

# Bicontinuous Zeolitic Imidazolate Framework ZIF-8@GO Membrane with Enhanced Hydrogen Selectivity

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**S** Supporting Information

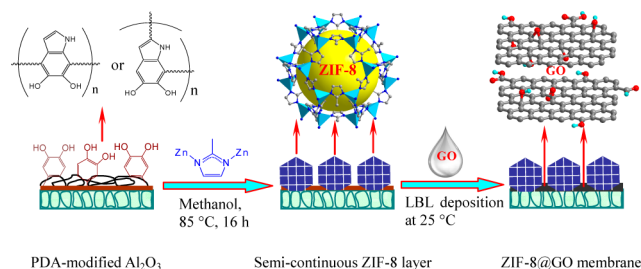
**ABSTRACT:** Through layer-by-layer (LBL) deposition of a graphene oxide (GO) suspension on a semicontinuous ZIF-8 layer, we have developed a novel bicontinuous ZIF-8@GO membrane. Since only the gaps between the ZIF-8 crystals are sealed by the GO layer due to capillary forces and covalent bonds, the gas molecules can only permeate through the ZIF-8 micropore system (0.34 nm). Therefore, the ZIF-8@GO membranes show high hydrogen selectivity. At 250 °C and 1 bar, the mixture separation factors of H<sub>2</sub>/CO<sub>2</sub>, H<sub>2</sub>/N<sub>2</sub>, H<sub>2</sub>/CH<sub>4</sub>, and H<sub>2</sub>/C<sub>3</sub>H<sub>8</sub> are 14.9, 90.5, 139.1, and 3816.6, with H<sub>2</sub> permeances of about 1.3 × 10<sup>-7</sup> mol·m<sup>-2</sup>·s<sup>-1</sup>·Pa<sup>-1</sup>, which is promising for hydrogen separation and purification by molecular sieving.

Separation of mixtures and purification of raw products play significant roles in industrial processes. In comparison with conventional separation processes such as distillation and adsorption, membrane-based separations are very promising due to their lower energy consumption.<sup>1</sup> In the past two decades, porous materials such as zeolites, carbons, silica, and metal–organic frameworks (MOFs) have been used to prepare molecular sieve membranes.<sup>2–28</sup> Recently, the two-dimensional graphene oxide (GO) with controllable surface chemistry emerged as a promising candidate for the fabrication of a fundamentally new class of molecular sieve membranes due to its high stability and easy fabrication.<sup>29–34</sup> By simple vacuum filtration or layer-by-layer (LBL) deposition of GO suspensions, molecular<sup>30</sup> or ionic<sup>31</sup> sieving GO membranes with a sharp size cutoff have been developed. However, it should be noted that with increasing the thickness of the GO membrane, its permeability decreases sharply.<sup>30</sup> It is found that even sub-micrometer-thick GO membranes are completely impermeable to liquids, vapors, and gases since the GO membranes are too tightly packed to let the molecules go through.<sup>29</sup> Therefore, it is still a big challenge to develop highly permselective GO molecular sieve membranes.

In order to increase the permeance, besides the development of ultrathin (nm-sized) GO membranes,<sup>30</sup> an alternative road is to insert nanoparticles between GO nanosheets to enlarge its spacing.<sup>31,32</sup> Attributed to the presence of plenty of functional groups in the GO framework, such as hydroxyl, epoxide, carboxyl, and carbonyl groups, GO is an optimum starting material for forming uniform and stable hybrid composites. Especially, hybrid composites based on GO and MOFs have

drawn much interest due to their unique properties.<sup>35–37</sup> Therefore, it can be expected that high-performance GO-based mixed-matrix membranes (MMMs) can be formed by incorporating MOFs into the GO layer. Generally, to prepare MMM, nanoparticles are mixed with an organic polymer and then dried and separated from the substrate to obtain a self-supporting membrane.<sup>38–41</sup> Since the thickness of the MMM is significantly larger than the diameters of the embedded particles, most particles are completely surrounded by the polymer matrix. Consequently, both selectivity and permeance of MMM are strongly influenced by the matrix.<sup>39–41</sup> Actually, a ZIF-8@GO MMM (Supporting Information (SI), Figure S1), which was prepared by simple incorporation of ZIF-8 (ZIF = zeolitic imidazolate frameworks, a subfamily of the most promising MOF structures because of their outstanding hydrothermal stability<sup>42,43</sup>) particles into the GO layer, displays low gas separation performances, since most transport channels of ZIF-8 are blocked by GO (SI, Table S1).

