Chapter

Metal Organic Frameworks-Based Optical Thin Films

Cheng-an Tao, Jianfang Wang and Rui Chen

Abstract

Metal-organic frameworks (MOFs) are organic-inorganic hybrid materials with ordered pore structures assembled by metal centers and organic ligands through coordination bonds, but conventionally they are mostly in powder form. In recent years, metal-organic framework films have received increasing attention due to their potential applications in nanotechnology and nanodevices. The intrinsic ultrahigh porosity of MOFs may lead to a low refractive index of MOF materials. In addition, over 70,000 types of MOFs exist, and their properties can be tuned through the adoption of different metal motifs, organic ligands, or crystal morphologies. These characteristics make MOFs a potential new generation of optical thin film materials. In this chapter, the fabrication methods of MOF thin films, the optical properties of MOF optical thin films, and their application in optical sensors were described.

Keywords: metal-organic frameworks, thin film, fabrication method, optical property, refractive index, sensor, naked eye detection

1. Introduction

An optical film refers to a type of optical dielectric material that is attached to a surface of an optical device and is composed of a thin and uniform layered medium that propagates a light beam through an interface [1]. Commonly used optical films include: reflective films, antireflection films, polarizing films, interference filters, and beamsplitters [2]. Although there are many mature technologies and commercial products, with the increasing requirements of modern optics and optoelectronic devices, the exploration of new optical films is still the focus of current research.

Metal-organic frameworks (MOFs) are a class of porous materials that have developed rapidly in the past 20 years [3, 4]. They are crystalline materials that are composed of inorganic metal ions or metal-oxo cluster nodes and organic bridging ligands through coordination bonds. Due to the diversity of metal ions and organic bridging ligands, and the diversity of coordination linkages, there are theoretically unlimited types of MOFs, and more than 70,000 species have been reported so far, which are still increasing. MOFs have many inherently excellent properties, such as rich and tunable pore structure (pore size, pore shape, and pore opening), large specific surface area, regulatable chemical microenvironment, and good thermal stability [5–7]. They also can show special luminescent properties, magnetic properties, electrical conductivity, catalytic properties, etc. by selecting a particular metal ion or ligand. These properties make MOFs materials of great potential applications in many fields, such as gas adsorption and storage [8], separation [9], catalysis [10, 11], drug delivery and sustained release [12], medical imaging [12], luminescent materials, sensing [13–16], and so on.

In the field of optical films also, MOFs can be useful. Its almost infinite variety, tunable optical properties, and some of the inherently superior properties described above make it an excellent material for building optical films. However, MOFs are usually prepared in bulk or in powder form. Preparation of MOFs into a flat and uniform optical film is a prerequisite for their application. The optical properties of optical films are their core properties. How to effectively control their optical properties is a key issue in the study of MOF optical films. Therefore, in this chapter, firstly, five major methods for preparing MOF optical films—spin-coating, dip-coating, self-assembly, direct growth, and step-by-step liquid phase epitaxy (LPE) methods—were introduced, and a comparison of them was made under the consideration of the same MOF as the model. Then, the method of determination of refractive index of MOF films was described. The change of the linkers and post-modification of bridged ligands to control the optical properties of MOF optical films were discussed. At last, MOF thin films used as optical sensors were presented, including monolayer MOF thin films, MOF film-based 1DPC, and MOF film-combined optical fiber.

2. Fabrication methods of MOF thin films

At present, a series of methods have been developed to prepare MOF films [17, 18], but the flatness of most of the resulting films cannot meet the requirements of optical films. To date, there are mainly five typical methods to produce MOF optical films with high quality.

2.1 Spin-coating method

Spin coating is widely used in microfabrication of functional oxide layers on glass or single crystal substrates using sol-gel precursors, where it can be used to create uniform thin films with nanoscale thicknesses [19]. Hinterholzinger et al. [20] reported the fabrication of one-dimensional photonic crystals (1DPCs, also called Bragg stacks) based on zeolitic imidazolate framework (ZIF)-8 by spin coating for the first time. 1DPC was composed of multilayer of alternative ZIF-8 layers and titanium dioxide layers. In 2013, Lotsch's group [21] fabricated MOF thin films by spin-coating a MOF nanoparticle suspension onto a flat substrate. Two kinds of MOFs have been explored: one is copper trimesate ($Cu_3(BTC)_2$, also known as HKUST-1, HKUST = Hong Kong University of Science & Technology), which contains Cu (II)-paddlewheel-type nodes and trimesate struts, and the other one is the isoreticular metal-organic framework-3 (IRMOF-3, zinc amino-terephthalate).

