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Preparation of Iridescent 2D Photonic Crystals by using a Mussel-Inspired Spatial Patterning of ZIF-8 with potential applications in optical switch and chemical sensor

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KEYWORDS: **Iridescent, Photonic Crystals, Polydopamine, MOF patterning, Optical switch and Chemical sensor**

ABSTRACT: In this work, spatial patterning of thin dense zeolitic imidazolate framework (ZIF-8) pattern was generated using photolithography and dopamine coating. A unique reversible two-color iridescent pattern can be easily obtained for potential applications in sensing and photonics.

INTRODUCTION: The optical phenomenon of iridescence appears on certain surfaces in which color changes with the angle of observation or the angle of illumination[1]. Iridescence is observed in a broad range of animal taxa ranging from marine copepods to terrestrial insects and to birds, such as the iridescent exoskeleton of a golden stag beetle, the paua shell of Haliotis iris, wings of Morpho didius, Tachinid fly and avian tissues[2]. These iridescent features play an important role in signaling and communication, thermoregulation and photoprotection and vision enhancement [1]. The artificial structural coloration/iridescent thin films are composed of periodic stacks of layers with alternating high and low refractive indices. Such structure can be achieved through a variety of approaches including layer-by-layer deposition, Langmuir–Blodgett, self-assembly of organic dielectric materials and so on. These advanced materials have found many applications in low-loss resonators, switches, sensors, optical fibers, display devices and so forth[3].

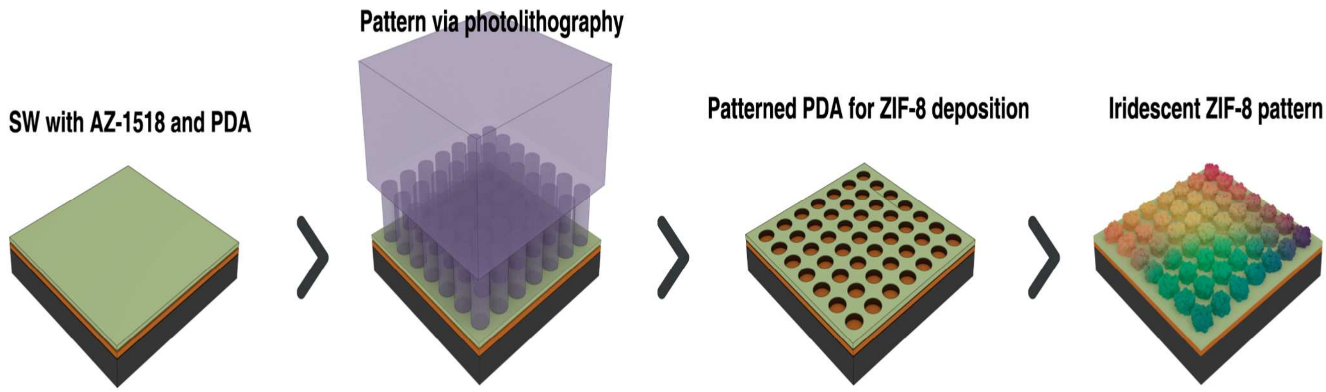


Figure 1 Iridescent ZIF-8 pattern preparation procedure:satge1: a clean silicon wafer was coated by PDA followed by a second layer of positive photoresist; stage 2: circular holes (pattern) were created by UV photolithography; stage 3: the pattern was immersed in ZIF-8 precursor solution; stage 4: the localized ZIF-8 was appeared by removing the unexposed regions of the positive photoresist using isopropanol (for details see supporting information)

Metal organic frameworks (MOFs) have drawn a growing attention due to their high specific area, nanometer-sized cavities, regular channels, satisfactory stability and chemical tailorability. These fascinating properties enable MOFs to be applied in adsorption, storage, filtration, and catalysis[4-6]. The non-iridescent structural coloration of MOF thin film due to the film-thickness-dependent optical interference in the visible light region has been reported[7-8]. Iridescence properties of MOFs can potentially be exploited in photonics and sensing applications and thus of significant interest. However, the fabricate MOFs material with iridescent property has remained a technical challenge, possible due to the difficulty in precise control of the MOFs thickness at a macroscopic scale.

