Metal–Organic Frameworks

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A Solvent-Free Hot-Pressing Method for Preparing Metal–Organic-Framework Coatings

*Yifa Chen[+], Siqing Li[+], Xiaokun Pei[+], Junwen Zhou, Xiao Feng, Shenghan Zhang, Yuanyuan Cheng, Haiwei Li, Ruodan Han, and Bo Wang**

Abstract: *Metal–organic frameworks (MOFs), with their well-defined pores and rich structural diversity and functionality, have drawn a great deal of attention from across the scientific community. However, industrial applications are hampered by their intrinsic fragility and poor processability. Stable and resilient MOF devices with tunable flexibility are highly desirable. Herein, we present a solvent- and binder-free approach for producing stable MOF coatings by a unique hot-pressing (HoP) method, in which temperature and pressure are applied simultaneously to facilitate the rapid growth of MOF nanocrystals onto desired substrates. This strategy was proven to be applicable to carboxylate-based, imidazolate-based, and mixed-metal MOFs. We further successfully obtained superhydrophobic and "Janus" MOF films through layer-by-layer pressing. This HoP method can be scaled up in the form of roll-to-roll production and may push MOFs into unexplored industrial applications.*

Metal–organic frameworks (MOFs)[1] are porous crystalline materials synthesized by covalently joining metal ions or clusters with organic linkers, and they are considered to be promising candidates for gas storage, separation, catalysis, sensing, and drug delivery.[2] However, with their inherent nature as inorganic coordination materials, MOF crystals are often brittle and can break down into tiny particles or fine powders. These can easily clog reactors and pipes during separation, catalysis, and other industrial applications; needless to say, severe material loss will inevitably occur when flushing with fluids (gas or liquid). Therefore, the fabrication of MOFs into granules, membranes, films, or fibers is required for these important industrial processes.[3]

The fabrication of MOFs into the above-mentioned devices, especially those with substrates, is mainly achieved by in situ growth of MOFs and other deposition methods with/without binders or additives.[4] In situ growth of MOF devices is an important and straightforward approach where the MOF crystals gradually form and grow on certain substrates by solvothermal synthesis; microwave, ultrasound, or electrochemical deposition; or low-temperature self-assembly in solution, among other methods.[5] Other approaches include some rather sophisticated deposition methods such as secondary growth on seeding layers, spray-coating, gel-layer procedures, colloidal dip-coating deposition, Langmuir–Blodgett layer-by-layer deposition, and colloidal Langmuir–Blodgett deposition.[6] Some important reports have presented inspiring results in controlling the location of individual crystals and the thickness of defect-free MOF layers, as well as various MOF species with specifically designed pore sizes and structures.[7] However, from a practical perspective, MOF layers obtained by using these methods can suffer from poor stability or fragility, and they often require tedious time/energy-consuming processes. Another practical way to fabricate MOFs is mixing MOF particles with suitable binders or additives to give a paste for shaping into uniform granules or free-standing membranes.[8] However, binders and other additives can lower the ratio of active species and may block the pores/channels of MOFs, thus further dampening the performance of the final products. Indeed, it is still challenging to efficiently fabricate stable and binder-free MOF coating layers, especially on flexible substrates on a large scale. An alternative facile approach toward robust MOF coatings on various substrates is thus highly desirable.

Herein, we present a novel strategy for synthesizing MOFs under solvent- and binder-free conditions by using a hot-pressing (HoP) method, in which hot pressing under 200 °C for only 10 minutes can turn a powder of the starting materials into highly stable MOF coatings on various substrates, including metal foils, cloths, and fibers (Scheme 1). Under applied temperature and pressure, MOF precursors, metal ions, or organic linkers can rapidly react with the surface functional groups or metal sites on the surface of the substrates to form the first layer, and then the growth of MOF layer can occur. Consequently, this HoP method can provide high affinity for MOF nanocrystals to attach onto the surface of flexible substrates, thus enhancing the resilience of such MOF-coated devices. We show that HoP can be successfully applied as a robust method for MOF fabrication. Not only does this approach consistently yield MOF devices with various MOF structures, but it also allows easy access to mixed-metal MOF coatings (Figure 1).

