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Molecularly imprinted colloidal array as a colorimetric sensor for label-free detection of *p*-nitrophenol

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Abstract

We report on the synthesis of a label-free *p*-nitrophenol (PNP) responsive crystalline colloidal array (CCA) based on the combination of photonic crystal and molecular imprinting technique. This novel sensing material was prepared by a self-assembly approach using PNP imprinted colloidal spheres and was characterized by a three-dimensional (3D) ordered opal structure in which numerous recognition sites were created during imprinting. The PNP recognition swelled the colloidal spheres, leading to a red shift of the diffraction wavelength of the CCA due to the lattice spacing change and the effective diffractive index change. The relationship between the diffraction wavelength of the CCA and the size of the colloidal spheres were studied and the size of the molecularly imprinted colloidal spheres was optimized to 200 (±5) nm by adjusting the recipe composition during the emulsifier-free emulsion polymerization. As a result, color change due to the diffraction light shift which is related to PNP concentrations can be observed. The results showed that the diffraction wavelength of the molecularly imprinted colloidal array (MICA) red-shifted more than 50 nm

in response to 30 mM of PNP with a detection limit of 1 mM PNP. The color change of the MICA from green to red was observed. The imprinting efficiency of the molecularly imprinting, the effect of buffer pH and the selectivity were also investigated. We achieved a facile colorimetric detection method for PNP without sample treatment.

Keywords: photonic crystal, molecular imprinting, colorimetric detection, crystalline colloidal array

1 Introduction

As an endocrine disrupting compound (EDC), *p*-nitrophenol (PNP) has harmful effects for public health [1, 2]. Methods have been developed for the detection of PNP in water. As described in the literature, solid-phase extraction [3] and high-performance liquid chromatography (HPLC) [1] have been applied for the analysis of PNP in water as well as an on-line method using solid-phase extraction coupled to supercritical fluid chromatography[4]. In addition, thin layer chronopotentiometry [5] and an interfaced plasma chromatograph/mass spectrometer technique[6] have been reported for the detection of phenolic pollutants. Generally, these methods need special instruments or time-consuming and laborious sample derivation. Therefore, it is still useful and highly desirable to develop a new, convenient method for detecting PNP and other EDCs.

Photonic crystals exhibit unique structural color on the basis of Bragg diffraction if the lattice spacing is appropriate [7, 8]. Responsive photonic crystals (RPCs) with properties that can be tuned by external stimuli have important applications as biological and chemical sensors [9-11]. Molecular imprinting is a well-established technique for the preparation of highly selective polymers with specific recognition ability [12, 13]. To improve the selectivity of RPCs, Li et al. coupled molecular imprinting with photonic crystals to create self-reporting specific sensors that detect proteins, medicines and biomarkers [14-16]. Our group also prepared molecularly imprinted photonic crystals to detect glucose and nerve agents [17, 18]. Most RPCs mentioned above have a three dimensional (3D), interconnected porous, inverse opal structure within a hydrogel matrix formed by crystalline colloidal array (CCA)

templating methods. However, formation of high-quality RPCs with inverse opal structure over a large area usually takes hours, days, or even months to complete, and the wet etching of the crystal template may also destroy the hydrogel matrix. Imprinted template molecules must be washed away from the fragile inverse opal, which may further destroy the hydrogel. Thus, fabrication difficulties have provided a major driving force to develop alternative approaches to classic, inverse opal RPCs.

Most recently, our group first reported on a molecularly imprinted colloidal array prepared by combining photonic crystal and molecular imprinting technique to detect PNP [19]. This proof of principle sensor was fabricated by a self-assembly approach using molecularly imprinted colloidal spheres with a diameter of 280. In aqueous solution, PNP swelled the imprinted colloidal spheres, which increased the lattice spacing, thus shifted the diffraction wavelength. The advantage of this approach is that the imprinted colloidal spheres act both as a recognition element which recognizes the target molecule, and as a signal transfer element which causes the diffraction shift. Usually, the ordered array of an opal crystalline colloidal array collapses easily in aqueous solution. To prevent the destruction of the CCA, we stabilized the ordering of the CCA with adhesive tape. This preliminary work confirmed the feasibility of the concept described above; however, it was only primary efforts without complete characterization. First, the original diffraction wavelength (without PNP in aqueous solution) of the molecularly imprinted colloidal array (MICA) was out of visible color region (more than 770nm), which is not appropriate for a colorimetric sensor if it further red shifts. Secondly, the optical response mechanism of diffraction wavelength red shift has not been

fully understood. In addition, the PNP sensing environment effect, such as pH, reusability of the sensor was not investigated neither.

Herein, as an improvement of our previous work and further demonstration that the developed principle is applicable for colorimetric detection, we report in full detail for the designing and synthesis of a MICA film as a visible indicator for PNP in surface water. The procedure to prepare our photonic crystal sensor is easier than previous inverse RPCs as described above. MICAs with the diffraction wavelength in visible light region were fabricated and exhibit a selective PNP colorimetric indicator. The swelling of the colloidal spheres due to PNP recognition increases the lattice spacing and the filling factor of the CCA both red shift the diffraction wavelength. The effect of pH, the reusability and some surface water detection using the MICAs were finally investigated.

