# Chem Soc Rev

Chemical Society Reviews rsc.li/chem-soc-rev



ISSN 0306-0012



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Cite this: Chem. Soc. Rev., 2017, 46, 5730

# Surface-supported metal-organic framework thin films: fabrication methods, applications, and challenges

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Surface-supported metal-organic framework thin films are receiving increasing attention as a novel form of nanotechnology. New deposition techniques that enable the control of the film thickness, homogeneity, morphology, and dimensions with a huge number of metal-organic framework compounds offer tremendous opportunities in a number of different application fields. In response to increasing demands for environmental sustainability and cleaner energy, much effort in recent years has been devoted to the development of MOF thin films for applications in photovoltaics, CO<sub>2</sub> reduction, energy storage, water splitting, and electronic devices, as well as for the fabrication of membranes. Although existing applications are promising and encouraging, MOF thin films still face numerous challenges, including the need for a more thorough understanding of the thin-film growth mechanism, stability of the internal and external interfaces, strategies for doping and models for charge carrier transport. In this paper, we review the recent advances in MOF thin films, including fabrication and patterning strategies and existing nanotechnology applications. We conclude by listing the most attractive future opportunities as well as the most urgent challenges.

Received 3rd May 2017 DOI: 10.1039/c7cs00315c

rsc.li/chem-soc-rev

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Christof Wöll is Director of the Institute of Functional Interfaces at the Karlsruhe Institute of Technology (since 2009). He studied Physics at the University of Göttingen and received his PhD in 1987 at the Max-Planck-Institute of Dynamics and Self-Organization. In 1996, he took over the chair for Physical Chemistry at the University of Bochum (until 2009) and founded the collaborative research center SFB 588. He has received several awards including

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the van't Hoff Prize of the German Bunsen Association. He is a member of the "Deutsche Akademie der Naturforscher Leopoldina" and is the Spokesperson of the German Physical Society (DPG) Surface Physics Division (since 2016). His research activities focus on fundamental processes in Surface Physics and Surface Chemistry, in particular development and advancement of techniques for the characterization of molecular adsorbates and oxide surfaces as well as metal–organic frameworks (MOFs and SURMOFs). Metal–organic frameworks (MOFs),<sup>1</sup> also referred to as porous coordination polymers (PCPs),<sup>2</sup> are constructed by coordinating metal or metal-oxo clusters, acting as nodes, and organic building blocks, referred to as linkers. MOFs exist as many different types. The existing MOFs, about 20 000 in 2013<sup>3</sup> and more than 70 000 in early 2017,<sup>4</sup> have been obtained by combining roughly 100 different nodes with roughly 1000 different ditopic, tritopic, or quadrutopic linkers. The number of MOFs that have an associated theoretical description is roughly 1 million. Considering that more than 100 million organic compounds have been synthesized so far,<sup>5,6</sup> which are all, in principle, suitable as MOF linkers after additional functionalization, there is virtually no upper limit to the number of possible structures.

Originally developed for applications<sup>7</sup> in gas storage,<sup>8</sup> gas separation,<sup>9–12</sup> and catalysis,<sup>13</sup> in recent years it has been shown that these porous, crystalline solids also have huge potential in completely different areas. In these novel application fields, their mechanical, electronic, optical, thermoelectric, and magnetic properties mainly provide the basis for innovative device concepts.

For many advanced applications in nanotechnology, it is mandatory that the MOFs, usually obtained in the form of powders, are deposited on solid substrates. This is particularly evident in the case of electrical applications.<sup>14</sup> In this review, we will focus on the methods to produce such thin films. We will distinguish essentially the different types of MOF thin films: (1) SURMOFs (surface-supported metal-organic frameworks) fabricated using layer-by-layer methods, where the orientation and film thickness can be well-controlled; (2) electrochemically deposited MOF thin films; (3) MOF thin films made using chemical vapour deposition (CVD); and (4) casted MOF thin films, where essentially powders made using conventional solvothermal synthesis are cast onto a substrate. Although MOF thin films retain the intrinsic properties of the corresponding powder MOFs in principle, the possibility of also realizing multi-heteroepitaxy (in particular in connection with a layer-by-layer synthetic technique) opens up additional architectures, including the creation of well-defined organic-organic interfaces. SURMOFs thus allow for design architectures that cannot be achieved using MOF powders. In this review, these aspects will be demonstrated using examples such as photovoltaics for solar energy conversion, electrochemical/photocatalytic CO<sub>2</sub> reduction, water splitting, the fabrication of components for information technology, including memory devices and field-effect transistors (FETs), energy storage, including supercapacitors and batteries, and thermoelectric devices.

Tremendous effort has been devoted to the development of new synthetic methods to fabricate monolithic, crystalline, and highly oriented SURMOF thin films with high structural quality and low defect density.<sup>15–24</sup> In recent years a number of MOF thin film-related reviews focusing on the multitude of aspects exposed in this rapidly developing field were published in different journals, reflecting the substantial attention received by these new "Designer Solids". Among these, the overview papers published more than five years ago (*Chem. Soc. Rev.*, 2009,<sup>15</sup> 2011,<sup>17</sup> 2012;<sup>19</sup> *Chem. Rev.*, 2012;<sup>18</sup> *Sci. China: Chem.*, 2011<sup>16</sup>) are certainly still very valuable. These earlier papers, however, do not cover the new, often unexpected applications of MOF thin films which have emerged in the past 2-3 years. These more recent developments are also not covered in the excellent reviews with a main focus on device fabrication published in 2014 by Falcaro<sup>25</sup> and by Allendorf<sup>26</sup> in *Chem.* Soc. Rev., and are also not one of the main topics in the highly valuable discussion by H. Kitagawa in APL Materials,<sup>20</sup> with the latter mainly focusing on characterization of MOF thin films using synchrotron XRD. Very recently, two compilations of papers were published, one in 2016 by Zhuang et al. in Coord. Chem. Rev. concentrating on the growth mechanism of MOF thin films,<sup>22</sup> and one in 2017 by Stassen et al. in Chem. Soc. Rev. with a focus on MOF applications in electronic and sensor devices.<sup>27</sup> In view of the rapid development of the field with many unforeseen, new applications emerging we provide here an up-to-date discussion of recent, MOF-thin-film-based device applications.

This review starts with a list of supporting substrates that have, in the past, been successfully used for the deposition of MOF thin films. We will then focus on new emerging synthetic strategies and novel applications of MOF thin films. Powder MOFs and their applications are not in the scope of this review. We will conclude our overview by providing a list of challenges that must be overcome with regard to MOF-based device fabrication, *e.g.*, thin-film quality, interface stability, electrical and thermal conductivity, charge carrier mobility, electron and hole recombination, and defect concentration.

### Fabrication methods

#### Substrates for the fabrication of MOF thin films

The choice of an appropriate substrate and suitable surface modification is crucial for the deposition of MOF thin films. Different strategies have been developed to support the coating of planar solid (Si, Au, FTO, ITO, etc.), flexible (plastic), and nonplanar substrates (metal oxide or polymer particles, metal foams, etc.). Since spray procedures have been recently developed that allow, in principle, the realization of continuous processes, there are virtually no limitations on the dimensions and types of solid substrates that can act as a substrate for MOF thin film deposition. In many cases, however, the functionalization of the substrates is crucial, in particular for the quasi-epitaxial deposition of MOF thin films. A number of applications involving charge transfer, e.g., electrocatalytic CO2 reduction, water spitting, and photovoltaics, require conducting substrates and high quality substrate/MOF interfaces. Table 1 provides a list of solid substrates and the corresponding deposition procedures that have been used successfully to deposit MOF thin films.

Numerous synthetic strategies, including liquid-phase epitaxy (LPE), chemical vapor deposition (CVD), atomic layer deposition (ALD), substrate-seeded heteroepitaxy (SSH), bottom-up modular assembly (BMA), spin coating techniques (SCT)<sup>28</sup> and electrochemical fabrication (ECF), have been developed for the fabrication of metal-organic framework thin films. In many cases, the formation of the thin films allowed for specific applications.<sup>29–32</sup>

		MOFs	Fabrication method	Ref.
Planar	Au/SAM	MOF-5, ZIF-8	Solvothermal mother solutions	33 and 34
		HKUST-1	Solvothermal solution	35
		HUKST-1 and $[M_2(L)_2(P)]$	Layer-by-layer or liquid-phase epitaxy	36 and 37
		HKUST-1 and Fe-MIL-88B-NH <sub>2</sub>	Gel-layer synthesis	38
		[Zn(bdc)(4,40-bipy) <sub>0.5</sub> ](MOF-508)	Liquid-phase epitaxy	39
		Rho-ZMOF-1	Solvothermal growth	40
		$Fe(py)_2[Pt(CN)_4]$	Liquid-phase layer-by-layer synthesis	41
	Si	MIL-89	Colloidal deposition method	42
		NAFS-1	Langmuir-Blodgett layer-by-layer deposition	43
		ZIF-8 and $[Cu(pzdc)_2(pyz)]$	Dip coating in mother solution	34 and 44
		MIL-101(Cr)	Dip coating from colloidal solution	45
		HKUST-1	Mother solution	46
		DA-MOF	Layer-by-layer fabrication	47
	ITO/FTO	Cu-TCPP	Drop-casting method	48
		MOF-525	Solvothermal method	49
		NU-1000, UiO-66, HKUST-1, Al-MIL-53	Electrophoretic deposition	50
		Pd-porphyrin Zn-SURMOFs	Liquid-phase epitaxy	51
		Re-SURMOF	Liquid-phase epitaxy	52
		Eu-HBPTC	Electrodeposition	53
		Co-TCPP	Solvothermal preparation	54
		Zn(NDI-X)	Deposition	55
	Polymer	HKUST-1	Mother solution	56 and 57
	1 01911101	MIL-47	Mother solution in MW	58
	Metal slice	HKUST-1	Electrochemically and mother solution	59 and 60
		$[Zn_2(btc)_2]$	Mother solution	61
		$Cu_{2}(bdc)_{2}$	Spin-casting method	28
	Alumina	MII -101(Cr)-NH-	Din costing	62
	Aluinna	$WIL^{-101}(CI)^{-1VII_2}$	Dip coating	02
Non-planar	Porous metal	HKUST-1	Seeded growth	63
		ZIF-8	Mother solution in MW	64 and 65
		ZIF-7	Seeding, then mother solution in MW	66-68
		ZIF-22	Mother solution	69
		[Cu <sub>2</sub> (ndc) <sub>2</sub> (dabco)]	Stepwise dosing of reactants	70
		IRMOF-3/MOF-5	Mother solution	71 and 72
		[Al(bdc)]MIL-53	Seeding, then mother solution	73
		MIL-96	Seeded growth	73
		[Cu(hfipbb)(H2hfipbb) <sub>0.5</sub> ]	Seeded growth	74
		Co-H <sub>3</sub> TBTC	In situ growth	75
	Si foam	HKUST-1 and ZIF-8	Layer-by-layer method	76
	ZnO nanowire	ZIF-CoZn	Solution method	77
	Capillary column	$Cu_2(D-cam)_2P$	Liquid-phase epitaxial growth	78
	AAO	Sr/Eu-imidazolate	In situ coating	79
	$Fe_3O_4$	HKUST-1	Liquid-phase epitaxy	80 and 81
	Silk	TMU-4, TMU-5	Liquid-phase epitaxy	82
	Polystyrene fiber	MOF-199	Electrospinning	83
	TiO <sub>2</sub>	MIL-125	Single-step hydrothermal synthesis	84
	SiO <sub>2</sub>	HKUST-1	Laver-by-laver method	85

Since the number of approaches developed is already fairly large, it is reasonable to divide them into two different categories: (i) solution-based fabrication of MOF thin films, a process in which the MOF thin films are fabricated on a substrate immersed in a single or different solutions containing the reactants, *e.g.*, metal precursors and organic ligands, and (ii) vacuum-based fabrication of MOF thin films, a process in which the MOF thin films are fabricated on a substrate under vacuum conditions using gas-phase reactants.

#### (i) Solution-based fabrication of MOF thin films

**Liquid-phase epitaxy (LPE).** Among the well-established MOF thin-film fabrication schemes, liquid-phase epitaxy (LPE), established by Wöll and coworkers, is one of most frequently used synthetic strategies for SURMOFs.<sup>37</sup> In the LPE process illustrated in Fig. 1(a), there are two central key issues: (i) a functionalized

substrate and (ii) a deposition process where the substrates are immersed in solutions containing individual reactants instead of a mixture of reactants using a conventional solvothermal process. Because of their importance, these two steps will be discussed in more detail.

**Substrate functionalization.** One of the most convenient ways to achieve a surface terminated by a particular functional group is the deposition of self-assembled monolayers (SAMs) on the primary substrate. SAMs expose organic surfaces terminated by, *e.g.*, -COOH,<sup>90</sup> -OH,<sup>91</sup>  $-NH_2$ ,<sup>92</sup> and  $-pyridine^{93}$  moieties. These functional groups can be used to anchor either the metal or metal-oxo nodes and organic linkers, thus nucleating the growth of MOF thin films. For more details on this aspect of SAM-induced MOF nucleation see the recent review by Zhuang *et al.*<sup>22</sup> Under favorable conditions, this can lead to the formation of oriented MOF thin films with a high degree of structural perfection. In several cases, it



**Fig. 1** (a) Schematic representation of the LPE approach for the growth of SURMOF thin films on a SAM-functionalized substrate in a layer-by-layer fashion. This approach involves repeated cycles of immersion in solutions of the metal precursor and solutions of organic ligands. Between steps, the material is rinsed with solvent. Reproduced from ref. 86 with permission from John Wiley & Sons, copyright 2009; (b)  $Cu_3(BTC)_2$  (HKUST-1) grown on OH- and COOH-terminated SAM-modified gold surfaces with different growth orientations. Reproduced from ref. 35, with permission from American Chemical Society, copyright 2007. Established setups for the fabrication of SURMOF thin films by utilizing the LPE approach in a layer-by-layer fashion. (c) High-throughput spray setup, reproduced from ref. 87 with permission from John Wiley & Sons, copyright 2011; (d) spin-coating setup, reproduced from ref. 28 with permission from American Chemical Society, copyright 2015; flow-based automation setup, reproduced from ref. 89 with permission from Royal Society of Chemistry, copyright 2015, and the resulting SURMOF thin films onto various substrates with corresponding setups.

has been demonstrated that the growth orientation of SURMOF thin films can be controlled by using different functional groups<sup>35,86</sup> (Fig. 1(b)) or by tuning the density of functional groups.<sup>94</sup>

**Separation of reactants.** In contrast to the "one-pot" reaction scheme used for the solvothermal synthesis of powder MOFs, the reactants are separated in the LPE process. The metal or metal-oxo clusters acting as nodes and the organic linkers are deposited on the surface sequentially in a layer-by-layer fashion (Fig. 1(a)). After optimization of the reaction conditions, this process results in the formation of compact SURMOFs, which are well-defined, highly oriented MOF thin films with controllable film thickness and homogeneity. In favorable cases, the surface roughness can be reduced down to the nm scale.<sup>95</sup>

With the demand for more efficient fabrication of large-scale SURMOF thin films with good qualities for industrial applications, a lot of effort has been devoted to the design and building of fabrication setups based on the LPE process, such as high-throughput spray,<sup>87</sup> large-area spray,<sup>96</sup> spin coating,<sup>28</sup> dipping robot,<sup>88</sup> and flow-based automation.<sup>89</sup> An overview is provided in Fig. 1(c)–(f). With these setups, large-scale, compact, and homogeneous SURMOF thin films<sup>97</sup> on various substrates can

be prepared. A number of representative examples are displayed in Fig. 1 (bottom).