$Zn(2\text{-mIM})_2$ (ZIF-8)-coated carbon cloth (denoted as ZIF-8@Carbon cloth) was prepared by first spreading a powdered mixture of $Zn(OAc)_2$, 2-methylimidazole, and polyethylene glycol (PEG) onto a section of carbon cloth (2-mIM =

[*] Y. Chen,[+] S. Li,[+] X. Pei,[+] Dr. J. Zhou, Prof. Dr. X. Feng, S. Zhang, Y. Cheng, H. Li, R. Han, Prof. Dr. B. Wang
Key Laboratory of Cluster Science, Ministry of Education of China
School of Chemistry, Beijing Institute of Technology
5 South Zhongguancun Street, Beijing, 100081 (P.R. China)
E-mail: bowang@bit.edu.cn
Homepage: http://bowang.bit.edu.cn
[+] These authors contributed equally to this work.
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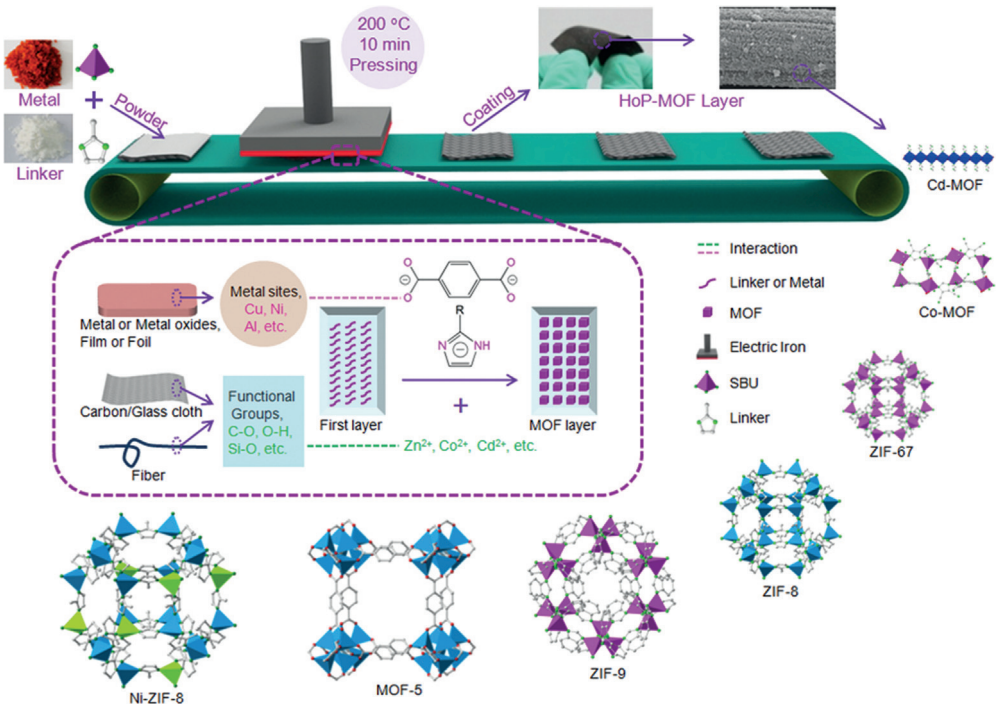

Scheme 1. Schematic presentation of the hot-pressing (HoP) method for MOF coating. SBU = Secondary Building Unit.

2-methylimidazolate). After that, 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 (Section S2-1 in the Supporting Information). The loading level of ZIF-8 was 7.12 g m^{-2} and could be tuned from 3.01 to 9.76 g m^{-2} by adjusting the quantity of precursors (Figures S4, S5 and Table S1 in the Supporting Information). Similarly, other MOF coatings were obtained under similar conditions (carboxylate-based and imidazolate-based MOFs; Figure 1). Notably, introducing heterogeneity into the predetermined crystalline framework can endow the material with unprecedented performance.[9] Nickel-doped Ni-ZIF-8@Carbon cloth was also obtained through the addition of nickel nitrate to the raw materials (Section S2-8 in the Supporting Information, Figure S15).[10] It should be noted that PEG was applied to enhance the initial diffusion of metal ions and consequently facilitate rapid growth of the MOF crystals, and all residual PEG was completely removed after synthesis (Figure S6), as in the case of other solid-phase MOF syntheses.[11]

