Supporting Information

Solution-Processable Porous Graphitic Carbon from Bottom-Up Synthesis and Low-Temperature Graphitization

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1. General Information

Starting materials, reagents, and solvents were purchased from Aldrich, Alfa Aesar, TCI, and Acros, and were used as received without further purification unless otherwise specified. Analytical thin-layer chromatography (TLC) tests were performed on glass that was precoated with silica gel 60-F254 (Sorbtech). Flash column chromatography was carried out using a Biotage® Isolera™ Prime. Solution phase $^1$H- and $^{13}$C-NMR spectra were obtained on Bruker Ascend 400 MHz spectrometers at room temperature. Chemical shifts are reported in ppm relative to the signals corresponding to the residual non-deuterated solvents (for $^1$H NMR: CDCl$_3$ $\delta$ = 7.26 ppm; for $^{13}$C NMR: CDCl$_3$ $\delta$ = 77.16 ppm). High-resolution Atmospheric Pressure Chemical Ionization (HR-APCI) mass spectra were performed using a Thermo Fisher Scientific Q Exactive Focus. Thermogravimetric analysis (TGA) data were collected on Mettle-Toledo TGA-DSC-1 at a heating rate of 20 °C min-1 from 30 °C to 900 °C under N$_2$ atmosphere. Powder X-ray diffraction (PXRD) was obtained with a Bruker D8-Focus Bragg-Brentano X-ray Powder Diffractometer equipped with a Cu sealed tube ($\lambda$ = 1.54178 Å) at 40 kV and 40 mA.
2. Synthesis

Monomers Synthesis

DAB: A mixture of 1-(2-iodophenyl)ethan-1-one (12.3 g, 50 mmol), Cu powder (31.8 g, 500 mol) and Copper(I) thiophene-2-carboxylate (47.7 g, 250 mmol) in DMSO (500 mL) was heated at 70 °C for 24 h. After the reaction was cooled down to room temperature, the precipitate was filtered out. The filtrate was poured into water. The white precipitate was filtered and washed with water. The crude product was purified by column chromatography (SiO$_2$, hexanes : EtOAc = 5:1) to yield DAB as a white solid (4.0 g, 67%).

$^{1}$H NMR (400 MHz, Chloroform-d): δ 7.73 (dd, $J = 7.5, 1.7$ Hz, 2H), 7.52-7.41 (m, 4H), 7.16 (dd, $J = 7.5, 1.7$ Hz, 2H), 2.25 (s, 2H).

$^{13}$C NMR (100 MHz, Chloroform-d): δ 201.68, 140.68, 138.76, 131.11, 130.78, 128.62, 127.67. HRMS (APCI): calcd for C$_{16}$H$_{14}$O$_2$ [M+H]$^+$ m/z=239.1067; found m/z=239.1063.

PGC-Pr: A 20 mL vial was charged with DAB (0.50 g, 2.1 mmol) and MSA (3 mL). The mixture was sonicated for 5 min. The resulting orange solution was heated to 90 °C for 1 h. Then the temperature was increased to 150 °C and kept for 24 h in a flask open to the air. The black solid was filtered, washed with methanol, and further washed by boiling THF in a Soxhlet extractor. The remaining solid was vacuum dried to give a black solid PGC-Pr (0.41 g, quantitative). Subsequently, the solid was annealed at various temperatures under N$_2$ for 3 h to afford PGT-T (PGC-300, PGC-400, PGC-500, PGC-600, PGC-700, PGC-800, and PGC-1000 respectively). N$_2$ flow rate: 100 mL min$^{-1}$. Temperature ramp rate: 2 °C min$^{-1}$. 


Figure S1. $^1$H (400 MHz, CDCl$_3$, RT) and $^{13}$C NMR (100 MHz, CDCl$_3$, RT) spectra of DAB monomer.
3. Porosity Measurements and Stability Tests

N₂ sorption isotherms at 77 K were measured with a Micromeritics ASAP 2020 surface area and pore size analyzer. Prior to the gas adsorption measurements, the sample was degassed for 10 h at 120 °C. All three materials showed type I isotherms in the lower pressure region with increased adsorption at higher pressure. The partial pressure range for the calculation of Brunauer-Emmett-Teller (BET) specific surface areas of samples was obtained from the corresponding Rouquerol plots, where the V(1-P/P₀) is continuously increasing along with P/P₀.¹ ² Pore size distribution data were calculated from the N₂ sorption isotherms based on the Nonlocal Density Functional Theory (NLDFT) method in the Micromeritics ASAP 2020 software package (assuming slit pore geometry).¹ All three materials showed primarily micropores at 1.2 ~ 1.5 nm, with a small population of broadly distributed mesopores. Due to the amorphous nature and possible interpenetration, the pore sizes and their distributions were not heavily dependent on their ideal crystalline structures. The mesopores were attributed to reaction defects formed during the Suzuki polymerization and interparticulate voids of the amorphous solid.³