**MOFs suited for the fabrication of SURMOFs.** The fabrication of high quality SURMOFs can be achieved by the layer-by-layer approach in combination with well-established setups shown in Fig. 1(c)–(f). It has to be noted that the selection of metal nodes for construction of SURMOFs is limited to the paddle-wheel structure metal linkers, like copper acetates and zinc acetates, while the use of organic linkers is unlimited by using the LPE approach in a layer-by-layer fashion. The organic linkers with either dicarboxylic acids at *meta-/para*-positions or a N-group at *para*-positions can be adopted to fabricate 2-D SURMOFs (SURMOF 2) and 3-D SURMOFs (pillared SURMOFs), respectively. The spray setup shown in Fig. 1(c) is well-suited for the fabrication of HKUST-1 and 2-D SURMOFs, while the spin coating, dipping robot and flow automation setups shown in Fig. 1(d)–(f) have been demonstrated to be appropriate tools for the fabrication of 3-D SURMOFs.

#### Interfacial synthesis

The interfacial synthesis of MOF thin films can take place either at the interface between two immiscible solutions or at the air–liquid interface *via* self-coordination of metal ions and organic linkers, which results in the formation of free-standing MOF thin films as shown in Fig. 2.

**Liquid–liquid interface.** The liquid–liquid interfacial synthesis of MOF thin films was first reported by Ameloot *et al.*<sup>98</sup> MOF formation occurs at the 2D interface created by two immiscible phases. A key requirement is the different solubility of the organic and inorganic solvents (Fig. 2(a)). When the two solvents are brought into contact, crystal-lization takes place only at the liquid–liquid interface,

resulting in the formation of a free-standing and uniform MOF thin film. Using this rather straightforward one-pot synthesis scheme, the growth rate of the free-standing MOF thin films is determined by the different diffusion rates of the MOF precursors in the respective solvent.

The liquid–liquid interface synthetic approach has been applied to a large variety of MOF structures, including ZIF-8,  $^{9,98-100}$  MOF-5 and MOF-2,  $^{101}$  Cu<sub>3</sub>(BTC)<sub>2</sub>,  $^{98,100,102,103}$  MIL-53 (Al),  $^{104}$  and [Cu<sub>2</sub>(ndc)<sub>2</sub>(dabco)]<sub>n</sub> (ndc = 1,4-naphthalene dicarboxylate; dabco = 1,4-diazabicyclo[2.2.2]octane).  $^{105}$ 



**Fig. 2** Left: Liquid–liquid interfacial synthesis. (a) Interfacial preparation of a MOF layer using a biphasic synthesis mixture consisting of an aqueous metalion-containing solution (blue) and an organic ligand solution (purple). Crystallite formation takes place primarily at defects remaining in the layer, resulting in self-completing growth. Transparent lighter blue octahedra correspond to new nucleation events resulting from bond formation between metal ions and ligand molecules that meet. (b) Overview of the process. Both immiscible liquids are supplied by syringe pumps to a T-junction, where the formation of aqueous solution droplets in the continuous organic phase takes place. (c) Scanning electron micrographs of hollow [Cu<sub>3</sub>(BTC)<sub>2</sub>] capsules crushed with a needle tip showing its hollow interior. (d) Cross-sectional view of the capsule wall, showing its thin and uniform thickness. (a–d) Reproduced from ref. 98 with permission from Nature publishing group, copyright 2011. Right: Air–liquid interfacial synthesis. (e) Schematic illustration of the assembly process of PdTCPP-Cu MOF nanosheets (NAFS-13) at the air/liquid interface with the crystalline structure of NAFS-13 shown in the inset. (f) Schematic illustration of the post-injection methodology employed in the fabrication of NAFS-13 nanosheets. (g and h) Brewster angle microscopy (BAM) images obtained using a 532 nm green laser at an incident angle of 53.12° (Brewster angle) with respect to the air/water interface normal taken during the formation of the NAFS-13 nanofilms fabricated by post-injection. (e–h) Reproduced from ref. 106 with permission from Nature publishing group, copyright 2013.

Moreover, the liquid–liquid interfacial synthetic approach enables the fabrication of differently formed MOF thin layers, *e.g.*, shaped as 3D hollow capsules as in Fig. 2(b).<sup>98</sup> In the case of Cu<sub>3</sub>(BTC)<sub>2</sub> (BTC, 1,3,5-benzenetricarboxylic acid), an aqueous phase containing 7.2 g of cupric acetate monohydrate and 100 g of 1–4 wt% polyvinyl alcohol (liquid 1) was injected through a hollow needle in a co-flowing stream of the organic solution (liquid 2, 0.353 g BTC in 20 g of 1-octanol) flowing through polytetrafluoroethylene tubing. Nucleation and growth of [Cu<sub>3</sub>(BTC)<sub>2</sub>] occurs at the interface where the two solutions start to contact *via* a ligand exchange between the carboxylate groups of the bridging copper acetate ligands and the carboxylic acid groups of the BTC ligands. This leads to the formation of hollow capsules of Cu<sub>3</sub>(BTC)<sub>2</sub> with a uniform diameter of 375 ± 15 µm and a pinhole-free capsule wall with a uniform thickness of 1.5–2 µm as shown in Fig. 2(c) and (d).

**Air–liquid interface.** Similar to the liquid–liquid interface, the air–liquid interface offers an excellent platform to assemble two-dimensional (2D) MOF nanosheets.<sup>101,106,107</sup>

Makiura and coworkers reported a new methodology for the synthesis of crystalline, uniform, and large-scale NAFS-13 nanosheets using an air-liquid interfacial synthetic approach. In this approach, first the molecular building units are pre-oriented at the water surface by spreading an ethanolic solution on a water subphase, as shown in Fig. 2(e).<sup>106</sup> In a second step, the metal nodes present in the water subphase coordinate to the molecular linkers, thus initiating MOF formation. The synthetic procedure is schematically presented in Fig. 2(f). In this particular case, the molecular building unit was 15,10,15,20-tetrakis(4-carboxyphenyl)porphyrinato-palladium(II) (PdTCPP). A solution of PdTCPP in ethanol was then spread onto 1 mM Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O aqueous solution. The tetratopic PdTCPP molecules coordinate to copper ion joints, resulting in the formation of 2D NAFS-13 (PdTCPP-Cu) nanosheets lving flat on the air/water interface. These 2D MOF plates consist of a 2D "checkerboard" motif of PdTCPP units linked by binuclear  $Cu_2(COO)_4$  paddle wheels with a µm-scale domain size and a sheet thickness of 3 Å, as displayed in Fig. 2(g) and (h).

#### Bottom-up modular assembly (BMA)

The bottom-up modular assembly approach for the fabrication of ultrathin MOF thin films was established by H. Kitagawa and coworkers.<sup>20,43,108–111</sup> The MOF thin films comprising metalloporphyrin building units and metal ion struts with a well-controlled growth direction and film thickness were constructed by combining layer-by-layer growth using the Langmuir–Blodgett (LB) method.

A schematic illustration of this procedure is shown in Fig. 3. In this case, CoTCPP (5,10,15,20-tetrakis(4-carboxyphenyl)porphyrinato-cobalt(II)) and pyridine (py) were used as molecular building blocks or linkers. A solution of CoTCPP in chloroform/ methanol was spread onto an aqueous solution containing the metal source, CuCl<sub>2</sub>·2H<sub>2</sub>O. Reaction of the subphase metal salt with the organic linkers at the interface between the two immiscible solvents, chloroform and H<sub>2</sub>O, resulted in the formation of a 2D CoTCPP thin film (CoTCPP-py-Cu), similar to the interfacial synthesis described above. In a second step, the 2D Molecular building units Top view of CoTCPP-py-Cu 2D array



**Fig. 3** Schematic illustration of the fabrication of NAFS-1 with bottom-up modular assembly by combining a layer-by-layer growth technique with the Langmuir–Blodgett method. Reproduced from ref. 43 with permission from Nature publishing group, copyright 2010.

CoTCPP-py-Cu sheets were transferred onto a Si(100) (or quartz) substrate using an LB scheme. Repeating this process several times yielded stacked MOF nanofilms (NAFS-1, nanofilms of metal–organic frameworks on surface no. 1). The thickness of these structurally well-defined films is controlled by the number of deposition cycles. The crystallinity, preferred orientation, and homogeneity of the fabricated NAFS-1 films were characterized using synchrotron X-ray diffraction (XRD,  $\lambda = 1.554$  Å) with two different scattering geometries: out-of-plane mode and in-plane mode. The XRD patterns yield the lattice parameters a = b = 1.6460(3) nm and c = 0.9380(3) nm, and indicate that the 2D NAFS-1 nanosheets are tidily stacked in the film with a perfect preferential [001] orientation. They are almost parallel to each other with an average tilting angle of  $0.3^\circ$ .

Unlike the fabrication of 2D nanofilms at an interface, including an air/liquid interface<sup>112</sup> and a liquid/liquid interface (two immiscible solutions),<sup>113</sup> Zhang and coworkers<sup>114,115</sup> developed a surfactant-assisted approach for producing ultrathin 2D MOF nanosheets that can be transferred to the substrate *via* the Langmuir–Schäfer method for further use.

This approach allows the fabrication of ultrathin 2D bimetallic M-TCPP(Fe) MOF nanosheets (M = Co, Cu, and Zn, TCPP(Fe) = Fe(m)tetra(4-carboxyphenyl)porphine chloride) with a thickness of



**Fig. 4** (a) Schematic illustration of the surfactant-assisted synthesis of 2D Co-TCPP(Fe) nanosheets. The MOF layers are drawn in alternating blue and red to clarify the layered structures. (b) AFM and (c) TEM images of 2D Co-TCPP(Fe) nanosheets. Inset: The corresponding SAED pattern of a 2D Co-TCPP(Fe) nanosheet with the electron beam perpendicular to its basal plane. (d) Schematic illustration of the assembly process for the preparation of 2D nanosheet-based MOF thin films. Reproduced from ref. 115 with permission from John Wiley & Sons, copyright 2016.

sub-10 nm. As an example, the synthesis of 2D Co-TCPP(Fe) nanosheets is illustrated in Fig. 4(a). The surfactant molecule, *i.e.*, PVP (polyvinyl pyrrolidone), was introduced during the synthesis and can be selectively attached on the MOF surface, modulating the anisotropic growth of Co-TCPP(Fe). This leads to the formation of ultrathin 2D Co-TCPP(Fe) nanosheets with a thickness of sub-10 nm, as shown in Fig. 4(b) and (c). Furthermore, the resulting 2D Co-TCPP(Fe) nanosheets were dispersed into solutions, forming 2D MOF suspensions for the fabrication of MOF thin films using a bottom-up modular assembly approach, as shown in Fig. 4(d).

#### Substrate-seeded heteroepitaxy (SSH)

The SSH method differs from the LPE growth of SURMOFs by directly using a solid substrate as a metal source. This contrasts with the LPE method, where both reactants (metal-containing nodes and organic linkers) are provided as a solution.



**Fig. 5** (a) Construction of  $Al_2(OH)_2TCPP$  MOF from (b) rod-shaped aluminum oxide nodes connected by porphyrin linkers (H<sub>4</sub>TCPP) to give a 3D MOF. (c) SEM images of octahedral Ag NCs are subjected to ALD deposition of alumina, followed by addition of TCPP linkers to make (d) MOF-enclosed Ag NCs, OH-nano-Ag  $\subset$  MOF. Reproduced from ref. 116 with permission from American Chemical Society, copyright 2015.

Yang, Yaghi, and coworkers first demonstrated the potential of the SSH method for the case of Ag nanocrystals (NCs) coated with a thin metal oxide.<sup>116</sup> The thin metal oxide film was deposited onto the Ag NCs using atomic layer deposition (ALD). MOF formation was initiated by simply immersing the oxide-coated NCs into a solution of suitable organic linkers, as shown in Fig. 5. The reaction of the molecular building block with the metal ions from the oxide substrate then yielded MOF thin films.

To yield larger-area MOF thin films, the Ag NCs were first drop-cast on a silicon substrate (Fig. 5(c)). Subsequently, a conformal alumina film with controlled thickness was deposited at 60 °C by employing an ALD process. Using trimethylaluminum and water as precursors,  $Al_2O_3$  films were deposited with a deposition rate of 0.1 nm per cycle. MOF deposition was then performed by immersing the alumina-coated Ag NCs into solutions of the TCPP linker in *N*,*N*-dimethylformamide (DMF)/water mixtures at 140 °C in a microwave reactor.<sup>117</sup> After a reaction time of 10 min, the formation of OH-nano-Ag $\subset$ MOFs was observed (Fig. 5(d)).

Using a similar approach, Falcaro and coworkers achieved a substrate-seeded heteroepitaxial growth of  $Cu_2(BDC)_2$  MOF thin films using  $Cu(OH)_2$  nanotube arrays as a source for metal ions,<sup>118</sup> as shown in Fig. 6(a) and (b).

