

Chapter 1

Ordered Responsive Materials for Sensing Applications

Qiang Matthew Zhang, Siyuan Guo, Jiaqi Duan and Michael J. Serpe

Abstract Detection of small molecules, macromolecules, and biomolecules is of utmost importance for protecting human health and ensuring our well-being. Therefore, a tremendous amount of research goes into the development of novel sensing motifs with increased sensitivity and selectivity to analytes, with very short analysis times, and ease of usability. Of these technologies, 1D, 2D and 3D ordered materials receive a lot of attention due to low cost and visual color change in presence of analytes. These materials were composed of a close packed array of particles or nanocavities, which are capable of interacting with wavelengths of light in the visible region. These interactions lead to constructive and destructive interference of the light in the assembly, resulting in specific wavelengths of light being reflected. Analytes cause shrinking or swelling of these materials and a concomitant change in the critical dimensions of the materials optical components, yielding color changes. This is very convenient, as the naked eye can be used as the “detector”. In this review, we cover many examples of 1D, 2D and 3D ordered materials for sensing applications, ending with examples of other significant sensing technologies.

1.1 Introduction

The beautiful and vivid colors of many objects found in nature (e.g., beetles, butterflies, and the opal gemstone) have fascinated many for ages. Unlike many other colored materials found in nature, which exhibit color due to the absorbance of light by small molecule chromophores, the examples above exhibit color as a result of light interacting with components of the material’s structure and resulting constructive and destructive interference. For example, opal gemstones are composed of an ordered

Q.M. Zhang · S. Guo · J. Duan · M.J. Serpe (✉)
Department of Chemistry, University of Alberta, Edmonton, AB T6G 2G2, Canada
e-mail: michael.serpe@ualberta.ca

© Springer International Publishing Switzerland 2016
M.J. Serpe et al. (eds.), *Photonic Materials for Sensing, Biosensing and Display Devices*, Springer Series in Materials Science 229,
DOI 10.1007/978-3-319-24990-2_1

close packed array of particles (typically silica), which are capable of interacting with visible wavelengths of light (via reflection/refraction/diffraction), leading to constructive/destructive interference, and their brilliant visual colors [1]. More generally, when light impinges on a material with refractive index periodicity, it is reflected/refracted/diffracted from each of the structure's interfaces. This light, under suitable conditions, interferes constructively/destructively and reflects/transmits certain wavelengths of light according to the well-known Bragg equation, modified for photonic crystals, as given [2–5]:

$$m\lambda = 2nd \sin \theta \quad (1.1)$$

where m is the diffraction order, λ is the wavelength of the reflected light, n is the mean refractive index of the periodic structure, d is the lattice period of the crystalline direction of propagation of light, and θ is the angle between the incident light and diffraction crystal planes.

Structured photonic materials can be classified as one-dimensional (1D), two-dimensional (2D), or three-dimensional (3D), depending on if the periodicity of their structure is in 1D, 2D, or 3D, respectively. Structured photonic materials play an important role in telecommunications [6], information processing and storage [7], solar cells [8], and other important applications [9]. Furthermore, chemical and biological sensors with visual color readouts can be developed by combining photonic materials with stimuli-responsive materials that change conformation in response to external stimuli such as pH [10, 11], ionic strength [12], solvent [13], vapors [14], temperature [15], and light [16]. In this review, we highlight the most relevant examples of structured photonic materials (photonic crystals) and devices for sensing applications. The general approach is based on the ability of species of interest (analyte) to induce changes in the spacing and/or refractive index of the structural elements of the devices [17, 18]. These changes together lead to observable optical property changes, i.e., color changes. Compared with complicated analytical instruments that can be used for sensing, structured photonic materials exhibit many advantages as sensors including: their low cost, ease of signal readout (a visual color change), and simple operation.

1.2 One-Dimensional Ordered Materials

In recent years, due to the development of simple bottom-up techniques, various functional one-dimensional ordered materials (1DOMs) were fabricated [19]. 1DOMs are typically layered structures, the layers being composed of materials with different refractive indices. One of the most common examples of 1DOMs is a Bragg stack typically used for light filtering applications. 1DOMs can also be fabricated from materials that are sensitive to their environment, i.e., they change dimensions as a function of the environmental conditions. These materials exhibit the very interesting and useful ability to change color; the color can be indicative of

their surroundings. Recently, a variety of materials have been used to prepare functional and responsive 1DOMs such as inorganic materials [20], organic/inorganic hybrid materials [21], and polymer or organic materials [22].

In one example, $\text{SiO}_2/\text{TiO}_2$ 1DOMs were prepared by alternatively exposing a surface (glass or silicon) to solutions of $\text{Si}(\text{OEt})_4$ and TiCl_4 via dip-coating, followed by curing/solidification of the layers via controlled thermal treatments to form $\text{SiO}_2/\text{TiO}_2$ layers [20]. As can be seen in Fig. 1.1, alternate deposition of two types of mesoporous layers (presenting different framework composition and/or porosity) gives rise to the desired one-dimensional periodicity in the z-dimension. The sequence of deposition and treatments is essential to obtain ordered 1DOMs with substantial porosity. After thermal treatment, the pore structures are interconnected with neighboring pores, resulting in the accessibility and transport of host molecules. The authors then used the devices for sensing applications, using them to detect dihexadecyl phosphate (DHDP), which selectively binds to the

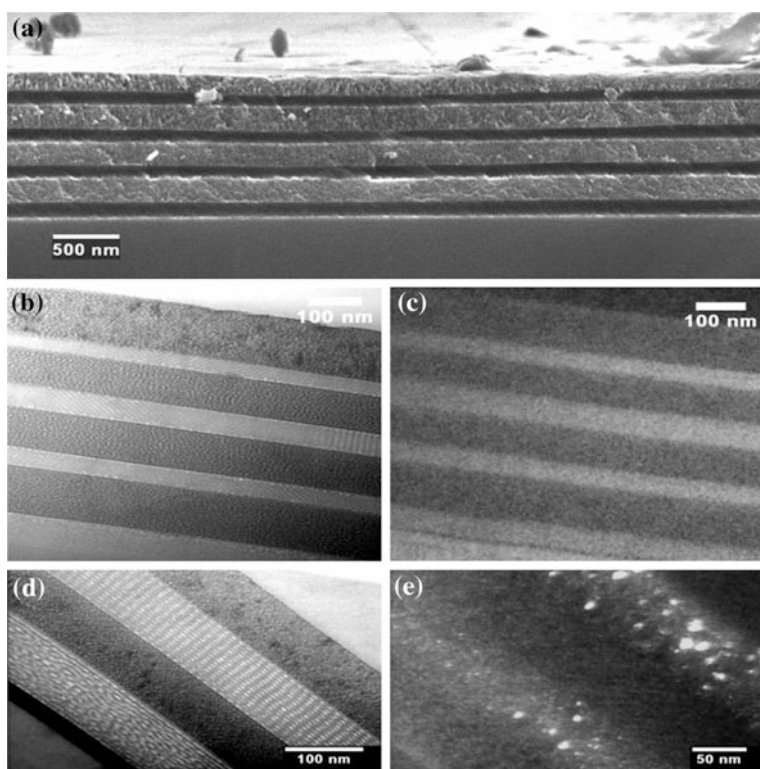


Fig. 1.1 Electron microscopy images of mesoporous Bragg multilayers. **a** FESEM, **b** TEM, and **c** energy-filtered mapping analysis of an 8-layered Bragg reflector, $4 \times (\text{SF-TF})$; dark grey Ti, light grey Si. **d** TEM of a $2 \times (\text{SF-TB})$ multilayer (see the experimental section for terminology), showing two ordered mesophases with different pore size. **e** Dark-field image of sample presented in (d); crystalline anatase domains are observed as *bright spots*. Reproduced with permission [20]

titania sites. Once DHDP enters the ordered mesopores of the material, it increases the refractive index of the titania layer. That leads to a dramatic change in the device's optical properties, as shown in Fig. 1.2.

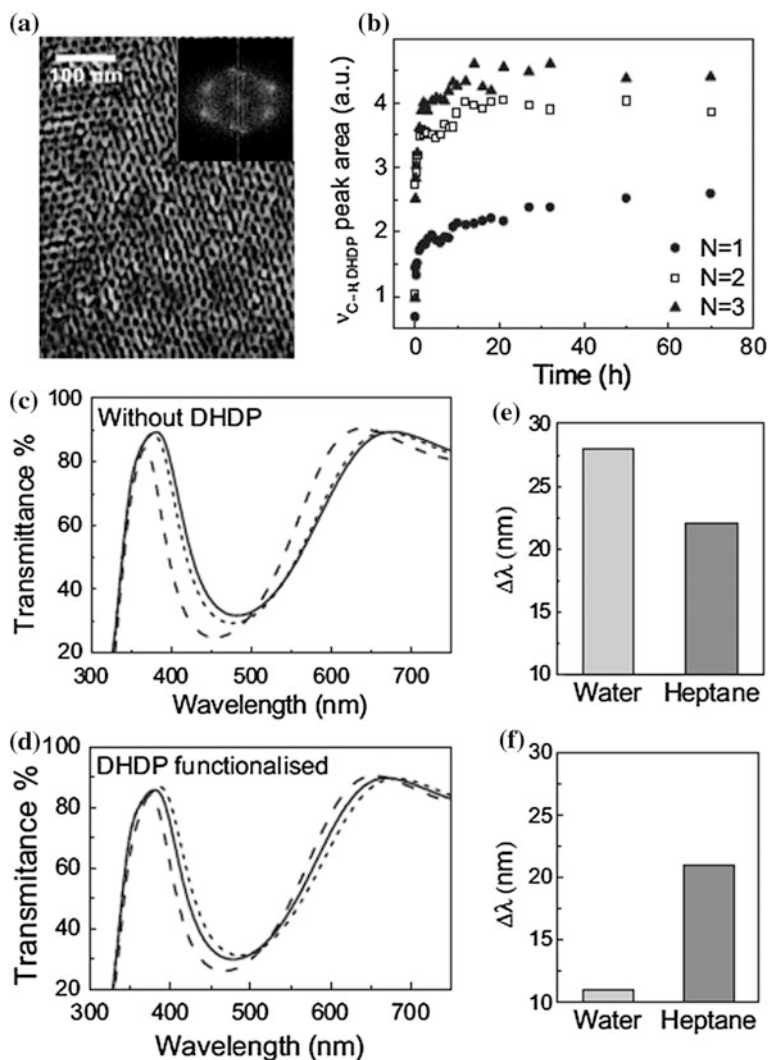


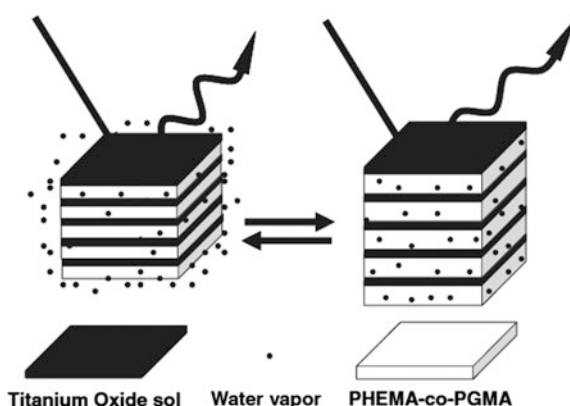
Fig. 1.2 Analysis of accessibility and the effect of functionalization on the optical response. **a** FESEM top view of the most external layer of a $4 \times$ (SF-TF) multilayer showing the presence of ordered open pores on its surface. The *inset* corresponds to the Fourier transform of the image. **b** Kinetics of DHDP molecule uptake for multilayers of the same composition possessing a different number of layers. **c** Transmission spectra of $3 \times$ (SF-TB) pristine stack (dashed line); same multilayer after immersion in water (solid line), and heptane (dotted line). **d** Same optical measurements for a DHDP-functionalized mesoporous $3 \times$ (SF-TB) stack. **e, f** Bar graph showing the different Bragg diffraction shifts obtained for the pristine and DHDP-functionalized mesoporous multilayers shown in (c, d). Reproduced with permission [20]

In another example, an organic/inorganic hybrid 1DOM was prepared by alternate deposition of titania sol and poly(2-hydroxyethylmethacrylate-co-glycidyl methacrylate) (PHEMA-co-PGMA) films via spin coating (Fig. 1.3) [23]. Their optical properties were tuned by changing the number, and thickness, of the layers. By changing the spacing and/or the refractive index of the layers, the devices can interact with the entire visible spectral range. Due to the interaction of PHEMA-co-PGMA with water vapor, the 1DOMs can be used as a sensor for environmental humidity, changing color over the full spectral range as humidity is varied (Fig. 1.4). Specifically, at high humidity the color of the 1DOM was red, which changes to blue at low humidity. It was shown that this behavior could be repeated more than 100 times (Fig. 1.4).

