Supporting information

Hollow ceramic fiber supported ZIF-8 membrane with enhanced gas separation performance prepared by hot dip-coating seeding

Kai Tao, Lujie Cao, Yichao Lin, Chunlong Kong * and liang Chen *

Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo, Zhejiang 315201, China. Tel: (+86) 574-8665023; Email: chenliang@nimte.ac.cn, kongchl@nimte.ac.cn.

*To whom correspondence should be addressed.

Experimental details

Materials:

All chemicals were used as supplied: $ZnCl_2$ (>99%, Sinopharm Chemical Reagent Co., Ltd), $Zn(NO_3)_2 \cdot 6H_2O$ (>99%, Sinopharm Chemical Reagent Co., Ltd), 2-methylimidazole (Hmim: >99%, Alfa Aesar), HCOONa (Sinopharm Chemical Reagent Co., Ltd), CH_3OH (>99%, Sinopharm Chemical Reagent Co., Ltd).

α-Al_2O_3 hollow ceramic fiber tube (HCT: i.d.: 2.5 mm, o.d.: 3.5 mm, pore size: 200 nm, porosity: 30%-40%, Hyflux Co., Ltd.) was cut into 70 mm in length. The support was cleaned with acetone in an ultrasonic cleaner, dried at 383 K for 12 h, and then calcined at 773 K for 6 h to remove greasy matter.

Synthesis of ZIF-8 nano seeds

ZIF-8 nano seeds were prepared according to the report by Cravillon.[1] Typically, 2.20 g of $Zn(NO_3)_2 \cdot 6H_2O$ and 4.87 g of Hmim were dissolved in 25 ml of CH_3OH, respectively. Then, two solutions were combined. The mixture was stirred at room temperature for 5 h. ZIF-8 nano seeds were collected by centrifugating (8500 rpm, 10 min) and washing with CH_3OH (5

times), and then dried overnight at 80 ^{o}C.

Preparation of seed layer by hot dip-coating

0.3 g ZIF-8 powder was dispersed in 19.7 g deionized water under sonication to obtain a seed suspension (1.5 wt%). To facilitate the dispersion, the ZIF-8 was carefully ground in an agate mortar before sonication. To prevent the deposition of ZIF-8 seeds inside the support, both ends of the support were sealed with Teflon tapes, and then placed in preheated oven (150 ^{o}C) for at least 4 h. Finally, the hot HCT support was dipped into the above suspension for about 20 s in contact with suspension and was withdrawn vertically and dried at 80 ^{o}C for 4 h.

Synthesis of ZIF-8 membrane by secondary growth

0.66 g of Hmim and 0.272 g of HCOONa were dissolved in 25 ml methanol. A solution consisting of 0.55 g $ZnCl_2$ and 25 ml of methanol was added to the above solution and sonicated for 5 min. A seeded HCT support with both ends of tube sealed by Teflon tapes was mounted on a home-made Teflon holder and placed vertically in Teflon lined stainless steel autoclave filled with synthesis solution so that the ZIF-8 membrane was formed on the outside of tube. The secondary growth was carried out at 120 ^{o}C for 8 h. After the crystallization, the membrane was washed thoroughly with methanol and soaked in methanol for 12 h. Then, the membrane was dried at a vacuum oven at 60 ^{o}C for 24 h. The membrane was stocked in a vacuum desiccator before permeation tests.

Characterization:

