Metal-Organic Frameworks for Metal-Ion Batteries: Towards Scalability

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Abstract

Metal-organic frameworks (MOFs), being a family of highly crystalline and porous materials, have attracted particular attention in material science due to their unprecedented chemical and structural tunability. Next to their application in gas adsorption, separation, and storage, MOFs also can be utilized for energy transfer and storage in batteries and supercapacitors. Based on recent studies, this review describes the latest developments about MOFs as structural elements of metal-ion battery with a focus on their industry-oriented and large-scale production.

1. Introduction

Global energy consumption is growing every year, which is associated with active social and economic development. However, limited natural energy resources and climatic changes, caused by their extraction and use, call into question the previous pace of development. In this sense, the development of new green technologies that ensure the energy storage in batteries and energy transfer in an environmentally friendly way is becoming more relevant than ever. Global industrial auto giants such as Mercedes also support such transition to green energy. Despite unprecedented successes in the development of such batteries and accumulators, chemical and physical limitations of existing (organic, inorganic and hybrid) materials yet hinder the wide commercial application and require new solutions in material science. For instance, limited life of the batteries and their cycle stability, physical and chemical stability of structural elements, limited charge/discharge rates, capacity, as well as recyclability of the batteries [1] are cornerstones of the future technology of the clean energy. In this sense, metal–organic frameworks (MOFs) can be considered as new attractive candidates to meet the requirements of next-generation energy storage devices [2].

Emerged over 20 years ago [3], MOFs have become one of the key materials in chemistry and crystal engineering. Being as a family of highly crystalline and porous materials, MOFs are composed of metal nodes and organic ligands linked by coordination bonds. Their "LEGO" nature possesses an unlimited structural and compositional versatility, providing the desired chemical and physical properties [4]. Due to synthetic design, MOFs' properties such as crystal structure, porosity, stability, and conductivity can be tailored for specific applications. Therefore, such synthetic versatility of MOFs allows one to optimize the functional properties for energy storage [5], since the needs of each device are different.

Today, MOFs, depending on their designed properties, are utilized as the main structural elements of the batteries (Fig. 1): electrodes, solid-state electrolyte, separator and potentially contacts with the metallic conductivity [6-10]. There are many reviews covering the design [5,11-16] fabrication, operation, limitations, and prospects of specific MOFs as individual structural elements such as cathodes and anodes [17-26], electrolytes and separators [27-30]. However, the problem associated with the creation of scalable MOFs for mass (as BASF, MOF-WORX, and NuMat make [31-34]) and large-scale production with focus on energy applications has not been addressed. Here we discuss the latest developments about MOFs as structural elements of metal-ion battery focusing on their industry-oriented production by thin film technology: spin coating and recently developed chemical vapour deposition.

2. Discussion

Generally, metal-ion batteries are composed of three major components: anode and cathode with different chemical potentials, immersed in an ion-conducting and electri-
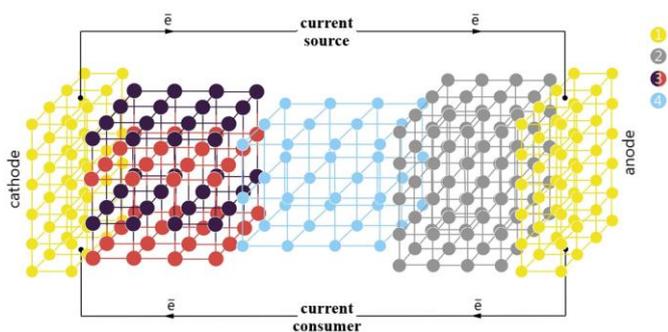
Fig. 1 Schematic illustration of MOFs (porous coordination polymers) as solid-state electrolytes (4), cathode (3) and anode (2) coating as well as potential electronic conductors (1)

cally insulating electrolyte (Fig. 1). The electrochemical reactions in such batteries are the following: metal ion diffusion within the electrode, charge transfer at the interface between the electrodes and electrolyte, and metal ion transport through the electrolyte. Herein, the recharging of the batteries (i.e. current source) occurs in a "rocking-chair" fashion: metal ions transfer between cathode and anode during charge/discharge cycles (Fig. 1). During discharge (i.e. current consumer), metal ions travel from the anode to the cathode, while electrons move externally from the anode to the cathode.