Recently, Goedel and colleagues proposed the preparation of bicontinuous zeolite LTA composite membranes through a “float casting” strategy,<sup>44</sup> where relative large zeolite LTA crystals were embedded in a polymer sheet in such a way that each particle penetrates both surfaces of the polymer sheet. Therefore, the zeolite LTA pore is the dominant transport channel for molecular sieving. Following the concept of “bicontinuity”, in the present work, we report the preparation of supported bicontinuous ZIF-8@GO membranes based on the treatment of ZIF-8 layer by a GO solution (Figure 1). Since



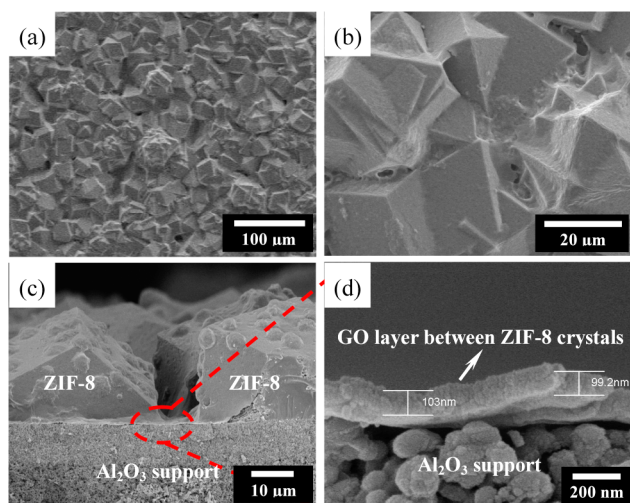
**Figure 1.** Scheme of preparation of bicontinuous ZIF-8@GO membranes through layer-by-layer deposition of graphene oxide on the semicontinuous ZIF-8 layer which was synthesized on a polydopamine-modified alumina disk.

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only the gaps between the ZIF-8 crystals are filled with GO due to capillary forces and covalent bonds,<sup>37</sup> the gas molecules can only permeate through the ZIF-8 micropore system (0.34 nm). Therefore, it can be expected that the ZIF-8@GO membranes will display a high molecular sieve performance for the separation of H<sub>2</sub> (0.29 nm) from larger gas molecules.

The preparation of a bicontinuous ZIF-8@GO membrane on polydopamine (PDA)-modified Al<sub>2</sub>O<sub>3</sub> is schematically shown in Figure 1. By simple immersion of the Al<sub>2</sub>O<sub>3</sub> disks in a buffered aqueous solution of dopamine (pH 8.5) for 20 h at room temperature, dopamine spontaneously polymerizes into PDA and deposits on the Al<sub>2</sub>O<sub>3</sub> surface.<sup>18</sup> After solvothermal reaction at 85 °C for 16 h (see SI), rhombic ZIF-8 crystals have interspersed the PDA-modified Al<sub>2</sub>O<sub>3</sub> surface and formed a semicontinuous ZIF-8 layer (SI, Figure S2). After repeated LBL deposition of GO suspension for five cycles, all gaps between the ZIF-8 crystals are completely sealed by a GO layer due to capillary forces and covalent bonds,<sup>37</sup> thus forming a dense ZIF-8@GO membrane (Figure 2a,b). The sealing of the spaces



