Photonic crystal gas sensors based on metal–organic frameworks and polymers

Jianan Wei, Zhihao Yi, Liu Yang, Ling Zhang, Junchao Yang, Molin Qin* and Shuya Cao*

A photonic crystal (PC) is an optical microstructure with an adjustable dielectric constant. The PC sensor was deemed a powerful tool for gas molecule detection due to its excellent sensitivity, stability, online use and tailorable optical performance. The detection signals are generated by monitoring the changes of the photonic band gap when the sensing behavior occurs. Recently, many efforts have been devoted to improving the PC sensor’s detection performance and reducing technical costs by selecting and refining functional materials. In this case, metal–organic frameworks (MOFs) with a large specific surface, tunable structural properties and polymers with unique swelling properties have attracted increasingly attention. In this review, a systematic review of PC gas sensors based on MOFs and polymers was carried out for the first time. Firstly, the optical properties and gas sensing mechanism of PCs were briefly summarized. Secondly, a detailed discussion of the structural properties and rapid preparation methods of distributed Bragg reflectors (DBRs), opals and inverse opals (IOPCs) was presented. Thirdly, the recent advances in MOF, polymer and MOF/polymer-based PC sensors over the past few years were summarized. It should be noted that the sensitivity and selectivity enhancement strategy by appropriate material species selection, organic ligand functionalization, metal-ion doping, diverse functional material arrays, and multi-component compounding were analyzed in detail. Finally, prospects on PC gas sensors are given in terms of preparation methods, material functionalization and future applications.

1 Introduction

Currently, there are numerous analytical techniques such as chromatography, mass spectrometry, electrochemistry, fluorescence, Raman, and many others used to detect chemical gas species like volatile organic compounds (VOCs) and organic phosphorus compounds. Gas sensors could be a possible alternative to complex analytical instruments that have high power consumption, cost and size.1 In recent years, there has been a significant improvement in sensor design along with advances in micro- and nano-fabrication technology and the use of newly designed materials, leading to the development of high-performance gas sensors.2 An ideal sensing technology would be portable, inexpensive, and able to selectively and sensitively detect hazardous species with few false positives.3

Optical sensors have developed rapidly and made great progress due to their strong anti-electromagnetic interference ability, rapid response time, room temperature operation and offline monitoring, where signals can be monitored farther from the sensing location, thus correspondingly making optical sensors promising devices for gas sensing applications. The most widely used optical gas sensing technique is absorption spectroscopy. However, it requires a long absorption length. Particularly, in the context of miniaturized absorption spectrometers for lab-on-chip applications, absorption detection may not be sensitive enough due to their short absorption length.

Over the past few decades, researchers have committed themselves to controlling the optical properties of materials. The concept of PCs was proposed in 1987 almost independently by S. John from Bell Labs and E. Yablonovitch from Princeton University. Historically, it was as long ago as 1887 that a one-dimensional (1D) PC was studied by Lord Rayleigh, who showed the existence of high reflectivity of light over a well-
defined wavelength range known as the stop-band.¹ There are many natural PC structures in nature. Most objects’ color results from the selective reflectance and absorption of incident light.³ There are three main ways for animals to produce color, namely pigment, bioluminescence or structural color.⁴⁵ To date, it has been shown that parts of the structure of a variety of animals or plants, such as Hibiscus trionum and Tulipa species,⁶ the wings of a butterfly or moth,⁷–⁹ the outer stripes of fish,¹⁰ or the outer skin texture of a chameleon,¹¹ exhibit the properties of PCs. These structures serve as a model for the advancement of artificial PCs.¹²–¹⁴ Some literature studies reviewing the characteristics, functionalization, and applications of PCs have been published over the past few years. For instance, Li et al.¹⁵ systematically summarized the progress of the basic structure, classification, main features and preparation methods of PCs and categorized and prospected PC-based sensors with different principles. Wang¹⁶ carried out a comprehensive summary of one-, two- and three-dimensional MOF-based photonic crystal gas sensors based on structural differences. There are limited reviews summarizing the application of MOF, polymer or MOF/polymer composite-based PC sensors, especially for the selection or functional modulation of functional materials to improve sensitivity and selectivity. Differing from traditional materials demonstrating limited variation of the effective refractive index or lattice spacing due to the intractability of their structure or pore sizes, MOFs with a large specific surface area and tunable structure properties and polymers with unique swelling properties could lead to short-term changes in the effective refractive index or lattice spacing when in contact with gases.

In this paper, the recent advances in MOF, polymer and MOF/polymer-based PC sensors over the past ten years were summarized. The sensitivity and selectivity enhancement strategy by appropriate material species selection, organic ligand functionalization, metal-ion doping, diverse functional material array, and multi-component compounding were analyzed in detail. We believe that the topics that we have discussed will provide technical support for fabricating MOF and polymer-based photonic crystals with excellent detection performance.

2 Optical properties

As an optical simulation of electron band theory, photon band theory can be used to calculate the dispersion characteristics of light in any PC structure and predict the existence of a photonic bandgap (PBG). The formation of a band gap is explained based on Bragg diffraction and the subsequent constructive interference of reflected light from a periodic structure.¹² The physical origin of the band gap can be understood via observing the electric field distribution at the upper and lower edges of the band gap. For a band structure as shown in Fig. 1(I), there are two ways to place an electric field with this wavelength in the medium. The nodes of the electric field can be placed at the center point of each layer of low electrolytic constant material, or at the center point of each layer of high electrolytic constant material, and any other position will be symmetrical. This leads to the opening of a gap in the dispersion relationship, forming the photonic band gap.