Standard procedure: **PGC-800** (50 mg) solid material was suspended in 10 mL of each following solutions (1) 12 M HCl at 80 °C for 7 days; (2) 14 M NaOH in H₂O/MeOH at 80 °C for 7 days; (3) 50 equiv. NaBH₄ in MeOH at 80 °C for 7 days; (4) chromic acid solution (0.1 M K₂Cr₂O₇ in concentrated H₂SO₄) for 3 days; or (5) 98% TfOH for 7 days. Afterwards, the solid material was collected by filtration, washed with H₂O and MeOH, and dried in vacuum. Subsequently, the remaining solid was subjected to solid state CP-MAS NMR and nitrogen adsorption isotherm tests.

As expected for a graphitic carbon-based material, **PGC-800** demonstrated excellent stability after extended treatments in harsh chemical conditions, including acids (12 M HCl at 80 °C, 7 days; or 98% TfOH, 7 days), base (14 M NaOH in H₂O/MeOH at 80 °C, 7 days), reducing agent (50 equiv. NaBH₄ in MeOH at 80 °C, 7 days), and oxidant (0.1 M K₂Cr₂O₇ in concentrated H₂SO₄). BET surface area and conductivity remained mostly intact through all treatments, demonstrating that the fully graphitized backbone endowed the material with exceptional chemical stability.
Figure S2. $N_2$ adsorption isotherms (a) and BET surface areas (b) of PGC-800 after each treatment.
4. Fourier Transform Infrared Spectroscopy (FT-IR)

Fourier transform infrared spectroscopy (FT-IR) spectra were recorded by ZnSe attenuated total reflection on a Shimadzu IRAffinity-1S spectrometer. FT-IR peaks corresponding to aromatic carbonyl groups at 1670–1707 cm\(^{-1}\) were observed in both monomer DAB and PGC-Pr, indicating the incomplete conversion of the ATC reaction. The finger print feature of 1,2-disubstituted benzene rings at 748 cm\(^{-1}\) and 1,3,5-trisubstituted benzene rings at 880, 810, and 695 cm\(^{-1}\) were observed in PGC-Pr,\(^4\) due to the incomplete graphitization without annealing.

Figure S3. Full FT-IR spectra (a) and aromatic fingerprint region FTIR spectra of DAB, PGC-Pr, PGC-600, and PGC-1000.
5. Solid-State NMR

Solid-state CP/MAS $^{13}$C NMR spectra were obtained on a Bruker Avance 400 MHz spectrometer with 4 mm CP/MAS probes and MAS rates of 10 kHz at room temperature. The spectra of DAB showed the signal of $sp^3$ methyl groups at 30 ppm and acetyl groups (C=O) at 200 ppm (the splitting was ascribed to the rotamers), while no distinct signals were observed for PGC-Pr, indicating the high degree of polymerization.$^5$ Both PGC-Pr and PGC-600 showed peaks in 120-130 ppm range, indicating the dominant presence of $sp^2$ carbons. The peak of PGC-1000 was not measurable due to the presence of strong paramagnetism.

Figure S4. Solid-state CP/MAS $^{13}$C NMR spectra of DAB, PGC-Pr and PGC-600.
6. X-ray absorption near-edge structure (XANES)

C K- and O K- XANES measurements were carried out at the National Synchrotron Light Source II of Brookhaven National Laboratory beamline SST-1 operated by the National Institute of Standards and Technology. Measurements were performed in partial electron yield (PEY) mode with a nominal resolution of 0.1 eV. The PEY signal was normalized to the incident beam intensity of a clean gold grid to eliminate the effects of any incident beam fluctuations and optics absorption features. The $\pi^*$ feature in the O K-edge data represents the transition of O 1s electrons to $\pi^*$ C=O states derived from the acetyl groups. The decrease in the intensity of this feature for PGC-600 relative to PGC-Pr points to a loss of C=O moieties. The broad feature centered at 540.7 eV can be assigned to the transitions of O 1s core-level electrons to $\sigma^*$ C–O and C=O states of acetyl groups and other oxygen-containing functionalities.

![XANES data at the O K-edge of PGC-Pr and PGC-600.](image)

**Figure S5.** XANES data at the O K-edge of PGC-Pr and PGC-600.
7. Film Fabrication and Scanning Electron Microscope (SEM) Images

