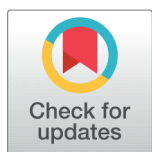


Photonic Crystals: A Review as Promising Tool for the Selective Detection of Toxic Gases



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Photonic crystals (PhCs) based sensing nanotechnology has gained a lot of attention because of its unique structural and morphological characteristics. With the potential utility, these PhC materials are promising as sensitive, selective, economical, portable, and visually detectable gas/vapor sensors for environment quality monitoring. This review focuses on current progress in the natural and artificial PhCs for gas sensing. We will discuss different PhCs including morpho butterfly wings and their nanostructure mimics, porous silicon, Bragg stacks, and colloidal crystals. Moreover, their fabrication techniques for PhCs sensing materials, structural modifications, and sensing mechanisms will be analyzed. In this review article, we highlighted the problem and solution as emerging trends for recent advances in PhCs-based sensors and their applications in environmental monitoring and pollution control. Furthermore, this study envisions new methodologies for PhCs-based sensors that will be highly advanced and effective.

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Keywords: Photonic crystals, Gas sensing, Morpho wings, Porous silicon, Bragg stacks, Colloidal crystals

INTRODCUTION

Photonic crystals (PhCs) are specialized periodic optical structures that trap light. PhCs have a bandgap in which a specific wavelength of light is entrapped and the diffraction grating phenomenon occurs.¹⁻⁶ PhCs

have a specified periodic array of atoms that's why these are classified into 1 dimensional (1D), 2 dimensional (2D), and 3 dimensional (3D) on the base of their structure as shown in Figure 1.⁷ The simplest PhCs are 1D because these comprise of alternating layers of substances with various dielectric con

stants. Light with a frequency of definite array acts as Bragg's mirror in 1D PhCs.^{8,9} 2D PhCs are those having a variable refractive index in two directions. Etching, spin coating, or confined convective assembly techniques are used to synthesize 2D PhCs.^{10–12} 3D PhCs have spatial 3 dimensional; opal and inverse opal are substantial examples of 3D structures. The main synthetic route to preparing PhCs is bottom-up self-assembly including gravity or vertical deposition. These consist of nanometer or sub-micrometer size spheres such as poly(methyl methacrylate), polystyrene, or silica.^{13–16}

Various colors exhibit materials with different dielectric constants. The motion of photons can be affected by these materials similar to the effect of electrons motion in semiconductor crystals. The periodic arrangement of arrays in dielectric substances develops a photonic bandgap that is specified for propagation to certain frequencies or wavelengths of light while another light is permissible to move. These light controlling properties insert excellent properties in PhCs that made them the ideal optics^{17–20}. Therefore, PhCs are very important substances because of their application diversity in every field of life.

PhCs are one of the promising tools in gas sensing due to their large surface area, and unique optical and structural properties. These have great advantages over traditional sensing devices including sensitivity, portability, constancy, and online monitoring of results^{21–23}. As discussed earlier, PhCs is the dielectric material having periodicity in their periodic lattice. Light propagation and reflection through the holes produce various colors. Bragg's law explains the diffraction mechanism of PhCs that was proposed by Yablonovitch and John.^{24–26}

$$2nds\sin\theta = m\lambda$$

In this equation, n is the refractive index, d is spacing between lattice

plates, ' m ' is diffraction order, λ shows the wavelength of the incident light, and θ is the glancing angle of the material.^{27,28} PhCs enhance the sensitivity, selectivity, and fluorescence due to photonic bandgap within a specified wavelength that's why these are the most advanced sensor for vapor/gas sensing.

PHOTONIC CRYSTALS FOR GAS SENSING

Volatile organic compounds (VOCs) and other toxic gases are contaminating the environment through various emission sources and have become a major concern of air pollution. These vapors affect human health and cause human diseases such as cancer, nausea, skin irritation, memory impairment, and visual disorders.^{29–32}

represents various VOCs profiles related to air quality. There are some traditional sensors present to detect the gas/vapor but these have some disadvantages including less sensitivity, and selectivity, and do not bear environmental conditions. In contrast to traditional sensors, optical sensors are very fast, selective, and have a long lifetime that's why optical sensors have commercialization potential but there is a marketable difficulty because of their expensiveness.^{33,34} The optical sensor converts light signals into analytical useful signals. Optical sensors have diverse applications in the field of environmental safety, agriculture, diagnostics, and energy^{35–37}. There is a necessity for a longer interaction path for the conventional optical sensor. This longer interaction path needs more space and volume that's why its size becomes large. This problem is solved by incorporating a mirror that multiplies the interaction between the gas and radiation. In this way, the size of the optical device decreased. However, its cost is high and restricted to following a hard fabrication process. PhCs replaced the traditional optical sensors due to their small size, low cost,

high sensitivity, selectivity, robustness, and easy manufacturing process. The size of a PhC-based optical sensor is less than 1 cm which provides a platform for portability and on spot detection of the analytes^{33,38,39} as shown in Figure 2. We will review various PhC-based optical sensors for gas/vapor sensing including morpho butterfly wing nanostructure, porous silicon, multilayer films, and colloidal array PhCs.

Morpho butterfly wing and their mimic nanostructure

PhCs are natural architecture present in stones, birds, and animals. The color of butterfly wings and chameleons is one of the major examples of the PhCs. These natural PhCs are low-cost and selective in their response. The color of butterfly wings is due to the diffraction of light between photonic multilayers and pigmentation (in some species). When the angle of incident light changes, color also changes which gives evidence of the nanostructure network. Morpho butterfly structure consisted of different layers of chitin and air with varying refractive indexes.^{42–44} Kim et al. used rigorous coupled-wave analysis to calculate diffraction efficiencies of the morpho butterfly wings. Other structural variations were also studied including thickness, material index, and grating width to evaluate optical properties as shown in Figure 3.⁴⁵

There is also a biological pattern associated with morpho butterfly that functionalizes the surface. This photonic security of the butterfly made it responsive to different analytes that's why morpho wings have wide applications in gas sensing. When volatile compounds come in contact with the wing's structure the color changes occur. That is why it is used in different optical sensing devices. When vapors entrap into the nanoarchitec-

