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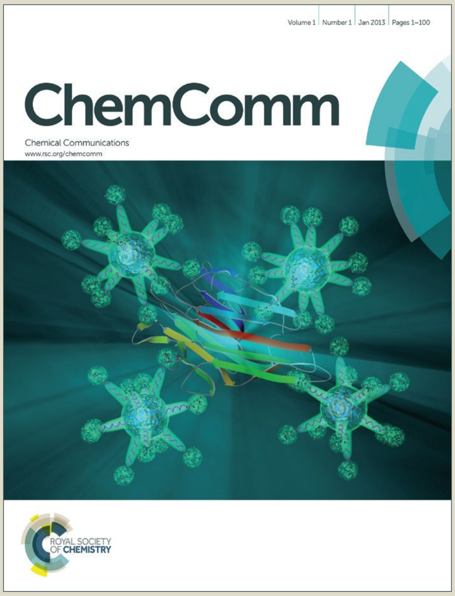

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COMMUNICATION

Superhydrophobic Zeolitic Imidazolate Framework ZIF-90 with High Steam Stability for Efficient Recover of Bioalcohols

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Superhydrophobic zeolitic imidazolate framework ZIF-90 with high steam stability is prepared through post-functionalization via an amine condensation reaction. The developed superhydrophobic ZIF-90 shows highly promising as an effective and reusable adsorbent for bio-alcohols recovery.

Due to the emerging scarcity of fossil resources and the critical environment concerns, the development of renewable and clean energy sources such as bioalcohols has drawn increasing interest in the recent years. [1] Bioalcohols are usually produced from biomass through fermentation with a low alcohol concentration in aqueous medium. Therefore, it is prerequisite to extract and recover the bioalcohols from the fermentation broth before it can be used as biofuels. Distillation is a conventional technology for the separation of alcohol/water mixture. However, it involves high energy-consuming boiling and condensing processes. Adsorptive separation by using porous materials is regarded as one of the most competitive methods due to its energy-saving and environmentally friendly. So far, various materials including activate carbons, polymeric resins and zeolites have been developed for the separation of alcohol/water mixture. [2-6] However, these adsorbents have a strong affinity to water, resulting in a low adsorption capacity and effectiveness. Therefore, the development of a novel adsorbent with high adsorption performance remains an urgent challenge.

In the past ten years, metal–organic frameworks (MOFs) have received considerable interest because of their potential applications in gas adsorption and storage, membrane separation, chemical sensor, and drug delivery. [7-12] In particular, zeolitic imidazolate frameworks (ZIFs), a subfamily of MOFs based on transition metals and imidazolate linkers, [13, 14] have emerged as a novel type of porous material for the fabrication of molecular sieving membranes due to their zeolite-like properties such as permanent porosity, uniform pore size, exceptionally thermal and chemical stability. [15-21] Further, ZIFs are also promising adsorbents for the recovery of bio-alcohols due to their tunable pore size and adjustable internal surface properties. [22, 23] It is well recognized that the adsorption performances of the adsorbents is determined no only by their open pore structures and surface areas, but also their hydrophobicity. [3, 24] Therefore, the development of superhydrophobic absorbents with open pore structures, high stability and large surface areas is of special interest. To the best of our knowledge, so far no studies on synthesis and application of superhydrophobic ZIFs have been reported.

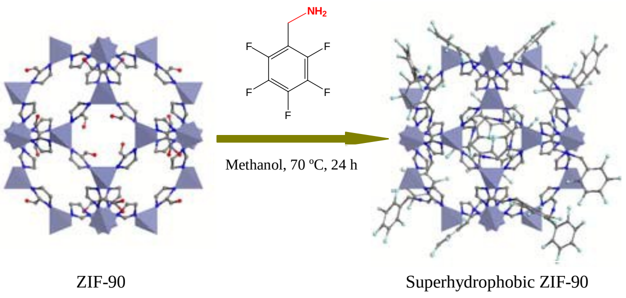

Fig. 1. Scheme of the synthesis of superhydrophobic ZIF-90 via an amine condensation reaction.

