belongs to the thiol group in DTT (Figure S1a) and the peaks at 2.68, 2.82, 3.27 ppm, which are attributed to the epoxy group in BGF (Figure S1b) disappear. Meanwhile, new peaks at 5.16 and 4.69 ppm attributed to $-\text{OH}$ appear clearly (Figure S1c). Due to stronger electron-donating effect of the newly formed groups, the proton resonances ascribed to benzene rings shift up-field (from 6.85-7.92 ppm to 6.77-7.87 ppm). Moreover, the integral area ratio of various protons on the obtained polymers, i.e. $(k+l):(i+j+m+n):(o+h):(e+f+s+p):(d+g+r+q):(a^'+b^'):(c'^+d'):(b+c+t+u):...$
(a+v+w+z) is about 2 : 4 : 2 : 4 : 2 : 6 : 2 : 8 (Figure S1c), which is in good agreement with the theoretical ratio.

The $^{13}$C NMR spectrum is shown in Figure S2a, in which the signals from 100 to 165 ppm are attributed to aromatic carbons from four benzene rings. Three groups of signals around 70 ppm can be assigned to the carbon in -C-O. The resonance at 36 ppm is attributed to the carbon in -C-S. The FTIR spectrum is displayed in Figure S2b. A strong broad peak is found at 3400 cm$^{-1}$ which is attributed to stretching vibration of -OH, indicating that these hydroxyl groups might form strong multiple hydrogen bonds. Due to the presence of benzene ring structures, an absorbent signal is found at 3040 cm$^{-1}$, which belongs to stretching vibration of aromatic C-H. Meanwhile, the skeleton vibrations of aromatic rings are found at 1605, 1510 and 1450 cm$^{-1}$, respectively. The peaks at 2928 cm$^{-1}$ and 2854 cm$^{-1}$ are assigned to the asymmetric and symmetric stretching vibrations of -CH$_2$-, respectively. The peaks at 822 and 740 cm$^{-1}$ are attributed to out-of-plain vibration of aromatic C-H and -CH$_2$-, respectively. The broad peak from 700-500 cm$^{-1}$ is ascribed to the stretching vibration of C-S. The molecular weight and its distribution for P(BGF-a-DHBDT) were studied by GPC measurements. As shown in Figure S2c, the number average molecular weight of P(BGF-a-DHBDT) is 8710 Da and the molecular weight distribution $M_w/M_n$ is 2.28. The thermal properties of P(BGF-a-DHBDT) were investigated through TGA and DSC measurements. The decomposition temperature of P(BGF-a-DHBDT) is around 300 °C (Figure S2d). The glass transition temperature ($T_g$) is 110 °C (Figure S2e) and
Figure S2. Characterizations of the P(BGF-a-DHBDT) alternating copolymer. (a) $^{13}$C NMR spectrum in DMSO-$d_6$, (b) FTIR spectrum, (c) GPC curve, (d) TGA curve and (e) DSC curve.

No crystal melting peaks are found on the DSC curve, indicating that P(BGF-a-DHBDT) is an amorphous polymer. The high $T_g$ is favorable for the structure stability during the conversion of HPSs to porous HCSs by the high temperature pyrolysis.
2.2 Characterizations of the aggregates of the P(BGF-α-DHBDT) alternating copolymer

**Figure S3.** DLS curve of the P(BGF-α-DHBDT) assemblies. The inset shows a digital photograph of the P(BGF-α-DHBDT) assemblies in aqueous solution, which exhibit a stable bluish turbid solution and an obvious Tyndall effect.

**Figure S4.** (a) Photograph, (b) SEM image at a low magnification, (c) SEM image at a higher magnification and (d) TEM image of the HPSs.
**Figure S5.** Size distribution plots of (a) the HPSs and (b) HCSs, based on the statistical analyses of ca. 200 particles on the SEM images.