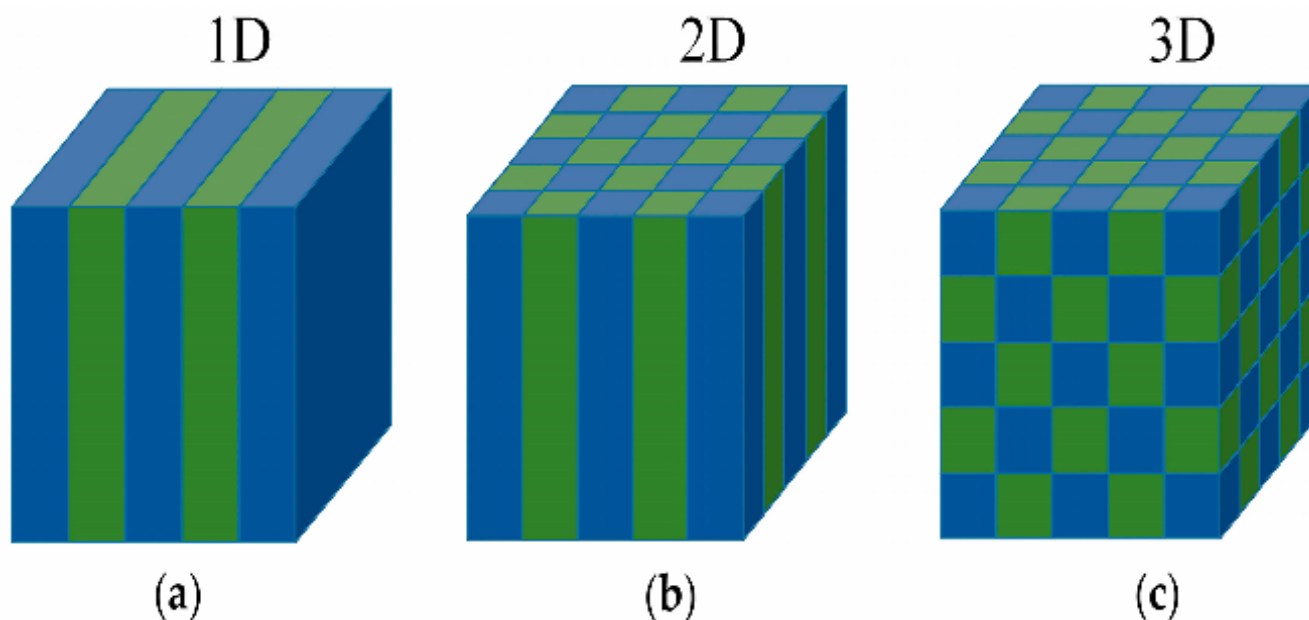


Figure 1. 1D, 2D, and 3D photonic crystals representation.⁷

Table 1. VOCs profile regarding air quality caused by the anthropogenic emissions in atmospheric environment.^{40,41}

VOCs Class	Distinctive VOC analytes	Threshold limit values (TLV)
Aldehydes	Formaldehyde Acetaldehyde Propanol	0.1 TWA 25 TWA 0.1 TWA
Ketones	Acetone 2-Butanone	250 TWA 200 TWA
Alcohols	Methanol Ethanol 1-Propanol	200 TWA 1000 TWA 200 TWA
Esters	Ethyl acetate	400 TWA
Carboxylic acid	Acetic acid	10 TWA
Alkanes	Ethane Propane Butane Pentane Hexane Heptane Octane Nonane Decane	N/A N/A 1000 TWA 1000 TWA 50 TWA 400 TWA 300 TWA 200 TWA N/A
Alkene	Ethylene Propylene Butylene 1,3-Butadiene	200 TWA 500 TWA 250 TWA 2 TWA
Alkynes	Acetylene	N/A
Aromatics	Benzene Ethylbenzene Styrene Toluene Xylene	0.5 TWA 20 TWA 10TWA 20 TWA 100 TWA
Halohydrocarbons	Chloroform Dichloromethane Dichloroethane Chlorobenzene	10 TWA 50 TWA 100 TWA 10 TWA

ture, the capillary condensation mechanism of the vapors explains its optical response.^{46–48} Couple-wave analysis method analyzes the diffraction efficiencies of the wings. Different parameters are also evaluated to analyze optical performance. Membrane thickness of closely packed grating nanoarchitecture shows color changes in response to environmental changes (vapors presence).^{49,50}

Potyrailo et al. fabricated a multi-variable photonic sensor based on mor-

pho scales to sense different gases. Photonic sensors were fabricated by using photolithography and chemical etching techniques. This is a new development in this field to develop artificial sensors after getting inspiration from natural species.⁴⁶ Blue butterflies have a quasi-ordered nanocomposite structure with embedded air holes and these nanostructures lead to the detection of different volatile organic compounds (VOCs) with high selectivity. The exposure of different VOCs

changes the bandgap of the cavities and capillary condensation occurs. Pitzer et al. designed a vapor-mixing setup and spectral changes were evaluated. They reported a direct relation between spectral shift and vapor concentration. The sensitivity and selectivity are altered by the modification of the surface through atomic layer deposition and ethanol pretreatment.⁵¹

The composite of different metals and metal oxide with morpho butterfly wings enhances their response

