ChemComm

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View Article Online
View Journal | View Issue

Cite this: *Chem. Commun.*, 2013, **49**, 10269

Received 12th July 2013,
Accepted 5th September 2013

DOI: 10.1039/c3cc45252b

www.rsc.org/chemcomm

A new microporous carbon material synthesized *via* thermolysis of a porous aromatic framework embedded with an extra carbon source for low-pressure CO_2 uptake†

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Pre-introducing an extra carbon source into the porous aromatic framework of PAF-1 followed by thermolysis affords a new microporous carbon material, which demonstrates a CO_2 uptake capacity of 93 $cm^3\ g^{-1}$ (equivalent to 4.1 mmol g^{-1} or 18.2 wt%) at 295 K and 1 bar.

The steady increase of CO_2 levels in the atmosphere over the past several decades has urged the development of viable carbon dioxide capture and sequestration (CCS) technologies to reduce the greenhouse emissions.[1] Current technologies are dominated by amine-based web-scrubbing systems, which are energy-costly, corrosive and inefficient.[2] This thus prompts the exploration of alternative approaches for CCS, and physisorption of CO_2 using porous materials holds great promise due to the facile regeneration process.[3]

Advanced porous materials such as porous organic polymers (POPs) (including conjugated microporous polymers (CMPs),[4] porous aromatic frameworks (PAFs),[5] and porous polymer networks (PPNs)[6]) and metal–organic frameworks (MOFs)[3,7] have recently been intensively investigated for CO_2 capture application. However, POPs usually exhibit very low CO_2 uptake capacities at ambient temperatures and pressures due to the low CO_2 adsorption enthalpies as a result of the lack of strong CO_2 binding sites,[6d] whereas MOFs typically possess poor water/chemical stabilities.[3e] Porous carbon materials, which feature high thermal/water/chemical stabilities, diverse availability and facile regeneration, have also been explored for CO_2 capture application.[8] Nonetheless, the large pore sizes together with broad pore size distributions lead to low CO_2 adsorption capacities, typically 2–3 mmol g^{-1} at 25 °C under 1 bar, for most porous carbon materials.[8c,d] Various studies on CO_2 capture in MOFs have suggested that pore size plays an important role in CO_2 capture performances, and narrow pores of $\sim$4 Å to $\sim$8 Å could facilitate CO_2 adsorption due to the fact that the potential fields of the opposite pore walls can overlap thus strengthening the interaction with CO_2 molecules.[3e,9] Direct thermolysis of MOFs or MOFs embedded with additional carbon sources to prepare ordered porous carbon materials with reduced pore sizes has recently been demonstrated,[10] but the pore size distributions are usually not very uniform thus unfavorable for CO_2 uptake at low pressure. Direct carbonization of highly porous PAFs to reduce the pore size in order to enhance CO_2 uptake capacity has also been recently reported,[11] but the enhancement was not very dramatic due to the remaining pore size being over 1.0 nm. To further narrow down the pore size with uniform distribution, herein, we report a new strategy of pre-introducing an extra carbon source into a PAF followed by carbonization, which afforded a new microporous carbon material with a small pore size of 5.4 Å thus facilitating a high CO_2 uptake capacity of 4.1 mmol g^{-1} at 295 K and 1 bar.

We selected PAF-1[12] for "proof-of-concept" studies considering its relatively large pore size and framework robustness as well as readiness for post-synthetic modification. To introduce an extra carbon source into PAF-1 (Scheme 1), we first post-grafted it with sulfonic acid, which can serve as the catalytic site for the polymerization of furfuryl alcohol (FA).[10b,13] The resulting PAF-1-SO_3H was then stirred in FA for two days, during which the adsorbed FA was catalyzed by the grafted sulfonic acid to polymerize within the pores of PAF-1. After careful filtration and washing with ethanol to remove FA physically adsorbed on the exterior surface, the obtained FA–PAF-1-SO_3H composite was heated at 900 °C under an inert gas atmosphere for 8 h to afford the carbonized material, which is designated as PAF-1/C-900.

