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The Growth Mechanism of a Conductive MOF Thin Film in Spraybased Layer-by-layer Liquid Phase Epitaxy

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Abstract: The layer-by-layer liquid-phase epitaxy (LBL-LPE) method is widely used in preparing metal-organic framework (MOF) thin films with the merits of controlling thickness and out-of-plane orientation for superior performances in applications. The LBL-LPE growth mechanism related to the grain boundary, structure defect, and orientation is critical but very challenging to study. In this work, a novel "in-plane self-limiting and self-repairing" thin-film growth mechanism is demonstrated by the combination study of the grain boundary, structure defect, and orientation of Cu₃(HHTP)₂-xC thin film via microscopic analysis techniques and electrical measurements. This mechanism results a desired highquality MOF thin film with preferred in-plane orientations at its bottom for the first time and is very helpful for optimizing the LBL-LPE method, understanding the growth cycle-dependent properties of MOF thin film, and inspiring the investigations of the biomimetic selfrepairing materials.

Introduction

Due to the highly designable framework and pore structures, metal–organic frameworks (MOFs) are attracting increasing research interests.^[1] Usually, MOFs in thin-film form exhibit better performances than powder samples in the applications, such as thermoelectricity, gas separation, and sensing.^[2] Many methods, including layer-by-layer liquidphase epitaxy (LBL-LPE), Langmuir–Blodgett LBL growth, in situ growth, electrochemical deposition, interface selfassembly, post-synthesis polymerization and solvent-free hot pressing, have been developed to prepare MOF thin films.^[3]

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Among them, LBL-LPE is superior in controlling the growth of MOF thin films, especially in out-of-plane orientation and thickness.^[4] In generally, the LBL-LPE thin film growth processes are mainly studied by grazing incidence X-ray diffraction, quartz crystal microbalance, atomic force microscope (AFM), ultraviolet-visible spectroscopy and infrared spectra.^[5] The important structure information, such as out-of-plane orientation, thickness, morphology, and roughness have been successfully revealed by these techniques.^[5] However, the microcosmic changes, such as grain boundary, structure defect, and in-plane orientation during LBL-LPE processes have not been provided yet. This situation has significantly hampered the optimization of the LBL-LPE technique to obtain higherquality MOF thin films for application. It is very desired while still challenging to further reveal the above-mentioned microcosmic changes related growth mechanism of MOF thin film in LBL-LPE.^[4a,6]

Compared with other MOFs, the electrically conducting MOFs (EC-MOFs) are a relatively newly-emerging type.^[7] The combination of conductivity and porosity makes them very attractive in various fields like electrocatalysis, battery, supercapacitor, field-effect transistors and sensors.^[8] Monitoring the electron and mass transport of EC-MOFs in the LBL-LPE process may reveal the desired thin film growth mechanism that cannot be achieved by the previous researches. To the best of our knowledge, such a work has not been reported yet.

Herein, the growth mechanism of the LBL-LPE process was studied with a representative conductive MOF, Cu₃-(HHTP)₂ (Scheme 1). LBL-dependent measurements of Cu₃(HHTP)₂ thin film, including direct current (DC) measurements, alternating current (AC) measurements and chemiresisitve gas sensing were conducted. The observed variation of the charge and mass transport during thin film growth reveals the desired microcosmic changes, including grain boundary, defect, and in-plane orientation. Through a systematical analysis of the above data, an "in-plane selflimiting and self-repairing" growth mechanism for LBL-LPE of EC-MOF has been successfully revealed, which improves the grain boundary and defect of MOF thin film during the thin film growth has been observed. A highquality MOF thin film with not only out-of-plane orientation but also preferred in-plane orientation at its bottom part has been observed for the first time.

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Scheme 1. Schematic illustration of spray-based LBL-LPE thin film growth and properties evolution of $Cu_3(HHTP)_2$ and its simulated crystal structure.