Metal-organic frameworks demonstrate high potential to optimize the performance of metal-ion batteries. This is facilitated by a number of their distinctive properties such as porosity, redox behavior, various types of conductivity (ionic and electronic), encapsulation of various molecules and ions, etc. Fig. 1 demonstrates a schematic diagram of a metal ion battery with highlighted areas corresponding to MOFs as cathodes, anodes, solid-state electrolytes and separators.

First, we consider MOFs as cathodes and anodes. Generally, metal-organic frameworks are semiconductors in nature, in some cases the band gap reaches up to 5 eV. Nevertheless, there are compounds with the lower band gap possessing hopping electronic conductivity. The mechanisms of electronic transport in MOFs are the following [35-37]: through-bond, through-plane, through-space, redox-hopping, and guest-promoted pathways. This provides an opportunity to utilize ZIF-8 ($Zn(mIm)_2$, where mIm = 2-methylimidazolate), metal-ion batteries, addressing two issues: providing electron transport and insertion/extraction of ions due to redox activity [38-40]. Nam et al. [38] were able to combine these two properties and provide a prototype of the metal-ion battery with a cathode entirely made of two-dimensional MOF ($Cu_3(HHTP)_2$, where HHTP - 2,3,6,7,10,11-hexahydroxytriphenylene) with an electronic conductivity of 0.2 S cm^{-1} (Fig. 2a). Also, Li et al. [40] demonstrated similar approach, but for the anode (Fig. 2b).

Deposition of metal-organic frameworks on the anodes also allows one to improve the capacitive characteristics of metal-ion batteries due to insertion/extraction of various ions through the MOF layer. This makes it possible to increase the effective anode area without changing the dimensional characteristics of the device, which, in its turn, promises miniaturization of existing batteries. A number of papers [41-48], considering such an approach, demonstrate the achievement of significant results in current densities, charge capacity, and cyclic stability. The mechanism of insertion/extraction of ions is also described in details in [44] using the example of aluminum-based MOF (Fig. 3). In addition, the deposition of MOFs on the cathodes possesses the similar effect, which has been considered by the authors of [48-52].
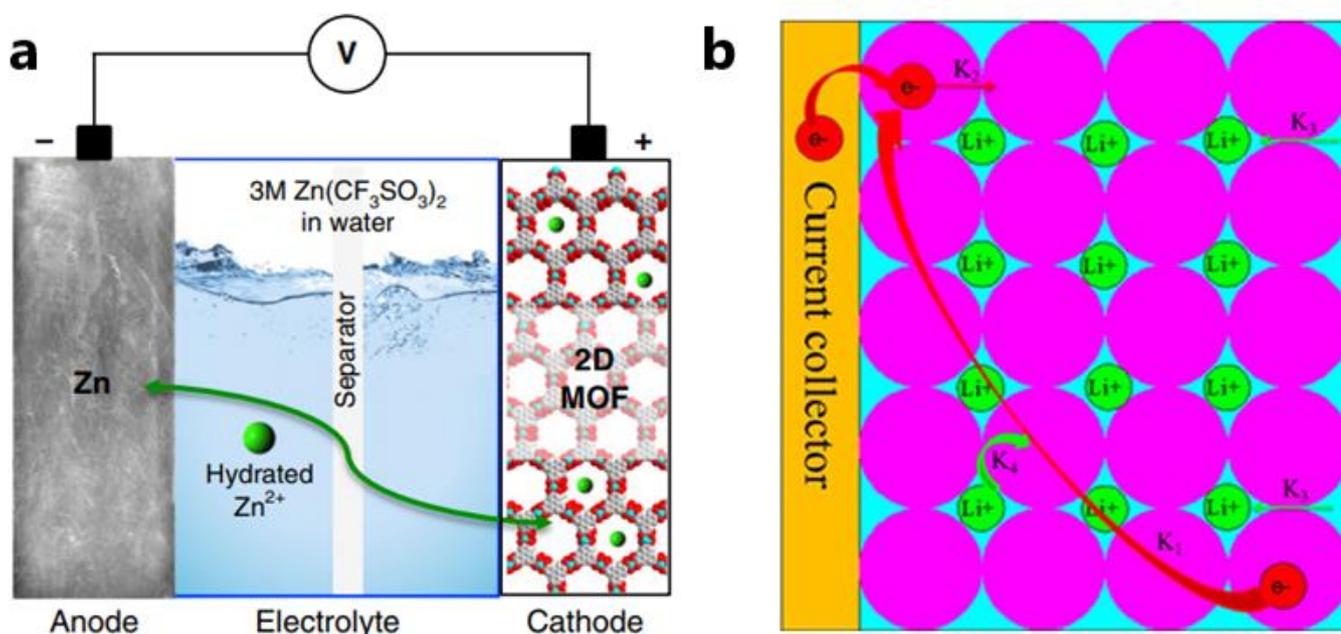