Powder X-ray diffraction (PXRD) patterns of PAF-1/C-900 (Fig. S1, ESI†) display two broad peaks at around 23° and 43°, corresponding to carbon (002) and (101) diffractions respectively. These results indicate the amorphous feature of PAF-1/C-900. Transmission electron microscopy (TEM) studies suggest that PAF-1/C-900 exhibits wormhole-like micropores (Fig. 1), and it is essentially amorphous, which is consistent with PXRD analysis.

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† Electronic supplementary information (ESI) available: Detailed procedures for preparation of materials, gas sorption measurements, PXRD patterns, and plots of gas sorption isotherms. See DOI: 10.1039/c3cc45252b

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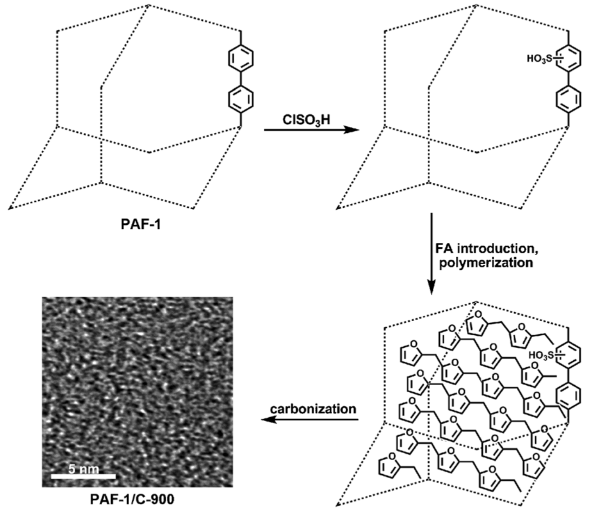

Scheme 1 Schematic illustration of the procedures for the preparation of PAF-1/C-900.

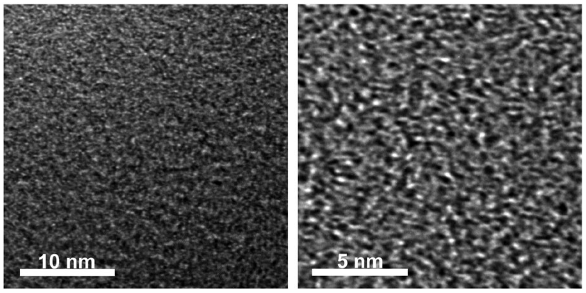

Fig. 1 TEM images of PAF-1/C-900 at different magnifications.

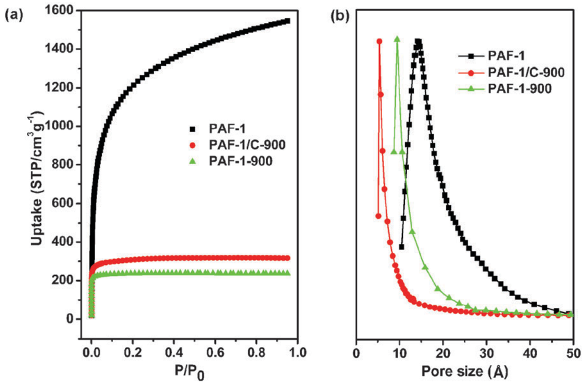

Fig. 2 (a) N_2 adsorption isotherms at 77 K and (b) pore size distributions (H–K model) for PAF-1, PAF-1/C-900, and PAF-1-900.

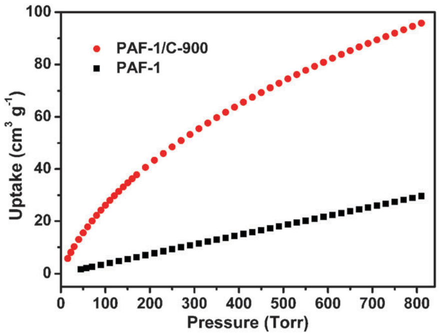

Fig. 3 CO_2 adsorption isotherms of PAF-1/C-900 and PAF-1 at 295 K.

