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Bioinspired angle-independent photonic crystal colorimetric sensing†

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An angle-independent photonic crystal (PhC) colorimetric sensor was developed by using a stimuli-response hydrogel to replicate the template arrays of isotropic photonic crystal beads (PCBs) for the detection of Hg^{2+}.

Colorimetric sensing, which can provide a direct visual indication of chemical reaction events in real time without the use of sophisticated instruments, has become an important detection method in clinical diagnosis, environmental monitoring, and so on.[1] A variety of colorimetric sensors have been exploited based on the processes of structural change of organic dyes, catalysis of enzymes, aggregation of gold nanoparticles, and so on.[2] Among all the materials explored in the colorimetric sensing, photonic crystals (PhCs) have received much consideration owing to their vivid structural colors.[3] By using stimuli-responsive polymers as skeleton materials of the PhCs, a series of colorimetric sensors for the ionic strength, temperature, solvent, biomolecules, and so on, have been well demonstrated.[4] In these cases, the PhCs show different structural colors when observed from different angles due to the effect of Bragg diffraction, thus they should be observed at a fixed incidence angle for the comparison of the stimuli-responsive color changes or the diffraction peak shifts. This intrinsic characteristic of angle dependence is disadvantageous for the construction of versatile colorimetric sensors and hinders the practical applications of the PhCs. Thus, the development of novel PhC colorimetric sensors with the feature of angle independence is eagerly anticipated.

In contrast, through the long eons of evolution, many natural creatures have created various excellent photonic nanostructures that can show desired structural colors.[5] For example, in the feathers of some birds, there exist amorphous arrays of β-keratin particles, which impart these feathers with uniform structural colors, while the nanostructures in the *Parides sesostris* butterfly are composed of several differently orientated domains of identical tetrahedral structure, which offer excellent reflectivity over a broad angle range.[6] Thus, Nature is indeed an ideal school for the design and fabrication of photonic materials.[7] In this regard, researchers have made progress in developing angle-independent PhCs through the self-assembly of amorphous colloidal arrays[8] or using spherical colloidal crystal clusters as elements of the materials.[9] However, these bioinspired photonic nanostructures have not been applied in construction of sensors.

In this communication, we present the desired PhC colorimetric sensor films with the feature of angle independence. Taking inspiration from the photonic nanostructures in the butterfly, we designed and fabricated the films with inverse opal structure by replicating the template arrays of isotropic photonic crystal beads (PCBs). The scaffold polymer of the inverse opal structure film was a target-responsive aptamer hydrogel. When the film was exposed to a target solution, the binding interaction between the aptamer and its target would change the conformation of the aptamer hydrogel and trigger the shrinkage of the hydrogel. This reaction could be observed as an angle-independent color change of the sensor film or could be detected as a deviation-free blue shift in the Bragg diffraction peak position, which could be used for quantitative estimation of the concentrations of the target with a high accuracy. This feature of the film confers itself to be an ideal colorimetric sensor for practical applications.

As a proof of concept, the PhC colorimetric sensor with the promised feature was fabricated by using a stimuli-responsive hydrogel as a scaffold polymer of the PhC film. The fabricating process and working principle of our colorimetric sensor are illustrated in Fig. 1a. The sensor was fabricated by replicating the template arrays of the isotropic PCBs. These PCBs were prepared by self-assembling of silica nanoparticles in microfluidic droplets.[10] It could be found that the PCBs were with good monodispersities and brilliant structural colors, as shown in Fig. 1b. The feature of the colors of the PCBs should be ascribed to the orderly arranged

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† Electronic supplementary information (ESI) available: (I) Methods and characterization; (II) the photographs of the reacted and the free-bending films; (III) the performance of the sensor; (IV) the selectivity of the sensor; (V) the sensor performance in real water samples. See DOI: 10.1039/c3cc42122h

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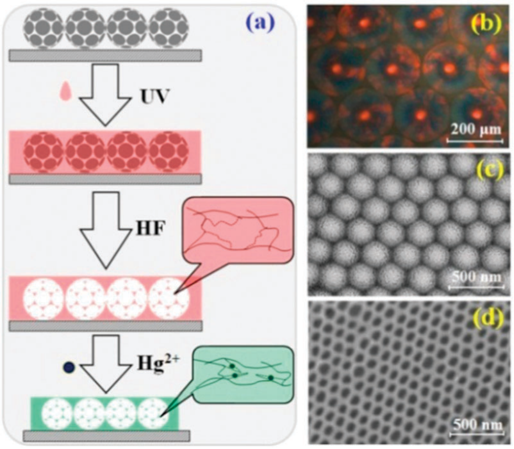