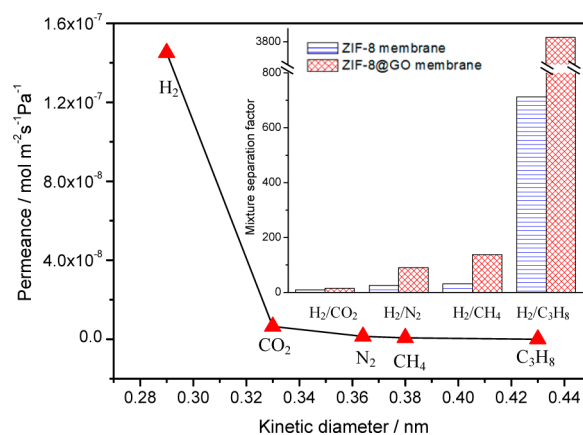
**Figure 2.** Top view (a,b) and cross-section (c,d) FESEM images of the bicontinuous ZIF-8@GO membrane prepared on porous Al<sub>2</sub>O<sub>3</sub> disk.

between the ZIF-8 crystals was further confirmed by the cross-section view (Figure 2c,d, and SI, Figure S3). A dense GO layer with about 100 nm thicknesses is formed between firmly stuck ZIF-8 crystals, and no cracks, pinholes, or other defects are visible in the GO layer (SI, Figure S4). The coverage of the GO layer can be controlled by adjusting the LBL process and the concentration of GO suspensions (SI, Figure S5). However, with higher GO coverage, more ZIF-8 crystals are covered by the GO layer, thus reducing the “real membrane area” for gas permeation, which results in a lower permeance of the ZIF-8@GO membrane.

The formation of ZIF-8@GO membrane was also confirmed by X-ray photoelectron spectroscopy (XPS). As shown in Figure S6 (SI), after LBL deposition of GO on the ZIF-8 layer, the enhancement of the intensity of O 1s (from GO) and the presence of C=O and C–O (from GO), as well as the reduction of the intensity of N 1s (from ZIF-8), indicate the formation of a GO layer on the ZIF-8 surface. On the other hand, the intensities of all peaks from the ZIF-8 layer are completely unchanged, indicating that the thickness of the GO layer on ZIF-8 crystals is less than 2 nm since the depth of XPS probe is about 2 nm. From this experimental finding we can

conclude, that there is no blocking GO layer on the ZIF-8 crystals to maintain the transport channels through the ZIF-8. The formation of a pure and highly crystalline ZIF-8@GO membrane was confirmed by X-ray diffraction (XRD), which indicates that all peaks match well with those of ZIF-8 and GO besides the Al<sub>2</sub>O<sub>3</sub> signals of the support (SI, Figure S7).<sup>15,18</sup>

The volumetric flow rates of the single gases H<sub>2</sub>, CO<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>, and C<sub>3</sub>H<sub>8</sub> as well as the 1:1 binary mixtures of H<sub>2</sub> with CO<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>, and C<sub>3</sub>H<sub>8</sub> were measured by using the Wicke–Kallenbach technique (SI, Figure S8).<sup>20,23</sup> The gas permeances and separation factors are listed in Table S2 (SI). Figure 3



**Figure 3.** Single gas permeances of different gases through the ZIF-8@GO membrane at 250 °C as a function of their kinetic diameters. The inset gives the mixture separation factors.

shows the permeances of the single gases through the ZIF-8@GO membrane as a function of the kinetic diameters of the permeating molecules. As shown in Figure 3 and Table S1, the H<sub>2</sub> permeance of  $1.45 \times 10^{-7} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$  is much higher than those of the other gases, and there is a clear cutoff between H<sub>2</sub> and the other larger gases. All the single gas permeances of the ZIF-8@GO membrane are lower than those of the ZIF-8 membrane.<sup>18</sup> In particular, for the molecules with a kinetic diameter larger than the crystallographic pore size of ZIF-8 (0.34 nm), like CH<sub>4</sub> (0.38 nm) and C<sub>3</sub>H<sub>8</sub> (0.43 nm), the gas permeances decrease more intensely. At 250 °C and 1 bar, the ideal separation factors of H<sub>2</sub> from CO<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>, and C<sub>3</sub>H<sub>8</sub> are 22.4, 102.8, 198.3, and 5870.1, respectively, which by far exceed the corresponding Knudsen coefficients (4.7, 3.7, 2.8, and 4.7), suggesting that the ZIF-8@GO membrane displays a high hydrogen selectivity.

