

## CHEMICAL, THERMAL AND BIO-RESPONSIVE POLYSTYRENE BASED- PHOTONIC CRYSTALS: A MINI-REVIEW

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### ABSTRACT

The potential uses for photonic crystals have attracted a lot of research interest. They can be employed as sensors thanks to their clearly defined physical properties, such as reflectance/transmittance, higher degrees of sensitivity producing precise detection limits, and the sparkling visual quality they present in the visible range of wavelengths. Connecting incident, reflected, and transmitted light to optical fibers allows for the sensing applications, which are then analyzed in distant locations. Responsive PhCs can be fabricated to sense chemicals, thermal and biological stimuli based on these characteristics. Evaluation of the product's cost-effectiveness and measurement accuracy in comparison to alternative approaches are essential for any sensing technology to be long-term viable. The minimal water absorption, rigidity, and low manufacturing costs of polystyrene make it a highly desirable material. This article examined some significant recent research on polystyrene-based photonic crystals that are thermo-, chemically-, and biologically sensitive.

**Keywords:** Photonic crystals, polystyrene, sensor.

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## 1. INTRODUCTION

Numerous technologies have achieved real-time detection with great selectivity and sensitivity thanks to the advancement of analytical methodologies. With a low limit of detection and limit of quantitation, gas chromatography-mass spectroscopy (GC-MS) is frequently employed to measure the concentration of volatile targets [1-2]. Ion mobility spectroscopy (IMS), which is now frequently employed in airport security inspections, is excellent at finding explosive gases [3]. With its quick detection, high sensitivity, and simple modification capabilities, the electrochemical sensor transforms chemical signals into electrical impulses [4-5]. However, the use of these technologies is severely constrained due to expert operation, rigid measurement requirements, expensive equipment, and other factors. Without any additional equipment, a perfect sensor should react swiftly and intuitively to the type and concentration of the object. The industrial revolution era, which has resulted in an explosion of hundreds of new items, includes nanostructures [6–15]. Due to their high surface-to-volume ratios, these products exhibit a number of special qualities, including improved strength, chemical reactivity, or conductivity; altered electronic bandgap energy (optical characteristics); customized functionality; and increased selectivity and sensitivity [15–24]. Based on these, photonic crystals (PhCs) have emerged as the optimal sensing nanostructured material for detection with the human eye by modifying their structural color in a particular environment through the design of their chemical constituents [25]. PhCs sensors, which feature label-free, visible, and on-site detection capabilities, have demonstrated widespread use in the fields of quick screening and point-of-care diagnostics when compared to conventional biochemical sensors [26].

Polystyrene has received a lot of attention among the materials used in the creation of photonic crystals because of its low water absorption capacity, stiffness, and affordable production prices [13]. For reaching high performance in sensing applications in this context, polystyrene-based photonic crystals constitute an exciting solution. In fact, since many photonic architectures have been extensively studied and used in photonic sensing (e.g., ring resonator, surface Plasmon resonance (SPR) - based sensors, microdisks, and microspheres, to name a few), polystyrene-based-PhCs exhibit a strong optical confinement of light to a very small volume, enabling the detection of chemical species with dimensions of nanometers [27]. Additionally, extremely

high performance can be attained in ultra-compact sensor chips by integrating them with microfluidic systems and applying cutting-edge chemical surface functionalization processes. A LOD of less than 20 pM for anti-biotin, which equates to less than 4.5 fg of bound material on the sensor surface and fewer than 80 molecules in the modal volume of the integrated microcavity, has been empirically and theoretically proven to have ultra-high performance [28]. Many gases, including CO<sub>2</sub>, CH<sub>4</sub>, and CO, exhibit absorption lines in the mid-IR wavelength range, leading to the development of polystyrene-based-PhC sensors as mid-IR gas sensors. Other uses mentioned in the literature deal, among other things, with the detection of temperature, pressure, stress, and humidity readings [28].