As shown above, the HoP method is applicable to different kinds of MOFs to form uniform coatings. We then expanded this method to different substrates. Specifically, we selected six flexible substrates (carbon cloth, anodic aluminum oxide film (AAO), nickel foam, copper foil, glass cloth, and glass fiber) and produced ZIF-8 coatings through the same general procedure. Notably, according to the scanning electron microscopy (SEM) images, the ZIF-8 particles are uniformly attached on the surfaces for all of the substrates, and nitrogen sorption tests verify that the microporosity of ZIF-8 is retained in all cases (Table S1, Figures S16–22).

Combined with their flexible properties, the production of MOF coatings on these substrates can be easily scaled up to the centimeter or meter scale. We first demonstrated this by continuously pressing ZIF-8 precursors on a large piece of glass cloth (50 cm × 10 cm) back and forth three times to yield ZIF-8@Glass cloth (Figure 2 a–c and Section S2-10 in the Supporting Information). Through HoP, we further grew ZIF-8 on a long single glass strand (50 cm in length, a bundle of glass fibers) under similar conditions (Figure 2 d–g). This represents an additional[5g,12] method for fabricating uniformly distributed MOF nanoparticles on a linear substrate.

The robustness of a device is one of the critical prerequisite for practical applications, since it determines the durability of the device under harsh conditions.[13] Abrasion resistance tests were performed through adhesion with adhesive tape or scratching continuously with sandpaper. ZIF-8@Carbon cloth obtained through the HoP method can maintain its structure and morphology and possesses superior performance compared with ZIF-8@Carbon cloth obtained by using the traditional solvothermal method (Section S3-1 in the Supporting Information, Figures S23–25). Mechanical stirring and KOH aqueous solution treatment further confirmed the mechanical and chemical stability of ZIF-8@Carbon cloth (Figures S26–27). Such high robustness can be attributed to the strong affinity between the MOF and the substrate. As shown by XPS studies, a new O 1s peak attributed to Zn−O appeared at 530.1 eV for carbon cloth after being treatment with zinc acetate by HoP compared with untreated carbon cloth; such a peak was absent for solvothermal-treated carbon cloth (Section S3-2 in the Supporting Information, Figure S28).[14]

The excellent stability of the HoP MOF-coated devices sets a solid basis for the introduction of other properties to devices. Superhydrophobicity, for example, can be achieved through combination with another hydrophobic layer[15] by means of layer-by-layer HoP. A superhydrophobic film with a 151° contact angle was prepared after hot-pressing 1H,1H,2H,2H-perfluorooctyltriethoxysilane onto the surface of a piece of ZIF-8@Carbon cloth (Figure 3 a, b, Figure S29 and Section S3-3 in the Supporting Information). We then