The molecular sieve performance of the ZIF-8@GO membrane was further confirmed by the separation of 1:1 binary mixtures of H<sub>2</sub> with CO<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>, and C<sub>3</sub>H<sub>8</sub> at 250 °C and 1 bar. Comparing with the H<sub>2</sub> single gas permeance, the H<sub>2</sub> permeance in mixtures shows only a slight reduction, with a H<sub>2</sub> permeance of  $(1.27\text{--}1.35) \times 10^{-7} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$ , indicating that the larger molecules (CO<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>, and C<sub>3</sub>H<sub>8</sub>) have only a slight influence on the permeation of the highly mobile H<sub>2</sub>. Similar experimental findings were also observed on ZIF-90<sup>23</sup> and ZIF-8<sup>15,18</sup> membranes. As shown in the inset of Figure 3 and in Table S2, for the 1:1 binary mixtures, the mixture separation factors of H<sub>2</sub>/CO<sub>2</sub>, H<sub>2</sub>/N<sub>2</sub>, H<sub>2</sub>/CH<sub>4</sub>, and H<sub>2</sub>/C<sub>3</sub>H<sub>8</sub> on the GO-modified ZIF-8 membrane are 14.9, 90.5, 139.1, and 3816.6, respectively, which are much higher than those of the ZIF-8 membrane (8.9, 16.2, 31.5, and 712.6).<sup>18</sup> As shown in previous reports,<sup>15,18</sup> CH<sub>4</sub> can easily pass a ZIF-8 membrane

due to lattice flexibility. In the present work, probably the rigid GO layer around the ZIF-8 crystals can constrict lattice flexibility of ZIF-8, thus preventing larger molecules (like CH<sub>4</sub> and C<sub>3</sub>H<sub>8</sub>) to enter the pores. Further, the LBL deposition of GO can reduce nonselective transport pathway through intercrystalline defects (SI, Figure S9) by covalent bonds, thus markedly enhancing the separation selectivity. Indeed, both FT-IR and Raman spectra of the ZIF-8@GO composite confirm the formation of Zn–O covalent bonds between the ZIF-8 and the GO, which is helpful for the formation of dense ZIF-8@GO membranes (SI, Figure S10). Further, it is found that the gas separation performance of ZIF-8@GO membranes is also much higher than that of the Al<sub>2</sub>O<sub>3</sub>-supported GO membrane (SI, Figure S11, Table S1). Since the preparation of semicontinuous ZIF-8 layer and LBL deposition of GO are controllable, a high reproducibility of the preparation of ZIF-8@GO membrane can be found (SI, Table S3).

ZIF-8, one of the most studied MOF structures, is of special interest for the fabrication of molecular sieve membranes for H<sub>2</sub> separation,<sup>15–18</sup> CO<sub>2</sub> separation,<sup>14</sup> and the separation of alkanes from alkenes.<sup>17,19</sup> Since the pore size of ZIF-8 membrane (0.34 nm) is in between the molecular sizes of H<sub>2</sub> (0.29 nm) and CH<sub>4</sub> (0.38 nm), the separation of H<sub>2</sub> with CH<sub>4</sub> was usually performed to investigate the separation performance of ZIF-8 membranes. Bux et al. prepared the first H<sub>2</sub> selective ZIF-8 membrane with a H<sub>2</sub>/CH<sub>4</sub> selectivity of 12.6 and a H<sub>2</sub> permeance of  $0.6 \times 10^{-7}$  mol·m<sup>-2</sup>·s<sup>-1</sup>·Pa<sup>-1</sup> through microwave heating.<sup>15</sup> Jeong et al. reported a H<sub>2</sub> selective ZIF-8 membrane with a H<sub>2</sub>/CH<sub>4</sub> selectivity of 13.0 and a H<sub>2</sub> permeance of  $1.7 \times 10^{-7}$  mol·m<sup>-2</sup>·s<sup>-1</sup>·Pa<sup>-1</sup>.<sup>16</sup> Lai and colleagues prepared high permeability ZIF-8 membranes on hollow YSZ fiber prepared by secondary growth method, with a H<sub>2</sub>/CH<sub>4</sub> selectivity of 13.0 and H<sub>2</sub> permeance of  $12.3 \times 10^{-7}$  mol·m<sup>-2</sup>·s<sup>-1</sup>·Pa<sup>-1</sup>.<sup>17</sup> Inspired by the bioadhesive ability of marine mussel, we have successfully synthesized high H<sub>2</sub> selective ZIF-8 membranes on PDA-modified Al<sub>2</sub>O<sub>3</sub> disks with a H<sub>2</sub>/CH<sub>4</sub> selectivity of 31.5 and H<sub>2</sub> permeance of  $1.9 \times 10^{-7}$  mol·m<sup>-2</sup>·s<sup>-1</sup>·Pa<sup>-1</sup>.<sup>18</sup> Recently, Nair and colleagues synthesized high H<sub>2</sub> selective ZIF-8 membrane on organic hollow fibers by interfacial technique,<sup>26</sup> which can be easily produced and are relatively cheap. Compared with literature data of mixed-gas separation on ZIF-8 membranes (SI, Figure S12) and other MOF as well as zeolite membranes (SI, Table S4), our ZIF-8@GO membrane also shows high separation selectivity and comparable permeance, and it far exceeds the Robeson “upper bound” of polymeric membranes for the separation of H<sub>2</sub>/CH<sub>4</sub> mixtures.<sup>45,46</sup> It is worth to note that other GO-based membranes, such as LTA@GO membranes (SI, Figure S13), can be easily fabricated through LBL deposition of GO on the semicontinuous LTA layer, confirming the universality of this method.

