Electronic Supplementary Material (ESI) for Nanoscale.

Label-free and pH-sensitive colorimetric material for the sensing of urea

Lu Li[a,b], Yue Long[b] , Jinming Gao[a], Kai Song*[b] and Guoqiang Yang[c]

a. *Shaanxi Key Laboratory of Natural Products & Chemical Biology, College of Science, Northwest A&F University, Yangling 712100, China*

b. *Laboratory of Bio-Inspired Smart Interface Sciences, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, China*

Email: songkai@mail.ipc.ac.cn

c.*Beijing National Laboratory for Molecular Sciences, Key Laboratory of Photochemistry, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China*

Materials and chemicals

Tetraethoxysilane (TEOS), methacrylic acid (MAA), ethylene glycol dimethylacrylate (EGDMA), ammonia, formamid, methylurea and 1,3-Dimethylurea were purchased from Alfa Aesar. Acetamide, 2, 2'-Azobis(isobutyronitrile) (AIBN) were obtained from Arcos Organics. Urease was purchased from TCI. Urea, anhydrous ethanol, hydrofluoric acid and other affiliated chemicals were all obtained from Beijing Chemical Industries. All of the solvents and chemicals used were of analytical quality and were used without further purification unless indicated. Common glass slides (Microscope slide, 76.2 mm long, 25.4 mm wide, 1 mm thick) were purchased from Sail Brand (Shanghai, China). Polymethyl methacrylate (PMMA) slides (25 mm long, 15 mm wide and 1mm thick) were from local suppliers.

Characterization

The morphology and microstructure of the silica colloidal crystals and photonic films were characterized using the scanning electron microscope (SEM, model JEOL S4800). Optical Bragg diffractions were tested by a fiber spectrometer (AvaSpec-2048, Avantes). These spectra were taken with light impinging perpendicular to the film. The diameter of collection spot was approximately 2 mm. The photopolymerization was performed in UV light at 24 W (Jiapeng limited company, Shanghai). The color change of the IOPP films was recorded using a common digital camera.

Formation of photonic crystal templates

The silica colloidal microspheres were synthesized by using an approach based on the Stöber method with certain modifications as follow. In a typical preparation process, anhydrous ethanol (100 mL), deionized water (6 mL) and ammonia (4 mL) were mixed in a 250 mL flask and stirred gently with a magnetic stirrer at 35℃ in a water bath. Then TEOS (6 mL) was quickly added and the resulting reaction mixture was left overnight. The size of the silica particles can be tuned in the range of 180–360 nm by changing the reactant ratio or conditions. The monodispersed silica particles were obtained by centrifugation followed by rinsing 8 times using anhydrous ethanol to remove the residues. The resulting product was then dispersed in anhydrous ethanol (Volume concentration 0.5%). Common glass slides were cut to the same as the PMMA slides, and were treated with and immersed in a H_2SO_4/H_2O_2 mixture (7:3, v/v) for 24 h. All 5 mL vials for the formation of colloidal crystal templates were treated as well. The glass slide was well-cleaned by rinsing with deionized water, ethanol several times and dried with nitrogen. The silica colloidal microspheres were placed into 5 mL clean vials and a clean glass slide was placed vertically into each vial for photonic crystal growth. After complete volatilization of ethanol, photonic crystal templates were obtained. In this work, monodispersed silica spheres with a diameter of about 220 nm were used (Fig. S1).

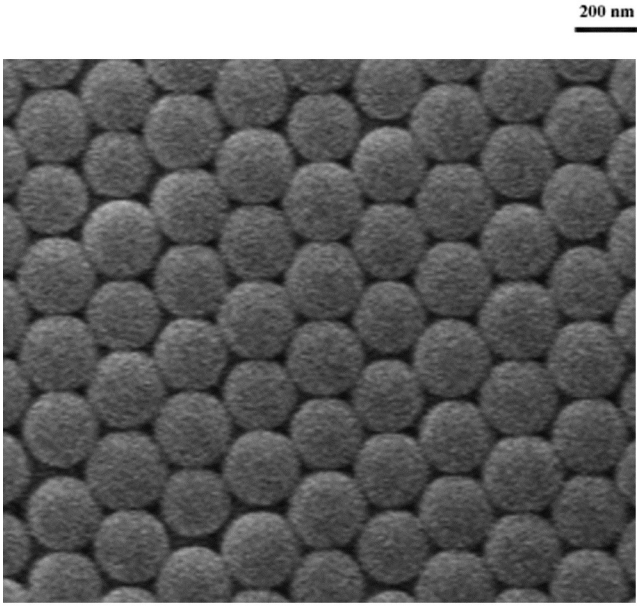

Fig. S1: SEM image of the used photonic crystal template.