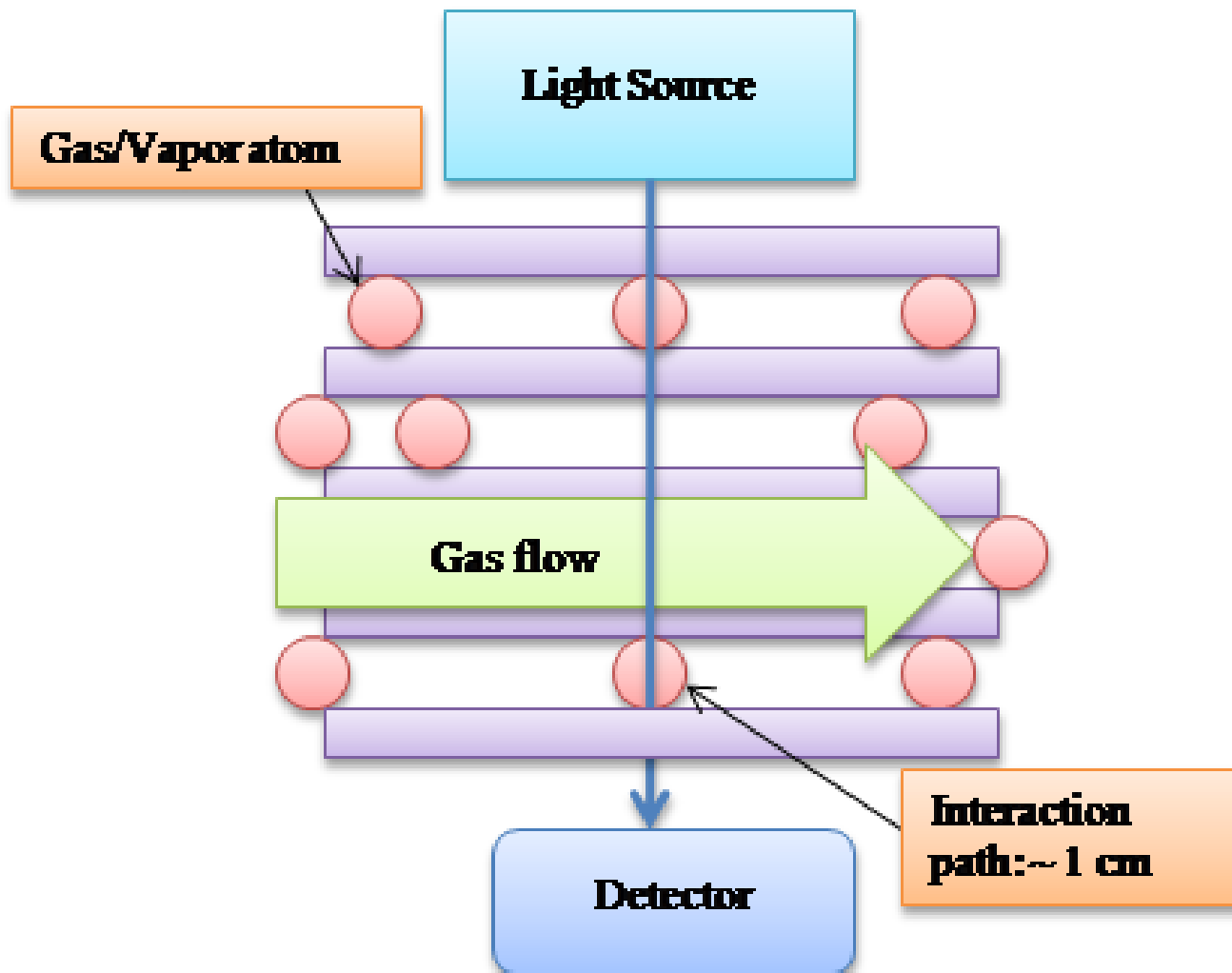


Figure 2. Working principle of a photonic crystal for sensing vapor/gas.

towards the analyte. Jiaqing He et al. synthesized a modified photonic structural framework of Morpho wing scales with Pd nanostrips. The coupling of plasmonic and optical resonant coupling modes in Pd nanostrips produced a sharp reflectance peak and enhanced the light-matter interaction. The reflectance of the Pd-modified butterfly wing increased after the exposure to H_2 . Figure 4 explained the structural medication of the morpho wing after Pd insertion. Pd nanostrips-biophotonic structural framework achieved a detection limit of less than 10 ppm for H_2 .⁵²

Yang et al. used the self-deposition sintering method to fabricate an amor-

phous/nanocrystal hybrid TiO_2 -based butterfly wing structure (ANH- TiO_2 -BW). Original nanoarchitecture was established due to a hybrid configuration. ANH- TiO_2 -BW configuration-based sensor was very conductive toward the acetone vapors because of its structural morphologies. The lowest detection limit for the acetone was 5 ppm at room temperature. The structural porosity made it very fast towards the acetone vapors.⁵³ First time, Silver et al. reported modified morpho wings from nano-structured phosphor materials to investigate the optical properties of photonic structures. The morpho wings were filled with two types of

phosphor solutions; $Y_2O_3:Eu^{3+}$ phosphor or $TiO_2:Eu^{3+}$ phosphor. The sample was dried at 100 °C followed by annealing. Morpho butterfly pleides were synthesized with two different phosphors materials.⁵⁴

The hypodermal process was used to fabricate 3D microporous $Co_3O_4@C$ and butterfly wings were taken as templates. The combination of nanoarchitecture with Co_3O_4 and Carbon skeleton enhance the sensitivity. Different characterization tools were used to understand the structural morphologies. The sensor exhibited excellent response towards VOCs at low temperature.⁵⁵ The microfabrication of

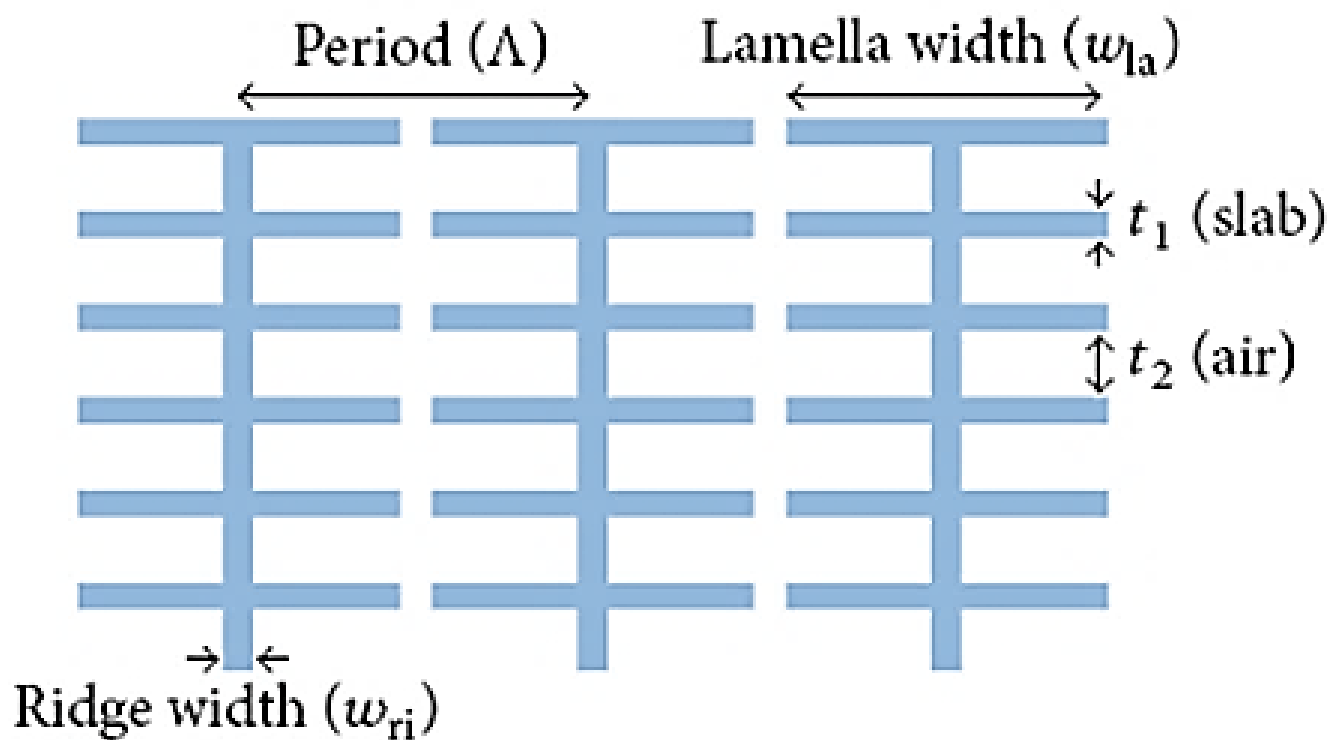


Figure 3. Schematic diagram of Morpho photonic structures for calculation purposes.⁴⁵