The diffraction properties of PCs can be described using eqn (1) (Bragg’s law and Snell’s law).²²

\[ m\lambda = 2d(n_{\text{eff}}^2 - \sin^2 \theta)^{1/2} \]  

where \( d \) represents the distance between particle planes, \( n_{\text{eff}} \) is the mean effective refractive index (RI), \( \theta \) and \( \lambda \) are the angle and wavelength of the reflected light, respectively, and \( m \) is the order of reflection. It can be seen that when the dielectric constant changes periodically, the change of the effective refractive index and lattice spacing will cause the shift of the maximum reflection peak, and the magnitude of the offset can

---

Liu Yang received his PhD degree from the State Key Laboratory of NBC Protection for Civilian in China in 2007. He is now an Associate Professor at the State Key Laboratory of NBC Protection for Civilian, China. His current research interests include the areas of toxic chemical sensors and rapid on-the-spot detection of harmful materials.

Ling Zhang obtained her MS degree in analytical chemistry from Sichuan University in 2019 and received her PhD degree in materials physics and chemistry from Sichuan University in 2019. Currently, she is a postdoctoral researcher at the Academy of Military Sciences. Her current research interests include stretchable/flexible sensors, photonic crystal gas sensors, wearable electronics, and laser-assisted nano/micro-fabrication.

Junchao Yang graduated from Tianjin University in 2012 with a bachelor’s degree in electronic science and technology. In 2015, he graduated from the State Key Laboratory of Nuclear, Biochemical and Chemical Engineering with a master’s degree in environmental engineering. Since 2020, he has been studying for a PhD, mainly engaged in semiconductor sensor technology research.

Molin Qin received his PhD degree from the Research Institute of Chemical Defense in 2015. He is now a research associate at the Research Institute of Chemical Defense. His current research interests include the areas of sensitive materials and sensing technology of chemical agents.

Shuya Cao received his MS degree from the State Key Laboratory of NBC Protection for Civilian in China in 1996. He is now a Professor at the State Key Laboratory of NBC Protection for Civilian, China. His current research interests include the areas of toxic chemical sensors and rapid on-the-spot detection of harmful materials.
be further used as a signal for gas sensing. For opal PC or inverse opal photonic crystal (IOPC) structures with 3D ordered pores, Mie scattering determined by the radius of the medium is equally effective in changing the position of the PBGs.

When a light beam passes through the gas chamber, the corresponding light intensity at the detector can be expressed by eqn (2):

$$I = I_0 e^{-\frac{aL}{d_0}}$$

(2)
where $a$ is the absorption coefficient of the material, $f$ is the filling factor, $c$ is the velocity of light, $L$ is the light–matter interaction length, $n$ is the RI of the slab material, and $v_g$ is the group velocity. The simple and common method we use to set up relatively long interaction paths (Fig. 1(II)), which is in the range of 10 to 50 cm, or large interaction volumes due to the weak interaction between gaseous analytes and light. However, for the PC sensor, as shown in Fig. 1(III), both the DBRs formed by alternating different dielectric layers and the opal and inverse opal structures have reduced interaction lengths compared to the conventional gas sensors. The multiple scattering of the light inside the PC increases the effective optical range of the incident light, compensates for the absorption losses, and improves the efficiency of light utilization, which in turn improves the sensitivity.

3 Fabrication and sensing parameters

3.1 DBRs

1D PCs – distributed Bragg reflectors, Bragg reflector/mirrors or dielectric mirrors – were first demonstrated in crystalline solids with atomic spacing comparable to the incident X-ray wavelength, resulting in the specular reflection of certain wavelengths at specific angles. Fig. 2(I) shows a DBR consisting of alternating layers of two transparent media with a thickness of $h_1$ and $h_2$ and an actual refractive index of $n_1$ and $n_2$ ($n_1 > n_2$), respectively. It is worth noting that once the number of alternating periodic layers exceeds the threshold, the reflection intensity becomes saturated. Light is partially refracted at each interface, reflected, and transmitted. The lattice spacing and layer refractive index define whether interference between reflected (transmitted) beams is constructive (disruptive) at a particular wavelength, which in turn defines the spectral region of the PBG. DBR sensors rely on two main diffusion mechanisms: porous structures and polymers. A typical

![Diagram of DBR fabrication and sensing](image)
mesoporous structure, named after Knudsen diffusion, specifies that molecules diffuse through membranes whose pore size is comparable to or larger than the osmotic molecule.

In addition to the DBRs mentioned above, the etching of 1D porous silicon has also attracted the attention of researchers. In 2005, Pacholski et al. demonstrated a simple method for electrochemical etching of multilayer porous silicon and used it in bioassays, which required only control of current density and etching time to enable etched porous silicon structures to differentiate targets in the vertical direction based on their molecular size. If one etched layer was properly designed, it can act as a reference for the other etched layer while achieving correction for composition drift and matrix effects. As shown in Fig. 2(II), other researchers constructed PCs by staining porous silicon with a chemically specific colorimetric indicator or permeating polystyrene with a reference channel for the detection of ammonia and the nerve agent diisopropyl fluoroephosphate (DFP). Spin coating, dip coating or layer-by-layer deposition (Fig. 2(III)) is a process driven by centrifugal or capillary forces during solvent evaporation, which is very suitable for 1D DBR structures. Spin-coating is based on the periodic multi-layer stacking of two different types of materials, with centripetal force that allows the dispersed material to spread evenly on the substrate. The use of thicker dispersions or polymer additives in the spin coating process can increase the viscosity of the material, resulting in a more homogeneous film. Sol-gel materials, on the other hand, are usually assembled by dipping. Solution aging, solvent evaporation, matrix extraction velocity, and temperature equilibrium are effective conditions for achieving ordered, uniformly thick mesoporous membranes. The reason why this method is incredible is that specialized aging, thermal stabilization, and template removal steps are performed after each layer is deposited, which makes the impregnation assembly process of mesoscopic structural materials quite laborious and time-consuming. The layer-by-layer deposition method, despite offering very low interfacial roughness, high compositional control and good stability, is time consuming for hundreds of adsorbed layers. This method usually requires drying and annealing steps between each subsequent layer, but it does not require complex fabrication steps such as colloidal crystal growth or template removal. It is worth noting that one of the critical drawbacks of this structure is that the photon band gap and structure color change with the viewing angle, which affects the indication of color change and the accuracy of the image display. Inspired by the hexagonal pit array on the elytral surface of a male beetle Chlorophila obscuripennis, Kou et al. used a transfer printing technique to fabricate the first array of bionic micro-sized bowls (Fig. 3), enabling responsive PCs for environmental visual sensing. P(AM-MBA)/TiO2 and P(MMA-EGDMA-AA)/TiO2 films were transferred to bowls on a polydimethylsiloxane surface, and this nanomaterial-based photonic film displayed angle-independent colors even after twisting, stretching, washing and rubbing.

