Supporting Information for

Full-Color CO_2 Gas Sensing by Inverse Opal Photonic Hydrogel

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Experimental

Chemicals and Instruments: All reagents used were analytical-reagent grade and used without further purification unless otherwise specified. Ethylene glycol dimethylacrylate (EGDMA) was obtained from Arcos. Polyethylene glycol-170 dimethylacrylate (MW ≈ 330) and 2-hydroxy-2-methylpropiophenone (HMPP, photo-initiator) were obtained from TCI. 2-Hydroxyethyl methacrylate (HEMA) and dimethyl aminopropyl methacrylamide (DMAPMA) were obtained from Sigma-Aldrich. Other chemicals and pure gases were supplied by local suppliers. Pure water was obtained from Milli-Q Advantage A10 ultrapure water system. Phosphate buffer solutions were made by mixing 0.01 M KH_2PO_4 (aq.) with different quantities of 0.1 M NaOH (aq.) and HCl (aq.) and their pH were measured with a pH meter. 10 ml vials and common glass slices of 50 mm*10 mm were immerged in a piranha solution for 24 h, following rinsing with deionized water in ultrasonic bath for three times and then dried for use. The SEM pictures of the colloidal crystals and inverse opal films were obtained from a FEISirion200 SEM with an accelerating voltage of 10 kV. Before imaging, the samples were arc-coated with a thin gold film. The evaluation of the optical characteristics was obtained by Ocean Optic Maya 2000 fiber optic spectrometer. All reflectance spectra were measured at near-normal incidence to the (111) planes. Images of the photonic films were recorded by a digital camera under a LED lamp. Element analyze was taken by Vario-ELIII IRMS element analyzer.

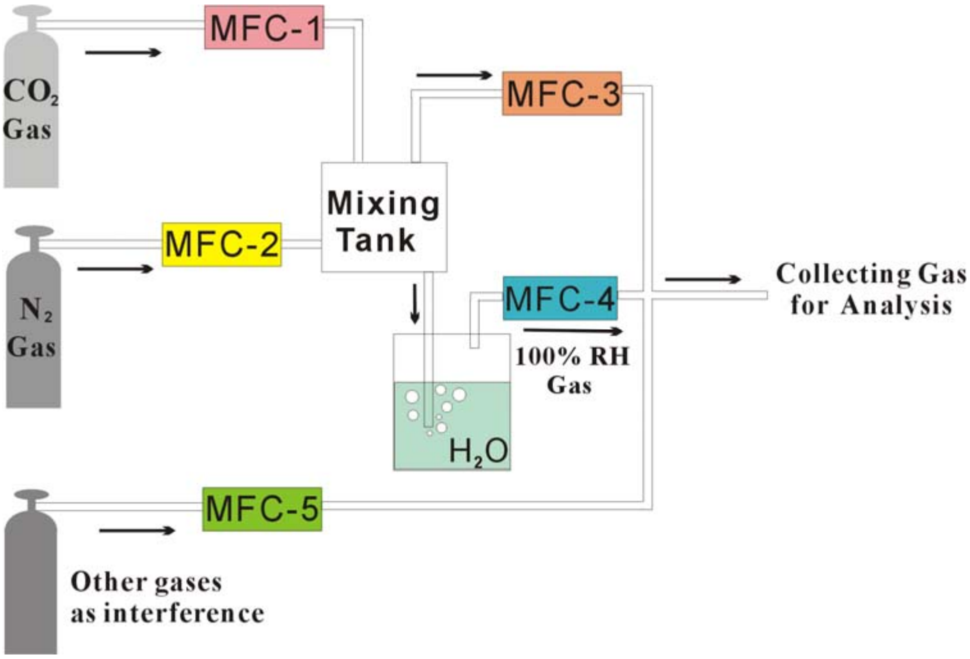
Synthesis of Monodisperse SiO_2 Particles: Firstly, 1.6g tetraethoxylsilane (TEOS) and 36 ml anhydrous ethanol were mixed in a 100 ml flask, stirred intensively with a magnetic beater at 25^{o}C, and then pouring in the mixture of 1.5mL ammonia and 1.7mL deionized water. After 18 h, the colloidal particles were obtained by centrifugation and rinsed using anhydrous ethanol for 4 times to expunge residues. The diameter of the SiO_2 particles is about 190 nm as showed in Scheme 1a.

Preparation of Silica Colloidal Crystals: The obtained monodisperse SiO_2 particles were dispersed in anhydrous ethanol to form a SiO_2 colloidal solution in 1.1 wt%, and then allotted into 10mL cleaning vials. The glass slice was put vertically into each vial. After complete volatilization of ethanol for 5-7 days in 25 ^{o}C, SiO_2 colloidal crystal was formed on both sides of the glass slice. There were about 17 layers of the SiO_2 particles which could be seen from the SEM image in Scheme 1a, with a refraction maximum of 448 nm (see Fig.S12).

Formula of homogeneous monomer precursor for the CO_2 sensitive photonic films: 144 µl DMAPMA (0.80 mmol), 200 µl MAA (1.88 mmol), 145 µl HEMA (1.20 mmol), 13.2 µl PEG170-DMA (0.04 mmol), 7.5 µl EGDMA (0.04 mmol) and 4 µl HMPP (photo-initiator) were mixed in 240µl methanol. MMA and HEMA were used to control the hydrophobicity of the hydrogel. If the hydrogel was too hydrophobic, the film would not be wetted again after dried, while an excessively hydrophilic film could not adhere to the PMMA substrate. Two cross-linkers were used to maintain rigidity and flexibility of the hydrogel system at the same time.

