Electronic Supplementary Information

Creating Extra Pores in Microporous Carbon via a Template Strategy for Remarkable Enhancement of Ambient-Pressure CO₂ Uptake

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1. Experimental Details

All reagents were purchased from Sigma-Aldrich or Alfa and used as received unless otherwise indicated. Tetrakis(4-bromophenyl)silane\textsuperscript{[1]} and PPN-4\textsuperscript{[2]} were synthesized according to the procedures reported in literature.

1.1 Synthesis of PPN-4

To a solution of 2,2’-bipyridyl (1.41 g, 9.04 mmol), bis(1,5-cyclooctadiene)nickel(0) (Ni(COD)\textsubscript{2} , 2.5 g, 9.04 mmol), and 1,5-cyclooctadiene (COD, 0.18 mL, 9.12 mmol) in anhydrous DMF/THF (150 mL/225 mL) add tetrakis(4-bromophenyl)silane (1.27 g, 2.0 mmol), and the mixture was stirred at room temperature under argon atmosphere overnight. Then, the mixture was cooled in ice bath, 6 mol/L HCl solution (125 mL) was added, the resulting mixture was stirred for another 12 h. The precipitate was collected, then washed with Methanol (6 × 100 mL), and H\textsubscript{2}O (6 × 100 mL), respectively, and dried in vacuo to produce PPN-4 as off-white powder.

1.2 Synthesis of PPN-4/C600

The powder of PPN-4 was heat-treated in a horizontal quartz reactor under an N\textsubscript{2} flow, and heated to 600 ºC with a heating rate of 5 ºC/min, the sample was pyrolyzed at 600 ºC for 8 h to afford the carbon material designated as PPN-4/C600-Si. Then the obtained PPN-4/C600-Si was soaked into a 2 M KOH solution at 120 ºC under hydrothermal conditions for two days followed by washing with water and methanol to afford the final microporous carbon material designated as PPN-4/C600.

1.3 Synthesis of PPN-4/C800 and PPN-4/C1000

The synthesis procedures of PPN-4/C800 and PPN-4/C1000 were similar to PPN-4/C600 except the heat-treated temperature at 800 ºC and 1000 ºC respectively.

2. Characterizations

PXRD patterns were collected on a Bruker D8 Advance X-ray diffractometer. Gas sorption experiments were carried out on a surface area analyzer ASAP-2020. N\textsubscript{2} gas
sorption isotherms were measured at 77 K using a liquid N₂ bath. CO₂ sorption isotherms were collected at 273 K using a water-ice bath and at 295 K with a water bath. Prior to the measurements, the samples were degassed for 10 h at 180 °C.

**Fig. S1.** Powder XRD patterns of the porous carbons PPN-4/C600, PPN-4/C800 and PPN-4/C1000.

**Fig. S2.** Powder XRD patterns of the PPN-4.
Fig. S3. Powder XRD patterns of the PPN-4/C600-Si.
Fig. S4. The comparison of EDS analysis of PPN-4/C600-Si (a) and PPN-4/C600 (b).
Fig. S5. N$_2$ sorption isotherms for PPN-4, PPN-4/C600-Si and PPN-4/C600. (adsorption: filled; desorption: open; PPN-4: black squares; PPN-4/C600-Si: red circles; PPN-4/C600: blue triangles).

Fig. S6. N$_2$ sorption isotherms for PPN-4, PPN-4/C800-Si and PPN-4/C800. (adsorption: filled; desorption: open; PPN-4: black squares; PPN-4/C800-Si: red circles; PPN-4/C800: blue triangles).
**Fig. S7.** N\textsubscript{2} sorption isotherms for PPN-4, PPN-4/C1000-Si and PPN-4/C1000. (adsorption: filled; desorption: open; PPN-4: black squares; PPN-4/C1000-Si: red circles; PPN-4/C1000: blue triangles).

**Table S1** Surface areas/pore sizes of PPN-4 and carbonized samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>(S_{\text{BET}}) (m\textsuperscript{2} g\textsuperscript{-1})</th>
<th>Pore size(^b) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPN-4</td>
<td>2882</td>
<td>12.7</td>
</tr>
<tr>
<td>PPN-4/C600-Si</td>
<td>636</td>
<td>5.0</td>
</tr>
<tr>
<td>PPN-4/C600</td>
<td>1323</td>
<td>4.7</td>
</tr>
<tr>
<td>PPN-4/C800-Si</td>
<td>662</td>
<td>5.2</td>
</tr>
<tr>
<td>PPN-4/C800</td>
<td>1373</td>
<td>4.8</td>
</tr>
<tr>
<td>PPN-4/C1000-Si</td>
<td>443</td>
<td>5.2</td>
</tr>
<tr>
<td>PPN-4/C1000</td>
<td>1152</td>
<td>4.8</td>
</tr>
</tbody>
</table>

\(a\) \(S_{\text{BET}}\) was calculated in the partial pressure \((P/P_0)\) range of 0.01 to 0.1 which gives the best linearization.

\(b\) Maxima of the pore size distributions calculated using the Horvath-Kawazoe (HK) model for microporous carbon and DFT model for PPN-4.
Fig. S8. Pore size distributions for PPN-4, PPN-4/C600-Si and PPN-4/C600.

Fig. S9. Pore size distributions for PPN-4, PPN-4/C800-Si and PPN-4/C800.
Fig. S10. Pore size distributions for PPN-4, PPN-4/C1000-Si and PPN-4/C1000.

Fig. S11. CO$_2$ adsorption isotherms of PPN-4, PPN-4/C800-Si and PPN-4/C800 at 298 K. (PPN-4: black squares; PPN-4/C800-Si: red circles; PPN-4/C800: blue triangle)
Fig. S12. CO$_2$ adsorption isotherms of PPN-4, PPN-4/C1000-Si and PPN-4/C1000 at 298 K. (PPN-4: black squares; PPN-4/C1000-Si: red circles; PPN-4/C1000: blue triangle).

Fig. S13. CO$_2$ adsorption isotherms of PPN-4, PPN-4/C600-Si and PPN-4/C600 at 273 K. (PPN-4: black squares; PPN-4/C600-Si: red circles; PPN-4/C600: blue triangle).

References