Results and Discussion

In the crystal structure of $Cu_3(HHTP)_2$, Cu ions and HHTP ligands coordinate with each other to form an extended twodimensional hexagonal π -conjugate layer. These layers further assemble with a slipped-parallel (ab) packing model to construct a porous honeycomb structure (scheme 1 and Figure S1).^[8h] Cu₃(HHTP)₂ thin films (denoted as Cu₃-(HHTP)₂-xC, xC=the growth cycle) were prepared by the spray-based LBL-LPE method on the hydroxyl-functionalized substrate with pre-patterned gold electrodes (Scheme 1, details see Supporting Information).^[9] Firstly, the substrate was sprayed with the solution containing Cu ions to coordinate with -OH at its surface and then rinsed with ethanol to remove the redundant Cu ions. Next, the substrate was sprayed with HHTP ligands to coordinate with Cu ions on it and then rinsed again with ethanol to remove the unreacted ligands to accomplish the first growth cycle. The above processes were repeated to epitaxially grow Cu₃(HHTP)₂-xC in a LBL-LPE manner. Figure S1 shows the in-plane and out-of-plane XRD pattern of Cu₃(HHTP)₂ film with a thickness of 200 nm. The high intensity diffraction peaks in the in-plane pattern measured by using a grazing-incidence XRD (GIXRD) technique show the high crystallinity of the thin film in ab plane. All of the peaks in the in-plane pattern could be assigned to (hk0), and the peak in the out-of-plane pattern could be assigned to (001). These results indicate Cu₃(HHTP)₂ film grows epitaxially along c axis and in high orientation. However, it should be noticed that the peak of (002) is weaker and broader than these of (hk0), suggesting a relatively worse long-range order packing along c axis due to weaker interaction among the layers.

FT-IR spectra and conductivity analysis show profound differences between HHTP ligand and $Cu_3(HHTP)_2$ film, excluding the possibility of the formation of crystalline thin films for the HHTP ligands (Figure S2 and S3).

To explore the growth mechanism, $Cu_3(HHTP)_2-xC$ films were firstly characterized by AFM at each growth cycle (Figure 1a–h and S4). The grain size, roughness, and thickness of these thin films were statistically analyzed (Figure 2a, 2b and S5). In the whole growth process, $Cu_3(HHTP)_2-xC$ shows a grainy surface with most of the grain size < 40 nm in transverse diameter (Figure 1a–h and 2b). Specifically, at the first growth cycle, island-like nuclei are deposited on the sapphire surface. Compared with the average roughness



Figure 1. a–h) Topography of $Cu_3(HHTP)_2$ -xC in AFM images, i) schematic diagram of growth mechanism of $Cu_3(HHTP)_2$ -xC.

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Angew. Chem. Int. Ed. 2022, 61, e202212797 (2 of 6)
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Figure 2. a) Growth cycle dependent analysis of thickness and roughness of Cu₃(HHTP)₂-xC, b) particle size analysis of Cu₃(HHTP)₂-xC, c) SEM cross-sectional view of Cu₃(HHTP)₂-20C, and d) schematic illustration of electrode, e) log(|1|)-Voltage curves of Cu₃(HHTP)₂-xC, and f) growth cycle dependent $log(\sigma)$ curve of Cu₃(HHTP)₂-xC.

 (R_a) of the substrate (0.3 nm), the first growth cycle increases the R_a to ≈ 0.7 nm (Figure 1a, 1b and 2a). The DC measurement of $Cu_3(HHTP)_2$ -1C shows a nonlinear I-Vcurve and very low current, indicating a bad electron transport pathway and confirming the discontinuous contact among the grains in the AFM image (Figure S6b). In the second growth cycle, the average transverse diameter of the nuclei does not change obviously, but they grow from "islands" to "mountains" with an obvious increment in height, resulting in an increased roughness of 2.47 nm (Figure 1c and 2a). Meanwhile, a large number of new nuclei with much smaller sizes can be observed to fill the gaps among the "mountains" (Figure 1c). A thin film with improved integrality has been obtained in this growth cycle, which shows a quasi-linear I-V curve and increased current (Figure S6c). The third growth cycle further improves the integrality of the thin film while with similar grain size and roughness as these in the second cycle (Figure 1d). In this cycle, a uniform and continuous thin film has been obtained, which is further demonstrated by the good linearity of its I-V curve (Figure S6d).

Further growth cycles do not obviously change the surface morphology of $Cu_3(HHTP)_2$ -xC (x=4-20). The average surface roughness of these thin films keeps ≈ 2.2 nm with little fluctuation (Figure 2a). Meanwhile, the SEM and AFM images of the cross-section of $Cu_3(HHTP)_2$ -xC demonstrate a successful epitaxial growth (Figure 2a and S5). Their thickness homogeneously increases with an average of ≈ 2 nm per cycle (Figure 2a). The cross-section of the thin film clearly shows a dense bottom and rough top profile and

Angew. Chem. Int. Ed. 2022, 61, e202212797 (3 of 6)

the proportion of the dense bottom to the rough top increases with the growth cycle increment (Figure 2c and S7).