Fig. 1 (a) Schematic illustration of the fabrication process of the PhC hydrogel colorimetric sensor and its application in the detection of Hg^{2+}. (b) Photographs of PCB arrays. (c and d) SEM images of the surface of the PCBs (c), and their replicated inverse structure (d).

structure of their composed silica nanoparticles (Fig. 1c). Because of this structure, the PCBs and the film constructed by the PCBs possess a photonic band gap (PBG) property and show the corresponding structural color or characteristic reflection peak. The peak value (λ) can be estimated from the Bragg–Snell equation:

$$\lambda = 2D(n_{\mathrm{eff}}{}^2 - \cos^2\theta)^{1/2} \tag{1}$$

where n_{eff} is the average refractive index of the beads, D is the diffracting plane spacing, and θ is the Bragg angle of incidence of the light. From the equation, it is conceived to construct the colorimetric sensor film with the function of tunable parameters in the law by using the stimuli-responsive hydrogel to replicate the nanostructure, as shown in Fig. 1d.

The achieved colorimetric sensor film with inverse opal structure was fabricated by replicating the template arrays of the PCBs followed by template etching. In contrast to the general colloidal crystal film, which was directly self-assembled from nanoparticles on a planar substrate and showed an obvious color variation at different positions and viewing angles, the film derived from the replication of the PCB arrays could display identical structural colors when it was viewed at different angles (Fig. 2a and b). This should be ascribed to the spherical symmetry of the PCBs, which infer them with identical photonic responses independent of the rotation of the axes. Thus, the colorimetric sensor film was imparted with the same angle independent feature as their PCB elements (Fig. 2c). It was found that at different viewing angles, the film displays a constant reflection peak position, which was the same as that under normal incidence ($\theta = 90°$). Thus, eqn (1) could be simplified as $\lambda = 2Dn_{\mathrm{eff}}$. The intensity of the film scattering light was not uniform under different detecting angles, it decreased with the decrease in the Bragg angle, thus the reflection intensity was angle-dependent. However, it is still possible to carry out the sensitive colorimetric detection of the corresponding target by using the target-responsive hydrogel to construct the sensor film, as the angle-dependent color changes were avoided and the result could only represent the response of the film to the target.

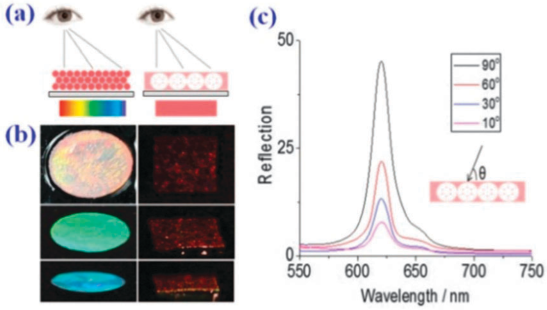

Fig. 2 (a and b) Schematic illustration and photographs of the colloidal crystal film (left) and the PCB-replicated film (right) at different viewing angles, the latter displays identical structural colors. (c) The reflection spectra of the PCB-replicated hydrogel film measured at different incidence angles.

Here, the Hg^{2+} responsive aptamer-crosslinked hydrogel was employed as the scaffold polymer of the colorimetric sensor films. To achieve this hydrogel, the Hg^{2+} responsive aptamer was co-polymerized with the pre-gel solution and acted as the cross-linker of the hydrogel network. When the Hg^{2+} was absent, the aptamers adopted a random coil structure. In contrast, the aptamer could selectively bind to the Hg^{2+} and form a hairpin-like structure of the T–Hg^{2+}–T complex.[11] The formation of this structure could trigger the shrinkage of the hydrogel, and induce a decrease in the diffracting plane spacing of the PhC nanostructure. The colorimetric sensor film could report this process as a blue shift of its structural color or reflection peak. The color changes could be used to qualitatively estimate the target ions, while the shift value of the diffraction peak could produce a quantitative result for the target ions.

Generally, it was beneficial for sensitive colorimetric detection by using a hydrogel scaffold with a high shrinking ratio, which could be realized by reducing the concentration of pre-gel solution or increasing the ratio of crosslinked probe ssDNA aptamers. In our experiment, we used a pre-gel solution of the acrylamide monomer, poly(ethylene glycol) diacrylate (PEGDA) and acryloyl-modified aptamer cross-linker. We fixed the concentration of the monomer and the aptamer cross-linker, and investigated the effect of PEGDA concentration on the PhC hydrogel film. It was found that the prepared colorimetric hydrogel film showed high light transmittance and its reflection spectra were undetectable when the concentration of PEGDA was lowered to 0.5%. Upon increasing the concentration to 1%, the prepared film exhibited obvious color and detectable reflection spectra. A further increase in the PEGDA concentration could enable the hydrogel to have better PhC quality but the possible shrinking ratio was also reduced. Therefore, 1% PEGDA was used to fabricate the PhC hydrogel film for the colorimetric detection in the following experiment.