Preparation of the CO_2 sensitive photonic film: After degassing by nitrogen for 10 min, the homogeneous monomer precursors (8-10 µl for each side) were dropped onto silica arrays with two PMMA slices (50 mm*10 mm*1.5 mm) covered on each side. The colorful SiO_2 colloidal crystal would become transparent, indicating the successful infiltration. The sandwich was photo-polymerized under an UV light at 365 nm for 90 minutes. After that, the sandwich was put into -20 ^{o}C deep freezer for 20 minutes to separate double slices. The PMMA slides were immerged into 1.5 wt% hydrofluoric acid solution to fully etch the silica colloids. After washed by deionized water, the inverse opal film on PMMA substrate was ready for tests. The resulting inverse opal hydrogel sensor was about 1 cm wide, 4 cm length (as shown in Fig.1a and Fig.2a) and 20 µm thick, with a 2 µm inverse opal structure on the surface.

Gas Sensing: Gas streams containing CO_2 in different concentrations were prepared by mixing CO_2 gas from the premixed tank with nitrogen gas and other gases as interference. (see Scheme S1) Digital mass flow controllers were used to control the desired concentrations and relative humidity. CO_2 concentrations, interference gas concentrations and humidity were confirmed by FTIR analysis and an electronic gas sensor (MX6 IBRID, Industrial Scientific). For all sensing experiments, the volume of pure water was fixed in 1.85 mL for 0.15 mL gas mixture and 1 mL for 1 mL gas mixture as the closed container had a total volume of 2 mL. (The reasons why we use pure water to carry out the detection rather than buffer solution were that: Firstly, CO_2 could change the micro-pH of film more effectively in pure water than in buffer solution. For example, if we use 1.85 mL of 10 mM pH=10.14 carbonate - bicarbonate buffer solution for the detection, then we need 0.207 mL 100% CO_2 to decrease the pH from 10.14 to 9.16 where the stopband only red shifts for 50 nm according to Fig.S1b. However, in pure water, 0.2 mL 100% CO_2 could red shift the stopband of the film for 220 nm according to Fig.S3, which demonstrated the sensing in pure water was more sensitive. Secondly, pure water is much easier to obtain and preserve in real application.) The gas mixtures was injected into the closed container and sealed inside with the inverse opal film, consistent with the atmospheric pressure. After-exposure images were acquired after the diffraction maxima reached the equilibrium. Experimental standard deviation of the diffraction maxima measurement was smaller than ± 2 nm.



Scheme S1. Gas mixing rig used for CO_2 sensing in this work. MFC = mass flow controller (including gas valves).

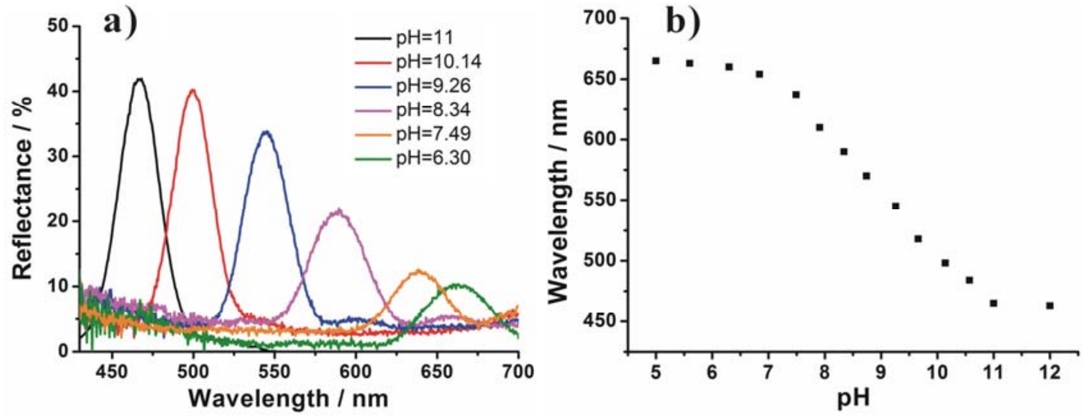


Figure S1. a) The reflectance spectrum of the CO_2 sensitive inverse opal film in 0.01 M buffer solutions with diversified pH. b) Plots of diffraction maxima of the photonic film versus the pH in the buffer solutions.