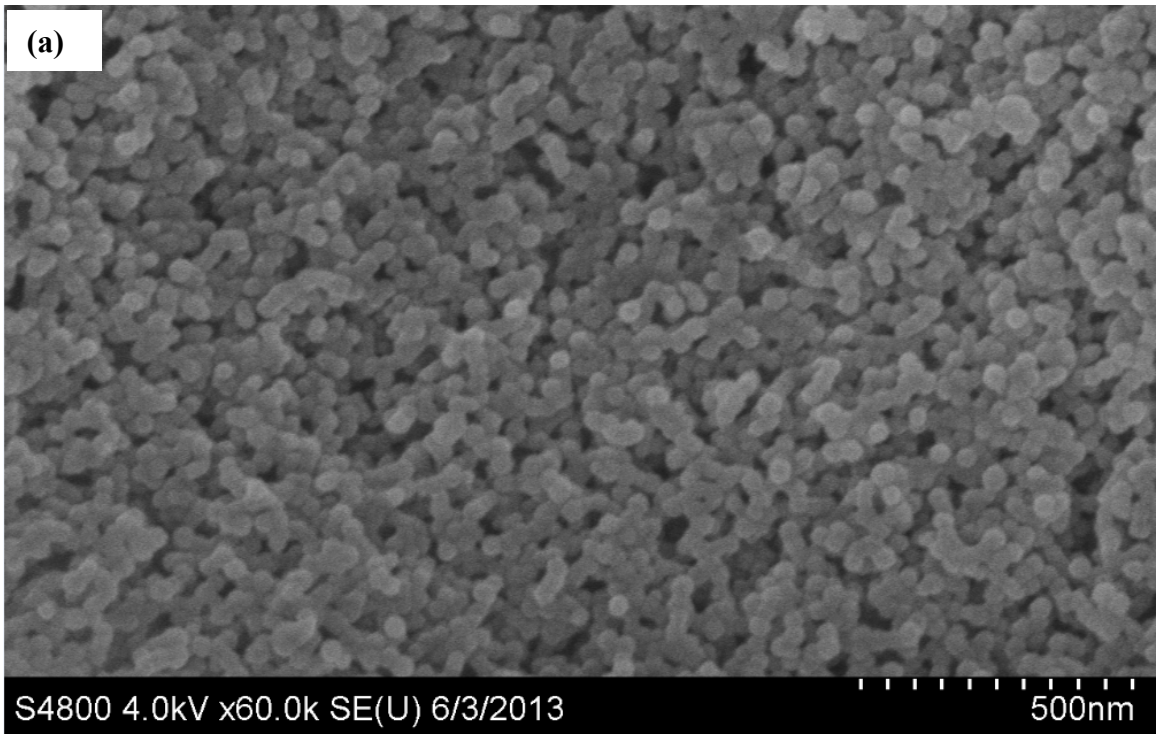
XRD data of the products were collected on a Bruker AXS D8 Advance diffractometer using CuKα (λ= 1.5406 Å) radiation at a voltage of 40 kV and 40 mA. The powder diffraction pattern was scanned over the angular range of 5°-60° (2θ) with a step size of 0.02°. Scanning electron microscopy (SEM) images were obtained from a field emission scanning electron microscope (Hitachi S-4800).

Gas permeation test:

Single gas permeation experiments were tested in a home-made permeation apparatus by pressure drop method. The supported ZIF-8 membrane was sealed in a permeation module with silicone O-rings. The tested gas was fed to the outside of the membrane. The feed stream was pressurized, while downstream pressure was maintained at atmospheric pressure. The pressure difference through the membrane was maintained at 0.1 MPa in the single gas

permeation test. The gas flow rate was determined by a soap film bubble flow meter. The permeance (A) is calculated by the expression: A = n/(P×S), where n is the molar flow rate of permeate (mol/s), S is the membrane area (m^2), and P is the transmembrane pressure drop (Pa), respectively. The ideal separation factor (D) is defined as follow: D=A1/A2, while Al and A2 are the permeance for gas 1 and gas 2, respectively. Before each test, the permeation module was purged for at least 1 h. Average values of 5 runs of test from at least two membranes synthesized at the same conditions were present.

Results



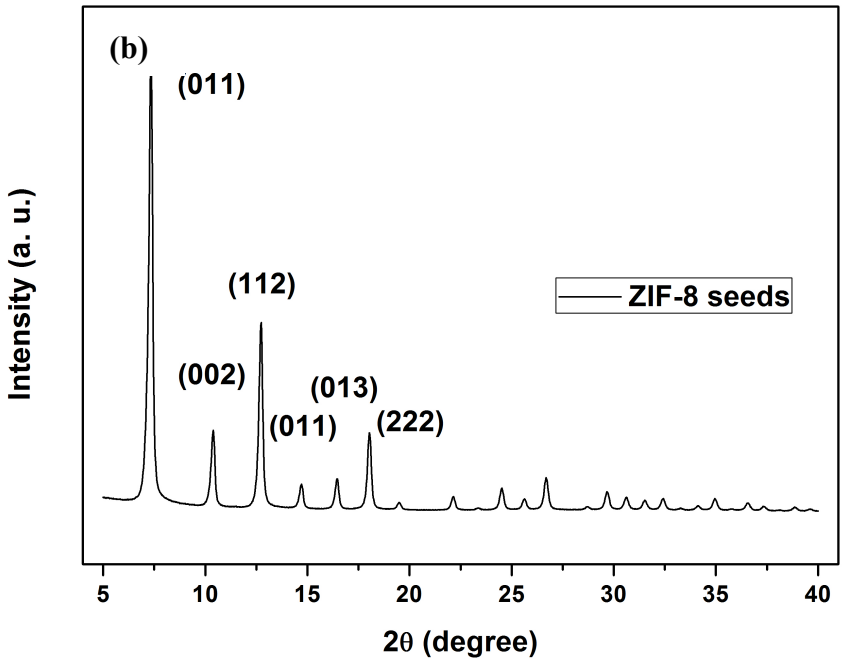


Fig. S1. SEM image (a) and XRD pattern (b) of pure ZIF-8 seeds.