Polymeric 1DOMs can also be fabricated using polyelectrolyte multilayers with alternating porosities, i.e., porous and less porous materials [24]. Layers were prepared via assembly of poly(acrylic acid) (PAA), poly(allylamine hydrochloride) (PAH), and poly(sodium 4-styrenesulfonate) (SPS) in specific combinations, which exhibit reflectivity bands in the visible region of the spectrum. This system was used to detect various solvent vapors, and the data is shown in Fig. 1.5. The change in the device's optical properties upon exposure to the various vapors is a result of selective solvation of the layers, leading to swelling/deswelling of the assembly, and the concomitant optical response (both a wavelength shift and a change in transmitted light intensity). As can be seen in Fig. 1.5, exposing the devices to saturated vapors of either water, ethanol, acetone, or toluene, yields a decrease in the reflectivity of the devices, and a shift of the transmitted peak to longer wavelengths.

Another class of 1DOMs was prepared via self-assembly of block copolymers into lamellar stacks, which consist of alternating layers of nonswellable glassy layers and swellable gel layers. The swelling of gel layers by some solvents can cause an increase in the distance between the glassy layers, and a change of the layer's

Fig. 1.3 Schematic of organic/inorganic hybrid 1DOMs generated by alternated spin-coating of titania sol and PHEMA-co-PGMA. Reproduced with permission [23]



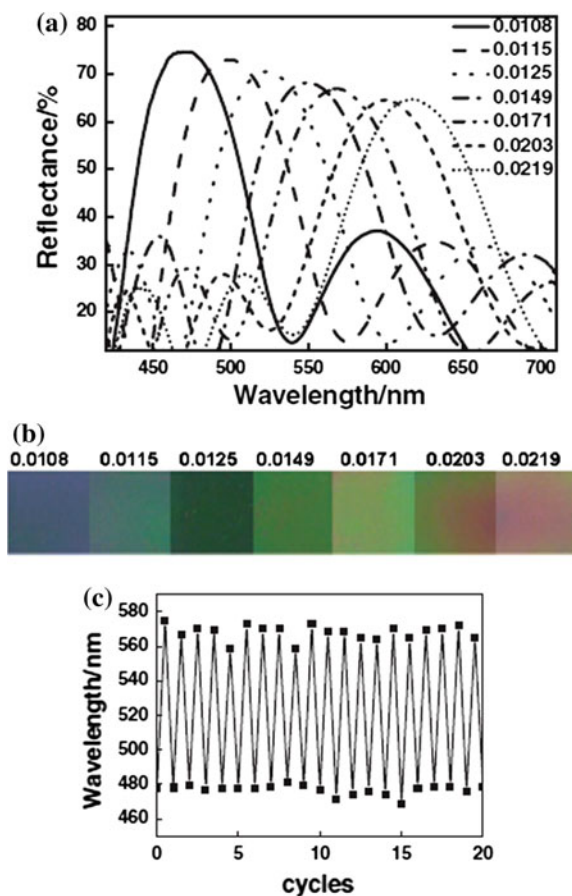


Fig. 1.4 **a** Sensitivity of the 1DOMs towards water vapor; **b** color variation of the 1DOMs with water-vapor concentration; **c** swelling–deswelling cycles of the 1DOMs with water-vapor concentration at 0.0177. The total number of layers is ten. Reproduced with permission [23]

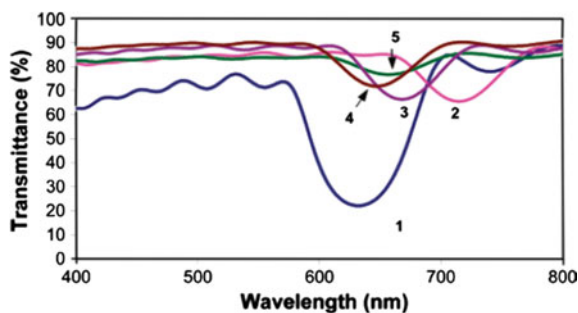


Fig. 1.5 Transmittance spectra of a treated $[(\text{PAH}/\text{PAA})_8-(\text{PAH}/\text{SPS})_{50}]_9$ film in air (1) and after exposure to water (2), ethanol (3), acetone (4), and toluene (5) vapors. Reproduced with permission [24]

refractive index, which results in strong reflectivity change and a shift of the stop-band position to longer wavelengths (Fig. 1.6) [22]. The block copolymer can be quaternized using iodomethane, which was used as a colorimetric humidity sensor.

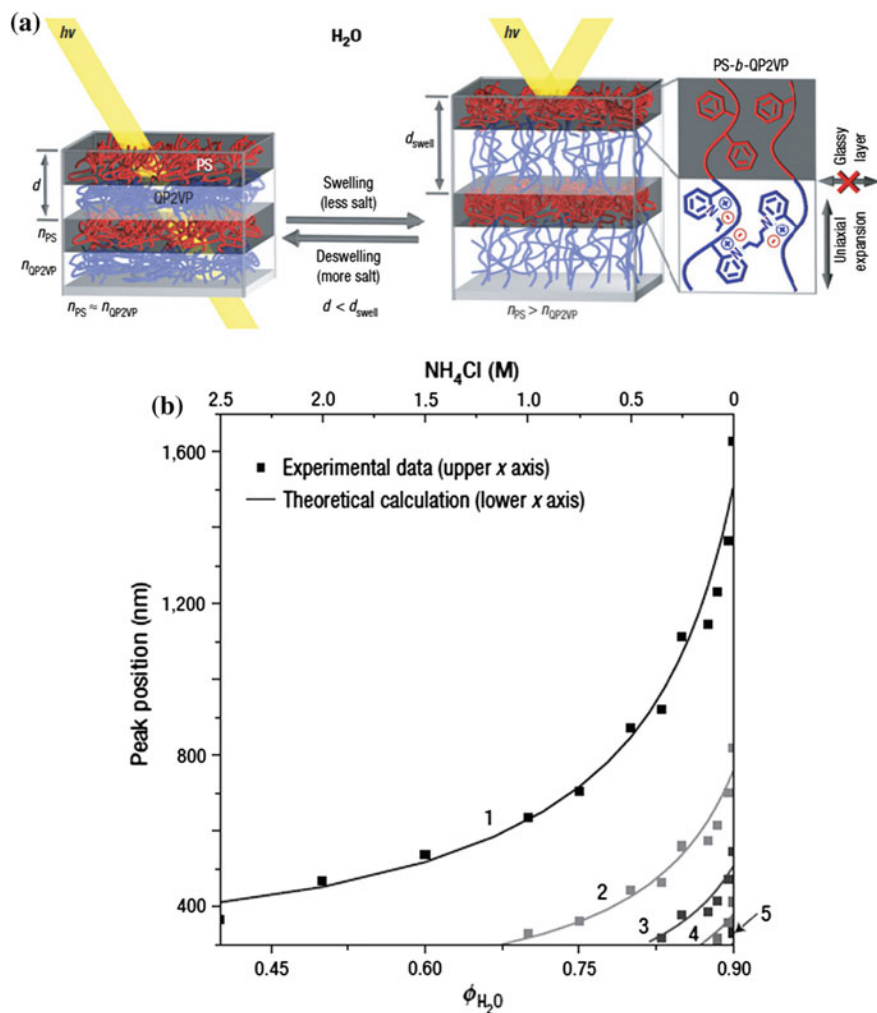


Fig. 1.6 **a** Schematic diagram of the structure of photonic gel film and the tuning mechanism. The photonic gel film was prepared by self-assembly of a diblock copolymer (PS-*b*-QP2VP). Swelling/deswelling of the QP2VP gel layers (blue) by aqueous solvents modulates both the domain spacing and the refractive-index contrast, and accordingly shifts the wavelengths of light reflected by the stop band. The hydrophobic and glassy polystyrene layers (red) limit expansion of the gel layers to the direction normal to the layers. **b** The change of stop-band position by approximately 575 % from 364 to 1627 nm as a function of the NH_4Cl concentration (symbols), or versus ϕ_{H_2O} (solid line) for each band. Reproduced with permission [22] (Color figure online)

Its sensitivity and dynamic range can be modulated by varying the pyridinium's counter ion or by varying the molecular weight of the block copolymers [25].

The Serpe group recently showed that layered poly(N-isopropylacrylamide) (pNIPAm) microgel-based materials could be used to sense pH, glucose, proteins and DNA [26–33]. These devices were constructed by “painting” responsive microgels onto an Au coated glass substrate [27]. Following further treatment, another Au layer was deposited onto the microgel layer. As can be seen in Fig. 1.7, [29] this yields a mirror-dielectric-mirror structure akin to a classic Fabry–Perot etalon. When the device is immersed in water, the microgels swell and separate the Au layers from one another. Light impinging on the structure can enter the microgel-based cavity and resonate between the two Au layers, which results in specific wavelengths of light being reflected/transmitted according to the following equation:

$$m\lambda = 2nd \cos \theta \quad (1.2)$$

where λ is the wavelength maximum of the peak(s), m is the peak order, n is the refractive index of the dielectric, d is the spacing between the mirrors, and θ is the angle of incidence [26]. A reflectance spectrum from a representative etalon can be seen in Fig. 1.7.

Many functional groups, such as carboxylic acid, amine, and boronic acid groups, were incorporated into the microgels. In one example, carboxylic acid groups were deprotonated at high pH, which led to microgel swelling due to Coulombic repulsion in the microgel network, as well as osmotic swelling [29]. The swelling of the microgels increased the distance between the mirrors, which leads to a change of the visible color of the devices, and a red shift in the position of the peaks in the device reflectance spectrum. The optical properties of spatially isolated regions of a single etalon can be changed independently in response to pH, as can be seen in Fig. 1.8 [29].

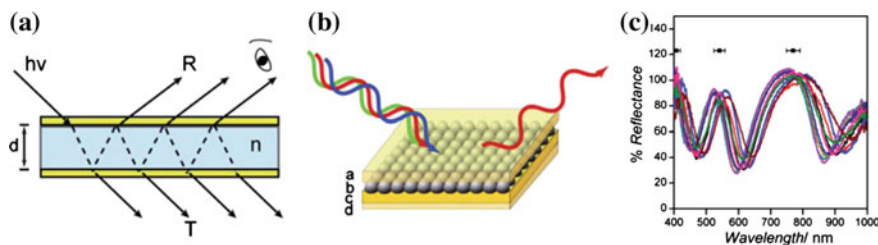


Fig. 1.7 **a** Schematic of a traditional Fabry-Perot etalon (d , distance between two mirrors; n , refractive index of the dielectric). **b** Schematic structure and proposed mechanism for our poly (N-isopropylacrylamide) microgel based etalons fabricated by sandwiching **(b)** a microgel layer between **(a, c)** two reflective Cr/Au surfaces, all on **d** a cover glass. **c** Reflectance spectra for an etalon immersed in pH 3.0 solution at 25 °C at 10 randomly chosen regions. The data points above each peak are the average peak positions and associated standard deviations for the respective peaks in the 10 individual spectra. Reproduced with permission [29]

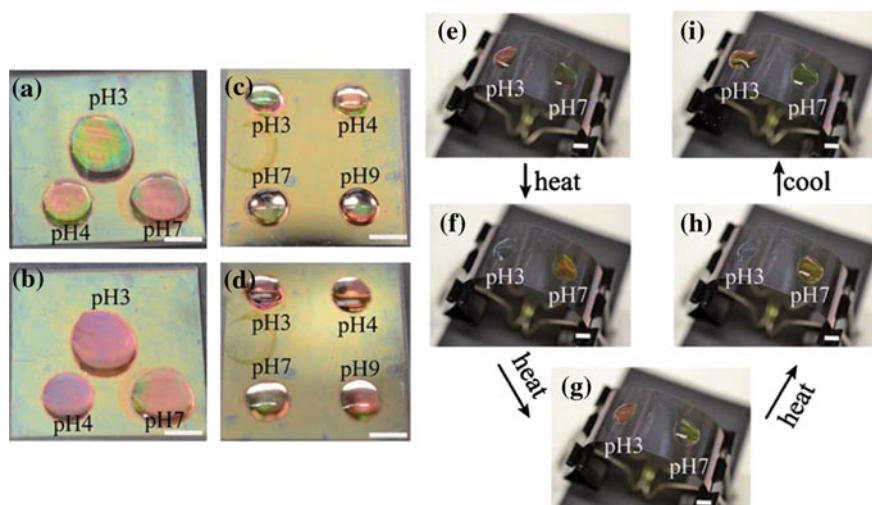


Fig. 1.8 Photographs of an etalon with solutions of various pH spotted on a single surface (**a, c, e, i**) 25 °C and (**b, d, f, g, h**) 37 °C. **f** 3 min after heating; **g** 5 min after heating; **h** 6 min after heating. In each panel, the scale bar is 5 mm. Reproduced with permission [29]

The devices were also used to sense glucose [34]. To accomplish this, microgels modified with 3-aminophenylboronic acid (APBA) were synthesized. In a basic buffer the boronic acid moieties on the APBA ($pK_a = 8.2$) were hydroxylated such that the boron possesses a negative charge (Fig. 1.9). The binding of glucose is favored for boronic acids in the charged state. As glucose binds, more boronic acid groups must convert to the charged state in order to maintain the equilibrium. In the presence of glucose, the bound state is preferred promoting more hydroxylation of the boron atoms into a charged form, leading to an increase in the Coulombic repulsion inside the microgel, which results in a swelling response. In the etalons this will be observed as a red shift, according to (1.1).