In this case, the growth was initiated by immersing the substrates in a saturated ethanolic solution of  $H_2BDC$  at room temperature. After an immersion time of 5 min, aligned  $Cu_2(BDC)_2$  crystals perpendicular to the nanotube surface were observed; see



**Fig. 6** Substrate-seeded heteroepitaxial growth of Cu<sub>2</sub>(BDC)<sub>2</sub> on singlecrystal Cu(OH)<sub>2</sub>. (a) Ligand (H<sub>2</sub>BDC)-containing solution is placed in contact with the Cu(OH)<sub>2</sub> nanobelt. (b) Cu<sub>2</sub>(BDC)<sub>2</sub> MOFs are heteroepitaxially grown on the Cu(OH)<sub>2</sub> nanobelt. (c and d) Crystal structures of both Cu(OH)<sub>2</sub> and Cu<sub>2</sub>(BDC)<sub>2</sub> MOFs. (e) SEM images of Cu<sub>2</sub>(BDC)<sub>2</sub> MOFs epitaxially grown on aligned Cu(OH)<sub>2</sub> nanobelt films and (f) magnified image. (g) Cu<sub>2</sub>(BDC)<sub>2</sub> MOF films on a SiC substrate. (h) Aligned Cu<sub>2</sub>(BDC)<sub>2</sub> MOFs deposited on a flexible substrate (cellophane). Reproduced from ref. 118 with permission from Nature publishing group, copyright 2017.

Fig. 6(e) and (f). Detailed X-ray diffraction (XRD) and transmission electron microscope (TEM) analyses revealed the *P*2 symmetry for the fabricated epitaxial Cu<sub>2</sub>(BDC)<sub>2</sub> thin film, with lattice parameters a = 10.90 Å, b = 5.89 Å, and c = 10.90 Å. This thin film has excellent lattice match with the Cu(OH)<sub>2</sub> nanotubes with *P*4 symmetry and lattice parameters a = 10.61 Å, b = 5.80 Å, and c = 10.61 Å, as shown in Fig. 6(c) and (d).

In addition, the substrate-seeded heteroepitaxy approach has been demonstrated to also permit the fabrication of large-scale epitaxial MOF thin films with unrestricted substrate size and rigidity, as displayed in Fig. 6(g) and (h). Using this approach, the fabrication of MOF thin film-based devices on flexible and large-scale substrates can be achieved.

#### **Electrochemical deposition (ECD)**

In general, three different approaches have been described for the fabrication of MOF thin films *via* electrochemical methods:

(i) anodic deposition, (ii) electrophoretic deposition,<sup>50</sup> and (iii) cathodic deposition. The basic concepts of these three methods are schematically illustrated in Fig. 7(a)–(c), respectively.<sup>21</sup>

In the anodic deposition process (Fig. 7(a)),<sup>119</sup> a metallic electrode was used by electrochemically dissolving metal anodes using high positive voltages. As described first by Müller and coworkers at BASF,<sup>120</sup> the electrochemically generated metal ions readily react with organic linkers contained in the electrolyte, and MOF thin films grew on the anode.

Inspired by the simplicity of this approach, anodic electrochemical MOF deposition has been widely used to fabricate various types of MOF thin films on metallic substrates, including HKUST-1  $(Cu_2(BTC)_3, BTC = benzene-1.3.5-tricarboxylic acid)$  on Cu electrodes,<sup>59</sup> Zn<sub>3</sub>(BTC)<sub>2</sub> on Zn plates,<sup>121</sup> MIL-100 (Fe) on Fe anodes,<sup>122</sup> and Zn(TPTC) (H<sub>3</sub>TPTC=1,3,5-tris[4-(carboxyphenyl)oxamethyl]-2,4,6-trimethylbenzene) on Zn plates (Fig. 7(d) and (g)).<sup>119</sup> In some cases, nonmetallic substrates were coated with a metallic film to provide the metal source, e.g., in the case of Cu<sub>2</sub>(BTC)<sub>3</sub> grown on Cu-coated glass.<sup>123</sup> Note that not all metals are suitable for anodic deposition; in some cases, the associated corrosion processes prohibit the growth of homogeneous MOF adlayers.<sup>124</sup> Apart from the fabrication of homogenous MOF thin films on metallic anodes, more heterogeneous MOF coatings have been grown on oxide layers doped with metal ions, such as Tb-BTC on ZnO substrates doped with Tb(III) (ZnO(Tb)).<sup>125</sup>

An alternative approach is electrophoretic deposition (EPD). In this process, illustrated in Fig. 7(b), two conductive electrodes are immersed in solutions containing surface-charged MOF particles. When a voltage is applied between the two electrodes, the created electric field drives the MOF particles toward the oppositely charged electrode, thus leading to the formation of MOF thin films. The EPD process has been successfully demonstrated by Farha, Hupp, and coworkers<sup>50</sup> to fabricate HKUST-1, Al-MIL-53, UiO-66, and NU-1000 on conductive fluorine-doped tin oxide (FTO) substrates, as shown in Fig. 7(e) and (h).

The cathodic deposition of MOF thin films was developed by Dincă and coworkers.<sup>124,126</sup> In this process, schematically shown in Fig. 7(c), the inert electrodes (WE, working electrode; CE, counter electrode) are used as chemically inert separators. They only act as sources of electrons without participating in the MOF-forming reactions. The key step in cathodic deposition is to obtain a local alkaline region near the cathode where the organic ligands are deprotonated. This can be achieved by the reduction of oxoanions (NO<sub>3</sub><sup>-</sup>) forming hydroxide or probase moieties (Fig. 7(f)). The "deprotonated" organic ligands react with metal precursors in solution and induce the crystallization of MOF particles at the cathode surface, resulting in the formation of MOF thin films (MOF-5, Zn<sub>4</sub>O(BDC)<sub>3</sub>, Fig. 7(i)).

#### Powder MOF-based deposition (PMD)

There are several possibilities for producing MOF thin films from powder MOFs that are obtained from standard solvothermal synthesis schemes. The following procedures have been used successfully in previous work: (i) direct deposition of as-synthesized powder MOFs onto a substrate by facial drop-casting or the spincoating method, using a suspension of MOF particles or mixtures



**Fig. 7** Schematic representation of the electrochemical fabrication of MOF thin films with (a) anodic deposition, (b) electrophoretic deposition, and (c) cathodic deposition. (d, e and f) Structure of Zn-TPTC, NU-1000, and MOF-5 fabricated with anodic deposition, electrophilic deposition, and cathodic deposition, respectively. (g, h and i) SEM images of the resulting MOF thin films of Zn-TPTC, NU-1000, and MOF-5, respectively. (d and g) Reproduced from ref. 119 with permission from Nature publishing group, copyright 2016. (e and h) Reproduced from ref. 50 with permission from John Wiley & Sons, copyright 2014. (f and i) Reproduced from ref. 124 with permission from Royal Society of Chemistry, copyright 2014.

of such suspensions and Nafion solution;<sup>127–129</sup> (ii) coating of a MOF particle suspension containing an additional polymeric binder to obtain MOF-based mixed matrix membranes;<sup>130,131</sup> and (iii) *in situ* deposition of powder MOF thin films on substrates into the reactant solutions during the solvothermal MOF synthesis process.<sup>132</sup>

The direct deposition of as-synthesized powder MOFs on solid substrates can be achieved using an advanced technique, namely electrospray deposition, as shown in Fig. 8(a).<sup>133</sup> For this process, an  $\alpha$ -alumina substrate was heated to a temperature of 160 °C before electrospray deposition. The voltage was applied to the capillary-containing precursor (ZIF-7) solutions. The precursor solution was sprayed onto the hot substrate. The fast evaporation of the solvents then leads to the formation of well-defined ZIF-7 thin films. Qiu and coworkers<sup>134</sup> developed a method which uses electrospinning to obtain a MOF-based mixed-matrix membrane, as illustrated in Fig. 8(b). The electrospinning solution was prepared by mixing a suspension of

ZIF-8 seed crystals with PVP to obtain solutions with the appropriate uniformity and moderate viscosity. This suspension was then loaded into a syringe and electrospun by applying a 12 kV voltage at a distance of 15 cm to form the ZIF-8/PVP composite fiber coating. The resultant coating was then used as a seed layer for the synthesis of high-quality ZIF-8 membranes.

Very recently, Wang and coworkers<sup>135</sup> developed a solventand binder-free approach for producing stable MOF coatings using a unique hot-pressing (HoP) method, as schematically shown in Fig. 8(c). This method consists of hot pressing MOF precursors, metal ions, or organic linkers on the substrates, where they can rapidly react with the surface functional groups or metal sites forming the first layer. Then the MOF layer grows under the applied temperature and pressure. The process converts the MOF powder into a highly stable MOF coating. This approach has been successfully applied to various substrates (carbon cloth, anodic aluminum oxide film (AAO), nickel foam, copper foil, glass cloth, and glass fiber).



**Fig. 8** Schematic diagram of (a) electrospray deposition for synthesizing ZIF-7 membranes on hot alumina (160 °C). Reproduced from Melgar *et al.*<sup>133</sup> (b) Electrospinning process for ZIF-8 on a microporous SiO<sub>2</sub> wafer. Reproduced from ref. 134 with permission from Royal Society of Chemistry, copyright 2012. (c) Hot-pressing (HoP) method for the fabrication of ZIF-8 on glass cloth (a) and (b) and glass fiber (c)–(e). Reproduced from ref. 135 with permission from John Wiley & Sons, copyright 2016.

As an example,  $Zn(2-mIM)_2$  (ZIF-8)-coated carbon cloth was prepared by first spreading a powdered mixture of  $Zn(OAc)_2$ , 2-methylimidazole, and polyethyleneglycol (PEG) onto a section of carbon cloth. Next, the section was covered with a piece of aluminum foil, packed, and then heated with an electric iron at 200 °C for 10 minutes. Flexible carbon cloth supporting a ZIF-8 coating with uniformly distributed ZIF-8 particles (*ca.* 100 nm) was thus obtained after washing with ethanol. The loading level of ZIF-8 was 7.12 g m<sup>-2</sup> and could be tuned from 3.01 to 9.76 g m<sup>-2</sup> by adjusting the quantity of the precursors. Using this method, other uniform MOF coatings, such as Cd-MOF, Co-MOF, ZIF-67, ZIF-9, MOF-5, and Ni-ZIF-8, were successfully fabricated on carbon cloth. Moreover, this method can be further extended to mass production using a roll-to-roll machine.

(ii) Vacuum-based fabrication of MOF thin films. Most of the reported protocols for the deposition of MOF thin films involve chemical reactions occurring in organic solvents. For many microelectronic manufacturing processes, however, solution-based fabrication of MOF thin films has severe disadvantages due to potential contamination from the MOF synthesis solutions.<sup>136</sup> In this context, vacuum-based thin film deposition techniques have a number of advantages. In the following, we will present two variants of vacuum-based fabrication of MOF thin films, namely chemical vapor deposition (CVD) and atomic layer deposition (ALD) as shown in Fig. 9.

#### Chemical vapor deposition (CVD)

Chemical vapor deposition (CVD) of films and coatings involves the adsorption and subsequent chemical reaction of gases with the surface of a substrate. This deposition method can also produce coatings with tightly controlled dimensions, *e.g.* on curved or inner surfaces, *e.g.*, the inside of tubes. In 2016, Ameloot and coworkers fabricated uniform ZIF-8 MOF thin films using chemical vapor deposition<sup>137</sup> (ZIF-8: (zinc-(2-methylimidazolate)<sub>2</sub>)) that had a controlled thickness. A substrate with a rather complicated shape, silicon pillar arrays, as well as a patterned substrate was successfully coated as shown in Fig. 9 (left).

The CVD approach employed in this work consisted of two steps: first is metal-oxide deposition, and this is followed by a vapor-solid reaction step (Fig. 9(a)). In the first step, the metal-oxide (ZnO) thin film with a thickness of 3–15 nm was deposited onto Si pillar arrays using ALD. MOF growth was then initiated by exposing the ZnO-coated Si pillar arrays to the vaporized organic linker, 2-methylimidazole (HmIM), at 100 °C for 30 min. The resulting highly crystalline and uniform ZIF-8 thin films are shown in Fig. 9(b) and (c).

#### Atomic layer deposition (ALD)

ALD<sup>139</sup> is also a chemical gas phase thin-film deposition technique, but, unlike CVD, it utilizes "self-limiting" surface



**Fig. 9** Left: (a) Chemical vapor deposition of ZIF-8 thin films. The procedure consists of a metal oxide vapor deposition (Step 1) and a consecutive vaporsolid reaction (Step 2). Scanning electron microscopy (SEM) images of (b) ZIF-8 coated silicon pillar arrays and (c) manufactured ZIF-8 patterns. Reproduced from ref. 137 with permission from Nature publishing group, copyright 2016. Right: (d) Schematic illustration of the ALD process to fabricate MOF thin films. The ALD process consists of a metal precursor and organic linker pulses separated by an inert gas on the substrate to yield a monolayer of the MOF thin film. The desired film thickness can be achieved by controlling the repetitions of both precursors. (e and f) The structure of fabricated Ca-BDC using ALD with different forms. Reproduced from ref. 138 with permission from American Chemical Society, copyright 2016.

reactions that better control the film thickness. The ALD technique<sup>139</sup> relies on sequential, self-saturating gas-in-surface reactions. After saturating a surface with a volatile precursor, the reactor chamber is purged with an inert gas to avoid reactions between the different precursors. Subsequently, the surface is saturated with a second, different precursor. The process for the ALD fabrication of MOF thin films is schematically illustrated in Fig. 9(d)<sup>138</sup> and consists of two sequential steps: (1) deposition of one monolayer of volatile metal precursors on the substrate, and (2) subsequent deposition of the second layer of volatile organic linkers. Repeating steps (1) and (2) allows thin films to be grown with the desired thickness.

Crucial to successful deposition is the choice of appropriate volatile precursors.<sup>140,141</sup> Karppinen and coworkers<sup>138</sup> successfully fabricated a Ca-BDC MOF thin film (Fig. 9(e) and (f)) on Si using Ca(thd)<sub>2</sub> (thd: 2,2,6,6-tetramethyl-3,5-heptanedione) and BDC (1,4-benzenedicarboxylic acid) as volatile precursors. The two reactants were kept in glass crucibles inside the ALD reactor during deposition. The sublimation temperatures were set to 190 °C for Ca(thd)<sub>2</sub> and 180 °C for BDC.

Nilsen and coworkers<sup>142</sup> reported the fabrication of UiO-66 in an all-gas-phase process with the aid of ALD, using sequential reactions of the substrates with ZrCl<sub>4</sub> and 1,4-benzenedicarboxylic acid. The intermediate product obtained using the ALD process, an amorphous organic–inorganic hybrid film, was then converted into a crystalline UiO-66 MOF thin film by exposure to acetic acid vapor.