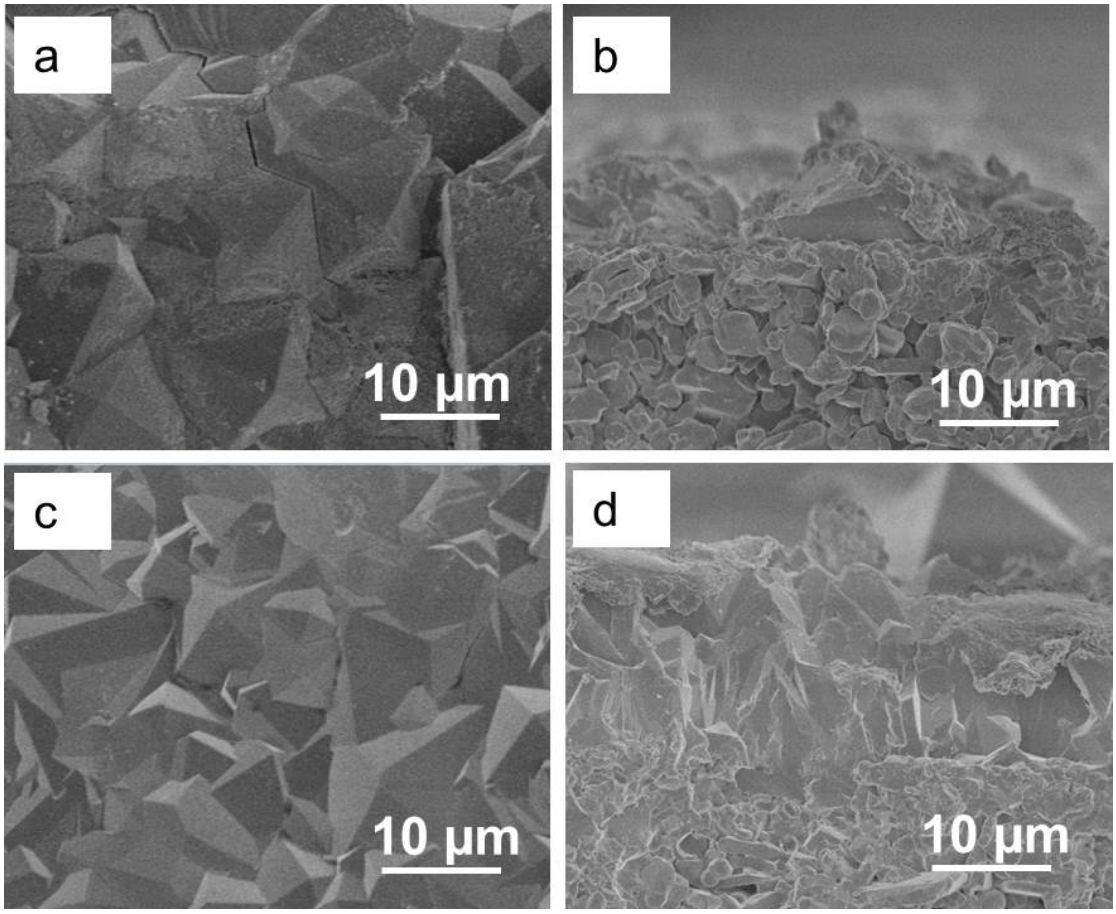


Fig. S2 SEM image of ZIF-8 membranes synthesized with different seeding methods: a,b: dip-coating and e,f: hot dip-coating (ZIF-8 content: 0.5 wt%); a,c: top-view; b,d,:

cross-section view.

Table s1. Comparison of permeability properties of ZIF-8 synthesized with different seeding methods.