Recently, Yaghi and co-workers have developed a novel SOD topology ZIF-90 through solvothermal reaction of Zinc (II) and imidazolate-2-carboxyaldehyde (ICA). [25] ZIF-90 shows not only highly stable but also permanent microporosity with a narrow

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pore size (~3.5 Å) and high BET surface area (1270 $m^2 \cdot g^{-1}$). Especially, the presence of free aldehyde groups in the ZIF-90 framework allows the covalent functionalization of ZIF-90 with amine groups via an imine condensation reaction. Based on the imine condensation reaction, we have developed a covalent post-functionalization strategy to enhance the molecular sieve performances of the ZIF-90 membrane. [26, 27] Indeed, the postsynthetic modification of MOFs is well known as an effective and versatile strategy to improve their physical and chemical properties. [28-32] Due to the presence of the free aldehyde groups in the ZIF-90 framework, ZIF-90 is an ideal candidate for the post-functionalization through host-guest reactions, generating a large number of topologically identical but functionally diverse ZIF-90 with fine-tuned and optimized properties. [25-29] In the present work, we report the synthesis of superhydrophobic ZIF-90 for bioalcohols recovery through post-functionalization of ZIF-90 with pentalfluorobenzylamine via amine condensation reaction (Fig. 1 and Fig. S1). It can be expected that the fluorinated ZIF-90 will show high hydrophobicity and thus is promising for bioalcohols recovery.

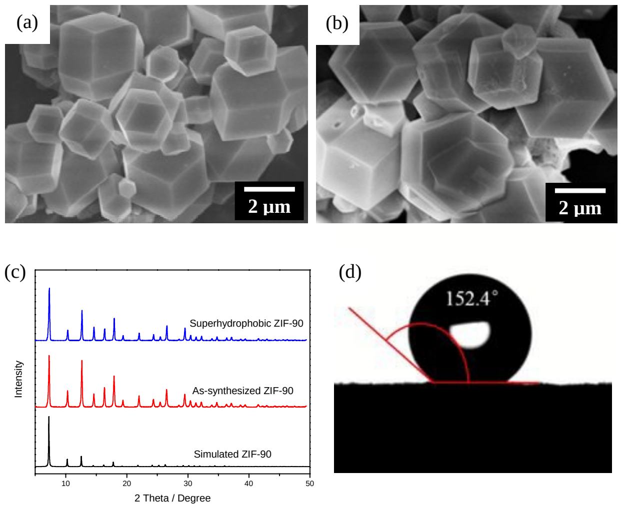

Fig. 2. FESEM images of ZIF-90 (a) and superhydrophobic ZIF-90 (b), XRD patterns of ZIF-90 and superhydrophobic ZIF-90 (c), measurement of contact angle with water for the superhydrophobic ZIF-90 (d).

Pentalfluorobenzylamine was synthesized according to the procedure reported elsewhere with minor modification (Fig. S2, the details see Supporting Information). [33] The formation of pentalfluorobenzylamine is confirmed by Fourier transform infrared (FT-IR) and ^{1}H-NMR nuclear magnetic resonance (NMR) spectra (Fig. S3). The ZIF-90 was prepared by the solvothermal reaction of zinc (II) nitrate tetrahydrate, sodium formate, and ICA in methanol. [34] As shown Fig. 2a, well-defined ZIF-90 crystals with dodecahedral morphology and size of about 2.0±0.5 μm are prepared after solvothermal synthesis for 24 h at 85 °C. For covalent post-functionalization, the as-prepared ZIF-90 crystals were immersed in a solution of pentalfluorobenzylamine in methanol, and then refluxed for 24 h at 70 °C. The post-functionalization of ZIF-90 with pentalfluorobenzylamine was confirmed by FT-IR spectroscopy and X-ray photoelectron spectroscopy (XPS). As shown in Fig. S4, the C=O band of the aldehyde at 1678 cm^{-1} is replaced by the C=N bond of the imine at 1630 cm^{-1}. The presences of aromatic C-C band at 1510 cm^{-1} and F-C band at 1030, 1125, 1235 cm^{-1} suggest that pentalfluorobenzylamine has been grafted on the ZIF-90 after post-modification. As shown in Fig. S5 and Table S1, after post-modification, the intensity of O1s and Zn2p peaks reduce much and a new F1s peak emerges with high intensity, confirming that pentalfluorobenzylamine has successfully reacted with the aldehyde groups of ZIF-90. Since the kinetic diameters of pentalfluorobenzylamine is much larger than the pore size of the ZIF-90, the pentalfluorobenzylamine is difficult to go into the ZIF-90 cage. Therefore, the post-synthetic modification reaction mainly occurs at the external surface of the ZIF-90 particles, as shown in Fig. S6. [35] The successful post-functionalization of ZIF-90 was further confirmed by N_2 adsorption isotherm. As shown in Fig. S7a, the N_2 adsorption isotherm for ZIF-90 showed a steep rise in the low-pressure region, indicating the permanent porosity of the ZIF-90 framework. [34] The calculated BET surface area of ZIF-90 in the present work is about 1182 $m^2 \cdot g^{-1}$, which is in good agreement with the previous report. [34] However, after post-functionalization, the pore aperture of the fluorinated ZIF-90 is severely constricted, leading to a low N_2 adsorption (Fig. S7b).