The fabrication of MOF thin films can be also realized by using an ALD-assisted approach, where metal oxide films formed on the substrate by ALD serve as nucleation layers to promote the heterogeneous nucleation for the growth of MOF thin films (see previous paragraph).<sup>116,143</sup>

# Applications

After presenting different strategies for the fabrication of MOF thin films, now we focus on the huge potential of MOF thin films for several areas of nanotechnology.

We would like to point out that applications of MOF thin films are not a mature field yet. Rather, this research area is evolving quickly and new, not previously anticipated applications are emerging. Very often, the fact that one particular growth method was used for an application did not result from a careful comparison of available methods but rather from the preferences of the laboratory where the application idea was conceived. We foresee that with time, different MOF thin film preparation methods will be used for different types of applications. At present, we feel it is too early to provide rules suggesting a particular MOF thin film deposition method for a given application. The same applies to cost efficiency – certainly, in the context of commercial products, this aspect will become important at some point.

We are convinced that the availability of such crystalline, porous, monolithic thin films will affect nanotechnology in a similar or even more pronounced way as self-assembled monolayers.<sup>144</sup> While applications in the areas of photovoltaics, CO<sub>2</sub> reduction, water splitting, electronic devices, and energy

storage are already quite impressive, we foresee many further cases where the enormous potential of MOFs will be used for novel applications.

#### Photovoltaics

It has been demonstrated that photovoltaic device performance can be improved by integrating MOF powders into other materials to form composites, such as MIL-125/perovskite,<sup>84</sup> Mg-BTC/polymer,<sup>145</sup> Cu-BTC/carbon nanotubes,<sup>146</sup> ZIF-8/dye,<sup>147</sup> PPF-4/TiO<sub>2</sub><sup>148</sup> and UiO-67/Cu<sub>2-x</sub>S/CdS.<sup>149</sup> Instead of discussing applications where MOFs are mixed with conventional materials, we will focus on novel device architectures based on the unique properties of MOF thin films.

One of the appealing properties of MOFs is that they offer a straightforward strategy to build up solids from molecular building units, thus allowing the unique properties of organic compounds to be exploited in constructing novel designer materials. An instructive example is the fabrication of solids from porphyrin building blocks. Porphyrins are a class of organic molecules that exhibit a number of interesting properties.<sup>150</sup> One of them is its large efficiency for absorbing visible light. Although the potential of porphyrins to fabricate organic photovoltaic cells that capture sunlight and convert it into electricity was realized early and motivated several studies,<sup>51</sup> the performance of the corresponding devices has been hampered by the lack of fabrication methods that yield well-ordered porphyrin thin films.

Here, the MOF-approach offers the striking advantage that, with porphyrin-based organic linkers, molecular thin films with a high structural quality can be prepared in a straightforward fashion. So far, two different concepts have been presented for MOF-based photovoltaic (PV) devices: (i) the fabrication of a dye-sensitized solar cell (DSSC)-like SURMOF PV device,<sup>51,145-147,151-154</sup> and (ii) an all-solid-state SURMOF PV,<sup>52,84,149,155,156</sup> as illustrated in Fig. 10(b) and (d).

MOF thin films and SURMOFs are well suited as photoactive layers, as demonstrated for a wide variety of MOF compounds including Ru-BTC,<sup>151</sup> Cu-BTC,<sup>152</sup> Al<sub>2</sub>(BDC)<sub>3</sub>,<sup>155</sup> MIL-125(Ti),<sup>156</sup> Co-NDC (NDC = 2,6-naphthalenedicarboxylic acid),<sup>153</sup> and Ru(n)-polypyridyl Zr(n).<sup>154</sup> In all these cases, homogeneous, monolithic SURMOFs with a thickness of around 300 nm were grown on transparent, conductive substrates (FTO or TiO<sub>2</sub>/FTO) using the LPE method. Although their performance is still inferior to that reported for OPV devices using conventional organic materials,<sup>157–159</sup> we foresee major advances in this area. In particular, it should be possible to overcome the relatively poor light absorption in the red-light region by optimizing the absorption of the organic linkers used to fabricate the SURMOFs.

A series of porphyrin-based SURMOFs prepared by the LPE approach have been assembled into functioning DSSC-like and all-solid-state photovoltaic devices by Liu, Wöll, and coworkers.<sup>51,52</sup> These epitaxially-grown porphyrin SURMOF thin films exhibit superior absorption capability in the red part of the spectrum and thus outperform MOFs fabricated with phenyl-based organic linkers.<sup>160</sup> Furthermore, in principle, the



**Fig. 10** (a) Schematic drawing of the LPE approach to fabricate porphyrinbased SURMOF thin films with a series of porphyrin linkers in a layer-by-layer fashion. Reproduced from ref. 270 with permission from Nature publishing group, copyright 2012. (b–d) Architectures of porphyrin–SURMOF thin filmbased photovoltaic devices and (c)–(e) their corresponding J-V curves. (b) and (c) reproduced from ref. 51 with permission from John Wiley & Sons, copyright 2015. (d) and (e) reproduced from ref. 52 with permission from Royal Society of Chemistry, copyright 2016.

porphyrin-based systems exhibit the potential to enhance directional exciton transport.<sup>161,162</sup>

It is well known that the metalation of the porphyrin rings and the attachment of electron donating groups to the porphyrin skeleton can substantially enhance the efficiency of photoinduced charge carrier generation.<sup>163,164</sup> In fact, using this strategy, record values of  $\varphi = 3.0 \times 10^{-1}$  have been obtained.<sup>52</sup> However, for this particular case, the overall power-to-electricity conversion efficiency was rather low (<1%). This poor performance most likely results from a high rate of electron–hole recombination events, possibly a result of the relatively slow charge carrier mobility. In future work, the linkers will have to be modified further to increase the charge carrier mobility.

Richards, Howard, and coworkers recently reported photon upconversion using multilayer SURMOFs fabricated using heteroepitaxy. These films are efficient in transforming low-energy light to high-energy light *via* photon upconversion (UC) by triplet–triplet annihilation (TTA).<sup>165</sup>

The SURMOF hetero-multilayers used in this work exhibit a (001) orientation and were prepared by the LPE approach using paddle-wheel Zn-acetate as a metal building unit and Pd(II) 5,15-diphenyl-10,20-di(4-carboxyphenyl) porphyrin (Pd-DCP) and 4,4'-(anthracene-9,10-diyl)dibenzoate (ADB) as organic linkers. The resulting hetero-SURMOF thin films thus contain a sensitizer layer, Zn-Pd-DCP (denoted as B), sandwiched by two emitter layers, Zn-ADB (denoted as A), as shown in Fig. 11(a) and (b).

The chromophores within the sensitizer B layer are excited with green (532 nm) photons. At this wavelength, the emitter A layer is transparent. The singlet lifetime of the sensitizer Pd-DCP in the B layer is less than 10 ps, and almost all absorbed photons initially generate triplet states in B due to such fast intersystem crossing in the sensitizer layer. The triplets that, by diffusion, reach and cross the B–A heterojunction *via* Dexter electron exchange will be collected in the A layer. Once trapped in the A layer, pairs of triplets can decay *via* TTA-UC, as evidenced by the emission of higher-energy blue photons. Therefore, the observation of upconverted blue emission coming from the sample (Fig. 11(c)–(e)) is direct evidence that the SURMOF–SURMOF heterojunction is of sufficient quality for excitons to move across it.



Fig. 11 (a) SEM cross section of a three-layer emitter–sensitizer–emitter (A–B–A) SURMOF heterostructure on a Si substrate. (b) Out-of-plane XRD diffractograms of A, B, and A + B. (c–e) Photographs of an encapsulated B–A structure under 532 nm laser irradiation. To exclude oxygen, this sample was encapsulated between two glass cover slips in a glovebox with an inert atmosphere. Two-component epoxy was used to seal the slides together. This is visible as the scattering, roughly circular form around the pinkish square heterostructure of the upconverting film. Reproduced from ref. 165 with permission from John Wiley & Sons, copyright 2016.

The structural quality of these well-defined, crystalline heterojunctions exceeds that of normal organic/organic interfaces (*e.g.*, between organic polymers or for interfaces prepared using PVD growth of hetero-organic layers). SURMOF heterojunctions thus offer the prospect of studying the Dexter transfer of triplet excitons over such organic/organic interfaces using theoretical methods.

#### CO<sub>2</sub> reduction

The reduction of  $CO_2$  to higher-value chemical products is an energetically and kinetically challenging chemical process. Two of the most important possibilities for bringing about the individual endothermic multielectron reaction steps required for this process are electrocatalysis and photocatalysis. Depending on the final product, multiple electrons have to be transferred: two for the production of carbon monoxide and formic acid, four for formaldehyde, six for methanol, and eight for methane. Because of its huge importance, extensive effort has been devoted to the development of molecular catalysts for  $CO_2$  reduction.<sup>166,167</sup>

It has been demonstrated that MOFs acting as efficient catalysts for carbon dioxide reduction can be designed in a straightforward fashion using organic linkers containing well-established molecular catalysts. Deposition of the corresponding MOF thin film directly on a conductive electrode yields a photo/electrocatalytic device that can be characterized using established procedures. Surface-supported MOF thin films exhibit a number of advantages with regard to  $CO_2$  reduction, including a large number of catalytic sites and enhancement of the local concentration of  $CO_2$  around the catalytic active centers inside the MOF cavities. In addition, they benefit from (i) elimination of the deactivation process such as by aggregation of the highly active catalyst, (ii) separation of the catalysts from the reaction solution, and (iii) promotion of light-induced charge separation.<sup>168</sup>

Previous examples illustrating the potential of MOF thin films as efficient electro- and/or photo-catalysts for the reduction of  $CO_2$  are presented in Fig. 12(d) and (h).

To achieve electrocatalytic reduction of CO<sub>2</sub>, Yang, Yaghi, *et al.*<sup>169</sup> deposited a novel porphyrin-containing MOF (AL<sub>2</sub>(OH)<sub>2</sub>TCPP-M, TCPP = 4,4',4'',4'''-(porphyrin-5,10,15,20-terayl)tetrabenzoate, M = Zn, Co, Cu) thin film on an alumina-coated conductive carbon disk electrode using a substrate-seeded heteroepitaxy method (see the section Fabrication methods).

The electrocatalytic performance was determined using a standard three-electrode setup with a titanium counter electrode, an Ag/AgCl reference electrode, and CO<sub>2</sub>-saturated purified 0.5 M potassium carbonate as the electrolyte. In the case of  $AL_2(OH)_2$ TCPP-Co, a current density of 5.9 mA cm<sup>-2</sup> was achieved. In fact, this MOF-based electrocatalytic cell exhibited excellent stability when operated at -0.7 V *vs.* RHE for up to 7 h. The selectivity to yield CO reached 76% (24% for H<sub>2</sub>), with a turnover frequency (TOF)  $\approx 200$  h<sup>-1</sup>.

A different approach to fabricate MOF thin-film heterocatalysts for the reduction of CO<sub>2</sub> to CO was reported by Farha, Hupp, and coworkers.<sup>170</sup> They deposited Fe-porphyrin-based MOF thin films (Fe\_MOF-525) onto an FTO substrate using the electrophoretic method (see previous section). The electrolysis was performed using a 1 M CO<sub>2</sub>-saturated TBAPF<sub>6</sub> acetonitrile solution at -1.3 V vs. NHE. They reached a maximum current density of 2.3 mA cm<sup>-2</sup>. After operating for more than 30 min, a slow degradation of the electrocatalyst was observed. The Faradaic efficiency with regard to CO production amounted to 54 ± 2% (45 ± 1% for H<sub>2</sub>) with a turnover number (TON) of 272 and an average turnover frequency (TOF) of 64 h<sup>-1</sup> (after 4 hours of electrocatalysis).

Using a different approach, Liu, Sun, and coworkers<sup>171</sup> found that, by controlling the orientation of the SURMOF thin film, the Faradaic efficiency for CO production can be increased substantially. Using the LPE approach, they grew a monolithic Re-SURMOF thin film with (001) orientation on an FTO substrate. For these high-quality MOF thin films, the Faradaic efficiency was found to increase to 93  $\pm$  5% for CO (TON<sub>CO</sub> 580) at -1.6 V vs. NHE.

By appropriate selection of the MOF - in particular the organic linkers used to construct the MOF - as well as the electrolytes, the electrocatalytic reduction of CO<sub>2</sub> can yield various products. Kulandainathan and workers<sup>172</sup> investigated the electrocatalytic activity of HKUST-1 thin films immobilized on a glassy carbon (GC) electrode with Nafion in CO<sub>2</sub>-saturated N,N-dimethylformamide (DMF) containing tetrabutylammonium tetrafluoroborate (TBATFB). These authors found that the HKUST-1/GC can reduce CO2 to yield oxalic acid with a Faradaic efficiency of 51%. For carbon paper electrodes coated with thin films of another MOF, Zn-BTC,<sup>173</sup> again in an ionic liquid electrolyte (1-butyl-3methylimidazolium perchlorate (BMIMClO<sub>4</sub>)), CO<sub>2</sub> was reduced to various products including CH<sub>4</sub>, CO, and H<sub>2</sub> at -2.2 V vs. Ag/Ag<sup>+</sup>, with Faradaic efficiencies of 88.3  $\pm$  3.8%, 6.8  $\pm$  2.1%, and 4.9  $\pm$ 1.0% for CH<sub>4</sub>, CO, and H<sub>2</sub>, respectively. These electrodes were stable for at least 2 h.

Several studies demonstrated that MOF materials also exhibit great potential for the photocatalytic conversion of CO<sub>2</sub> to CO; see Fig. 12(h). Yang, Yaghi, and coworkers<sup>174</sup> used a particular MOF built from Zr-containing nodes,  $Zr_6O_4(OH)_4(-CO_2)_{12}$ , which are connected by BPDC and ReTC linkers (Fig. 12(a)). The resulting face-centered cubic Ren-MOF contains 12 coordinated Zr-based metal clusters which are interconnected by 21 BPDC and 3 ReTC linkers; see Fig. 12(f). The  $Re_n$ -MOF film was deposited on Ag nanocubes via the solvothermal method forming Ag  $\subset$  Re<sub>n</sub>-MOF; see Fig. 12(g). The photocatalytic reduction of CO<sub>2</sub> was carried out in a CO<sub>2</sub>-saturated acetonitrile/triethylamine mixture (MeCN/TEA = 20:1), where TEA served as a sacrificial electron donor. The highest turnover on Ag 
Re<sub>3</sub>-MOF-16 nm resulted in 7 fold enhancement of photocatalytic activity over Re<sub>3</sub>-MOF under visible light, and there was no activity observed without Re<sub>n</sub>-MOF. This striking performance improvement in the presence of the Ag clusters was explained by the plasmonic properties of the Ag particles. Under irradiation with visible light, plasmons excited in the Ag nanocubes generate highly intensified near-surface electric fields, which are in fact substantially higher than the incident electromagnetic field. The catalytic Re3-center contained in the MOF coating of the Ag nanocubes therefore experiences highly intensified electric fields and, as a result, shows substantially higher photocatalytic activity.