Sample	Gas separation selectivity			H_2 permeance
	H_2/N_2	H_2/CH_4	H_2/CO_2	$molm^{-2}s^{-1}pa^{-1}$
Blank	-	-	-	3.5 E-05
D	2.9	2.5	3.3	3.9 E-06
H1	3.7	2.8	3.4	1.4 E-06
H2	9.2	10.8	5.4	7.3E-07
Knudsen sel.	3.78	2.83	4.7	-

D: dip-coating, ZIF-8: 1.5 wt %

H1: hot dip-coating, ZIF-8: 0.5 wt %

H2: hot dip-coating, ZIF-8: 1.5 wt %

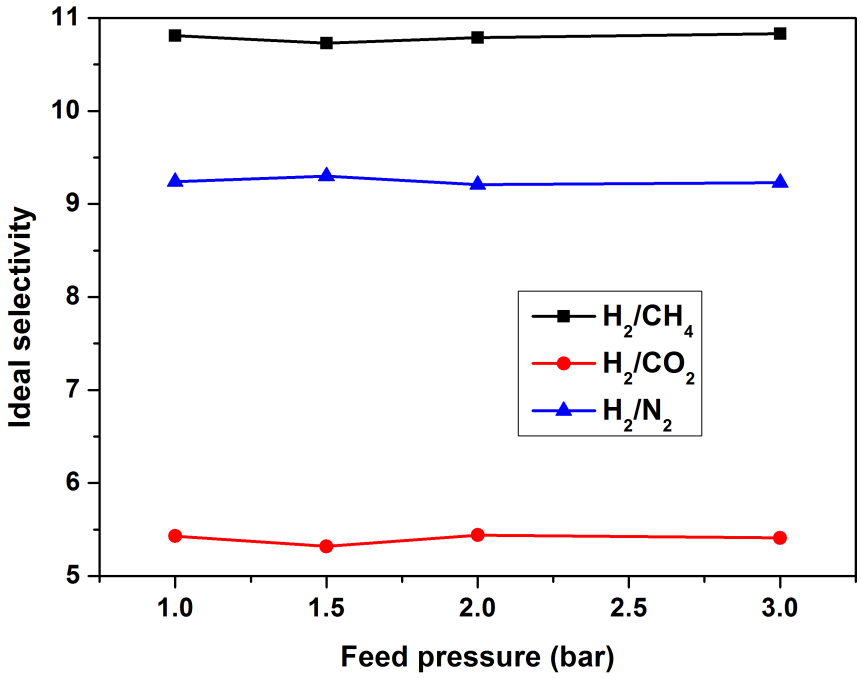


Fig. S3 The ideal selectivity of as-synthesized ZIF-8 membrane as a function of feed pressure at room temperature.

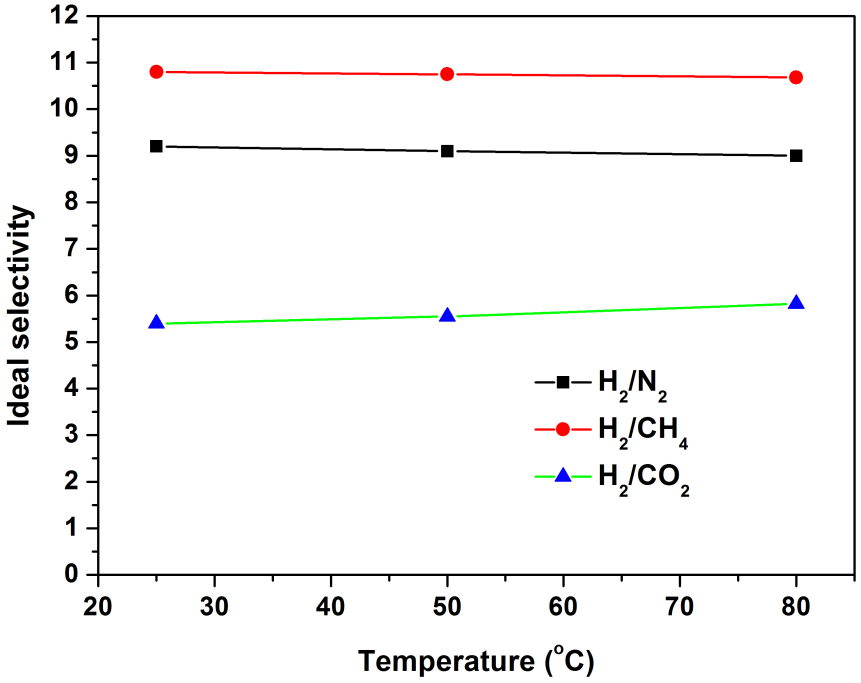


Fig. S4 The ideal selectivity of as-synthesized ZIF-8 membrane as a function of temperature at feed pressure of 1 bar.