DAB monomer (150 mg) was dissolved in MSA (1 mL) to form the reaction solution. The solution was drop-cast onto a 6” X 6” glass substrate and sandw Iched between another piece of glass of the same size. These glass substrates were pre-treated by spraycoating a thin layer of PTFE to prevent undesired adhesion of the membrane onto the glass. Two pieces of 150 mm-thick micro cover glass slides were placed in between (Figure S5a). The sandw iched system was heated at 110 °C for 24 h. After the reaction, the freestanding PGC membrane was detached from the glass substrate and soaked in methanol for 45 min. It was then taken out and soaked in another batch of clean methanol. After repeating twice, the membrane was dried in air. The following annealing processes were conduct under the same condition as power samples. Field-emission scanning electron microscopic (SEM) images were collected using the FEI Quanta 600 FE-SEM.
Figure S6. (a) Graphic representation of thin film fabrication using an MSA solution of the monomer. Top view SEM images of PGC film (b), PGC-600 film (c), and PGC-1000 film (d). Cross-sectional view SEM images of PGC film (e), PGC-600 film (f), and PGC-1000 film (g).
8. Conductivity

Conductivity of PGC and $p$-PPN films was evaluated by a four-point probe method. The electrical resistance was measured with a Keithley 2450 SourceMeter. The thickness of the pellet was measured using scanning electron microscopy. The electrical conductivity was calculated based on the slope of the I-V plots.
Figure S7. I-V plots from 4-probe conductivity measurement of PGC and p-PPN films pyrolyzed at different temperatures.
| Name          | Pyrolysis Temperature / °C | Electrical Conductivity / S cm⁻¹ | Reference |
|--------------|----------------------------|----------------------------------|-----------|
| PGC-300      | 300                        | 1.31 X 10⁻⁸                      |           |
| PGC-400      | 400                        | 4.92 X 10⁻⁷                      |           |
| PGC-500      | 500                        | 2.07 X 10⁻⁴                      |           |
| PGC-600      | 600                        | 0.031                            |           |
| PGC-700      | 700                        | 13.3                             |           |
| PGC-800      | 800                        | 36.4                             |           |
| PGC-1000     | 1000                       | 94.8                             |           |
| RuO₂/ACNF    | 800                        | 0.59                             | This work |
| PPSα-CD      | 800                        | 0.62                             | 6         |
| URC-700      | 700                        | ~0                               | 7         |
| URC-800      | 800                        | ~0.25                            |           |
| URC-900      | 900                        | ~2.75                            | 8         |
| URC-1000     | 1000                       | ~4.10                            |           |
| URC-1100     | 1100                       | ~4.40                            |           |
| 1300-CC      | 1300                       | 14.97                            |           |
| 1300-Ni-GCM  | 1300                       | 25.75                            | 9         |
| 1300-Ani-GCM | 1300                       | 24.75                            |           |
| NGPCs-850    | 850                        | 6.93                             | 10        |
| PAC-10       | 1000                       | 6.23                             | 11        |
| GPAN-1000    | 1000                       | 5.32                             | 12        |
| GPAN-1800    | 1800                       | 51.01                            |           |
| GPAN-2200    | 2200                       | 75.91                            |           |
| C-800        | 900                        | 0.19                             | 13        |
| C-1400-3     | 1400                       | 54.5                             | 14        |
9. X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) analysis was carried out with Omicron XPS/UPS system with Argus detector using Omicron’s DAR 400 dual Mg/Al X-ray source. The deconvoluted C 1s spectra were assigned as follows: 283.3 eV for carbon of the acetyl groups [H₃C(C=O)], 284.4 eV for sp² carbon, 285.4 eV for sp³ carbon, 289.1 eV for C=O, 287.7 eV for O-C-O.¹⁵-¹⁶ DAB monomer showed the corresponding ratio of 2:2:12 for methyl:acetyl (C=O):biphenyl groups. Without pyrolysis, PGC-Pr was revealed to have decent amount of acetyl groups. Pyrolysis significantly diminished acetyl groups, and the ratio of sp²/sp³ carbon increased from 1.485 (PGC-Pr) to 1.847 (PGC-600) to 3.745 (PGC-1000), confirming the increased degree of graphitization.
Figure S8. C 1s XPS spectra and deconvolution for (a) PGC-Pr, (b) PGC-600, (c) PGC-1000, and (d) DAB.
10. Elemental Analysis

Carbon, hydrogen, and nitrogen elemental analysis was carried out by Perkin-Elmer Model 2400 CHN Analyzer at operating temperature of 950°C. The content of oxygen and other elements was estimated by subtracting the carbon, hydrogen, and nitrogen contents. In PGC-Pr, a relatively low carbon content was observed due to the low degree of graphitization, the presence of residual unreacted functional groups, and entrapped solvent. With higher pyrolysis temperatures, carbon content gradually increased, while hydrogen, oxygen, and other element content decreased. This observation was in consistent with the FT-IR, solid-state NMR, XPS, and conductivity results.

Table S2. Elemental analysis of PGC-Pr, PGC-600, and PGC-1000.

|          | C (%) | H (%) | N (%) | O and Other (%) |
|----------|-------|-------|-------|-----------------|
| PGC-Pr   | 77.79 | 9.84  | N/A   | 12.37           |
| PGC-600  | 90.51 | 4.04  | N/A   | 5.45            |
| PGC-1000 | 93.91 | 2.84  | N/A   | 3.25            |
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