Based on the above observations, an "in-plane (parallel to the substrate) self-limiting and out-of-plane (perpendicular to the substrate) epitaxial growth" mechanism for Cu₃-(HHTP)₂-xC is proposed (Figure 1i). The observed conductivity and small roughness of Cu₃(HHTP)₂-1C indicate Cu₃(HHTP)₂ is very easy to form "nuclei" during the first spray process. The amount of these "nuclei" is big enough to make them get close with each other to form a quasiconnected thin film, which results a different I-V curve from that of the substrate. From the second growth cycle, the grain size and roughness of the thin films change little, while the thickness increases homogeneously. These results indicate the nucleation and the growth of the surface grain at the "in-plane" direction have a balanced speed, which results in a self-limiting process. In each cycle, the growth of the surface grain is always restricted to <40 nm by the newborn nuclei due to the limited in-plane space. Notably, this growth model is quite different from the reported one, where the nuclei continuously grow up.^[5a,b,d,g,10] The dense packing of the cross-sectional view of thin films indicates the newborn nuclei can fuse tightly with the original grain in the following growth cycles. Different from the in-plane direction, the out-of-plane shows a homogeneous epitaxial growth mode due to the unlimited space.

To reveal more details of this thin film growth mechanism, the charge/mass transfer properties of Cu₃(HHTP)₂**xC** were studied. I-V curves measured by the two-electrode method were used to calculate the electrical conductivity of Cu₃(HHTP)₂-xC (Figure 2d and S6). As shown in Figure 2d, different from a perfect single crystal thin film which has a thickness-independent conductivity, the conductivity of Cu₃-(HHTP)₂-xC presents a thickness-dependent conductivity in a logarithmical model (Figure 2e and 2f). This result indicates there are a large amount of grain boundaries and defects in the thin film. Interestingly, at the first 10 cycles, the conductivity of Cu₃(HHTP)₂-xC increases dramatically from 3.8×10^{-7} to 2.1×10^{-3} S cm⁻¹, ≈ 5500 times. After that, the increment of the conductivity gradually saturate. These phenomena suggest the grain boundary and defects among the grains are gradually fixed during thin film growth.

To further analyze the grain boundary, AC complex impedance spectroscopy measurements were performed in the frequency range of 10^{-1} to 10^{6} Hz. With the increasing growth cycle, the diameter of the semicircle in the Nyquist plots of Cu₃(HHTP)₂-xC gradually decreases (Figure 3a). The experimental impedance data are fitted with an equivalent circuit which consists of the resistances and constant phase elements of bulk (R_b) , grain boundary (R_{gb}) and contact (R_c), respectively (Figure 3a inset and S8) and the obtained resistances are shown in Figure 3b. It has been well known that the $R_{\rm b}$ and $R_{\rm gb}$ should be inversely proportional to the thickness of the thin film. However, with the increase of the growth cycle, the R_{b} and R_{gb} decrease with a power function model rather than a linear model, indicating the decrease of the resistances is much faster than the increase of the growth cycle (Figure S8). This unusual



Figure 3. Growth cycle-dependent measurements: a) AC impedance spectra, insert: equivalent circuit, b) resistances of bulk grain boundary resistance and contact, insert: the first derivative of log R-cycles curve, c) gas sensing. d-f) HR-TEM and the corresponding FFT pattern of Cu₃(HHTP)₂-30C.

phenomenon suggests an unexpected self-repaired crystallinity and grain boundary during the LBL-LPE processes. This speculation is well consistent with the observations of AFM and SEM, which show a dense thin film by grain fusion (Figure 1 and S7). Moreover, it is also observed that at the first 5 cycles, the total resistance of the thin film is mainly contributed by $R_{\rm b}$, which is ≈ 10 times higher than R_{sb} and R_c . Then, R_b decreases faster than R_{sb} and they reach a similar value at around the 15th cycle. After that, R_{gb} gradually dominates the total resistance of the thin film. The first derivative of the log R-cycles curve is also conducted to obtain the coefficient of resistance change (K) with the growth cycles (Figure 3b inset). It clearly shows that the decrease of R_b , R_{gb} and R_c slows down and gradually approaches a saturated value after the 10th growth cycle, demonstrating that the crystallinity and grain boundary of the thin film have been remarkably improved after 10 growth cycles. After that, the thin film can be grown with stable quality.