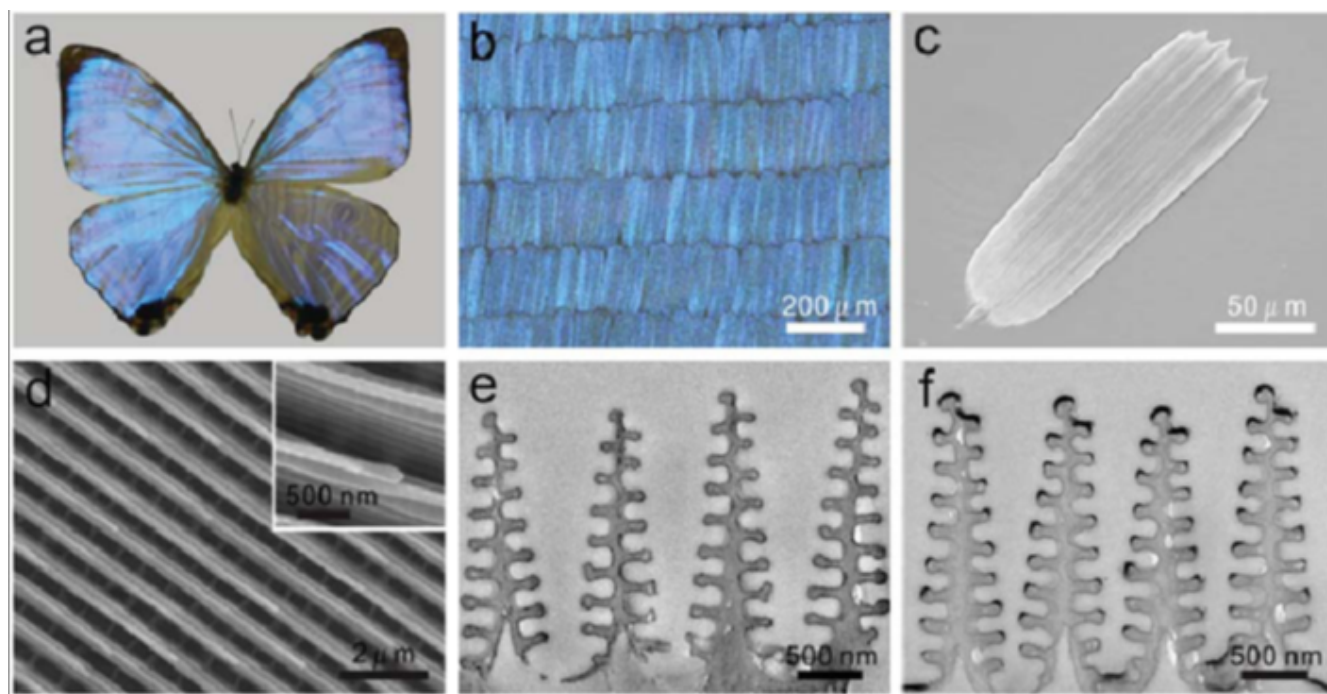


Figure 4. Structural modification in Morpho butterfly wing before and after Pd insertion. (a) Morpho butterfly (b) Optical microscopy image of the stacked scales (c) SEM image of stacked scales (d) Top SEM view of photonic structure (e) TEM image for scale ridges with lamella structures (f) TEM image of modified Pd nanostrips coated lamella.⁵²

morpho-wing based nanoarchitecture in atomic layer was performed to study the vapor response towards artificial photonic nanostructures. Two structures were developed: one was obtained by the combination of TiO_2 and Al_2O_3 , and the second combining HfO_2 and Al_2O_3 . First time, an ALD-Morpho like structure was reported to detect the vapors.⁵⁶ There are different metal oxides with morpho wings including ZnO ⁵⁷, SiO_2 ⁵⁸, and SnO_2 ⁵⁹ was also fabricated for different applications.

The coloring polymers were also combined with Morpho wings to investigate their optical response. Zhang and Chen reported the nanofabrication and coloration studies of artificial morpho wings. The artificial nanoarchitecture framework was based on electron beam lithography combined with LOR dissolution and aligned with color polymers (lamellae multilayers). Maxwell's equations were used to understand the relationship between coloration and genomic dimensions. Spectral measurements were taken carefully for characterization purposes.⁶⁰ First time, natural photonic crystals response was evaluated towards trace chemical warfare agents (CWAs). Dimethyl methylphosphonate (a nerve agent simulant) and dichloropentane (a mustard gas simulant) were detected through modified nanostructured wings of the morpho butterfly. PhCs response was evaluated under visible light. It was also suggested that there are several parameters including material selection, spacing, functionalization, and structure of PhCs which affect the response of the sensor towards the CWA stimulants.⁶¹

Porous silicon Photic crystals

Porous silicon (PSi) PhCs are very significant optical sensors because of their unique sensing characteristics and large surface area. Different size pores have different morphology and characteristics. PSi PhC is one of the ideal optical sensors because the fabrication of such sensing structures is not applica-

ble in other porous material. PSi PhCs have been used for the detection of different VOCs because absorbance of VOCs on the surface of PSi changes the refractive index. The ultimate result of these changes gives a reflection peak and response is evaluated.^{62–65} Kumeria et al. fabricated a colorimetric sensor based on PSi PhC through electrochemical anodization technique. The sensor exhibited color changes when it was exposed to alcohol.⁶⁶ Chun and Miskelly monitored a specified PSi PhCs film by hyperspectral and color imaging when it was exposed to different organic vapors. The response was recorded in the concentration range of 100 to 3,000 mgm^3 . Different solvents were discriminated through hyperspectral imaging, while specificity was not attained from color camera data as shown in Figure 5.⁶⁷

In a new study, colorimetric pSi PhCs was synthesized with two rest bands, one is appropriate activated indicator dye with corresponding optical absorbance and other clear spectral section that specifies a reference. Octadecylsilane was added to modify the inner pore walls and indicator dye was embedded into PhC mesoporous matrix. Various indicator dyes were used for different analyte of interests and results were evaluated by measuring the reflectance spectrum of white light that exhibited colorimetric variations with the detection limit of 14ppm, 5 ppm, and 114ppb for HF, HCN, and, DFP respectively.⁶⁸