Recently, spatial positioning of MOFs for micro patterns has opened new lines of research for MOFs applications such as energy production, optics, drug delivery, bioreactors, sensing, and molecular transport. Herein, we describe how the spatial patterning of ultra-thin zeolitic imidazolate framework (ZIF-8) films on a polydopamine (PDA)-coated silicon wafer (SW) can lead to a surface with novel iridescent properties. The PDA platform can induce the rapid growth of dense thin ZIF-8 films and form patterned iridescent films by using a simple photolithography approach. The utility of photolithography using photoresist/masks makes it possible to create different types of patterns including circular dots. The unique combination of ZIF-8/PDA films and regular patterns endows the surface structural coloration and iridescent property. Without PDA sub-layer, the ZIF-8 patterns can be still created but the iridescent property cannot be observed.

The photonic crystal structure is composed of dielectric materials with an ambient/ZIF-8/PDA configuration that can reflect specific wavelengths of visible light by creating conditions that promote selective constructive/destructive interferences. The light reflectivity (Reflectance, R) of the configuration is directly related to the refractive index (n) and extinction coefficient (k) of the ZIF-8/PDA layers according to the following equation[9]:

$$\boldsymbol{R} = \frac{[(n_{Zif8}-n_{PDA})^2+(K_{Zif8}-K_{PDA})^2]}{[(n_{Zif8}+n_{PDA})^2+(n_{Zif8}+n_{PDA})^2]} \qquad (1)$$

Therefore, more differentiated refractive indices or extinction coefficients between the ZIF-8 and PDA component can lead to a stronger reflection of the visible light.

ZIF-8 is chemically robust and thermally stable with the sodalite (SOD) zeolite-type structure that has small pore apertures (3.4 Å) and large cavities (11.6 Å)[8]. There are a variety of protocols to control the position of dense MOF thin film patterns with an appropriate thickness. But the fabrication process can be complicated and the prepared patterns can subject to poor mechanical stability[10]. In addition, these patterns do not have the structural coloration feature. In this work, we proposed a rapid, facile and versatile strategy towards ZIF-8 patterns. As shown in Figure 1, the silicon wafer (SW) was firstly coated with a layer of polydopamine (PDA), and then the pattern was generated using photolithography technique (see Supporting Information). In this work, the ZIF-8 synthesis solution contained 0.137 g $Zn(NO_3)_2$ and 2.83 g 2-methylimidazole in 50 ml MQ water in room temperature. The catechol groups of PDA could chelate Zn^{2+} ions from the solution and induce the subsequent growth of ZIF-8. The high functional group density and strong bond provide enough nucleation sites to make the film dense and uniform. Scanning probe microscopy revealed that the PDA layer has a thickness of around 60 nm (Figure 2a), while the ZIF-8 patterns have a thickness of less than 800 nm (see Figure 2b). The average roughness of SW substrate, the PDA layer, and ZIF-8/PDA layer are 2.64, 5.9 and 30.8 nm on a 1 μm × 1 μm scale, respectively (see Figure S1 in SI). As we can see in Figure 2c and d, the scanning electron microscopy (SEM) images demonstrate that a uniform dense film formed on the silicon surface whereas no continuous film but dispersed ZIF-8 crystals (0.5-2 μm) were observed on the slide without PDA coating. Immersing in ZIF-8 precursor solution for 30 min is sufficient to form the dense thin film for the PDA treated SW, and the scattered crystals began to appear after 60 min of deposition (Figure S2). X-ray diffraction measurements confirmed the existence of ZIF-8 crystal structure in the films (Figure S3). Figure 3a shows that the ZIF-8 thin film without PDA intermediate layer does not exhibit any colors while a greenish color appeared for PDA coated SW samples. Although the sample with PDA intermediate layer holds the greenish color, the color does not change distinctively as the angle of view or the angle of illumination changed (video M1). However, when circular ZIF-8 patterns (400 μm diameter and 800 nm thickness, Figure 3b) were created on the PDA coated silicon wafer, an interesting iridescence phenomenon could be observed. The color of pattern changed from green to pink by only about 20^o change in the viewing angle (Figure 3c and Video M2). It should point out here that a Xenon arc lamp was used to simulate visible light to test the iridescent property of our pattern.