**Fig. 4** (I) The diagram of PMMA-CA fabrication. (II) (a and b) Color of the droplet surface changes rapidly after entering the low-pressure environment. (c and d) Change of color is more and more obvious, and the droplet edge reaches green faster than the middle. (e) Whole gas–liquid interface turns green. (f and g) As the droplet gradually evaporates, the edges begin to dewet and the color changes from green to blue. (h and i) Uniform particle layer on the liquid surface is gradually pulled and divided at last, resulting in fragmentation. (j) Particle layer on the liquid surface eventually spreads out onto the substrate in a fragmented state and even forms a hole.
3.2 Opal and inverse opal PCs

In addition to the natural opal structure, three-dimensional structures made of polystyrene (PS), polymethylmethacrylate (PMMA) and silicon dioxide (SiO2) nanorods arranged in an orderly fashion on a silicon or glass substrate are called opal PCs and are usually in the hcp arrangement.\textsuperscript{42,43} The opal PCs are used as templates, which are infiltrated into the pores or deposited with functional materials and then removed, resulting in IOPCs. An IOPC, as an opal replica composed of a suitable high RI material, featuring a fcc lattice of air spheres, should possess a full PBG between the eighth and ninth bands of its photonic band structure.\textsuperscript{44} The criteria of high RI contrast and minimal absorption in the desired wavelength range pose a substantial challenge to material selection.

Opal structures are usually constructed through “controlled evaporation” or “vertical deposition” methods, and the whole process takes a long time, about one to three days.\textsuperscript{45,46} During the evaporation-induced process, shrinkage of the colloid itself or capillary-driven aggregation leads to an increase in tensile stresses parallel to the substrate plane, and when the in-plane stresses reach a critical value, cracks are formed to release strain energy. However, cracks are considered harmful and should be avoided in most studies for devices. Katherine R. et al. successfully utilized the basic principles of crack formation in composite opals to produce patterned colloidal wafers with uniform size and geometry, including opals, composite opals and anti-opals, and the patterned substrates were reusable.\textsuperscript{47}

In order to overcome the problem of the long preparation cycle of three-dimensional PC colloidal arrays, Fan et al.\textsuperscript{48} proposed a method for rapid self-assembly to prepare three-dimensional PC colloidal arrays (Fig. 4(I)). Nitrogen blowing induces and enhances the convection of the particles, and heating accelerates the evaporation of the suspension and promotes the self-assembly process. The formation of colloidal arrays at the gas–liquid interface by capillary force reduces the preparation time to less than a few minutes compared to the...
long cycle times of traditional methods. The low-pressure-assisted evaporation (LPAE) method reduces the days needed for evaporation to minutes or even seconds. Zhang et al. achieved ultrafast preparation of homogeneous colloidal crystals by suppressing the coffee ring effect in droplet flash evaporation. The low-pressure environment can greatly increase the evaporation rate, which accelerates the capture of colloidal particles by the gas–liquid interface and their instantaneous self-assembly into ordered structures (Fig. 4(II)). Apart from the above-mentioned strategies, highly charged monodisperse carboxyl-functionalized hybrid colloidal nanoparticles can be covalently assembled in seconds (≈20 s) by repulsion-induced precipitation assembly (RIPA) under strong repulsive forces. The double roller film-forming (DRF) process also produces high-quality polymer PC films from a homogeneous slurry of core/shell particles in a matter of seconds.

The template sacrifice method is the most commonly used method to prepare IO structures, which usually removes the opal template by high temperature calcination or solvent etching after the deposition of the functional material and ultimately obtains structures with high porosity and periodic interconnecting pores (Fig. 5(I)). The construction of the opal template is the core of the technique. Functional materials deposited in IOPC arrays (DRF) process typically include metal oxides (ZnO, TiO₂, and SiO₂), metal–organic frameworks (MOFs), and a diverse range of polymers, a process that can be accomplished through a combination of procedures such as sol–gel, spray pyrolysis, atomic layer deposition (ALD), chemical vapor deposition (CVD), and electrospray deposition. As shown in Fig. 5(II), in addition to the conventional drop-injection of functional materials onto the prepared opal templates, the co-assembly of functional materials with the opal precursor liquid is also an effective method to prepare IOPC templates. In ALD and CVD processes, thin layers of functional materials from the vapor-phase precursor are deposited on a template. Wang et al. combined microfluidics and template technology to prepare hydrogel PC microparticles (HPCMs) with an anti-opal structure (Fig. 5(III)). The inner aqueous phase containing monodisperse silica NPs flowed through a co-fluidic microfluidic device to form monodisperse mono-emulsion droplets induced by the strong shear action and interfacial tension of the outer silica oil phase. The formed emulsion droplets were then collected in hydrophobic polytetrafluoroethylene (PTFE) containers to keep the emulsion droplets perfectly spherical. After complete evaporation of water, monodisperse silica colloidal crystal particles were obtained.

