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Published in:

ACS applied materials & interfaces

Published: 11/08/2019

Document Version:

Post-print, also known as Accepted Author Manuscript, Peer-reviewed or Author Final version

Publication record in CityU Scholars:

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Published version (DOI):

[10.1021/acsami.9b08592](https://doi.org/10.1021/acsami.9b08592)

Publication details:

He, Y., Sun, M., Zhao, Q., Shang, J., Tian, Y., Xiao, P., Gu, Q., Li, L., & Webley, P. A. (2019). Effective Gas Separation Performance Enhancement Obtained by Constructing Polymorphous Core-Shell Metal-Organic Frameworks. *ACS applied materials & interfaces*, 11(33), 30234-30239. <https://doi.org/10.1021/acsami.9b08592>

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Effective Gas Separation Performance Enhancement Obtained by Constructing Polymorphous Core-Shell Metal-Organic Frameworks

*Yingdian He^a, Qinghu Zhao^a, Jin Shang^{*b,c}, Yuanmeng Tian^c, Ke Xie^a, Penny Xiao^{a,e}, Qinfen Gu^{*d}, Paul A. Webley^{a,e}*

a. Department of Chemical and Biomolecular Engineering, The University of Melbourne, Victoria 3010, Australia.

b. School of Energy and Environment, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong SAR

c. City University of Hong Kong Shenzhen Research Institute, 8 Yuexing 1st Road, Shenzhen Hi-Tech Industrial Park, Nanshan District, Shenzhen, China

d. Australian Synchrotron (ANSTO), 800 Blackburn Rd, Clayton, Victoria 3168, Australia.

e. Cooperative Research Center for Greenhouse Gas Technologies (CO2CRC), Melbourne, Australia.

KEYWORDS: gas adsorption; metal-organic frameworks; core-shell

ABSTRACT

We report a new polymorphous core-shell MOF in the form of a 3D-MOF core wrapped in a 2D-layered MOF shell by applying a general acid-solvent synergy synthesis. This hybrid material can achieve high adsorptive selectivity/capacity simultaneously, which provides a new route for elevating gas separation performance by constructing multi-functional core-shell materials.

Metal-organic frameworks (MOFs) or porous coordination polymers (PCPs) have attracted increasing attention due to their applications in adsorptive gas separation over the past few decades thanks to their ultra-high surface area and tuneable pore chemistry.¹⁻⁴ Most porous MOFs feature large pore volume and surface area and thus can provide relatively high adsorption capacity for all components in the gas mixture, but result in relatively low selectivity based on equilibrium adsorption.⁵⁻⁷ A few MOFs possessing uniform pore/channel size similar to the gas molecules could offer very high selectivity based on the molecular sieving mechanism, but lack of sufficiently high capacity due to the reduced overall pore volume.⁸⁻¹⁰ Particularly, flexible MOFs as a unique family of MOFs, generally exhibit high adsorption selectively attributed to their structural responsiveness to the inclusion of certain guest molecules.^{4, 11-12} It is highly desirable to develop MOFs that combine both high adsorption selectivity and high capacity. In order to take full advantage of the merits of MOF materials for gas separation, a core-shell MOF composite constructed from a high adsorption capacity MOF-Core (MOF-C) as the high capacity gas storage core and a MOF-Shell (MOF-S) with high gas selectivity as the outer shell to achieve merits of both simultaneously.

Generally, construction of the core-shell structure in MOF families is a challenging and less studied area. Several pioneering studies have proven the possibility of constructing the core-shell MOFs and demonstrated their exceptional capabilities for versatile applications.¹³⁻¹⁸ For example, $[\text{Zn}_2(\text{ndc})_2(\text{dabco})]_n$ and $[\text{Zn}_2(\text{ndc})_2(\text{dpndi})]_n$ with different pore surface functionality were integrated into one single crystal via face-selective epitaxial growth strategy (where ndc = 1,4-naphthalene dicarboxylate, dabco = 1,4-diazabicyclo[2.2.2]octane and dpndi = N,N'-di(4-pyridyl)-1,4,5,8-naphthalenetetracarboxydiimide).¹⁹ The heterogeneous crystals offer potential to integrate sorption, separation, and reaction properties in one functional material. Another core-shell product was obtained by a seeded growth technique on MOF-5 (Zn_4O clusters with BDC) with IRMOF-3 (Zn_4O clusters with ABDC), where BDC = 1,4-benzene dicarboxylate and ABDC = 2-amino benzene-1,4-dicarboxylate. Interestingly, the N_2 uptake of IRMOF-3@MOF-5 and MOF-5@IRMOF-3 are approximately $820 \text{ cm}^3/\text{g}$ which is between that of MOF-5 ($920 \text{ cm}^3/\text{g}$) and IRMOF-3 ($750 \text{ cm}^3/\text{g}$). The identical topology of the two structures, multilayered crystals in forms of MOF-5@IRMOF-3@MOF-5 and IRMOF-3@MOF-5@IRMOF-3, were produced successfully by applying the same technique.²⁰ A core-shell architecture built from two isostructural compounds $\text{Co}_2(\text{ad})_2(\text{CH}_3\text{CO}_2)_2$ (named bio-MOF-11, where ad = adeninate) and $\text{Co}_2(\text{ad})_2(\text{C}_4\text{H}_9\text{CO}_2)_2$ (bio-MOF-14), can integrate the benefits of two structures for selective adsorption CO_2 over N_2 with high water stability.²¹ However, for these reported successful examples, the structures of the shell and the core component are topologically identical, predominately on a basis of the growth of the shell out of the core by an epitaxial mechanism. This limits the development of core-shell MOFs to certain MOF families. Therefore, a new synthetic strategy is required to construct core-shell MOFs which feature structural diversity between the shell and core materials so as to extend the structural multiformity of composite.

