

Supporting Information

Bioinspired angle-independent photonic crystal colorimetric sensing

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I Methods and Characterization

Chemicals and Materials. The Hg²⁺ aptamer (5'-NH₂-(CH₂)₆-TTCTTTCTTCCCCTTGTGTT-(CH₂)₆-NH₂-3') was synthesized by Invitrogen Biotechnology Co., Ltd (Shanghai, China) and purified by standard desalting.

Acrylamide (98%, AA) and mercury(II) perchlorate were purchased from Alfa Aesar China Ltd. Acrylic acid N-hydroxysuccinimide ester, poly(ethylene glycol) diacrylate (PEGDA, MW 700) and 2-hydroxy-2-methylpropiophenone photoinitiator were purchased from Sigma (St. Louis, MO, USA). All other metal ion reagents were of analytical reagent grade and were used without further purification or treatment. 2-(N-Morpholino)ethanesulfonic acid (MES) and tris(hydroxymethyl)aminomethane (Tris) were purchased from Aladdin. Milli-Q (Millipore, Bedford, MA) water with ultraviolet (UV) sterilization was used throughout the experiment.

Characterization. The co-flow microfluidic device used for PCBs generation was homemade.

Photographs of the beads were obtained with an Olympus microscope (Olympus BX51) equipped with a CCD camera (Media Cybernetics Evolution MP5.0). Photographs of CPCHs were obtained with a Canon digital camera (EOS 5D Mark II). Reflection spectra of PhCs were obtained at a fixed glancing angle utilizing an optical microscope equipped with a fiber-optic spectrometer (Ocean Optics, USB2000-FLG). The microstructures of the PhCs were characterized by a scanning electron microscopy (SEM, Hitachi, S-300N).

Generation of Template PCBs. The PCBs were fabricated by the droplet template method. The aqueous 20 wt% silica particles suspension and oil were injected into the microfluidic device and the aqueous suspension was broken into droplets by the oil flows in the microfluidic channel. The droplets were collected into a container filled with the Hexadecane oil containing 1% hypermer 2296 surfactant. The water in the droplets was evaporated at 80 °C over night. After solidification, the silica PCBs were calcined at 800 °C for 3 h to improve their mechanical strength.

Fabrication of aptamer-crosslinked PhC hydrogel film. The pre-gel solution used for the aptamer-crosslinked PhC hydrogel film was composed of 10% (v/v) AA, 1% (v/v) PEGDA, 3',5'-acryloyl-modified aptamer (1 mM) and 1% (v/v) photoinitiator. The 3',5'-acryloyl-modified aptamer was obtained by mixing the acrylic acid N-hydroxysuccinimide ester (50 mM) and 3',5'-aminoalkyl-modified aptamer (10 mM) in 50 mM Na₂CO₃/NaHCO₃ buffer solution at pH 9.0 for 12 h.

The aptamer-crosslinked PhC hydrogel film were replicated from the voids of the template PCBs. To make sure the pre-gel solution could fill the void fully, the PCBs were firstly treated with piranha solution (30% hydrogen peroxide / 70% sulfuric acid) for 6 h. After washing with water and drying by nitrogen flow, the PCBs were immersed in the pre-gel solution for 1 h. Then the beads with the pre-gel solution was injected into the polymerization cell, which consisted of two quartz disks separated by 250 μm thick Parafilm spacers. Gently shaken the cell and a close packed monolayer beads film were formed. Then the cell was exposed to 365 nm UV light (100 W, 10 min) for the polymerization of the pre-gel solution in and out of the PCBs. Finally the aptamer-crosslinked PhC hydrogel film were obtained after removing the template PCBs by hydrofluoric acid (1%) for 2 h. The resulting PhC hydrogel film was rinsed with pure water to remove any unreacted prepolymer and stored in the hydrated state before use.