After post-functionalization, no remarkable differences in the ZIF-90 morphology are found between the as-prepared and the fluorinated ZIF-90 (Fig. 2b). As deduced from the X-ray diffraction (XRD) pattern (Fig. 2c), the high crystallinity of the ZIF-90 structure is kept unchanged after post-modification, even after being boiled in water for 24 h (Fig. S8). Further, from thermogravimetric analysis (TGA) (Fig. S9), both the as-prepared and fluorinated ZIF-90 show a similar plateau region without significant weight loss in the temperature range 80~300 °C, even after the measurement of water stability (Fig. S10). These results indicate that the fluorinated ZIF-90 shows high thermal and chemical stability.

The hydrophobicity of the fluorinated ZIF-90 was evaluated by the measurement of water contact angle (CA). As shown in Fig. 2d, the surface of fluorinated ZIF-90 shows a water CA of about 152.4°, while water CA of the surface of the as-prepared ZIF-90 is 93.9° (Fig. S11), suggesting that the hydrophobicity of the ZIF-90 can be significantly enhanced through post-functionalization with pentafluorobenzylamine. Such surface superhydrophobicity should be attributed to the cooperation of both microporous morphological structures and strongly hydrophobic chemical compositions of the fluorinated ZIF-90, which are two well-known key factors for the surface superhydrophobicity. [24, 36]

The hydrophobicity of the fluorinated ZIF-90 was further confirmed by the removal of alcohols from alcohol/water mixtures. To evaluate the adsorption capacity of the fluorinated ZIF-90 for recovery of alcohols from alcohol/water mixtures, the superhydrophobic ZIF-90 powders were added into ethanol/water mixture which was dyed by red oil for clarity, and then keeping stirring for 2 h. After a following selective adsorption of ethanol for 20 h, the fluorinated ZIF-90 powders which have adsorbed ethanol were separated by a simple filtration. As shown in Fig. S12c, the mother solution become colourless and transparent after the removal of fluorinated ZIF-90 powders by filtration, indicating ethanol has been fully recovered and removed by the fluorinated ZIF-90. In deeded, according to the analysis of gas chromotograph (GC), 98% ethanol has been removed from the ethanol/water mixture (Fig. 3). On the contrary, only 7% ethanol can be removed from the ethanol/water mixture by using the as-prepared ZIF-90 as adsorbent (Fig. S13). Besides ethanol, the superhydrophobic ZIF-90 also displays high adsorptive separation performances for removal of other bioalcohols such as methanol, iso-propanol and butanol as well as its mixtures (Fig. 3). Further, the superhydrophobic ZIF-90 can be easily regenerated by simple thermal regeneration under vacuum at 65 °C, and the superhydrophobic ZIF-90 still shows highly active after five successive cycles of separation due to its high stability, with almost constant alcohol removal percent (Fig. S13). From the TGA measurement of the superhydrophobic ZIF-90 which has fully adsorbed ethanol, a similar plateau region without significant weight loss in the temperature range 80~300 °C is still observaed, and the initial weight loss is about 20% at 30~80 °C due to the release of ethanol (Fig. S14). These results are in good agreement with our supposition that the superhydrophobic ZIF-90 is very promising to be used as an effective and reusable adsorbent for bio-alcohols recovery from aqueous solution.