The Serpe group has also shown that etalons could be used for biosensing application [35]. In an early study, they showed that biotinylated polycationic polymer can penetrate through the Au overlayer of an etalon resulting in the collapse of a negatively charged microgel layer (due to electrostatics-mediated crosslinking), and a blue shift of the reflectance peaks. The extent of the peak shift depended on the amount of biotinylated polycation added to the etalon; high polycation concentration yielded a large shift, and vice versa. This phenomenon was exploited to sense the concentration of streptavidin in solution at μM concentrations, as detailed in Fig. 1.10. To accomplish this, the polycation, poly(allylaminehydrochloride) (PAH) was modified with biotin. Excess amounts of PAH–biotin were exposed to various amounts of streptavidin leaving behind specific amounts of unbound PAH–biotin—the amount of PAH–biotin unbound is inversely related to the streptavidin concentration. Biotin modified magnetic particles were added to the solution, which bound to the PAH–biotin–streptavidin complex, and an

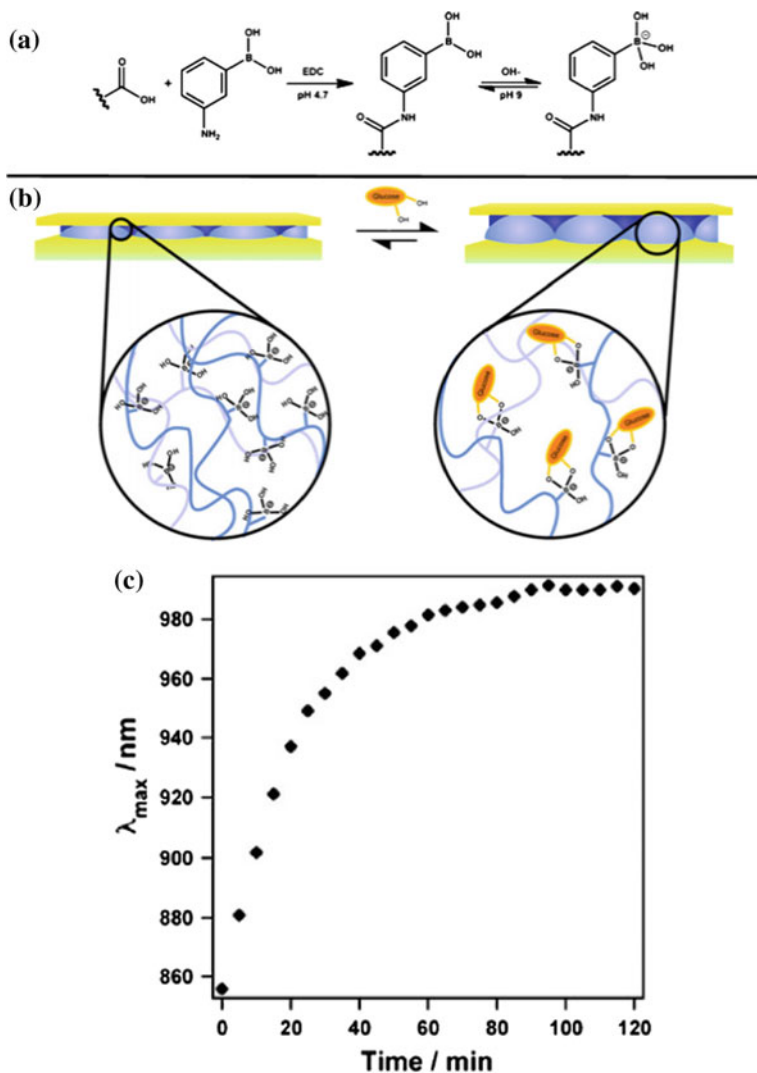


Fig. 1.9 Reaction scheme for **a** the functionalization of the acrylic acid moieties on the microgel with 3-aminophenylboronic acid (APBA) followed by the activation of the boronic acid with base, **b** a cartoon depiction of the glucose responsivity of an APBA functionalized microgel etalon at pH 9, **c** the peak position for the most red-shifted peak is plotted as a function of time after glucose introduction. Total spectral shift is 134 nm. Reproduced with permission [34]

external magnet was used to remove the magnetic particles bound with PAH–biotin–streptavidin from the solution. The solution containing the excess, unbound PAH–biotin was subsequently added to the pNIPAm-co-AAc etalon stabilized in pH 7.2 solution. The PAH–biotin was able to penetrate the etalon and crosslink the

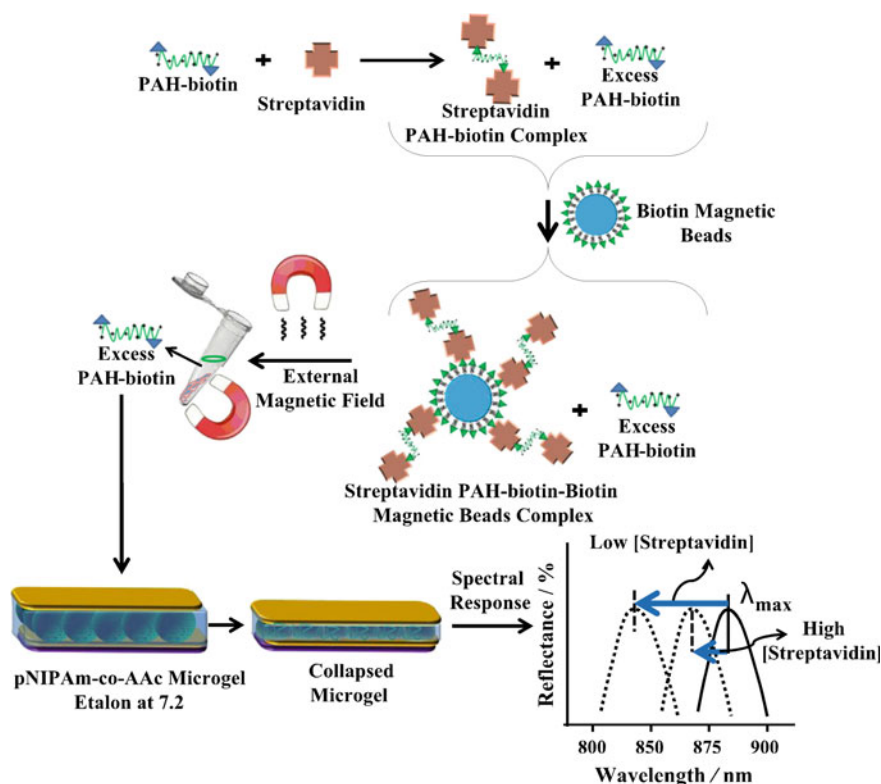


Fig. 1.10 Streptavidin (the analyte) is added to an excess amount of biotin-modified poly (allylamine hydrochloride) (PAH). The streptavidin-biotin-PAH complex is then removed from solution using biotin modified magnetic particles, leaving behind free, unbound PAH. The unbound PAH is subsequently added to a pNIPAm-co-AAc microgel-based etalon immersed in aqueous solution at a pH that renders both the microgel layer and the PAH charged. As a result, the etalon's spectral peaks shift in proportion to the amount of PAH-biotin that was added. This, in turn can be related back to the original amount of streptavidin added to the PAH-biotin. Reproduced with permission [35]

microgels, causing them to collapse resulting in a blue shift of the etalon's spectral peaks (Fig. 1.10). As can be seen, in this concentration range, the extent of the blue shift depends linearly on the amount of PAH-biotin added to the etalon, which can be easily related to the amount of streptavidin in initially added to the PAH-biotin. Etalons of this type are very interesting because unlike most biosensors, a large signal is obtained for low analyte concentration, as can be seen in Fig. 1.11 [35].

The Serpe group has also shown that etalons can be used to detect μM concentrations of target DNA in solutions [32]. This is a direct result of the polyanionic nature of DNA, and its penetration into the microgel layer of etalons composed of positively charged microgels. Specifically, when the DNA interacts with the positively charged microgels, electrostatic crosslinking results, causing the microgel

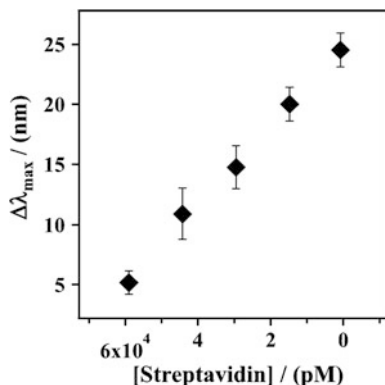


Fig. 1.11 Cumulative shift of the etalon's reflectance peak upon addition of the indicated amounts of streptavidin to PAH–biotin 100:1. The pNIPAm-co-AAc microgel-based etalon was soaked in pH 7.2 throughout the experiment, while the temperature was maintained at 25 °C. Each data point represents the average of at least three independent measurements, and the error bars are the standard deviation for those values. Reproduced with permission [35]

layer to collapse, leading to a shift in the position of the reflectance peaks to lower wavelength. The extent of shift can be related to the concentration of target DNA present in the sample solution, as shown in Fig. 1.12.

