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Electronic Supplementary Information

Fluorescence enhancement film sensor for highly effective detection of Bi³⁺

ions based on SiO₂ inverse opal photonic crystals

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Fig. S1 SEM images of REP infiltrated SiO₂ IOPC films fabricated from PS microspheres with diameters of (a) 350, (b) 450, (c) 600 nm, and (d) non-periodic SiO₂ porous film, respectively. The scale bar is 2 μ m. (e) Reflectance spectra of SiO₂ IOPCs before (solid line) and after (dash line) infiltration of REP molecules, followed by reaction with Bi³⁺ ions (dot line). They were recorded at normal incidence of the (111) plane of PCs. (f) Reflectance spectra of SiO₂ IOPCs and REP-SiO₂ IOPCs measured at 45° from the (111) plane of PCs.

The reflectance spectra have a little red-shift after infiltration of REP because small quantities of REP may induce tiny variation in the effective refractive index of PC. In addition, the stopband width becomes a little broader due to the higher relative dielectric contrast after infiltration of REP.¹ The reflectance spectra of the REP-SiO₂ IOPCs after reaction with Bi³⁺ ions demonstrated that there are no obvious stopband shifts compared with those of REP-SiO₂ IOPCs because the introduction of very small quantities of Bi³⁺ ions has not obvious effect on the effective refractive index of the PC.



Fig. S2 SEM images of co-assembly opal PC films composed of PS microspheres with diameters of (a) 350 nm, (b) 450 nm, (c) 600 nm, and (d) non-periodic co-assembly film, and their corresponding reflection spectra (e), noted as PC_{350} , PC_{450} , PC_{600} , and F_{Non} , respectively. The scale bar is 2 μ m.

The PS microspheres arranged in an orderly face-centered cubic arrangement and the SiO_2 colloidal crystals infiltrated uniformly into the voids of the PS microspheres. The reflectance spectra shows that the photonic stopbands of PC₃₅₀, PC₄₅₀, and PC₆₀₀ are at 754, 893 and 1346 nm, respectively. For non-periodic co-assembly film, there is no obvious reflectance peak.



Fig. S3 The measurement of fluorescence spectra. (a) A sample is positioned along the diagonal in a quartz cuvette. (b) The schematic illustration of excitation light and emission light on the surface of IOPC.



Fig. S4 Fluorescence spectra of different REP-SiO₂ IOPC sensors, the non-periodic SiO₂ porous film (PF_{Non}) and the control sample Glass immersed into the Bi³⁺ aqueous solution for 8 min at a concentration of 100 μ M (pH = 6.0), and the REP infiltrated IOPC₄₅₀ immersed into pure water ($\lambda_{ex} = 350$ nm).



Fig. S5 Fluorescence spectra of REP-SiO₂ IOPC₄₅₀ film sensor immersed into different metal ions at each concentration of 100 μ M and pH 6.0 ($\lambda_{ex} = 350$ nm). The mixed solution (Mix-Bi³⁺) is composed of all metal ions listed in this figure including Bi³⁺ ions, each at a concentration of 100 μ M and pH 6.0.



Fig. S6 FL intensities at 553 nm when the sensors were immersed into solutions at different concentrations of Bi^{3+} and Fe^{3+} ions (pH = 6.0), respectively. ($\lambda_{ex} = 350$ nm)



Fig. S7 Fluorescence spectra of REP-SiO₂ IOPC₄₅₀ film sensor immersed into drug containing bismuth solution prepared from bismuth potassium citrate and general Bi³⁺ ions aqueous solutions ($\lambda_{ex} = 350$ nm)

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Table S1. Comparison of the REP-SiO₂ $IOPC_{450}$ sensor with other reported methods for the determination of Bi³⁺ ions

Method	Linear range (nM)	LOD (nM)	Ref.
Dielectric Barrier Discharge Atomic Absorption Spectrometry Coupled with Hydride Generation		5.26 nM	2
Hydride generation atomic absorption spectrometric	0.19–5.98 nM	0.057 nM	3
dispersive liquid–liquid microextraction coupled with electrothermal atomic absorption spectrometer	1.44–38.28 nM	0.335 nM	4
Adsorptive Stripping Voltammetry	0.1–400 nM	0.05 nM	5
Adsorptive Stripping Voltammetry	2–200 nM	0.94 nM	6
Resonance light scattering	38.28–12537.08 nM	9.09 nM	7
Nanodrop spectrophotometric	0.479-334.96 nM	172.27 nM	8
Colorimetric	400–8000 nM	10 nM	9
Fluorometric	500–30000 nM	150 nM	10
Fluorometric	2.39–478.51 nM	0.766 nM	11
Fluorometric		2775.39 nM	12
Fluorometric	10000–35000 nM	2690 nM	13
Fluorometric	10–400 nM	0.1 nM	This work

Table S2 Fluorescence intensity comparison of the REP-SiO₂ IOPC sensor when exposure to Bi^{3+} aqueous solution and bismuth potassium citrate solution

Concentrations Fluorescence intensity Samples	100 nM	220 nM
Bi ³⁺ aqueous solution	118.65	184.27
Bismuth potassium citrate solution	122.74	178.84

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