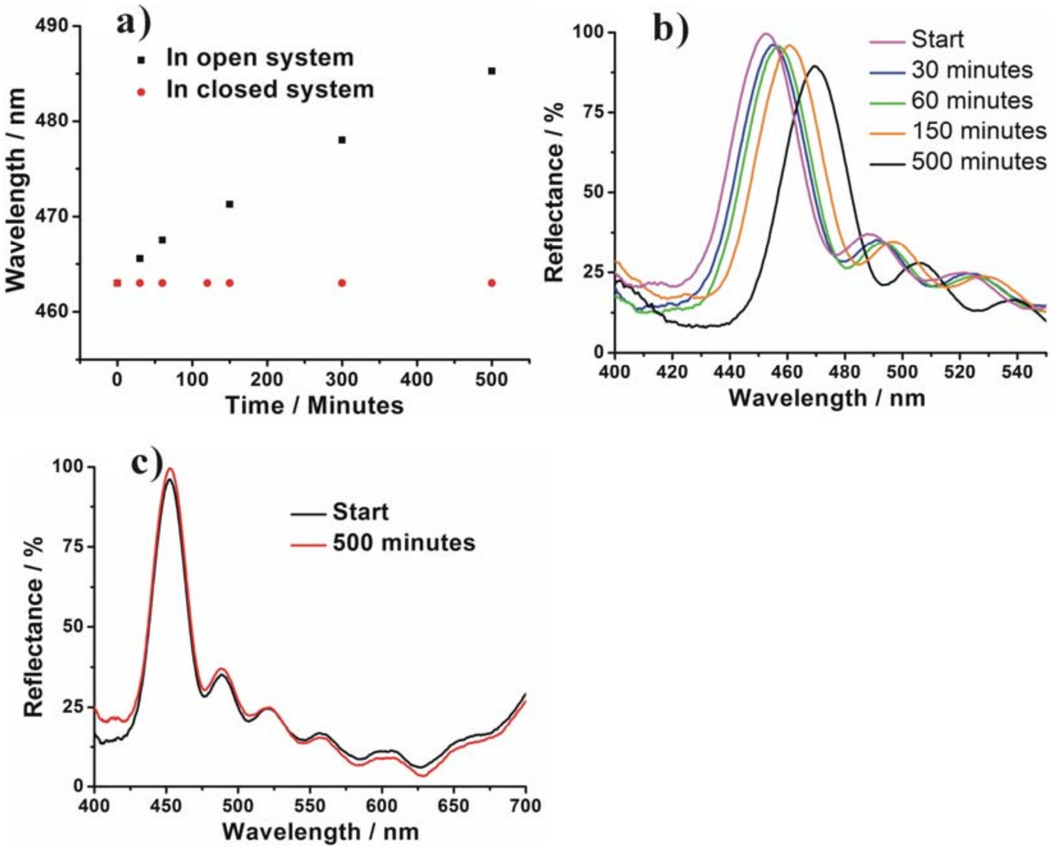


Figure S2. a) Plots of diffraction maxima of CO_2 sensitive inverse opal film versus time in pure water. b) The reflectance spectra of the photonic film in 1.85 mL pure water exposed to air. c) The reflectance spectra of the photonic film in 1.85 mL pure water in a closed container.

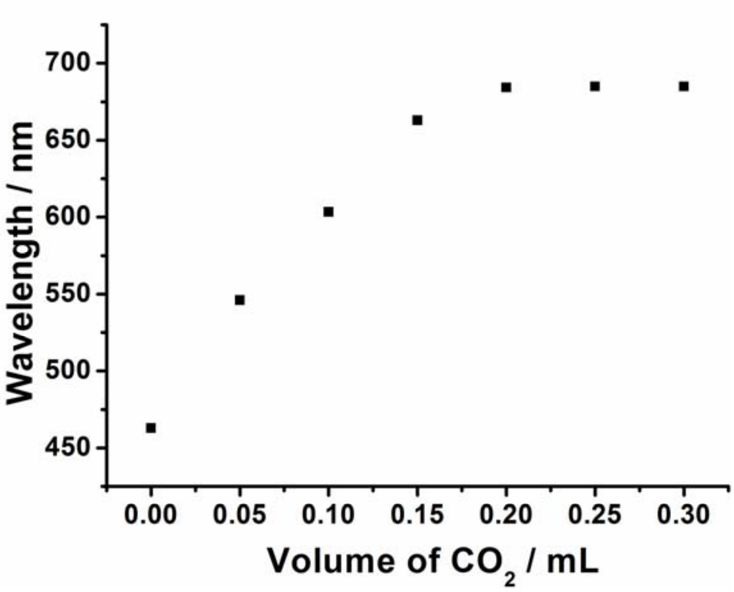


Figure S3. Plots of diffraction maxima of the photonic film versus the volumes of CO_2 (V_{CO2}).

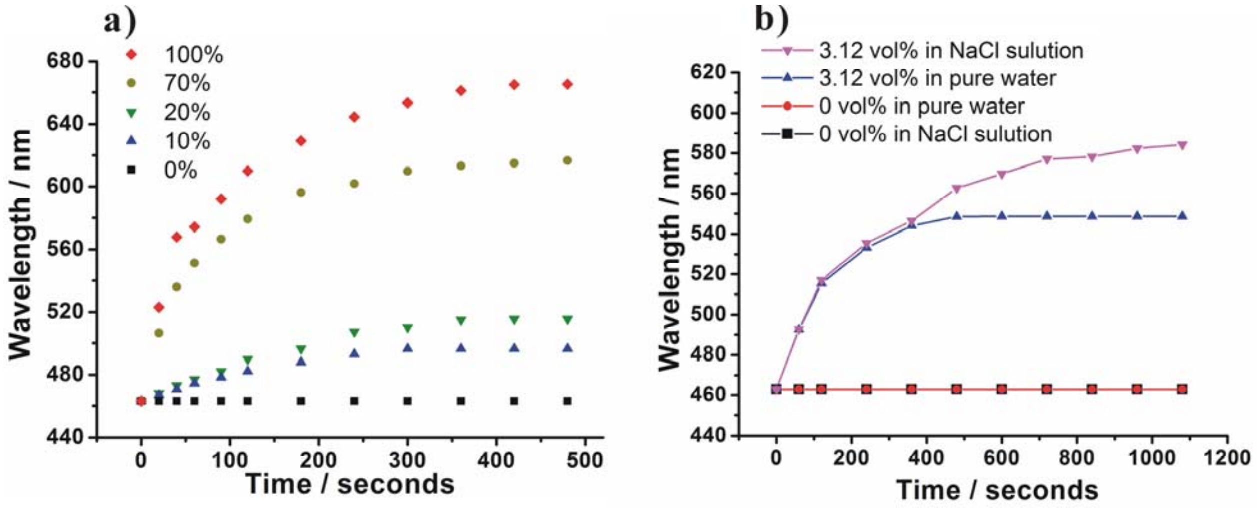


Figure S4. Diffraction shift kinetics of the photonic film a) after 0.15 mL CO_2/N_2 mixtures in different concentrations being injected into the closed container; b) after 1 mL CO_2/N_2 mixtures being injected into pure water and 0.01 M NaCl solution.