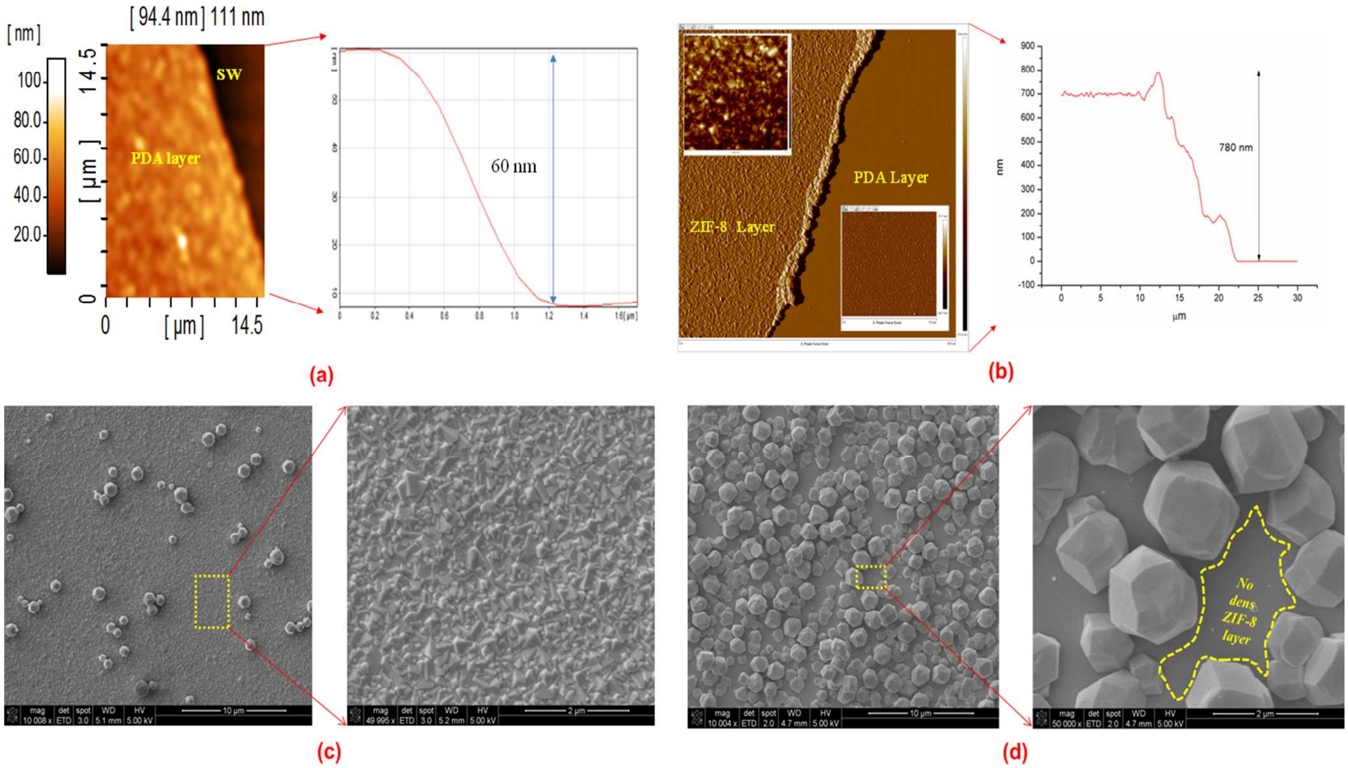


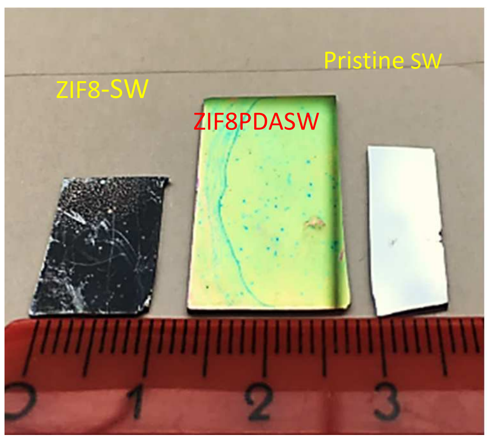
Figure 2 AFM images and thickness profile of PDA layer coated on clean SW (dark region) (a)and ZIF-8 pattern and its corresponding thickness profile (b), and the effect of PDA coating on the ZIF-8 film formation on silicon wafer (immersion time 3hr); dense ZIF-8 deposition with PDA coating (c) and ZIF-8 deposition without PDA coating (d)