**Fig. 12** Electrocatalytic CO<sub>2</sub> reduction. (a) Molecular structure of cobalt-metalated TCPP linker, (b) crystal structure of  $Al_2(OH)_2$ TCPP-Co MOF, (c) SEM image of the MOF catalyst film integrated in a conductive substrate with plate-like morphology, and (d) schematic illustration of the functional CO<sub>2</sub> electrochemical reduction system. Reproduced from ref. 169 with permission from American Chemical Society, copyright 2015. Photocatalytic CO<sub>2</sub> reduction. (e)  $Zr_6O_4(OH)_4(-CO_2)_{12}$  secondary building units are combined with BPDC and ReTC linkers to form (f) a face-centered cubic  $Re_n$ -MOF. (g) TEM image of  $Ag \subset Re3$ -MOF showing  $Re_3$ -MOF constructed on the surface of an Ag nanocube. (h) Schematic illustration of  $Re_n$ -MOF coated on an Ag nanocube for plasmon-enhanced photocatalytic conversion of CO<sub>2</sub>. Reproduced from ref. 174 with permission from American Chemical Society, copyright 2017.

The photocatalytic performance of MOFs can be substantially enhanced by MOF thin films coated on other materials. Wang and coworkers  $^{168}$  reported that coating graphitic carbon nitride (g-C\_3N\_4) with Co-ZIF-9 to form a co-catalyst facilitates the adsorption of CO<sub>2</sub> and promotes light-induced charge separation, leading to high photocatalytic activity for CO<sub>2</sub> conversion to CO upon visible light illumination under mild reaction conditions. Ye and coworkers<sup>175</sup> demonstrated that a UiO-66 thin film coated on nanosized carbon nitride nanosheets via the electrophoretic method can substantially suppress electron-hole pair recombination in the carbon nitride nanosheet. This occurs due to the electron transfer from the photoexcited carbon nitride nanosheet to UiO-66, which supplies long-lived electrons for the reduction of CO<sub>2</sub> molecules captured in UiO-66. As a result, the photocatalytic activity for the CO<sub>2</sub> conversion to CO was enhanced 1.6 fold with a UiO-66/carbon nitride nanosheet heterogeneous photocatalyst.

#### Water splitting

The ability to split water, a rather abundant source of hydrogen, into  $O_2$  and  $H_2$  opens up many opportunities to convert sunlight into chemical energy. Basically, the water splitting reaction can be divided into two half reactions: first, water oxidation (oxygen evolution reaction (OER)) and, second, water reduction (hydrogen evolution reaction (HER)); see Fig. 13(a).

Usually, the formation of H–H and O=O bonds in and from water is inherently slow or requires high electrochemical potentials.

To overcome these limitations, it is necessary to employ electrocatalysts to lower the overpotentials for driving water oxidation and proton reduction. In recent years, MOF-based thin-film electrodes have been demonstrated to exhibit great potential for promising photo- and/or electrocatalytic water splitting.<sup>176–179</sup>

To further enhance the photo- and/or electrocatalytic performances of MOF-based catalysts, a wide variety of novel linkers and nodes have been designed with the goal of optimizing the MOF catalytic activity. These approaches include (i) integration of  $\pi$ -conjugated organic ligands into the framework to prolong the electron-hole recombination time, <sup>128,183</sup> (ii) incorporation of molecular catalysts,184 semiconductor quantum dots,185 metal nanoparticles,<sup>176</sup> and metal ions<sup>132</sup> into MOF thin films; and (iii) fabrication of ultrathin 2D MOF nanosheets (UMOFNs). This last approach offers several advantages, including rapid mass transport, superior electron transfer, and extremely high percentages of exposed catalytic active surfaces with coordinatively unsaturated metal sites to ensure high catalytic activity; and distinct surface atomic structures and bonding arrangements that are easily identifiable and tunable.<sup>181</sup> Wang and coworkers<sup>181</sup> reported a 2D ultrathin NiCo bimetal-organic framework (NiCo-UMOFNs), with a space group of C2/m consisting of two metal nodes, Ni and Co, connected via a benzenedicarboxylic acid (BDC) linker (Fig. 13(a), left) and a thickness of  $\sim$  3 nm (Fig. 13(b), right). In this structure, both the Co and Ni atoms are octahedrally coordinated by six O atoms, and these pseudo-octahedra are further edge/corner connected with each other

along the [010]/[001] direction in the (200) crystallographic plane, forming 2D bimetal layers separated by BDC molecules.

The NiCo-UMOFNs were coated onto glassy carbon (GC) and copper foam using the powder MOF-based deposition approach, as described previously in the Fabrication methods section.

The electrocatalytic performance of NiCo-UMOFNs was characterized using a three-electrode electrochemical cell using NiCo-UMOFNs/GC or NiCo-UMOFNs/Cu as a working electrode, and Pt wire and an Ag/AgCl electrode as a counter electrode and reference electrode, respectively, in a 1 M KOH aqueous solution.

The ultrathin NiCo-UMOFNs exhibited high electrocatalytic activity for the OER. The NiCo-UMOFNs/GC showed an overpotential of only 250 mV, and the corresponding current density amounted to 110 mA cm<sup>-2</sup>. A slightly different electrode based on NiCo-UMOFNs/Cu demonstrated an even lower overpotential of 189 mV at current densities of 10 mA cm<sup>-2</sup>. Moreover, the NiCo-UMOFNs exhibited an impressive long-term stability (200 h) in alkane solutions (applied voltage of 1.48 V *vs.* Ag/AgCl, corresponding to an overpotential of 0.25 V). These values are clearly

superior to those of commercial  $RuO_2\text{-}based$  electrocatalysts, where the anodic current decay amounts to 60.3% after operation times of  $\sim\!11$  h. $^{181}$ 

The significantly higher electrocatalytic activity of NiCo-UMOFNs for the oxygen evolution reaction (OER) is attributed to coordinatively unsaturated metal sites within the porous ultrathin NiCo-UMOFN layers. Such special sites provide pronounced catalytic activity for MOFs<sup>186,187</sup> and improve the electrocatalytic activity. Farha, Hupp, and coworkers<sup>182</sup> reported an acid-stable proton-conducting metal-organic framework material (NU-1000) that is solvothermally grown on an FTO electrode and substantially accelerates the electrochemical hydrogen evolution. The NU-1000 MOF used in this work consists of  $Zr_6(\mu_3-O)_4(\mu_3-OH)_4(OH)_4(OH_2)_4$  nodes and a TBAPy<sup>4-</sup> linker ( $H_4$ TBAPy = 1,3,6,8-tetrakis(*p*-benzoic acid)pyrene), as shown in Fig. 13(a). After the MOF thin film formation, the Ni-S (a material comprising nickel and sulfur; its main product is Ni<sub>3</sub>S<sub>2</sub> after 2 min electrodeposition) was electrodeposited on NU-1000/FTO. This procedure resulted in a hybrid multilayer of an NU-1000 Ni-S electrocatalytic device as shown in Fig. 13(c).



**Fig. 13** (a) Left: Thin sheets of Ni–Co metal–organic frameworks (MOFs) as anodic oxygen evolution electrocatalysts under alkaline conditions. The inset shows the structure of the Ni–Co MOF electrocatalyst. Right: Nu-1000\_Ni–S thin films as cathodic hydrogen evolution electrocatalysts under acidic conditions. The inset shows the structure of the NU-1000\_Ni–S electrocatalyst. Modified based on ref. 180 with permission from Nature publishing group, copyright 2016. (b) Right: TEM image of ultrathin NiCo-UMOFNs. Left: Polarization curves of NiCo-UMOFNs, Ni-UMOFNs, Co-UMOFNs, RuO<sub>2</sub>, and bulk NiCo-MOFs in an O<sub>2</sub>-saturated 1 M KOH solution at a scan rate of 5 mV s<sup>-1</sup>. The dotted horizontal line is a guide for the eye showing a current density of 10 mA cm<sup>-2</sup>. Reproduced from ref. 181 with permission from Nature publishing group, copyright 2016. (c) Left: Cross-sectional SEM image of NU-1000\_Ni–S films. Right: J-V curves of four types of electrodes: bare FTO (dotted black), FTO\_NU-1000 (dotted red), FTO\_Ni–S (black), and NU-1000\_Ni–S (red). Reproduced from ref. 182 with permission from Nature publishing group, copyright 2015.

The NU-1000\_Ni–S exhibits excellent electrocatalytic performance for the hydrogen evolution reaction (HER). In aqueous HCl solutions at pH 1, the hybrid material can deliver a catalytic current of 10 mA cm<sup>-2</sup> at an overpotential of just 238 mV – a sizable (*ca.* 200 mV) decrease in the overpotential relative to electrocatalysts built with MOF-free Ni–S films. The significant improvement in electrocatalytic activity for the HER has been attributed to the ability of the proton-conductive MOF to favorably modify the immediate chemical environment of the sulfide-based catalyst.

#### **Electronic devices**

The use of metal–organic frameworks for the fabrication of sensor devices involves a large area of research activities, which has been well documented in previous reviews.<sup>15,17,26,188–191</sup> We would like to mention, however, the recent work by Stavila *et al.* who used a MOF thin film grown on an acoustic device surface using the layer-by-layer method for the detection of volatile hydrocarbons.<sup>192</sup>

In this context, we will mainly focus on applications where MOF thin films are used as an active component, *i.e.* not just as an insulating material. Certainly, the particular properties of MOFs make them attractive candidates also for taking over a passive role in conventional electronic circuits (e.g. as low dielectrics devices<sup>193-195</sup>). After it was demonstrated that MOFs can be rendered with electric conductivity, either by loading with appropriate molecules<sup>196,197</sup> or by using appropriate linkers,<sup>198</sup> a number of MOF-based electronic devices were presented.14,25,26 Since the presence of electrical contacts is mandatory in these applications, the deposition of thin films on conducting substrates is a key requirement. The essential properties of electronic devices, such as electric conductivity,<sup>197,199-201</sup> thermoelectric behavior,<sup>202</sup> and magnetism,<sup>203,204</sup> can be improved by designing new types of MOFs or integrating guest species into MOFs. This is due to their tunable chemical and physical properties. Electronic active MOF materials can be fabricated for use in electronic devices such as a MOF-based memory device (memristor)<sup>205,206</sup> or the MOF-based field-effect transistor (FET).207

**Memristor.** The realization of a MOF thin film-based memristor was reported by Redel, Baumgart, Wöll, and coworkers using lithographical methods.<sup>208</sup> The performance of the SURMOF device is quite different from an earlier, MOF single-crystal based memristor as reported by Grzybowski and coworkers,<sup>205</sup> in particular as regards switching speed, which is much higher for the crystalline HKUST-1 films prepared by LPE (see the Fabrication methods section).

The SURMOF-based nanodevice was fabricated using nm-thick HKUST-1 films sandwiched between a conductive support (SAM/Au/Si), serving as a bottom electrode, and a lithographically fabricated top-electrode (Au/Al), as schematically shown in Fig. 14(a).

The resistive switching of this HKUST-1 SURMOF device was characterized using a parameter analyzer. In a typical switching cycle, the device changes to a higher resistance ( $R_{OFF}$ ) state at  $V_{RESET}$  and to a lower resistance ( $R_{ON}$ ) state at  $V_{SET}$  by applying a slow voltage ramp between -0.8 V to +0.8 V. This is typical behavior for nonvolatile resistive random access memory (RRAM).



**Fig. 14** (a) Illustration of a SURMOF test device structure with an Au/ SURMOF/Al/Au stack and SURMOF film and measurement setup. (b) Switching cycle of 10.5 nm thick HKUST-1 SURMOF devices without ferrocene loading. (c) Schematic drawing of HKUST-1 SURMOF loaded with ferrocene and (d) corresponding switching cycles. (a–d) Reproduced from ref. 208 with permission from John Wiley & Sons, copyright 2016.

The bipolar switching characteristics for a 10 nm thick HKUST-1 SURMOF device without ferrocene are shown in Fig. 14(b). During a slow voltage sweep from 0 to -0.8 V, there was transition to a low-resistance state. Inversely, during a slow voltage sweep from 0 to 0.8 V, a transition back to the high-resistance state is observed. After ferrocene was loaded into the pores of HKUST-1 (see Fig. 14(c)), a more regular switching behavior also occurred due to the lowered resistance within the SURMOF layer. This resistance resulted because of the increased conductivity from loading ferrocene into the pores of HKUST-1, as shown in Fig. 14(d). These results reveal the huge flexibility of MOF materials with regard to applications in SURMOF-RRAM devices.

**Dielectrics.** Because of their rather small dielectric constants, MOF materials are considered to be suitable candidates to fabricate low-*k* dielectrics layers.<sup>209–212</sup> It has been demonstrated that the dielectric constant is strongly dependent on the form of the MOFs; *i.e.*, low-*k* powder MOFs become high-*k* when they exist in the form of MOF thin films.<sup>119</sup>

Cao and coworkers reported an interpenetrated MOF thin film-based high-*k* dielectric device<sup>119</sup> (Fig. 15(a)). The MOF thin film was prepared using the electrochemical deposition method (anodic deposition, see the Fabrication methods section), which contains an interpenetrated structure with 1,3,5-tris[4-(carboxy-phenyl)oxamethyl]-2,4,6-trimethylbenzene (H<sub>3</sub>TBTC) as an organic building unit and Zn as the metal node (Fig. 15(b) and (c)).

The interpenetrated MOF thin film-based dielectrics possess a dielectric constant (k) of 19.5 at a frequency of 1 MHz, which is much larger than those of most previously reported MOFs except for ferroelectric MOFs. In contrast, the powder MOFs only exhibit a small k of 5.9, which is still substantially larger than most of the previously reported MOFs having a typical dielectric constant less than 4 (Fig. 15(e)).