Our group [16, 22–24] successfully applied this method to construct many other MOF thin films, such as iron (III) terephthalate MIL-88B (MIL = Materials of Institut Lavoisier), aluminum terephthalate MIL-53, MIL-101(Cr), and their analogs. We [16] reported the first example of flexible MOF optical thin film fabricated by spin coating (**Figure 1**). The flexible NH_2-MIL-88B(Fe) was chosen as the model, and nanorods of NH_2-MIL-88B(Fe) were prepared by hydrothermal method, and then MOF optical films prepared by spin-coating. The thickness of the film was nearly proportional to both suspension concentration and rotation cycles, and inversely proportional to the spin speed. And the rod-shaped MOFs tended to be aligned parallel to the substrate due to rotational shear forces. It provides the basis for subsequent application of properties.

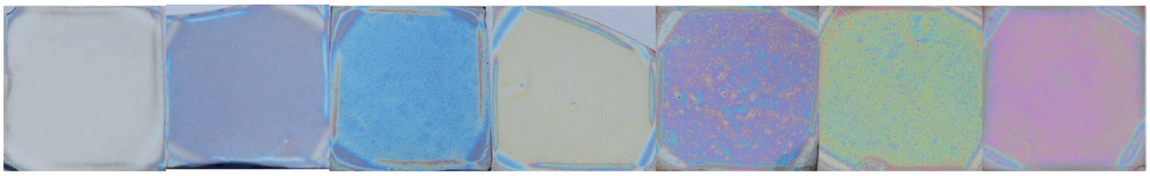

Figure 1.
Photograph of a series of NH_2-MIL-88B films deposited on silicon wafers with various concentrations (from left to right: 0.5, 1, 2, 3, 4, 5, and 6 wt%) by spin-coating method. Reproduced from Ref. [16] with permission from The Royal Society of Chemistry.

2.2 Dip-coating method

As a popular alternative to spin coating, dip-coating methods are frequently employed to produce thin films from sol-gel precursors for research purposes, where it is generally used for applying films onto flat or cylindrical substrates [25]. In 2009, Gérard Férey et al. [26] first synthesized a colloidal dispersion of MIL-89, and then prepared a MIL-89 optical film by a dip-coating method. The film with a surface roughness of approximately 3 nm is very uniform. Subsequently, the team used microwave method to obtain nanoscale MIL-101(Cr) [27], MIL-100(Cr) [28], and MIL-100(Fe) [28], and prepared optical films using them by a similar dip-coating method. The MOF films are deposited from MOF nanoparticles naturally, and their surface roughness is about half of the size of MOF nanoparticles. The premise of this method is to obtain MOF nanoparticles with better dispersibility. MIL-100(Al) particles prepared by the same method cannot be used to fabricate optical thin films because of their large particle size (>500 nm) [28].

2.3 Self-assembly

Self-assembly is a process in which a disordered system of preexisting components forms an organized structure or pattern as a consequence of specific, local interactions among the components themselves, without external direction. The building blocks of self-assembly are not only molecules, but span a wide range of nano- and mesoscopic structures. In 2014, Prof. Huo [15] proposed a method for self-assembly of MOF nanoparticles. First, the nanoparticles of UiO-66 (UiO = University of Oslo) were prepared; then, their surface was modified with polyvinylpyrrolidone (PVP), and finally dispersed in mixture of water and ethanol (v:v = 1:1) to obtain a dispersion. A glass substrate was inserted into the water in a culture dish, and a small amount of the above dispersion was dropped on the surface of the water. Then, the MOF nanoparticles were rapidly spread to the surface of the water, and a 2% sodium dodecyl sulfonate (SDS) solution was dropped to make the MOF dispersion closely arranged into a single layer film. The film was transferred out to obtain a monolayer MOF film on the glass substrate. The MOF multilayer films can be obtained by repeating the process.

2.4 Direct in situ growth

MOFs prepared by direct in situ growth usually produce thick and rough membranes or dispersive particles. Lu et al. [14] successfully constructed ZIF-8-based optical thin films via a direct growth method that functioned as selective sensors for chemical vapors and gases. They immersed a glass substrate or silicon wafer in a newly prepared ZIF-8 growth solution (2-methylimidazole and $Zn(NO_3)_2$ in methanol) at room temperature. After 30 min of growth, a uniform ZIF-8 film of about 50 nm was obtained. More importantly, this process can be repeated, and the thickness of each subsequent growth was increased by about 100 nm, and the resulting film exhibited a very bright structural color. The color changes as the thickness increases, as shown in **Figure 3**. The method has the advantages of mild reaction conditions, fast growth rate, easy control of thickness, and easy removal of solvent in MOFs after reaction.