The optical interference mechanism is known responsible for producing structural color [1]. Interference colors of an iridescent surface are produced when light interacts at boundaries of layers with different refractive indices (here air-ZIF-8 and ZIF-8-PDA layers). Depending on the dimensions of the layers, lights of certain wavelengths constructively interfere to generate colors, whereas the remaining lights destructively interfere [11].

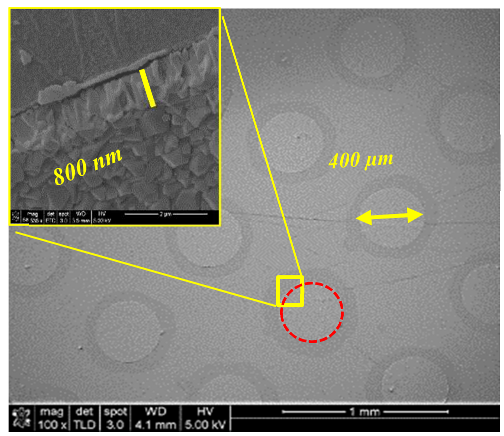
We used diffuse reflection spectroscopy to study the optical properties of ZIF-8-PDA layers. Since the composite coating layer is not thin enough to let the light transmit, only absorption and reflection contribute to the iridescent structure. Diffuse reflectance and absorption results demonstrate how the periodic pattern behaves according to different incident light wavelengths. Figure 4a shows the different reflection results between circular ZIF-8-PDA patterns and pristine SW. As a result, the selective reflection of different wavelengths from the patterned crystals leads to the iridescence properties[12]. The intensity and wavelength of the reflected light mostly depend on periodicity, refractive index ratio and the density of circular patterns. As shown in Figure 3c, the structure exhibited a reversible two-color iridescent property from green to pink and vice versa according to a different angle of view. The peak shown in Figure 4a around 561 nm reveals that the structure reflects green color due to constructive interference. Pink is not considered as a spectral color and encompasses different wavelengths with different propagation wave vectors. We monitored the angle-based reflectance with a high-resolution camera. As shown in Figure 4b, the change of viewing angle can lead to different reflected color: from green (10°) to pink (20°) and then back to green at 40°. The effect of circular ZIF-8 pattern diameter and thickness were examined in Figure

S4. It was observed that reducing the pattern diameter from 400 to 100 μm did not change the color of the structure (see Figure S4 a). However, when the pattern thickness was reduced to 440 nm by simply reducing the immersion time a bluish color was observed (see Figure S4 b and c). According to *Lu et al.* [8], the relation between film's refractive index and film thickness at normal incidence follows n=mγ/2l where "m" is an integer and "n" is the thin film's refractive index. Therefore, the higher the thickness is the lower the film's refractive index is. According to Equation 1, refractive indices difference between layers for creating iridescent structure is desired.

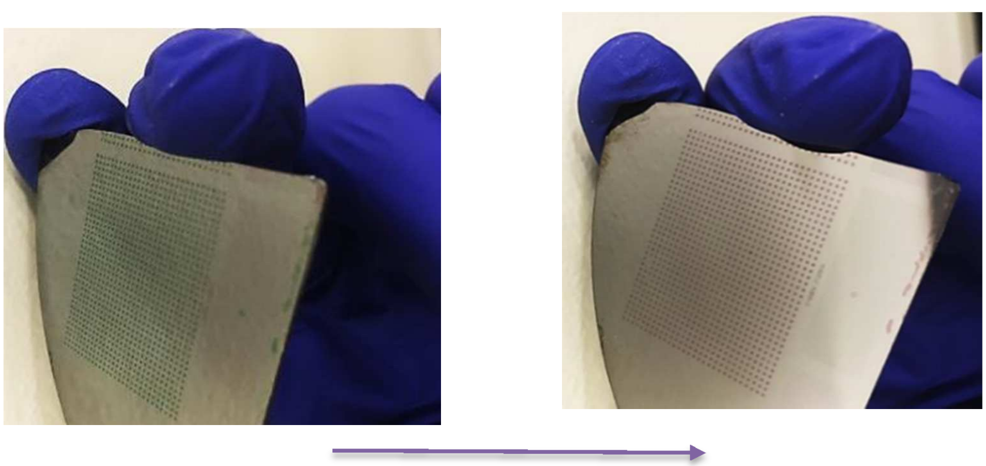
The iridescent ZIF-8 patterns have a potential to be used for a variety of applications such as signaling, sensing, security printing, optical switches and filters, and for decorative purposes. Here, as a proof of concept, two different applications were introduced: optical switch and a single-use sensor for the detection of silver ions in water.