The N_2 adsorption isotherm collected at 77 K (Fig. 2a) reveals that PAF-1/C-900 exhibits typical type-I adsorption behavior, a characteristic of microporous materials. Its uptake capacity at the saturation pressure (P/P_0 = 0.95) is 316 cm^3 g^{-1}, which is much lower than that of PAF-1 (1546 cm^3 g^{-1}). This means a dramatic drop in the Brunauer–Emmett–Teller (BET) surface area from 4246 m^2 g^{-1} for PAF-1 to 1174 m^2 g^{-1} for PAF-1/C-900 (Table S1, ESI†). Direct carbonization of PAF-1 at 900 °C also led to a remarkable decrease in surface area of the resulting material, PAF-1-900, which exhibits an even lower BET surface area of 923 m^2 g^{-1} as derived from the N_2 adsorption isotherm at 77 K. Pore size distribution analysis based on the Horvath–Kawazoe (HK) model (Fig. 2b), which is widely employed for micropore size analysis,[14] indicates that the pore size of PAF-1/C-900 is predominantly distributed around 5.4 Å in comparison with 14.5 Å for PAF-1 and 9.4 Å for PAF-1-900 (Table S1, ESI†). These results thus highlight the effectiveness of our strategy in further narrowing down the pore size by pre-introducing an extra carbon source compared with the direct carbonization method.

Given that the pore size of PAF-1/C-900 falls in the range of 4 Å to 8 Å, we decided to assess its low pressure CO_2 adsorption performances. CO_2 adsorption isotherms collected at 295 K show that PAF-1/C-900 can adsorb a large amount of CO_2 with an uptake capacity of 93 cm^3 g^{-1} (equivalent to 4.1 mmol g^{-1} or 18.2 wt%) under 1 atm of pressure, meaning an enhancement by a factor of 2.4 compared to parent PAF-1 (27 cm^3 g^{-1} or 1.2 mmol g^{-1} or 5.3 wt%) under the same conditions (Fig. 3). A higher uptake capacity of 135 cm^3 g^{-1} (or 6.0 mmol g^{-1} or 26.5 wt%) is observed for PAF-1/C-900 at 273 K and 1 bar. In comparison, at 295 K and 1 bar, PAF-1-900 exhibits a lower CO_2 uptake capacity of 79 cm^3 g^{-1} (or 3.5 mmol g^{-1} or 15.5 wt%) and a much lower CO_2 adsorption capacity of 26 cm^3 g^{-1} (or 1.2 mmol g^{-1} or 5.1 wt%) is observed for carbonized poly(FA) (Fig. S4, ESI†). These results thus validate our strategy of pre-introducing an extra carbon source into a PAF followed by carbonization for enhancing the CO_2 uptake capacity. It is worth noting that the CO_2 uptake capacity of PAF-1/C-900 at 295 K and 1 bar is among the highest for porous carbon materials reported thus far.[15] PAF-1/C-900 outperforms P-C450[10] (4.5 mmol g^{-1} at 273 K and 1 bar) which is resulted from directly carbonizing PAF-1 at 450 °C without introducing an extra carbon source, and it also surpasses the sulfonic acid grafted porous organic polymers, PPN-6-SO_3H (3.6 mmol g^{-1} at 295 K and 1 bar) and PPN-6-SO_3Li (3.7 mmol g^{-1} at 295 K and 1 bar);[6b] yet it is comparable to the aliphatic amine-tethered porous organic polymer, PPN-6-CH_2DETA (4.3 mmol g^{-1} at 295 K and 1 bar).[6a] The CO_2 uptake capacity of PAF-1/C-900 at 295 K and 1 bar also exceeds that of ZIFs (*e.g.* 9.1 wt% for the best ZIF of ZIF-78[7d] at 298 K and 1 bar),[3c,e] most MOFs (*e.g.* 15.4 wt% for mmen-Cu-BTTri[7c] and 15.2 wt% for bio-MOF-11[7e] at 298 K and 1 bar)[3c,e] and most zeolite materials (*e.g.* 3.1 mmol g^{-1} for Na-A[16b] at 298 K and 1 bar)[16] under similar conditions.