2.5 Step-by-step liquid phase epitaxy (LPE)

Step-by-step liquid phase epitaxy alternately deposits metal and organic ligand precursors on a functionalized surface, and the two are assembled by layer-by-layer growth to obtain a MOF film (also called surface-anchored MOF, SurMOF). The MOF prepared by this method has precisely controlled thickness and growth orientation, and the thickness can be regulated by the number of cycles of growth. In 2007, Wöll et al. [29] successfully used this method to prepare crystalline MOF films, such as two-component MOFs, HKUST-1, which alternately deposit copper acetate and BTC (BTC = trimesate) ligands on –COOH or –OH-modified gold substrate. The method is further used to prepare ternary layered MOFs composed of two organic ligands, such as $[Cu(bdc)_2(dabco)_2]$ (bdc = 1,4-benzenedicarboxylic acid; dabco = 1,4-diazabicyclo[2.2.2]octane) [30], $[Zn_2(+/-)(cam)_2dabco]$(cam = (1R,3S)-(+)-camphoric acid) [31], $Fe(pz)[Pt(CN)_4]$(pz = pyrazine) [32, 33], DA-MOF$(M(L)_2(P)_2)$((M = Cu or Zn; L = naphthalene dicarboxylate or 2,3,5,6-tetrafluoroterephthalic acid); P = dabco) [34], and so on.

The orientation of SurMOF can be regulated by different functional groups on the surface. For example, modifying the carboxyl or hydroxyl groups on the surface of the substrate allows the growth direction of HKUST-1 to be [111] and [100], respectively, under suitable conditions [29]. On the pyridyl- or carboxyl-modified surface, the growth direction of $[Cu(bdc)_2(dabco)_2]$ is [100] and [001], respectively [30].

Unfortunately, it usually takes a long time to obtain a thicker film of MOFs due to the layer-by-layer growth mechanism. To overcome this shortcoming, researchers further combined this method with the spray method [35, 36], the spin-coating method [37], and the dip-coating method [38], and thereby developed a few improved methods for rapidly preparing the MOF films. Wöll et al. [36] alternately sprayed a solution of $Cu_2(CH_3COO)_4 \cdot H_2O$ and BTC on a substrate modified with a coordinating group by a high-pressure carrier gas to obtain a HKUST-1 film. The thickness of the cyclic growth can reach 10 nm, and the growth rate of the method is increased by two orders of magnitude compared with the original method. In 2016, Eddaoudi group [37] combined the LPE method with the spin-coating method to achieve the growth of MOF films by spin-coating the metal salt solution and the organic ligand solution on the substrate, respectively. $Cu_2(bdc)_2 \cdot xH_2O$, $Zn_2(bdc)_2 \cdot xH_2O$, HKUST-1, and ZIF-8 films were successively prepared on the surface of substrates such as gold and alumina, which is more effective than traditional LPE methods. MOF films with thicknesses ranging from nm to μm are available. However, compared with the conventional LPE, the roughness of the obtained MOF film is remarkably increased. Particularly, the MOF films having too much growth cycle or growing on a porous substrate are difficult to use as optical films.

In 2014, Benes team [38] at the University of Twente developed a step-by-step dip-coating method that yielded thicker, dense MOFs in a single cycle. They dipped the silicon wafer vertically into the $ZnCl_2$ solution for 30 min, and then pulled it out at a certain rate (0.1–4 mm/s). After washing, it was immersed in the 2-methylimidazole solution for 30 min, then pulled out again, and then washed again. ZIF-8 film can be obtained by drying naturally in a culture dish, wherein the rate of each pulling is controlled to be the same, wherein the thickness of the film can be controlled by the pulling speed. The thickness of the ZIF-8 film is about 100 nm at