Taking the advantage of the gas sensing nature of $Cu_3(HHTP)_2$ -xC, the gas molecule can be used as a probe to further confirm the growth cycle-dependent change of the defect and grain boundary. Usually, the charge and mass transportability of $Cu_3(HHTP)_2$ -xC together dominate the sensing response value. However, H₂ has a very small kinetic diameter and can easily penetrate MOFs such as Cu_3 -(HHTP)₂ with a pore size larger than 1.8 nm.^[11] Therefore, the growth cycle-dependent response to H₂ mainly reflects the change of the charge transport in $Cu_3(HHTP)_2$ -xC. As

Angew. Chem. Int. Ed. 2022, 61, e202212797 (4 of 6)

shown in Figure 3c, the response of Cu₃(HHTP)₂-xC to 100 ppm H₂ increases dramatically for the first 5-10 growth cycles. After that, the response value varies very little. This result indicates the charge transportability has been optimized after 10 growth cycles, confirming the results in DC and AC measurements. Comparatively, NH₃ has a bigger kinetic diameter and a much stronger interaction with Cu₃(HHTP)₂-xC than H₂. Therefore, its transport in the pore of Cu₃(HHTP)₂ is limited. Different from H₂, NH₃ reaches its highest value at the first ≈ 10 growth cycles and then decreases obviously. Since the charge transport has been optimized at the first ≈ 10 growth cycle, the decrease of the response to NH₃ suggests the degraded mass transport of Cu₃(HHTP)₂-xC. This result confirms that there are plenty of defects facilitating the mass transport in the thin film less than 10 growth cycles and then they have been selfrepaired with the thin film growth.

Angewandte

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The slices of Cu₃(HHTP)₂-30C were peeled off from the substrate to reveal more details of the thin film structure. Figure 3d and S11 show the high-resolution TEM images with the electron beam perpendicular to the slices. The thicker part of the slice has an image with different contrast, indicating it contains the rough top surface of Cu₃(HHTP)₂-**30C** (Figure S11). The Fast Fourier transfer (FFT) pattern of the TEM image shows the diffraction cycles of (hk0) of the crystal structure, confirming its polycrystal nature. Notably, none of (001) can be found (Figure S11 inset), suggesting Cu₃(HHTP)₂-xC grows along the (001) direction orientedly. Differently, the thinner part of the slice has homogeneous contrast, indicating it belongs to the smooth bottom of Cu₃(HHTP)₂-30C (Figure 3d, 3f and S12). Its high-resolution TEM image in thousands of square nanometers shows orderly arranged lattice fringes. Different from the thicker part, the thinner part shows bright diffraction points in its FFT pattern (Figure 3e and S12 inset). Notably, these diffraction points can be divided into only a few sets of hexagonal lattice points rather than diffraction cycles. Thus, the bottom part of Cu₃(HHTP)₂-**30C** has a preferred orientation in the *ab* plane of the crystal structure. Since the area of these lattice fringes is larger than the observed grain size in the TEM and AFM images (Figure S12 and 1), the grains at the bottom part of Cu₃(HHTP)₂-30C should have fused to form a mesocrystal structure. These observations confirm the results of growth cycle-dependent DC, AC and gas sensing measurements very well. Due to the self-limiting growth, the grains in the thin film have a nanoscale size and thus high surface energy. When they connect with each other to form a thin film, the system should have high energy. To reduce the energy, the defects and grain boundary at the bottom part of the thin film are gradually self-repaired by a recrystallization process during spray processes. On the other hand, it has been known that the coordination bonding among metal ions and organic ligands is reversible with the assistance of solvent, which lays the foundation for the self-repairing process. Notably, the oriented growth of MOF thin film along the direction perpendicular to the substrate is commonly obtained by the LBL-LPE method, while the oriented growth along the basal plane of the substrate was reported for the first time.