The quantitative behavior of the colorimetric assay was assessed with different concentrations of Hg^{2+} under the optimized conditions (pH 8.0 buffer A, 30 min reaction time). At the beginning, the film showed a red color and a reflection peak at 620 nm. Upon addition of Hg^{2+}, the PhC hydrogel film displayed a remarkable structural color change and diffraction wavelength shift (Fig. 3). The color changes were bright and obvious, which could be used for the Hg^{2+} determination based on a calibration color chart. It was worth mentioning that the PhC hydrogel film also

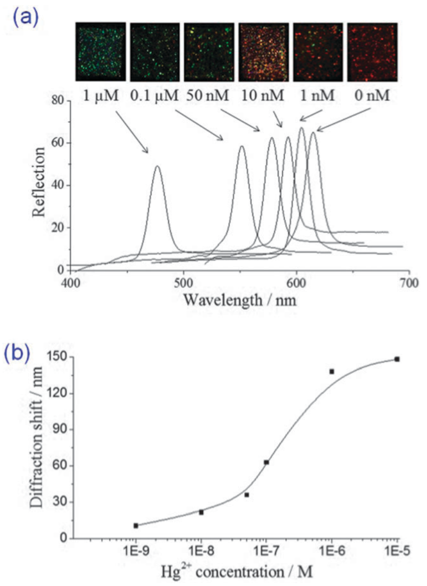

Fig. 3 (a) Photographs and reflection spectra of the colorimetric PhC film at different concentrations of Hg^{2+}; (b) effect of Hg^{2+} concentration on the shift of the diffraction wavelength of the film.

exhibited angle independent performance during all the processes of the assays whether it was in the planar or the free-bending state (Fig. S1, ESI†). The diffraction wavelength was also blue shifted corresponding to the increase in the Hg^{2+} concentration. Fig. 3b presents the peak shift value of the colorimetric hydrogel film as a function of Hg^{2+} concentration. It could be found that the shift value increased with an increase in the Hg^{2+} concentration and saturated at 10 μM Hg^{2+}. A wide range of Hg^{2+} concentrations from 1 nM to 10 μM was detectable by our method. As the toxic level for Hg^{2+} defined by the US Environmental Protection Agency in drinking water is below 10 nM, our proposed Hg^{2+} sensors may have many practical values.

In addition to the sensitivity, a successful colorimetric sensor should also show high selectivity to its corresponding targets. This is particularly important in the detection of Hg^{2+} because of the common coexistence of other heavy metals. In our research, the selectivity of the colorimetric sensor film for Hg^{2+} was evaluated by testing the response of the sensor film to other environmentally relevant metal ions, including Pb^{2+}, Ag^{+}, Mn^{2+}, Zn^{2+}, Mg^{2+}, Ca^{2+}, Al^{3+}, Ba^{2+}, Fe^{3+}, Cu^{2+} and Cr^{3+} at a concentration of 10 μM. It was found that only the solution of Hg^{2+} could cause a significant diffraction shift of the film, and the film displayed an undetectable optical response to the control metal ions (Fig. S3, ESI†). Thus, our colorimetric sensor film showed good selectivity to Hg^{2+} against other relevant metal ions. This indicated the possibility of its application in real samples.

To demonstrate the practical value of our colorimetric sensor, it was used for detecting Hg^{2+} in both tap and lake water samples. For the tap water, the sample was collected after discharging tap water for 30 min and boiled for 5 min to remove chlorine. The lake water sample collected from XuanWu Lake was first filtered to remove solids. Recovery was investigated by adding a known amount of a standard Hg^{2+} solution into the water sample and comparing the measured value to the same amount of Hg^{2+} presented in the solution prepared by Mini-Q. It was found that the recovery reached ideal percentages of 94–96% (Table S1, ESI†), which suggested that our colorimetric sensor was largely free from the matrix effect of real water samples.

In conclusion, we have developed a new type of PhC colorimetric sensor film by replicating the template arrays of the optical isotropic PCBs. By employing an Hg^{2+}-responsive aptamer hydrogel as the scaffold polymer, the achieved film could report the concentration of Hg^{2+} as a remarkable structural color change and diffraction wavelength shift. Both the color change and the reflection shift were used for the qualitative determination of the concentration of target Hg^{2+}. The results showed that our colorimetric sensor film could detect a wide range of Hg^{2+} concentrations with high accuracy. The detection limit of Hg^{2+} satisfactorily met the sensitivity requirements of the US EPA in drinking water. As the colorimetric detection can be achieved without the aid of sophisticated instrumentation, our technique could be further applied in diverse areas such as forensic analysis, medical diagnostics, and environmental monitoring.

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