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A flexible imprinted photonic resin film templated by nanocrystalline cellulose for naked-eye recognition of sulfonamides

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ABSTRACT

An optical sulfonamides sensor is fabricated based on a molecular imprinted resin templated by nanocrystalline cellulose. A chiral nematic imprinted composite film is synthesized which is subsequently treated with removal of templates to generate a red reflecting photonic film. The film shows a naked-eye color response to sulfanilamide, which is related to reassemble imprinted sites in the chiral nematic structure, resulting in a yellow reflecting film. Upon exposure to various antibiotics, it can be simultaneously in selectively response to three sulfonamides. This strategy facilitates enormously potential application of the resin as battery-free and portative optical monitoring sensors.

Introduction

Sulfonamides (SAs) are one of broad-spectrum antibiotics that commonly incorporated in the human medicines and feedstuff additives. It is widespread used in the treatment of antiinflammatory, antiviral agents and anticancer [1,2]. Through excretion, these drugs reach in the environment and have caused a large-scale water contamination due to their chronicity and toxicity [3–5]. Many researchers have tried some selective and effective approaches for the detection of the sulfonamides, including different spectroscopic and imaging methodologies, or novel magnetite techniques [6,7]. In addition, someone utilized a surface acoustic wave technique to identify sulfamethizole [8]. In contrast, a real-time, convenient and easy-to-use recognition technology of SAs pollution that does not require professional equipment and tedious sample preparation is a large challenge. An optical molecular sensor based on responsive color change in available optical material system, even “naked-eye”, will be appealing.

Photonic crystals [9–11] that are able to reflect the diffraction of light in the visible spectrum on base of the photonic band gap (PBG) [12–14]. As a promising material, An area of attractive interest lies in the potential of optical sensors to develop the naked-eye recognition. The sensors show targeted analyte triggers refractive index achieving the change of wavelength and intensity of diffracted light into optical visible. To date, some investigators have used the naked-eye molecular detection [15–17], whereby selectivity was introduced by molecular imprinted polymers (MIPs)[18,19]. Incorporation of MIPs into suspension arrays to construct a photonic material could achieve the selective optical responses for imprinted template by the change of refractive index. For example, Lu et al. recently reported a molecularly imprinted colloidal array photonic crystal to visually detect 2,4,6-trinitrotolune [17]. However, patterned array substrates are easily influenced by the ambient environment resulting in weaken or confusion of photonic property and thus inhomogeneity in color. Moreover, the specific imprinted cavities distribute on the smaller surface areas than suspension assays and hence prohibitive for the potential of molecular imprinting technology. Recently, much attention has been drawn to the use of liquid crystals (LCs) to synthesize porous photonic materials [20–22], which arises from itself inherent ordered hierarchical structure by self-assemble [23]. Most importantly, LCs have advantages in rich of raw materials and their characteristic 1D photonic structure is easy for fabrication. Some reports have showed that, cholesteric liquid crystals incorporated with functional imprinted recognition groups, such as crown ether, dimethyloctadecyl[3-(trimethoxysilyl)propyl] ammonium chloride, benzoic acid for the molecular optical recognition [24–26]. The patterned pores in these materials are uniformly inserted in the each layer of materials to ensure functional sites more efficiently accessing to analytes.

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Nevertheless, these photonic materials just respond to single analytes on the one hand, and on the other hand, cholesteric liquid crystals are normally formed from aromatic polyester, which leads to adverse aqueous recognition and high cost of production [27]. In contrast, nanocrystalline cellulose (NCC) liquid crystals are obtained from cellulosic biomass and advantage in water solubility, resource-rich and consumption-low. Some of them as the natural biotemplate have been already applied to many mesoporous photonic patterns with chiral nematic structure [28–31]. Recently, our group has successfully synthesized a photonic fluorescent silica film based on NCC for detection of nitrobenzene [32]. Cachelin et al. demonstrated the combine of chiral nematic liquid crystals and reactive chiral dopants constructing an optical acetone sensors [33]. Some researchers recently reported CNC-based chiral nematic photonic films for humidity sensor [34,35]. Therefore, the fabrication of an imprinted chiral nematic nanostructure photonic material based on NCC is achievable. Meanwhile, the ideal materials can be selectively triggered by imprinted template, leading to the light response, and the optical change can be discernable by the naked eye.

Herein, we report on a molecular sensor based on a chiral nematic photonic resin film and demonstrates a remarkable optical response and recognition toward sulfonamides selectively, whereby introducing hydrophilic, flexible, easy to implement molecular imprinted resin. The variation of photonic film ascribes to the change in the average refractive index and simultaneously the swell of chiral nematic structure during the recognition process. The photonic film can be in response to three sulfonamides as the color contrast of film was clearly visible to the naked eye. This research into molecular optical sensor as a responsive photonic film is anticipated to extend unique horizons in pollution monitoring.