Conclusion

In summary, the evolution of grain boundary and defect during the MOF thin film growth was revealed for the first time by electric measurements to meet the challenge in the mechanism study of the widely-used LBL-LPE thin film preparation method. As results, a novel "in-plane selflimiting and self-repairing" thin film growth mechanism was disclosed, which results an unprecedentedly high-quality Cu₃(HHTP)₂ thin film with out-of-plane orientation through whole thin film and in-plane orientation at its bottom part. The mechanism changes our long-term apparent understanding of the polycrystalline MOF film prepared by the LBL-LPE method and may inspire the preparation of desired single-crystal MOF thin film. This work not only provides a useful electric method to study the MOF thin film growth mechanism, but also helps to optimize the thickness of MOF thin film for the best performances in various applications.

Supporting Information includes experimental details and characterization data.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: Gas Sensing \cdot Layer-by-Layer Growth \cdot Liquid Phase Epitaxy \cdot Metal–Organic Frameworks \cdot Thin Film

Angew. Chem. Int. Ed. 2022, 61, e202212797 (5 of 6)

2022, 61, e202116396; Angew. Chem. 2022, 134, e202116396; f) P. Geng, L. Wang, M. Du, Y. Bai, W. Li, Y. Liu, S. Chen, P. Braunstein, Q. Xu, H. Pang, Adv. Mater. 2022, 34, 2107836; g) T. Luo, G. T. Nash, Z. Xu, X. Jiang, J. Liu, W. Lin, J. Am. Chem. Soc. 2021, 143, 13519-13524; h) J. P. Zhang, H. L. Zhou, D. D. Zhou, P. Q. Liao, X. M. Chen, Natl. Sci. Rev. 2018, 5, 907-919; i) G. K. Gao, Y. R. Wang, S. B. Wang, R. X. Yang, Y. Chen, Y. Zhang, C. Jiang, M. J. Wei, H. Ma, Y. Q. Lan, Angew. Chem. Int. Ed. 2021, 60, 10147-10154; Angew. Chem. 2021, 133, 10235-10242; j) A. Dhamija, C. K. Das, Y. H. Ko, Y. Kim, R. D. Mukhopadhyay, A. Gunnam, X. J. Yu, I. C. Hwang, L. V. Schafer, K. Kim, Chem 2022, 8, 543-556; k) W. Gong, H. Xie, K. B. Idrees, F. A. Son, Z. Chen, F. Sha, Y. Liu, Y. Cui, O. K. Farha, J. Am. Chem. Soc. 2022, 144, 1826-1834; 1) M. H. Yu, B. Space, D. Franz, W. Zhou, C. He, L. Li, R. Krishna, Z. Chang, W. Li, T. L. Hu, X. H. Bu, J. Am. Chem. Soc. 2019, 141, 17703-17712; m) S. Geng, E. Lin, X. Li, W. Liu, T. Wang, Z. Wang, D. Sensharma, S. Darwish, Y. H. Andaloussi, T. Pham, P. Cheng, M. J. Zaworotko, Y. Chen, Z. Zhang, J. Am. Chem. Soc. 2021, 143, 8654-8660; n) B. Dinakar, A. C. Forse, H. Z. H. Jiang, Z. Zhu, J. H. Lee, E. J. Kim, S. T. Parker, C. J. Pollak, R. L. Siegelman, P. J. Milner, J. A. Reimer, J. R. Long, J. Am. Chem. Soc. 2021, 143, 15258-15270; o) H. An, J. Song, T. Wang, N. Xiao, Z. Zhang, P. Cheng, S. Ma, H. Huang, Y. Chen, Angew. Chem. Int. Ed. 2020, 59, 16764-16769; Angew. Chem. 2020, 132, 16907-16912.