Recently, the Serpe group prepared etalons from lipase loaded microgels (also containing pyridine) that were capable of sensing triglyceride concentration [36]. The lipase inside of the microgels can degrade triglyceride into glycerinum and fatty acid, which could attach to the microgels by acid-base reaction with pyridine

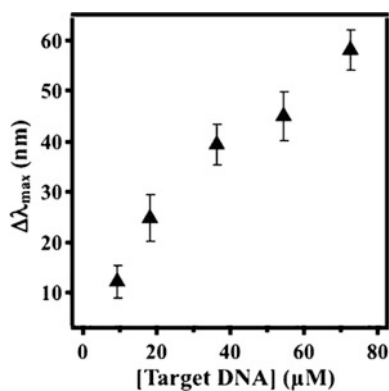


Fig. 1.12 Shift of a reflectance peak for a pNIPAm-co-APMAH etalon upon addition of separated TDNA solution of different concentrations. The pNIPAm-co-APMAH microgel-based etalon was soaked in pH 7.2 solution throughout the experiment, while the temperature was maintained at 25 °C. Each point in the plot represents the average of at least three independent measurements, and the error bars are standard deviation for those values. A new device was used for each experiment. Reproduced with permission [32]

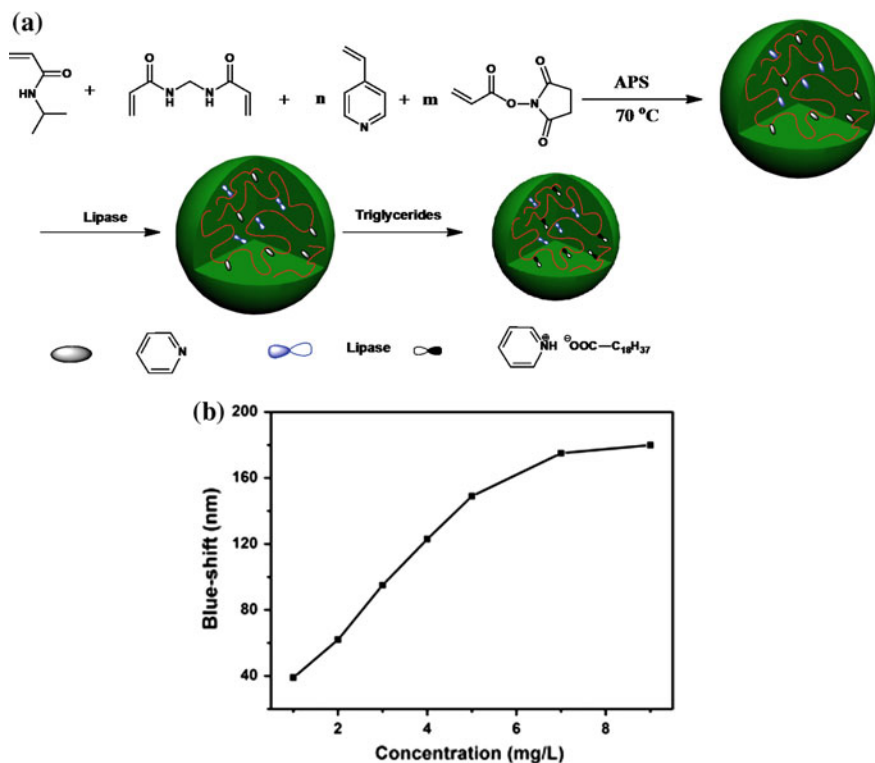


Fig. 1.13 **a** Microgel synthesis scheme; **b** blue-shift as function of triglyceride concentration. Reproduced with permission [36]

(Fig. 1.13). The introduction of fatty acid into microgels increased hydrophobicity of microgels, resulting in their collapse and a concomitant blue-shift in peaks of the reflectance spectrum. As can be seen in Fig. 1.13, the extent of the blue-shift depended on triglyceride concentration [36].

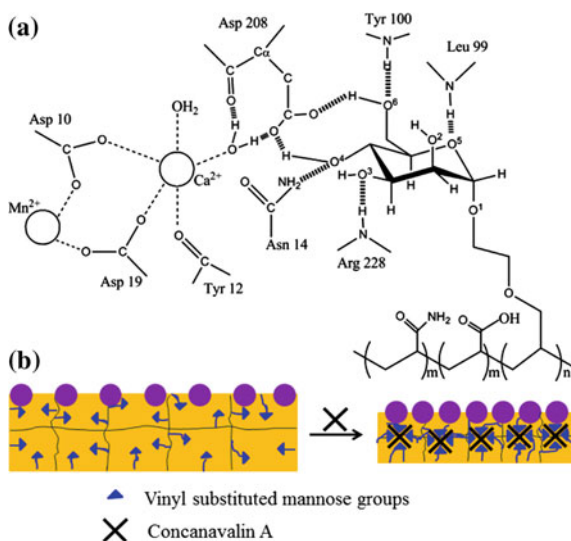
1.3 Two-Dimensional Ordered Materials

Two-dimensional ordered materials (2DOMs) possess structural periodicity in two spatial directions [37]. Generally, they are prepared using top-down methods such as photolithography, etching techniques and chemical methods [1]. Here, we mainly focus on 2DOMs prepared by chemical methods. 2DOMs diffract light at wavelengths that depend on their 2D array element spacing. These 2DOMs have been developed for the visual determination of pH, ionic strength, charged surfactants, and proteins in aqueous media [37].

Carbohydrate-functionalized 2DOMs were fabricated by attaching polystyrene (PS) particles onto a hydrogel surface (Fig. 1.14) [38]. Lectin–carbohydrate interactions create hydrogel crosslinks that collapse the hydrogel, which decreases the 2D particle spacing. This mannose containing 2D photonic crystal sensor detects Concanavalin A (Con A) through shifts in the 2D diffraction wavelength. Con A concentrations can be determined by measuring the diffracted wavelength or visually determined from the change in the observed visual color. Figure 1.15 shows the dependence of the diffraction wavelength maximum of the 2DOMs sensor as a function of the Con A concentration. In the absence of Con A, the 2D array diffraction maximum occurs at 600 nm. The diffraction wavelength blue shifts with increasing Con A concentrations; at 2 mg/mL, the diffraction blue shifts to 554 nm. The inset photograph in Fig. 1.15 clearly shows the visual color changes as a function of Con A concentration. Thus, Con A concentrations can be roughly determined by visually observing color changes of the sensor. The 2D photonic crystal sensors are completely reversible and can monitor Con A solution concentration changes. The detection limit for Con A was determined to be 0.02 mg/mL (0.7 μ M).

A stimuli-responsive 2DOM made of a polyelectrolyte gel with an monolayer inverse opal structure was developed [39]. To prepare these 2DOMs, a monolayer of a PS colloids was first assembled into an ordered array on a glass or silicon substrate, onto which a solution of quaternized poly-(2-vinyl pyridine) (qP2VP) was spin-coated. The PS monolayer was then selectively removed by dissolution in toluene. Finally, a mechanically stable inverse opal 2DOMs was obtained after thermal crosslinking at 120 °C. Figure 1.16 shows the SEM images of a 2DOM prepared by using a monolayer of close packed PS spheres with 470 nm diameter. From the SEM images, it can be seen that a thin layer covers the void spaces, and

Fig. 1.14 Mechanism of **a** Con A attachment to mannose attached to hydrogel. **b** Shrinkage and particle spacing decrease in Man-1 hydrogel sensor that results from Con A binding. Reproduced with permission [38]



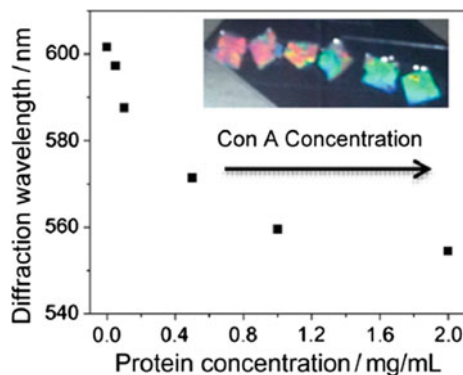


Fig. 1.15 Dependence of normalized diffraction spectra of the 2DOMs mannose hydrogel sensors upon Con A concentration in 0.1 M NaCl aqueous solutions that contain 1 mM Ca^{2+} and 0.5 mM Mn^{2+} . Reproduced with permission [38]

replicates the hexagonal packing of the opal monolayer that was initially present. The critical dimension of the resulting 2DOMs depends on the diameter of the template PS spheres. The evidence of the top layer and the height of the voids can be obtained from the cross-section SEM image in Fig. 1.16b.

P2VP is a weak polycation, and the pyridine group can be protonated at acidic pH, resulting in fast and substantial swelling. Transmission spectra of a 2DOMs exhibit 6, 15, 29 and 26 nm red-shifts in response to pH 5, 4, 3 and 2, respectively, as shown in Fig. 1.17a. Therefore, the variation of pH conditions can be readily read out from the wavelength shift of the 2DOMs. More importantly, the varying hues from purple, blue, green to yellow upon different pH conditions (pH 5–2) were observed (Fig. 1.17b). Therefore, this material can be used as a pH sensor.

An ion sensor has been prepared by using a similar 2DOM structure. In this case, PS particles self-assembled into 2D ordered structure in hydrogel thin films, which was functionalized using 4-acryloylamidobenzo-18-crown-6 (4AB18C6). 4AB18C6 is a molecular recognition agent, which responds specifically to Pb^{2+}

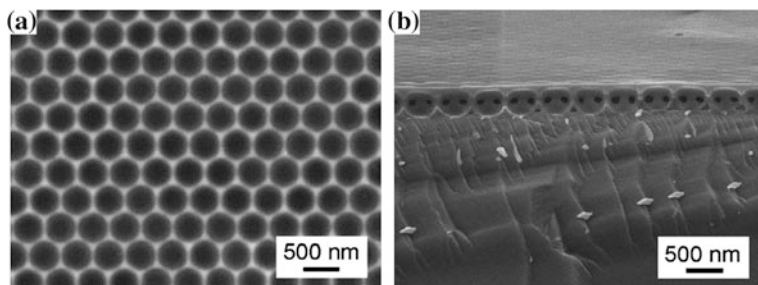


Fig. 1.16 SEM images of the 2DOMs based on a monolayer inverse opal of polyelectrolyte gel on a silicon wafer: **a** top-view and **b** side-view. Reproduced with permission [39]

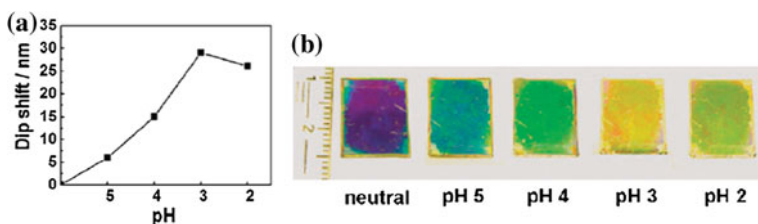


Fig. 1.17 Transmission dip shift (a) and interference colors (b) of 2DOMs in response to different pH conditions. Reproduced with permission from [39]

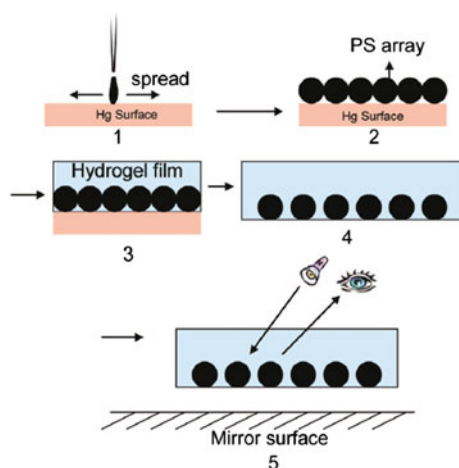


Fig. 1.18 Fabrication of a 2-dimensional (2-D) photonic crystal for sensing applications. 1, 2 PS particles self-assembled into a 2-D close-packed array. 3 A hydrogel film is polymerized around the 2-D array. 4 The swollen hydrogel with the embedded 2-D array is peeled from the glass substrate. 5 Diffraction from the 2-D array/hydrogel sandwich is monitored visually. Reproduced with permission from [40]

(Fig. 1.18) [40]. When exposed to Pb^{2+} solution, 4AB18C6 selectively incorporated with Pb^{2+} , which increased the charge density in the polymer network. This resulted in hydrogel swelling and correspondingly increased the distance between PS particles, which led to a color change of the thin film.

1.4 Three-Dimensional Ordered Materials

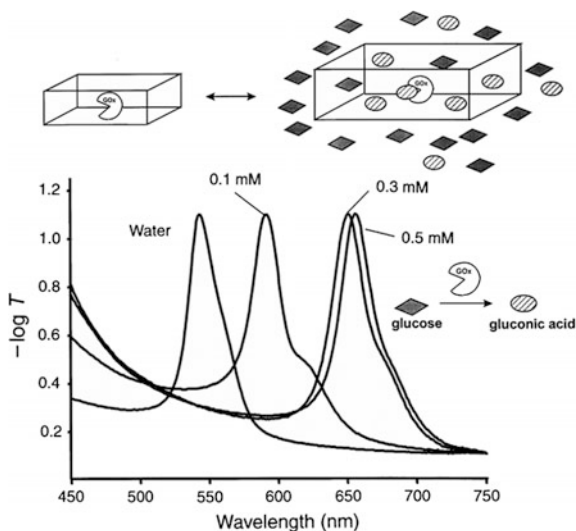
Three-dimensional ordered materials (3DOMs) have structures ordered periodically in three spatial directions [41, 42]. The most common example of a 3DOM is the opal gemstone, which consists of a close-packed ordered array of silica colloids—this is also known as a colloidal crystalline array (CCA) [43, 44]. Inspired by

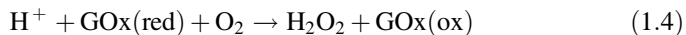
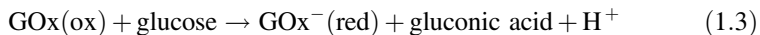
nature, color tunable 3DOMs have been fabricated in the lab by entrapping CCAs in stimuli responsive hydrogels [45–47]. The CCA exhibits visual color, similar to an opal gemstone, but interestingly allows the color to be tuned by the swelling and deswelling of the hydrogel in response to external stimuli [48–50].