Experimental section

Materials

All compounds were obtained from standard suppliers without purification unless otherwise noted. Aqueous dispersions of nanocrystalline cellulose (NCC) were obtained from acid-catalysed hydrolysis of degreasing cotton (3.5 wt%, pH = 2.4) in a procedure described previously [36].

Characterizations

UV–vis/near-IR studies were carried out on a Shimadzu UV-3600Plus spectrophotometer (Japan) in transmission mode. CD spectroscopy experiments were was recorded using a JASCO J-815 spectrometer (Japan) and the beam path was perpendicular to the surface of films in a quartz cuvette. Infrared spectra was collected on a Nicolet iS50 FT-IR spectrometer (America) with a Smart orbit diamond slide-on ATR. Polarized optical micrographs (POM) were measured from images obtained with a BM-58XCC microscope with crossed polarizers. TEM images were collected on a JEOL JEM-2100 (HR) at an accelerating voltage of 200 kV with a LaB6 filament, Thermo Scientific (Japan). SEM images were performed on the Hitachi S4700 FE-SEM (Japan). The samples were fractured into small pieces by liquid nitrogen, and using double-sided adhesive tape to paste them in aluminum stubs, and spraying gold or gold-palladium in their fracture surface. Static contact angle images were collected with KSV CM 20 (Finland). XRD patterns were obtained on a Shimadzu XRD-6100Lab (Japan) at 10–80° with 7°/min. All images taken with the polarizers in a perpendicular (crossed) arrangement were necessary unless otherwise stated and analyzed using LAS software.

Synthesis

Preparation of SAs-imprinted resol precursor

A base-catalyzed polymerization method was employed to synthesize a soluble, low-molecular-weight, imprinted resol precursor. The preparation process use for reference to the procedure reported by MacLachlan MJ [37]. The imprinted polymer was presented with phenol and formaldehyde, which can introduce abundant hydroxyls and ether linkages into the precursor. In the preparation procedure, 0.61 g (6.50 mmol) of phenol was melted at 40–42 °C, and followed by the addition of 20% NaOH (aq; 0.13 g, 0.65 mmol) slowly over 10 min with stirring. 1.05 g (13.0 mmol) of formalin was added dropwise below 50 °C, and then the optimal weight 100 mg of sulfanilamide as imprinted template were added. The reaction mixture was then stirred at 70–75 °C for 1 h. After cooling to room temperature, the reaction mixture was neutralized to pH = 7.0 using 0.6 M HCl (aq) solution. Water was removed under vacuum below 50 °C, and then a viscous product was obtained and dissolved in ethanol before the precipitate was removed by filtration. Ethanol was removed by evaporation and the final product was dissolved in a water/ethanol (85/15 v/v %) solvent mixture to make a 30 wt% solution.

Synthesis of chiral nematic composite film

A representative example described the preparation of the composite resin film (≈30 μm). 14 ml of the aqueous NCC suspension (3.5 wt%, pH = 2.4) was sonicated for 15 min and then mixed with 800 μl imprinted precursor solution at room temperature for 2 h with stirring. The homogenous solution was then transferred in 7 ml portion to two 100 mm polytetrafluoroethylene Petri dishes and allowed to dry for 48 h at ambient conditions. The obtaining composite films need to be thermopolymerized in an oven at 75 °C for 24 h.

Removal of templates to construct the photonic imprinted resin film

Firstly, NCC was removed from the composite films using NaOH (aq.) solution. In a typical procedure, about 200 mg of the composite films were placed in a beaker containing 100 ml of 16% NaOH (aq) solution and heated at 70 °C for 12 h with gentle magnetic stirring. The films were then brought to room temperature and transferred to a beaker containing vast deionized water at room temperature. The films were then washed with copious amount of deionized water periodically to remove NaOH until the washings proved to be neutral by pH paper. Secondly, the SAs template was remove from composite films by extractant of methanol–water (4:1, v/v) with the assistance of ultrasound, which was repeated eight times. Films were washed as mentioned and allowed to air-dry at ambient conditions. Finally, the 72 mg of photonic imprinted resin film was obtained after the templates removed step by step.

Naked-eye recognition of sulfonamides

The imprinted films were used for quantitative analysis and naked-eye recognition of sulfonamides. For quantitative analysis, different concentrations of sulfanilamide solutions were used to induce the films (about 2 × 2 cm) for 30 min resting on watch-glass at room temperature. The unbound analytes were washed away with vast pure water, and then drying with air heater. The transmission spectra of the DRs were measured after the analytes binding to the imprinted sites. For naked-eye recognition of sulfonamides, the films were put into many watch-glass and incubated by the a various of antibiotics (6 mg/ml) with methanol/water (3:7, v/v) solvent. The mixed solvent can be better to solve the problem that a few antibiotics are poor water solubility. After reaction, the films were washed away with vast pure water. Then the transmission spectra of the films were measured as mentioned.

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