From a technical perspective, PhC-based photonic sensors, such as integrated planar photonic crystals and photonic crystal optical fibers (PCFs), are appropriate for multiplexing and label-free detection. For instance, a large-scale chip-integrated PhC sensor microarrays for biosensing on an SOI-based platform has recently been proposed and proven [29–30]. The creation of PhCs often uses conventional and CMOS-compatible technological techniques, such as electron-beam lithography, inductively coupled plasma (ICP) etching, and plasma enhanced chemical vapor deposition (PECVD), making these sensors appropriate for mass-market and low-cost production. As an illustration, Burratti et al. (2018) created high-quality polystyrene (PS) 3D-PCs, also known as opals, with a filling factor  $f$  that was close to the ideal value of 0.74 and had a strong response to various concentrations of methanol (MeOH) vapor [31]. In this article, several experiments using polystyrene-based photonic crystals for chemical, thermal, and biomolecular sensing were covered.

## 2. ADJUSTING THE PHOTONIC BAND GAP

According to Bragg-law, Snell's any stimulus that can alter either the periodicity or the refractive index contrast (or both) of the PhC can cause a change of the PBG (equation 1):

$$\lambda_{\max} = \frac{2}{m} d \sqrt{n_{\text{eff}}^2 - \sin^2\theta}$$

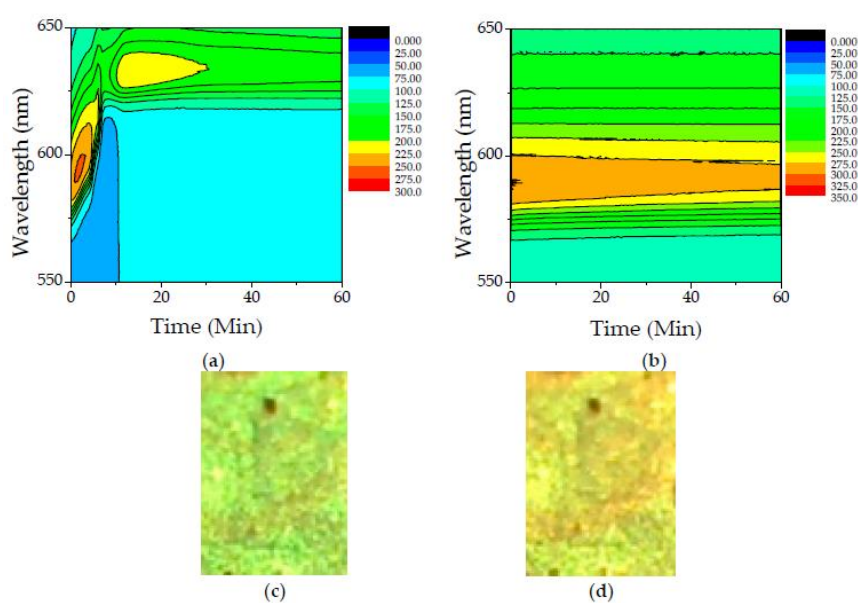
equation 1

where  $\lambda_{\max}$  is the maximum reflection (photonic band gap) peak's wavelength,  $d$  is the lattice constant,  $m$  is the order of diffraction,  $n_{\text{eff}}$  is the effective refractive index, and  $\theta$  is the angle at which the light is incident on the PhC [32]. The fact that many methods can be used to determine the effective refractive index is notable [32]. The literature reports a lot of different external stressors that have the power to modify PBG. Chemical, thermal, magnetic, biological, mechanical, optical, and electrical stimuli are a few prominent examples.

### **Chemical Stimuli**

The interaction between a soft structure (such as a hydrogel) and a specific chemical species is one of the most popular ways to tune the PBG using chemical approaches. For instance, the contact with ions may cause the soft structure to expand and contract, changing the geometrical characteristics of the PhC and shifting the photonic band gap [33–34]. Additionally, using this method will allow for the construction of pH sensors by detecting  $\text{H}^+$  ions [34]. A different category of chemically tuned PhCs entails the incorporation of porous materials, where the refractive index is modulated by the infiltration of vapors or liquids [32]. High-quality polystyrene (PS) 3D-PCs, also known as opals, with a filling factor  $f$  close to the ideal value of 0.74 were created by Burratti *et al.* (2018) and examined for their optical response in the presence of various concentrations of methanol (MeOH) vapor [35]. The reflectance spectra showed energy shifts when methanol was present in the photonic crystal voids. Due to a linear relationship between the vapor concentration and the maximum reflectance band wavelength, the concentration of methyl alcohol vapor can be deduced. We put the system's time stability and reversibility to the test. 5% (v/v0) was calculated as the limit of detection (LOD), where  $v$  was the volume of methanol and  $v_0$  was the total volume of the solution (methanol and water). At normal incidence ( $Q = 0$ ), the reflectance of PS photonic crystals was also investigated in the presence of various methanol/water vapor concentrations. For the case of pure methanol, Figure 1a depicts the color map of the reflectance peak as a function of time. The maximum red shift in this instance was roughly 48 nm and was attained quite quickly (about 10 min). After 30 minutes, the reflectance band's intensity (represented by the figure's color scale) reached a plateau. The creation of a thin coating of condensed methanol on the PC surface may have contributed to the first increase in reflectance. To evaluate the optical sensor's response in the