2 Experimental

2.1 Materials

p-Nitrophenol (PNP), *m*-nitrophenol (MNP), *o*-nitrophenol (ONP), phenol, 3-aminophenol (3-AP), sulfuric acid and hydrogen peroxide (30% water solution) were purchased from China National Medicines Co. Ltd and used as received. Methyl methacrylate (MMA), acrylamide (AM) and potassium peroxydisulfate was purchased from Xilong Chemical Co. Ltd. MMA was purified by passing through an Al_2O_3 column before usage. Methanol (HPLC grade) was purchased from Yuwang Industrial Co. Ltd. All solvents and chemicals are of reagent quality and were used without further purification unless specially described.

Glass slides (50×24×0.12 mm) were obtained from Weiss Experiment Products Co. Ltd, China. Before use, glass slides were immerged in H_2SO_4/H_2O_2 mixture (7:3) for 12 h, and then rinsed with deionized water in ultrasonic bath three times. Adhesive tape was obtained from Deli Stationery, China.

2.2 Preparation of PNP imprinted colloidal spheres

Monodisperse PNP imprinted colloidal spheres were prepared by emulsifier-free emulsion polymerization using a four-neck round-bottom flask which contained a reflux condenser, and a Teflon stirrer, powered by a mechanical stirrer. The flask also contained a temperature sensor and a nitrogen inlet. The reaction flask was charged with 255 mL of pure water containing varying amounts of MMA**,** AM and PNP. A nitrogen atmosphere and a stirring rate of 300 rpm were maintained throughout the reaction. This solution was deoxygenated by bubbling with nitrogen for half an hour. After thorough deoxygenation, the temperature was increased to 80±1℃, and a solution of 0.6g potassium peroxydisulfate in 15 mL water was injected. The reaction was left to reflux for 45 min. After polymerization, the monodisperse PNP imprinted colloidal spheres were separated from the resulting emulsion by centrifugation at 5500 rpm for 5min. To remove the template molecules, imprinted colloidal spheres were then washed with acetic acid/methanol/deionized water (1:4:5, v/v), methanol/deionized water (1:1, v/v) and deionized water respectively. As a control experiment, non-imprinted colloidal spheres were also prepared in the same manner in the absence of PNP.

2.3 Formation of MICA films

The monodisperse PNP imprinted colloidal spheres were fully dispersed in deionized water (0.25-0.35 wt %) and then were added into a clean Petri dish. Clean glass slides were placed vertically into a Petri dish to allow colloidal crystal array growth. After complete evaperation of deionized water, MICAs were formed on both sides of each glass slide and then transferred to an adhesive tape.

2.4 Characterization of imprinted colloidal spheres and MICA

Binding isotherms were measured to determine the adsorption capacity of imprinted colloidal spheres. PNP (0.1-1.5 mg mL^{-1}) prepared in 1.0 mL methanol: deionized water (6:4, v/v) was incubated with 10 mg imprinted colloidal spheres for 1 h at room temperature. After incubation and separation of the colloidal spheres by centrifugation, the residual concentration of PNP in the supernatant was determined by HPLC (Shimadzu LC-20A HPLC system) with a SPD-20A UV detector. A 250 × 4.6 mm Promosil C8 analytical column (Agela Technologies) was used. Methanol-water (5.5:4.5, v/v) was used as the mobile phase at 1 mL min^{-1}. The injection volume was 20 μL and the UV detection wavelength was 260 nm. The isotherms and the capacity were obtained by the regression of adsorption data using Prism (GraphPad Software, Inc.).

The reflection of the MICA was recorded using an Avaspec-2048TEC UV/Vis spectrometer with an AvaLight-DH-S-BAL light source and a FC-UV600-2-SR fiber optic reflection probe. The MICA films were equilibrated in deionized water before recording reflection measurements. The MICA films were cut to 5 mm × 5 mm and incubated in phosphate buffer

(pH = 6.0, 0.04 M) for 5 min before each UV-vis scan, and were then incubated into 0-30 mM PNP solutions respectively. After detection, the film was rinsed with a methanol/water (1:1, v/v) solution 3 times for recovery.

The color changes of the MICA films were photographed using a common digital camera under a daylight lamp. After sputter coating the MICA with a thin layer of Au, the size and morphology was examined using Scanning Electron Microscopy (S-4800, HITACHI).

3 Results and discussion

3.1 Preparation of MICA

Figure 1a displays the experimental procedure employed for the construction of PNP MICA, including the polymerization of imprinted colloidal spheres, the self-assemble of the CCAs, and the stabilization of the CCAs by using an adhesive tape.