In good agreement with the previous reports of ZIF-8 membrane,<sup>18</sup> with increasing permeation temperature from 25 to 250 °C at 1 bar, the H<sub>2</sub> permeance of the ZIF-8@GO membrane increases from  $2.1 \times 10^{-8}$  to  $1.3 \times 10^{-7}$  mol·m<sup>-2</sup>·s<sup>-1</sup>·Pa<sup>-1</sup>, and the H<sub>2</sub>/CH<sub>4</sub> mixture separation factor rises from 30.3 to 193.8 (SI, Figure S14). At low temperature, mainly CH<sub>4</sub> is adsorbed in the ZIF-8 pores, thus blocking the diffusion of the highly mobile H<sub>2</sub>. As temperature increases, less CH<sub>4</sub> is adsorbed, and thus more H<sub>2</sub> can diffuse in the resulting free volume, leading to an enhancement of H<sub>2</sub> permeance.<sup>18,23</sup> The ZIF-8@GO membrane has been tested for longer than 72 h at 250 °C, and the separation performance of the ZIF-8@GO

membrane remains unchanged (SI, Figure S15), suggesting that the ZIF-8@GO membrane has a high thermal stability. Also the ZIF-8@GO membrane consistently displays a high stability in the presence of steam, and both H<sub>2</sub> permeance and H<sub>2</sub>/CH<sub>4</sub> selectivity are unchanged for at least 72 h (Figure S15). The slight reduction of the H<sub>2</sub> permeance can be attributed to the parallel permeation of H<sub>2</sub>O and H<sub>2</sub> through the ZIF-8 pore since the kinetic diameter of H<sub>2</sub>O is only 0.26 nm, which is smaller than the pore size of ZIF-8 with 0.34 nm. Further, the ZIF-8@GO membrane can keep its high H<sub>2</sub> permselectivity when the H<sub>2</sub> partial pressure increases from 0.5 to 1.5 bar (SI, Figure S16).

In conclusion, in the present work we have successfully prepared a novel bicontinuous ZIF-8@GO membrane with high hydrogen permselectivity. Through LBL deposition of GO, only the gaps between the ZIF-8 crystals in the layer are sealed by the GO layer due to capillary forces and covalent bonds. Thus, the gas molecules can only permeate through the open ZIF-8 micropores. The linker distortion of the ZIF-8 seems to be suppressed by the GO layer which results in improved hydrogen selectivities. At 250 °C and 1 bar, the mixture separation factors of H<sub>2</sub>/CO<sub>2</sub>, H<sub>2</sub>/N<sub>2</sub>, H<sub>2</sub>/CH<sub>4</sub>, and H<sub>2</sub>/C<sub>3</sub>H<sub>8</sub> are 14.9, 90.5, 139.1, and 3816.6, respectively, with H<sub>2</sub> permeances of about  $1.3 \times 10^{-7}$  mol·m<sup>-2</sup>·s<sup>-1</sup>·Pa<sup>-1</sup>. This high separation selectivity combined with its high hydrothermal stability recommends the developed ZIF-8@GO membrane as a promising candidate for gas separation.