A CCA/hydrogel-based system was developed by Asher's group, which could be used for noninvasive glucose sensing in tear fluid. The sensor was designed and used in contact lenses or in ocular inserts under the lower eyelid. It exhibits different colors when exposed to different glucose concentrations. The concept is that users could monitor glucose concentration by viewing the color of the sensor [51–53]. In another example, Asher's group fixed highly charged monodisperse PS colloids into a hydrogel network. Boronic acid derivatives were incorporated into the hydrogel backbone, rendering them glucose responsive [52]. Glucose can interact with the boronic acid derivative to form glucose boronate crosslinks, therefore higher glucose concentration results in higher crosslink density and the hydrogel shrinks leading to a blue shift of reflectance spectra.

Another CCA/hydrogel-based glucose sensor was prepared by incorporation of a periodic array of PS spheres with different geometries into a polyacrylamide hydrogel [55]. The enzyme glucose oxidase was also incorporated into this system, which allowed the material to sense glucose (Fig. 1.19) [54]. These materials exhibited Bragg diffraction in the visible wavelengths [54]. Glucose solutions caused the hydrogel to swell, resulting in a red shift of the diffracted light. The hydrogel swelling is a result of the formation of reduced glucose oxidase after reaction with glucose, which is anionic at neutral pH. This charged state causes the hydrogel to swell. The reduced glucose oxidase is reoxidized by O_2 ; all these reactions are detailed in reactions (1.3) and (1.4).

Fig. 1.19 Visible extinction spectra showing how diffraction depends on glucose concentration for a 125-mm-thick CCA glucose sensor. Reproduced with permission [54]





No response was observed using similar concentrations of sucrose or mannose, because of the enzyme selectivity.

CCA/hydrogels were also used to monitor hydrogel volume-phase transitions using Bragg diffraction in response to pH changes [56]. In this case, hydrogels were composed of poly(acrylic acid) (PAAc), which has a pK_a of ~ 4.7 . Therefore, the PAAc groups will be protonated/deprotonated in response to pH and will induce volume-transitions; these solvation state changes causes the lattice spacing of the colloidal crystal to change, which can be detected as optical property (color) changes. From this, a detailed hydrogel volume-phase transition model has been built, which accurately models swelling with no adjustable parameters.

Poly(hydroxyethyl methacrylate) hydrogel-based CCAs were also prepared and used as a pH sensor [57]. To accomplish this, the surfaces of monodisperse silica particles were coated with a thin layer of PS-co-SPS (sulfonated PS). Surface charge groups were introduced into the system due to the negative SPS block. The resulting highly charged monodisperse silica particles were self-assembled into a CCA in deionized water. Polymerization of hydroxyethyl methacrylate (HEMA) occurred around the CCA to form a pHEMA-CCA. The silica particles were etched away using hydrofluoric acid to produce a three-dimensional periodic array of voids in the HEMA-CCA, i.e., an inverse opal. The authors also fabricated a CCA by utilizing a second polymerization to incorporate carboxyl groups into the HEMA-CCA. This system can be used to model the pH dependence of diffraction of the HEMA-CCA using Flory theory, which predicts polymer conformation in solutions, and can be used to determine polymer network elasticity [19]. These sensors exhibited reversible pH response in different ionic strength solutions.

An unusual feature of the pH response above is the hysteresis in response to titration. The kinetics of equilibration are very slow due to the ultralow diffusion constant of protons in the carboxylated CCA as predicted earlier by the Tanaka group [58]. In spite of its simplicity, the long response time of the hydrogel photonic crystal materials has limited their utility. This results from the slow diffusion of analytes in the hydrogel, which act to change their optical properties. New procedures to fabricate CCA hydrogels were developed to reduce the response time. The Lee Group demonstrated a mechanically robust CCA hydrogel that exhibited fast response kinetics. This was done by fabricating the materials using templated photo-polymerization of hydrogel monomers within the interstitial space of a self-assembled colloidal crystal, as shown in Fig. 1.20 [59].

By a rigorous optimization of photopolymerization conditions, the pH sensors show a response time of less than 10 s in response to solution pH changes. Lee's inverse opal hydrogels primarily consists of void spaces interconnected by holes (Fig. 1.20), once the voids are connected, the diffusion of proton can take place both

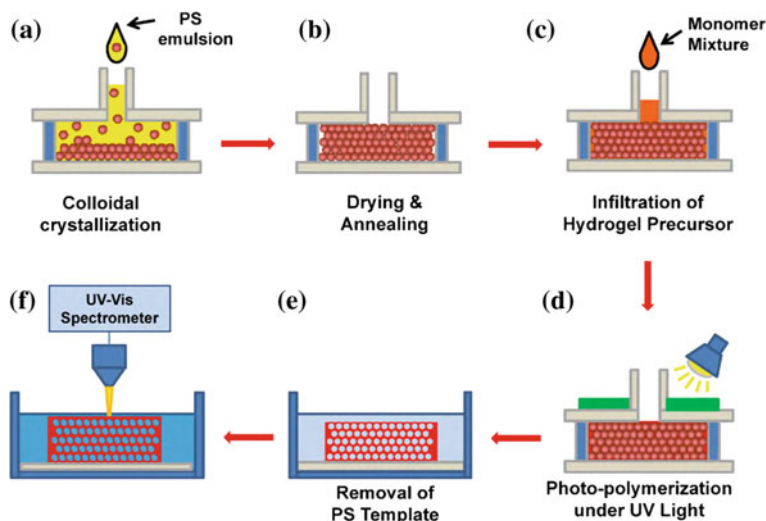


Fig. 1.20 Schematic illustration of fabrication procedures. Reproduced with permission [59]

through the void space and the hydrogel network [59]. Most ionic species are expected to diffuse rapidly through the voids, and then into the hydrogel, resulting in an aqueous diffusion limited response time. Repeated pH changes revealed that the sensor has a long lifetime (>6 months) without change of the response time or reproducibility in pH-induced color change. Mangeney's group also fabricated a novel CCA for sensing solution pH, with enhanced pH response by incorporating a planar defect inside the CCA hydrogel, as shown in Fig. 1.21a [60]. Figure 1.21b shows the SEM images of the colloidal-crystal template with an embedded planar defect layer and the resultant photonic polymer hydrogel films.

In a more biologically relevant application, a creatinine (a molecular marker of renal dysfunction) sensor has been fabricated by immobilizing creatinine deiminase (CD) into polyacrylamide hydrogel. The hydrogel was functionalized with two recognition molecules, CD enzyme and a 2-nitrophenol (2NPh), and swells as a result of two sequential reactions: hydrolysis of creatinine by the enzyme CD, which releases OH, and increases the pH within the gel—this leads to a concomitant deprotonation of 2NPh. The overall effect is an increased hydrophilicity (and charge) of the hydrogel, causing the hydrogel to swell (Fig. 1.22) yielding a red shift in diffraction [61]. In another example, by covalently linking the amine groups of cholesterol oxidase (ChOx) to an epoxide-functionalized CCA (from acrylamide and glycidyl methacrylate), a photonic crystal-based sensor capable of detecting cholesterol with concentrations up to 5 mM could be fabricated [62].

In recent years, 3DOMs have been used to sense specific analytes. Generally speaking, to achieve molecular recognition, recognition motifs will be incorporated into the photonic crystal system and the recognition process will change the photonic crystal ordered structure/spacing, leading to a color change. One way this can

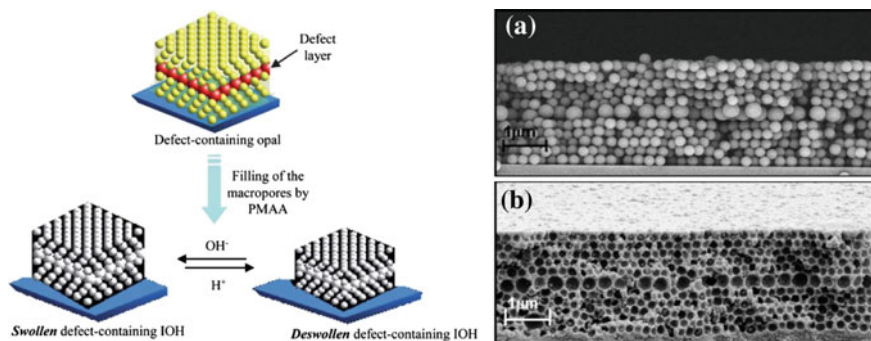


Fig. 1.21 **a** Schematic illustration of the defect-containing opal and inverse opal hydrogel (IOH) films. **b** SEM images of **(a)** the colloidal-crystal template with embedded planar defect layer of larger particles and **(b)** the resulting inverse opal hydrogel film with a defect layer of larger macropores. The resulting materials consists of a three-dimensional, highly-ordered, and interconnected macroporous array of poly(methacrylic acid), which is sensitive to pH. Reproduced with permission [60]

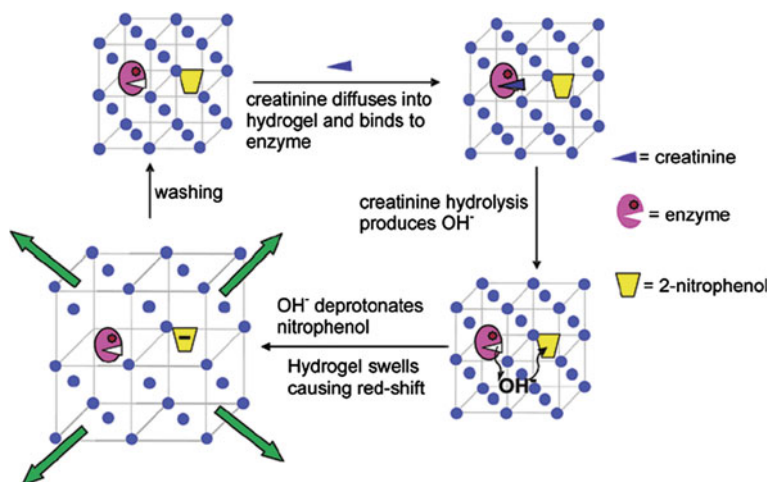


Fig. 1.22 Schematic depiction of the creatinine sensor concept. Creatinine deiminase causes the production of hydroxide ions. In a second step, 2-nitrophenol is deprotonated. The increased solubility of the phenolate ion and its negative charge causes the swelling in the polymer. Reproduced with permission [61]

be achieved is via molecular imprinting. Molecular imprinting is a technique used to create nanocavities inside a polymer network that are capable of binding specific molecules. This is achieved by incorporating the molecules of interest into the gels, followed by their extraction. The resulting cavities left in the gel are now chemically and conformationally templated to rebind the imprinted molecule. These nanocavities work as artificial antibodies which can recognize target molecule

through the specific shape and binding site between them and target molecules [63]. Combination of molecular imprinting and photonic crystal technology to prepare a photonic crystal based sensor can yield label-free colorimetric detectors [64–67].

Bisphenol A (BPA) is a common monomer for synthesis of plastics and epoxy resins. However, recent studies have found out BPA is an emerging contaminant which can disrupt the endocrine system and potentially cause cancer [68]. By molecular imprinting, numerous nanocavities were created in polymethyl methacrylate (PMMA) spheres, which can specifically target BPA (Fig. 1.23) [26]. The monodisperse PMMA spheres can be made into a 3DOMs that has been used as optical sensor. Once the sensor was exposed to BPA solution, binding occurred due to the hydrogen bonding and spatial effects, changing the diffraction peak intensity [65].

In another example, this method was used to detect atrazine that is a widely used in pesticide. This pesticide has recently shown up as a contaminant in drinking water and consumption of this pesticide above the maximum contaminant level (MCLs) has been associated with adverse human health effects. Li's group develop atrazine-imprinted photonic polymers (MIPP) (Fig. 1.24) [66]. First, silica colloids were deposited onto a glass substrate and formed a 3D ordered array as a template. Pre-gel solution containing template molecule (atrazine) was filled into the void space of the 3D ordered array. After polymerization, silica and the atrazine molecular templates were removed from the hydrogel film, forming highly ordered porous arrays with specific nanocavities capable of recognizing atrazine through noncovalent interaction. When exposed to different concentration of atrazine, the device's color visually changed.