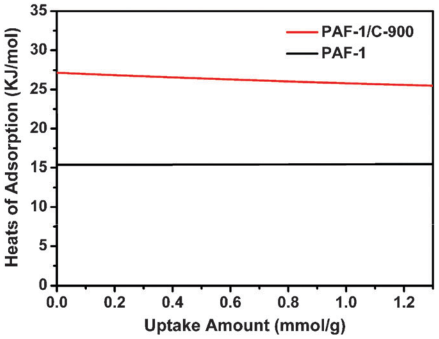

Fig. 4 Heats of adsorption of CO_2 for PAF-1/C-900 and PAF-1.

It has been well-documented that narrow pores can strengthen the interaction between pore walls and CO_2 molecules due to the overlap of potential fields of the opposite pore walls.[3e,9,17] We calculated the heats of adsorption (Q_{st}) of CO_2 for PAF-1/C-900 and PAF-1 based on the CO_2 adsorption isotherms at 273 K and 295 K using the virial method.[18] As shown in Fig. 4, PAF-1/C-900 exhibits a Q_{st} of $\sim$27.0 kJ mol^{-1} at zero-loading, which is 11.6 kJ mol^{-1} higher than that of PAF-1 (Q_{st} of 15.4 kJ mol^{-1}). These results further validate the contribution of narrow pores to the remarkable enhancement of CO_2 uptake in PAF-1/C-900.

In summary, pre-introducing an extra carbon source into PAF-1 followed by carbonization at 900 °C afforded a microporous carbon material, PAF-1/C-900, with a small pore size of $\sim$5.4 Å. As a result of the substantially reduced pore size, PAF-1/C-900 demonstrates remarkable enhancement of CO_2 uptake capacity at 295 K and 1 bar by a factor of $\sim$2.4 and a dramatic increase in Q_{st} of CO_2 by 11.6 kJ mol^{-1} at zero-loading compared to the parent PAF-1. The strategy of pre-introducing extra carbon sources into the POP materials followed by thermolysis represents a promising approach to create microporous carbon materials with very narrow pores ($<$8 Å), which could hold promise for CO_2 capture applications. Ongoing work in our laboratory includes the design and synthesis of other types of functional porous materials for application in CO_2 capture, sensors and catalysis.

The authors acknowledge the University of South Florida for financial support of this work.