Angewandte

Chemie

- [2] a) Y. Zhao, H. Zeng, X. W. Zhu, W. Lu, D. Li, *Chem. Soc. Rev.* 2021, *50*, 4484–4513; b) H. Yuan, N. Li, W. Fan, H. Cai, D. Zhao, *Adv. Sci.* 2022, *9*, 2104374; c) R. B. Lin, S. C. Xiang, W. Zhou, B. L. Chen, *Chem* 2020, *6*, 337–363; d) Q. Qian, P. A. Asinger, M. J. Lee, G. Han, K. Mizrahi Rodriguez, S. Lin, F. M. Benedetti, A. X. Wu, W. S. Chi, Z. P. Smith, *Chem. Rev.* 2020, *120*, 8161–8266; e) L. Sun, B. L. Liao, D. Sheberla, D. Kraemer, J. W. Zhou, E. A. Stach, D. Zakharov, V. Stavila, A. A. Talin, Y. C. Ge, M. D. Allendorf, G. Chen, F. Leonard, M. Dinca, *Joule* 2017, *1*, 168–177.
- [3] a) L. Heinke, C. Wöll, Adv. Mater. 2019, 31, 1806324; b) W. Li, G. Yang, A. Terzis, S. Mukherjee, C. He, X. An, J. Wu, B. Weigand, R. A. Fischer, Adv. Mater. 2021, 33, 2006980; c) Y. Lin, W. H. Li, Y. Wen, G. E. Wang, X. L. Ye, G. Xu, Angew. Chem. Int. Ed. 2021, 60, 25758-25761; Angew. Chem. 2021, 133, 25962-25965; d) S. Sakaida, K. Otsubo, O. Sakata, C. Song, A. Fujiwara, M. Takata, H. Kitagawa, Nat. Chem. 2016, 8, 377-383; e) H. Yuan, J. Tao, N. Li, A. Karmakar, C. Tang, H. Cai, S. J. Pennycook, N. Singh, D. Zhao, Angew. Chem. Int. Ed. 2019, 58, 14089-14094; Angew. Chem. 2019, 131, 14227-14232; f) X. J. Yu, Y. M. Xian, C. Wang, H. L. Mao, M. Kind, T. Abu-Husein, Z. Chen, S. B. Zhu, B. Ren, A. Terfort, J. L. Zhuang, J. Am. Chem. Soc. 2019, 141, 18984-18993; g) W. Li, S. Mukerjee, B. Ren, R. Cao, R. A. Fischer, Adv. Energy Mater. 2022, 12, 2003499; h) Y. Zang, F. Pei, J. H. Huang, Z. H. Fu, G. Xu, X. L. Fang, Adv. Energy Mater. 2018, 8, 1802052; i) X. Chen, J. J. Dong, K. Chi, L. J. Wang, F. Xiao, S. Wang, Y. Zhao, Y. O. Liu, Adv. Funct. Mater. 2021, 31, 2102855; j) X. Ma, Y. Chai, P. Li, B. Wang, Acc. Chem. Res. 2019, 52, 1461-1470.
- [4] a) Z. G. Gu, J. Zhang, *Coord. Chem. Rev.* 2019, *378*, 513–532;
 b) S. Hurrle, S. Friebe, J. Wohlgemuth, C. Woll, J. Caro, L. Heinke, *Chem. Eur. J.* 2017, *23*, 2294–2298; c) H. K. Arslan, O. Shekhah, J. Wohlgemuth, M. Franzreb, R. A. Fischer, C. Wöll, *Adv. Funct. Mater.* 2011, *21*, 4228–4231; d) R. Zhai, Z. Gu, J. Zhang, *Sci. China Chem.* 2020, *50*, 857–866.
- [5] a) Q. Li, J. Gies, X. J. Yu, Y. Gu, A. Terfort, M. Kind, *Chem. Eur. J.* **2020**, *26*, 5185–5189; b) J. Lau, A. E. Trojniak, M. J. Maraugha, A. J. VanZanten, A. J. Osterbaan, A. C. Serino, M. L. Ohnsorg, K. M. Cheung, D. S. Ashby, P. S. Weiss, B. S. Dunn, M. E. Anderson, *Chem. Mater.* **2019**, *31*, 8977–8986;

© 2022 Wiley-VCH GmbH

a) N. Hanikel, X. Pei, S. Chheda, H. Lyu, W. Jeong, J. Sauer, L. Gagliardi, O. M. Yaghi, *Science* 2021, *374*, 454–459; b) C. Gu, N. Hosono, J. J. Zheng, Y. Sato, S. Kusaka, S. Sakaki, S. Kitagawa, *Science* 2019, *363*, 387–391; c) F. Chen, D. Lai, L. Guo, J. Wang, P. Zhang, K. Wu, Z. Zhang, Q. Yang, Y. Yang, B. Chen, Q. Ren, Z. Bao, *J. Am. Chem. Soc.* 2021, *143*, 9040– 9047; d) L. Yang, P. Cai, L. Zhang, X. Xu, A. A. Yakovenko, Q. Wang, J. Pang, S. Yuan, X. Zou, N. Huang, Z. Huang, H. C. Zhou, *J. Am. Chem. Soc.* 2021, *143*, 12129–12137; e) L. L. Ling, W. Yang, P. Yan, M. Wang, H. L. Jiang, *Angew. Chem. Int. Ed.*