Fig. 2 The concept for the MOF as a cathode (a) [38] and anode (b) [40]

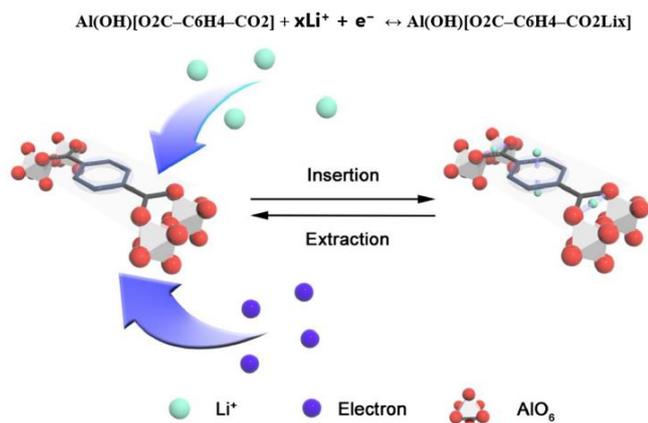$$Al(OH)[O2C–C6H4–CO2] + \mathbf{xLi^+} + \mathbf{e^-} \leftrightarrow Al(OH)[O2C–C6H4–CO2Lix]$$

Fig. 3 The mechanism of insertion/extraction of various ions through MOF layer [44]

Utilization of metal-organic frameworks as an active medium for ion transport is the other side of the story. The porous structure provides ion transport through the MOF, which allows one to consider it as a solid-state electrolyte [53-59]. The reason to use MOF as a solid-state electrolyte is dictated, first, by a decrease in the toxicity of the resulting metal-ion batteries. Indeed, the common liquid electrolytes are extremely toxic, which makes the process of disposal quite difficult and expensive. Such toxicity also makes existing batteries extremely unsafe for use in electronic devices for children. In this sense, the transition from the liquid electrolytes towards solid-state ones can improve this issue and allows the batteries to be recyclable. In addition, a number of metal-organic frameworks demonstrate promising operation characteristics under the extreme conditions: high temperatures,

mechanical stress, directed thermal action, etc. A number of recent research works [54-59] prove the validity of this suggestions through the embedding of metal-organic frameworks as an additional layer [58] (Fig. 4c) or making the energy device based on MOF as an active layer [57] (Fig. 4a,b). Also, a review of potentially suitable compositions of MOFs as solid-state electrolytes can be found in [59].