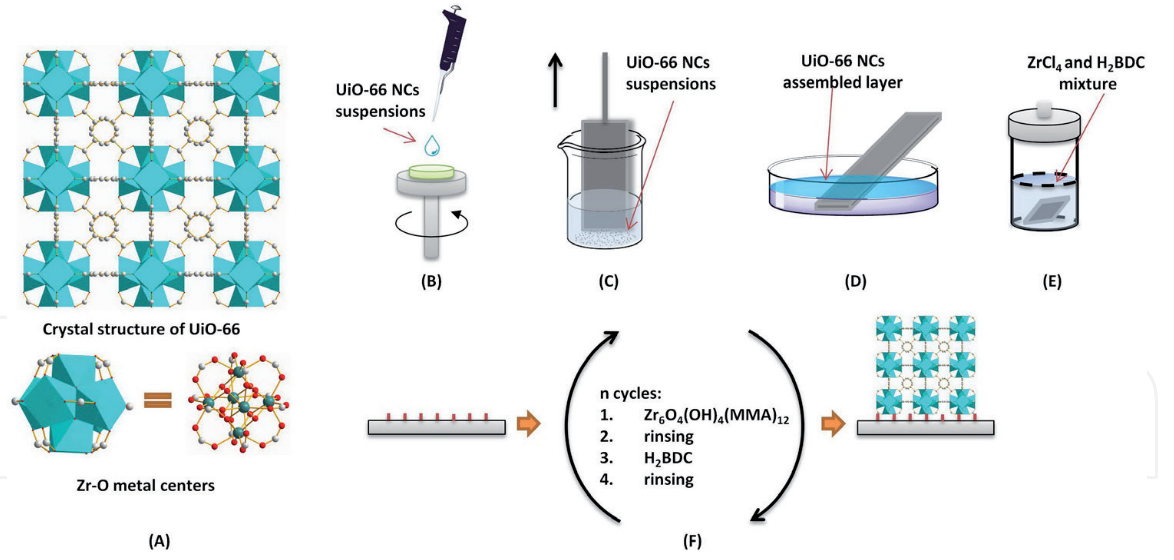

Figure 2.
(A) Crystal structure of UiO-66, consisting of Zr-O metal centers connected by terephthalate linkers. Zr, cyan; C, gray; O, red; H, omitted. (B–F) Illustration of five fabrication methods of MOF optical thin film: (B) spin coating, (C) dip coating, (D) self-assembly, (E) direct in situ growth, (F) LPE method [39].

a pulling rate of 1 mm/s. If the rate is too large or too small, the film thickness will increase. This method has not been extensively studied and has not been reported for the suitability of other types of MOFs.

2.6 Comparison

The above-mentioned five methods have shown success in preparation of MOF thin films, but there is still lack of systematic research on the performance and potential application of the MOF films from the aspects of optical films. Moreover, for the same MOF system, there is a lack of detailed comparison on these preparation methods. Recently, our group [39] chose UiO-66 as a model to prepare UiO-66 thin films by the above-mentioned five methods, respectively (**Figure 2**). The resultant thin films were denoted as OTF-SP, OTF-DP, OTF-SA, OTF-DG, and OTF-LPE, respectively. The qualities of the films were quantitatively analyzed using surface roughness. The arithmetic average roughness, Ra, is the arithmetic average value of filtered roughness profile and the root mean squared roughness. The OTF-SP film has the best flatness, while the OTF-DG has the worst roughness (Ra = 40.3 nm). The roughness of MOF thin films made of octahedral UiO-66 nanocrystals is generally higher than that of spherical MOF nanoparticles-based thin films [23, 24, 27]. For the dip-coated films, the more the depositions, the larger the roughness due to accumulation. For the self-assembled films, the trend is just the opposite. Their roughness decreases with the increase of depositions, thanks to the interleaved filling of following nanocrystals.

3. Optical properties of MOF optical thin films

At present, the research on optical properties of MOF optical films is still relatively preliminary, mainly focusing on the determination of their optical constants, especially the refractive index, and the regulation of optical constants.

3.1 Determination of optical constants

Refractive index is one of the important properties and parameters of optical films (such as antireflective coatings, high reflectivity coatings, polarizing films, long/short wave filters, etc.). The main method for determining the optical constant of an optical film of MOFs is an ellipsometry method. Férey et al. [26] reported the optical film of MIL-89 prepared by the dip-coating method and determined its refractive index at 700 nm. Since MIL-89 is a flexible MOF, its refractive index is larger after absorption of water vapor. The change was reduced to 1.45. They used an ellipsometer to monitor the change in refractive index with the water vapor pressure. They also measured the refractive indices of MIL-101(Cr) [27], MIL-100(Cr) [28], and the MIL-100(Fe) [28] optical films at 700 nm, which are 1.18, 1.17, and 1.43, respectively. The optical film prepared by the spin-coating method inevitably has interparticle pores, so the determined values of the refractive index are the effective refractive indices of the MOF optical films, not the intrinsic refractive indices of the MOF materials themselves. Ranft et al. [40] also measured the refractive index of the HKUST-1 optical films prepared by spin coating using ellipsometry, and found it was only 1.20, while Redel et al. [41] studied the refractive index of HKUST-1 optical film prepared by LPE method, and found it was 1.39 at 750 nm, which was much larger than that of the spin-coated HKUST-1 film, and close to the intrinsic refractive indices of HKUST-1, benefiting from the compactness of the optical film prepared by LPE method.

