

## Supporting Information

### **A stepwise crosslinking strategy toward lamellar carbon frameworks with covalently connected alternate layers of porous carbon nanosheets and porous carbon spacers**

Junlong Huang,<sup>a</sup> Yanhuan Lin,<sup>a</sup> Shaohong Liu,<sup>\*a</sup> Qiantong Liu,<sup>a</sup> Yiwei Sun,<sup>a</sup> Yeru Liang,<sup>a</sup> Yongming Chen,<sup>b</sup> Ruowen Fu<sup>\*a</sup> and Dingcai Wu<sup>\*a</sup>

<sup>a</sup> *Materials Science Institute, PCFM Lab and GDHPRC Lab, School of Chemistry, Sun Yat-sen University, Guangzhou 510275, P.R. China.*

<sup>b</sup> *School of Materials Science and Engineering, Sun Yat-sen University, Guangzhou 510275, P.R. China.*

E-mail: wudc@mail.sysu.edu.cn, cesfrw@mail.sysu.edu.cn, liushh27@mail.sysu.edu.cn

## EXPERIMENTAL PROCEDURES

### Preparation of PTEPM-*b*-PS block copolymers

Reversible addition fragmentation chain transfer polymerization (RAFT) was used to synthesize the block copolymers. In a typical synthesis process, 41 mg chain transfer agent cumyl dithiobenzoate (CDB) and 2.5 mg initiator 2, 2'-azobisisobutyronitrile (AIBN) were dissolved in a flask with 11.375 g monomer triethoxysilyl propyl methacrylate (TEPM) (molar ratio TEPM : CDB : AIBN = 523 : 10 : 1). After 1 h under N<sub>2</sub> purge, the flask was sealed and put into an oil bath of 60 °C and stirred for 19 h. The reaction was stopped by opening the flask and cooling down to room temperature. After that, the mixture was precipitated into a large excess of methanol/water mixture (7 : 3 by volume, about 200 mL) three times and then centrifuged. After freeze-drying for 24 h, PTEPM<sub>79</sub> was collected.

Next, 0.42 g PTEPM<sub>79</sub> was dissolved in a flask with 6.28 mL styrene (St) (molar ratio PTEPM<sub>79</sub> : St = 1 : 3000) and then sealed and purged with N<sub>2</sub> for 1 h. Subsequently, the flask was put into an oil bath of 90 °C and stirred for 5 h. After that, the product was diluted with an appropriate amount of tetrahydrofuran (THF) (about 10 mL) and precipitated by a large amount of methanol (about 150 mL). After filtration and vacuum-drying at 40 °C, PTEPM<sub>79</sub>-*b*-PS<sub>125</sub> was obtained. Other PTEPM-*b*-PS block copolymers were synthesized according to the above procedure.

### Self-assembly of PTEPM-*b*-PS

At first, a bulk polymeric film was prepared by dissolving 0.8 g PTEPM<sub>79</sub>-*b*-PS<sub>125</sub> into an appropriate amount of THF (about 25 mL) and slowly evaporating solvent for

4 days. After drying at 60 °C in vacuum for 6 h, the bulk polymeric film went through microphase separation by annealing in a vacuum oven at 120 °C for 48 h. After that, lamellar block copolymer PTEPM<sub>79</sub>-*b*-PS<sub>125</sub> was obtained.

### **Crosslinking of PTEPM microphases**

The lamellar block copolymer PTEPM<sub>79</sub>-*b*-PS<sub>125</sub> was soaked in diluted hydrochloric acid (10%) and stirred for 24 h at room temperature. After filtration and drying at 80 °C in vacuum, *x*PTEPM<sub>79</sub>-*b*-PS<sub>125</sub> was obtained.

### **Hypercrosslinking of PS microphases**

6 g AlCl<sub>3</sub> was completely dissolved in 30 mL CCl<sub>4</sub> and 20 mL nitrobenzene in a three-necked flask equipped with reflux condenser and heated to 75 °C. Next, 0.2 g solid *x*PTEPM<sub>79</sub>-*b*-PS<sub>125</sub> was added to start the Friedel-Crafts hypercrosslinking reaction. The reaction was kept at 75 °C and stirred for 48 h, terminated by adding 50 mL mixture of ethanol and water (1 : 1 by volume) slowly. The product was filtered off, washed with mixture of acetone and 10% hydrochloric acid (3 : 1 by volume) three times, and then washed with distilled water three times. After drying at 80 °C in vacuum, *x*PTEPM<sub>79</sub>-*b*-*x*PS<sub>125</sub> was obtained.