**Figure S6.** A typical TEM image of an ultrathin slice of HPSs embedded in epoxy resin at a low magnification. As shown in this figure, most of the particles are hollow. The reason that some of the particles do not show cavities is because the slicing did not pass through their cavities during the sample preparation of the ultrathin slices.
2.3 Characterization of the carbon materials obtained by pyrolysis of the uncrosslinked HPSs

**Figure S7.** SEM image of the product after the pyrolysis of the uncrosslinked HPSs at 800 °C under N₂ atmosphere. The uncrosslinked HPSs lose their spherical morphology after pyrolysis, giving irregular plate-like carbons.
2.4 Characterization of the CL-HPSs

The BGF units of P(BGF-α-DHBDT) HPSs was crosslinked through the Scholl reaction according to reported literature.\textsuperscript{5,6} The reaction was performed in chloroform at 58 °C with AlCl\textsubscript{3} as catalyst. As shown in Figure S8a, the color of the self-assembly powders changes from white to brown after crosslink. Moreover, as shown in Figure S8b and Figure S8c, the SEM and TEM images show that the spherical morphology are not destructed but well retained after crosslink.

\textbf{Figure S8.} Characterization of the CL-HPSs. (a) Photograph, (b) SEM image, and (c) TEM image.

After crosslinking, the resultant crosslinked HPSs (CL-HPSs) are stabilized, and cannot be dissolved in the good solvent, such as DMF. As illustrated in the inset of Figure S9, the CL-HPS/DMF solution shows a clear Tyndall effect, indicating the existence of colloidal particles. On the contrary, the uncrosslinked HPSs are easily dissolved in DMF and the particles are thereby disappeared in the DMF solution. As a result, no Tydall effect is observed from the DMF solution of HPSs. DLS measurements give an average diameter ($D$) of 358 nm with a polydispersity index (PDI) of 0.133 for CL-HPSs (Figure S9) in DMF, which is close to the size of HPSs in water (Figure S3). In other words, the CL-HPSs are stable and cannot be
disassociated.

**Figure S9.** DLS curve of CL-HPSs in DMF (0.5 mg/mL), a good solvent for the copolymer. The inset shows a digital photograph of the DMF solution of CL-HPSs (the inset left) and HPSs (the inset right) irradiated with a laser light. A clear Tyndall effect was observed for the DMF solution of CL-HPSs, indicating that they are stable in DMF. On the contrary, no Tyndall effect was observed for the uncrosslinked HPSs in DMF.

### 2.5 Characterization of the N₂ adsorption/desorption behavior of HPSs and CL-HPSs.

**Figure S10.** N₂ adsorption/desorption isotherms of (a) HPSs and (b) CL-HPSs before pyrolysis.
2.6 Characterization of the structural and chemical nature of HCSs and A-HCSs

Figure S11. (a) The XRD and (b) Raman spectrum for HCSs, (c) XRD and (d) Raman spectrum for A-HCSs.

XRD patterns and Raman spectroscopy were investigated to further study the microstructures of HCSs and A-HCSs. As shown in Figure S11a and Figure S11c, XRD patterns of HCSs and A-HCSs exhibit three broad peaks at 13.8°, 26.5° and 43.1°, respectively, which are characteristics of amorphous carbon. Two broad peaks at 26.5 (d = 0.336 nm) and 43.1 (d = 0.210 nm) corresponding to the (002) and (100) diffraction mode⁷-⁹ indicate the pseudographitic crystallite in the turbostratic carbon structure while a wide peak at about 13.8 (d = 0.642 nm) is ascribed to amorphous carbon¹⁰ possibly derived from the uniform microporous structure. Raman spectra exhibit two peaks of “D-band” at 1350 cm⁻¹ and “G-band” at 1590 cm⁻¹ (Figure S11b and Figure S11d), further confirmed that HCSs and A-HCSs were Partially
graphitized amorphous carbon. The “D-band” is derived from a breathing mode of A_{1g} symmetry in six fold aromatic rings which only becomes active when defects exist. The “G-band” is ascribed to E_{2g} symmetry which involves the in-plane bond stretching motion of sp^2 carbon atom pairs. It exists in all sp^2 sites (both in rings and in chains)^{11-14}. The intensity ratio of D to G band (I_G/I_D) is widely used as probe to calculate the degree of graphitization in carbon materials. In our case the I_G/I_D are 1.01 and 1.03 for HCSs and A-HCSs, respectively. The almost same I_G/I_D values indicated that chemical activation by KOH has little impact on bonding state of carbon and the degree of graphitization. Moreover, One overtone band of 2D is observed at 2850 cm^{-1} on Raman spectra.