Firstly, monodisperse PNP imprinted colloidal spheres with a diameter of 200 (±5) nm were synthesized by emulsion-free polymerization. The size of the PNP imprinted colloidal spheres can be tuned in the range of 150 to 280 nm by changing the polymerization conditions. After removing the PNP, recognition sites were created inside the colloidal spheres. Due to the non-covalent bonds between PNP and functional monomer MMA and AM, these recognition can recognize PNP specifically. Secondly, highly ordered close-packed MICA was prepared by a vertical deposition method on glass substrates. During the MICA formation, constant temperature (30℃) and humidity (50%) were necessary to produce a highly ordering MICA with minimum defect. It should be noted that the MICAs on the surfaces of the glass slides

lack stability when incubated in aqueous solutions and cannot be used in practical applications. Thermal treatment has been used to stabilize CCAs on glass slides [20], but the colloidal spheres melt at high temperature. CCAs can be imbedded inside a hydrogel matrix [10, 14, 21], however, infiltration of hydrogel precursor solution may also destroy the crystal array. Thus, in our case, the MICAs were stabilized by being transferred from glass substrates to an adhesive tape. Once stuck to adhesive tape for stabilization, MICA films showed good physical stability. The MICAs on adhesive tapes exhibited bright structural color. Figure 1b shows the MICA with 200 nm colloidal spheres on adhesive tape with green structure color.

3.2 Optimization of the size of colloidal spheres

For a close-packed CCA, the diffraction wavelength of CCA changes as the size of colloidal sphere changes which results in the alterations of CCA lattice constant. In order to prepare MICAs with a desired visible structural color, PNP imprinted colloidal spheres with diameters of 150 nm, 200 nm, 250 nm and 280 nm were prepared using the recipes listed in Table 1. It was found that the average size of the colloidal spheres can be adjusted by changing the reaction parameters including the amount of monomers and initiator, temperatures, and rotation speed. Herein, the colloidal spheres with different diameters were obtained by varying the amount of monomers. After polymerization, PNP was washed off by organic solvents, leaving the monodisperse PNP imprinted colloidal spheres. As a control experiment, non-imprinted colloidal spheres were also prepared in the same manner in the absence of PNP.

All of these imprinted colloidal spheres with diameters of about 150 nm, 200nm, 250nm and 280nm readily form close-packed CCAs by a vertical deposition method, which strongly diffract light of a specific visible wavelength. SEM images of the MICAs fabricated by different sized spheres are displayed in Figure 2. As shown in Figure 2, the colloidal particles were arranged into a 3D close-packed face-centered cubic (FCC) structures through self-assembly. On the other hand, the highly ordered periodic opal structure of the MICA leads to highly specific surface areas, which enabled them rapidly and sensitively respond to target analytes.

For photonic crystals with FCC structure, the maximum diffraction wavelength follows Bragg's Law (1),

$$m\lambda = 2n_{\text{eff}}d \sin \alpha \qquad (1)$$

where m is the diffraction order, λ is the wavelength of the diffracted light, n_{eff} is the effective refractive index of the CCA, d is the interplanar spacing, and α is the angle of incidence. Because of the close-packed CCA in this study, the diffraction wavelength λ could be varied by changing the diameter of the colloidal spheres. The prepared 150, 200, 250, and 280 nm MICAs diffracted 370, 509, 630, and 756 nm at normal angle respectively (Figure 3a), and different structural colors were observed. As we can see in Figure 3b, the diffracted wavelengths of 200 and 250 nm MICAs lie in visible light region, green and red colors are observed. However, MICAs containing 150 and 280 nm colloidal spheres diffracted UV and near infrared light respectively. No structural color could be observed for 150 nm MICA. It

can be seen that 280 nm MICA shows violet structural color even though the diffracted wavelength is out of visible region. This structural color could be attributed to the second order diffraction of the MICA. For MICAs containing 250 nm colloidal spheres, there would be no significant color change for any further red shift, because it diffracts red light. Thus, the colloidal spheres with a diameter of 200 nm were selected for the following investigations.

3.3 Sensing properties of MICA

MMA and AM were chosen as functional monomers for the recognition of PNP. The binding capacities of PNP on the molecularly imprinted colloidal (MIC) spheres were analyzed, and the results are shown in Figure 4a. It was observed that the adsorption amount of PNP on the imprinted colloidal spheres increased with an increasing PNP concentration. The adsorption capacity was approached equilibrium at the high concentration. This result suggested that the imprinted spheres possessed a large number of specific binding sites within the colloidal spheres. The adsorption capacity of imprinted spheres to PNP can be calculated according to binding isotherm as 331 μmol g^{-1}, while for the non-imprinted colloidal (NIC) spheres the adsorption capacity is 84 μmol g^{-1}. Imprinting effect, defined as the ratio of the capacities between imprinted colloidal spheres and non-imprinted colloidal spheres, is 3.4. A satisfactory imprint was achieved.

The traditional molecular imprinting technique only affords thousands to millions highly specific binding pockets or recognition elements that possess the ability to recognize specific target molecules. As a sensing element, the integration of these recognition elements with an

appropriate transduction element is required. In our case, due to the 3-D ordered CCA structure, the signal can be generated by the MICA itself through Bragg diffraction, and the molecular recognition process can be directly transferred into readable optical signals.