Hg²⁺ Detection. The aptamer-crosslinked PhC hydrogel film was first equilibrated in buffer A (20 mM NaNO₃, 8 mM Tris nitrate, pH 8.0) in a polypropylene tube (diameter: 1.2 cm). To detect Hg²⁺ or other metal ions, different concentrations of Hg²⁺

or 100 μM other metal ions were introduced to incubate the PhC hydrogel film in test tubes at 25 $^{\circ}\text{C}$ for 30 min. After extensively wash with buffer A, the reflection spectra of the PhC hydrogel film were measured in buffer A at room temperature.

II The photographs of the reacted and the free-bending films.

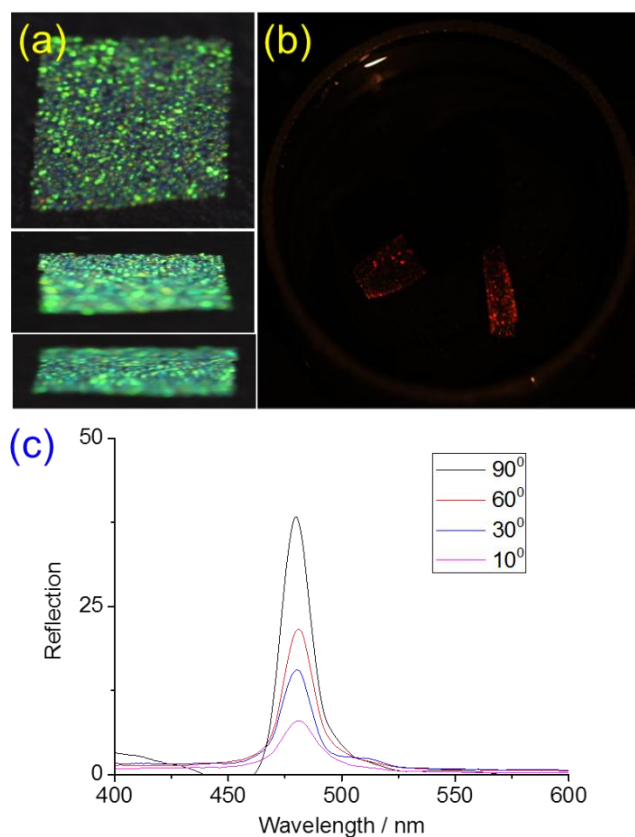


Fig. S1 (a) The photographs of the angel-independent PhC hydrogel film after reacted with 1 μM Hg^{2+} . (b) The photograph of a PhC hydrogel film under free-bending state in solution. (c) The reflection spectra of the PhC hydrogel film after reacted with 1 μM Hg^{2+} measured under different incident angles.

III The selectivity of the sensor.

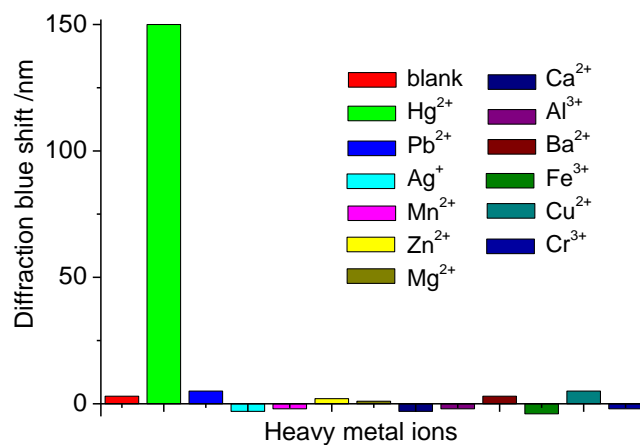


Fig. S2 Diffraction peak shift values of the colorimetric sensor film selectivity towards 10 μM diverse metal ions.

IV The sensor performance in real water samples.

Table S1. Determination of Hg²⁺ in different water samples.

Sample	Added amount (nM)	Measured amount (nM)	Recovery (%)	RSD (% , n = 3)
Tap water	50	48	96	5.2
Lake water	50	47	94	4.7