The increasing focus on industrially applicable MOFs [31-34] for microelectronics and energy applications highlight significant limitations of common solution methods and emphasizes the need for more scalable technologies like Roll-on approach, which is highly needed for production of portable batteries. The possibility of the scaling of the synthesis of functional MOFs is directly related to the development of technologies for the growth of high-quality crystals in the form of thin films. To address this issue, first, we consider spin coating approach [60-64]. This is one of the simplest methods for MOF scalability allowing the deposition of MOF films on different rigid and flexible substrates (metal, semiconductor or dielectric) with different morphologies. The method consists of the interaction of droplets of two solutions (an organic ligand and a metal salt) on the surface of a rotating substrate (Fig. 5a) [60]. Due to the high rotation speeds of the substrate, the resulting film has relatively good uniformity in thickness and composition (Fig. 5b).

The heating of the substrate can be also applied to increase both the rate of synthesis and the crystallinity. The authors of [61] obtained a 150 nm film on an aluminum electrode at a rotation speed of 3000 rpm and a substrate temperature of 140 °C, which can potentially
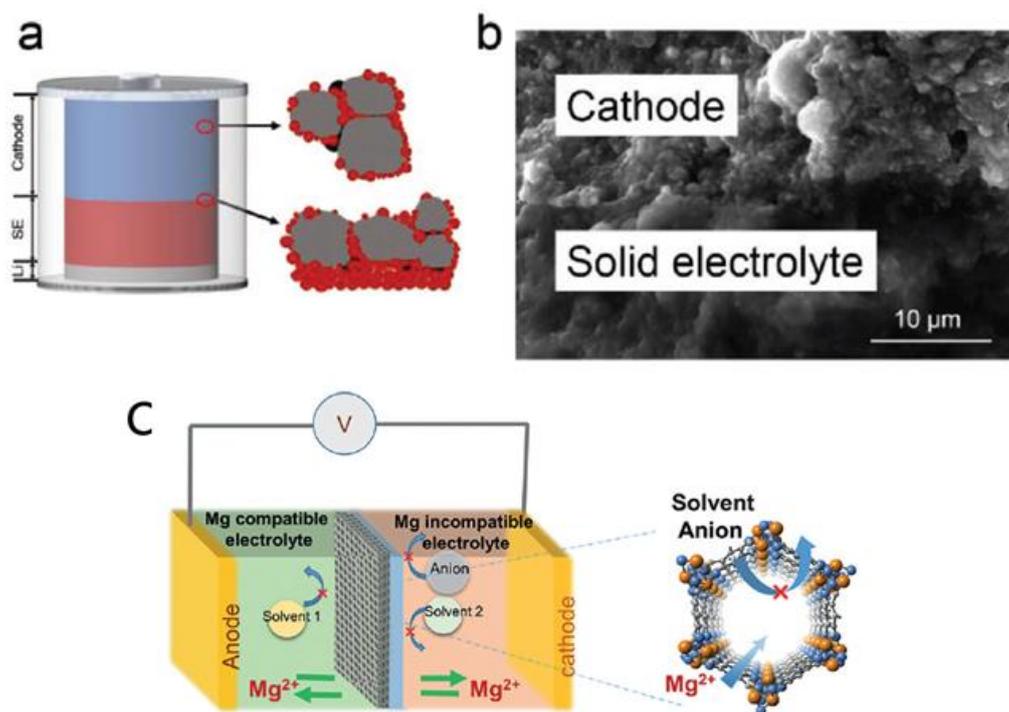