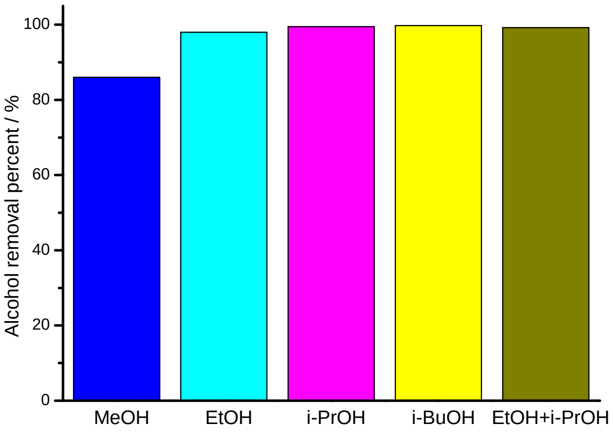

Fig.3. Adsorptive separation performance of the superhydrophobic ZIF-90 for removal of alcohols from alcohols/water mixtures.

In conclusion, based on an amine condensation reaction between the aldehyde groups of ZIF-90 and amine groups of pentafluorobenzylamine, we have developed a facile post-functionalization road for preparation of superhydrophobic ZIF-90. After post-functionalization, the water CA can be enhanced from 93.9° to 152.4°, while both the dodecahedral morphology and SOD structure of ZIF-90 remain unchanged due to its high stability. The developed superhydrophobic ZIF-90 displays high adsorptive separation performance for the recovery of bio-alcohols. At 20 °C, more than 98% bio-alcohols (ethanol, iso-propanol and butanol) can be recovered and removed from bio-alcohol/water mixture. These properties recommend the superhydrophobic ZIF-90 as a promising candidate for industrial bio-alcohols recovery.