Figure S12. EDX spectra of HCSs (a) and A-HCSs (b).
**Figure S13.** Characterizations of the A-HCSs: (a) SEM image, the inset shows a TEM image of an ultrathin slice; (b) HR-TEM image of an ultrathin slice; (c) N2 adsorption/desorption isotherm of the HCSs; (d) the pore size distribution curve calculated by the DFT method.

SEM and TEM images reveal the retention of the hollow spherical structure for the activated HCSs (A-HCSs) and the nearly unchanged microporous structure in the A-HCSs (Figure S13a,b). The N$_2$ adsorption-desorption analysis of the A-HCSs shows a combined isotherm of Types I and II with a small hysteresis loop (Figure S13c), indicating the presence of small mesopores, which most likely arises from the interconnection of partial micropores after the KOH activation. The average pore size of the A-HCSs is 0.8 ± 0.3 nm, almost identical to that of the unactivated HCSs. The pore size distribution of the major peak for the A-HCSs is slightly broadened (Figure S13d) and the volume fraction of the micropores has barely changed (from 0.76 to
0.79, Table 1 in the main text). These results therefore confirm that the original pore structure and size are largely retained. Similar to the HCSs, the A-HCSs consist of partially graphitized carbons with a high degree of graphitization ($I_G/I_D = 1.03$, Figure S11). The C content of the A-HCSs is measured to be ca. 93 at.%, almost unchanged in comparison with that of HCSs (Table 1 and Figure S12). The high carbon content and high degree of graphitization facilitate the charge transfer in the carbon matrix of the A-HCSs.
2.7 Evaluation of the capacitive performance of HCSs and A-HCSs as electrode materials for supercapacitors.

**Figure S14.** CV curves of A-HCSs as electrodes at different scan rates in 6 M KOH electrolyte solution.

**Figure S15.** The galvanostatic charge/discharge curve of HCSs without KOH activation at a current density of 1 A g$^{-1}$ in 6 M KOH electrolyte solution.
2.8 Comparison of the electrochemical performance of carbon materials in our work with those reported in some literature.

Table S1 Comparison of the electrochemical performance of carbon materials in our work with those reported in some literature.

| Sample names                                                      | Electrolyte | SSAs /m² g⁻¹ | Cₛ / F g⁻¹ | Literature   |
|------------------------------------------------------------------|-------------|---------------|------------|--------------|
| A-HCSs                                                           | 6M KOH      | 2580          | 292        | This work    |
| Melamine resin-functionalized GOs                                | 1M LiPF₆    | 1040          | 210        | Ref.15       |
| Nitrogen-containing mesoporous carbon spheres                    | 1M LiPF₆    | 1460          | 160        | Ref.16       |
| Commercial activated carbons                                     | 1M TEA-BF₄ | 2347          | 112        | Ref.17       |
| Nitrogen-doped porous carbonaceous nanofibers                    | 6M KOH      | 562           | 202        | Ref.18       |
| Nitrogen-doped graphene hydrogels                                | 5M KOH      | N/A           | 190        | Ref.19       |
| CNT                                                              | 7M KOH      | 644           | 57         | Ref.20       |
| Graphene/polyaniline composite paper                             | 1M H₂SO₄    | 94            | 233        | Ref.21       |
| PF-resin                                                         | 6M KOH      | 2445          | 234        | Ref.22       |
| KOH-activated nitrogen-doped porous carbons                      | 6M KOH      | 2970          | 259        | Ref.23       |
| Hydrothermal reduction of graphene oxide dispersions              | 5M KOH      | 215           | 220        | Ref.24       |
| Three-dimensional graphene-based frameworks                       | 1M H₂SO₄    | 350           | 226        | Ref.25       |
| Reduced graphene oxide paper                                     | 6M KOH      | 630           | 255        | Ref.26       |
| Ordered mesoporous carbon monolith                               | 6M KOH      | 1800          | 186        | Ref.27       |
| PDU-15                                                           | 6M KOH      | 1410          | 200        | Ref.28       |
| Carbon nanospheres                                               | 2M H₂SO₄    | 1312          | 95         | Ref.29       |
| Nitrogen-doped Hollow Carbon Spheres                             | 1M H₂SO₄    | 427           | 160        | Ref.30       |
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