Herein, we report a new polymorphous MOF composite constructed from a 3D rigid MOF as the core and a 2D layered flexible MOF as the shell obtained by crystal phase-converting in an “outside-in” fashion. Importantly, this core-shell MOF composite integrates the high adsorption capacity of the core MOF and the ideal selectivity of the shell MOF, which demonstrates the desired properties for the potential practical application in gas separation.

Inspired from our previous studies on structural conversion of a layered MOF to achieve enhanced selectivity,⁸ we designed a new core-shell composite to realize both high adsorption capacity and selectivity in the system. To be specific, we fabricated a “gate keeping” shell around the “storage” core so that undesired gas molecules (e.g. N₂) can be excluded from entering the internal pores within the core. The key to achieve this goal is the control of both the morphology and thickness of the shell, which we have accomplished as shown below. The core-shell MOF composites were synthesized by simply soaking the core single crystals (MOF-C) in a concentrated 1,3-Bis(4-pyridyl)propane (BPP) solution with a small amount of acetic acid addition and heated to 105 °C for various time lengths (Figure 1, S1). A detailed synthesis route is provided in Supporting Information.

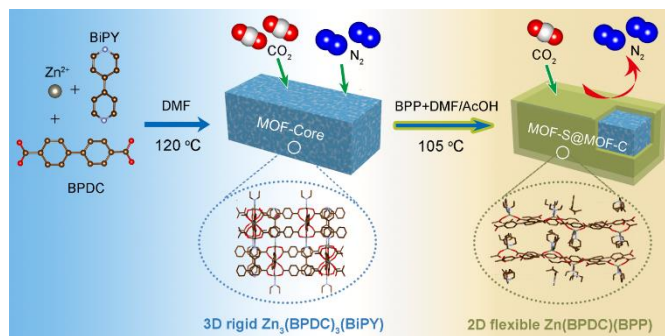


Figure 1. Schematic illustration of acid-solvent synergy synthesis for the core-shell MOF-S@MOF-C composite with enhanced gas separation performance.

Interestingly, the morphologies of the samples with the 4-days reaction time exhibited same columnar-like single crystals and remained the shape similar to the parent MOF-C, as evidenced by our microscope observations (Figure 2a, 2b). In addition, the core-shell composite showed considerably rougher surface compared with that of the pristine MOF-C crystals (Figure S4). This may be due to a dramatic difference existing in the structural topologies between MOF-S and MOF-C crystals in this case, with the ligand exchange proceeding to certain extent, the surface of parent single crystals cracked into smaller crystals as indicated from the optical microscope images and SEM images (Figure S3) of MOF-S (Figure 2c). Basically, the structural transformation from MOF-C to MOF-S involved a substantial change of the crystal morphology at a critical point when the intactness of the parent crystals cannot remain upon the ligand exchange. In this case, the crystals of the sample after 7-days exchange time lost their single crystal nature caused by crystal micro strain and lattice mismatch. *In-situ* optical microscope observation of the synthesis process indicates the polymorphous structure (with MOF-S@MOF-C composites having the same crystal morphology as the parent MOF-C) for the samples with certain exchange time. To further confirm the formation of the core-shell structure, we conducted TEM experiments on the sample with 6-days exchange time. The cross-section of one typical core-shell MOF single crystal was prepared by focus ion beam (FIB) cutting method (Figure S2) and the TEM image clearly shows the interface between the core and shell crystal phases (Figure 2d).

