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Creating extra pores in microporous carbon *via* a template strategy for a remarkable enhancement of ambient-pressure CO₂ uptake†

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In this work, we illustrate a template strategy to create extra pores in microporous carbon for enhancing ambient-pressure CO₂ uptake, as exemplified in the context of carbonizing the silicon-containing POP, PPN-4, followed by removal of the silicon template. The resultant PPN-4/C600 demonstrates a remarkable enhancement of CO₂ uptake capacity at 295 K and 1 bar by a factor of 2.3 compared to the parent PPN-4.

Over the past several decades, the emission of CO₂ as greenhouse gas in the atmosphere has been recognized as an environmental problem.¹ Current technologies addressing this issue are dominated by energy-intensive, corrosive and inefficient amine-based wet-scrubbing systems.² Adsorptive technologies that exploit physisorption of CO₂ onto surfaces of porous materials have gained momentum due to the facile regeneration process.³

Porous organic polymers (POPs)⁴ have recently been advanced as new types of porous materials for CO₂ capture application due to their high surface areas and adjustable pore size. Compared with other widely investigated porous materials of metal-organic frameworks (MOFs),^{3,5} POPs usually feature high thermal and water/chemical stabilities due to the covalent bonding nature of the framework construction, which makes them a promising platform for CO₂ capture.^{4g} However, high-surface area POPs commonly lack strong interactions between CO₂ and the surface, typically affording very low CO₂ uptake capacities at ambient temperatures and pressures.⁶ Some strategies have been employed to enhance CO₂ adsorption ability in porous organic polymers such as grafting aliphatic amines for chemically binding CO₂ molecules^{7a} and creating electro-static fields to polarize CO₂

molecules by sulfonate.^{7b} Moreover, direct carbonization of POP materials to create microporous carbon materials also provides another feasible strategy to enhance the uptake ability for CO₂ capture.⁸ Recently, we illustrated an efficient strategy to enhance the CO₂ uptake ability by pre-introducing an extra carbon source into POPs followed by carbonization to create microporous carbon materials with narrow pore size, thus increasing the CO₂ adsorption enthalpies.^{8a} Besides increasing the adsorption enthalpies, creating extra pores in porous materials would represent another appealing way to enhance CO₂ capture capacity. Herein, we report a strategy to create extra pores by removal of the silicon template in porous carbon materials derived from carbonizing silicon-containing POPs.

We selected PPN-4⁹ as a “proof-of-concept” model because of its rigid and silicon-containing framework. To obtain the desired porous carbon, we heated three samples of PPN-4, one each to 600 °C, 800 °C, and 1000 °C under an inert gas atmosphere for 8 h affording carbonized materials. The obtained samples were then soaked in KOH solutions at 120 °C for two days to remove the silicon templates. The resultant carbon materials were designated as PPN-4/C600, PPN-4/C800 and PPN-4/C1000, respectively (Scheme 1).

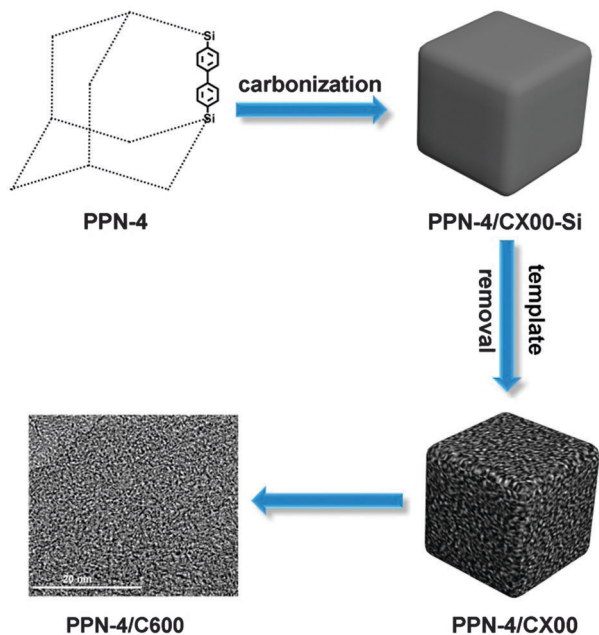
Powder X-ray diffraction (PXRD) patterns of the three samples (Fig. S1, ESI†) display two broad peaks around 23° and 43°, corresponding to carbon (002) and (101) diffractions respectively. The results thus indicate the amorphous feature of these carbon materials. Transmission electron microscopy (TEM) studies suggest that the three samples exhibit wormhole-like micropores (Fig. 1), and the materials are essentially amorphous, consistent with the PXRD analysis. EDX analysis indicates that the KOH treatments lead to complete removal of the silicon templates (Fig. S4, ESI†).