DS-*x*PTEPM-*b*-*x*PS were synthesized utilizing 0.1 g *x*PTEPM-*b*-PS as precursors, which were dispersed in 30 mL CCl<sub>4</sub> for 48 h to form homogenous mixture. Then the dispersion was added into a heated mixture of 5 mL CCl<sub>4</sub>, 2 g AlCl<sub>3</sub> and 15 mL nitrobenzene, and stirred at 75 °C for 48 h. The subsequent treatment process was the same with *x*PTEPM<sub>79</sub>-*b*-*x*PS<sub>125</sub>.

### **Preparation of PCSs-PCNs**

The as-prepared  $x$ PTEPM<sub>79</sub>- $b$ - $x$ PS<sub>125</sub> was carbonized at 800 °C in N<sub>2</sub> flow for 3h with a heating rate of 5 °C min<sup>-1</sup>, leading to formation of C- $x$ PTEPM- $b$ - $x$ PS. Next, 0.1 g C- $x$ PTEPM- $b$ - $x$ PS was soaked in mixture solution of 1 mL ethanol, 2 mL hydrofluoric acid and 2 mL distilled water for 18 h. After centrifugation, the product was washed with distilled water and ethanol. After drying at 80 °C, PCSs-PCNs was obtained.

DSCNs was synthesized with DS- $x$ PTEPM- $b$ - $x$ PS as carbon precursors through the same treatment processes with PCSs-PCNs.

### **Preparation of C- $x$ PTEPM- $b$ -PS**

$x$ PTEPM<sub>79</sub>- $b$ -PS<sub>125</sub> was treated with the same carbonization and silica etching procedures as  $x$ PTEPM<sub>79</sub>- $b$ - $x$ PS<sub>125</sub> to yield C- $x$ PTEPM- $b$ -PS.

### **Preparation of C- $x$ PTEPM**

PTEPM was soaked in diluted hydrochloric acid (10%) and stirred for 24 h at room temperature. After filtration and drying at 80 °C in vacuum, the as-obtained  $x$ PTEPM underwent the same carbonization and silica removal processes with  $x$ PTEPM<sub>79</sub>- $b$ - $x$ PS<sub>125</sub> to obtain C- $x$ PTEPM.

### **Preparation of C- $x$ PS**

PS was synthesized by using atom transfer radical polymerization (ATRP). Typically, a Schlenk flask was charged with 27.43 mL St, 0.69 mL ethyl  $\alpha$ -bromoisobutyrate, 0.053 g CuBr<sub>2</sub>, and 1.5 mL N, N, N', N', N''-pentamethyl diethylene triamine. After purging N<sub>2</sub> for 20 min, 0.344 g CuBr was added to the solution quickly. After another 1 h under N<sub>2</sub> purge, the flask was sealed and put into

an oil bath of 90 °C and stirred for 18 h. The reaction was stopped by opening the flask and cooling down to room temperature. Afterwards, the product was diluted with an appropriate amount of THF (about 20 mL), passed through a column of neutral alumina, and precipitated into a large amount of methanol (about 400 mL). After filtration and vacuum-drying at 40 °C, PS was obtained.

Next, 0.2 g PS powder went through the same hypercrosslinking treatment process with  $x$ PTEPM<sub>79</sub>-*b*-PS<sub>125</sub> to yield  $x$ PS. Subsequently,  $x$ PS was carbonized at 800 °C in N<sub>2</sub> flow for 3h with a heating rate of 5 °C min<sup>-1</sup> to obtain C- $x$ PS.