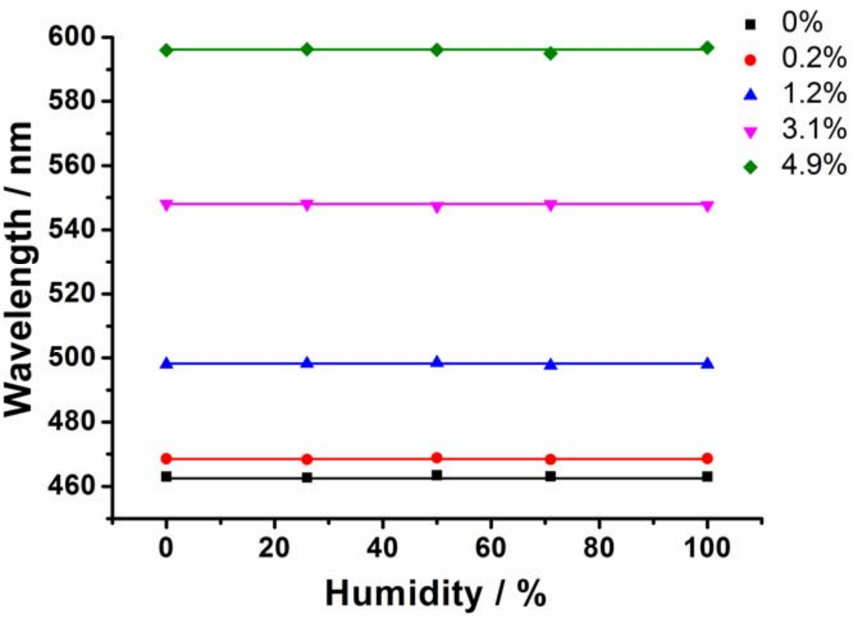


Figure S5. Plots of diffraction maxima of CO_2 sensitive inverse opal film versus humidity of 1 mL CO_2/N_2 mixture with different CO_2 concentrations.

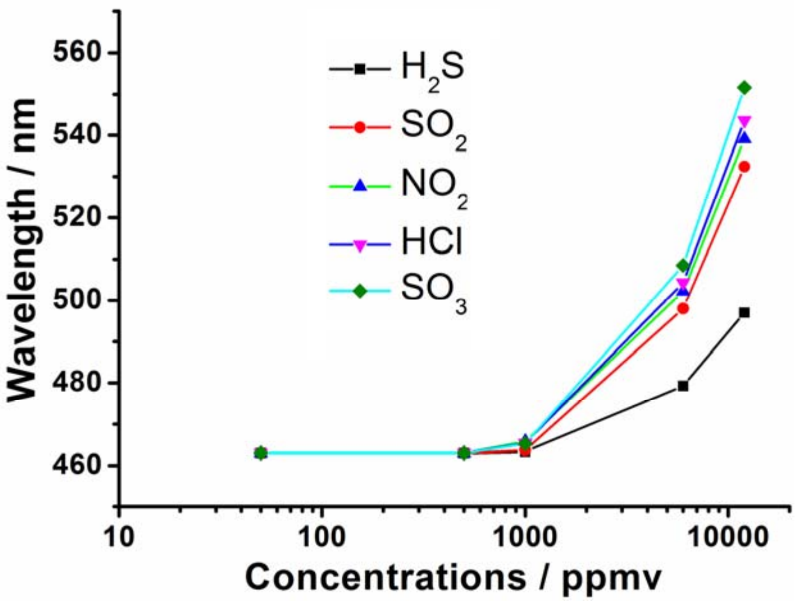


Figure S6. Plots of diffraction maxima of CO_2 sensitive inverse opal film versus concentrations of different acidic gases in 1 mL gas mixture with nitrox.