N₂ sorption isotherms collected at 77 K (Fig. 2, Fig. S5–S7, ESI†) reveal that PPN-4/C600, PPN-4/C800 and PPN-4/C1000 exhibit typical type-I adsorption behavior, characteristic of microporous materials. Their uptake capacity at the saturation pressure ($P/P_0 = 0.95$) is 380 cm³ g⁻¹, 384 cm³ g⁻¹ and 333 cm³ g⁻¹, respectively. These results are much lower than that of PPN-4

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Scheme 1 Schematic illustration of the procedures for the preparation of PPN-4/CX00 ($X = 6, 8, \text{ or } 10$).

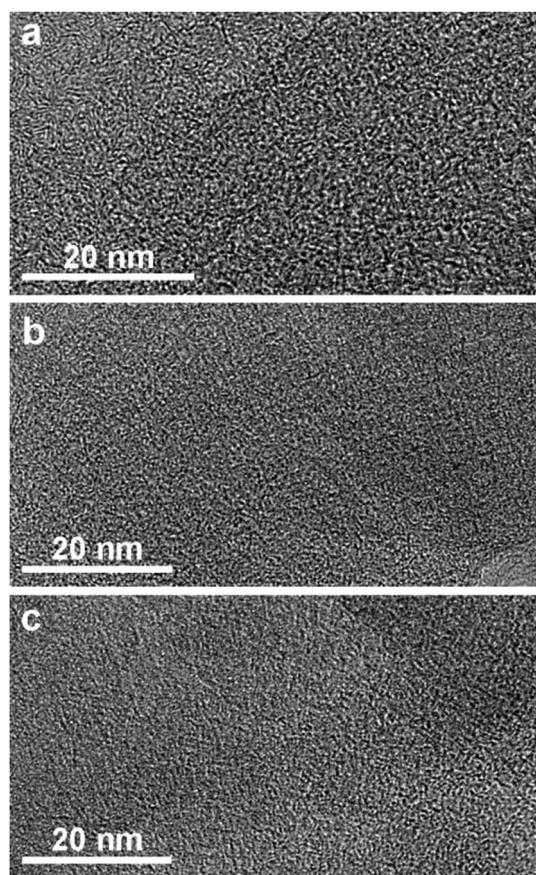


Fig. 1 TEM images of PPN-4/C600, PPN-4/C800, and PPN-4/C1000.

($1262 \text{ cm}^3 \text{ g}^{-1}$). This means a dramatic drop in the Brunauer–Emmett–Teller (BET) surface area from $2882 \text{ m}^2 \text{ g}^{-1}$ for PPN-4

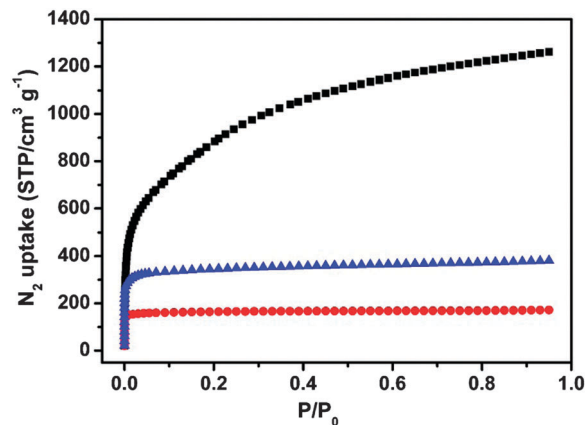


Fig. 2 N_2 adsorption isotherms for PPN-4 (black), PPN-4/C600-Si (red), PPN-4/C600 (blue) at 77 K.