**Fig. 15** Schematic drawing of (a) a MOF-based dielectric device and (b) the two-fold interpenetrated MOF architectures. (c) SEM images of MOF thin films prepared at a voltage of 3 V for 60 s. (d) Schematic of the space-charge distribution in the MOF thin film and in bulk MOFs. (e) Dielectric constant of a MOF film and powder MOFs after removal of the guest molecules during the heating process. Reproduced from ref. 119 with permission from Nature publishing group, copyright 2016.

The excellent dielectric properties, both of MOF thin films and powder MOFs, can be well explained due to the large density and the total polarizability of the molecules within the interpenetrated materials. The superior performance of MOF thin films over powder MOFs is attributed to the spacecharge relaxation phenomenon of the polar guest molecules within MOF thin films, as shown in Fig. 15(d).

Field-effect transistors (FETs). Xu and coworkers reported MOF-based field-effect transistors.<sup>207</sup> The semiconducting MOF used, Ni<sub>3</sub>(HITP)<sub>2</sub>, consisted of HITP-6HCl (HITP = 2,3,6,7,10,11-hexaminotriphenylene) organic linkers and NiCl<sub>2</sub>·6H<sub>2</sub>O nodes. MOF thin films were prepared using the interfacial synthetic approach (air–liquid interface). The resulting Ni<sub>3</sub>(HITP)<sub>2</sub> layers with a room-temperature conductivity of 40 S cm<sup>-1</sup> were transferred onto a SiO<sub>2</sub>/Si wafer substrate by a simple stamping process. To realize the FET, top electrodes were deposited using a PVD process, while the substrate served as the gate. The device geometry is shown in Fig. 16(a) (left).

The performance of this first MOF-based FET is demonstrated by the *I/V* characteristics displayed in Fig. 16(b) (left). The linear  $I_{ds}-V_{ds}$  curves and the gradual slope increase with  $V_{ds}$  revealed a p-type behavior of the MOF material. They also demonstrate an impressive performance of the charge carrier transport due to the short layer distance (3.5 Å), which is short enough to create sufficient orbital overlap between adjacent layers through  $\pi-\pi$ interactions. Xu's work not only provides a good method to prepare high quality MOF thin films, but also takes a key step forward in the research of MOF-based electronic devices.

Zheng, Zhang, and coworkers reported the first application of a MOF thin film in organic field-effect transistors (OFETs).<sup>213</sup> The OFET device was fabricated on MOF/SiO<sub>2</sub>/Si, which was coated with a semiconducting polymer of PTB7-Th (poly[4,8bis(5-(2-ethylhexyl)thiophene-2-yl)benzo[1,2-*b*:4,5-*b*']dithiophene*co*-3-fluorothieno[3,4-*b*]thiophene-2-carboxylate]) and two top Au electrodes on the semiconducting film, as displayed in Fig. 16(a) (right).

The HKUST-1 SURMOF thin film was prepared by the LPE approach to modify the SiO<sub>2</sub> dielectric layer in the OFETs. The authors found that the performance of the HKUST-1/SiO<sub>2</sub>-based OFETs, such as charge mobility, threshold voltage, and current on/ off ratio, was significantly improved compared to that of the bare dielectric layer SiO<sub>2</sub>. The OFET modified with three LPE dipping cycles of HKUST-1 SURMOF exhibited a hole mobility of  $(1.15 \pm 0.23) \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and a threshold voltage less than 10 V (Fig. 16(b) (right)). This performance is superior to that of an OFET without HKUST-1 SURMOF coating (average hole mobility of  $5.17 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and threshold voltage larger than 13 V).

The performance enhancement of the device is mainly attributed to the highly crystalline, homogeneous, and low-k HKUST-1 SURMOF grown on the SiO<sub>2</sub>/Si substrate and the smaller interface trap density in the OFET.

**Thermoelectrics.** Talin and coworkers reported the first MOF thin film-based thermoelectric device.<sup>202</sup> For their proof-of-principle device they used the liquid-phase epitaxy approach to deposit (111) oriented Cu<sub>3</sub>(BTC)<sub>2</sub> films with a thickness of ~ 200 nm onto a quartz substrate with pre-patterned Au contacts.<sup>85</sup> The SURMOF-coated electrode was then partially immersed in a TCNQ/methanol solution to load TCNQ (7,7,8,8-tetracyanaoquinodimethane) molecules into the MOF pores, thus obtaining an electrically conducting TCNQ@Cu<sub>3</sub>(BTC)<sub>2</sub> thin film device.

The thermoelectric properties of the  $TCNQ@Cu_3(BTC)_2$  thin film were measured using Peltier temperature control elements to create a temperature gradient (cold and hot), and an IR camera to measure the temperature gradient as displayed in Fig. 17(a) and (b).

Plots of thermovoltage *versus*  $\Delta T$  measured at 40 °C and the Seebeck coefficient as a function of the average temperature are shown in Fig. 17(c) and (d), respectively. The obtained Seebeck coefficient of 375  $\mu$ V K<sup>-1</sup> is surprisingly large, it is comparable to that of the best organic materials<sup>214</sup> and exceeds that of Bi<sub>2</sub>Te<sub>3</sub>.<sup>215</sup> As shown in Fig. 17(e) and (f), the linear behavior of electrical conductivity as a function of temperature is consistent with a temperature-activated charge carrier transport with an energy barrier of 0.052 eV, and the power factor with a value of 0.057  $\mu$ W m<sup>-2</sup> K<sup>-1</sup> at room temperature is about two orders of magnitude lower than the best organic and inorganic materials due to the relatively lower electrical conductivity of TCNQ@Cu<sub>3</sub> (BTC)<sub>2</sub>. In combination with *ab initio* calculations, the observed large positive Seebeck coefficient resulted from the hole transport in the MOF valence band and the low thermal conductivity value is most likely due to the presence of disorder within the MOF thin film.

#### Energy storage via MOF-based capacitors and batteries

**Supercapacitor.** A supercapacitor or an electric double-layer capacitor (EDLC) is a high-capacity electrochemical device with huge capacitance values. They are of interest for applications



Fig. 16 Left: (a) Schematic representation of  $Ni_3$ (HITP)<sub>2</sub>-based porous FETs and electrical characteristics of FETs. (b) Output and transfer curves. Reproduced from ref. 207 with permission from American Chemical Society, copyright 2016. Right: (a) Obtained OFET device and schematic structure of OFET with the interfacial modification of SiO<sub>2</sub> dielectric layers by HKUST-1 SURMOF. (b) Output characteristic and transfer characteristic of the OFET device with HKUST-1 (three cycles)/SiO<sub>2</sub>/Si. Reproduced from ref. 213 with permission from American Chemical Society, copyright 2017.



**Fig. 17** Thermoelectric characterization of the MOF thin film devices. (a) Schematic of the measurement. (b) Example of an IR image taken during one of the measurements. The electrical contacts appear cold in the image because of their different emissivity compared with the MOF. (c) Thermovoltage as a function of the applied temperature difference. (d–f) Seebeck coefficient, conductivity and power factor as a function of the average temperature, respectively. The dashed lines are linear fits. Reproduced from ref. 202 with permission from John Wiley & Sons, copyright 2015.

requiring many rapid charge/discharge cycles. Supercapacitors do not use the conventional solid dielectric of ordinary capacitors. These devices instead store electrical energy either in the electrochemical double layer (EDL) formed by the electrolyte ions on the surface of the electrode, or electrochemically by redox reactions involving the surface regions of electrode materials. Research on supercapacitors has focused on achieving higher energy densities. To further increase the capacity, new electrode materials are required with good electrical conductivity, high surface area, and tailored pore sizes. Since they meet many of these criteria, MOF thin films are promising candidates for the fabrication of supercapacitors.



**Fig. 18** Structural schematics of Ni<sub>3</sub>(HITP)<sub>2</sub>. (a) Molecular structure of Ni<sub>3</sub>(HITP)<sub>2</sub>. (b) Relative size of pores, electrolyte Et<sub>4</sub>N<sup>+</sup> and BF4<sup>-</sup> ions, and acetonitrile solvent molecules, shown in a space-filling diagram of idealized Ni<sub>3</sub>(HITP)<sub>2</sub>. Green, lime, blue, gray, brown, and white spheres represent Ni, F, N, C, B, and H atoms, respectively. Performance of Ni<sub>3</sub>(HITP)<sub>2</sub> electrodes in a symmetrical supercapacitor cell up to 1 V. (c) Cyclic voltammetry at a scan rate of 10 mV s<sup>-1</sup> at increasing cell voltage. (d) Galvanostatic charge and discharge curves at current densities of 0.5, 1.0, and 2.0 A g<sup>-1</sup>. Reproduced from ref. 216 with permission from Nature publishing group, copyright 2016.

One of the first realizations of such MOF-based energy storage devices was reported by Dincă and coworkers, who fabricated a conductive MOF electrode to build a stable super-capacitor with high areal capacitance.<sup>216</sup> A conductive MOF, Ni<sub>3</sub>(HITP)<sub>2</sub>, consisting of 2,3,6,7,10,11-hexaaminotriphenylene linkers and Ni metal nodes, was synthesized using solvothermal methods. The bulk materials (see Fig. 18(a) and (b)) exhibited an electrical conductivity greater than 5000 S m<sup>-1</sup> and a surface area of 630 m<sup>2</sup> g<sup>-1</sup>.

Coating the supercapacitor electrodes was performed by manually pressing  $Ni_3(HITP)_2$  powder into a Pt mesh in an electrolyte consisting of tetraethylammonium tetrafluoroborate (TEABF<sub>4</sub>) and acetonitrile (ACN).

Typical capacitive behaviors of  $Ni_3(HITP)_2$  with nearly rectangular and triangular traces were observed in the cyclic voltammetry (CV) and galvanostatic charge and discharge of a two-electrode symmetrical supercapacitor cell (Fig. 18(c) and (d)).

At a low discharge rate of 0.05 A  $g^{-1}$  the gravimetric capacitance is 111 F  $g^{-1}$ , which is in the same range as activated carbons and higher than that for carbon nanotubes. Normalized to the specific surface area, the value obtained for Ni<sub>3</sub>(HITP)<sub>2</sub>, 18 F cm<sup>-2</sup>, is higher than that observed for any carbon material except graphene. The excellent supercapacitor performance of Ni<sub>3</sub>(HITP)<sub>2</sub> is attributed to the improvement in the double layer capacitance from the electrolyte movement within the 1D channels of Ni<sub>3</sub>(HITP)<sub>2</sub>.

Kang, Yaghi, *et al.* reported that nanocrystal MOFs (nMOFs) can be doped with graphene and then used as electrode



Fig. 19 (a) Structure and morphology of nMOF-867 constructed with  $Zr_6O_6(CO_2)_{12}$  and 2,20-bipyridine-5,50-dicarboxylate (BYDC). (b) Schematic representation of nMOF supercapacitors. (c) Areal capacitance of the highest nMOF supercapacitor (nMOF-867) and comparison to activated carbon and graphene. Reproduced from ref. 217 with permission from American Chemical Society, copyright 2014.

materials for supercapacitors.<sup>217</sup> The best nMOF with the highest capacitance, nMOF-867, was synthesized from  $Zr_6O_6(CO_2)_{12}$  and 2,2'-bipyridine-5,5'-dicarboxylate (BYDC) building units under solvothermal conditions, as shown in Fig. 19(a).

Fabrication of nMOF films with a thickness of 2  $\mu$ m occurred by spin coating a nMOF/graphene/hexane dispersion on the cleaned Ti substrates. These were assembled in a coin-shaped supercapacitor with a separator (monolayer polypropylene separator membranes) and an electrolyte (1.0 M tetraethylammonium tetrafluoroborate ((C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>NBF<sub>4</sub>) in acetonitrile), as shown in Fig. 19(b). It is expected that, by charging the device, the positive and negative ions of the electrolyte move in opposite directions through the separator and into the MOF pores. During discharge, the ions migrate out of the pores because of their high porosity and the openness of their structure, which should result in high capacity for storing ions and the robust cycling of ions within the cell, respectively.

Among 23 nMOF-based supercapacitors, nMOF-867 exhibits excellent performance and properties as a supercapacitor. It has stack and areal capacitances of 0.64 and 5.09 mF cm<sup>-2</sup>, respectively, which are about six times those of supercapacitors made from benchmark commercial activated carbon and graphene materials, as shown in Fig. 19(c).

**Batteries.** The use of metal-organic frameworks for the fabrication of batteries is very appealing. In the past few years, a number of device concepts based on several different MOF materials have been proposed, including Li batteries,<sup>218–237</sup> Li–S batteries,<sup>238–241</sup> Li–O<sub>2</sub> batteries,<sup>242</sup> redox flow batteries,<sup>243</sup> sodium batteries,<sup>244,245</sup> and alkaline batteries.<sup>246</sup> The use of MOF thin film electrodes for Li, Li–S, and Li–O<sub>2</sub> batteries has been recently reviewed by Deng<sup>247</sup> and Wang.<sup>248</sup> Here, the use of MOF thin-film electrodes for the realization of the emerging dual-ion battery, alkaline battery, redox flow battery, and sodium ion battery, which have not been covered in previous reviews, will be presented.

Li, Liu, and coworkers reported MOF electrodes as electrocatalysts for aqueous zinc-polyiodide redox flow batteries.<sup>243</sup>



**Fig. 20** (a) Schematic of the MOF-based zinc-polyiodide redox flow battery (ZIB). Electrochemical performances of the pristine GF and the MOF-modified GF electrodes. (b) Charge/discharge curves. (c) Energy efficiency with different current densities. Reproduced from ref. 243 with permission from American Chemical Society, copyright 2016.

In these applications, the powder MOFs (MIL-125-NH<sub>2</sub>, UiO-66- $CH_3$ ) were deposited on graphite felts (GFs) using a powder MOF-based deposition method (see the Fabrication methods section), as illustrated in Fig. 20(a).

The performance of MOF-based flow cells is shown in Fig. 20(b) and (c). For both UiO-66-CH<sub>3</sub> and MIL-125-NH<sub>2</sub>-based electrodes, there was improved electrochemical activity and reversibility toward the redox couple of  $I^-/I_3^-$  compared to pristine graphite powders. The charge/discharge curves in Fig. 20(c), recorded for MIL-125-NH<sub>2</sub>-based electrodes, demonstrated the smallest overpotentials (highest discharge voltage and lowest charge voltage) among all of the samples.