Notes and references

1 R. K. Pachauri, A. Reisinger, IPCC Fourth Assessment Report, Intergovernmental Panel on Climate Change, 2007.
2 (*a*) J. Johnson, *Chem. Eng. News*, 2004, **82**, 36; (*b*) C. Wang, H. Luo, D. Jiang, H. Li and S. Dai, *Angew. Chem., Int. Ed.*, 2010, **49**, 5978.
3 (*a*) Z. Yong, V. Mata and A. E. Rodrigues, *Sep. Purif. Technol.*, 2002, **26**, 195; (*b*) S. Ma and H.-C. Zhou, *Chem. Commun.*, 2010, **46**, 44; (*c*) J.-R. Li, Y. Ma, M. C. McCarthy, J. Sculley, J. Yu, H.-K. Jeong, P. B. Balbuena and H.-C. Zhou, *Coord. Chem. Rev.*, 2011, **255**, 1791; (*d*) Y.-S. Bae and R. Q. Snurr, *Angew. Chem., Int. Ed.*, 2011, **50**, 11586; (*e*) K. Sumida, D. L. Rogow, J. A. Mason, T. M. McDonald, E. D. Bloch, Z. R. Herm, T.-H. Bae and J. R. Long, *Chem. Rev.*, 2012, **112**, 724; (*f*) J. Liu, P. K. Thallapally, B. P. McGrail, D. R. Brown and J. Liu, *Chem. Soc. Rev.*, 2012, **41**, 2308; (*g*) Z. Zhang, Y. Zhao, Q. Gong, Z. Li and J. Li, *Chem. Commun.*, 2013, **49**, 653.
4 (*a*) A. I. Cooper, *Adv. Mater.*, 2009, **21**, 1291; (*b*) M. G. Rabbani, A. K. Sekizkardes, O. M. El-Kadri, B. R. Kaafarani and H. M. El-Kaderi, *J. Mater. Chem.*, 2012, **22**, 25409; (*c*) X. Zhu, C. C. Tian, S. M. Mahurin, S. H. Chai, C. M. Wang, S. Brown, G. M. Veith, H. M. Luo, H. L. Liu and S. Dai, *J. Am. Chem. Soc.*, 2012, **134**, 10478; (*d*) Y. Zhu, H. Long and W. Zhang, *Chem. Mater.*, 2013, **25**, 1630; (*e*) Y. Xu, S. Jin, H. Xu, A. Nagai and D. Jiang, *Chem. Soc. Rev.*, 2013, DOI: 10.1039/c3cs60160a.
5 (*a*) T. Ben and S. Qiu, *CrystEngComm*, 2013, **15**, 17; (*b*) T. Ben, C. Pei, D. Zhang, J. Xu, F. Deng, X. Jing and S. Qiu, *Energy Environ. Sci.*, 2011, **4**, 3991; (*c*) H. Ma, H. Ren, X. Zou, F. Sun, Z. Yan, K. Cai, D. Wang and G. Zhu, *J. Mater. Chem. A*, 2013, **1**, 752; (*d*) X. Zou, H. Ren and G. Zhu, *Chem. Commun.*, 2013, **49**, 3925.
6 (*a*) W. Lu, J. P. Sculley, D. Yuan, R. Krishna, Z. Wei and H.-C. Zhou, *Angew. Chem., Int. Ed.*, 2012, **51**, 7480; (*b*) W. Lu, D. Yuan, J. Sculley, D. Zhao, R. Krishna and H.-C. Zhou, *J. Am. Chem. Soc.*, 2011, **133**, 18126; (*c*) D. Yuan, W. Lu, D. Zhao and H.-C. Zhou, *Adv. Mater.*, 2011, **23**, 3723; (*d*) J. P. Sculley, J.-R. Li, J. Park, W. Lu and H.-C. Zhou, *Sustainable Technologies, Systems & Policies*, DOI: 10.5339/stsp.2012.ccs.16.
7 (*a*) A. R. Millward and O. M. Yaghi, *J. Am. Chem. Soc.*, 2005, **127**, 17998; (*b*) S. R. Caskey, A. G. Wong-Foy and A. J. Matzger, *J. Am. Chem. Soc.*, 2008, **130**, 10870; (*c*) A. Demessence, D. M. D'Alessandro, M. L. Foo and J. R. Long, *J. Am. Chem. Soc.*, 2009, **131**, 8784; (*d*) R. Banerjee, H. Furukawa, D. Britt, C. Knobler, M. O'Keeffe and O. M. Yaghi, *J. Am. Chem. Soc.*, 2009, **131**, 3875; (*e*) J. An, S. J. Geib and N. L. Rosi, *J. Am. Chem. Soc.*, 2010, **132**, 38; (*f*) R. Vaidhyanathan, S. S. Iremonger, G. K. H. Shimizu, P. G. Boyd, S. Alavi and T. K. Woo, *Science*, 2010, **330**, 650; (*g*) B. Li, Z. Zhang, Y. Li, K. Yao, Y. Zhu, Z. Deng, F. Yang, X. Zhou, G. Li, H. Wu, N. Nijem, Y. J. Chabal, Z. Lai, Y. Han, Z. Shi, S. Feng and J. Li, *Angew. Chem., Int. Ed.