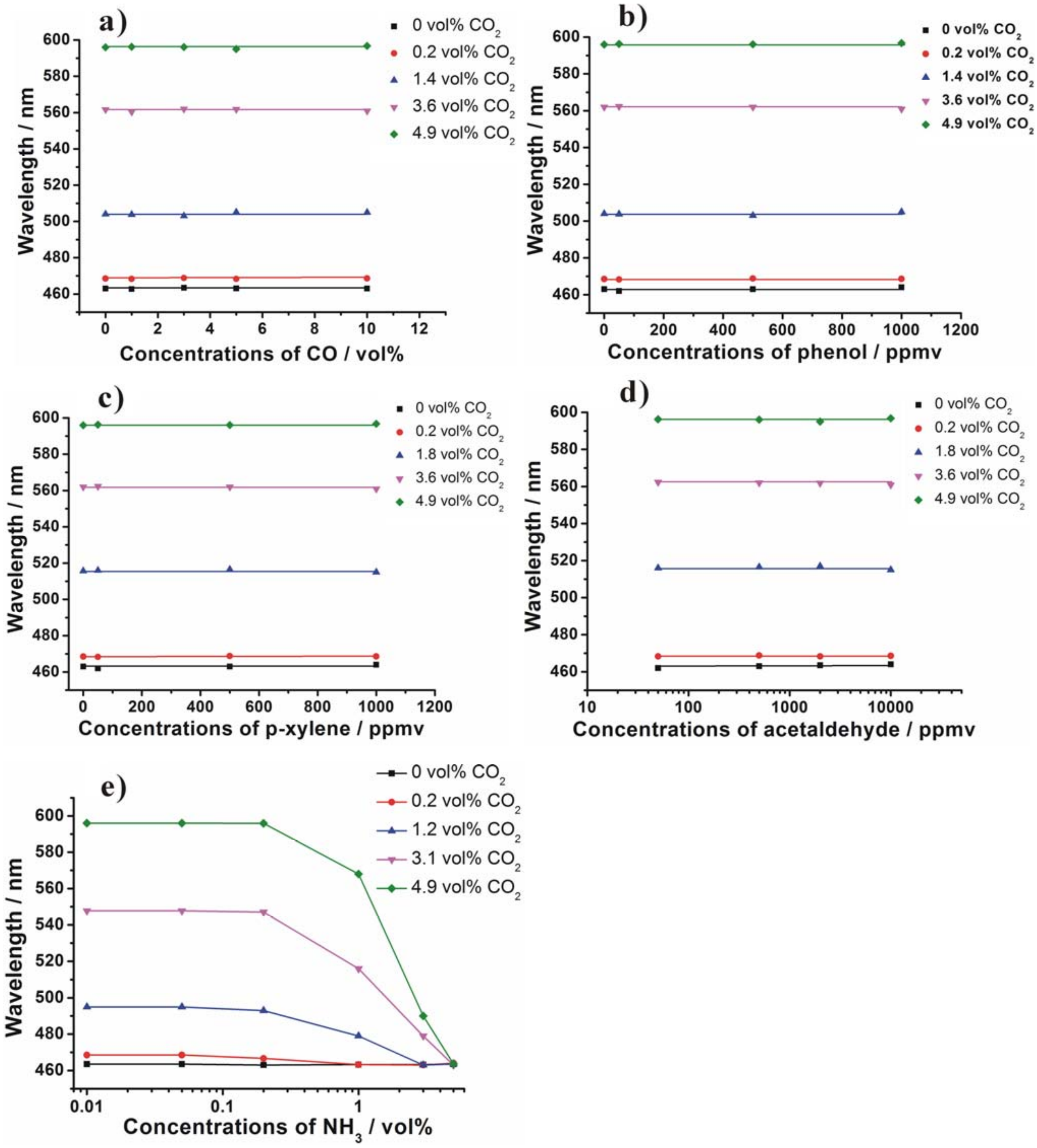


Figure S7. Plots of diffraction maxima of CO_2 sensitive inverse opal film versus the concentrations of (a) CO, (b) phenol, (c) p-xylene, (d) acetaldehyde), (e) NH_3 in 1 mL CO_2/N_2 mixture with different CO_2 concentrations.