The MacLachlan group recently prepared photonic materials from nanocrystalline cellulose films, and used supramolecular templating to yield a sensor

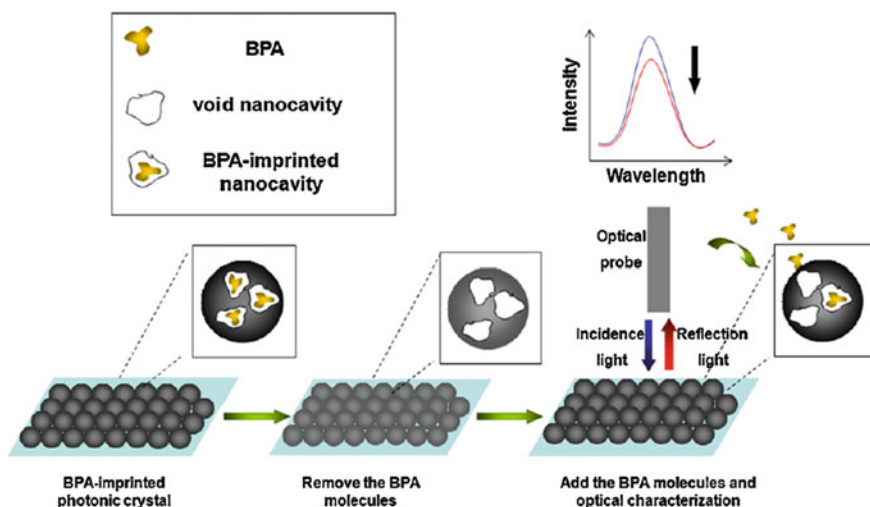


Fig. 1.23 Experimental procedures for the reflectometric detection of BPA using an imprinted nanocavity opal photonic crystal sensor. Reproduced with permission [65]

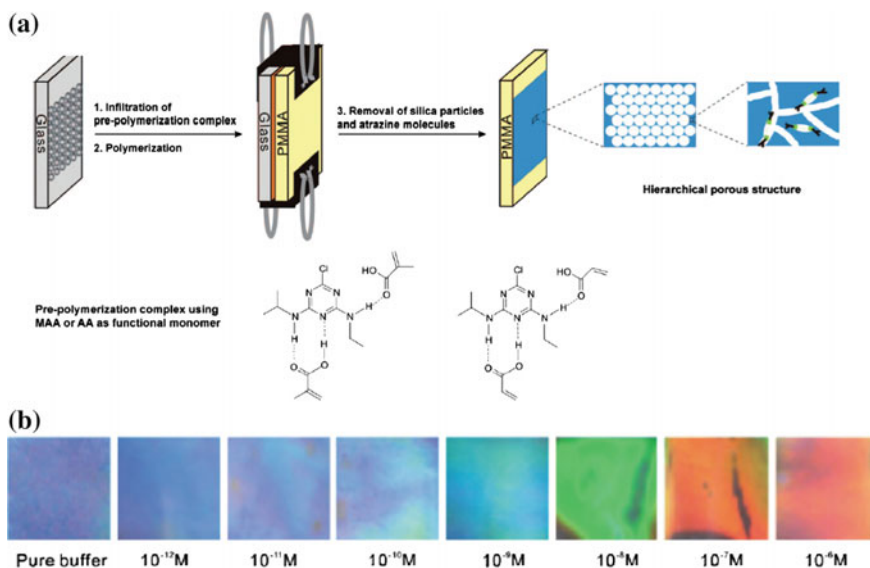


Fig. 1.24 **a** Schematic illustration of the procedure used for the preparation of the molecularly imprinted photonic polymer (MIPP). **b** Color change induced by exposure to atrazine at different concentrations. Reproduced with permission [66]

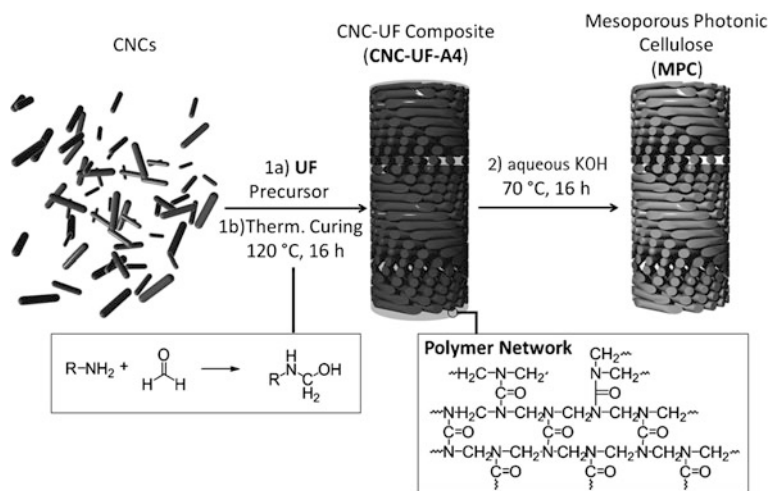


Fig. 1.25 Synthetic route to generate mesoporous photonic cellulose (MPC). An aqueous suspension of CNCs is combined with a UF precursor. Following evaporation-induced self-assembly, a CNC-UF composite with chiral nematic order is obtained. Thermal curing of the composite is followed by treatment with aqueous KOH to yield MPC. Reproduced with permission [71]

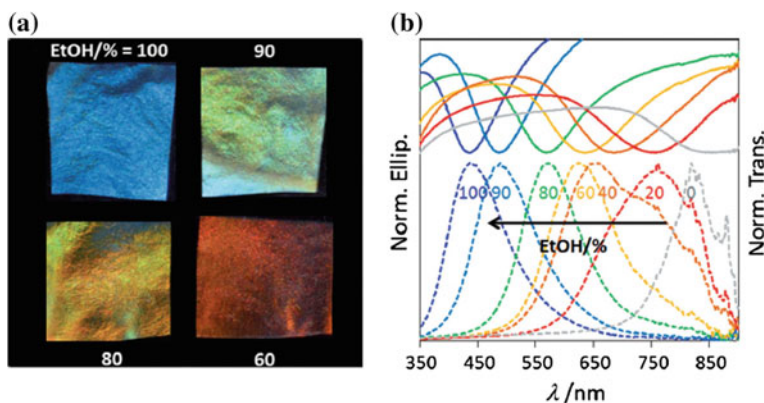


Fig. 1.26 Sensing performance of the functional MPC films. **a** Photographs and **b** UV/Vis (solid lines) and CD spectra (dashed lines) of MPC soaked in EtOH/H₂O at different ratios as indicated. Reproduced with permission [71]

[69–71]. A schematic depiction of the device preparation is shown in Fig. 1.25. Briefly, chiral nematic cellulose films were synthesized by the self-assembly of cellulose nanocrystals (CNCs) in the presence of a resin precursor. The mixture was dried overnight under ambient conditions, followed by heat curing at 120 °C to complete the polymerization. Subsequently, CNCs were removed from resin, generating a periodic mesoscopic structure with a photonic band gap. The periodicity can be tuned by changing the reaction conditions, and therefore the optical property and potential application of these materials can be controlled. These films showed a rapid red shift of their reflection peak when immersed in polar solvents (Fig. 1.26). Also, film colors depend on solvent polarity and composition, which can be observed by the naked eye (Fig. 1.26b). The vibrant visible colors could be tuned from 430 nm in pure ethanol to 840 nm in pure water (Fig. 1.26).

1.5 Other Noteworthy Photonic Materials for Sensing

Trinitrotoluene (TNT) is one of the most widely used and well-known explosives that can be used as a weapon and is a threat to our security. Another potential threat to human security is the use of biological warfare and nerve gases. Over the years, researchers worldwide have been developing sensors for weapons of mass destruction, but most of them are limited by sensitivity, selectivity and/or reliability [72]. Conjugated polymer-based molecular wires has been used for sensing these dangerous chemicals [73]. Molecular wires are molecular-scale objects, which conduct electrical current. The use of molecular wires significantly enhances the chemosensory response. A number of advanced sensing technologies have been developed based on this approach. Nomadics Inc. who markets Fido produces devices capable of detecting very

low levels of explosives, which is based on the chemoresistivity of molecular wires [74–77].

Porous silicon has also attracted significant attention for sensor applications. Tokranova et al. reported [78] a porous silicon microcavity (PSi MC) infiltrated with poly(2-methoxy-5-(2-ethylhexyloxy)-p-phenylenevinylene) (MEH-PPV) ($M_w = 139,000$) for TNT sensing. The unique architecture of the polymer/PS nanohybrid makes it very attractive for sensing of nitroaromatic compounds especially with low vapor pressure (e.g., TNT) because of the combination of high sensitivity (due to extra thin polymer film inside the PSi) with an intense optical signal (as a result of sufficient polymer mass adsorbed by the PSi). The PSi MC/MEH-PPV composite exhibited excellent sensitivity of TNT vapors significantly exceeding that of the conventional thin films of MEH-PPV deposited on flat Si. The spectral shift of the MC resonance peak upon TNT vapor exposure offers an additional advantage. Sensor specificity could be substantially improved by discriminating nitroaromatic explosives with low vapor pressure (spectral shift ~ 1 nm) from explosive interferants with medium and high vapor pressures (spectral shift $\sim$ several nanometers, e.g., dinitrotoluene, nitrotoluene). These PSi MC/polymer nanocomposites were used as a novel system for various applications in sensing and trace detection of toxic gases.

Interestingly, single crystal porous silicon (PSi) was also used for sensing applications. Because the optical signature of these photonic crystals is sensitive to the average refractive index of the structure, materials are able to absorb (and desorb) to the pore walls (and from the pore walls), which is the basis for biosensing. While the adsorption of materials to the pore walls causes a red-shift (if it has a higher refractive index than the material it replaces), the desorption of materials from the pore walls results in a blue shift (thus the average refractive index decreases). PSi photonic crystals can be made into very sensitive and selective label-free optical sensors by modifying the pore walls with the appropriate surface chemistry [79]. Interest in the use of PSi photonic crystals for biosensing arises from the fact that their optical signatures can be tuned by means of changing the porosity and periodicity of the multilayer photonic crystals, over the whole visible and infrared regions of the electromagnetic spectrum [80]. PSi biosensors have focused on affinity sensing motif for the detection of DNA [81, 82], proteins [83, 84] and microorganisms [85].

In a similar approach, a flexible photonic crystal cavity system was developed, which was consisted of a regular array of silicon nanowires embedded in a polydimethylsiloxane (PDMS) matrix that enables wide-range tuning of its resonance frequency (Fig. 1.27) [86]. This mechanical stretchable assembly exhibits a cavity resonance in the telecommunication band that can be reversibly tuned over 60 nm. Specifically, the optical response of the cavities towards various solvents, such as ethanol, isopropanol (IPA), and tert-butanol (TBA), was investigated. The swelling ratios were found to be 4, 9, and 21 %, respectively as shown in Fig. 1.28 at room temperature.