### 3.3 Sensing parameters

For the performance evaluation of the sensor, the following factors, namely sensitivity (S), limit of detection (LOD), standard deviation (σ), quality factor (Q) and good value (FOM), can be calculated using eqn (3)–(7), respectively:

\[
S = \frac{\Delta \lambda}{\Delta C} = \frac{\lambda_{\text{det}} - \lambda_{\text{origin}}}{C_{\text{det}} - C_{\text{origin}}} 
\]

\[
\sigma = \sqrt{\frac{\sum_{i=1}^{n} (\lambda_i - \bar{\lambda})^2}{n - 2}} 
\]

\[
Q = \frac{\lambda_{\text{peak}}}{\text{FWHM}} 
\]

\[
\text{FOM} = \frac{S}{\text{FWHM}} 
\]

where S is the sensitivity, σ is the standard deviation, \( \lambda_{\text{origin}} \) and \( \lambda_{\text{det}} \) are the original wavelength and detection wavelength, \( C_{\text{origin}} \) and \( C_{\text{det}} \) are the original concentration and detected concentration, respectively, FWHM is the half-peak width, and \( \lambda_{\text{peak}} \) is the wavelength corresponding to the maximum spectral radiation power.

### 4 Materials and applications of PCs

Porous nanoparticles (NPs) such as SiO₂, TiO₂, ITO, SnO₂ (ref. 60) and ZnO (ref. 61) have been successfully used in PC gas sensing. These metal oxides with small particle sizes and high refractive indices, are often used as high refractive index layers in DBR, opal or IOPC structures. Given that the NP based PCs rely on the change of the effective refractive index to generate a robust sensing signal, an unavoidable shortcoming of the above structure is the limited relative light shift of the resistive bands. Therefore, some studies have been dedicated to improving sensitivity and selectivity by constructing defective layers or compositing with other materials. For 1D PCs, defect preparation usually changes the symmetry of the whole structure by increasing the thickness of functional layers or by adding other responsive materials such as nanosheets or dyes in the layer-to-layer intervals. The selective detection of vapors of different molecular sizes in opals and IOPCs, usually by controlling the size of the aperture or by connecting different apertures in series, nanoparticles can be compounded with other materials such as noble metal monomers or metal oxides to enhance the resolution of the sensor.

To alleviate the detection limitations of DBR, opal or inverse opal-PCs composed of metal oxides for gas sensing, MOFs with strong adsorption and polymer molecules with strong solubility have been used in this field in recent years.

#### 4.1 Metal–organic framework-based PCs

Metal–Organic Frameworks (MOFs) are a type of crystalline inorganic–organic hybrid porous material consisting of metal clusters and organic ligands. Owing to their specific surface area, ordered pore structure, easy functionalization and tailor-able adsorption properties, MOFs are deemed ideal candidates for fabricating PC sensors. Hupp’s group prepared a DBR PC structure for the first time using a zeolite imidazolate framework (ZIF-8) as the gas sensing material in 2010. Subsequently, various MOFs including ZIF, UIO, HKUST, CAU and MIL have been employed in the construction of PC gas sensors. The types
### Table 1  Applications of MOFs in PC gas sensing

<table>
<thead>
<tr>
<th>MOF</th>
<th>Metal ions</th>
<th>Organic ligands</th>
<th>Composition of periodicity</th>
<th>Structure type</th>
<th>Target gas</th>
<th>LOD (ppm)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZIF-8</td>
<td>Zn$^{2+}$</td>
<td>2-Methylimidazole</td>
<td>Pt</td>
<td>SAM</td>
<td>Ethanol/H$_2$</td>
<td>—</td>
<td>63</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>TiO$_2$</td>
<td>DBR</td>
<td>Ethanol</td>
<td>—</td>
<td>64</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>—</td>
<td>OPC</td>
<td>n-BuOH</td>
<td>—</td>
<td>65</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>—</td>
<td>Acetone</td>
<td>—</td>
<td>—</td>
<td>66</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>NR</td>
<td>Acetone</td>
<td>60</td>
<td>—</td>
<td>67</td>
</tr>
<tr>
<td>QDs</td>
<td></td>
<td></td>
<td>PS</td>
<td>2D film</td>
<td>Acetone/acetoneitrile</td>
<td>—</td>
<td>69</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>—</td>
<td>HMSNSE</td>
<td>VOCs</td>
<td>—</td>
<td>70</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>—</td>
<td>—</td>
<td>Alcohols/water</td>
<td>—</td>
<td>71</td>
</tr>
<tr>
<td>ZIF-8@ZnO</td>
<td></td>
<td></td>
<td>TiO$_2$</td>
<td>DBR</td>
<td>Carbon tetrachloride</td>
<td>320</td>
<td>72</td>
</tr>
<tr>
<td>MIL-88A</td>
<td>Fe$^{3+}$</td>
<td>Fumaric acid</td>
<td>CB/PVDF</td>
<td>IOPC</td>
<td>Methanal</td>
<td>0.89</td>
<td>77</td>
</tr>
<tr>
<td>NH$_2$-MIL-88B</td>
<td>2-Aminoterephthalic acid</td>
<td>TiO$_2$</td>
<td>1D film</td>
<td>Ethanol</td>
<td>—</td>
<td>75</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>P(St-AA)</td>
<td>DBR</td>
<td>BTEX</td>
<td>0.22–3.70 g m$^{-3}$</td>
<td>76</td>
</tr>
<tr>
<td>MIL-101</td>
<td>Cr$^{3+}$</td>
<td>Terephthalic acid</td>
<td>TiO$_2$</td>
<td>DBR</td>
<td>Carbon tetrachloride</td>
<td>33</td>
<td>79</td>
</tr>
<tr>
<td>MIL-101-NH$_2$</td>
<td>2-Aminoterephthalic acid</td>
<td>TiO$_2$</td>
<td>1D film</td>
<td>Ethanol</td>
<td>33</td>
<td>79</td>
<td></td>
</tr>
<tr>
<td>UIO-66</td>
<td>Zr$^{4+}$</td>
<td>Terephthalic acid</td>
<td>GO/TiO$_2$</td>
<td>DBR</td>
<td>Chlorobenzene</td>
<td>13</td>
<td>80</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>—</td>
<td>OPC</td>
<td>Ethanol</td>
<td>—</td>
<td>81</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>—</td>
<td>IOPC</td>
<td>Chlorobenzene</td>
<td>1.64</td>
<td>82</td>
</tr>
<tr>
<td>UIO-66-NH$_2$</td>
<td>2-Aminoterephthalic acid</td>
<td>TiO$_2$</td>
<td>DBR</td>
<td>HCl</td>
<td>0.22</td>
<td>83</td>
<td></td>
</tr>
<tr>
<td>MOF-801</td>
<td>Fumaric acid</td>
<td>TiO$_2$</td>
<td>DBR</td>
<td>Humidity</td>
<td>15–95% RH</td>
<td>84</td>
<td></td>
</tr>
<tr>
<td>HKUST-1</td>
<td>Cu$^{2+}$</td>
<td>Trimesic acid</td>
<td>SiO$_2$</td>
<td>OPC</td>
<td>CS$_2$</td>
<td>0.5</td>
<td>85</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>—</td>
<td></td>
<td>Methanol</td>
<td>—</td>
<td>87</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>PS</td>
<td>IOPC</td>
<td>Ethanol</td>
<td>—</td>
<td>88</td>
</tr>
</tbody>
</table>