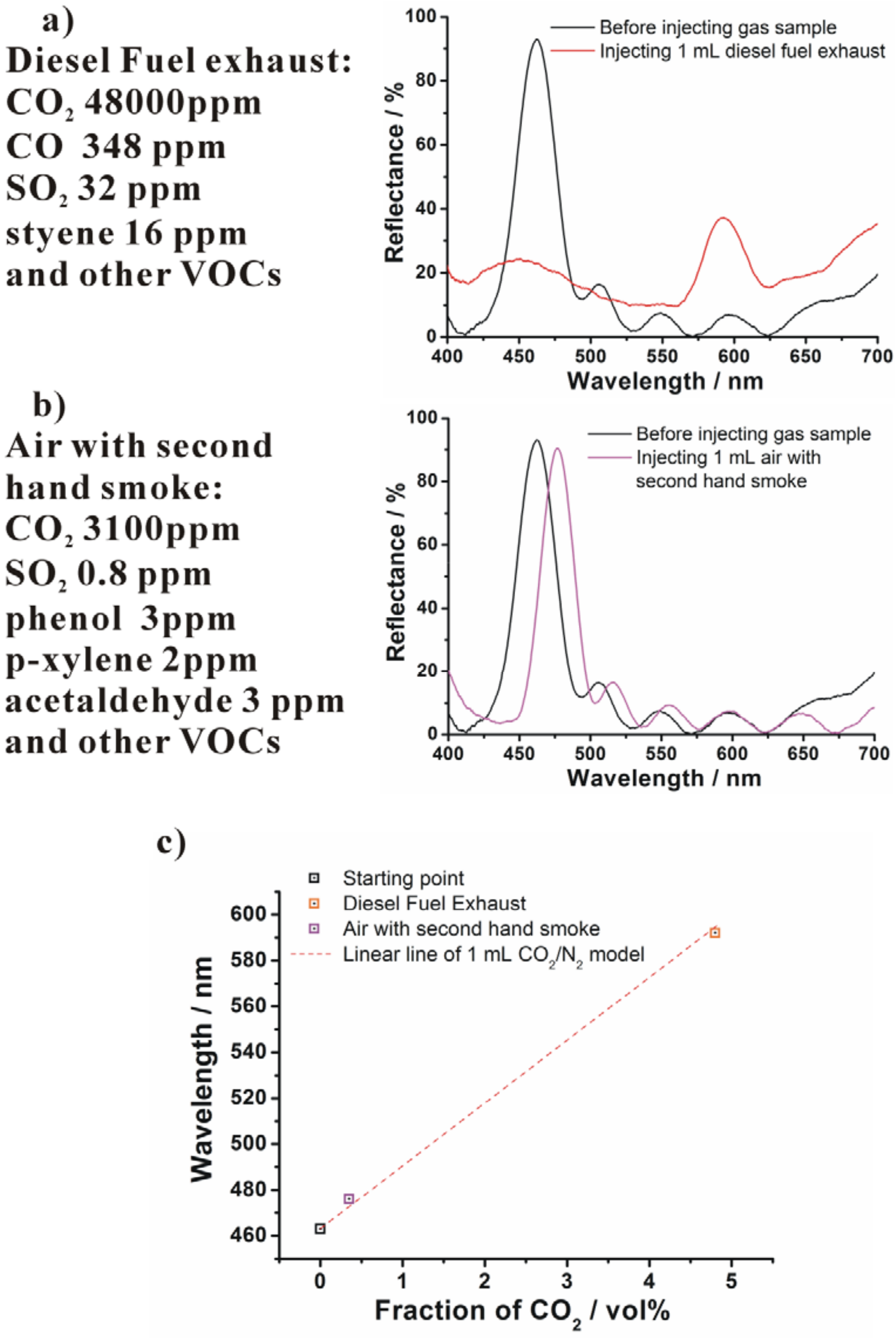


Figure S8. The reflectance spectra of the photonic film before and after the injecting of 1 mL a) diesel fuel exhaust and b) air with second hand smoke; c) the diffraction maxima compared with the linear line of 1 mL CO_2/N_2 model.

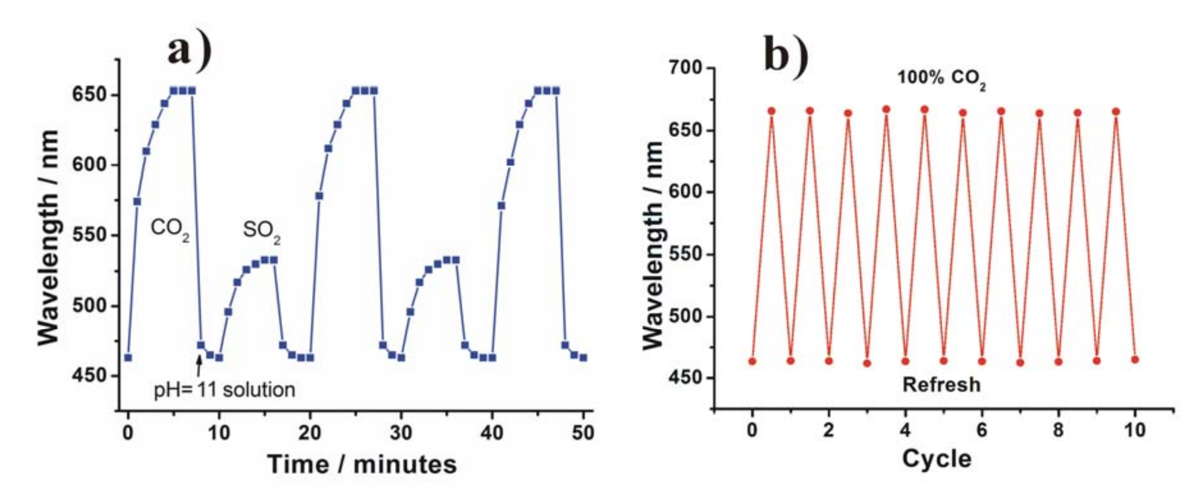


Figure S9. a) Diffraction maximum recorded in 5 cycles of the CO_2 sensitive inverse opal film treated by 0.15 mL 100% CO_2 – pH=11 ammonia solution – 0.15 mL 10% SO_2 –0.15 mL 100% CO_2– pH=11 ammonia solution – 0.15 mL 10% SO_2. b) Reversible switching of the diffraction light of the photonic film by repeated response-refresh processes.

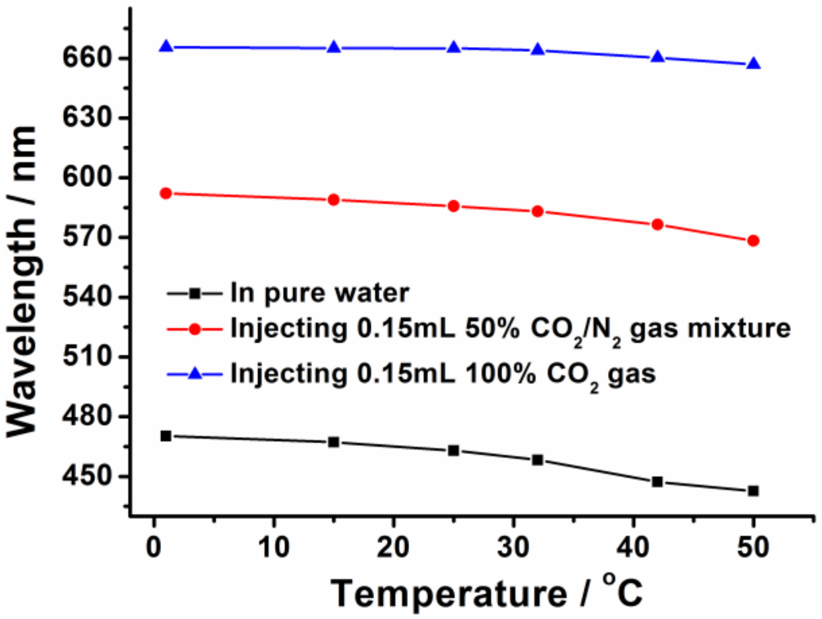


Figure S10. Plots of diffraction maxima of CO_2 sensitive inverse opal film versus the temperature of the pure water and the closed container.