Fig. 4 MOF as a solid-state electrolyte (a,b) [57] and separator film (c) [58]
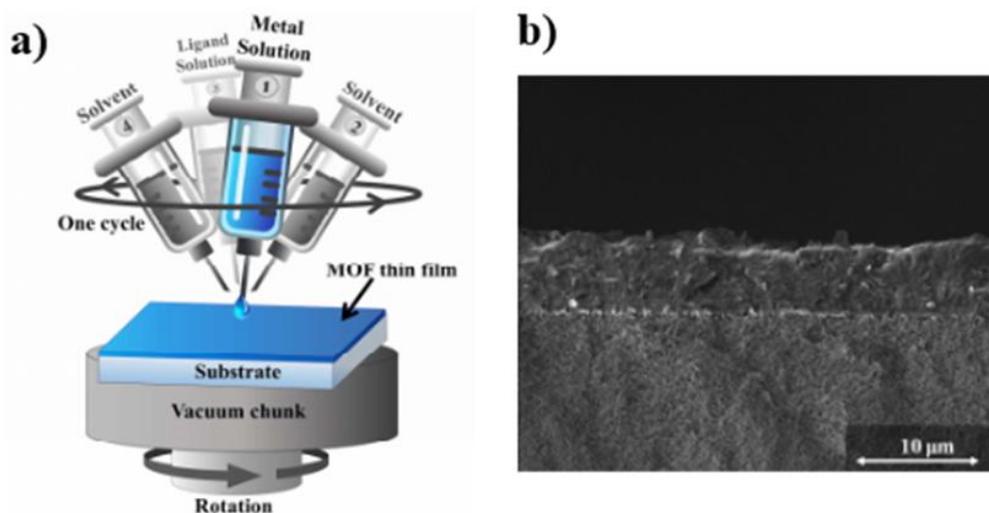
Fig. 5 Schematic illustration of spin-coating approach (a) and cross-section view of MOF thin film obtained by scanning electron microscopy (b) [60]

be used for the process of modifying the electrodes of metal-ion batteries. Chen et al. [62] also showed the possibility of spin-coating the flexible film with an electronic type of conductivity, which is interesting as electrode layers in the device of metal-ion batteries. Also, direct evidence of the validity of the spin-coating technology application follows from the paper [63] where Fan et al. modified the surface of the Zn-MOF anode by centrifugation. Finally, considering the battery, whose structure consists of multilayer MOFs as electrodes, electrolytes and separators (Fig. 1), the specific technology is required. In this sense, the spin-coating makes it possible to fabricate such multilayer structures, as evidenced by the results obtained in [64].

Next highly promising approach is chemical vapour deposition (CVD) [65-74]. Indeed, CVD as a non-solvent method is a well-known industrial approach for obtaining surfaces suitable for micro- and optoelectronics since the corrosion and contamination issues are solved. A variant of CVD, MOCVD (metal-organic CVD) is a standard process for laser diode, LED, and semiconductor manufacturing, meaning it can be used for MOF synthesis, as well. Following the research works on MOF CVD, common structures such as ZIF-8, ZIF-67 ($Co(mIm)_2$, where mIm = 2-methylimidazolate), HKUST-1 ($Cu_3(BTC)_2$, where BTC = benzene-1,3,5-tricarboxylic acid) and MIL-53 (Al-BDC, where BDC = 1,4 benzene dicarboxylic acid), recently utilized for energy storage [21], can be prepared as model thin films. However, in contrast to solution chemistry, the limited possibilities of CVD for using a variable concentration of various solvents significantly limit the resulting MOF topologies, while it is not an insurmountable problem for the method.

The general concept of MOF CVD is illustrated in Fig. 6. Rob Ameloot and co-workers describe this methods as a two-step procedure [65]: the deposition of the metal oxide layer on a support by, for instance, atomic layer deposition (ALD), followed by the exposure of this oxide coating
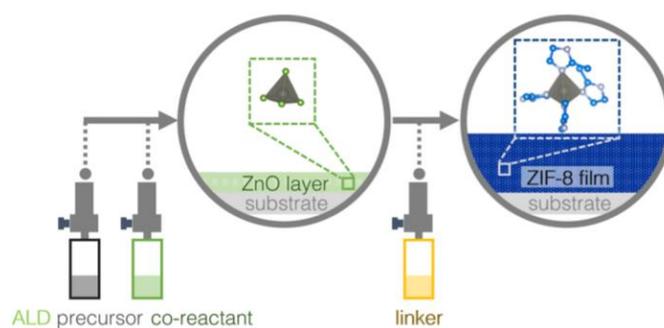