(please note: the significantly lower surface area compared with that of PPN-4 reported in ref. 9 could result from the much larger amounts of starting materials used in this work for the POP preparation) to $1322 \text{ m}^2 \text{ g}^{-1}$, $1372 \text{ m}^2 \text{ g}^{-1}$ and $1152 \text{ m}^2 \text{ g}^{-1}$ for PPN-4/C600, PPN-4/C800, and PPN-4/C1000, respectively (Table S1, ESI[†]). These results are consistent with the observations reported previously with similar thermal treatments,^{8a,b} and the decreasing surface area should be presumably due to the conversion of single-layered POP materials into multi-layered amorphous carbon materials. In comparison, the samples containing silicon templates exhibit lower BET surface areas with $636 \text{ m}^2 \text{ g}^{-1}$, $662 \text{ m}^2 \text{ g}^{-1}$ and $443 \text{ m}^2 \text{ g}^{-1}$ for PPN-4/C600-Si, PPN-4/C800-Si and PPN-4/C1000-Si, respectively. The large enhancement of the surface area after the template removal is indicative of the successful creation of extra pores. Pore size distribution analysis based upon the widely employed Horvath–Kawazoe (HK) model¹⁰ (Fig. S8–S10, ESI[†]) indicates that PPN-4/C600, PPN-4/C800, and PPN-4/C1000 exhibit pore sizes predominantly distributed around 4.7–4.8 Å, significantly smaller than PPN-4's pore size distributed around 12.7 Å (Table S1, ESI[†]). The pore sizes of PPN-4/C600, PPN-4/C800, and PPN-4/C1000 are comparable to those of PPN-4/C600-Si, PPN-4/C800-Si and PPN-4/C1000-Si with pore sizes distributed around 5.0–5.2 Å. These results thus highlight that the template removal strategy by carbonizing POP materials not only narrow down the pore size compared with their pristine materials but also can create extra pores in porous carbon materials.

Considering the reduction of pore sizes in comparison with the pristine material of PPN-4 as well as the significant enhancement of surface areas compared with silicon containing porous carbons, we decided to examine the ambient-pressure CO_2 adsorption performances of PPN-4/C600, PPN-4/C800 and PPN-4/C1000 (Fig. 3 and Fig. S11 and S12, ESI[†]). CO_2 adsorption isotherms collected at 295 K show that PPN-4/C600 exhibits the highest CO_2 uptake capacity among the three samples with a value of $87 \text{ cm}^3 \text{ g}^{-1}$ (equivalent to 3.9 mmol g^{-1} or 17.1 wt%) under 1 atm pressure. This means an enhancement by a factor of 2.3 when compared to the parent PPN-4 ($26 \text{ cm}^3 \text{ g}^{-1}$ or 1.2 mmol g^{-1} or 5.3 wt%) under the same conditions (Fig. 3). It also significantly outperforms PPN-4/C600-Si, which shows a CO_2 uptake capacity of

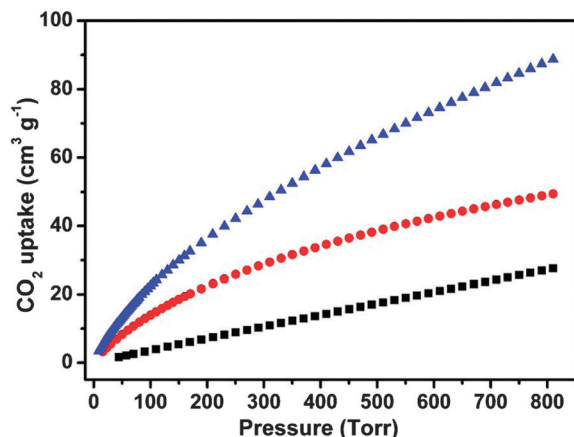


Fig. 3 CO₂ adsorption isotherms of PPN-4 (black), PPN-4/C600-Si (red), PPN-4/C600 (blue) at 295 K.