Appendix:

The temperature response of the CO_2 sensitive inverse opal here is reversible, which means the final results could be standardized by controlling the final temperature. For example, when

we carried out the detection for 50 % CO_2 gas mixture in pure water of 50 °C, the reflection wavelength could redshift from 463 nm to 568.3 nm. Then we decreased the temperature of the system down to 1 °C, the reflection wavelength could redshift to 592.1 nm. After that we increased the temperature of the system up to 25 °C, the reflection wavelength would finally blueshift to 585.7 nm, which was actually the same with the sensing result carried out in pure water of 25 °C in Fig.1b (main text).

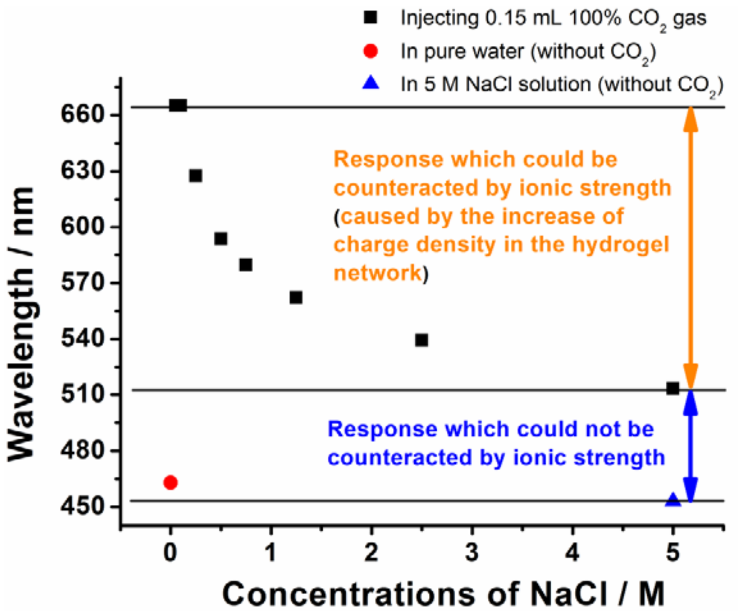


Figure S11. Plots of diffraction maxima of CO_2 sensitive inverse opal film versus the NaCl concentration in pure water.

Appendix:

According to the Flory-Huggins theory (P. J. Flory, Principles of Polymer Chemistry, Cornell University Press, Ithaca, New York, 1953.) of ionic network swelling, in the dilute polymer solution approximation, when the external electrolyte concentration is comparable with the fixed charge density of the polymer network, the equilibrium relation may be solved as the following equation:

$$q_m{}^{5/3} \cong \frac{\left(\dfrac{i}{2v_u S^{1/2}}\right)^2 + \dfrac{(0.5-\chi_1)}{v_1}}{v_e / V_o}$$

where q_m is the equilibrium swelling rate; i/v_u is the concentration of fixed charge referred to the unswollen network, S stands for the ionic strength; χ_1 indicates the polymer-solvent interaction parameter; v_1 indicates the volume fraction of the polymer in the hydrogel system and v_e/V_o expresses the degree of cross-linking.

Based on this theory, the response to CO_2 which could be counteracted by ionic strength was caused by the increase of fixed charge in the hydrogel network (marked by orange arrow, over 75% of the redshift). The rest of the response (marked by blue arrow) can be explained by the change of polymer-solvent interaction parameter because the resulting ion-pairs were much more hydrophilic than the non-ionic amino groups. Refractive index must have some effects on the response but it should be minor according to the previous reports of photonic hydrogel sensors. (Such as J. Am. Chem. Soc. 2000, 122, 9534; Adv. Mater. 2003, 15, 563.)

Thus, the CO_2 response is mainly resulted from hydrogel swelling and shrinking (by donnan potential caused by the increase of fixed charge in the hydrogel and the change of polymer-solvent interaction parameter).

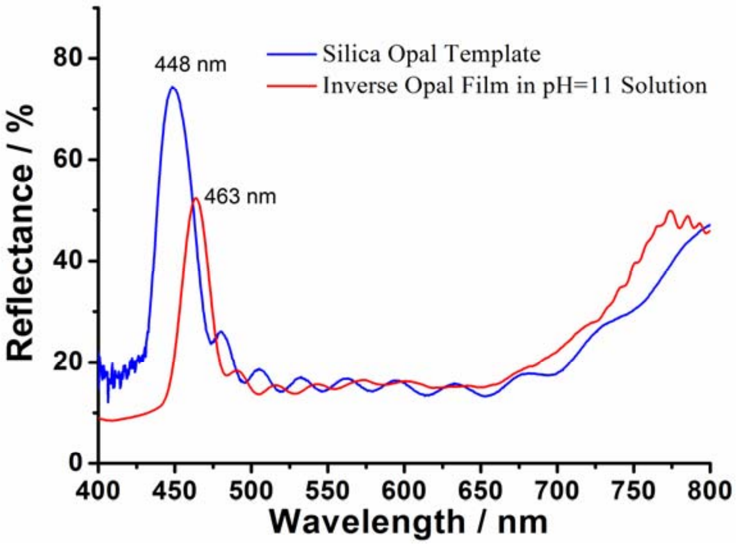


Figure S12. The reflectance spectra of the silica opal template and the resulting inverse opal film in this work.