The calculation of the interference fringes on the upper and lower surfaces of the optical film is another method to determine refractive index of an optical film. Lu et al. [14] determined the refractive index of the ZIF-8 film prepared by the direct growth method using this method. The value is 1.39, which is quite different from the value of 1.20 obtained by Ranft et al. [40], mainly because the ZIF-8 film prepared by Ranft et al. is composed of ZIF-8 nanoparticles, while for the dense ZIF-8 film reported by Lu et al. prepared by direct in situ growth, the value (1.39) of refractive index is closer to the that of the ZIF-8 bulk material [14].

Redel et al. [41] prepared two copper-carboxylic acid MOF Cu-BDC films on Si substrate by LPE method. The refractive index of the film was directly measured by spectroscopic ellipsometry, and the refractive index of a series of MOF films with the same Cu-BDC topology but different lengths of organic ligands was predicted. This study also showed the advantages of MOFs in optical applications: compared to the optical properties of traditional inorganic materials, MOF can be used as an optical film active material to adjust the optical properties by changing the composition or structure of the MOF.

For the UiO-66 films prepared by different methods, in general, their refractive index has this order: OTF-SP < OTF-DP < OTF-SA < OTF-LPE. The refractive index of OTF-LPE has the highest value, which can be considered as the intrinsic refractive index of UiO-66 due to the compactness and integrity of the film. The nanocrystal-based films can achieve a refractive index lower than 1.23, which is important for application as antireflection films. Such a low refractive index benefits from the cracks and voids between the UiO-66 nanocrystals. Assuming the intrinsic refractive index of UiO-66 was 1.512, the index of air is 1, the void percent in the film was estimated according to the effective medium theory [7, 23, 42]. The voids of OTF-SP, OTF-DP, and OTF-SA films are about 25, 30, and 23%, respectively.

3.2 Tuning of optical constants

The optical constants of MOF optical films can be regulated in various ways, such as changing the metal ion species, ligand type, crystal type, adsorbing guest molecules, and changing metal ions or ligands by post-modification. But many strategies have not been realized. The way of adsorbing guest molecules is more used in sensing. Here, the manners of changing linkers and post-modification of ligands are introduced to tune the optical constants of optical films.

3.2.1 Tuning through changing of the linkers

Our group [23] reported the regulation of the optical properties of MOF optical films by changing linkers with different functional groups. Five different ligands were selected and synthesized with chromium ions to obtain five MOFs of the same MIL-101 configuration, which were respectively recorded as MIL-101(Cr), NH_2-MIL-101(Cr), NO_2-MIL-101(Cr), OH-MIL-101(Cr), and $(NO_2)_2$-MIL-101(Cr), and the corresponding optical film was produced by spin coating. The refractive index and extinction coefficient of the MOF optical film changed with the change of linkers. The average refractive indices of MIL-101(Cr), NH_2-MIL-101(Cr), OH-MIL-101(Cr), and $(NO_2)_2$-MIL-101(Cr) optical films were 1.306, 1.268, 1.223, and 1.250, respectively. NO_2-MIL-101(Cr) has the lowest refractive index of only 1.208, which is lower than 1.22, making it have great potential in the preparation and application of antireflection coatings [43, 44].

The effect of ligand on the refractive index of MOF materials was further studied by eliminating the effect of porosity of the optical films. The order of the intrinsic refractive indices of MOFs is: $(NO_2)_2$-MIL-101(Cr) > NO_2-MIL-101(Cr) > NH_2-MIL-101(Cr) > OH-MIL-101(Cr) > MIL-101(Cr). The intrinsic refractive index of the MOF material in the same topology increases with the increase of the atomic density of the ligands.

The change of the extinction coefficient k is related to the electron-absorbing and electron-donating states of the ligands. It was found that the substitution of the electron-donating group was good at increasing the value of k, and the electron-withdrawing group would decrease k value.

3.2.2 Tuning through post-modification

Post-modification of ligands is also an effective means to change the optical constants of MOF optical films benefiting from abundant organic chemical reactions. Our group [24] reported the first example of successful regulation of optical films by post-modification of NH_2-MIL-53(Al) (see **Figure 3**). Propionaldehyde, valeraldehyde, and heptaldehyde with different carbon chain lengths were chosen as the modifier. After modification with propionaldehyde and valeraldehyde, the n_{eff} of the MOF optical films became larger as the carbon chain length increased, and the refractive index increased from 1.292 to 1.371 (propionaldehyde modification) and 1.424 (valeraldehyde modification). After heptaldehyde modification, the refractive index changed only slightly, from 1.292 to 1.299 (**Figure 3F**). This is because propionaldehyde and valeraldehyde have small molecular size and can effectively modify MOF, while heptaldehyde has a larger molecular size (10.7 Å) and finds it difficult to enter into the pores of MOF (8.5 Å), so the grafting rate is not high.