The flow cells with MIL-125-NH<sub>2</sub>-modified GFs or UiO-66-CH<sub>3</sub>-modified GFs serving as the positive electrodes both demonstrate higher energy efficiency values than those with pristine GFs. The energy efficiency values are improved by around 6.4% and 2.7%, respectively, at the current density of 30 mA cm<sup>-2</sup>, due to the Lewis acid sites in the MOFs that can act as catalytic sites to accelerate the electron transfer. These can accept electrons and facilitate the transport of electrons.

Long and coworkers reported a sodium battery based on a redox-active MOF.<sup>244</sup> In this case, the coating of the carbon cloth electrodes was carried out using the drop-cast method applied to a suspension of a redox-active MOF, Fe<sub>2</sub>(dobpdc) (dobpdc<sup>4–</sup> = 4,4'-dioxidobiphenyl-3,3'-dicarboxylate) and Fe<sub>2</sub>(dobdc) (dobdc<sup>4–</sup> = 2,5-dioxidobenzene-1,4-dicarboxylate).<sup>249</sup> The final device is shown in Fig. 21(a).



Fig. 21 (a) Structure of the Fe<sub>2</sub>(dobpdc) framework. Generalized schematic of how Fe<sub>2</sub>(dobpdc) operates in an electrochemical cell. For the electrochemical reduction, the anions, A<sup>-</sup>, can be tetrafluoroborate, hexafluorophosphate, bis(trifluoromethylsulfonyl)imide, or tetrakis(perfluorophenyl)borate. The cations, M<sup>+</sup>, can be lithium, sodium, or potassium. Half-cell performance of a prototype sodium battery with a 0.6 M NaPF<sub>6</sub> electrolyte in 30:70 EC/DMC. The theoretical capacity is 140 mA h g<sup>-1</sup>. (b) Cycle-rate dependence. (c) Change in capacity with cycle number at 1C. Reproduced from ref. 244 with permission from American Chemical Society, copyright 2015.

The performance of the redox MOF-based sodium battery is impressive, as evident from an inspection of the data shown in Fig. 21(b) and (c). The dependence of the charge/discharge rate on capacity within the resulting battery indicates that the much larger pore size and significantly closer iron-iron contacts within Fe<sub>2</sub>(dobpdc) are responsible for the fast kinetics. Upon partial oxidation of Fe<sub>2</sub>(dobpdc), the electronic properties of the material changed dramatically with enhanced charge-transfer mobility. The coulombic efficiency of the sodium half-cell was larger than 99% over 50 oxidation/reduction cycles. After 10 cycles, the cell capacity plateaued at approximately 90 mA h  $g^{-1}$ , which is more than double the capacity of other iron-based MOFs and is comparable to that of graphite intercalation compounds. The change in the discharge profile between the 10th and the 50th cycle reveals a slow decrease in the electrode kinetics for increasing cycle numbers, whereas the total capacity remained the same. The overall performance of this MOF-based battery is impressive, as the specific stored energy is comparable to that of graphite intercalation compounds.

Pei, Chen, *et al.* reported high-performance alkaline batterysupercapacitor hybrid devices based on a layered Ni-based MOF.<sup>246</sup> The Ni-MOF nanosheets were synthesized using NiCl<sub>2</sub>·6H<sub>2</sub>O and *p*-benzenedicarboxylic acid as building units under solvothermal conditions. The resulting structure comprises stacks of 2D layers, with typical thicknesses of 20–80 nm, a surface area of 295.7 m<sup>2</sup> g<sup>-1</sup>, and a pore size of 3.6 nm. The structure of this MOF is schematically depicted in Fig. 22(a).

In this case, the coating of the electrodes was accomplished by drop-casting a slurry of Ni-MOF, carbon black, and polyvinylidene difluoride dissolved in *N*-methyl-2-pyrrolidinone



**Fig. 22** (a) View of the structure of Ni-MOF along the *a*-axis. (b) Schematic illustration of the alkaline battery–supercapacitor hybrid device containing Ni-MOF and CNT-COOH as the positive and negative electrodes, respectively. The electrochemical measurements of an Ni-MOF//CNT-COOH device in a 3 M KOH + 0.1 M K<sub>4</sub>Fe(CN)<sub>6</sub> solution: (c) CV curves of the device in different potential windows at 10 mV s<sup>-1</sup> and (d) galvanostatic charge–discharge curves of the device at various current densities. Reproduced from ref. 246 with permission from Royal Society of Chemistry, copyright 2016.

onto nickel foam. A platinum foil was used as a counter electrode, a saturated calomel electrode (SCE) was the reference electrode, and the electrolyte was  $\text{KOH/K}_4\text{Fe}(\text{CN})_6$ . The device architecture is displayed in Fig. 22(b).

The performance of the MOF-based alkaline battery-supercapacitor hybrid device is shown in Fig. 22(c)–(f). The CV curves are nearly rectangular and symmetric in shape, and the device is stable up to an optimal electrochemical voltage window of 1.4 V. The specific capacity values calculated were 96.7, 90.7, 85.5, and 79.8 mA h g<sup>-1</sup> at current densities of 1, 2, 5, and 10 A g<sup>-1</sup>, respectively. The device exhibits an excellent electrochemical long-time cyclic stability for 3000 consecutive cycles at a current density of 10 A g<sup>-1</sup>, and it still retains 90.6% of its initial capacity. The device has an excellent electrochemical performance with a high-energy density of 55.8 W h kg<sup>-1</sup> and a power density of 7000 W kg<sup>-1</sup>, which are comparable to Li batteries and supercapacitors, respectively.

#### Membranes

Recent reports have demonstrated that MOF thin films have the notable potential to be used as a gas-phase membrane for

separating small molecules (CH<sub>4</sub>, CO<sub>2</sub>, H<sub>2</sub>, CO) and volatile organic compounds (hydrocarbons, alcohols).<sup>250–253</sup> Compared to other materials, MOFs offer the advantages of precise tunability of pore size and flexibility of the structural backbones.<sup>9–11</sup> Compared to thermodynamically driven separation methods such as distillation, a membrane-based process can substantially reduce the energy and capital cost of separating molecules on a large scale.<sup>254</sup>

Heinke and coworkers revealed that the permeate flux can be continuously adjusted using a photoswitchable MOF membrane, as schematically illustrated in Fig. 23(a).<sup>23</sup>

The photoswitchable MOF membrane containing Cu<sub>2</sub>-(AzoBPDC)<sub>2</sub>(AzoBiPyB) (AzoBPDC: 2-phenyldiazenyl-4,40-biphenyldicarboxylic acid; AzoBiPyB: (*E*)-4,40-(2-(phenyldiazenyl)-1,4phenylene dipyridine)) (Fig. 23(c)) was fabricated on an  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> substrate by LPE with a thickness of ~2 µm, as shown in Fig. 23(b).



Fig. 23 (a) Schematic illustration of tunable, remote-controllable molecular selectivity by a photoswitchable MOF membrane. (b) SEM cross-section image of the SURMOF membrane on the mesoporous  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. (c) The structure of Cu<sub>2</sub>(AzoBPDC)<sub>2</sub>(AzoBiPyB) with the azobenzene groups. The transition between *trans* and *cis* states can be tuned by irradiation with 365 nm and 455 nm light, respectively. (d) The separation of H<sub>2</sub>:CO<sub>2</sub> and N<sub>2</sub>:CO<sub>2</sub> mixtures. The membrane is irradiated by 365 nm and 455 nm light for 5 min each. The permeances of H<sub>2</sub> and CO<sub>2</sub> (left), as well as N<sub>2</sub> and CO<sub>2</sub> (right), are shown in black with the unit of mol s<sup>-1</sup> m<sup>-2</sup> Pa<sup>-1</sup>. The molecular selectivities (or separation factors) are shown in red. Reproduced from ref. 12 with permission from Nature publishing group, copyright 2016.

The azobenzene moieties can be switched from the *trans* to the *cis* configuration and *vice versa* by irradiation with ultraviolet or visible light, resulting in a substantial modification of the membrane permeability and separation factor due to the precisely adjusted pore volume. By controlling irradiation times or by simultaneous irradiation with ultraviolet and visible light, the separation for H<sub>2</sub>:CO<sub>2</sub> can be adjusted between 3 and 8 (N<sub>2</sub>:CO<sub>2</sub> = 5–8), as shown in Fig. 23(d).

## Challenges

The impressive number of MOF-based devices compiled in this review, most of them reported within the past five years, demonstrates the huge potential of this novel class of designer solids. The rapid increase in devices using these novel nanomaterials as active or passive components results from the unique combination of material properties of these molecular frameworks. Particularly important are their large surface areas, enormous porosity, tunable chemical properties, and physical (electrical, mechanical) properties. Crucial for many of the advanced applications is that several routes are available to produce well-defined thin films of this material with different thicknesses. We expect further rapid development of this field. Of the existing 70 000 MOF materials,<sup>4</sup> not all have been considered for applications other than gas storage and separation. Also, the number of possible MOFs is virtually infinite. Furthermore, the opportunity to load these porous nanomaterials with functional nanoclusters has only been explored in a few cases to date.<sup>255-262</sup> Considering this huge flexibility, we expect to see rapid further improvement of the existing devices and the development of completely new devices with novel, yet unforeseen, functionalities.

Regarding the fabrication of MOF-based materials, and in particular the fabrication of high-quality structures with low defect densities, a number of challenges in fabricating MOF materials must be overcome: (i) improving the thin-film quality; (ii) understanding the thin-film growth mechanism; (iii) controlling the defects; (iv) improving the interface stability; (v) enhancing the electrical conductivity; and (vi) enhancing the charge carrier mobility, reducing recombination rates, and improving the efficiency of charge separation. We will briefly explain these individual challenges below.

#### (i) Thin film quality

The fabrication of compact, homogeneous, oriented, pin hole-free, smooth, and crystalline surface-supported metal–organic framework thin films with controllable film thickness and scalable dimensions is a critical step toward their broader, large-scale application. MOF thin-film properties, including film thickness, film orientation, and density of film defects, have substantial influence on the performances of electronic and photovoltaic devices using MOF thin films as an active or passive component.<sup>263</sup> Among the existing approaches for the fabrication of MOF thin films, the LPE<sup>95</sup> and ALD methods have been demonstrated to be the most appropriate for quality. Notably, these two methods allow the film orientation to be controlled by deposition on an appropriately functionalized substrate.

So far, only little attention has been paid to the influence of thin-film quality on the performance of MOF thin-film devices. However, a thorough characterization of defect concentrations in thin films has indicated that, e.g., the LPE method results in MOF thin films with a defect density lower than that in the corresponding bulk material.<sup>264,265</sup> In the majority of applications discussed here, thin-film electrodes are coated with mixtures of MOF precursors and other additives, such as polymers or surfactants. For such heterogeneous systems, the morphology, homogeneity, defects, and compactness of the thin-film electrodes, as schematically represented in Fig. 24, are difficult to control; thus, it is difficult to determine the importance of these parameters on device performance. A more systematic analysis is only possible for all-MOF electrodes, e.g., those used by Yang, Yaghi, and coworkers,<sup>169</sup> or Liu, Sun, and coworkers<sup>171</sup> for CO<sub>2</sub> reduction. We foresee that optimization of growth conditions will lead to further improvements in these device characteristics.

A number of methods are available for characterizing MOF thin film properties such as thickness, morphology, composition, structure, orientation, and defects. Several methods are available for determining structural parameters. Quartz crystal



Fig. 24 The types of defects within MOF thin films. Modified based on ref. 266 with permission from Nature publishing group, copyright 2007.

microbalance (QCM), cross-sectional scanning electron microscopy (SEM), scanning probe microscopy (SPM), or transmission electron microscopy (TEM, mainly for free-standing MOF thin films)<sup>267</sup> are appropriate tools for determining the thickness of MOF thin films. In addition, SEM and SPM (thin film roughness) can also be used to characterize the morphology of MOF thin films. The composition of MOF thin films can be characterized by a number of analytical techniques, including infrared (IR),<sup>187</sup> Raman spectroscopy,<sup>197,262</sup> X-ray photoelectron spectroscopy (XPS),<sup>43</sup> and time-of-flight secondary ion mass spectrometry (TOF-SIMS).<sup>268,269</sup>

Conventional single crystal or powder X-ray diffraction (XRD), the standard methods for characterizing single crystal and powder MOFs fabricated using conventional methods, is not suited for determining the structural parameters of MOF thin films. Most important here are the so-called out-of-plane and in-plane XRD. A schematic illustration is shown in Fig. 25(a). In brief, out-of-plane measurements are performed in the typical ( $\theta$ -2 $\theta$ ) configuration.<sup>118</sup> With this method, which can be performed with laboratory equipment in a straightforward manner, the periodicity of the MOF thin films perpendicular to the substrate can be determined. For in-plane measurements, which can be most conveniently obtained using a synchrotron source, the periodicity parallel to a surface can be determined.

These two techniques have been widely used to characterize various types of MOF thin films. As an example, epitaxial SURMOF 2 thin films prepared using the LPE method<sup>270,271</sup> and Cu<sub>2</sub>(BDC)<sub>2</sub> fabricated on Cu(OH)<sub>2</sub> nanobelts using the SSH approach<sup>118</sup> are presented in Fig. 25(b) and (c), respectively. The in-plane and out-of-plane XRD patterns demonstrate that Cu<sub>2</sub>(BDC)<sub>2</sub> thin films are epitaxially grown on Au/SAMs and Cu(OH)<sub>2</sub> nanobelts with [001] orientation and a layer distance peak (010); these indicate the 2D structural characteristics of the Cu<sub>2</sub>(BDC)<sub>2</sub> thin films.

Moreover, Kitagawa and coworkers demonstrated the characterization of MOF thin films by utilizing other synchrotron XRD techniques.<sup>20,41,43,97,108–111,272–274</sup> Synchrotron X-rays are very well defined geometrically with µm-level beam sizes. Synchrotrons provide very intense beams of high energy X-rays, a million times more intense than laboratory-based X-ray systems with higher depth of penetration on the millimeter scale. As an example, synchrotron in-plane and out-of-plane XRD ( $\lambda = 1.555$  Å) patterns of a highly oriented crystalline Hofmann-type porous 2D MOF, a Fe(py)<sub>2</sub>[Pt(CN)<sub>4</sub>] (py: pyridine) thin film with preferred orientation along the [001] direction, are displayed in Fig. 25(d).