The sensing response of the MICA to PNP was examined in phosphate buffer solution (pH=6.0, 0.04 M). Figure 4b shows the sensing behavior of the MICA fabricated by using the 200 nm imprinted colloidal spheres. With an increasing of the concentration of target molecules, the diffraction peak red shifted gradually. Within 5 min, the wavelength increased from 613 to 668 nm when PNP increased to 30 mM. The color changes that accompany the peak shift of the Bragg diffraction also are visually evident. The MICA film in the phosphate buffer solution shows green color at the beginning. After the exposure to 10 mM and 30 mM PNP solution, the MICA film changed color to yellow and red, respectively (Figure 4c). For a better comparison, diffraction wavelength shifts vs. PNP concentration were plotted instead of the raw data (Figure 4d). Notably, this selective detection is relatively sensitive for PNP, as evident from the detection of 1 mM PNP solution. Compared with the detection limit of 0.2mg/L of traditional PNP detection method based on HPLC or Mass spectroscopy [1,3], the detection limit of MICA is still needed to improve. However, these traditional methods involve time-consuming sample preparation and expensive instruments. Our MICA provides a simple way and colorimetric detection for PNP. As a control experiment, a non-imprinted colloidal array (NICA) film with the same photonic structure was also constructed (Figure 4d). It exhibited only a minor shift when it was soaked in PNP solutions with the same concentration variation as the MICA film described above (Figure 4b). Although the detection

method based on the MICA is actually semi-quantitative, it did offer us a facile colorimetric detection method.

3.4 Sensing principles

This selective sensing mechanism can be attributed to the hydrogen bond interactions, electrostatic attraction and associated weak interactions between the target molecules of PNP and functional monomers. The target molecule and the specific binding sites of MICA produced a specific recognition by noncovalent bonds, and the process of recognition can swell the spheres. With increasing PNP concentration, the size of spheres increased, and results in an increase in the interplanar spacing followed by a reflection peak red shift (Figure 5a). Furthermore, the increase in the effective refractive index can be one of the factors causing the diffraction peak red shift. The hydrophilic functional comonomer AM makes the exterior of the colloidal spheres more flexible and soft [22]. In response to PNP adsorption, swelling of imprinted colloidal spheres caused the space between colloidal spheres to become occupied (Figure 5b). Thus, the filling factor of the CCA increases. The effective refractive index n_{eff} of the crystal is calculated as follows [23]:

$$n_{\mathrm{eff}}=\sqrt{f\cdot n_{\mathrm{m}}{}^{2}+(1-f)n_{\mathrm{v}}{}^{2}} \qquad (2)$$

Where f is the filling factor, n_m is the refractive index of the colloidal spheres, and n_v is the refractive index of the voids. In this research, n_v is the refractive index of the PNP solution and below the value of n_m. Once the voids are occupied, the filling factor increased, and the n_{eff} increased, eventually leading to the red shift of the reflection peak. According to Figure

5b, colloidal spheres swelled by about 10% in response to 20 mM PNP. The results in our research suggest that a close-packed MICA can swell in response to analytes and show a visual optical signal.

3.5 Response characteristics and reproducibility

To optimize the response of the MICA, the red shift of reflectance in response to 10mM PNP under different pH conditions was investigated (Figure 6a). Most PNPs (pKa=7.16) [24] exist as anions when the solution pH > pKa, and as a neutral molecule when the solution pH < pKa. As the pH of the PBS decreases, more and more PNP exists as its neutral molecule structure. When the pH value is too low in solution, more H^+ may affect the hydrogen bond between the PNP and the AM, leading to less PNP adsorption by the imprinted colloidal spheres. Generally, the experiment results showed that at pH=5 and pH=6, MICAs had better optical responses to the target. The selectivity test of the MICA was carried out by using its analogues, phenol, *m*-nitrophenol (MNP), *o*-nitrophenol (ONP) and 3-aminophenol (3-AP). It was seen that there were almost no diffraction wavelength changes in response to phenol, ONP, and 3-AP. The red reflection of the MICA shifted significantly in response to MNP, which has similar structure to PNP (Figure 6b). The reusability of the MICA was evaluated by an elution and rebinding method. From Figure 6c, it can be observed obviously that MICA possessed an ideal recoverability within five cycles and the standard error was just within 5%.

To test the possibility of utilizing the MICA to colorimetrically detect PNP from environmental samples, the MICA film was subjected to surface (from the Linglong Lake,

Beijing, China) and tap waters (Beijing, China) spiked with PNP. The results showed that the reflectance peak, in surface and tap water, shifted approximately 55 nm and 50 nm, respectively, towards 30 mM PNP. The color of the MICAs changed from green to red (Figure 7). A relative linearity of the response of the MICA to 1 to 30 mM PNP from surface and tap water is observed (r^2=0.971 and 0.985, respectively), and a LOD of 1 mM was achieved.

4 Conclusions

In summary, a simple and low cost colorimetric method to detect PNP was developed by self-assembling imprinted colloidal spheres into a close-packed CCA structure. Adhesive tape can be used to stabilize the CCAs. The result shows that the imprinted CCA has high selectivity and great regenerating ability in an aqueous environment. More importantly, MICA directly generates colorimetric signals, which is suitable for reporting recognition events without any necessary treatments of analytes. It is envisaged that the MICA could provide a promising alternative to current methods of onsite monitoring of PNP levels.