Different nanocomposites of PSi with metals, metal oxides, and hybrids were produced to enhance the response of PSi PhCs. Ahmed and Mehaney fabricated Porous silicon one-dimensional photonic crystals (PSi-IDPCs) for sensing purpose on the base of changes in refractive indices. Various metals (Al, Ag, Au, and Pt) were attached to PSi-IDPCs structure to enhance the Tamm/Fano resonances. First time, Tamm/Fano resonances were achieved in the PSi-IDPCs simultaneously. Transfer matrix method (TMM)

and Bruggeman's effective medium approximation (BEMA) were used to calculate the reflection spectra of the PSi-IDPCs. Among different metals, Ag/PSi-IDPC based sensor exhibited the highest response with the sensitivity of 5018 nm/RIU .⁶⁹ Finite differential time-domain (FDTD) tools were used to examine periodical lattice of silver-porous silicon (Ag-PSi). Different characteristics like porosity, layering and reflection, absorption, transmission were evaluated in the range of 400-750 nm. The reflection was directly proportional to porosity while it was inversely proportional to the number of layers. There was an inverse relationship between the reflection and number of layers. The results also revealed that transmission had an inverse relation to porosity⁷⁰. Fecteau and Frechette reported a modified sensor by deposition of Au film on 1D PhC based mesoporous silicon. A high-quality tamm structure was observed with the confirmation of a singularity in the ellipsometric angles.⁷¹

Peng et al. used electrochemical corrosion to fabricate macro-porous silicon (MPS) for gas detection. WO_3 nanofilms were deposited on MPS. The resulted WO_3 /MPS sensor was used to investigate gases at room temperature. WO_3 /MPS exhibited a good response towards NO_2 gas with the detection limit of 1 ppm. This experiment revealed that the addition of metal oxide with MPS PhC increases the sensitivity of the sensor. The sensor response towards ethanol vapors was also recorded which was lower than the NO_2 because of the selectivity of the WO_3 /MPS towards NO_2 gas.⁷² Similarly, tungsten oxide (WO_3) nanowires/porous silicon (PS) sensor-loaded nanoparticles of gold (Au) were developed. The sensor exhibited a good response against NO_2 gas. The sputtering method was used to synthesize Au-loaded WO_3 nanowires on a porous silicon substrate. The lowest detection limit of Au-loaded WO_3 nanowires/Psi-based sensor was

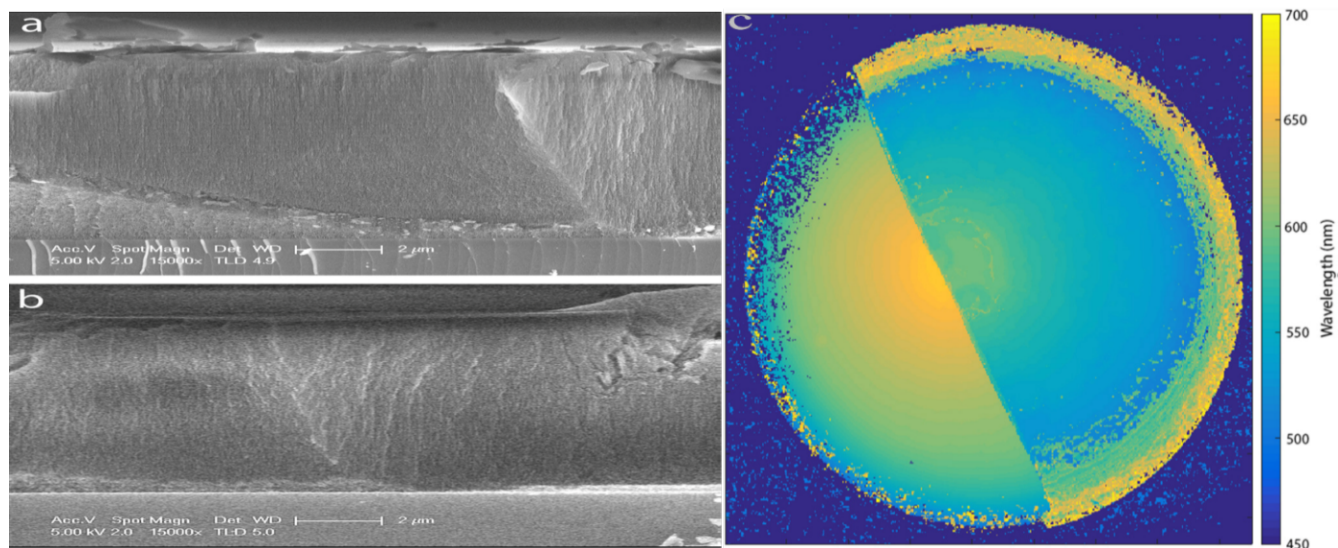


Figure 5. SEM image of porous Silicon (a) Oxidized side (b) Methylated side (c) False color map of porous silicon (wavelength of maximum rugate reflectance band).⁶⁷

recorded at 0.2 ppm–5 ppm at 25 °C.⁷³ Abed et al. incorporated nanoparticles of CuO mixed SnO₂ into the PSi layer. SnO₂ and CuO nanoparticles were attached to the PSi surface through chemical spray pyrolysis. Laser-assisted etching technique was used to synthesize SnO₂/CuO/Psi nanocomposite and morphological properties of the SnO₂: CuO nanoparticles changed with the content of CuO. An increase in the content of CuO produced various shapes of SnO₂ and SnO₂:CuO on the PSi surface. SnO₂(70%)/CuO(30%)/porous silicon nanocomposites sensor detected the NH₃ gas detected with high sensitivity (88%).⁷⁴ In a similar manner, various PSi metal oxide nanocomposites were synthesized such as ZnO⁷⁵, ZrO₂⁷⁶, and Al₂O₃.⁷⁷

Carbon nanomaterials have unique characteristics that enhance the sensitivity of the sensing material.⁷⁸ Sailor et al. patented nanocomposites of Carbon and Silicon materials to evaluate the photonic response.⁷⁹ C-dots nanostructures within various PSi Bragg reflectors contained optical properties. C-dots emission spectral features could be tuned and their fluorescence emission enhanced due to the overlapping of

PSi high reflection band with the peak wavelength of C-dots.⁸⁰ The precursor of Poly (furfuryl alcohol) (PFA) in PSi was used to fabricate Carbon/porous silicon composite films. A glassy carbon layer was coated into the internal structure of PSi. C₂ hydrocarbon gases were examined by the C/PSi composite-based optical sensor. The electrochemical anodization of moderate or high doped p-type silicon was performed to synthesize porous silicon templates. The reflectance spectrum and sensitivity varied with the carbon percentage in the photonic structure. The large surface area of the C/PSi composite enhanced the sensitivity of the sensor. 0.2% (v/v) was the lowest detection limit recorded for the C₂ hydrocarbons in a nitrogen carrier gas.⁸¹