---

**Fig. 6**  (I) Scheme illustrating the basic steps of color image analysis and determination of analyte-specific numerical codes. (a) Photographic images of an array assembled from TiO$_2$/ZIF-8, TiO$_2$/HKUST-1, and TiO$_2$-CAU-1-NH$_2$ BSs. (b) On the basis of average RGB intensities obtained for three measurements. (c) Image processing and calculation of AR (G, B) are performed for all investigated analytes, yielding a 9 × 9 matrix. (II) (a) Schematic representation of a multilayered photonic crystal comprising CAU-1 and TiO$_2$ nanoparticle layers; (b) crystal structure of CAU-1 with carbon atoms given in black, oxygen in red, aluminium-oxygen octahedra in turquoise and pores indicated by yellow and green spheres; (c) the two post-synthetic modification strategies of the framework applied in this work using (top) de-methoxylation of the SBU (CAU-1-SBU) and (bottom) amidification with hexanoic anhydride of the organic linker (CAU-1-Hex).
of MOFs and sensor structures employed in PC gas sensing research over the past 15 years are systematically summarized and listed in Table 1.

When target molecules are adsorbed, the refractive index of MOFs changes, and the maximum reflected wavelength changes accordingly. According to Brugmann’s effective medium approximation (EMA) theory, the refractive index change of the MOF layer is determined by its adsorption capacity and the refractive index of adsorbed vapor.99,100 Liu et al. coated HKUST-1 on a silicon substrate using an epitaxial growth method, followed by sputtering to deposit an indium tin oxide (ITO) layer with a thickness of 62–100 nm. By repeating the above process several times, a 1D PC gas sensor was fabricated and was able to detect ethanol or other gases.94 The ITO layer stood for the high refractive index component (n ≈ 2.0), while the HKUST-1 layer represented the low refractive index component (n ≈ 1.52). As a result, the BS multilayer films demonstrated high optical quality (the PBG reflectivity is about 1%).

The regulation of the sensing properties of MOF-based PC sensors requires the exchange of the MOF system because the adsorption properties are highly dependent on MOF types. This may be limited by synthetic constraints such as the availability of nanoparticulate MOFs. To confer differences in chemical selectivity in the MOF layer while keeping the entire PC backbone constant, Von Mankowski et al.95 developed a simple and gentle “post-assembly” modification strategy (Fig. 6). The 1D PC structure was spun-coated alternately with CAU-1 and TiO2, and the optical response to solvent gas exposure was studied using the original CAU-1-based sensor and its modifications, and the results showed enhanced analyte selectivity in the post-modified system.

For MOF-based PC sensors, the more direct factor affecting the performance of the sensors is the adsorption performance of the MOF towards the target gas. The size exclusion effect, pre-enrichment effect, affinity/hydrophobicity, and intermolecular forces including van der Waals forces, hydrogen bonds, and π-π bonds are all important factors affecting the adsorption effect.95,96 It’s meaningful to improve the physical and chemical properties of MOFs using various modification strategies.

4.1.1 Flexible MOF-based PCs. The MOFs’ flexibility is defined by their supramolecular host–guest interactions (type of ligand with functional groups for specific gases). When gas molecules were adsorbed, these flexible MOFs can change their lattice spacing “d” accordingly without apparent bond breaking. Compared with rigid MOFs, which only change the refractive index after adsorption, flexible MOFs demonstrated more sensitive signal response as a result of change in the refractive index contrast and unique “respiration effect”. In 2014, Hu et al.75 proposed the first 1DPC gas sensing structure based on amino group (-NH2) modified MIL-88B, and the simultaneous changes of the refractive index and lattice spacing made the spectrum show a more obvious redshift. Choosing an appropriate stable MOF as the function layer was beneficial to improve the sensor performance. Xing et al.76 fabricated an NH2-MIL-101-based 1D PC sensor for methanal detection, which exhibited high repeatability, long-term storage and thermal stability. The N–H groups favor the non-covalent bonding mechanism with the methanal molecule. Some MOF structures that are broadly defined as rigid may also have some flexible properties. For example, in addition to adsorbing molecules with sizes smaller than its pores, when ZIF-8 interacts with the benzene series whose sizes are larger than its inner pores, the imidazole portion of the ligand can be slightly rotated, and the pore size can be enlarged to allow access to the molecules, which shows an “open-door” effect,97 resulting in a satisfactory adsorption effect. Based on this, a 1D PC gas sensor with a ZIF-8/TiO2 structure98 prepared by a spin-coating method and a 3D PC gas sensor with a 3D opal structure99 prepared by a template-free method were used for the detection of the benzene series and DMMP, respectively.