presence of high levels of humidity and determine whether water can alter the reflected signal, a similar analysis was also carried out for pure water. For pure water, Figure 1b shows the maximum reflectance as a function of time. Figure 1c depicts a snapshot of the sample surface taken before exposure to methanol vapor, while Figure 1d depicts the same spot taken after exposure to methanol vapor for one hour. Clearly, the color has changed. The change in colour may be explained using a capillary condensation model for intermediate and high methanol concentrations. In order to completely comprehend the surprising energy shift discovered for very high methanol content, a swelling process of the PS spheres was also invoked.



**Fig.1.** Color maps of the reflectance spectra as a function of time: (a) pure alcohol and (b) pure water (0% v/v0 methanol). Colors are proportional to the intensity (counts) of the reflected signal. Photographs of the sample surface without methanol (c) and after one hour of exposition to methanol vapor (d) [35]

Self-assembled polystyrene nanobeads were employed by Burratti *et al.* (2018) to create a photonic crystal that might serve as an optical sensor [36]. This device uses a change in the reflectance spectrum brought on by the condensation of vapours inside the PC pores to identify the presence of several alcohols (methanol, ethanol, isopropanol, 1-propanol, and n-butanol). In particular, we found a significant wavelength redshift of the reflectance peak, which we

attributed to the system's increased effective refractive index as well as the PS spheres' expansion brought on by the alcohols. The PCs demonstrated total reversibility with every tested solvent, indicating that they can be reused multiple times. Due to the PC's surface nanostructuring, which inhibits water from penetrating the pores, such systems responded to water rather poorly. We investigated how our systems responded to a mixture of water and ethanol based on these characteristics in an effort to use them as prospective breathalyzers. A LOD of 2% vEthan/vtot, or 1167 ppm, was demonstrated by PS photonic crystals to be capable of sensing varying concentrations of ethyl alcohol in diverse water/ethanol mixtures. The ease of the synthesis process and the low cost of production make these devices viable candidates for further study, even though this limit is fairly high in comparison to other commercial breathalyzers.

According to Fenzl *et al.* (2012), photonic crystal arrays built on PDMS can be used to visually detect the presence of nonpolar solvents like gasoline and possibly a large number of other hydrocarbons, such as n-hexane [37]. Solvents generate varying degrees of swelling (and consequent color shifts) in the sensor, depending on their polarity. Methanol induces a 5-nm shift in a sensor film that has been calibrated with humid air, whereas ethanol generates a 20-nm shift that can already be seen. PDMS oil and n-hexane, which are less polar solvents, cause significant longwave shifts (by 137 and 151 nm, respectively) (Table 1). It was also demonstrated that, in ethanol/water combinations, the peak wavelength of reflected light increases linearly with increasing ethanol concentration. The peak wavelength and ethanol content were shown to be fairly linearly related in previous research using ethanol and methanol mixes. Response times are as fast as 1 s here, and any signal changes are entirely reversible. In addition, it was discovered that unlike many fluorescence-based sensors, these polymer films are not photobleached. This explains why photonic crystal-based sensing is superior to indicator-based techniques.