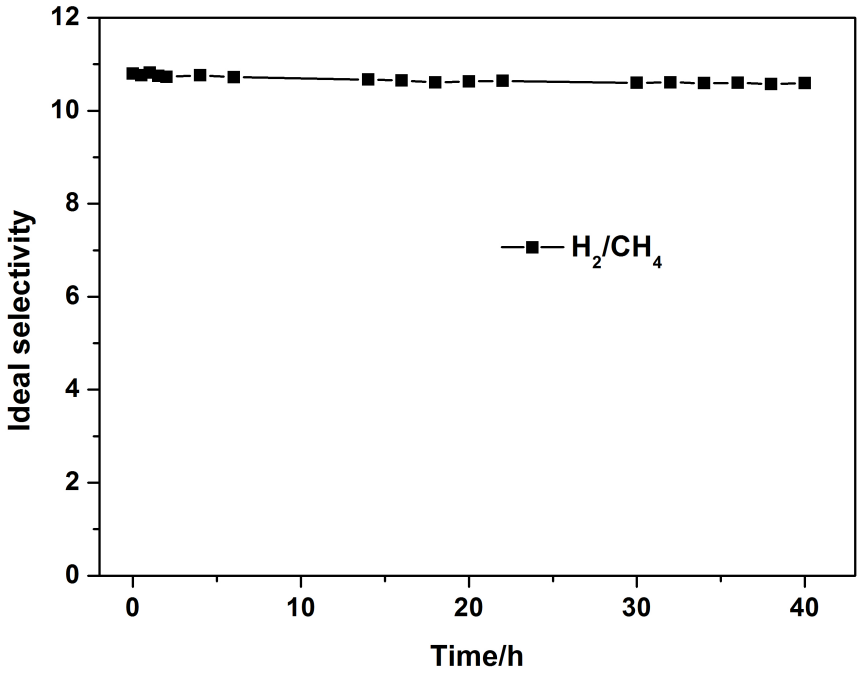


Fig. S5 Ieal H_2/CH_4 separation factor as-synthesized ZIF-8 membrane as a function of time at room temperature and feed pressure of 1 bar.

Tabel S2 Comparison of H_2 permselectivity of as-synthesized ZIF-8 membrane with reported MOF membranes.

Membrane	Support	Thickness	Reported permeances (10^{-8} mol $m^{-2}S^{-1}Pa^{-1}$)[a]							
			H_2	CH_4	N_2	CO_2	H_2/CH_4	H_2/N_2	H_2/CO_2	Ref
ZIF-8	Al_2O_3 disc	12	10	0.67	-	2	14.9	-	5.0	2
ZIF-8	Al_2O_3 disc	20	17.3	1.33	1.49	4.45	13.0	11.6	3.9	3
ZIF-8	Al_2O_3 disc	2.5	36	7.8	9	14	4.6	4.0	2.6	4
ZIF-8	TiO_2 disc	40	6.04	0.48	0.52	1.33	12.6	11.6	4.5	5
ZIF-8	Al_2O_3 disc	12	17	-	3.0	-	-	5.7	-	6
ZIF-8	Nylon disc	2.5	113	-	25	-	-	4.6	-	7
ZIF-8	Al_2O_3 disc	25	23.5	1.8	2.0	4.6	13.1	11.8	5.1	8
ZIF-8	Al_2O_3 tube	2	5730	-	371.1	336.1	-	15.4	17.0	9
$Cu_3(BTC)_2$	Al_2O_3 HCT[b]	13	7.25	1.25	1.01	0.55	5.8	7.2	13.2	10
ZIF-90	Al_2O_3 HCT	5	19.2	7.1	3.0	10.7	2.7	6.4	1.8	11
ZIF-8	Al_2O_3 HCT	6	99	36.7	39.6	3.1	2.7	2.5	32.3	12
ZIF-8	Al_2O_3 HCT	5	114	16.76	15.62	21.92	6.8	7.3	5.2	13
ZIF-7[c]	Al_2O_3 disc	2	4.55	0.31	0.22	0.35	14.7	20.7	13.0	14
ZIF-69	Al_2O_3 disc	50	6.50	1.85	-	2.5	3.5	-	2.6	15
ZIF-78	Al_2O_3 disc	4	11.1	1.73	1.91	1	6.4	5.8	11.1	16
ZIF-9-67	Al_2O_3 disc	35	1405	517	381	158	2.7	3.7	8.9	17
MOF-5	Al_2O_3 disc	40	80	39	30	25	2.1	2.7	3.2	18
MMOF	Al_2O_3 disc	20	1.21	-	0.34	0.34	-	3.6	3.6	19
IRMOF-3	Al_2O_3 disc	10	152	64.9	41.8	62.4	2.3	3.6	2.4	20
MIL-53	Al_2O_3 disc	8	49.4	16.4	13.6	11.0	3.0	3.6	4.5	21
MIL-96	Al_2O_3 disc	6	98.2	33.8	26.5	21.4	2.9	3.7	4.6	22
Ni-MOF-74	Al_2O_3 disc	25	1270	440	420	140	2.9	3.0	9.1	23
ZIF-8	Al_2O_3 HCT	20	72.9	6.75	7.92	13.5	10.8	9.2	5.4	This work