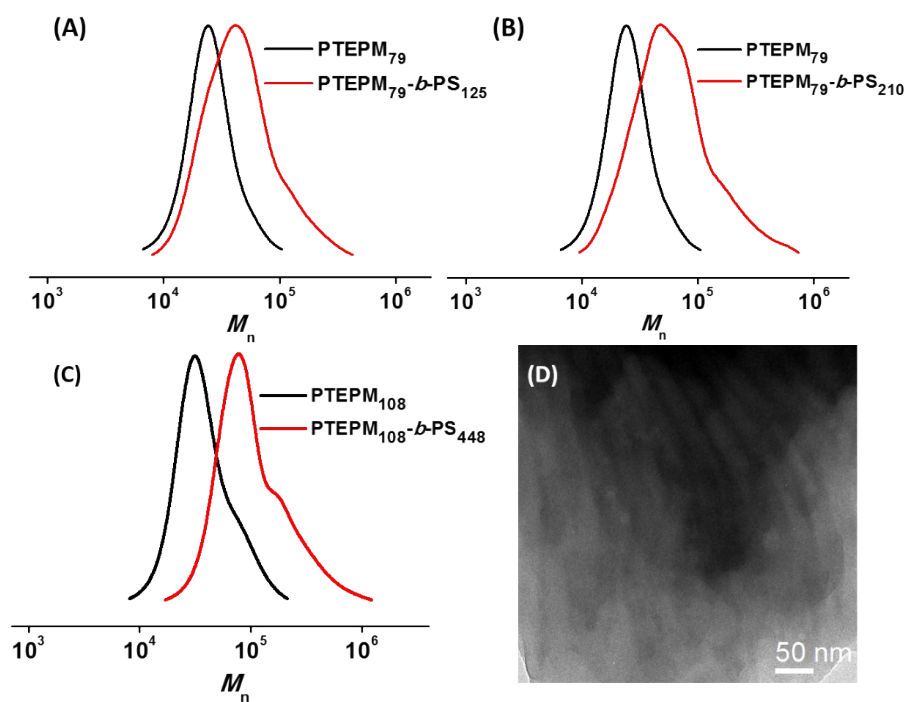
### **Sample characterization**

The molecular weight (MW) and polydispersity index (PDI) of PTEPM-*b*-PS were determined by a Waters Breeze 1515 gel permeation chromatography (GPC). The nanomorphologies were visualized by using a field-emission scanning electron microscopy (FESEM, Hitachi S-4800) and a transmission electron microscopy (TEM, Tecnai G2 Spirit). Pore structures were determined using a Micromeritics ASAP 2020 instrument at 77 K. Brunauer-Emmett-Teller (BET) and Langmuir surface areas were analyzed according to BET and Langmuir theories, respectively. Pore size distributions were calculated based on the original Density Function Theory (DFT). The Fourier-transform infrared spectra (FT-IR) were recorded on a Bruker TENSOR 27 infrared spectroscopy (Germany) by a KBr disk method. Thermogravimetric analysis (TGA, PE Pyris1 TGA) was carried out to characterize the thermal stability of PTEPM-*b*-PS,  $x$ PTEPM-*b*-PS, and  $x$ PTEPM-*b*- $x$ PS. The Raman spectra were determined by Laser Micro-Raman Spectrometer (Renishaw inVia). The electrical

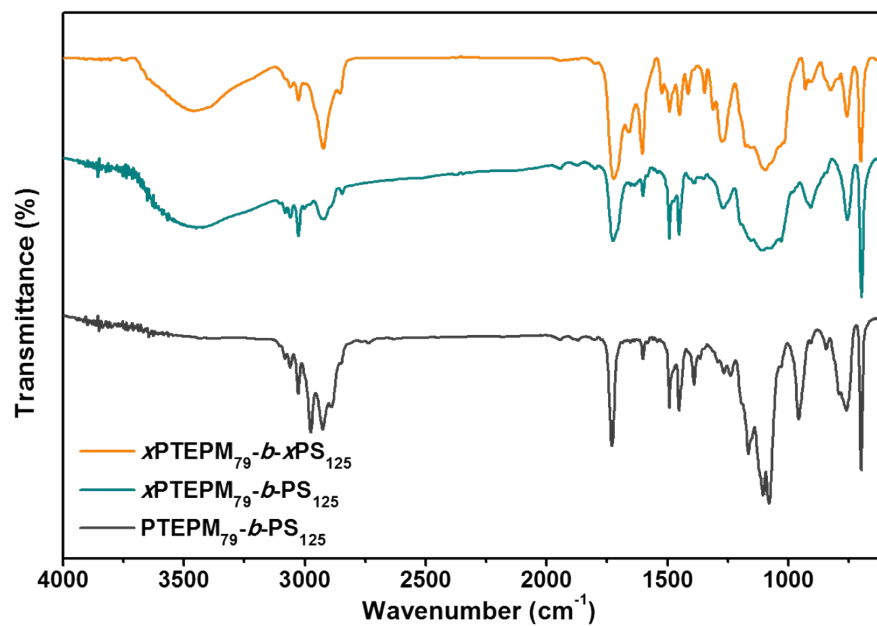
conductivity was measured by a ST2722-SZ four-probe resistivity measurement instrument.