**Table 1.** Reflected light of a thin film composed of polystyrene nanoparticles in polydimethylsiloxane in the presence of different solvents [37]

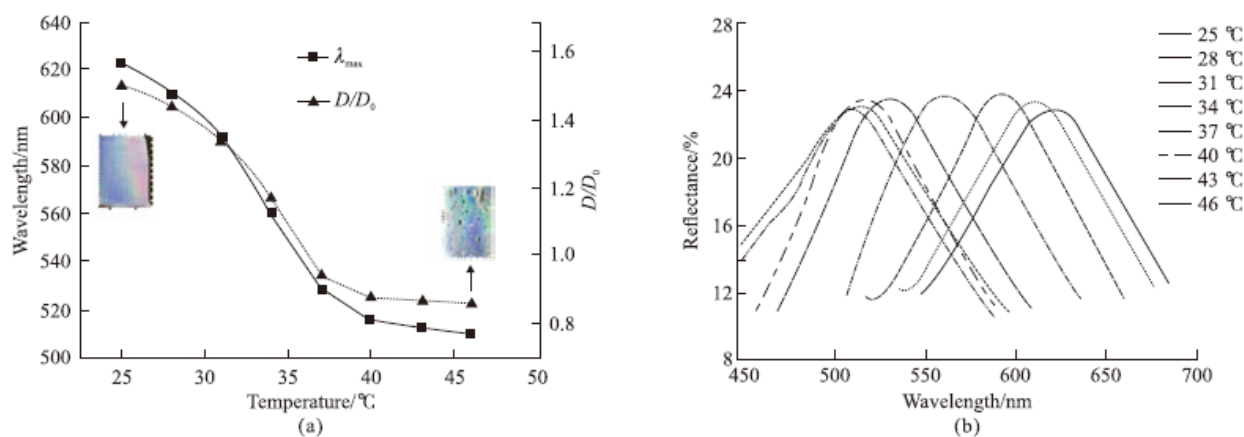
Solvent	Relative permittivity $\epsilon_r$	Swelling parameter $S$	Reflected wavelength/nm	Signal shift/nm
None	-	-	$420.6 \pm 0.7$	0
Water	78.36	1.00	$421.4 \pm 0.6$	0.8
Methanol	32.66	1.02	$426 \pm 4$	5
Ethanol	24.55	1.04	$440.9 \pm 1.4$	20
PDMS oil <sup>a</sup>	2.2	-	$557 \pm 2$	137
<i>n</i> -Hexane	1.88	1.35	$571 \pm 3$	151

<sup>a</sup> polydimethylsiloxane.

### Thermal Stimuli

The introduction of a temperature gradient makes it simple to adjust photonic crystals made from thermoresponsive materials, such as polymers or colloidal dispersions [38–39]. In order to create a thermally sensitive photonic crystal material, Zheng *et al.* (2021) formed a poly(*N*-isopropylacrylamide) (IONH<sub>PNIPAm</sub>) inverse opal nanocomposite hydrogel within the interstitial region of a polystyrene photonic crystal template [40]. The physically crosslinked nanocomposite hydrogels and PS photonic crystals have been combined for the first time to create the thermally responsive IONH<sub>PNIPAm</sub> films. The IONH<sub>PNIPAm</sub> films produced with this approach have a quick response time, strong mechanical stability, and self-healing capability. The manufactured IONH<sub>PNIPAm</sub> films feature beautiful color, thermoresponsiveness, and fluorescence properties. When the temperature increases from 25 °C to 46 °C, the observed phenomena or results show that the IONH<sub>PNIPAm</sub> films' Bragg diffraction wavelength will change to the blue (Figure 2). While the temperature fluctuates between 25 °C and 46 °C, the IONH<sub>PNIPAm</sub> films show outstanding cycle stability. Additionally, the IONH<sub>PNIPAm</sub> films have the ability to rapidly decrease Ag<sup>+</sup> in sunlight and generate bright blue fluorescence when excited by UV light (365 nm). They can therefore be used in the detection of Ag ions. This stimuli-responsive photonic crystal materials based on physically cross-linked inverse opal nanocomposite hydrogels with fast response and good mechanical stability are promising for applications in the fields of smart optical detectors, thermal-responsive sensors, and fluorescent sensing devices. They differ from chemically cross-linked IOH in that they have better mechanical stability and a faster response time.