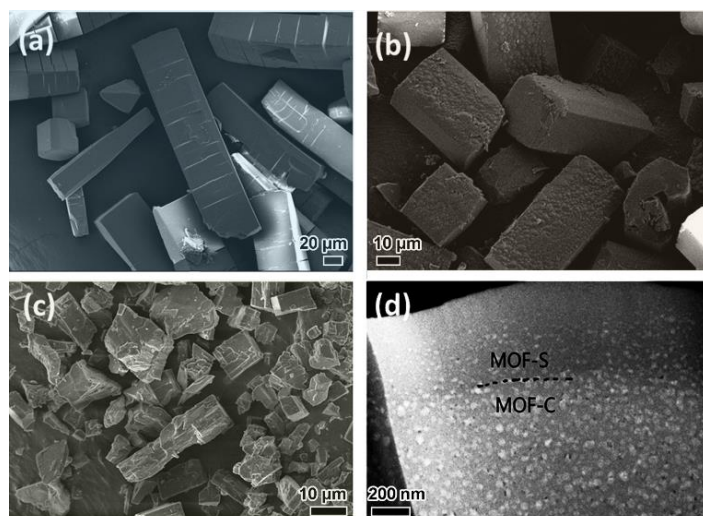


Figure 2. (a) SEM image of MOF-C crystals, (b) core-shell MOF-S@MOF-C composite after 4-days exchange reaction, and (c) MOF-S crystals after full conversion, (d) TEM image of a cross-section of the core-shell MOF-S@MOF-C composite prepared by focused ion beam (FIB) cutting.

To better understand the mechanism of the formation of the polymorphous core-shell MOF composite and the structural conversion from MOF-C to MOF-S in atomic scale, we conducted synchrotron X-ray powder diffraction (XRPD) experiment for the samples collected after various reaction periods, i.e. 3, 4, 6, 7, and 9 days, to monitor the crystal phase transformation or MOF-S shell growth during the ligand exchange process (Figure 3a). The parent MOF-C sample remained almost unchanged with 3-days exchange time, and a complete pure phase of MOF-S was formed after 9 days. The XRPD patterns indicate that the core-shell structure displayed an increasing ratio of MOF-S phase in MOF-S@MOF-C with increased ligand exchange time. For example, the MOF-S@MOF-C composite with 4-days reaction time contained approximately 40.1 wt % of parent MOF-C phase and 59.9 wt % of MOF-S phase on basis of the Rietveld refinement results from the XRPD data (Figure 3b). After 7-days exchange, phase composition reached 9.2 wt % of parent MOF-C phase and 90.2 wt % of MOF-S phase (Figure S5). It is worth noting that the ratio of the MOF-S and MOF-C is an average value considering the crystal size distributions due to

inevitable small crystal defect (Figure S3, S9). In addition, the ratio between MOF-S and MOF-C phases can be precisely controlled by changing reaction time, temperature, and acid concentration.

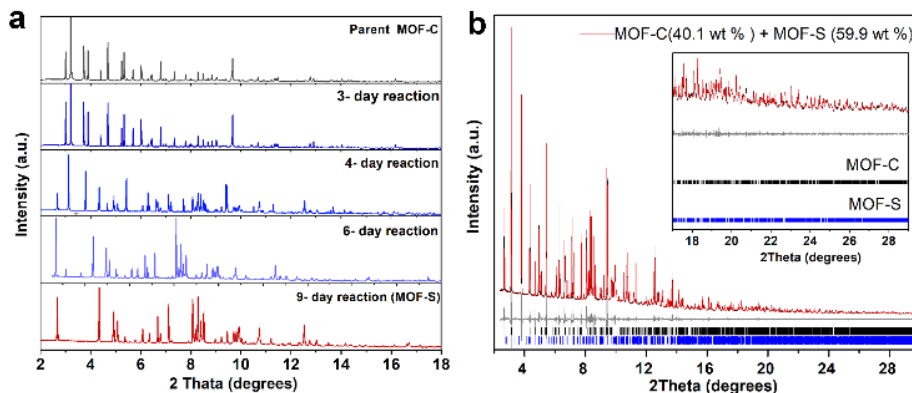


Figure 3. (a) Synchrotron X-ray powder diffraction (XRPD) patterns of pristine parent MOF-C, and samples with 3, 4, 6 (MOF-S@MOF-C) and 9 days (MOF-S) exchange time; (b) Rietveld refinement profile for the core-shell.

To verify our prediction of the enhanced gas separation performance on our rational designed core-shell MOF composite, we conducted CO₂ and N₂ sorption experiments on the 4-days exchanged sample as well as pure MOF-C and pure MOF-S for comparison. Notably, the shell layer from core-shell structure, MOF-S, blocked N₂ uptake at 77 K (Figure 4a). In contrast, the core material from the core-shell structure, MOF-C, adsorbed a substantial amount of N₂ (approximately 12 mmol/g at 1 bar and 77 K) at the same conditions (Figure 4a). As anticipated, the core-shell structure, MOF-S@MOF-C composite, displayed negligible N₂ uptake similar to MOF-S (Figure 4a). These results prove that our MOF-S@MOF-C composite inherits the property of the shell, that is, blocking N₂ due to molecular sieving.