Fig. 6 Schematic illustration of MOF CVD process [68]

to a vaporized linker resulting in a vapor-solid reaction towards the formation of the desired MOF structures. Following this approach, ZIF-8 films were obtained by Stassen et al. [65]. ZIF-8 was deposited on silicon pillars with a 25:1 aspect ratio by vapour-solid transformation of 25 nm ALD zinc oxide films. It is vital to mention the possibility of obtaining conformal coatings by such approach on various, often fragile, surfaces. Intriguing, the presence of water during synthesis promotes formation of a non-porous diamondoid $Zn(mIM)_2$ polymorph, but under high temperatures the water evaporation eliminates the chances of amorphous material to form.

Similar effect of lack of solvent has been demonstrated by Han et al. [66] who reported solvent-free HKUST-1 film deposition under vacuum conditions. They combined CVD and physical vapour deposition processes using layer-by-layer (LBL) growth where after each H_3BTC deposition cycle a monolayer Cu was grown again.

The group of Ameloot [67] also reported the growth of MOF based on Cu(II) and linkers 1,4-benzenedicarboxylic acid (H_2BDC) and trans-1,4-cyclohexanedicarboxylic acid (H_2CDC). The MOF-CVD method for these materials consists of two steps: vapour-phase deposition of copper or copper oxide films as a metal source, and a solid–vapour reaction between this precursor and the vaporised organic linker. It is important to note that depending on synthesis

conditions (dry or humid) diverse MOFs' structures were obtained. For H_2CDC linker humidity did not play a major role and porous CuCDC was normally formed. However, for H_2BDC linker, depending on the humidity level, CuBDC or CP-CuBDC structure similar to coordination polymer $[Cu_2(OH)_2(BDC)]$ could be obtained.

A number of emerging problems in the process of MOF-CVD, such as the incomplete conversion of the metal-oxide precursor to MOF, and the degradation of the organic ligand during deposition at elevated temperature were described [68-71]. A possible solution was proposed by Cruz et al. [68]: involving an increase of exposure time and decrease of the thickness of the metal-oxide precursor. Furthermore, the use of low-temperature synthesis (80 ºC) conditions to circumvent these challenges was explored for MAF-6 (RHO-Zn(eIm)$_2$, where eIm = 2-ethylimidazolate) [69], MAF-252 (Zn(dpt)$_2$, where dpt = 3-(2-pyridyl)-5-(4-pyridyl)-1,2,4-triazolate)) [70] (Fig. 7), ZIF-8 and ZIF-67 [71] structures.

Another issue comes from MOF-CVD method itself that allows obtaining MOFs with limited porosity [65-71]. This deteriorates a whole range of functional properties including ion transport. This issue can be overcome by accounting for the following factors [67,68]: (i) humidity has to be controlled since it can increase chances of amorphous intermediate formation, thus, affecting thin film roughness – the more humid conditions are, the rougher are the films produced; (ii) the thickness of metal-oxide precursor has to be controlled in order to fully convert it into MOF. Otherwise, it acts as a protecting shell that hampers further MOF growth. So far, only model MOFs with relatively simple topologies and short ligands have been synthesized by CVD, therefore, leaving room for further investigations of MOFs with more complex hierarchy and variable ion/electron conductivity.

The report by Stassin et al. [72] creates a basis for the direct comparison of the solvothermal and vapour deposition methods for the synthesis of functional and polymorphic MOFs. MOFs Al-MIL-53-Fum and Al-MIL-53-Mes (Al-MIL-68-Mes) were synthesized with and without modulators. When formic acid was used as a modulator, MOF crystallized at 80 ºC by CVD in the orthorhombic crystal system with *Pnma* space group. At the same time, modula-

tor-free product crystallized by solvothermal method in the monoclinic space group *P*21/*c*. The change of the modulator from formic to mesaconic acid led to formation of Al-MIL-53-Mes by CVD that crystallizes in the orthorhombic with *Pnma* space group. This work highlighted the principle possibility of the controlled synthesis of structurally diverse compounds via conscious vapour deposition synthesis.