Synthesis of inverse opal photonic crystal polymer (IOPP) films

Certain amounts of MAA, EGDMA and AIBN were sufficiently mixed in anhydrous methanol (Typical preparation process: 5 mM MAA, 1 mM EGDMA and 0.5 mL anhydrous methanol). Then the homogeneous mixture was degassed with nitrogen for 5 mines to remove the dissolved oxygen. The solution was infiltrated into the photonic crystal template which was covered with PMMA slide in a Petri dish. After the removal of excess precursors, photopolymerization was performed in an ice bath under a UV light at 365 nm for 3 h. The photonic templates were frozen in a 3D network of polymer. Afterward the film was immersed in 1% HF aqueous solution to remove the SiO_2. The inverse opal photonic crystal polymer was formed on the PMMA slide and then was rinsed thoroughly with deionized water several times. Finally, the resulting polymer was immersed in deionized water at room temperature still they reached a swelling equilibrium and then was ready for use (Fig. S2).

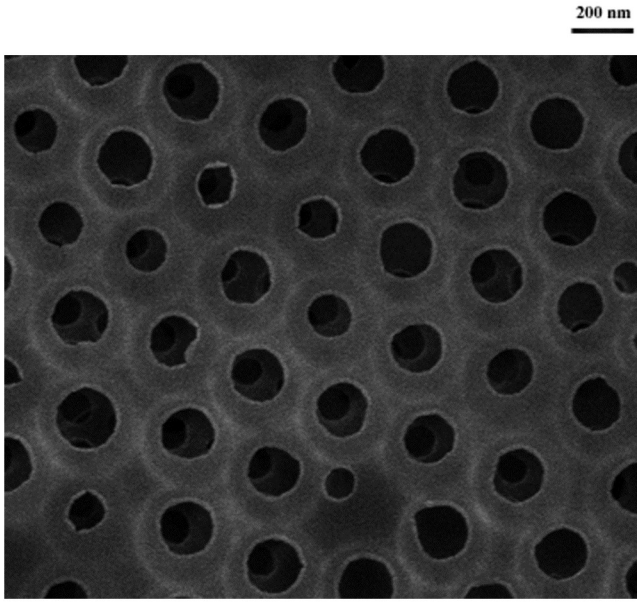

Fig. S2: SEM image of the formed IOPP film.

Detection of urea

Urease was firstly dissolved in deionized water (5 mL) to form an aqueous solution (0.2 mg/mL), to the resulting solution IOPP film was immersed before the addition of urea solution, and mixed evenly. The signal was measured when the IOPP film reached a swelling equilibrium after the catalytic reaction finished in the solution. The sensing property of the IOPP film was tested by immersing the analytes into the solution one after another from low to high concentrations.

Fig. S3: Optical response the films fabricated at 2:1 molar ratio of MAA and EGDMA.

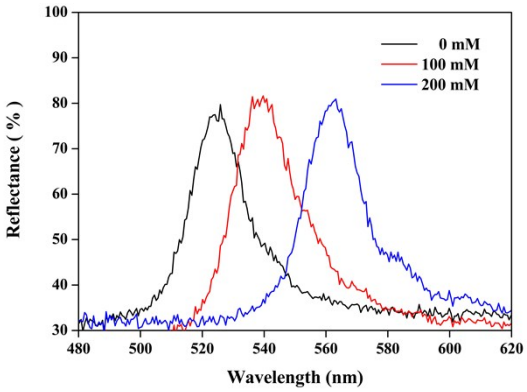

Fig. S3

Fig. S4: Optical response of the IOPP film with formamid and methylurea as inference molecules in urea solution.

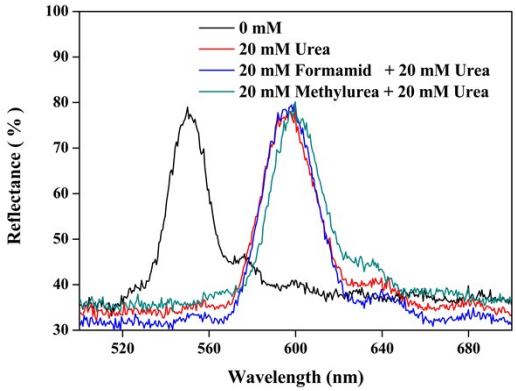

Fig. S4