4.1.2 Bimetalllic MOF-based PCs. The metal center coordination ability and electrostatic interaction between the target gas and the MOFs will also have an impact on the adsorption effect. Different types and proportions of metal doping can affect the overall physical properties of MOFs,98 such as conductivity, energy location in the metallic state, charge separation, and synergistic effects.99 And the above properties will ultimately affect the adsorption and desorption of MOFs in the sensor.100

Xing et al. prepared a bimetalllic ZIF-8 (Zn@Co) 1DPC gas sensor for chlorobenzene vapor detection.101 The doping of Co2+ improves the chemical heterogeneity and microporosity of ZIF-8, thereby enhancing the adsorption of the material.102 More significantly, the extra metal ions (Co and Ni) could also reduce the initial resistance of the MOF and improve the adsorption ability. Cao et al.99 developed a Co/Ni/Fe trimetallic oxide (CoNiFe-MOS-n)-based PC sensor by co-doing Co2+ and Ni2+ and oxidative pyrolysis of NH2-Fe-MIL-101. The decreased resistance is attributed to the increase of hole charge carriers of metal oxides induced by the incorporation of Co2+ in the sites of Fe3+ in p-type semiconductors. This CoNiFe-MOS-n-based PC sensor displays high sensitivity (560) and good selectivity to acetone vapors.

In addition to one-dimensional structures, the bimetalllic or polymetallic synergistic effect is also applied to three-dimensional structures. Wang et al. prepared a bimetalllic MIL-127 (Fe2M, M = Fe, Ni, Co, Zn) 3D PC gas sensor by simple evaporation-induced self-assembly for the detection of chlorinated hydrocarbons.100 The bimetalllic MIL-127 with redox-active open metal sites and mixed metal nodes generated peculiar surface properties and synergetic effects due to the doped Co element, which enhances the adsorption performance. From the adsorption site, the ionic properties of Co–O bonds are higher than those of Fe–O bonds, so this site will easily adsorb CCL4.

4.1.3 Diverse MOF array-based PCs. Tuning the MOFs’ framework through introducing functional groups or metal ion doping could precisely control the host–guest interactions between MOFs and target molecules. However, an unavoidable drawback of PC sensors constructed with a single MOF is their insufficient selectivity to distinguish among analytes with similar chemical properties. In this case, a photonic nose inspired by the olfactory system was developed by integrating diverse MOFs into one sensing device. The adsorption properties of photonic noses could be tailored by choosing MOFs with appropriate
Fig. 7 (a) Simulated color fingerprints of the photonic nose in saturated MeOH, EtOH, IPA, DCM, TCM, CTC, BEN, MCB and SM vapors. (b) PCA score plots based on lab values for the discrimination of saturated MeOH, EtOH, IPA, DCM, TCM, CTC, BEN, MCB and SM vapors. Sensing of paint vapors with different benzene contents: (c) schematic diagram of the detection process and (d) visual color fingerprints.

Table 2 Applications of polymers in PC gas sensing

<table>
<thead>
<tr>
<th>Analysis</th>
<th>Sensing material composition</th>
<th>Structure</th>
<th>LOD (ppm)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂O</td>
<td>PC/PVDF</td>
<td>DBR</td>
<td>—</td>
<td>105</td>
</tr>
<tr>
<td>VOCs</td>
<td>PDMS/PSPI</td>
<td>—</td>
<td>106</td>
<td></td>
</tr>
<tr>
<td>CCl₄</td>
<td>PMMA/V₂O₅</td>
<td>—</td>
<td>107</td>
<td></td>
</tr>
<tr>
<td>CCl₄/BTEX</td>
<td>CA/PPO</td>
<td>108</td>
<td>109</td>
<td></td>
</tr>
<tr>
<td>CTC, DCM, EA</td>
<td>(PDA/PDMA)ₙ(TiO₂/PSS)ₙ</td>
<td>110</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Toluene</td>
<td>CA/polystyrene (ZnO)</td>
<td>10</td>
<td>111</td>
<td></td>
</tr>
<tr>
<td>CCl₄ and aromatic homologues</td>
<td>PPO/CA</td>
<td></td>
<td>112</td>
<td></td>
</tr>
<tr>
<td>Humidity</td>
<td>P(AM-MBA)/TiO₂</td>
<td></td>
<td>113</td>
<td></td>
</tr>
<tr>
<td>Organic solvent vapor</td>
<td>P(MMA-AA)/TiO₂</td>
<td></td>
<td>114</td>
<td></td>
</tr>
<tr>
<td>Galden HT55</td>
<td>HY/PVK</td>
<td></td>
<td>115</td>
<td></td>
</tr>
<tr>
<td>Water/toluene</td>
<td>SEBS/PVA (ZrO₂)</td>
<td></td>
<td>116</td>
<td></td>
</tr>
<tr>
<td>Toluene et al</td>
<td>P(St-AA)/TiO₂</td>
<td>14.7–99.2</td>
<td>117</td>
<td>33</td>
</tr>
<tr>
<td>DCP</td>
<td>P(VC-co-BPA)/P(4VP-co-BPA)</td>
<td>IOPC</td>
<td>0.001 vol%</td>
<td>118</td>
</tr>
<tr>
<td>Water-based insecticide</td>
<td>Poly(HEMA)/poly(ETPTA)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alcoholos</td>
<td>P(HEMA-co-MA) in SiO₂</td>
<td></td>
<td>15.7–16.0</td>
<td>119</td>
</tr>
<tr>
<td>THF</td>
<td>P(PVS-b-DMAEMA) in SiO₂</td>
<td></td>
<td>120</td>
<td></td>
</tr>
<tr>
<td>THF/acetone</td>
<td>TPEP in SiO₂</td>
<td></td>
<td>121</td>
<td></td>
</tr>
<tr>
<td>Xylenes</td>
<td>P(VBC-co-MMA) in SiO₂</td>
<td></td>
<td>0.17–0.51</td>
<td>122</td>
</tr>
<tr>
<td>p-Xylene/toluene</td>
<td>PS CCA in PDMS</td>
<td></td>
<td>123</td>
<td></td>
</tr>
<tr>
<td>NH₃/HCl</td>
<td>PANI in TiO₂</td>
<td></td>
<td>124</td>
<td></td>
</tr>
<tr>
<td>TNT</td>
<td>MEH-PP in Psi MC</td>
<td></td>
<td>125</td>
<td></td>
</tr>
</tbody>
</table>

characteristic sensing features, and hence, photonic noses displayed low cross-responsivity to other analytes.