*, 2012, **51**, 1412; (*h*) S. D. Burd, S. Ma, J. A. Perman, B. J. Sikora, R. Q. Snurr, P. K. Thallapally, J. Tian, L. Wojtas and M. J. Zaworotko, *J. Am. Chem. Soc.*, 2012, **134**, 3363; (*i*) S. Xiang, Y. He, Z. Zhang, H. Wu, W. Zhou, R. Krishna and B. Chen, *Nat. Commun.*, 2012, **3**, 954; (*j*) W.-Y. Gao, W. Yan, R. Cai, K. Williams, A. Salas, L. Wojtas, X. Shi and S. Ma, *Chem. Commun.*, 2012, **48**, 8898; (*k*) J.-R. Li, J. Yu, W. Lu, J. Sculley, P. B. Balbuena and H.-C. Zhou, *Nat. Commun.*, 2013, **4**, 1538.
8 (*a*) A. Wahby, J. M. Ramos-Fernández, M. Martínez-Escandell, A. Sepúlveda-Escribano, J. Silvestre-Albero and F. Rodríguez-Reinoso, *ChemSusChem*, 2010, **3**, 974; (*b*) V. Presser, J. McDonough, S.-H. Yeon and Y. Gogotsi, *Energy Environ. Sci.*, 2011, **4**, 3059; (*c*) S. Himeno, T. Komatsu and S. Fujita, *J. Chem. Eng. Data*, 2005, **50**, 369; (*d*) Y. Zhao, L. Zhao, K. X. Yao, Y. Yang, Q. Zhang and Y. Han, *J. Mater. Chem.*, 2012, **22**, 19726.
9 P. Nugent, Y. Belmabkhout, S. D. Burd, A. J. Cairns, R. Luebke, K. Forrest, T. Pham, S. Ma, B. Space, L. Wojtas, M. Eddaoudi and M. J. Zaworotko, *Nature*, 2013, **495**, 80.
10 (*a*) B. Liu, H. Shioyama, T. Akita and Q. Xu, *J. Am. Chem. Soc.*, 2008, **130**, 5390; (*b*) H. L. Jiang, B. Liu, Y. Q. Lan, K. Kuratani, T. Akita, H. Shioyama, F. Zong and Q. Xu, *J. Am. Chem. Soc.*, 2011, **133**, 11854; (*c*) M. Hu, J. Reboul, S. Furukawa, N. L. Torad, Q. Ji, P. Srinivasu, K. Ariga, S. Kitagawa and Y. Yamauchi, *J. Am. Chem. Soc.*, 2012, **134**, 2864; (*d*) S. Lim, K. Suh, Y. Kim, M. Yoon, H. Park, D. N. Dybtsev and K. Kim, *Chem. Commun.*, 2012, **48**, 7447.
11 T. Ben, Y. Li, L. Zhu, D. Zhang, D. Cao, Z. Xiang, X. Yao and S. Qiu, *Energy Environ. Sci.*, 2012, **5**, 8370.
12 T. Ben, H. Ren, S. Ma, D. Cao, J. Lan, X. Jing, W. Wang, J. Xu, F. Deng, J. M. Simmons, S. Qiu and G. Zhu, *Angew. Chem., Int. Ed.*, 2009, **48**, 9457.
13 (*a*) S. Che, A. E. Garcia-Bennett, X. Liu, R. P. Hodgkins, P. A. Wright, D. Zhao, O. Terasaki and T. Tatsumi, *Angew. Chem., Int. Ed.*, 2003, **42**, 3930; (*b*) Q.-H. Yang, W. Xu, A. Tomita and T. Kyotani, *J. Am. Chem. Soc.*, 2005, **127**, 8956.
14 R. T. Yang, *Adsorbents: Fundamentals and Applications*, John Wiley & Sons, Hoboken, 2003.
15 (*a*) M. Sevilla and A. B. Fuertes, *Energy Environ. Sci.*, 2011, **4**, 1765; (*b*) M. Sevilla, P. Valle-Vigon and A. B. Fuertes, *Adv. Funct. Mater.*, 2011, **21**, 2781; (*c*) Y. Zhao, X. Liu, K. X. Yao, L. Zhao and Y. Han, *Chem. Mater.*, 2012, **24**, 4725.
16 (*a*) R. Krishna and J. A. vanBaten, *Langmuir*, 2010, **26**, 3981; (*b*) T.-H. Bae, M. R. Hudson, J. A. Mason, W. L. Queen, J. J. Dutton, K. Sumida, K. J. Micklash, S. S. Kaye, C. M. Brown and J. R. Long, *Energy Environ. Sci.*, 2013, **6**, 128.
17 S. Ma, *Pure Appl. Chem.*, 2009, **81**, 2235.
18 L. Czepirsky and J. Jagiello, *Chem. Eng. Sci.*, 1989, **44**, 797.