## ■ ASSOCIATED CONTENT

### ● Supporting Information

Experimental details; FESEM, XRD, XPS of the membranes; separation performances of ZIF-8@GO membrane. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

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## ■ REFERENCES

- (1) Ockwig, N. W.; Nenoff, T. M. *Chem. Rev.* **2007**, *107*, 4078.
- (2) Carreon, M. A.; Li, S. G.; Falconer, J. L.; Noble, R. D. *J. Am. Chem. Soc.* **2008**, *130*, 5412.
- (3) Lai, Z.; Bonilla, G.; Diaz, I.; Nery, J.; Sujaoti, K.; Amat, M. A.; Kokkoli, E.; Terasaki, O.; Thompson, R. W.; Tsapatsis, M.; Vlachos, D. G. *Science* **2003**, *300*, 456.
- (4) Yuan, W.; Lin, Y. S.; Yang, W. *J. Am. Chem. Soc.* **2004**, *126*, 4776.
- (5) Yan, Y. S.; Davis, M. E.; Gavalas, G. R. *Ind. Eng. Chem. Res.* **1995**, *34*, 1652.
- (6) Zhu, W.; Gora, L.; van den Berg, A. W. C.; Kapteijn, F.; Jansen, J. C.; Moulijn, J. A. *J. Membr. Sci.* **2005**, *253*, 57.