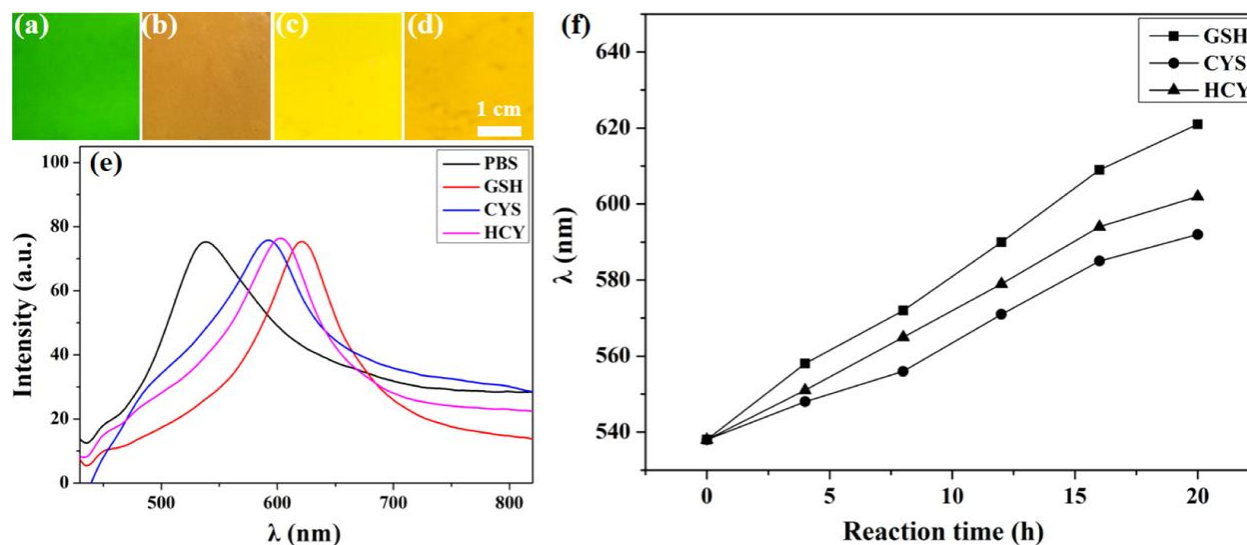
**Fig.2.** The peak wavelength of IONH<sub>PNIPAm</sub> from the Bragg diffraction spectrum and relative swelling ratio of IONH<sub>PNIPAm</sub> in different temperatures deionized water(a), and Reflectance spectra of IONH<sub>PNIPAm</sub> at different temperatures(b) [40]

When compared to prior investigations [41], El-Amassi *et al.* (2018) got a significantly greater peak shift employing a polystyrene polymeric material as a working layer. For instance, Banerjee (2009) discovered that a ternary photonic crystal can produce a peak shift of 0.355 nm while a binary photonic crystal may produce a peak shift of 0.350 nm. Bi<sub>4</sub>Ge<sub>3</sub>O<sub>12</sub> serves as the working layer in his ternary photonic crystal [42]. Although Banerjee (2009) achieved an intriguing outcome, it is still incomparable to El-Amassi *et al.* works. According to El-Amassi *et al.* (2018), the Si/polymer/SiO<sub>2</sub> structure of the ternary photonic crystal was proposed. At various temperatures, the transmission profile of this photonic structure was studied. It was discovered that as temperature rises, the transmission peak moves toward longer wavelengths. Thermo-optic and thermal expansion coefficients are responsible for this. A transmission peak shift of 0.368 nm per degree rise in temperature was obtained when the polymer "polycarbonate" was used, but a transmission peak shift of 0.380 nm per degree rise in temperature was obtained when the polymer "polystyrene" was used. It is found that the inclusion of the polymer layer between Si and SiO<sub>2</sub> to form a ternary photonic crystal significantly increases the temperature-sensitive transmission peak shift. A ternary photonic crystal made of Si, polymer, and SiO<sub>2</sub> would require a challenging N-period sputtering, spin coating, and sputtering process, it is worth highlighting. Future research may focus on identifying alternate transparent inorganic materials with the right characteristics.