5 Acknowledgments

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Table 1 Recipes and diameters of imprinted colloidal spheres

Sample	Diameters (nm)	MMA (ml)	AM (mmol)	PNP (mmol)
A	280	30	15	5
B	250	24	12	4
C	200	12	6	2
D	150	6	3	1

Figures

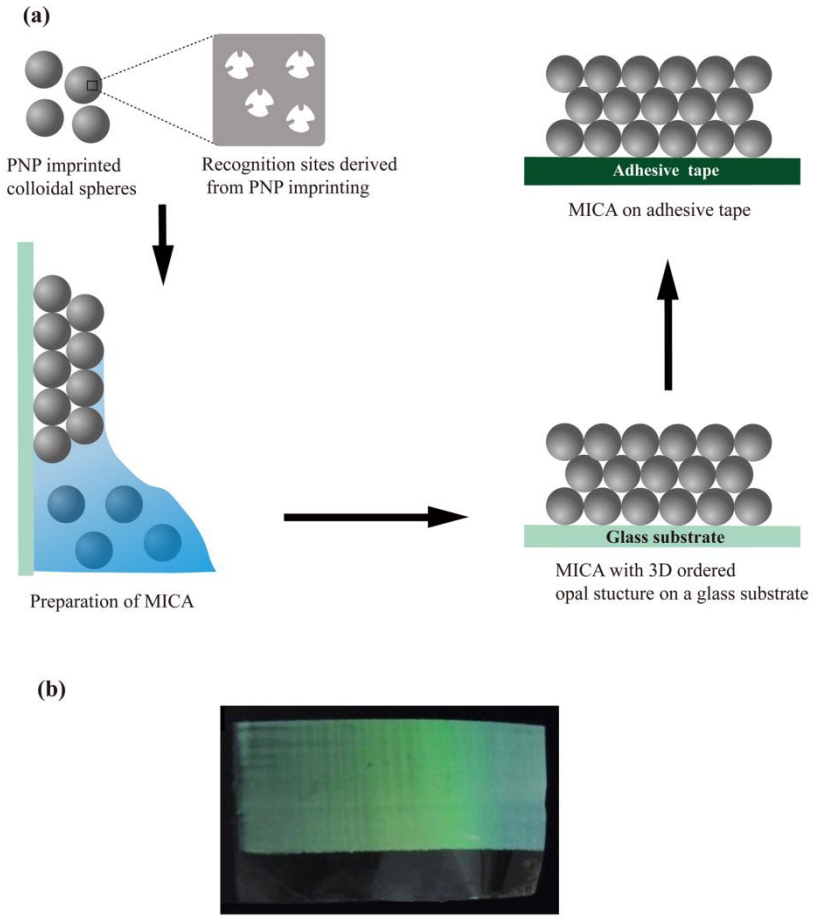

Figure 1. (a) Schematic illustration of MICA fabricating. Monodisperse PNP imprinted colloidal spheres were self-assembled into a 3-D ordered opal CCA structure on a glass substrate. Then the MICA was transferred onto an adhesive tape which conserving the intact opal structure. (b) Photograph of the MICA self-assembled by 200 nm colloidal spheres on adhesive tape with green structural color.

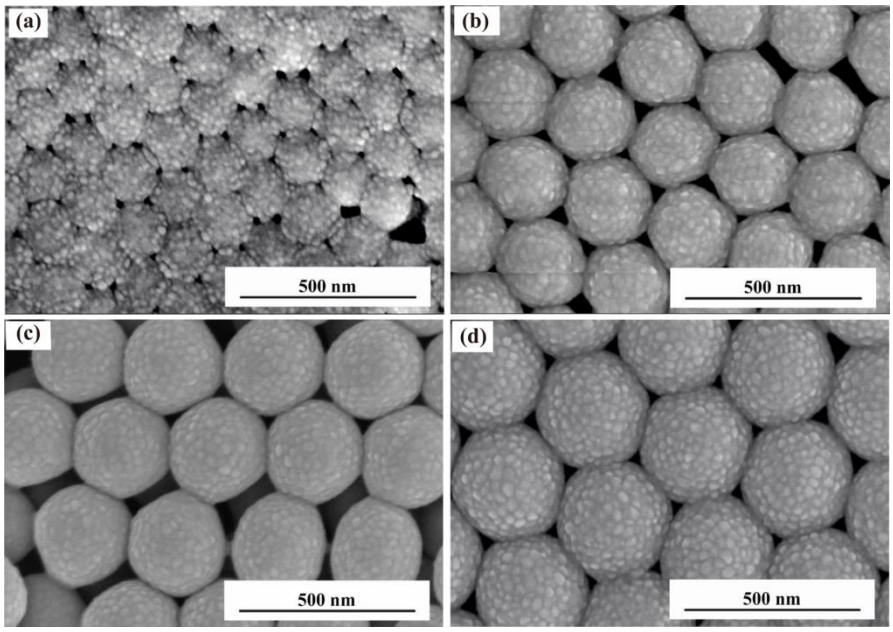

Figure 2. (a) SEM images of close-packed MICAs of different sizes, (a) 150 nm, (b) 200 nm, (c) 250 nm, and (d) 280nm.