c) M. Tu, R. A. Fischer, J. Mater. Chem. A 2014, 2, 2018–2022;
d) V. Stavila, J. Volponi, A. M. Katzenmeyer, M. C. Dixon, M. D. Allendorf, Chem. Sci. 2012, 3, 1531–1540;
e) J. Nan, X. Dong, W. Wang, W. Jin, N. Xu, Langmuir 2011, 27, 4309–4312;
f) O. Shekhah, Materials 2010, 3, 1302–1315;
g) C. Munuera, O. Shekhah, H. Wang, C. Woll, C. Ocal, Phys. Chem. Chem. Phys. 2008, 10, 7257–7261.

- [6] a) Z. B. Wang, C. Wöll, Adv. Mater. Technol. 2019, 4, 1800413;
 b) M. Tu, S. Wannapaiboon, R. A. Fischer, Inorg. Chem. Front. 2014, 1, 442–463; c) G. Delen, Z. Ristanovic, L. D. B. Mandemaker, B. M. Weckhuysen, Chem. Eur. J. 2018, 24, 187–195.
- [7] a) L. Sun, M. G. Campbell, M. Dinca, Angew. Chem. Int. Ed.
 2016, 55, 3566–3579; Angew. Chem. 2016, 128, 3628–3642;
 b) L. S. Xie, G. Skorupskii, M. Dinca, Chem. Rev. 2020, 120, 8536–8580.
- [8] a) H. Yuan, N. Li, W. Fan, H. Cai, D. Zhao, Adv. Sci. 2022, 9, 2104374; b) B. J. Zhu, D. S. Wen, Z. B. Liang, R. Q. Zou, Coord. Chem. Rev. 2021, 446, 214119; c) M. Wang, R. Dong, X. Feng, Chem. Soc. Rev. 2021, 50, 2764–2793; d) J. Liu, X. Song, T. Zhang, S. Liu, H. Wen, L. Chen, Angew. Chem. Int. Ed. 2021, 60, 5612–5624; Angew. Chem. 2021, 133, 5672–5684; e) H. B. Meng, Y. Han, C. H. Zhou, Q. N. Jiang, X. F. Shi, C. H. Zhan, R. F. Zhang, Small Methods 2020, 4, 2000396; f) X. Deng, J. Y. Hu, J. Luo, W. M. Liao, J. He, Top. Curr. Chem. 2020, 378, 27; g) M. Ko, L. Mendecki, K. A. Mirica, Chem.

Commun. **2018**, *54*, 7873–7891; h) V. R. Giménez, N. Almora-Barrios, G. Escorcia-Ariza, M. Galbiati, M. Sessolo, S. Tatay, C. Martí-Gastaldo, *Angew. Chem. Int. Ed.* **2018**, *57*, 15086– 15090; *Angew. Chem.* **2018**, *130*, 15306–15310.

- [9] a) M. S. Yao, X. J. Lv, Z. H. Fu, W. H. Li, W. H. Deng, G. D. Wu, G. Xu, Angew. Chem. Int. Ed. 2017, 56, 16510–16514; Angew. Chem. 2017, 129, 16737–16741; b) M. S. Yao, J. W. Xiu, Q. Q. Huang, W. H. Li, W. W. Wu, A. Q. Wu, L. A. Cao, W. H. Deng, G. E. Wang, G. Xu, Angew. Chem. Int. Ed. 2019, 58, 14915–14919; Angew. Chem. 2019, 131, 15057–15061.
- [10] a) O. Shekhah, H. Wang, D. Zacher, R. A. Fischer, C. Woll, Angew. Chem. Int. Ed. 2009, 48, 5038–5041; Angew. Chem. 2009, 121, 5138–5142; b) Z. Öztürk, M. Filez, B. M. Weckhuysen, Chem. Eur. J. 2017, 23, 10915–10924.
- [11] a) R. W. Day, D. K. Bediako, M. Rezaee, L. R. Parent, G. Skorupskii, M. Q. Arguilla, C. H. Hendon, I. Stassen, N. C. Gianneschi, P. Kim, M. Dinca, ACS Cent. Sci. 2019, 5, 1959–1964; b) A. Mähringer, A. C. Jakowetz, J. M. Rotter, B. J. Bohn, J. K. Stolarczyk, J. Feldmann, T. Bein, D. D. Medina, ACS Nano 2019, 13, 6711–6719.

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