(a)



(b)



Color changes as the angle of view changes
(Iridescence phenomenon)

(c)

Figure 3(a) Effect of PDA coating on the ZIF-8 thin film appearance, (b) SEM images of ZIF-8 patterns (400 μm) on silicon wafer, which were created by positive photoresist lithography, and (c) iridescence phenomenon of ZIF-8 patterns created on the silicon wafer

Potential applications: Optical switch and "turn-off" chemical sensor

A photoswitch defined as a sensor that can detect the presence in or change of light. The two-color iridescent behavior of the sample by alternating the view angle makes the film a potential candidate for an optical switch, as we demonstrated in following experiments. A 532 nm green laser (50 mW) was used to investigate the photo-switch-ability of the structure. First, the light was emitted to the surface of the structure at an angle of 10 degrees with the sample surface. Then the reflected light spot is recorded by a high-resolution camera. The angle then increased to 20 degrees and then reduced back to 10 degrees. Figure 4c shows the intensity of green color in the recorded photo at 10 and 20-degree angles. The diagram in the figure shows how green color intensity decreases when the angle is switched to 20 degree and increases when the angle switches back to 10 degrees.

The ability to accept guest molecules inside the cavity of ZIF-8 was previously used for sensing of chemical vapors and gases[8]. The luminescence quenching mechanism of ZIF-8 luminescence-based sensor was also utilized for the detection of metal ions and small molecules [13]. However, the iridescent quenching mechanism in response to sorption of analyte molecules on the ZIF-8/PDA thin film can also be used to detect chemicals. In this case, the ZIF-8 film is serving as both receptor to recognize molecules and transducer to generate a signal. Similar to the ZIF-8 luminescence-based sensors, the imidazole nitrogen sites within ZIF-8 are expected to play critical roles in the detection of molecules and ions [13-14] , when the iridescent quenching is responsible for the signal transduction. The ZIF-8/PDA patterns did not show the iridescent property after exposing to silver nitrate (1 mg/L) for 15 min (see Figure S5). As EDAX analysis in Figure S5d shows, the silver particles adsorbed on the circular patterns led to the switch-off for the iridescent behavior. Different concentrations of silver nitrate (0.05, 0.1, 0.2, 0.4 and 0.5 mg/L) were applied (immersion time: 15 min) to evaluate the sensitivity of the iridescent sensor. The iridescent quenching event was not observed for <0.1 mg/L concentration. There is also a possibility that Silver ions change ZIF-8 into ZnO nano rods resulting in the iridescent quenching as it reported by We et al.[15]. However, for such transformation a long-term exposure of ZIF-8 with silver ions is necessary. In order to study the effect of interfering ions 100 μl of a solution congaing Fe^{3+} ($Fe(NO_3)_3$) and Cu^{2+} ($Cu(NO_3)_2$) (10ppm each) were added to 50ml of 0.5 mg/ml Ag^+ solution. Iridescent samples were then immersed in the solution for two mins. The control is a solution without the interfering compounds. The comparison between the control solution and the solution with the interfering compounds revealed no difference. The experiment was repeated for a higher concentration of interfering ions (100 and 200 ppm). Iridescent quenching was observed within the first 30 sec at the higher concentration of interfering ions (see the exposed region in Figure S6). Therefore, the ZIF-8/PDA pattern with iridescent property has reasonable selectivity at low concentration of interfering ions.