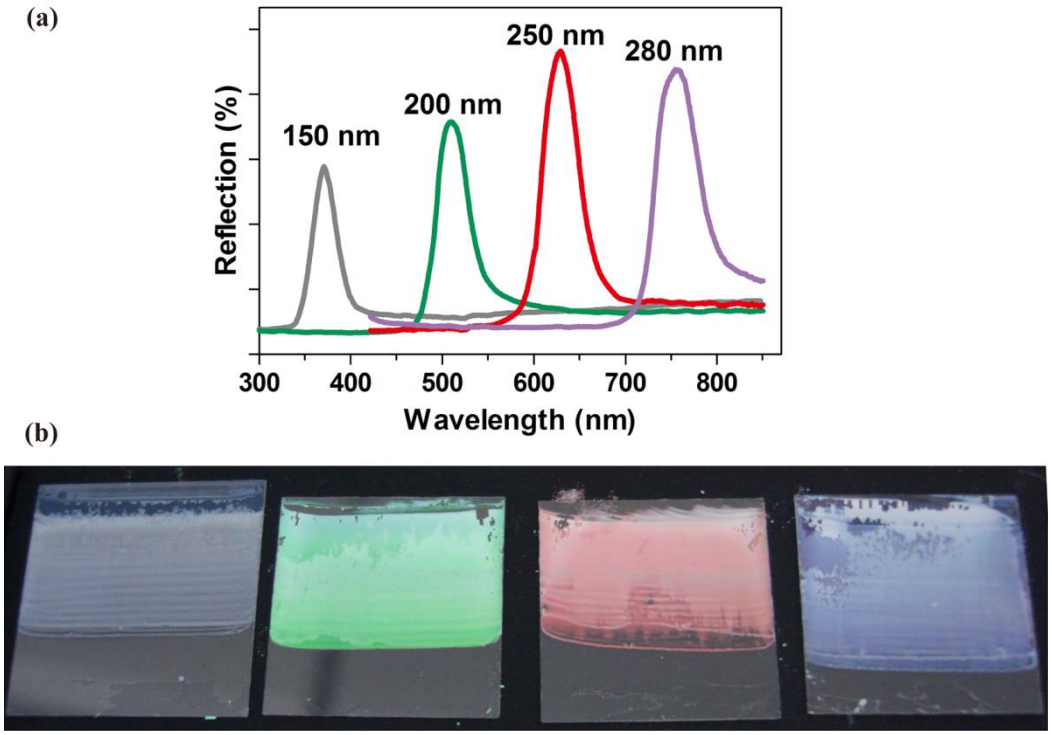

Figure 3. (a) Reflection spectra of MICAs self-assembled from different size of colloidal spheres. (b) Colors of the MICAs self-assembled from colloidal spheres with different size.