The first report of a photonic nose constructed from an array of 8 MOFs was presented by Gao et al.104 In order to realize the differences between the sensing units, four rigid MOFs with different pore sizes and specific surface areas (HKUST-1, UIO-66, MOF-808, and MIL-101 (Cr)) and four flexible MOFs with variable structures, i.e., NH2-MIL-88B, NH2-MIL-53 (Fe), MIL-53 (Al) and NH2-MIL-53 (Al), were used to prepare 1D PCs (Fig. 7). 8 DBR structure-based PC sensing units take advantage of the inherent adsorption capacity of the MOFs and were available for microscopic adsorption of VOCs within 1 s, enabling PCs (PCs) to produce color fingerprints for the differentiation of alcohols, halogenated hydrocarbons, and benzene saturated vapors of nine similar chemical properties. In addition, the performance of color fingerprinting in practical applications was verified by detecting benzene content in poor-quality paints using photonic noses.

Ranft et al.104 integrated multiple MOFs [ZIF-8, HKUST-1, and CAU-1-NH2] into a single sensing platform (named the tandem MOF Bragg stacks), and utilized the combined response of multiple MOF films for analyte detection such as methanol. The photographic images of samples before and after exposure to vapor were recorded and the corresponding RGB values were extracted by image analysis; the extracted values could be used to analyze the individual ability of the BS to distinguish between different analyt vapor, and the three MOF BSs showed a significantly different degree of differentiation between the analysts studied.

4.2 Polymer-based PCs

Stimulus-responsive polymers are a class of macromolecular systems with “intelligent” behavior. They can receive stimulus signals from the external environment and change the structure or state of their macromolecules to affect their physicochemical properties. Stimulus-responsive polymers are also one of the most widely used materials in PC gas sensors. Unlike MOFs, which focus more on changing the effective refractive index, the advantage of this material is that it can expand dramatically under gas stimulation to make the lattice spacing significantly larger, so that PC sensors can achieve a large wavelength shift and high detection sensitivity. Due to their good film-forming properties, easy functionalization, and adjustable flexibility, polymer materials were widely employed to fabricate one-dimensional PCs with multiple functions. Table 2 systematically summarizes the relevant applications of polymer-based PC sensors in recent years.

After the introduction of gas, the polymer network undergoes a volume phase transition (VPT) due to expansion, leading to the change of the particle spacing (Fig. 8). The expansion of the polymer and the diffusion of gases in the polymer increase as the glass transition temperature decreases, enabling higher sensitivity detection.106,107 One of the principles for selecting the polymers is to consider the influence of the similarity of solubility parameters between structures and analytes. The higher the similarity, the higher the sensitivity. For example, the solubility parameters of benzenes including benzene (9.02 cal1/2 cm−3/2), toluene (8.90 cal1/2 cm−3/2), xylene (8.79 cal1/2 cm−3/2), and 1,2,4-TMB (8.77 cal1/2 cm−3/2) are close to those of the aryl polymer polystyrene (8.5–8.6 cal1/2 cm−3/2), and thus the sensor prepared from polystyrene (PS) will exhibit a high response to these vapors whether in terms of polarity and solubility parameters.108

A polymer-based PC sensor can be used as a visual identifier to distinguish analytes based on their differences in solubility parameters and polarity. The interaction between the polymer and the analyte can also be explained by the Flory–Huggins parameter. Δδ2 is a function of the analyte molar volume (VΔ) and of the squared difference in the Hildebrand solubility parameter for the pairs; a smaller Δδ2 will lead to greater solubility. Based on the Flory–Huggins principle, PMMA,109 PDMS,110 PVDF111 and CA108 were widely employed to construct DBR-structured PC gas sensors. In addition to this, hydrogels112 or dimethyl aminopropyl methacrylamide (DMAPMA)113 have been used to construct three-dimensional anti-opal PCs for gas sensing. Unlike the use of polymers as a unit in a periodic structure, cholesterol liquid crystal polymer networks (CLCNs) can be regarded as a PC structure. Chen et al.114 prepared a PC gas sensor using a CLCN thin film for the detection of humidity and pH in the environment.

However, ideal sensing results, including sensitivity and selectivity, are not achieved based on similar solubility parameters alone. Therefore, modification or doping of polymers is an
effective and necessary approach to provide more specific adsorption sites.

4.2.1 Block copolymer-based PCs. In comparison with single polymer-based PC sensors, which usually have only one response mechanism, the use of block copolymers allows PC sensors to respond to two different external stimuli simultaneously.

Xu et al. prepared a block copolymer by combining an oxidation-responsive partial material (phenyl vinyl sulfide) with a pH-responsive partial material (N,N′-(dimethylamino)ethyl acrylate), which demonstrates dual response to ozone and pH by changing “n” and “d” to modulate the band gaps of PCs. Kim et al. prepared a PC sensor for environmental humidity detection with a self-assembled poly(styrene sulfonate–methylbutylene) (PSS-b-PMB) (PSS-b-PMB) block copolymer, in which hydrophobic PMB cylinders were dispersed in the PSS matrix. In terms of humidity levels, the PSS-b-PMB films self-revealed discernible reflective color changes covering almost the entire visible region from violet (RH = 20%) to red (RH = 95%).

4.2.2 Polymer composite-based PCs. Similar to the modification of block copolymers, hydrogels and nanoparticles could also be used as additives to dope with polymers by altering the physical or chemical properties of the polymer.