- (7) Xu, X.; Yang, W.; Liu, J.; Lin, L. *Adv. Mater.* **2000**, *12*, 195.
- (8) Huang, A.; Liang, F.; Steinbach, F.; Gesing, T. M.; Caro, J. *J. Am. Chem. Soc.* **2010**, *132*, 2140.
- (9) Shiβett, M. B.; Foley, H. C. *Science* **1999**, *285*, 1902.
- (10) de Vos, R. M.; Verweij, H. *Science* **1998**, *279*, 1910.
- (11) Ranjan, R.; Tsapatsis, M. *Chem. Mater.* **2009**, *21*, 4920.
- (12) Lu, G.; Hupp, J. T. *J. Am. Chem. Soc.* **2010**, *132*, 7832.
- (13) Li, Y.; Liang, F.; Bux, H.; Feldhoff, A.; Yang, W.; Caro, J. *Angew. Chem., Int. Ed.* **2010**, *49*, 548.
- (14) Venna, S. R.; Carreon, M. A. *J. Am. Chem. Soc.* **2010**, *132*, 76.
- (15) Bux, H.; Liang, F.; Li, Y.; Cravillon, J.; Wiebcke, M.; Caro, J. *J. Am. Chem. Soc.* **2009**, *131*, 16000.
- (16) McCarthy, M. C.; Varela-Guerrero, V.; Barnett, G. V.; Jeong, H.-K. *Langmuir* **2010**, *26*, 14636.
- (17) Pan, Y.; Wang, B.; Lai, Z. *J. Membr. Sci.* **2012**, *421–422*, 292.
- (18) Liu, Q.; Wang, N.; Caro, J.; Huang, A. *J. Am. Chem. Soc.* **2013**, *135*, 17679.
- (19) Kwon, H. T.; Jeong, H.-K. *J. Am. Chem. Soc.* **2013**, *135*, 10763.
- (20) Huang, A.; Bux, H.; Steinbach, F.; Caro, J. *Angew. Chem., Int. Ed.* **2010**, *49*, 4958.
- (21) Liu, Y.; Zeng, G.; Pan, Y.; Lai, Z. *J. Membr. Sci.* **2011**, *379*, 46.
- (22) Dong, X.; Li, Y. S. *Chem. Commun.* **2013**, *49*, 1196.
- (23) Huang, A.; Dou, W.; Caro, J. *J. Am. Chem. Soc.* **2010**, *132*, 15562.
- (24) Huang, A.; Wang, N.; Kong, K.; Caro, J. *Angew. Chem., Int. Ed.* **2012**, *51*, 10551.
- (25) Brown, A. J.; Johnson, J. R.; Lydon, M. E.; Koros, W. J.; Jones, C. W.; Nair, S. *Angew. Chem., Int. Ed.* **2012**, *51*, 10615.
- (26) Brown, A. J.; Brunelli, N. A.; Eum, K.; Rashidi, F.; Johnson, J. R.; Koros, W. J.; Jones, C. W.; Nair, S. *Science* **2014**, *345*, 72.
- (27) Huang, A.; Chen, Y.; Wang, N.; Hu, Z.; Jiang, J.; Caro, J. *Chem. Commun.* **2012**, *48*, 10981.
- (28) Gascon, J.; Kapteijn, F. *Angew. Chem., Int. Ed.* **2010**, *49*, 1530.
- (29) Nair, R. R.; Wu, H. A.; Jayaram, P. N.; Grigorieva, I. V.; Geim, A. K. *Science* **2012**, *335*, 442.
- (30) Li, H.; Song, Z.; Zhang, X.; Huang, Y.; Li, S.; Mao, Y.; Ploehn, H. J.; Bao, Y.; Yu, M. *Science* **2013**, *342*, 95.
- (31) Joshi, R. K.; Carbone, P.; Wang, F. C.; Kravets, V. G.; Su, Y.; Grigorieva, I. V.; Wu, H. A.; Geim, A. K.; Nair, R. R. *Science* **2014**, *343*, 752.
- (32) Mi, B. *Science* **2014**, *343*, 740.
- (33) Kim, H. W.; Yoon, H. W.; Yoon, S.-M.; Yoo, B. M.; Ahn, B. K.; Cho, Y. H.; Shin, H. J.; Yang, H.; Paik, U.; Kwon, S.; Choi, J.-Y.; Park, H. B. *Science* **2013**, *342*, 91.
- (34) Hu, M.; Mi, B. *Environ. Sci. Technol.* **2013**, *47*, 3715.
- (35) Jahan, M.; Bao, Q.; Yang, J.; Loh, K. P. *J. Am. Chem. Soc.* **2010**, *132*, 14487.
- (36) O'Neill, L. D.; Zhang, H.; Bradshaw, D. *J. Mater. Chem.* **2010**, *20*, 5720.
- (37) Kumar, R.; Jayaramulu, K.; Maji, T. K.; Rao, C. N. R. *Chem. Commun.* **2013**, *49*, 4947.
- (38) Jia, M.; Peinemann, K.-V.; Behling, R.-D. *J. Membr. Sci.* **1991**, *57*, 289.
- (39) Zimmerman, C. M.; Singh, A.; Koros, W. J. *J. Membr. Sci.* **1997**, *137*, 145.
- (40) Yang, T. X.; Xiao, Y. C.; Chung, T. S. *Energy Environ. Sci.* **2011**, *4*, 4171.
- (41) Ordoñez, M. J. C.; Balkus, K. J., Jr.; Ferraris, J. P.; Musselman, I. H. *J. Membr. Sci.* **2010**, *361*, 28.
- (42) Park, K. S.; Ni, Z.; Côté, A. P.; Choi, J. Y.; Huang, R.; Uribe-Romo, F. J.; Chae, H. K.; O'Keeffe, M.; Yaghi, O. M. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 10186.
- (43) Phan, A.; Doonan, C. J.; Uribe-romo, F. J.; Knobler, C. B.; O'Keeffe, M.; Yaghi, O. M. *Acc. Chem. Res.* **2009**, *43*, 58.
- (44) Kiesow, I.; Marczewski, D.; Reinhardt, L.; Mühlmann, M.; Possiwan, M.; Goedel, W. A. *J. Am. Chem. Soc.* **2013**, *135*, 4380.
- (45) Robeson, L. M. *J. Membr. Sci.* **1991**, *62*, 165.
- (46) Robeson, L. M. *J. Membr. Sci.* **2008**, *320*, 390.