**Table S1.** Structure parameters of PTEPM-*b*-PS with different molecular ratios and molecular weights.

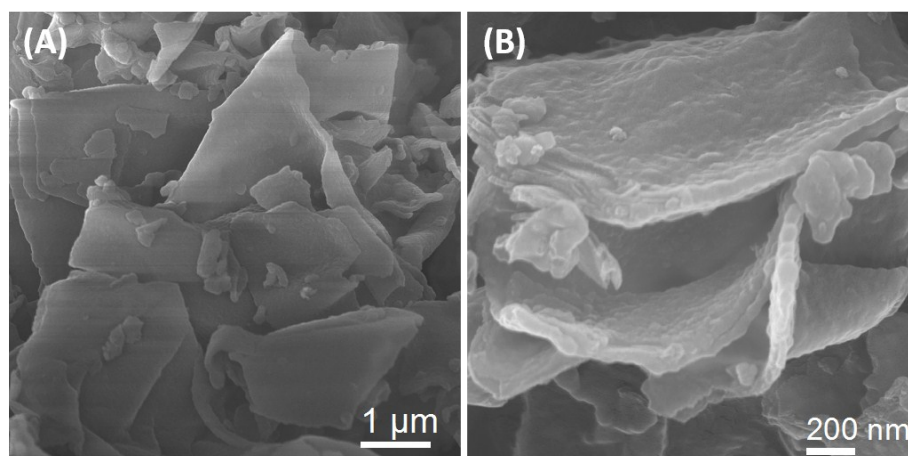
Sample	$M_n$	Fraction of PTEPM (%)
PTEPM <sub>79</sub>	22.8 K	-
PTEPM <sub>86</sub>	24.9 K	-
PTEPM <sub>108</sub>	31.5 K	-
PTEPM <sub>79</sub> - <i>b</i> -PS <sub>125</sub>	35.4 K	64
PTEPM <sub>79</sub> - <i>b</i> -PS <sub>210</sub>	44.3 K	51
PTEPM <sub>108</sub> - <i>b</i> -PS <sub>448</sub>	78.0 K	40



**Fig. S1** Molecular weight distribution curves of (A) PTEPM<sub>79</sub> and PTEPM<sub>79</sub>-*b*-PS<sub>125</sub>, (B) PTEPM<sub>79</sub> and PTEPM<sub>79</sub>-*b*-PS<sub>210</sub>, and (C) PTEPM<sub>108</sub> and PTEPM<sub>108</sub>-*b*-PS<sub>448</sub>. (D) TEM image of *x*PTEPM<sub>79</sub>-*b*-PS<sub>125</sub>.

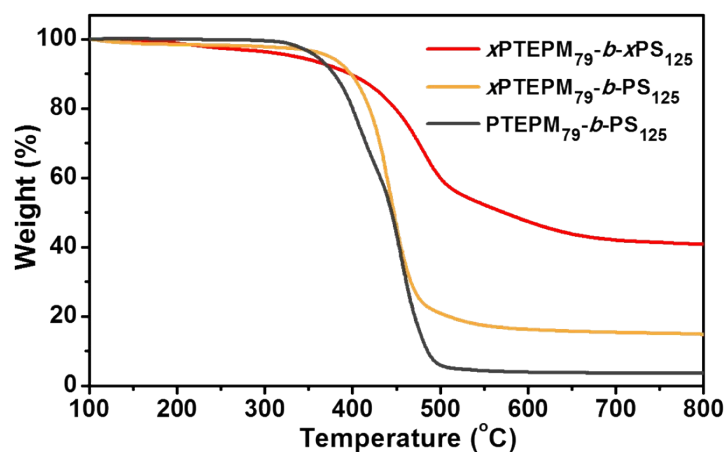


**Fig. S2** FT-IR spectra of PTEPM<sub>79</sub>-*b*-PS<sub>125</sub>, xPTEPM<sub>79</sub>-*b*-PS<sub>125</sub>, and xPTEPM<sub>79</sub>-*b*-xPS<sub>125</sub>.