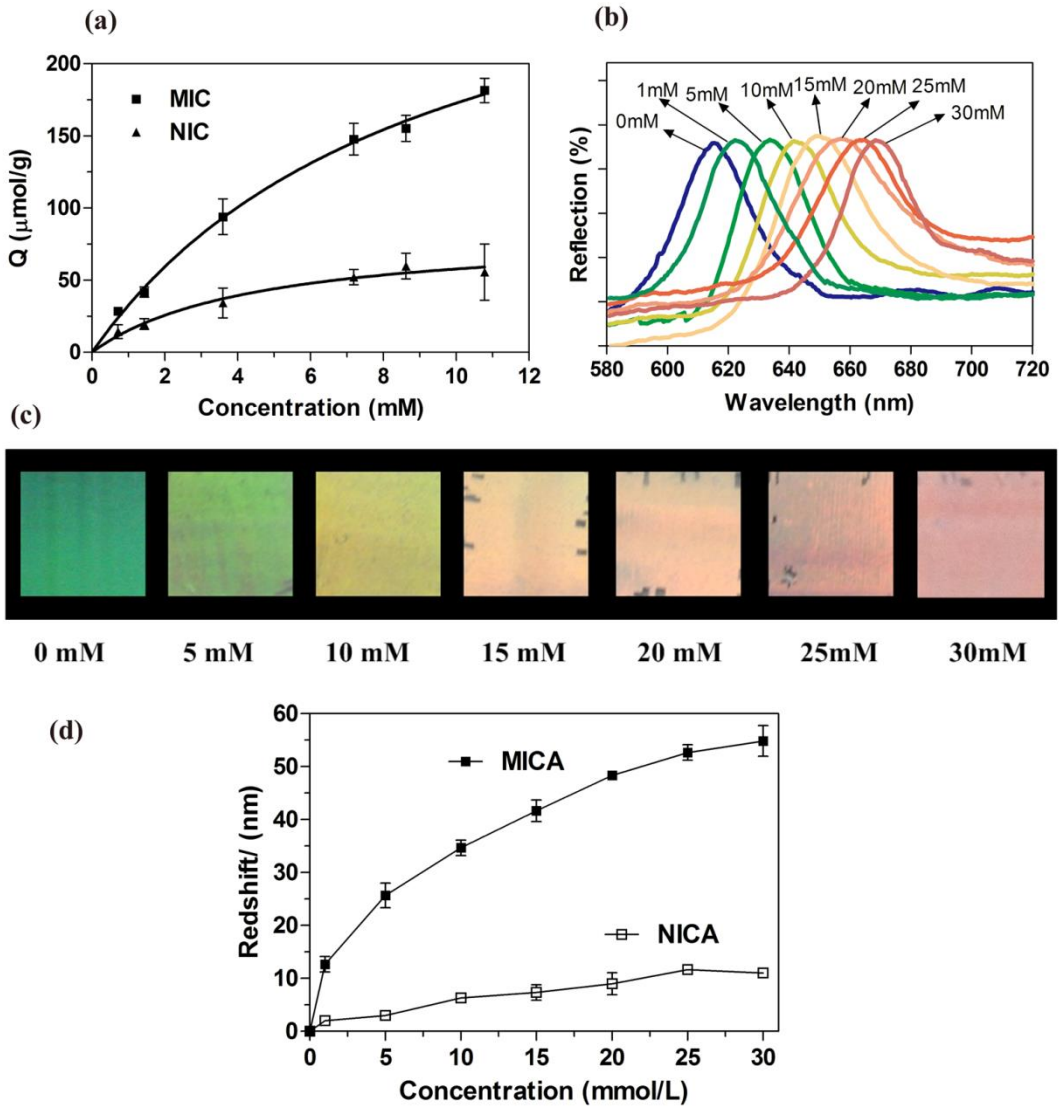

Figure 4. (a) Adsorption isotherms of PNP on imprinted colloidal spheres and non-imprinted colloidal spheres. (b) Optical response of MICA in response to PNP in phosphate buffer (pH=6.0, 0.04 M). (c) The induced color changes of the MICA film upon adsorption of PNP at different concentrations. (d) Plot of the Bragg diffraction shifts of the MICA and NICA in response to the PNP.

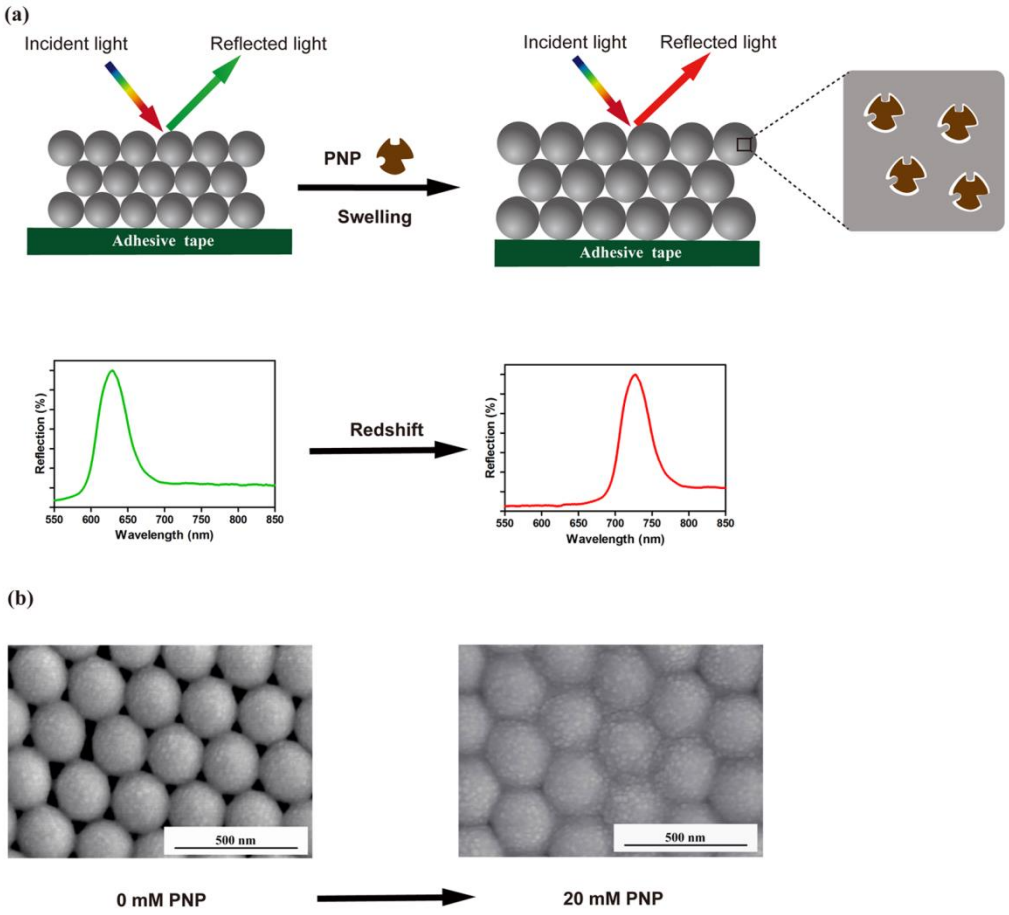

Figure 5. (a) Sensing principle of the MICA film. (b) SEM images of the MICA before and after adsorption of PNP.