In addition, the extinction coefficient (k) is the imaginary part of the complex refractive index and is another important parameter of the optical film. After post-modification, the extinction coefficient of the MOF optical film also changed significantly. This is due to the change in the electronic structure inside the MOFs after post-modification [41]. The stop band width of MOFs after modification decreased from 2.74 to 2.71 eV (propionaldehyde modification) and 2.68 eV (valeraldehyde modification), which is consistent with the change in k. After grafting, the optical properties of the material itself are tuned both due to changing the internal electronic structure of NH_2-MIL-53 (Al) and occupying its internal pore structure.

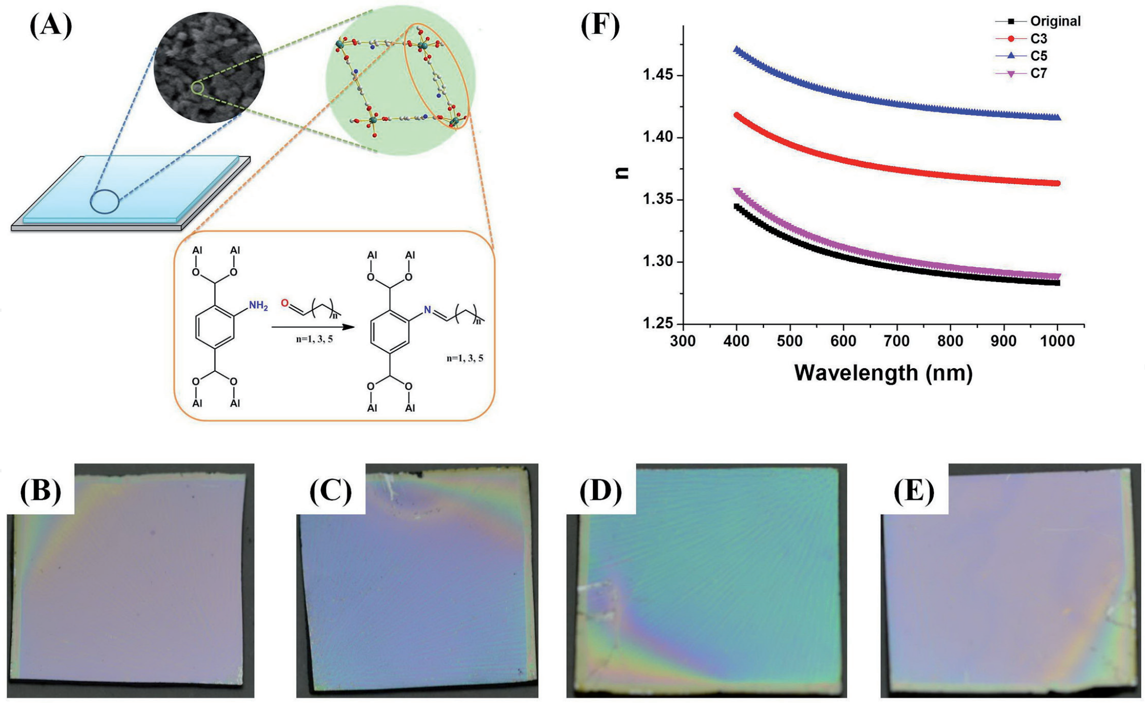

Figure 3.
(A) Scheme of tuning the optical properties through post-modification. Photographs of MOF optical thin film without modification (B), modified with propionaldehyde (C), pentanal (D), and heptanal (E). (F) The effective refractive index (n) of MOF optical thin films [24].

4. The application of MOF films in optical sensors

The application of MOF optical films in optical sensing is also essentially using the changes in optical properties, typically changes in the reflectance spectra (or colors) caused by the stimulation of target molecules.

4.1 Monolayer MOF thin films

Lu and Hupp [14] constructed a ZIF-8 monolayer film-based Fabry-Pérot device, which can serve as a selective sensor for chemical vapors and gases. The red shift of the reflection spectrum was observed within 1 min due to adsorption of propane. The sensor can distinguish n-hexane and cyclohexane due to their different sizes. It can also detect the ethanol from water/ethanol system with a limit as low as 0.3 vol%, corresponding to an ethanol vapor concentration of ca. 100 ppm.