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References

1 J. A. Turner, *Science*, 1999, **285**, 687-689.
2 S. J. T. Pollard, G. D. Fowler, C. J. Sollars and R. Perry, *Sci. Total Environ.*, 1992, **116**, 31-52.
3 A. Li, H. X. Sun, D. Z. Tan, W. J. Fan, S. H. Wen, X. J. Qing, G. X. Li, S. Y. Li and W. Q. Deng, *Energy Environ. Sci.,* 2011, **4**, 2062-2065.
4 T. Ono, T. Sugimoto, S. Shinkai and K. Sada, Nat. Mater., 2007, **6**, 429-433.
5 K. Zhang, R. P. Lively, J. D. Noel, M. E. Dose, B. A. McCool, R. R. Chance and W. J. Koros, *Langmuir*, 2012, **28**, 8664-8673.
6 K. Zhang, R. P. Lively, M. E. Dose, L. Li, W. J. Koros, D. M. Ruthven, B. A. McCool and R. R. Chance, *Microporous Mesoporous Mater.*, 2013, **170**, 259-265.
7 R. Banerjee, A. Phan, B. Wang, C. Knobler, H. Furukawa, M. O'Keeffe and O. M. Yaghi, *Science*, 2008, **319**, 939-943.
8 B. Wang, A. P. Cote, H. Furukawa, M. O'Keeffe and O. M. Yaghi, *Nature*, 2008, **453**, 207-211.
9 H. T. Kwon and H. K. Jeong, *J. Am. Chem. Soc.*, 2013, **135**, 10763-10768.
10 A. R. Millward and O. M. Yaghi, *J. Am. Chem. Soc.*, 2005, **127**, 17998-17999.
11 G. Lu and J. T. Hupp, *J. Am. Chem. Soc.*, 2010, **132**, 7832-7833.
12 Y. Lee, S. Kim, J. K. Kang and S. M. Cohen, *Chem. Commun.*, 2015, **51**, 5735-5738.
13 K. S. Park, Z. Ni, A. P. Cote, J. Y. Choi, R. Huang, F. J. Uribe-Romo, H. K. Chae, M. O'Keeffe and O. M. Yaghi, *Proc. Nat. Acad. Sci. U. S. A.*, 2006, **103**, 10186-10191.
14 X. C. Huang, Y. Y. Lin, J. P. Zhang and X. M. Chen, *Angew. Chem. Int. Ed.*, 2006, **45**, 1557-1559.
15 H. Bux, F. Liang, Y. Li, J. Cravillon, M. Wiebcke and J. Caro, *J. Am. Chem. Soc.*, 2009, **131**, 16000-16001.
16 Y. S. Li, F. Y. Liang, H. Bux, A. Feldhoff, W. S. Yang and J. Caro, *Angew. Chem. Int. Ed.*, 2010, **49**, 548-551.
17 Y. Pan and Z. Lai, *Chem. Commun.,* 2011, **47**, 10275-10277.
18 A. Huang, Y. Chen, N. Wang, Z. Hu, J. Jiang and J. Caro, *Chem. Commun.,* 2012, **48**, 10981-10983.
19 Z. Xie, J. Yang, J. Wang, J. Bai, H.Yin, B. Yuan, Ji. Lu, Y. Zhang, L. Zhou and Chunying Duan, *Chem. Commun.*, 2012, **48**, 5977-5979.
20 A. Huang, Q. Liu, N. Wang, Y. Zhu and J. Caro, *J. Am. Chem. Soc.*, 2014, **136**, 14686-14689.
21 A. Huang, W. Dou and J. Caro, *J. Am. Chem. Soc.*, 2010, **132**, 15562-15564.
22 K. Zhang, R. P. Lively, M. E. Dose, A. J. Brown, C. Zhang, J. Chung, S. Nair, W. J. Koros and R. R. Chance, *Chem. Commun.*, 2013, **49**, 3245-3247.
23 K. Zhang, K. M. Gupta, Y. Chen and J. Jiang, *AICHE J.*, 2015, *61*, 2763-2775.
24 X. Yao, Y. Song and L. Jiang, *Adv. Mater.*, 2011, **23**, 719-734.
25 W. Morris, C. J. Doonan, H. Furukawa, R. Banerjee and O. M. Yaghi, *J. Am. Chem. Soc.*, 2008, **130**, 12626-12627.
26 A. Huang and J. Caro, *Angew. Chem. Int. Ed.*, 2011, **50**, 4979-4982.
27 A. Huang, N. Wang, C. Kong and J. Caro, *Angew. Chem. Int. Ed.*, 2012, **51**, 10551-10555.

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28 H. Li, X. Feng, Y. Guo, D. Chen, R. Li, X. Ren, X. Jiang, Y. Dong and B. Wang, *Scientific reports*, 2014, **4**, 4366.
29 A. Karmakar, N. Kumar, P. Samanta, A. V. Desai and S. K. Ghosh, *Chem-Eur. J.*, 2015, **3**, 1521-3765.
30 Z. Wang and S. M. Cohen, *J. Am. Chem. Soc.*, 2007, **129**, 12368–12369.
31 E. Dugan, Z. Wang, M. Okamura, A. Medina and S. M. Cohen, *Chem. Commun.*, 2008, 3366-3368.
32 T. Gadzikwa, G. Lu, C. L. Stern, S. R. Wilson, J. T. Hupp and S. T. Nguyen, *Chem. Commun.*, 2008, 5493-5495.
33 B. Kumar Das, N. Shibata and Y. Takeuchi, *J. Chem. Soc. Perkin Trans,* 2002, **1**, 197–206.
34 Q. Liu, N. Wang, J. Caro and A. Huang, *J. Am. Chem. Soc.*, 2013, **135**, 17679-17682.
35 X. Liu, Y Li, Y Ban, Y Peng, H Jin, H. Bux, L. Xu, J. Caro and W. Yang, *Chem. Commun.*, 2013, **49**, 9140-9142.
36 L. Gao and T. J. McCarthy, *J. Am. Chem. Soc.*, 2006, **128**, 9052-9053.