For many applications, macroscale defects, such as pin holes or domain boundaries, are important (Fig. 24). They can be monitored efficiently using microscopic techniques (SEM, SPM,<sup>275</sup> TEM,<sup>276</sup> and confocal fluorescence microscopy<sup>277</sup>) due to their significant influence on a variety of properties,<sup>186,278–280</sup> including catalytic performance,<sup>281–283</sup> gas uptake,<sup>284–287</sup> separation efficiency,<sup>288–290</sup> electrical conductivity,<sup>291–293</sup> and optical band gap.<sup>187</sup>

Intrinsic and artificially created atomic-scale defects inside MOFs and in MOF thin films have received a lot of attention in recent years. Such defects, *e.g.*, lattice shrinkage of the MOF thin films<sup>273</sup> or unsaturated coordination sites of metal nodes, may result from a break in coordination bonds between organic

building units and metal nodes, a changed chemical state of metal nodes, or missing linkers<sup>294–298</sup> or clusters.<sup>299–301</sup>

These defects are difficult to see using microscopic techniques. The type of defects (*e.g.* domain boundaries, vacancies, interstitials, *etc.*) and defect concentration can be analyzed using a sophisticated combination of diffuse scattering, electron microscopy,<sup>267</sup> anomalous X-ray scattering, and pair distribution function measurements.<sup>276</sup> Alternatively, spectroscopic techniques such as X-ray photoelectron spectroscopy (XPS) and vibrational spectroscopy (FTIR)<sup>302</sup> are powerful tools for detecting and characterizing local microscale defects and probing their chemical and physical environment within a MOF thin film. Further, with the help of theoretical studies,<sup>264,296,303–308</sup> the scenarios of the structure–property relationships for MOF thin films can be established precisely.

Yang and co-workers<sup>309</sup> confirmed the presence of Cu vacancies in MOF-505 and their concentrations using XPS in combination with extended X-ray absorption fine structure (EXAFS) spectroscopy. Also for the HKUST-1 SURMOF thin films grown on an MHDA/Au substrate (Fig. 26(a)) defects within MOFs were characterized using XPS.<sup>264</sup> As shown in Fig. 26(b), the XP spectra indicate the existence of Cu<sup>+</sup> in the pristine HKUST-1 SURMOF thin film with a concentration of ~10%. The concentration of Cu<sup>+</sup> reaches ~40% when the sample is annealed at 420 K. The existence and significant increase in Cu<sup>+</sup> upon annealing indicated existing defects within the HKUST-1 SURMOF thin film, which can be further determined using vibrational spectroscopic techniques. Note, that such defects can have a pronounced influence on the diffusion of small molecules through the porous MOF materials.<sup>310</sup>

Vibrational spectroscopic techniques with various probe molecules like CO,<sup>264,311</sup> CO<sub>2</sub>, and CD<sub>3</sub>CN<sup>312–314</sup> are suitable for studying the defects present in low concentrations and buried within the MOF thin films. High-resolution ultrahighvacuum (UHV) FTIR has been demonstrated by Wöll and coworkers<sup>264</sup> to be a quality-control indicator for the defects that characterize the local environments of Cu<sup>2+</sup>-paddlewheel nodes, using CO as a probe molecule as shown in Fig. 26(c). In combination with density functional theory (DFT) calculations, the existence of mixed-valence Cu<sup>2+/+</sup> paddlewheel nodes was confirmed due to the linker vacancies.

Inspired by this pioneer work, Fischer and co-workers<sup>187</sup> designed a series of defective linkers (Fig. 26(d)) that artificially create defects within HKUST-1. The vibrational bands of CO observed in the UHV-PFIR spectra (Fig. 26(d)), together with DFT calculations, suggest that there is one CO molecule coordinating to a regular  $Cu_2^{II}(BTC)_4$  unit and two CO molecules coordinating to the defective  $Cu^{II}Cu^{I}(BTC)_3$  units with linker vacancies. This indicates the presence of defective units.

#### (ii) Thin-film growth mechanism

While the fabrication of MOF thin films from slurries by employing drop-casting or doctor-blade techniques are straightforward, the assembly of SURMOF thin films using LPE, the method which produces the highest-quality MOF thin films, is much more complicated. To date, the LPE thin-film growth

#### (a) XRD experimental setups for MOF thin films characterization



(b) SURMOF thin films fabricated with LPE method



(c) MOF thin films fabricated with SSH method



(d) MOF thin films fabricated with LPE method



**Fig. 25** (a) Schematic illustration of the XRD experimental setups for MOF thin films. Reproduced from ref. 118 with permission from Nature publishing group, copyright 2017. Selected examples of MOF thin films with the corresponding out-of-plane and in-plane XRD patterns for (b) SURMOF 2, (c)  $Cu_2(BDC)_2/Cu(OH)_2$ , and (d)  $Fe(py)_2[Pt(CN)_4]$  (py: pyridine) thin films. (b, c and d) Reproduced from ref. 270, 118 and 41 with permission from Nature publishing group, copyright 2012, 2017, and 2016, respectively.

mechanism has been extensively investigated with a focus on the substrate with different functional groups<sup>86</sup> and the density of functional groups,<sup>94</sup> growth kinetics using a quartz crystal microbalance (QCM),<sup>85</sup> the temperature influence using atomic force microscopy (AFM),<sup>315</sup> the surface energy dominated growth,<sup>316</sup> and the first-layer order of the growth using infrared spectroscopy (IR).<sup>317</sup> However, there has been a lack of systematic investigations into solvent effects, humidity effects, and dynamic growth monitoring in combination with *in situ* spectroscopic techniques. While most successful LPE processes for SURMOF growth are based on ethanol as a solvent, ZIF-8 SURMOFs with high structural quality can only be obtained using methanol as a solvent.<sup>318</sup>

#### (iii) Role of defects

Note that defects not only have negative properties. In some cases, *e.g.* as discussed in connection with catalytic properties in the previous paragraph, their effect is wanted. This is also true in connection with electronic (doping), optical (color centers) and magnetic effects. Highly relevant in this context is a quotation from a recent paper on the role of defects in organic materials by K. Müllen<sup>319</sup> "Unravelling the relationships between defects and material properties is a daunting task, but increased analysis and knowledge could be beneficial in many applications."

We feel that MOF thin films and in particular SURMOFs are very well suited to explore such relationships for the new and rapidly growing class of the metal-organic hybrid materials described in this review, since thin films are better suited for electrical and optical characterization and, more importantly, since defect densities can be controlled in MOF thin films in a straightforward fashion. For example, in the case of SURMOF high quality films with low defect densities can be produced.<sup>322</sup> In such high-quality films defects could then be introduced in a controlled fashion, e.g. by using "defective linkers"<sup>187</sup> or by heating.<sup>265</sup> Note, that with regard to the characterization of optical qualities, MOF thin films are much better suited than the powder materials available from solvothermal synthesis since scattering and refraction occurring at small particles makes the reliable recording of optical properties of powders a rather difficult task.

#### (iv) Interface stability

As yet, there have been no detailed investigations into the precise structure and quality of substrate/MOF or electrode/ MOF interfaces. Several studies have revealed, however, that the adhesion can be very strong. For example, in the case of HKUST-1/Au(111) films, detailed investigations using XRD have not observed delamination, despite the opposite sign of the thermal expansion coefficient (positive for the substrate, negative for the deposited MOF thin film) and even after several heating/ cooling cycles.<sup>320</sup> This experiment demonstrates that the anchoring of SURMOFs to appropriately functionalized substrates can be very strong.

Although the deposited MOFs themselves may be stable under harsh conditions (such as immersion into strong acidic or alkaline solutions), the anchoring may fail in such cases, as



**Fig. 26** (a) Schematic drawing of HKUST-1 grown on an MHDA/Au substrate. (b) XP spectra of HKUST-1/MHDA/Au at different temperatures. (c) Left: UHV-IRRAS spectra of CO adsorbed on activated HKUST-1/MHDA/Au at 110 K. The sample was annealed at 350 K and 420 K. Right: Cluster model of a MOF that is formed from  $Cu^{2+}$  dimers and 1,3,5-benzenetricarboxylic acid (BTC). Reproduced from ref. 264 with permission from John Wiley & Sons, copyright 2012. (d) Top: The defective BTC-like linkers. Bottom: UHV-FTIR spectra were obtained after representative defective MOF samples with different defective linkers L1–L4 exposed to various amounts of CO at 90 K. Reproduced from ref. 187 with permission from American Chemical Society, copyright 2014.

indicated in Fig. 27. Detailed investigations of these interfaces and their influence on, *e.g.*, charge transfer, are scarce. Without doubt, they will influence the electrical transport and govern the resistance of the corresponding contacts.

MOF thin-film deposition on substrates exposing functional groups results in the formation of MOF/SAM interfaces (Fig. 2(a)). Another type of interface is created within hetero-MOF multilayers. The boundary within "stacked" MOF layers results in MOF/MOF interfaces (Fig. 27(b)). Here, the defect density depends on the lattice match between the two adjacent MOF lattices, among other effects.<sup>321</sup> In Fig. 27(c), MOF thin films constructed using the metal ion source from the substrate will lead to the formation of "interfaced" interfaces; such



Fig. 27 Schematic illustration of the interface types of MOF thin films. (a) MOF/SAM interface, (b) MOF/MOF interface, and (c) "intercalated" interface. (b and c) Reproduced from ref. 321 with permission from American Chemical Society, copyright 2014, and ref. 118 with permission from Nature publishing group, copyright 2017, respectively.

interfaces are expected to be rather stable. Interface stability is particularly crucial for the use of MOF thin films in electrochemical devices, *e.g.*, for  $CO_2$  reduction and water splitting. Whereas SURMOF thin films fabricated using LPE or electrophoretic deposition methods have been observed to degrade already after two-hour electrocatalysis,<sup>170,171</sup> MOF thin films prepared by the substrate-seeded approach showed good performance even after operating for several hours.<sup>169</sup>

#### (v) Electrical conductivity

Electrical conductivity is a key requirement for applications of MOFs and MOF thin films as energy storage materials in supercapacitors and batteries. Most MOFs are characterized by a sizeable HOMO–LUMO gap and, correspondingly, are medium-to-large bandgap semiconductors<sup>322</sup> or insulators with poor electrical conductivity. To overcome this limitation and thus improve the electrical conductivity, several strategies have been proposed.

Particularly successful has been an approach, where the porosity of MOFs was utilized to load organic guest molecules (*e.g.* ferrocene<sup>323</sup> or TCNQ<sup>197</sup>) into the voids of the metal–organic framework. Using this strategy, the conductivity of MOFs can be substantially enhanced. In the case of TCNQ@HKUST-1 (TCNQ = 7,7,8,8-tetracyanoquinodimethane), electrical conductivity has been increased by six orders of magnitude.<sup>197</sup> A different strategy used to improve the electrical performance of MOFs is the synthesis of conductive polymers from suitable precursors loaded into the pores of the framework. After polymerization of the monomer EDOT (3,4-ethoxylene dioxy thiophene), the resulting PEDOT chains, poly(3,4-ethylenedioxythiophene),<sup>324</sup> rendered a substantially higher conductivity of the MOF–polymer composite.

Instead of enhancing the conductivity *via* introduction of guests within the frameworks, Dinca and coworkers reported new types of

MOFs with intrinsic conductive properties using highly conjugated linkers.<sup>325</sup> This approach has been successful in fabricating a supercapacitor with excellent energy storage properties.<sup>216</sup>

#### (vi) Charge carrier mobility, recombination, and separation

The use of MOFs as light-harvesting materials for photovoltaics or photocatalysis<sup>326</sup> has already been demonstrated for powder



**Fig. 28** (a) Scheme for donor/acceptor (D/A) molecule loading in MOF hetero-multilayers. Reproduced from ref. 321 with permission from American Chemical Society, copyright 2014. (b) Electron and hole transport between well-defined organic/organic interfaces in MOF thin-film materials. Reproduced from ref. 165 with permission from John Wiley & Sons, copyright 2016.

MOFs constructed with porphyrin derivatives as organic linkers. The performance was found to be superior to MOFs built from other types of organic linkers.<sup>327–331</sup>

To improve the performance of MOF-based photovoltaic devices, which is still rather low compared to that of other organic compounds,<sup>51,52,154,161</sup> light absorption and charge carrier mobility need to be further improved. At the same time, recombination rates need to be reduced and the efficiency of charge-carrier separation must be enhanced.<sup>332</sup> Whereas these goals call for an improvement in the organic linkers or the loading of guest molecules into the pores of MOF thin films, higher efficiencies for exciton dissociation and charge carrier separation might be achieved by creating optimized MOF/MOF heterojunctions between framework materials optimized for electron and hole transport, respectively, using hetero-epitaxy,<sup>165,321</sup> a different strategy consists of loading donor/acceptor (D/A)<sup>333</sup> molecules into the MOF thin films (Fig. 28).

# Conclusions and perspective

In summary, the design and fabrication of various surfacesupported metal–organic framework thin films have recently resulted in a number of novel devices. The use of MOFs for such advanced applications that require the attachment of electrodes to MOF materials was not foreseen when these porous coordination polymers were first introduced about 20 years ago.<sup>334</sup> The success in constructing devices from these materials, in areas such as photovoltaics for solar energy conversion,  $CO_2$  reduction, water splitting, electronic devices including memory devices and field-effect transistors (FETs), and energy storage including supercapacitors and batteries, now calls for a more intense investigation into the solution-based/ vacuum-based processes introduced to manufacture such MOF thin films.

Although MOF thin films have demonstrated attractive performance in previous studies, there is still a long way to go before these materials can be industrialized and commercialized. Besides, several challenges must be addressed before MOF thin films can be directly applied. We believe that, with more research effort, MOF thin films will be further extended into other unexplored fields.

# Author contributions

The manuscript was written through contributions from all authors. Both authors have approved the final version of the manuscript.

# Competing financial interest

The authors declare no competing financial interests.

# Acknowledgements

We thank Dr S. Begum, Dr H. Gliemann, Dr L. Heinke, Dr E. Redel, Dr J. Rinck and Dr O. Shekhah for a careful reading of the

manuscript. Prof. Z. Tian and Prof. L. Sun have provided valuable suggestions. Financial support from the National Basic Research Program of China (973 program) (2014CB239402), the Natural Science Foundation of China (NSFC 21673032), the Fundamental Research Funds for the Central Universities (DUT17LK21), the State Key Laboratory of Physical Chemistry of Solid Surfaces, Xiamen University (201507) as well as from the German Science council through SFB 1176 (project C4 and C6) and SPP1928 "COORNET" is gratefully acknowledged.

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