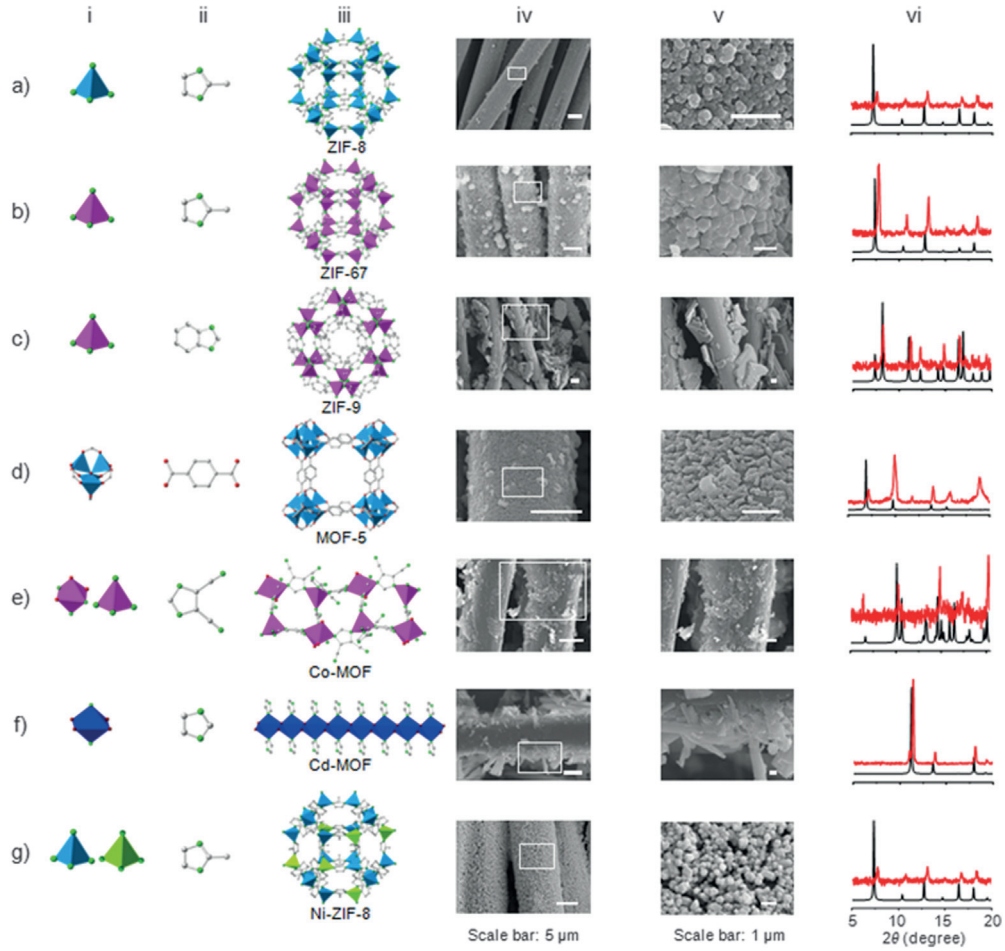

Figure 1. a) ZIF-8@Carbon cloth. b) ZIF-67@Carbon cloth. c) ZIF-9@Carbon cloth. d) MOF-5@Carbon cloth. e) Co-MOF@Carbon cloth. f) Cd-MOF@Carbon cloth. g) Ni-ZIF-8@Carbon cloth. SBUs (i), linkers (ii), and structures (iii) are presented for the corresponding MOFs. Zn, blue; Co pink; Cd dark blue; Ni light green; N green, O red. SEM images (iv, v) of the prepared MOF coatings at different magnifications. (v) shows a magnified image of the square box in (iv). PXRD patterns (vi) of MOF coatings with different structures and the corresponding experimental (red) and simulated (black) patterns are shown for each MOF-coated device.

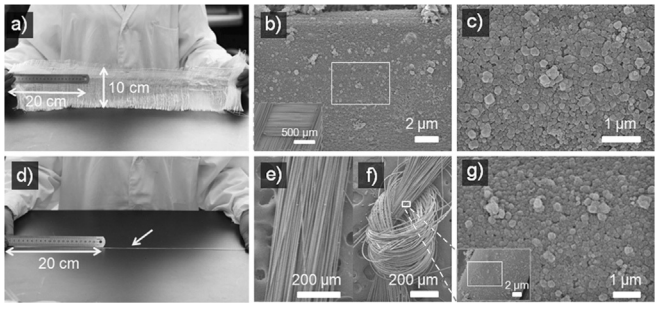

Figure 2. a) Photograph of the ZIF-8@Glass cloth on a large scale. b) SEM image of ZIF-8@Glass cloth. Inset: whole image SEM of the ZIF-8@Glass cloth. c) Magnified SEM image of the area highlighted in (b). d) Photograph of a ZIF-8@Glass fiber. e) SEM image of a straight ZIF-8@Glass fiber. f) SEM image of a twisted ZIF-8@Glass fiber. g) SEM images of twisted ZIF-8@Glass fiber. Inset: magnified image of the area highlighted in (f).

successfully achieved asymmetric MOF coatings by growing ZIF-8 and ZIF-67 on different sides of a section of copper foil, as indicated by powder X-ray diffraction (PXRD) and SEM (Figure 3c,d, Section S3-4 in the Supporting Information, Figure S30). "Janus" and layer-by-layer methods conducted with the HoP method might greatly increase the diversity and multi-functionality of MOF coatings, which would in turn open up a wide range of new applications.