Compared with the rigid pore structure of ZIF-8, the flexible pore structure of MOFs can change more significantly after adsorbing water or organic vapors. Our group [16] chose flexible NH_2-MIL-88B as a model MOF to fabricate a Fabry-Pérot device with a vivid color by spin-coating method. The NH_2-MIL-88B photonic film displayed high chemical selectivity, for example, acetone induced 380-nm redshifts, while water only led to a redshift of about 50 nm, and the color would change accordingly after absorbing the water or organic vapors (**Figure 4**), which can be observed by the naked eye. Depending on the nature of the organic solvent and their interaction with NH_2-MIL-88B, the selective breathing behavior of NH_2-MIL-88B promotes the excellent selectivity of the optical films.

4.2 MOF thin film-based one-dimensional photonic crystals

A one-dimensional photonic crystal (1DPC), also called Bragg stack, is a periodic nanostructure with a refractive index distribution along one direction [45].

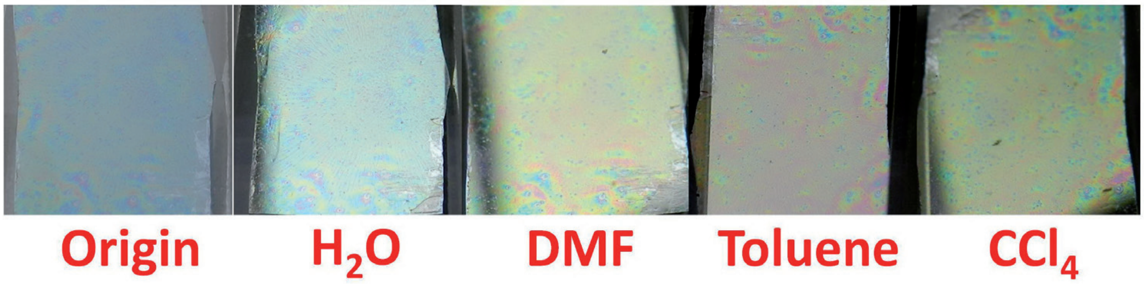

Figure 4.
Photographs of the NH_2-MIL-88B optical film upon exposure to various organic vapors. Reproduced from Ref. [16] with permission from The Royal Society of Chemistry.

Hinterholzinger et al. [20] presented the fabrication of 1DPC based on ZIF-8 and mesoporous titanium dioxide (TiO_2) for the first time. ZIF-8 is intended to impart molecular selectivity, and mesoporous TiO_2 is used to ensure high refractive index contrast and to guarantee molecular diffusion within the 1DPC. The 1DPC is sensitive and selective toward a series of chemically similar solvent vapors due to different sorption behavior of the photonic material to the solvent vapors.

In the consideration of replacing the rigid MOF with a flexible MOF, we [22] also prepared a 1DPC by alternately spin-coating NH_2-MIL-88B and TiO_2, wherein the TiO_2 layer functioned as a high-refractive index contrast. The optical properties (color, refractive index, etc.) of the 1DPCs can be adjusted by varying the number of depositions, and the thickness of the film. Benefiting from the flexible pore structure of NH_2-MIL-88B, the 1DPCs exhibited a highly selective response to different organic vapors, including dimethyl formamide, isopropanol, methanol, acetone, and ethanol