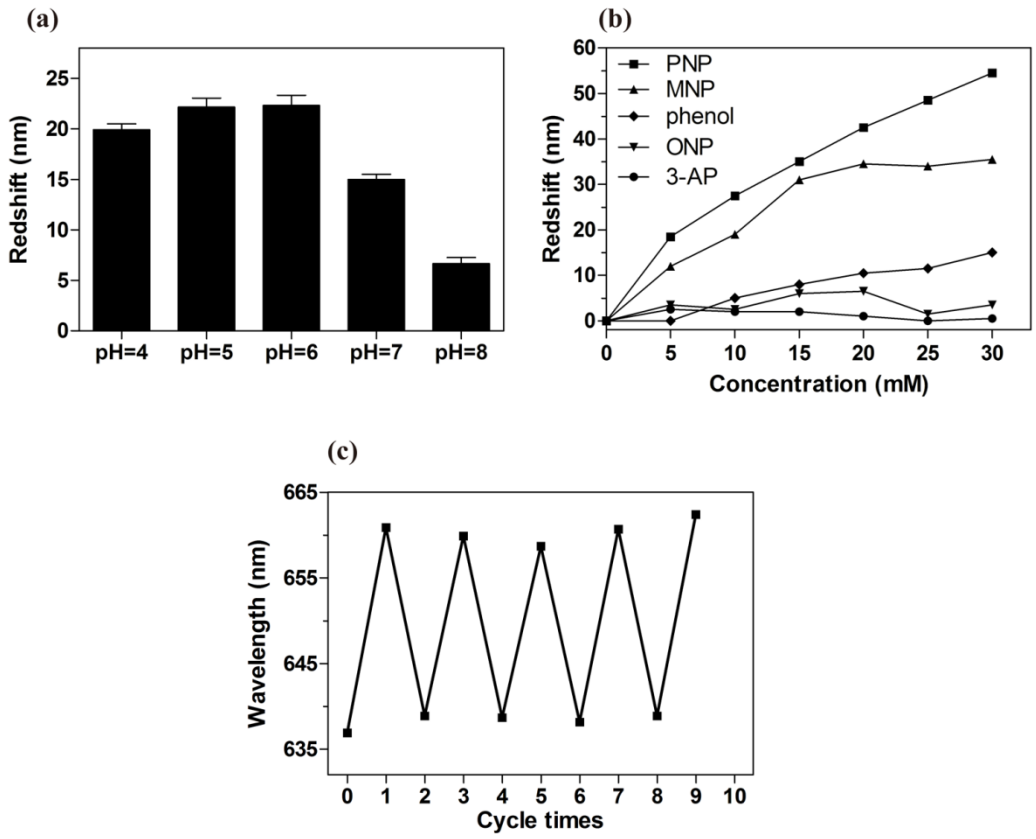

Figure 6. (a) The red shift of the MICA film in response to 10 mM PNP in phosphate buffer under various pH. (b) Red shift of MICA film in response to PNP and its analogues. (c) Recoverability of the MICA film incubated in a 10 mM PNP buffer and then recovered in a methanol/water (1:1, v/v) solution.

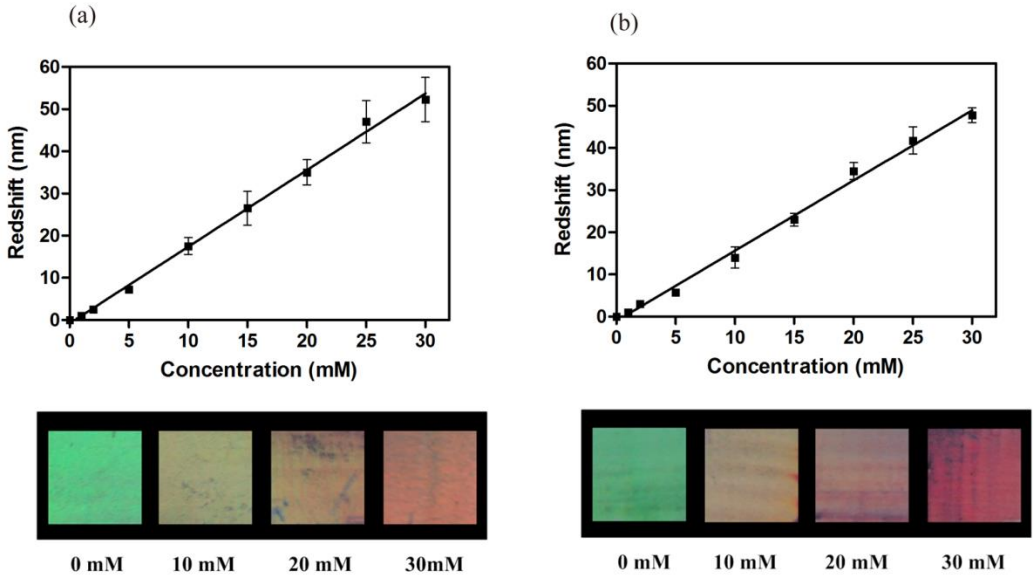

Figure 7. Reflection red shift of the MICA in response to various concentrations of PNP and their color changes in (a) surface water (from the Linglong Lake, Beijing, China) and (b) tap water (Beijing, China).