Given the multifunctionality of MOFs, the flexibility in terms of substrate, and the robustness of the HoP devices, a simple yet effective filtration device was constructed by replacing the filter element with the MOF-coated devices in a commercially available syringe filter (Figure 3e). In a typical As^V adsorption study, ZIF-8@Carbon cloth, ZIF-9@Carbon cloth, and ZIF-67@Carbon cloth showed excellent adsorption capacities of 27.2, 53.1 and 32.6 $mg\,g^{-1}\,m^{-2}$ (Figure 3f, Section S3-5, and Table S3 in the Supporting Information), respectively.[16]

We further set out to explore this method in mass production with a roll-to-roll hot-pressing machine. As presented in Figure S31, this roll-to-roll apparatus can accurately adjust the hot-pressing temperature, pressure, and working speed, thereby providing potential opportunities for industrial mass production.

In conclusion, we present an alternative facile and scalable hot-pressing (HoP) method for MOF coating that is generally applicable to various substrates. MOF-coated devices obtained through this method exhibit excellent uniformity and robustness, with well-maintained crystallinity and microporosity of the pristine MOFs. Furthermore, layer-by-layer and "Janus" approaches applied with HoP greatly increase the diversity and multifunctionality of the MOF coatings. Moreover, this method can be further extended to mass production with a roll-to-roll machine. We believe that our approach will open up exciting opportunities in a wide range of industrial applications that have so far been inaccessible for materials like MOFs, covalent-organic frame-

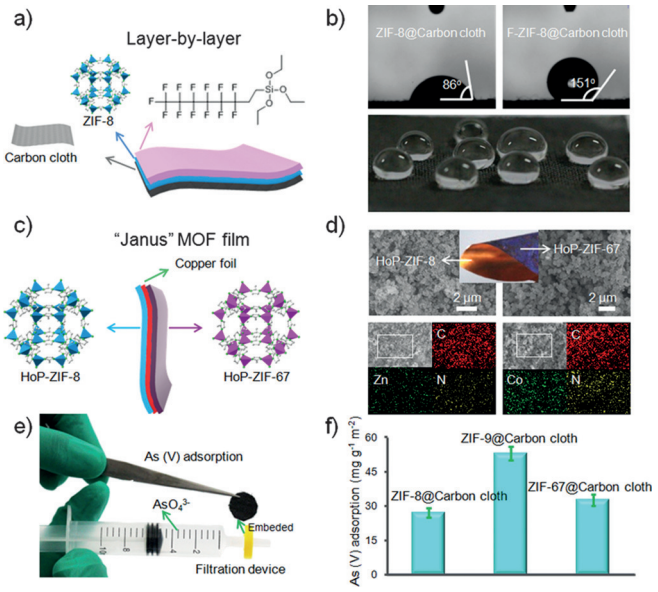

Figure 3. a) Schematic representation of "layer-by-layer" MOF coating. b) Hydrophobic properties of F-ZIF-8@Carbon cloth and ZIF-8@Carbon cloth (for comparison) after treatment in water for 6 h. Below is a photograph of water on the surface of F-ZIF-8@Carbon cloth. c) Schematic representation of a "Janus" MOF film. d) On the left is an SEM image and elemental mapping analysis of one side of the copper foil and on the right is the other side. Inset: photograph of a "Janus" MOF film. e) A filtration device constructed from MOF-coated carbon cloth (1 cm in diameter). f) As^V adsorption performances of ZIF-8@Carbon cloth, ZIF-9@Carbon cloth, and ZIF-67@Carbon cloth, where carbon cloth shows a value of 4.3 mg m^{-2} for comparison.

works (COFs),[17] conjugated microporous polymers (CMPs),[18] and other crystalline porous solids.[19]

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