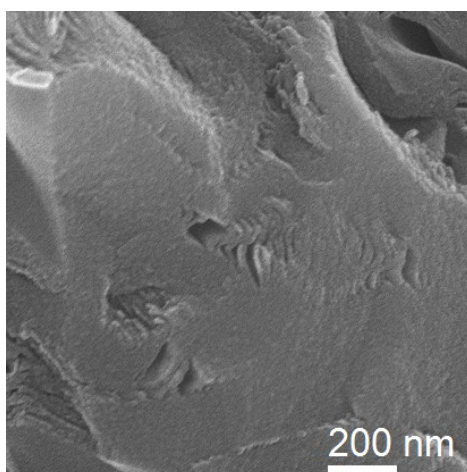


**Fig. S3** SEM images of (A) DS-xPTEPM-*b*-xPS and (B) the related DSCNs.

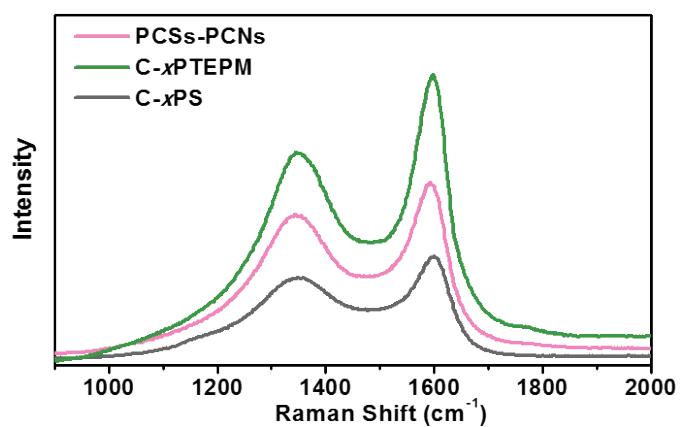




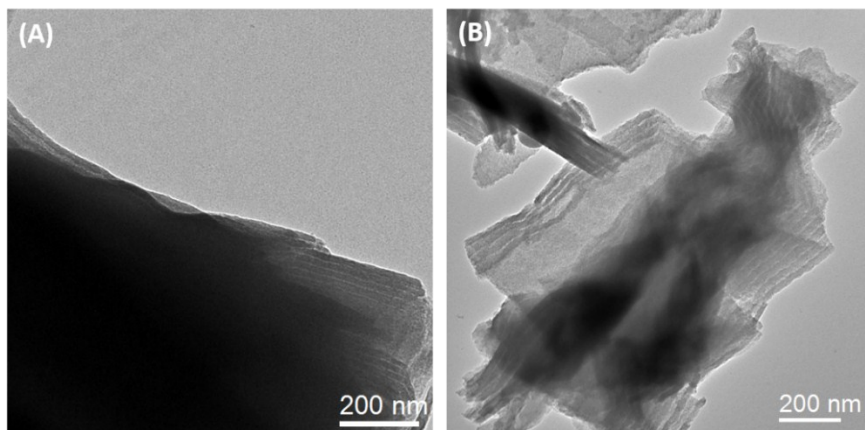
**Fig. S4** Thermogravimetric analysis curves of PTEPM<sub>79</sub>-*b*-PS<sub>125</sub>, xPTEPM<sub>79</sub>-*b*-PS<sub>125</sub>, and xPTEPM<sub>79</sub>-*b*-xPS<sub>125</sub>.



**Fig. S5** SEM image of C-xPTEPM-*b*-PS.



**Fig. S6** Raman spectra of PCSs-PCNs (pink), C-xPTEPM (green), and C-xPS (gray).



**Fig. S7** TEM images of PCSs-PCNs derived from (A) PTEPM<sub>79</sub>-*b*-PS<sub>210</sub> and (B) PTEPM<sub>108</sub>-*b*-PS<sub>448</sub>.