Multilayer photonic crystals

A combination of two different dielectric materials gives rise to a novel substance having unique electromagnetic properties and additional periodicity in bandgap structures. These multilayer systems have enhanced optical properties and can be used for controlled propagation of light. 1D photonic layers are

easy to fabricate as structural modification leads to directional changes in a single dimension.^{82–86} Development of porous photonic stacks gained a lot of interest in the mid-nineties. Different methods like vapor deposition and sputtering were used due to their simplicity and performance stability.^{87,88} Modern techniques like electrochemical etching, chemical and physical vapor deposition, wet deposition methods, and spin coating have enabled the controlled fabrication of nanoparticles, polymer, colloidal crystals, and metal oxide-based multilayer photonic crystals (MPhCs). Their porous structure, large surface area, vides optical response, and binding ability proved them very efficient in gas and vapor sensing.^{89–93}

Polymer nanoparticles based photonic crystals are a modern type of photonic crystals (PhCs) developed by using spin coating or self-assembly technique. These techniques have the special advantage of controlled nanoparticle size achieved by mixing different ratios of monomers and cross-linkers. Desired chemical properties can be attained by the introduction of specific functional groups that react with gas molecules.⁹⁴ Burratti

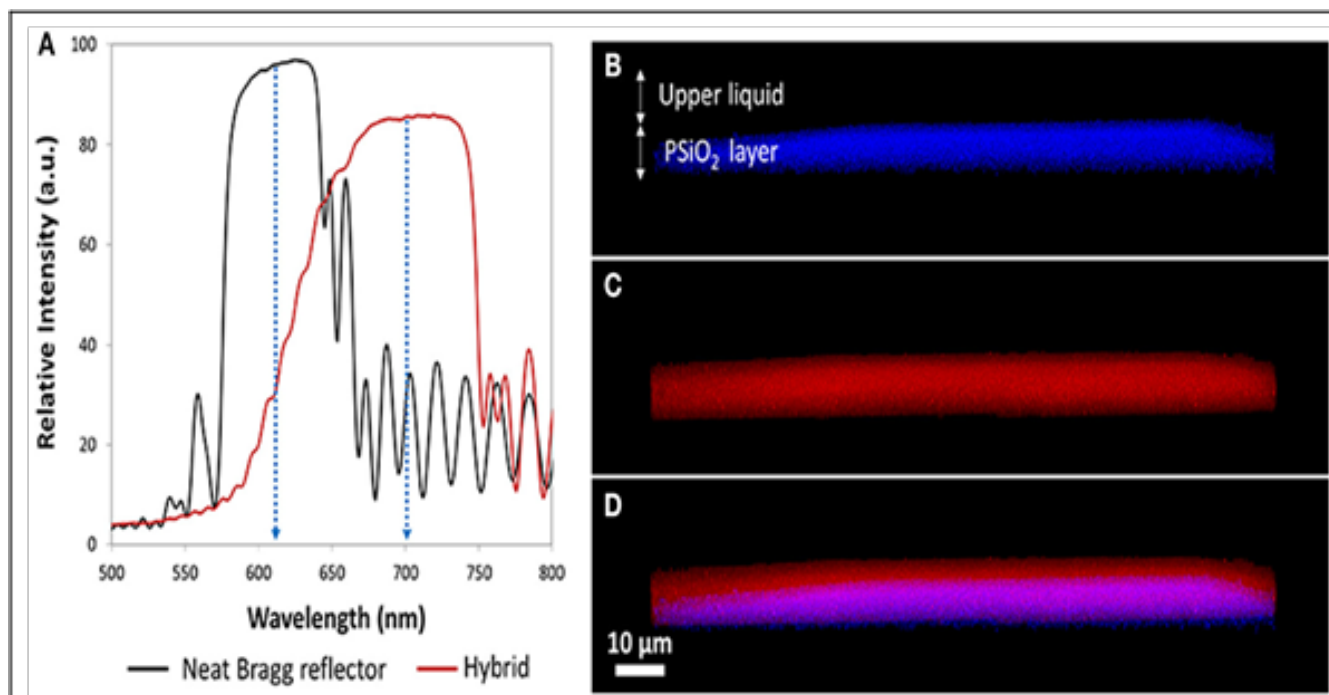


Figure 6. Reflection spectra of the PSiO_2 Bragg's reflector before and after the fabrication of C-dots and the 3D projection image of the PSiO_2 Bragg reflector/C-dots hybrid. (A) Reflection spectra of the PSi (before and after the fabrication of C-dots); (B) Photoluminescence of the PSiO_2 ; (C) Fluorescence signal (C-dots); (D) A, B combined view (C-dots within a porous layer).⁸⁰

et al. fabricated a multilayer PhCs-based colorimetric sensor for alcoholic vapor detection through self-assembled polystyrene nanospheres with an average diameter of 250 nm. The drop-casting technique was applied to introduce samples on the surface of a glass substrate. Thin films exhibited an excellent reflectance band and maximum reflection was observed at 600 nm. Adsorption of vapors resulted in swelling of polystyrene nanospheres. Change in reflectance peak (red shift) as time function was observed in the presence of ethanol, n-butanol, isopropanol, and n-propanol vapors. Water vapors did not show any change in reflection because of the hydrophobic properties of polystyrene. The sensor proved to be highly selective for VOC detection with a detection limit of 1167 ppm.⁹⁵ A multilayer PhC-based on stacks of organic and inorganic layers was fabricated for the detection of organic vapors. Different layers

were generated by alternate assembly of organic (polystyrene-acrylic acid) and inorganic (TiO_2) nanoparticles for visual detection of toxic hydrocarbons (benzene, toluene, and xylene) with a very fast response time of 1.5 seconds. The sensor was examined with a smartphone-based colorimetric study program that enabled optical detection and analysis of different hydrocarbons⁹⁶.