In another example, a sensor was fabricated by incorporation of a chemo-responsive hydrogel into a PSi transducer (Fig. 1.29) [87]. When exposed to the model analyte, which was the reducing agent tris(2-carboxyethyl) phosphine

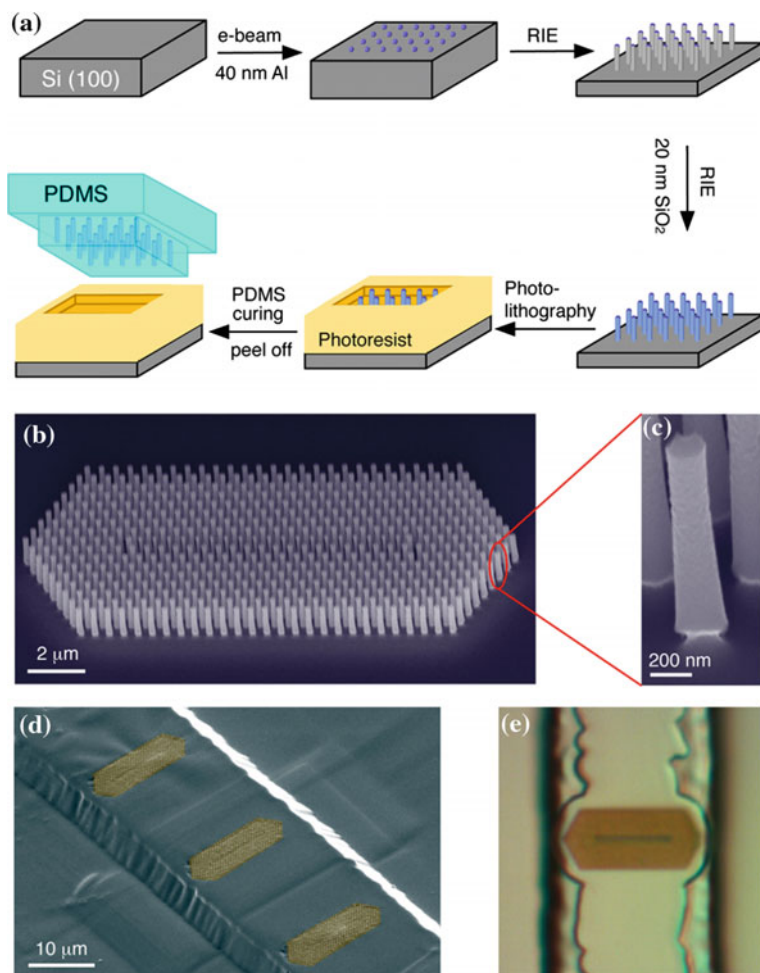


Fig. 1.27 Flexible PC cavities. **a** Schematic for flexible PC cavity fabrication: the PC patterns on a Si (1, 0, 0) wafer were made by electron-beam lithography; 40 nm Al was deposited as an etch mask; Si was etched to form Si nanowires; 20 nm of SiO₂ was deposited by atomic layer deposition; SiO₂ was selectively etched on the substrate; the nanowire bases were thinned by etching; a window by photolithography; pour and cure PDMS; and then finally peel off the PDMS. **b** Scanning electron microscope (SEM) image of the PC tilted at 45°. Design dimensions: regular nanowire diameter is 200 nm; defect nanowire diameter is 140 nm; nanowire length is 1.2 μm. The hexagonal lattice spacing is 500 nm. **c** Zoom-in view of an undercut NW at the PC edge, also tilted at 45°. **d** SEM image of the PDMS mesa structure containing several PC cavities. **e** Optical image of the top-down view of a PC embedded in PDMS. The *dark line* in the middle of the PC is the line defect. Reproduced with permission [86]

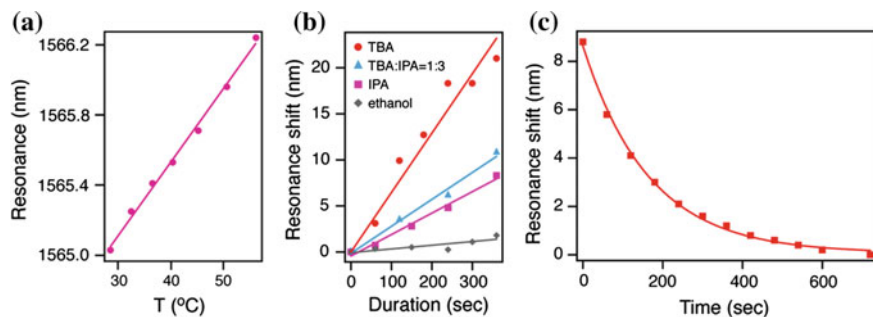


Fig. 1.28 Resonance shift as a function of temperature and solvent swelling. **a** Resonance peak red-shifted as temperature increased. **b** Resonance shift as a function of time that PDMS stayed in a solvent bath. **c** As TBA evaporated over time, the resonance moved back to the original position (without solvent swelling) with exponential time dependence. Reproduced with permission [86]

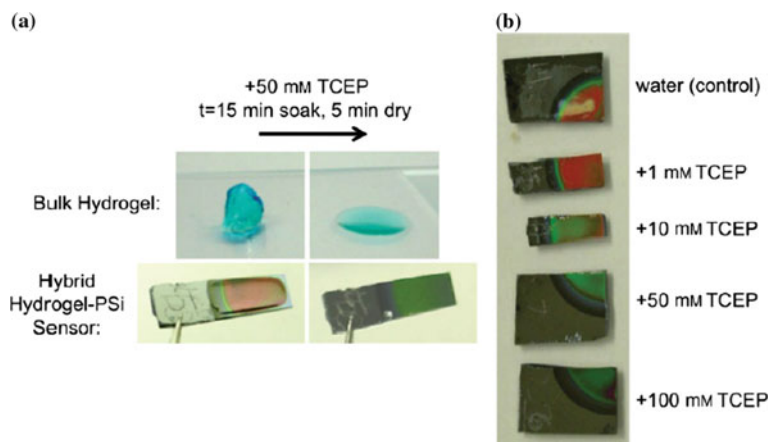


Fig. 1.29 Visual color readout of hybrid hydrogel-PSi sensor upon exposed to different concentration of TCEP. Reproduced with permission [87]

(TCEP), the disulfide bond used as cross-linker cleaves and thus the color of the sensor changes.

For biological sensing, it is desired that the sensing material be free from legitimate concerns of toxicity; these concerns have limited the use of CdSe quantum dots especially for in vivo imaging and sensing applications. For these reasons, there has been a quest to develop non-Cd-based quantum dots. Silicon nanocrystals (ncSi) have been identified as one of the best candidates; although they exhibit lower quantum efficiencies [88]. The Ozin group focused on the possibility of synthesizing colloiddally-stable monodispersed ncSi for in vitro fluorescence labeling of human breast tumor cells [88, 89].

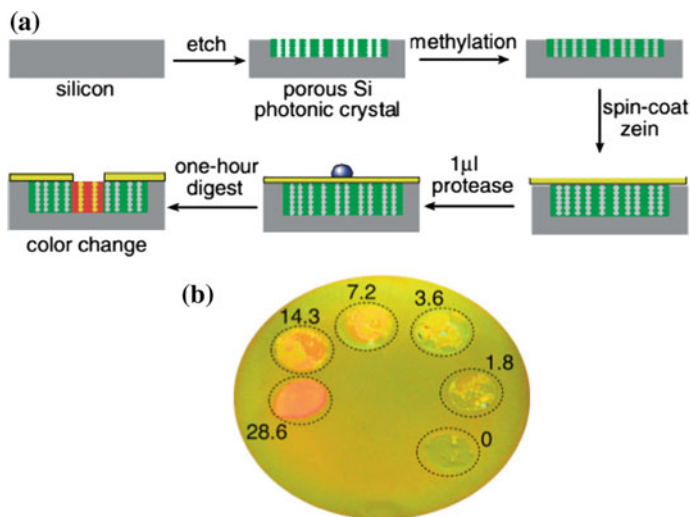


Fig. 1.30 **a** Enzymatic assay using a protein-coated porous Si photonic crystal; **b** Dilution series for active protease pepsin, showing the effect of pepsin concentration on the observed color change in the porous Si photonic crystal. Reproduced with permission [91]

Traditional staining technology to differentiate Gram (+) from Gram (−) bacteria is cumbersome. Miller's group proposed a simple way to realize reliable Gram (−) bacteria identification [90]. The authors designed and synthesized an organic receptor, tetratryptophan-tercyclopentane, designated TWTCP, which specifically binds to Gram (−) bacteria and functionalized porous silicon surface with this receptor. Only exposed to Gram (−) bacteria, the device exhibited red-shift. Sailor's group developed a porous Si photonic crystal probe to colorimetric monitor protease activity (Fig. 1.30) [91]. This method is highly sensitive even the picomoles in a 1 μ L can cause the probe's color to visually change. The introduction of protease will cause the total refractive index of the porous film to increase, generating a red shift.

Related to Si, TiO_2 has been used as a sensing material for biomolecules. This is primarily due to its large internal surface area, good biocompatibility, and broad application [92, 93]. Proteins can be directly immobilized on the pore surfaces of TiO_2 substrates by physical adsorption. The change of the diffraction peak shifts can be monitored to obtain information about the binding of analytes [92]. Photonic crystal biosensors (based on TiO_2) for measuring HIV viral load have recently been developed [93].

1.6 Summary

This chapter has reviewed only a portion of the available examples of photonic materials for sensing applications. The systems that were described primarily exhibited their unique optical properties due to refractive index periodicity (in 1D, 2D, or 3D), although, the final section of the chapter detailed alternative systems that can be used for sensing—primarily using porous Si. Many of the devices were fabricated using self-assembly processes, and relied on visual color changes for the readout. These facts made the devices not only easy and cost effective to fabricate, but allow them to be used without complex analytical instrumentation to get a result. The examples illustrated the exciting applications of such materials, and clearly demonstrated how the devices can be used to positively impact human health. While much progress has been made, many challenges still exist that prevent the use of these materials in everyday applications. For example, regarding sensing, polymers with enhanced sensitivities to specific species need to be developed and investigated. Furthermore, response times need to be enhanced and the ability of the devices to sense analytes in complex media (saliva, blood, urine) demonstrated. Regardless of the challenges, continuous development of such devices and related technologies makes us optimistic about the future positive impacts these materials can have on human life.

Acknowledgements MJS acknowledges funding from the University of Alberta (the Department of Chemistry and the Faculty of Science), the Natural Sciences and Engineering Research Council of Canada (NSERC), the Canada Foundation for Innovation (CFI), the Alberta Advanced Education and Technology Small Equipment Grants Program (AET/SEGP), Grand Challenges Canada and IC-IMPACTS. QMZ acknowledges financial support through an Alberta Innovates Technology Futures (AITF) Postdoctoral Fellowship.

References

1. J. Ge, Y. Yin, *Angew. Chem. Int. Ed.* **50**, 1492–1522 (2011)
2. P. Yeh, *Optical Waves in Layered Media* (Wiley, New York, 1988)
3. L. Hu, M.J. Serpe, *Chem. Commun.* **49**, 2649–2651 (2013)
4. F.H. Schacher, P.A. Rupar, I. Manners, *Angew. Chem. Int. Ed.* **51**, 7898–7921 (2012)
5. X. Ye, L. Qi, *Nano Today* **6**, 608–631 (2011)
6. S. Itabashi, H. Nishi, T. Tsuchizawa, T. Watanabe, H. Shinojima, R. Kou, K. Yamada, *IEICE Trans. Electron.* **E95C**, 199–205 (2012)
7. A. Chen, *Introduction to Polymer Photonics for Information Technology* (Crc Press-Taylor & Francis Group, Boca Raton, 2008)
8. C.X. Guo, G.H. Guai, C.M. Li, *Adv. Energy Mater.* **1**, 448–452 (2011)
9. S.Q. Feng, T. Lei, H. Chen, H. Cai, X.S. Luo, A.W. Poon, *Laser Photonics Rev.* **6**, 145–177 (2012)
10. A. Moutsopoulos, A.K. Andreopoulos, G. Lainioti, G. Bokias, G. Voyiatzis, J.K. Kallitsis, *Sens. Actuators B Chem.* **211**, 235–244 (2015)
11. H.B.D. Thai, J.K. Yu, Y.-J. Park, D.-R. Ahn, *Analyst* **140**, 2804–2809 (2015)