[a] permeances were tested at 25 ^oC.

[b] HCT: hollow ceramic fiber tube

[c] permeances were tested at 200 ^{o}C.

Reference

(1) J. Cravillon, S. Münzer, S.-J. Lohmeier, A. Feldhoff, K. Huber, M. Wiebcke, Chem. Mater., 21(2009) 1410-1412.
(2) H. Bux, A. Feldhoff, J. Cravillon, M. Wiebcke, Y.-S. Li, J. Caro, Chem. Mater. 23 (2011) 2262-2269.
(3) McCarthy M. C., V. Varela-Guerrero, G. V. Barnett, H.-K. Jeong, Lagmuir. 26 (2010) 14636-14641.
(4) Y. Pan, Z. Lai, Chem. Comm. 47 (2011) 10275-10277.
(5) H. Bux, F. Liang, Y. Li, J. Cravillon, M. Wiebcke, J. Caro, J. Am. Chem. Soc. 131 (2009) 16000-16001.
(6) H. Bux, F. Liang, Y. Li, J. Cravillon, M. Wiebcke, J. Caro, J. Am. Chem. Soc. 131 (2009) 16000-16001.
(7) Z. Xie, J. Yang, J. Wang, J. Bai, H. Yin, B. Yuan, J. Lu, Y. Zhang, L. Zhou, C. Duan, Chem. Comm. 48 (2012) 5977-5979.
(8) S. Zhou, X. Zou, F. Sun, F. Zhang, S. Fan, H. Zhao, T. Schiestel, G. Zhu, J. Mater. Chem. 22 (2012) 10322.
(9) A. Brown, J. Johnson, M. Lydon, W. Koros, C. Jones, S. Nair, Angew. Chem. Int. Ed. 51(2012) 10915-10618.
(10) G. Xu, J. Yao, K. Wang, L. He, P. A. Webley, C. Chen, H. Wang, J. Membr. Sci., 385-386 (2011) 187-193.
(11) Y. Pan, B. Wang, Z. Lai, J. Membr . Sci. 421-422 (2012) 292-298.
(12) Y. S. Li, F.-Y. Liang, H. Bux, W.-S. Yang, J. Caro, J. Membr. Sci., 354 (2010) 48.
(13) Y. Liu, E. Hu, E. A. Khan, Z. Lai, J. Membr. Sci., 353 (2010) 36.
(14) X. Dong, K. Huang, S. Liu, R. Ren, W. Jin, Y. S. Lin, J. Mater. Chem., 22 (2012) 19222.
(15) C. Zhang, Y. Xiao, D. Liu, Q. Yang, C. Zhong, Chem. Commun., 49 (2013) 600-602.
(16) Y. Yoo, Z. Lasi, H.-K. Jeong, Microporous Mesoporous Mater., 123 (2009) 100.
(17) R. Ranjan, M. Tsapatsis, Chem. Mater., 21 (2009) 4920.
(18) Y. Yoo, V. Varela-Guerrero, H.-K. Jeong, Langmuir, 27 (2011) 2652.
(19) Y. Hu, X. Dong, J. Nan, W. Jin, X. Ren, N. Xu, Y. M. Lee, Chem. Commun., 47 (2011) 737.
(20) J. Nan , X. Dong, W. Wang, W. Jin, Microporous Mesoporous Mater., 155 (2012) 90.
(21) D.-J. Lee, Q. Li, H. Kim, K. Lee, Microporous Mesoporous Mater. 163 (2012) 169.