Since the periodicity of the chiral nematic helical structure of cellulose nanocrystals (CNCs) matches the wavelength of visible light, CNC films can also be considered as a PC. After combining cellulose nanocrystals with the polymer, the hydroscopcity increased, and the color change detection performance improved. Duan et al. successfully prepared CNC–poly (ethylene glycol) (PEG) and CNC–glycerol composite films with stimulus response and iridescent colors, which exhibited reversible structural color changes when humidity changed due to reversible swelling and dehydration of the chiral nematic phase structure, while CNC–glycerol films produced a reversible stimulus response to hydrochloric acid gas. The response mechanism of the polymer-ionic liquid system is similar to that of hydrogels. A PC responsive material was developed by Smith et al. using the ionic liquid ethylguanidine perchlorate (EGP) as a poly (hydroxyethyl methacrylate) (pHEMA) organogel network to detect water vapor and ammonia. The Flory–Huggins interaction parameter of EGP increased a significant amount when the analyte absorbed into the organogel, leading to a longer time to reach sensing equilibrium and reduced reversibility. To solve this problem, one approach is to synthesize high performance optical polymers with high refractive indices, such as p(HB–PVS) with 1.68, PVK with 1.68 and poly (pentabromophenyl acrylate) with 1.71. Another method is to modulate its optical properties by doping with a material with a high refractive index. Song et al. synthesized a block copolymer with large differences in the refractive index using zirconium oxide (ZrO₂) nanoparticles to tune its optical constants. The strong hydrogen bonding between ZrO₂ and PEO resulted in the refractive index of the copolymer increasing from 1.45 to 1.70. A significant enhancement of the reflection was observed in the composite at about 398 nm (~250% increase) compared to the unmodified copolymer.

4.3 MOF/polymer composite-based PCs

In previous studies, researchers have attempted to achieve gas sensing by using a single polymer- or MOF-based PC. In fact, both polymer and MOF functional materials can be assembled into one PC structure simultaneously. This strategy not only overcomes the limitations of material selection, but also integrates the respective advantages of the two functional materials. When target vapor is introduced into the MOF/polymer structure, the lattice spacing change induced by the stimulated swelling of the polymer and the effective refractive index change caused by the adsorption capacity of the MOF will significantly enhance the sensing performance of MOF/polymer-based PCs. Kou et al. demonstrated the successful combination of a flexible MOF (NH₄–MIL-88B) and a functional polymer (P(St-AA)) for assembling a 1D PC colorimetric sensor. In addition to the synergistic effect of the MOF and polymer mentioned above, the rich pore structure of NH₄–MIL-88B could also facilitate the vapor molecular diffusion, thus further improving the detection sensitivity. Gao et al. prepared a 1D PC sensor for the visual sensing of VOC vapors in the highly toxic benzene series by integrating photo-crosslinked polymer-poly(styrene-benzophenyl acrylate) (P(St-BPA)) and a high-surface-area MOF (MIL-101 (Cr)). The detection limits of benzene series VOCs were as low as 0.06–3.45 g m⁻³.

5 Current development direction: difficulties and challenges

Low cost, integration, chip-based and easy on-site inspection are the very powerful features of PCs as a sensing structure. For researchers, there are also some problems and challenges that must be solved:

(1) Advances in the preparation method

Among the methods currently used for the preparation of DBR structures, whether MOFs or polymers, the most commonly used is the spin-coating method, which has the advantages of simplicity and structural stability. However, because nanoparticles, including MOFs, have heterogeneous particle sizes and are usually agglomerated, it is difficult to control the thickness and uniformity of the MOF layer during the spin-coating process, which leads to the degradation of the optical properties of the PCs. In terms of reproducibility and high spatial resolution,
small variations induced by the spin-coating process can also lead to different structural colors. This is a significant hindrance to the commercialization of various PC optics. For opal and antioptal structures, a three-dimensional structure is highly demanding for the monodispersity of nanoparticles such as MOFs, and the occurrence of agglomeration during either evaporation or sedimentation is detrimental to dry mass preparation. Based on this, the assembly process, particle-to-particle van der Waals forces, electrostatic forces, and gravity are given maximum attention, and a high-quality self-assembly process requires an optimal equilibrium relationship between the various forces. In addition, the time required for assembly should also be optimized, and achieving self-assembly in a short period of time (minutes or even less) is one of our concerns.

(2) Advances in materials

The selectivity of the material chosen for PC preparation to the target gas is an important factor in the sensitivity and specificity of the sensor. Methods to improve sensor sensitivity can be considered from two perspectives, high resolution through signal amplification (e.g., complex readout methods) and material improvement, including grafting functional groups onto the material to achieve specificity for sensitive adsorption. In the case of MOFs, it is possible to tailor the “adsorption site” to the properties of the target gas, e.g. by enhancing the hydrogen-bonded ligand or changing the metal ratio or constructing defects. The refractive index and flexibility of polymer materials are important properties to focus on, as high refractive index polymers will greatly enhance the integrity of the bandgap, and flexible polymers will be important for the future of smart wearable sensing.

(3) Advances in application

Both MOFs and polymers have limited selectivity for gases within the material itself, so selectivity remains a major challenge in this field. Sensor arrays have become a common compromise to mitigate the poor selectivity of individual conventional sensors. We can foresee that the adjustable pore size of MOFs for gas selection of different molecular sizes and the different solubility parameters that different polymers have will be an effective means of constructing array structures for the recognition of mixed gases. At the same time, most of the currently studied PC gas sensors are based on rigid materials such as Psi or SiO2 as the substrate structure, and are equipped with light sources, spectrometers and other auxiliary equipment, which hinders the miniaturization of the equipment in practical detection. Passive detection applications are one of the development directions worth exploring.

Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

Author contributions

Jianan Wei: conceptualization, methodology, data curation, investigation, formal analysis, visualization, and writing – original draft; Zhihao Yi: data curation, investigation, writing – review and editing, and supervision; Liu Yang: data curation, investigation, writing – review and editing, and supervision; Ling Zhang: resources and writing – review and editing; Junchao Yang: resources; Molin Qin: conceptualization, methodology, visualization, and writing – review and editing; Shuya Cao: supervision, resources, funding acquisition, and writing – review and editing.

Research funding

This work was supported by the Postdoctoral Fellowship Program of CPSF (GZB20230992).

Conflicts of interest

The authors declare no conflict of interest.

References

45 Y. Suh, Q. Pham, B. Shao and Y. Won, *Small*, 2019, 15, 1804523.