Distributed Bragg's reflectors (DBRs) are another type of polymer used as photonic crystals. These are fabricated through alternative thin films of different dielectric materials.⁹⁸ Paola et al. fabricated a multilayer stack of ZnO-polystyrene nanocomposites for the detection of toluene vapors. The proposed sensor was 10-fold more sensitive than the bare polystyrene reflector because of the enhanced optical response of the functionalized surface.⁹⁹ The same group also proposed a Flory-Huggins sensor

reflector for sensing VOCs. Alternative layers of inert cellulose acetate and active polystyrene modified with salinized ZnO nanoparticles formed a multilayer stack. Affinity-based attractions led to a change in UV-Visible optical response after the exposure of toluene, benzene, o-dichlorobenzene and CCL_4 vapors.¹⁰⁰ Kuchyanove et al. used multilayer porous silica films that formed hydrogen bonds between the silane group and ammonia leading to greater variations in optical properties. The proposed sensor was highly sensitive with a very low detection limit of 1 to 10^5 ppm.¹⁰¹ Some materials such as multilayer porous silicon PhCs have the ability to concentrate gas molecules or vapors with micro-capillary condensation phenomena.¹⁰² 1D multilayer porous thin film of mixed metal hydroxides (MMO) and TiO_2 were used as PhC-based sensors for the detection of various VOCs with relative humidity. Alternate layers of TiO_2

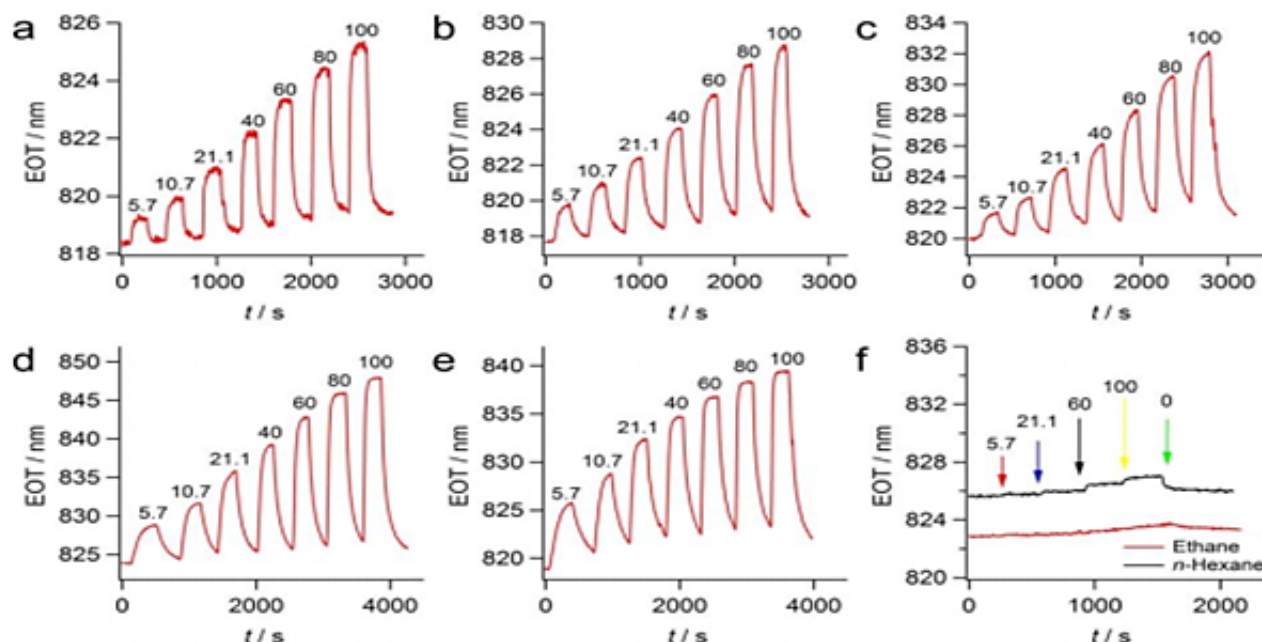


Figure 7. Response curves of multichannel silica nanolayer for altered concentrations of (a) benzene, (b) toluene, (c) chlorobenzene, (d) ethanol, (e) acetone, (f) ethane, and *n*-hexane. Related concentrations in the ppm range are marked on the top of the response curve.⁹⁷ Reproduced with permission from ref 97. Copyright 2018 ACS publications.

and double-layered metal hydro-oxides (LDH) were deposited by spin coating and calcination was performed to convert LDH into porous structured MMO. The variation in the thickness of the TiO₂ and MMO layer changes the reflection spectrum in the visible region. Unique color band variations were observed with the absorbance of VOCs on the surface of mesoporous holes.¹⁰³ A photonic multilayer nanochannel membrane of silica was fabricated by generating layer-bilayer stacks of nanometer thickness. The regular arrangement of ultra-thin channels with a diameter of 2.3 nm resulted in very high density (1012 cm⁻²) and a large surface area available for the attachment of molecules. Highly porous structures are reflected light in a constructive and destructive pattern of a specific wavelength. The attachment of vapors shifted the reflectometric interference spectrum to a higher wavelength. The lowest detection limit of the sensor was in the ppb range as shown in Figure 7.⁹⁷

Colloidal array photonic crystals

Colloidal crystals are highly ordered closely packed spheres that structurally resemble natural gemstone opal. These have a unique sub-micrometer diameter that enables light diffraction in the visible or near-infrared region. The diffraction wavelength can be altered by varying the assembly and diameter of colloidal arrays.^{104–106} Accumulation of vapors on the colloidal surface leads to a change in optical properties, resulting in structural color changes. Therefore, these have been widely used for gas sensing applications.^{107–109} Ling et al. fabricated a highly sensitive hybrid mesoporous PhC-based sensor by using fluorescent dye for qualitative and quantitative analysis of chemical vapors and gas mixtures. A change in color was observed by recording the fluorescence spectra of the excitation light.¹¹⁰

Metal oxides provide highly selective interactions, rigidity, and gas absorbing properties.¹¹¹ Yun et al. reported tin oxide (SnO₂) nanospheres

for the sensing of ethanol vapors. Different structural spheres were synthesized using different growth models and their sensitivity was checked at different ethanol concentrations. Results revealed that nanocones are more sensitive than hollow and amorphous core structures due to better changes in the diffraction of light.¹¹² Applying metal oxides to a heat-generating system increases their sensitivity and recovery time which is necessary for in-situ gas detection.^{113–115} 2D colloidal array of SnO₂ was fabricated on a selective surface of a micro-heater for the formaldehyde vapors detection. Monolayer self-assembly and thermal decomposition were used for homogenous chemical deposition of the SnO₂ metal layer. The sensor was selective with a very low detection limit of 6.5 ppb and a recovery time of 5.4 seconds.¹¹⁶ He et al. reported a porosity-controlled SnO₂ sphere for acetone detection. The electrostatic spraying method was applied for the fabrication of homogenous porous spheres while 3D polystyrene