## Bio-Stimuli

Photonic crystals can be easily functionalized with appropriate recognition groups that allow for the detection of specific biomolecules. Due to the change in color, colorimetric detection is quick and easy [43]. These sensors change their optical properties not only when in contact with classical biomolecules like sugars, creatinine or glucose, but also larger ones such DNA [44-45] and proteins [32]. Intracellular thiols (e.g., cysteine, homocysteine, and glutathione) play critical roles in biological functions. Glutathione is the most abundant cellular thiol which is important for preserving redox homeostasis in biosystems. By combining the self-assembly of monodisperse carbon-encapsulated Fe<sub>3</sub>O<sub>4</sub> nanoparticles (NPs) and in situ photopolymerization, Jia *et al.* (2019) demonstrated the construction of responsive photonic crystals (RPCs) for the selective detection of thiol-containing biomolecules [46]. Typically, a cross-linking agent with disulfide bonds was used to create the polyacrylamide-based PCs. It's interesting to note that the unique chemical reaction between thiol-containing biomolecules and disulfide bonds causes a reduction in the RPCs' degree of cross-linking, which causes the hydrogel to swell and the NP lattice spacing to increase. By detecting the diffracted wavelength or visually witnessing the structural color shift, the reduced glutathione ( $10^{-6}$  to  $10^{-2}$  mol/L) can be identified (Figure 3). Because different thiol-containing biomolecules react with disulfide bonds at different rates, the RPCs can also be used to identify various types of thiol-containing biomolecules by a simple color variation. This work offers a straightforward but efficient method for visualizing the identification of the thiol-containing biomolecules.



**Fig.3.** (a–d) Photographs and (e) corresponding reflection spectra of the RPCs at a fixed detection angle ( $90^\circ$ ) in (a) PBS solution (pH = 6.8), PBS solution containing  $10^{-3}$  mol/L (b) GSH, (c) CYS, or (d) HCY for 20 h, respectively. The scale bar in (d) applies to the others. (f) Diffraction wavelength of the RPCs treated in the aqueous solution containing  $10^{-3}$  mol/L GSH, CYS, or HCY for different durations [46]

A unique electrode based on GPCs with a low triggering potential was created for the first time for micromolecule detection in a distinct study by Wang et al. (2021) [47]. The monolayer photonic crystals that made up the GPC electrodes were created using PS spheres, and they also contained Au nanoparticles. In this work, photonic crystals nanomembrane played three distinct roles: (1) the surface of PS spheres can immobilize proteins due to the hydrophobic characteristics of polystyrene; (2) the monolayer-like photonic crystals structure self-assembled by PS spheres can enhance ECL intensity due to its light scattering effectiveness; and (3) GPCs electrodes made of photonic crystals and Au nanostructures integrated in the photonic crystals significantly lowered the triggered potential of the typical ECL. As a result, rather than the  $\text{Ru}(\text{bpy})_3^{2+}$  -COOH luminescent group, the common reactant TPrA was oxidized to start the ECL emission of the luminophore. The GPCs electrode-based ECL sensor had a starting potential of 0.95 V (vs SCE), which was about 300 mV lower than the potential of the  $\text{Ru}(\text{bpy})_3^{2+}$  -COOH electrochemical oxidation at the beginning of ECL. In the area of ECL analysis and detection, the decreased working potential provides many benefits. First off, a lower operating potential can prevent oxidation products from interfering with processes due to side

effects brought on by a high potential. Additionally, it lessened the oxidation of the electrode surface, which decreased electrode interference. The presence of hydroxide ions in the water phase can also cause the low triggered potential to lower the ECL background. Last but not least, it can lessen the electrochemical harm that can be done to delicate biomolecules and oligonucleotide sequences. A tetracycline immunity model was successfully built at the same time, demonstrating the viability and sensitivity of GPCs electrodes. This low triggered potential ECL method has the potential to address a number of issues brought on by high ECL potentials, taking into account the importance of GPCs electrodes in the field of analysis.

### 3. CONCLUSION

In this paper, noteworthy recent research on polystyrene-based photonic crystals that are chemically, thermally, and biologically sensitive was evaluated. These structures enable the transformation of an external stimulus into an instantly recognizable optical response, and they are often produced by means of straightforward and economical procedures. Due to their potential use in a variety of applications, including sensing, display, and lighting, these features have captured the interest of both the scientific community and business.

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