12. S. Sun, X.-Y. Hu, D. Chen, J. Shi, Y. Dong, C. Lin, Y. Pan, L. Wang, *Polym. Chem. Uk* **4**, 2224–2229 (2013)
13. Z. Zhang, D.S. Kim, C.-Y. Lin, H. Zhang, A.D. Lammer, V.M. Lynch, I. Popov, O.S. Miljanic, E.V. Anslyn, J.L. Sessler, *J. Am. Chem. Soc.* **137**, 7769–7774 (2015)
14. A. Afzal, N. Iqbal, A. Mujahid, R. Schirhagl, *Anal. Chim. Acta* **787**, 36–49 (2013)
15. Y.-J. Jin, B.S.-I. Kim, W.-E. Lee, C.-L. Lee, H. Kim, K.-H. Song, S.-Y. Jang, G. Kwak, *Npg Asia Mat.* **6** (2014)
16. Q.M. Zhang, X. Li, M.R. Islam, M. Wei, M.J. Serpe, *J. Mater. Chem. C* **2**, 6961–6965 (2014)
17. H. Wang, K.-Q. Zhang, *Sensors* **13**, 4192–4213 (2013)
18. C. Fenzl, S. Wilhelm, T. Hirsch, O.S. Wolfbeis, *ACS Appl. Mater. Interfaces* **5**, 173–178 (2012)
19. L.D. Bonifacio, B.V. Lotsch, D.P. Puzzo, F. Scotognella, G.A. Ozin, *Adv. Mater.* **21**, 1641–1646 (2009)
20. M.C. Fuertes, F.J. López-Alcaraz, M.C. Marchi, H.E. Troiani, V. Luca, H. Míguez, G.D.A. Soler-Illia, *Adv. Funct. Mater.* **17**, 1247–1254 (2007)
21. C. Kang, E. Kim, H. Baek, K. Hwang, D. Kwak, Y. Kang, E.L. Thomas, *J. Am. Chem. Soc.* **131**, 7538–7539 (2009)
22. Y. Kang, J.J. Walish, T. Gorishnyy, E.L. Thomas, *Nat. Mater.* **6**, 957–960 (2007)
23. Z. Wang, J. Zhang, J. Xie, C. Li, Y. Li, S. Liang, Z. Tian, T. Wang, H. Zhang, H. Li, *Adv. Funct. Mater.* **20**, 3784–3790 (2010)
24. L. Zhai, A.J. Nolte, R.E. Cohen, M.F. Rubner, *Macromolecules* **37**, 6113–6123 (2004)
25. Y. Kang, *Macromol. Res.* **20**, 1223–1225 (2012)
26. C.D. Sorrell, M.J. Serpe, *Adv. Mater.* **23**, 4088–4092 (2011)
27. C.D. Sorrell, M.C. Carter, M.J. Serpe, *Adv. Funct. Mater.* **21**, 425–433 (2011)
28. M.R. Islam, M.J. Serpe, *Chem. Commun.* **49**, 2646–2648 (2013)
29. L. Hu, M.J. Serpe, *J. Mater. Chem.* **22**, 8199–8202 (2012)
30. M.R. Islam, M.J. Serpe, *Macromolecules* **46**, 1599–1606 (2013)
31. M.R. Islam, M.J. Serpe, *Anal. Bioanal. Chem.* 1–7 (2014)
32. M.R. Islam, M.J. Serpe, *Anal. Chim. Acta* **843**, 83–88 (2014)
33. Q.M. Zhang, W. Xu, M.J. Serpe, *Angew. Chem. Int. Ed.* **53**, 4827–4831 (2014)
34. C.D. Sorrell, M.J. Serpe, *Anal. Bioanal. Chem.* **402**, 2385–2393 (2012)
35. M.R. Islam, M.J. Serpe, *Biosens. Bioelectron.* **49**, 133–138 (2013)
36. Q.M. Zhang, D. Berg, S.M. Mugo, M.J. Serpe, *Chem. Commun.* **51**, 9726–9728 (2015)
37. J.T. Zhang, L. Wang, D.N. Lamont, S.S. Velankar, S.A. Asher, *Angew. Chem. Int. Ed.* **51**, 6117–6120 (2012)
38. J.-T. Zhang, Z. Cai, D.H. Kwak, X. Liu, S.A. Asher, *Anal. Chem.* **86**, 9036–9041 (2014)
39. C. Li, B.V. Lotsch, *Chem. Commun.* **48**, 6169–6171 (2012)
40. J.-T. Zhang, L. Wang, J. Luo, A. Tikhonov, N. Kornienko, S.A. Asher, *J. Am. Chem. Soc.* **133**, 9152–9155 (2011)
41. Y. Cheng, Z. Yang, J. Liao, J. Qiu, Z. Song, Y. Yang, *J. Rare Earths* **33**, 599–603 (2015)
42. H. Wakayama, H. Yonekura, Y. Kawai, *Acs Macro Lett.* **2**, 284–287 (2013)
43. J. Jirasek, M. Vavro, J. Jiranek, *Chem. Listy* **103**, 647–651 (2009)
44. J.B. Lambert, G.O. Poinar, *Acc. Chem. Res.* **35**, 628–636 (2002)
45. J. Liao, Z. Yang, J. Sun, S. Lai, B. Shao, J. Li, J. Qiu, Z. Song, Y. Yang, *Sci. Reports* **5** (2015)
46. K.T. Hufziger, S.V. Bykov, S.A. Asher, *Appl. Spectrosc.* **68**, 1219–1223 (2014)
47. D. Yang, S. Ye, J. Ge, *Adv. Funct. Mater.* **24**, 3197–3205 (2014)
48. J.H. Holtz, S.A. Asher, *Nature* **389**, 829–832 (1997)
49. J.M. Weissman, H.B. Sunkara, A.S. Tse, S.A. Asher, *Science* **274**, 959–963 (1996)
50. D. Kang, J.E. MacLennan, N.A. Clark, A.A. Zakhidov, R.H. Baughman, *Phys. Rev. Lett.* **86**, 4052–4055 (2001)
51. V.L. Alexeev, S. Das, D.N. Finegold, S.A. Asher, *Clin. Chem.* **50**, 2353–2360 (2004)
52. M. Ben-Moshe, V.L. Alexeev, S.A. Asher, *Anal. Chem.* **78**, 5149–5157 (2006)
53. V.L. Alexeev, A.C. Sharma, A.V. Goponenko, S. Das, I.K. Lednev, C.S. Wilcox, D.N. Finegold, S.A. Asher, *Anal. Chem.* **75**, 2316–2323 (2003)

54. J.H. Holtz, S.A. Asher, *Nature* **389**, 829–832 (1997)
55. S.A. Asher, J. Holtz, L. Liu, Z. Wu, *J. Am. Chem. Soc.* **116**, 4997–4998 (1994)
56. K. Lee, S.A. Asher, *J. Am. Chem. Soc.* **122**, 9534–9537 (2000)
57. X. Xu, A.V. Goponenko, S.A. Asher, *J. Am. Chem. Soc.* **130**, 3113–3119 (2008)
58. S. Mafé, J.A. Manzanares, A.E. English, T. Tanaka, *Phys. Rev. Lett.* **79**, 3086–3089 (1997)
59. J. Shin, P.V. Braun, W. Lee, *Sens. Actuators B: Chem.* **150**, 183–190 (2010)
60. N. Griffete, H. Frederich, A. Maître, M.M. Chehimi, S. Ravaine, C. Mangeney, *J. Mater. Chem.* **21**, 13052–13055 (2011)
61. A.C. Sharma, T. Jana, R. Kesavamoorthy, L. Shi, M.A. Virji, D.N. Finegold, S.A. Asher, *J. Am. Chem. Soc.* **126**, 2971–2977 (2004)
62. M.K. Maurer, S.E. Gould, P.J. Scott, *Sens. Actuators B* **134**, 736–742 (2008)
63. K. Mosbach, O. Ramström, *Nat. Biotechnol.* **14**, 163–170 (1996)
64. Z. Wu, X. Hu, C.-A. Tao, Y. Li, J. Liu, C. Yang, D. Shen, G. Li, *J. Mater. Chem.* **18**, 5452–5458 (2008)
65. C. Guo, C. Zhou, N. Sai, B. Ning, M. Liu, H. Chen, Z. Gao, *Sens. Actuators B: Chem.* **166**, 17–23 (2012)
66. Z. Wu, C.A. Tao, C. Lin, D. Shen, G. Li, *Chem. A Eur. J.* **14**, 11358–11368 (2008)
67. Y.-X. Zhang, P.-Y. Zhao, L.-P. Yu, *Sens. Actuators B: Chem.* **181**, 850–857 (2013)
68. C.A. Staples, P.B. Dome, G.M. Klecka, S.T. Oblock, L.R. Harris, *Chemosphere* **36**, 2149–2173 (1998)
69. M.K. Khan, M. Giese, M. Yu, J.A. Kelly, W.Y. Hamad, M.J. MacLachlan, *Angew. Chem. Int. Ed.* **52**, 8921–8924 (2013)
70. K.E. Shopsowitz, J.A. Kelly, W.Y. Hamad, M.J. MacLachlan, *Adv. Funct. Mater.* **24**, 327–338 (2014)
71. M. Giese, L.K. Blusch, M.K. Khan, W.Y. Hamad, M.J. MacLachlan, *Angew. Chem. Int. Ed.* **53**, 8880–8884 (2014)
72. H. Xu, P. Wu, C. Zhu, A. Elbaz, Z.Z. Gu, *J. Mater. Chem. C* **1**, 6087–6098 (2013)
73. C.J. Cumming, C. Aker, M. Fisher, M. Fok, M.J. La Grone, D. Reust, M.G. Rockley, T.M. Swager, E. Towers, V. Williams, *IEEE Trans. Geosci. Remote Sens.* **39**, 1119–1128 (2001)
74. M.J. Marsella, P.J. Carroll, T.M. Swager, *J. Am. Chem. Soc.* **116**, 9347–9348 (1994)
75. M.J. Marsella, P.J. Carroll, T.M. Swager, *J. Am. Chem. Soc.* **117**, 9832–9841 (1995)
76. T.M. Swager, M.J. Marsella, *Adv. Mater.* **6**, 595–597 (1994)
77. Q. Zhou, T.M. Swager, *J. Am. Chem. Soc.* **117**, 12593–12602 (1995)
78. N.A. Tokranova, S.W. Novak, J. Castracane, I.A. Levitsky, *J. Phys. Chem. C* **117**, 22667–22676 (2013)
79. K.A. Kilian, T. Bocking, J.J. Gooding, *Chem. Commun.* 630–640 (2009)
80. B. Guan, A. Magenau, K.A. Kilian, S. Ciampi, K. Gaus, P.J. Reece, J.J. Gooding, *Faraday Discuss.* **149**, 301 (2011)
81. S. Chan, P.M. Fauchet, Y. Li, L.J. Rothberg, B.L. Miller, *Phys. Stat. Sol. A* **182**, 541–546 (2000)
82. V.S. Lin, *Science* **278**, 840–843 (1997)
83. H. Ouyang, L.A. DeLouise, B.L. Miller, P.M. Fauchet, *Anal. Chem.* **79**, 1502–1506 (2007)
84. K.-P.S. Dancil, D.P. Greiner, M.J. Sailor, *J. Am. Chem. Soc.* **121**, 7925–7930 (1999)
85. S. Chan, S.R. Horner, P.M. Fauchet, B.L. Miller, *J. Am. Chem. Soc.* **123**, 11797–11798 (2001)
86. C.L. Yu, H. Kim, N. de Leon, I.W. Frank, J.T. Robinson, M. McCutcheon, M. Liu, M.D. Lukin, M. Loncar, H. Park, *Nano Lett.* **13**, 248–252 (2013)
87. L.M. Bonanno, L.A. DeLouise, *Adv. Funct. Mater.* **20**, 573–578 (2010)
88. E.J. Henderson, A.J. Shuhendler, P. Prasad, V. Baumann, F. Maier-Flaig, D.O. Faulkner, U. Lemmer, X.Y. Wu, G.A. Ozin, *Small* **7**, 2507–2516 (2011)
89. M.L. Mastronardi, E.J. Henderson, D.P. Puzzo, G.A. Ozin, *Adv. Mater.* **24**, 5890–5898 (2012)
90. S. Chan, S.R. Horner, P.M. Fauchet, B.L. Miller, *J. Am. Chem. Soc.* **123**, 11797–11798 (2001)

91. M.M. Orosco, C. Pacholski, G.M. Miskelly, M.J. Sailor, *Adv. Mater.* **18**, 1393–1396 (2006)
92. J. Li, X. Zhao, H. Wei, Z.Z. Gu, Z. Lu, *Anal. Chim. Acta* **625**, 63–69 (2008)
93. H. Shafiee, E.A. Lidstone, M. Jahangir, F. Inci, E. Hanhauser, T.J. Henrich, D.R. Kuritzkes, B.T. Cunningham, U. Demirci, *Sci. Reports* **4**, 4116 (2014)

Photonic Materials for Sensing, Biosensing and Display
Devices

Serpe, M.J.; Kang, Y.; Zhang, Q.M. (Eds.)

2016, XV, 364 p., Hardcover

ISBN: 978-3-319-24988-9