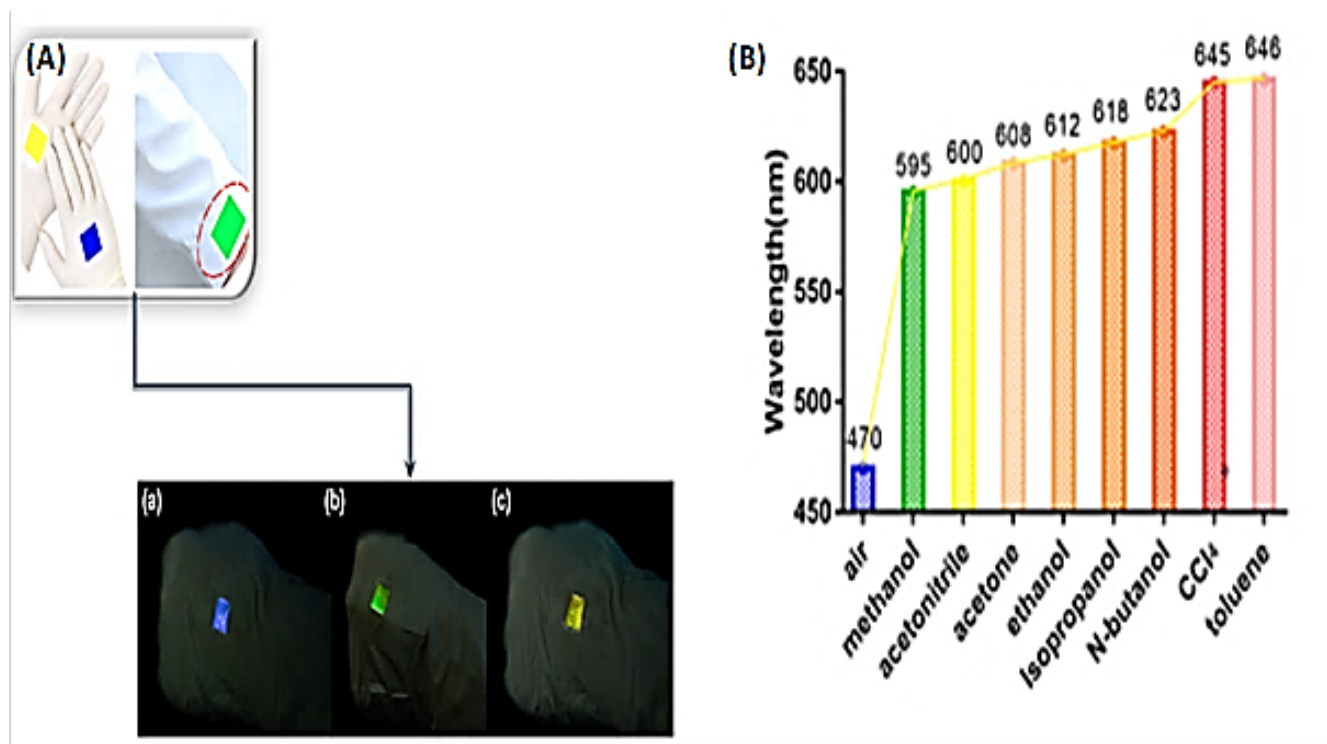


Figure 8. (A) Color changes of SMPCF sensor on glass rubber in response to (a) air, (b) methanol, and (c) acetonitrile. (B) Reflection spectrum of SMPCF sensor in response to different organic solvents.¹²⁷ Reproduced with permission from ref 127. Copyright 2019 ACS publications.

beads were developed by colloidal templating of polystyrene beads. Different characterization tools were used to understand the composition and morphology of the sensing material. The sensor exhibited a very low detection limit of 5 ppm with high selectivity.¹¹⁷

Polymer colloidal photonic crystals have found great interest in colloidal PhCs because of their high flexibility, functionalities, and unique optical properties.^{118,119} Zhang et al. developed polymer infiltrated silicon dioxide (SiO₂) inverse opal photonic crystal (IOPhC) to detect xylene vapors in air. The polymer was developed on the Inverse opal SiO₂ layer with 4-vinylbenzyl chloride-co-methyl MAA functional monomer. A resemblance in solubility parameters resulted in a higher affinity of polymer surface towards xylene vapors. The sensor exhibited a color change from green to red when exposed to the analyte with the detection limit of 0.51,

0.41, and 0.17 $\mu\text{g mL}^{-1}$ for ortho, para, and meta-xylene vapors.¹²⁰ Polymeric hydroxyethyl 2-Methacrylate film was used for the detection of carbohydrates and polyhydric alcohols. The film was fabricated with a self-assembly method followed by rinsing of deionized water to attain swelling equilibrium. A red-shift in wavelength from 520-780 nm was observed with the attachment of analyte molecules.¹²¹ Li et al. fabricated IOPhC film on SiO₂ nanosphere by using hydroxyethyl methacrylate as a monomer and Ethylene glycol dimethacrylate (EGDMA) as a cross-linker. The sensor selectively responded with a color change from green to red when exposed to different concentrations of p-Nitrophenol vapors.¹²² In another study, Chang et al. reported a colloidal photonic crystal-polydimethylsiloxane (PDMS) composite for VOCs detection. Nanoscale easy net process (NET) was used for the construction of colloidal crystal-PDMS

composite. The sensor detected VOCs vapors with high sensitivity and color changes were observed in the visible region.¹²³

Silk/cellulose fibers have found a recent application as a matrix for photonic materials due to mechanical strength, degradation ability, and low cost.^{124,125} An opal and inverse opal 2D and 3D cellulose photonic film (CPCF) was fabricated by using 2D and 3D PMMA arrays into carboxymethyl cellulose (CMC). The wavelength of diffracted light was controlled by changing the size and diameter of nanoparticles. A visible color change from violet to red was observed by exposing the fabricated CPCF to VOCs.¹²⁶ With an extension in PhCs technology, Dan et al. synthesized a wearable silk and cellulose composite, the composite was first dyed then its surface was functionalized with 3D polystyrene and polymethyl methacrylate (PMMA)

nanostructured colloidal arrays. The Resulted inverse opal silk methylcellulose photonic crystal film (SMPCF) was highly flexible. A redshift in wavelength with a color change from green to red was observed by exposing the sensor to different VOC vapors. The SMPCF sensor integrated on a rubber glove also exhibited excellent sensitivity and selectivity towards organic solvents including methanol, ethanol, acetonitrile, toluene, and acetone as shown in Figure 8.¹²⁷

CONCLUSIONS

Recent advances in photonic sensors have enhanced their applications in environmental monitoring and pollution control. Their fast response time, high sensitivity, and lower detection limit have proved them more attractive than other sensing devices. In this review, we have discussed recent advances in different types of photonic structures and improvements in their gas sensing properties. The sensitivity of the sensor mainly depends upon the change in the refractive index induced by gas or vapor adsorption. Recent modifications have led to the enhanced optical and gas adsorbing ability of photonic crystals making them an attractive tool for gas sensing in the environment. Two and Three-dimensional nanostructures have the ability to refract light in the visual region and color changes observe with the naked eye. Furthermore, in the future, key technologies of PhC-based sensors will explore new design methodologies for highly advanced and effective gas sensors.

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