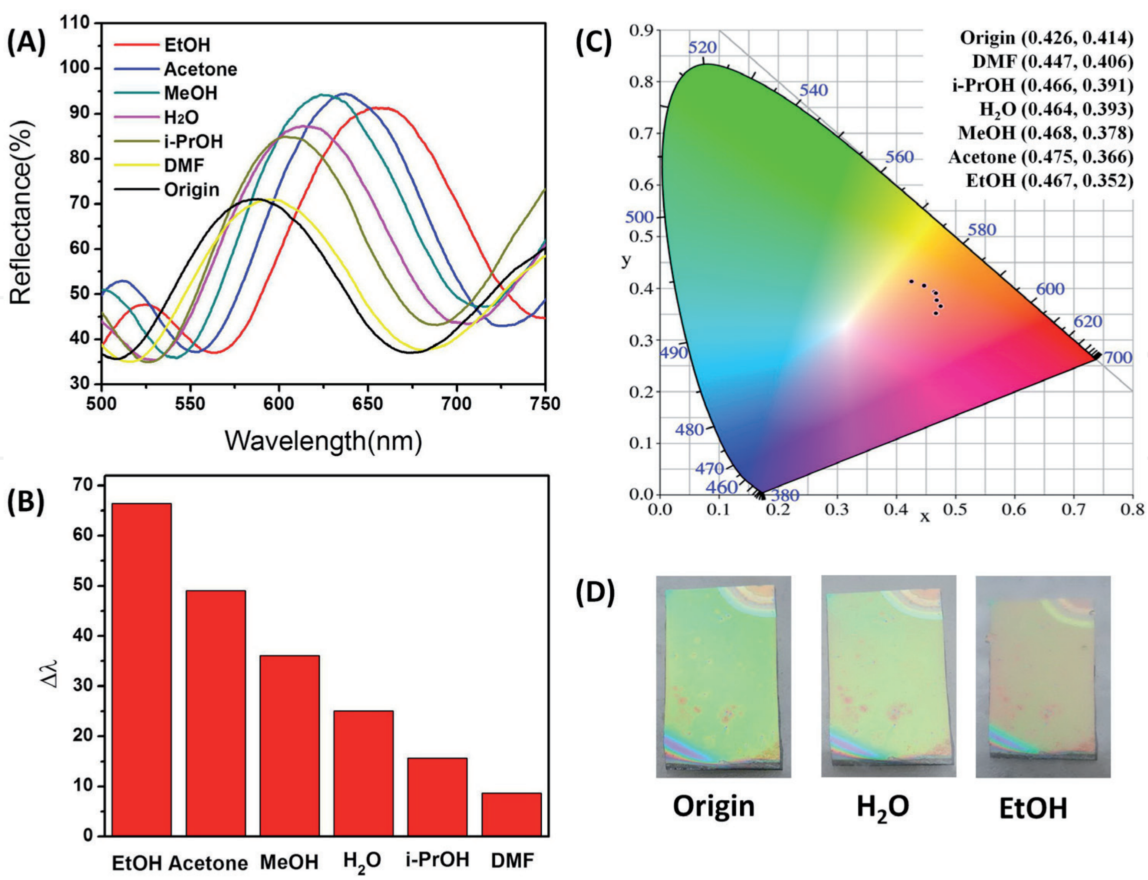

Figure 5.
(A) Reflection spectra, (B) shift of the photonic stop band, (C) chromaticity coordinates, and (D) typical images of the NH_2-MIL-88B/TiO_2 1DPCs upon exposure to various organic vapors. Reproduced from Ref. [22] with permission from The Royal Society of Chemistry.

(**Figure 5A–C**). Typically, the color of the 1DPCs in air and saturated vapors of water and EtOH were different, which can be observed by naked eye (**Figure 5D**). The 1DPC also can detect ethanol from 0 to 43.8 vol% in a water-ethanol mixture.

Liu et al. [46] described the fabrication of 1DPC by alternate deposition of HKUST-1 and indium tin oxide (ITO) layers by LPE method and sputtering method, among which HKUST-1 was used as low-refractive index layer, and ITO as high-refractive index layer. The 1DPC had a red shift response of only 38 nm for the adsorption of toluene because of the change in refractive index brought about by the adsorbing guest molecules.

4.3 MOF thin film on fiber surfaces

MOF thin films can be deposited not only on the flat surface but also on the nonplanar optical components, which further expands their use as optical sensors. Kim et al. [47] recently reported ZIF-8 films grown on linear fiber surfaces to create optical gas sensors, which are more sensitive to the target gases than Fabry-Pérot devices or 1DPCs based on normal incident light. The resultant sensors showed high sensitivity and selectivity to CO_2 gas relative to other small gases such as H_2, N_2, O_2, and CO. They also exhibited rapid (<tens of seconds) response time and excellent reversibility, which may be ascribed to the physisorption of gases into a nanoporous MOF. A refractive index-based sensing mechanism for the MOF-integrated optical fiber platform was proposed.

5. Conclusions

There are five major methods for preparing MOF optical films with high-quality spin coating, dip coating, self-assembly, direct growth, and LPE. Under the consideration of the same MOF (UiO-66) as the model, the MOF film prepared by spin coating has the best flatness, while the one prepared by direct growth is the worst one. The research on optical properties of MOF optical films is still in its early stage, mainly focusing on the determination and regulation of optical constants. The change of the linkers and post-modification of bridged ligands to control the optical properties of optical films have been realized. The application of MOF thin films in optical sensors can induce label-free optical sensors with variable colors exposed to various organic vapors. MOF films not only on the flat surface but also on the nonplanar surface (for instance fiber surface) can be served as optical sensors. They can have great selectivity due to different interactions between the target molecules with MOFs. In the future, the quality of optical films will be further improved, and a wide range of chemical modification methods will be applied to control the properties of optical films, which will further meet the needs of specific optical devices. MOF optical films are expected to become the next generation of optical materials.

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Conflict of interest

The authors declare no conflict of interest.

Author details

Cheng-an Tao*, Jianfang Wang and Rui Chen
College of Liberal Arts and Science, National University of Defense Technology, Changsha, China

*Address all correspondence to: taochengan@nudt.edu.cn

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