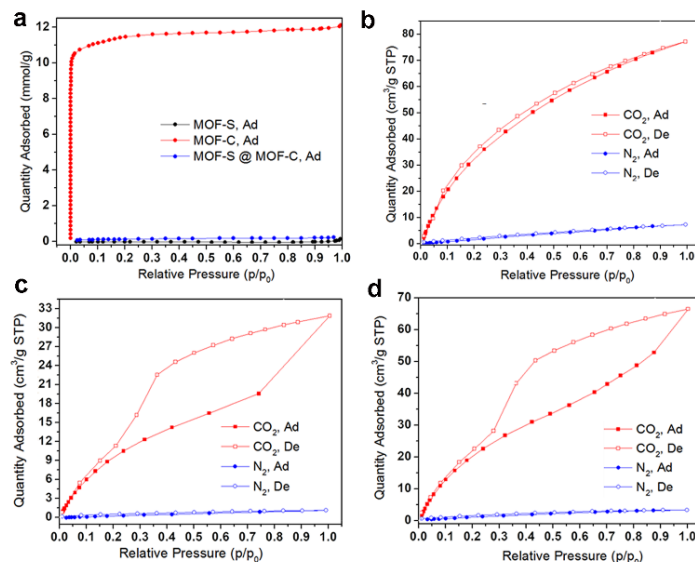


Figure 4. (a) N₂ adsorption isotherms at 77 K of MOF-C, MOF-S@MOF-C (the sample with 4-days exchange), and MOF-S (the sample with 9-days exchange), CO₂ and N₂ adsorption/desorption isotherms of (b) MOF-C, (c) MOF-S and the (d) MOF-S@MOF-C with 4-days exchange at 273 K.

We are to examine if the MOF-S@MOF-C composite also inherits the advantage of the MOF-C. From Figure 4b, MOF-C adsorbs approximately 77.5 cm³/g of CO₂ and 7.4 cm³/g of N₂ at 1 bar and 273 K. On the other hand, the MOF-S has much lower CO₂ adsorption capacity, around 31.5 cm³/g, and it adsorbs negligible amounts of N₂ (1.2 cm³/g) at the same condition. It is evident that the MOF-C exhibits higher CO₂ adsorption capacity but MOF-S has the advantage of high CO₂/N₂ selectivity. Very importantly, the adsorption properties of the core-shell MOF-S@MOF-C composite integrate the merits of the both single MOF structures, suggesting our designed core-shell composite works as expected. To be specific, MOF-S@MOF-C features considerably higher CO₂ adsorption capacity (66.8 cm³/g) compared with MOF-S (31.5 cm³/g), and higher CO₂/N₂ selectivity (20.9) than that of MOF-C (10.5). It is worth mentioning that a small percentage of pure MOF-S crystals can be expected in the MOF-S@MOF-C samples (Figure S3 shows a large number of very small crystals present), since the parent MOF-C crystals with smaller crystalline size

logically complete ligand exchange, which can be removed with a suitable manual sieve. This is likely the cause of the observed adsorption/desorption hysteresis from the flexible nature of the MOF-S structure.

Conclusions

In summary, we applied a novel strategy to construct a core-shell architecture of MOF-S@MOF-C composite which features the merits of both pure MOF-S and MOF-C materials in terms of high gas adsorption capacity and high gas selectivity, demonstrated by the enhanced CO₂/N₂ separation performance at 273 K. The 4-days exchanged MOF-S@MOF-C composite exhibited 212% higher CO₂ adsorption capacity compared with the value for pure MOF-S, and 199% CO₂/N₂ higher selectivity compared with the value for pure MOF-C. This innovated synthesis route potentially offers a universal method for constructing advanced core-shell MOF structures as we have demonstrated a potential generalization route of the solvent-acid synergetic ligand exchange.²² Having overcome the limitation in topological similarities to construct core-shell MOFs, a numerous combination of the MOFs with distinct structures and properties via the strategy reported in this study would open up a new horizon to enhance gas separation performances by rational designed polymorphous MOF composites.

ACKNOWLEDGMENT

JS gratefully acknowledges the financial support from the National Natural Science Foundation of China (21706224), the Research Grants Council of Hong Kong (CityU 21301817), and City University of Hong Kong Start-Up grant (7200524). Authors acknowledge Australian Research Council (ARC) funding (DP2013000024). SEM experiment was conducted by Dr.

Ranjeet Singh. TEM was conducted by Dr. Sergey Rubanov. Part of work was undertaken on the PD beamline, Australian Synchrotron (ANSTO).

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