Similar message was conveyed by a very recent work by Tu et al. [73], which described another approach to controlled MOF-CVD synthesis by using the so-called template vapor that arranges the MOF building blocks and promotes the formation of desired product. They found out that the reaction between zinc oxide and 4,5-dichloroimidazole (HdcIm) leads to the formation of either porous kinetic phase ZIF-71 [Zn(dcim)2] (dcim = 4,5-dichloroimidazolate) with RHO topology, or thermodynamically stable phase ZIF-72 (the same chemical formula as ZIF-71) with LCS topology. The addition of template vapors enabled formation of ZIF-71 at lower temperatures (120 ºC vs 160 ºC); however, at temperatures above 120 ºC it was impossible to avoid the phase transition from ZIF-71 to ZIF-72.

3. Conclusions

Conventional solution chemistry certainly remain the key approach for the synthesis of MOFs for diverse applications including electrochemical energy storage [74]. However, the increasing focus on industrially applicable MOFs [31-34] for microelectronics, optics [75] and energy application highlight significant limitations of the solution methods and emphasizes the need for more scalable and industry-oriented technologies. Here, we cover advanced methods, such as spin coating and vapour deposition techniques, allowing large-scale and fast productions of functional MOFs. These industrially oriented and scalable methods demonstrate high potential for producing the functional MOF thin films. Specifically, the CVD technique appears as the most optimal and promising method for the industrial manufacture of MOFs. The intense research during the past 5 years identified a number of technological challenges hampering the implementation of MOF-CVD and indicated avenues for their solution. The key challenges include the incomplete conversion of the metal-oxide precursor to MOF, the degradation of the organic ligand during deposition at elevated temperature [68-71], as well as growth of MOFs with limited porosity [65-71]. All these issues can potentially be addressed. Also, over the past year, the possibility of large-scale growth of MOFs with a structural diversity has been also demonstrated [73,74], which, we believe, will be one of the driving forces in MOF crystal engineering in the near future.

Concerning spin coating approach, there are still technological problems of MOF thin film fabrication such as a poorly controlled growth process, the influence of external
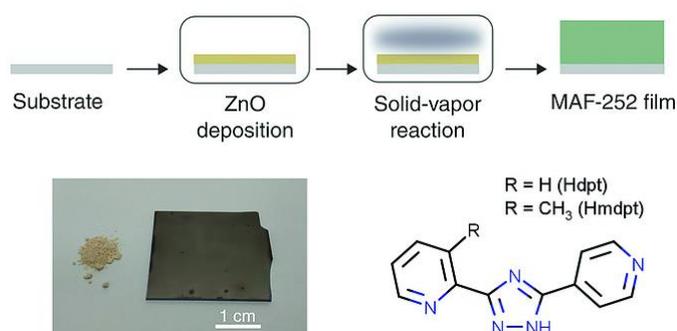
Fig. 7 The scheme of MAF-252 thin film fabrication with corresponding optical images of MAF-252 powder and large-scale film [70]

factors (mechanical vibrations, convection flows and in-sufficient automation), and a limited list of structural elements (especially ligands) involved in the crystal growth. The latter is associated with the high growth rate of thin films during the spin coating, which does not allow sufficiently large ligands (porphyrins, TBAPY etc.) to organize a porous periodic lattice. Finally, inhomogeneity of the film (domain structure) and a high degree of surface roughness limit the applicability of the method.

In our review, we also omitted the other industrially oriented methods for scalable MOF fabrication, such as electrochemistry, mechanochemistry and microwave-assisted synthesis. The reason for this is the rather high degree of development of these methods, which is reflected in the relevant reviews [76-81].

Acknowledgments

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