CONCLUSION: In summary, we constructed a MOF-based iridescent film by spatial patterning of ZIF-8 on a polydopamine coated silicon wafer through positive photolithography. The virtues of this approach include the one-step rapid growth of aqueous based ZIF-8 thin film, benign conditions, and versatile patterning using simple photoresist technology.

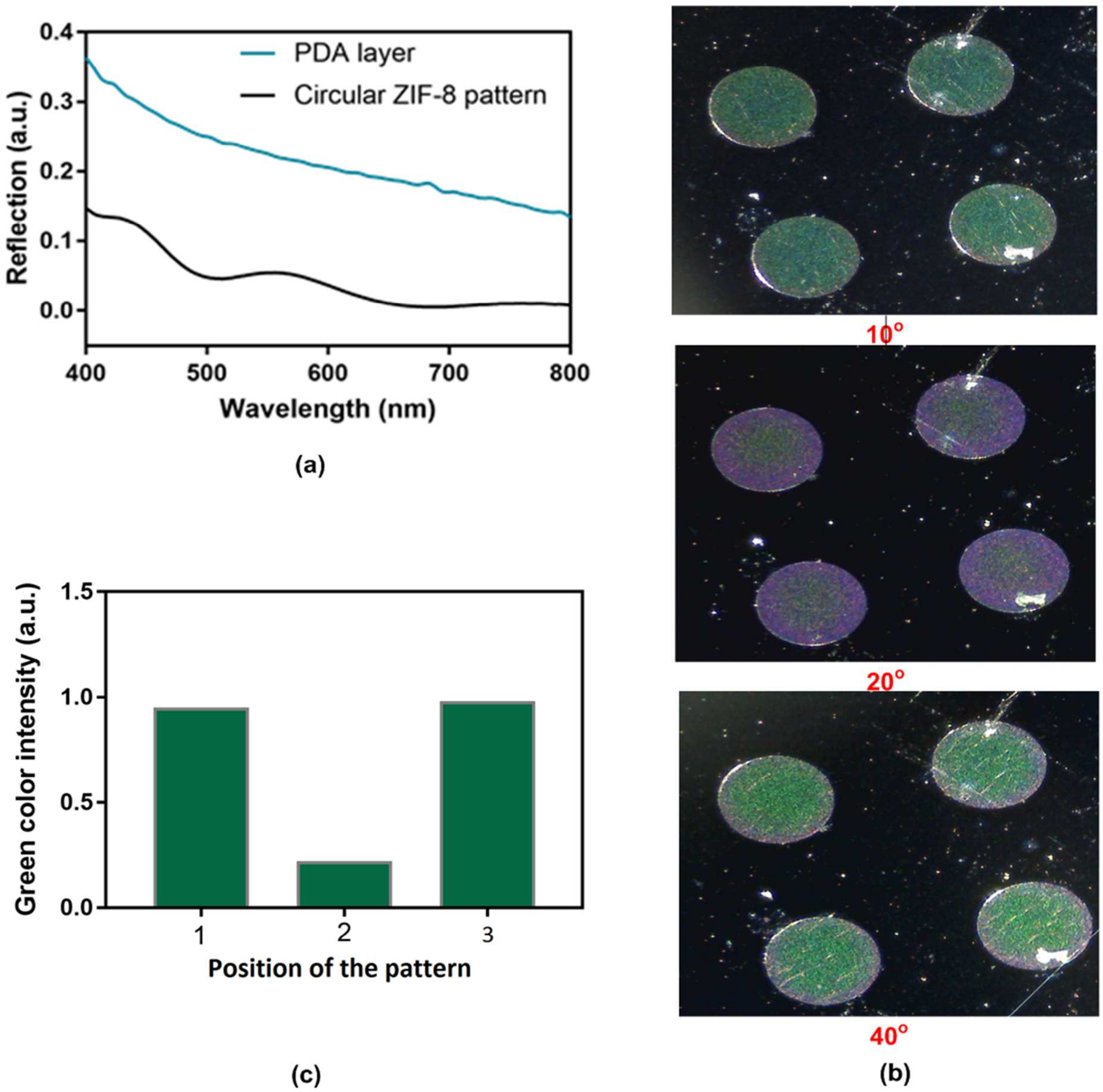


Figure 4 Comparison between the diffused reflectance of circular ZIF-8 patterns (green curve) and Bare SW reflectance spectrum (Black curve) (a), color sequential modifications of the sample due to change in the angle of view left 10, middle 20, right, 40 degree (b), and optical switch: alterations in green color