48 cm³ g⁻¹ (equivalent to 2.1 mmol g⁻¹ or 9.4 wt%) at 295 K and under 1 atm. We reason that the enhancement of ambient-pressure CO₂ uptake capacity in PPN-4/C600-Si and PPN-4/C600 compared with the pristine PPN-4 should be attributable to the narrow pores (<8 Å) that resulted from the carbonization process, in which the potential fields of the opposite pore walls can overlap thus strengthening the interaction with CO₂ molecules. Given their similar pore sizes, the higher CO₂ uptake capacity PPN-4/C600 than PPN-4/C600-Si should be due to its higher surface area as a result of the extra pores created by removal of Si in PPN-4/C600-Si. The boost of CO₂ adsorption is also observed at 273 K and 1 atm for PPN-4/C600 (134 cm³ g⁻¹ or 6.0 mmol g⁻¹ or 26.5 wt%) compared with PPN-4/C600-Si (78.5 cm³ g⁻¹ or 3.5 mmol g⁻¹ or 15.4 wt%) (Fig. S13, ESI†), further validating our strategy of creating extra pores *via* removal of the Si template for enhancing the CO₂ uptake capacity. It is noteworthy that the CO₂ uptake capacity of PPN-4/C600 at 295 K and 1 atm is among the highest for porous carbon materials reported thus far.⁸ PPN-4/C600 outperforms P-C450 (4.5 mmol g⁻¹ at 273 K and 1 bar),^{8b} FCDTPA-K-700 (3.71 mmol g⁻¹ at 298 K and 1.13 bar),^{8c} and is comparable to NC900 (3.9 mmol g⁻¹ at 298 K and 1 atm),¹¹ PAF-1/C-900 which resulted from carbonizing the POP, PAF-1 with the introduction of an extra carbon source (4.1 mmol g⁻¹ at 295 K and 1 atm).^{8a} PPN-4/C600 also surpasses the sulfonic acid grafted porous organic polymers, PPN-6-SO₃H (3.6 mmol g⁻¹ at 295 K and 1 bar) and PPN-6-SO₃Li (3.7 mmol g⁻¹ at 295 K and 1 bar),^{7b} yet remains comparable to the aliphatic amine-tethered porous organic polymer, PPN-6-CH₂DETA (4.3 mmol g⁻¹ at 295 K and 1 bar).^{7a} Moreover, the CO₂ uptake capacity of PPN-4/C600 at 295 K and 1 atm compares favorably to that of ZIFs (*e.g.* 9.1 wt% for the best ZIF of ZIF-78¹² at 298 K and 1 bar), most MOFs (*e.g.* 15.4 wt% for mmen-Cu-BTtri^{5c} and 15.2 wt% for bioMOF-11^{5e} at 298 K and 1 bar) and most zeolite materials (*e.g.* 3.1 mmol g⁻¹ for Na-A¹³ at 298 K and 1 bar) under similar conditions.

We tested the recyclability of PPN-4/C600 by simulating vacuum swing adsorption processes using an ASAP2020 analyzer, by putting the materials through cycles of saturation and vacuum, exposing the materials to CO₂ up to 1.1 bar at 295 K followed by

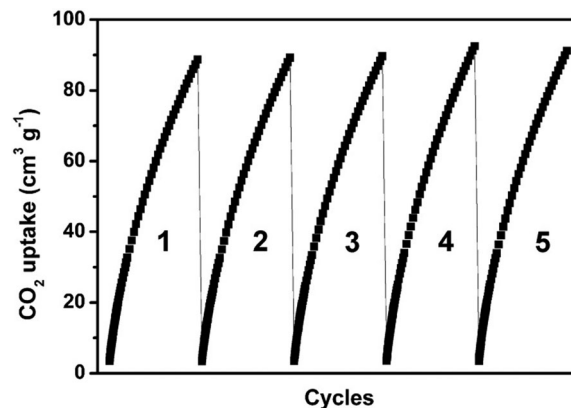


Fig. 4 The cycle experiments of CO₂ adsorption for PPN-4/C600.

high vacuum desorption for 30 min at room temperature. The results show no apparent loss in CO₂ capacity after five cycles (Fig. 4), indicating complete desorption during each regeneration cycle. The apparent lack of reduction in CO₂ capacity indicates that the adsorption mechanism in PPN-4/C600 primarily results from physical adsorption, allowing for non-energy intensive regeneration processes.

In summary, we demonstrated that the creation of extra pores by removal of the silicon template in porous carbon materials derived from carbonizing Si-containing POPs can afford high ambient-pressure CO₂ uptake capacity, as exemplified in the context of carbonizing PPN-4 followed by removal of the silicon template. The resultant PPN-4/C600 exhibits a remarkable enhancement of CO₂ uptake capacity at 295 K and 1 bar by a factor of 2.3 compared to the pristine PPN-4. The strategy of creating extra pores *via* removal of the template (*e.g.* Si in this work) represents a promising approach to boost CO₂ adsorption in microporous carbon materials for CO₂ capture applications. It could also be applied to other types of porous materials for various applications, and research along this line is currently underway in our laboratory.

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