Table S1. Determination of amino groups and the coresponding stopband redshifts

Formula Number	1	2	3	4
DMAPMA[a]	144 μl (0.8mmol)	100 μl (0.56mmol)	50 μl (0.28mmol)	0 μl
MMA[a]	200 μl (1.88mmol)	225 μl (2.12mmol)	255 μl (2.40mmol)	285 μl (2.68mmol)
Nitrogen Content of Monomers (Calculated)	4.52%	3.26%	1.70%	0%
Amine Content of Monomers (Calculated)	1.60 mmol/g	1.16 mmol/g	0.61 mmol/g	0 mmol/g
After polymerization and purification				
Gel Mass / Monomer Mass	0.89	0.85	0.86	0.86
Nitrogen Content (by Elemental Analysis)	5.11%	3.85%	2.69%	~ 0
Amine Groups Content (by Elemental Analysis)	1.83 mmol/g	1.38 mmol/g	0.96 mmol/g	~ 0 mmol/g
Amine Groups Content (by Titrimetry)	1.30 mmol/g	0.91 mmol/g	0.39 mmol/g	0 mmol/g
Maximum Redshift by 0.5 mL CO_2 （Normalized [b]）	0.47	0.24	0.043	~ 0

a. Other components of the homogeneous monomer precursors: 145 μl HEMA (1.20 mmol), 13.2 μl PEG170-DMA (0.04 mmol), 7.5 μl EGDMA (0.04 mmol), 4 μl HMPP (photo-initiator) and 240μl methanol.

b. $\Delta\lambda/\lambda_0$, here λ_0 was about 463 nm.

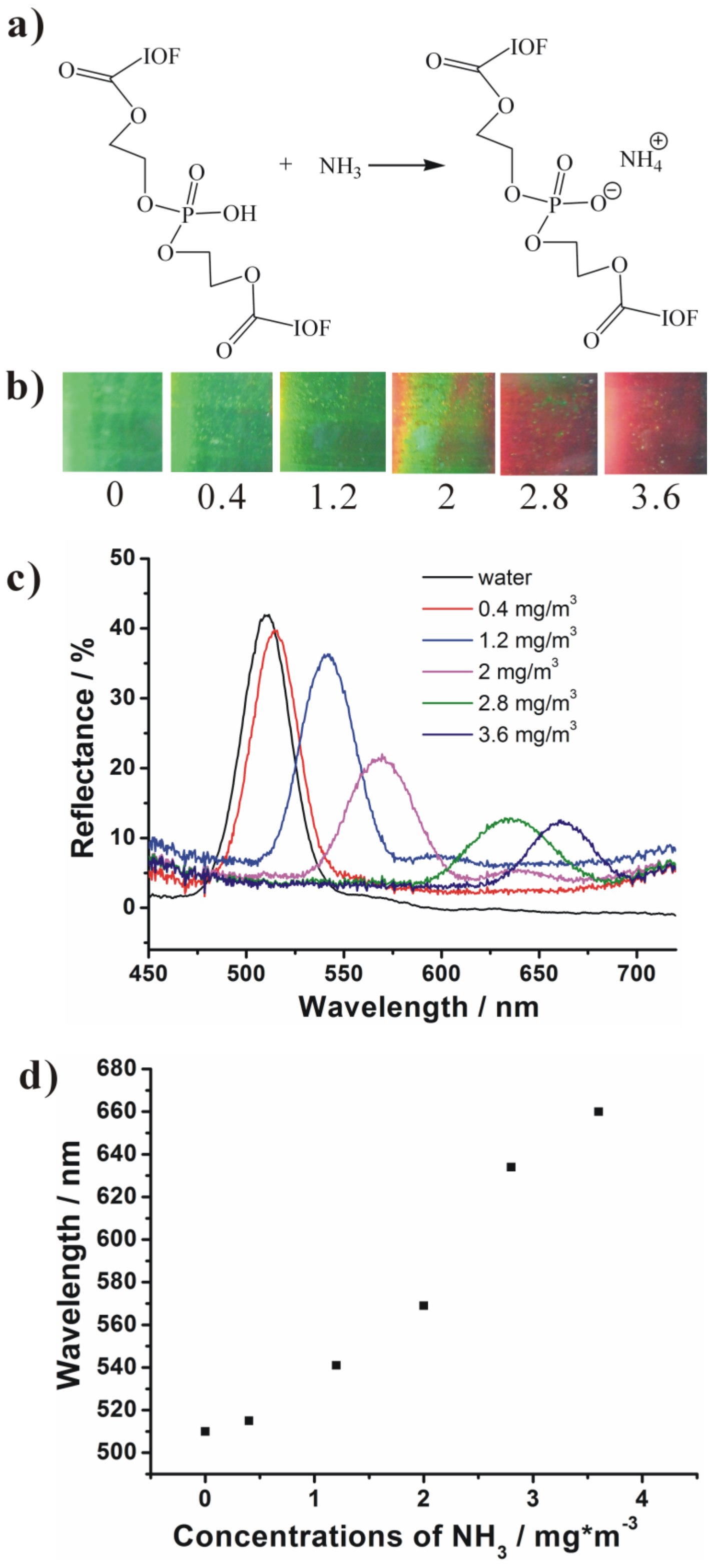


Figure S13. a) Operation of the phosphate-functionalized inverse opal film (IOF) for NH_3 sensing. b) The induced color change and c) the reflectance spectra of the phosphate-functionalized inverse opal film in 5 mL pure water after being bubbled with diversified NH_3/air mixtures of 25 L, unit: mg*m^{-3}. d) Plots of diffraction maxima of the photonic film versus concentrations of NH_3 in the air.