intensity for rotations of 10, 20 and 10 degrees, vertical axis demonstrates the normalized green color intensity while horizontal axis shows 10, 20 and 10 degree rotation (1, 2 and 3 refers to 10, 20 and 10 degree angle rotation) (c)

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Supporting Information. Materials and Methods, surface roughness of SW/MOF/PDA layers, effect of immersion time (min) on the formation of ZIF-8, XRD patterns, AFM analysis, effect of pattern thickness and diameter, and evidence of sensing of silver ions.

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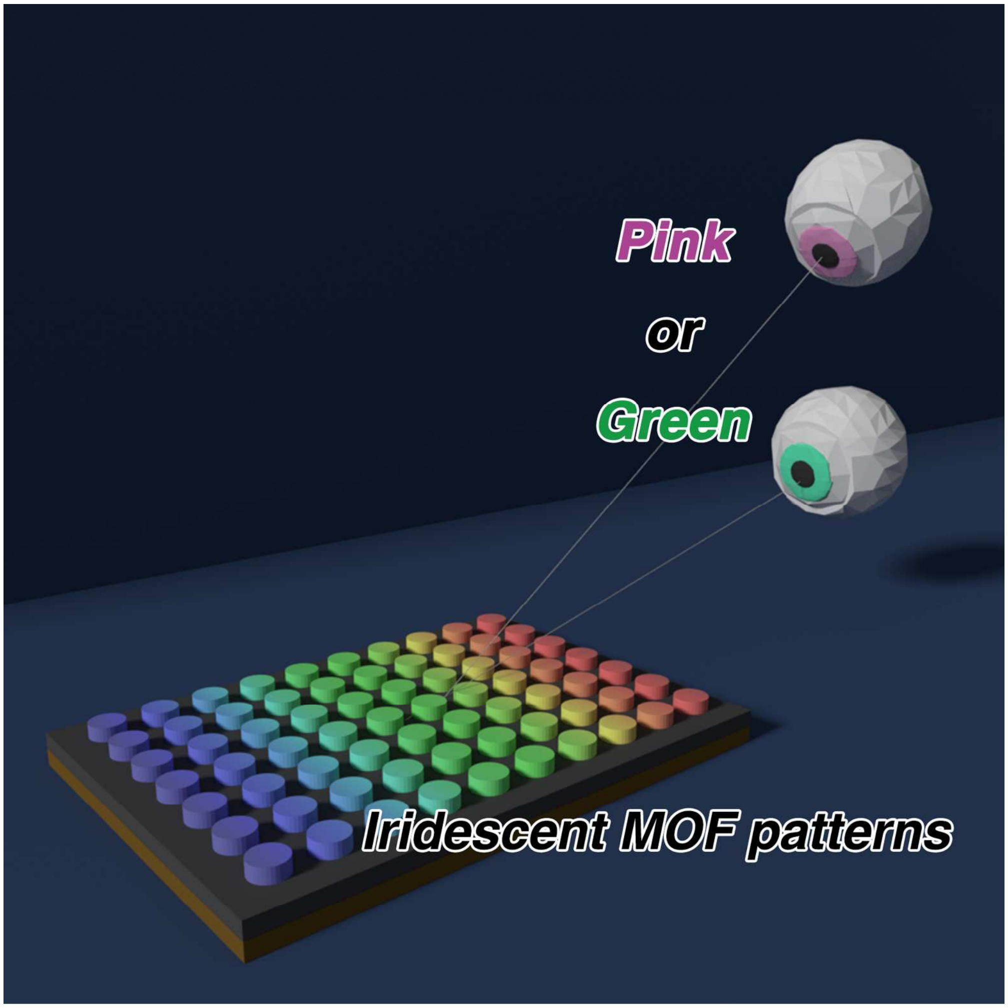

TOC Graphical abstract

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