Supporting Information

Ethanol-assisted Multi-sensitive Poly(vinyl alcohol) Photonic Crystal Sensor

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Experimental Part

CCA Preparation: A 10% (w/w) latex of monodisperse polystyrene (PS) colloids with diameter of 186 nm were prepared via emulsion polymerization as described elsewhere.[S1] The PS colloidal particles were filtered through glass wool and then cleaned via dialysis against ultrapure water (18 MΩ cm) for 14 days. The iridescent CCA solution was obtained due to Bragg diffraction once the excess ions were removed and the colloids were self-assembled. Concentrated CCA solution was achieved trough further dialyzing with gradient steps at 10%, 25% and 50% ethanol (Shanghai Lingfeng Chemical Reagent Co., Ltd) followed by shaking with ion-exchange resin (Bio-Rad mixed bed, AG 501-X8 (D) resin, 20-50 mesh).

GCCA Preparation: In a typical procedure,[S2] Poly(vinyl alcohol) (PVA, 99% hydrolyzed, DP = 1750 ± 50, Shanghai Chemical Agent Co., Ltd) powder was dissolved in water/ethanol (v/v = 1/1) at 90 °C for 2 h in N_2 atmosphere to form a 10% (w/w) homogeneous solution. When the temperature of the PVA solutions was lowered, the solutions were mixed with CCA solution (v/v = 2/1). Then a small amount of ion-exchange resin was added and the mixture was shaken until strong diffraction was visually apparent (10 min). We cut 2 layers of parafilm (125 µm thick, Chicago, IL) into a 10 mm × 30 mm × 250 µm spacer which was clamped between a set of glass slides to provide a uniform GCCA thickness. Then the pregel solution was injected into the chamber, and gelled at -18 °C for 4 h to form PVA GCCA. The GCCA hydrogel film can be easily removed from the cast after thawing at room temperature for 0.5 h. The resulting GCCA was cut into square pieces (approximately 10 mm × 10 mm) with a razor blade and stored in ultrapure water. The glassware used in all experiments was cleaned in a RCA solution (5:1:1 mixture of water, hydrogen peroxide (30%) and ammonia (28%)) at 75 °C for 30 min. The route for the fabrication of GCCA is illustrated in Figure 1.

Formation of Chemical Cross-Links: A 10 mm × 10 mm (250 µm thick) GCCA sample was placed in a wide mouth jar containing 50mL water. 1.5 mL of 10% glutaraldehyde solution and 0.5 mL of concentrated sulfuric acid were then added. The reaction was terminated by immersing the GCCA pieces in gently stirred ultrapure water after 4 h.

Functionalization of GCCA: To accomplish carboxylation of PVA GCCA, a chemically cross-linked GCCA was firstly exchanged from pure water to pure ethanol with 2 h equilibration, and the ethanol (50 mL) was replaced three times. The GCCA was placed into a 40 mL solution of ethanol dissolving 0.22 g of succinic anhydride, and 5 drops of pyridine was added as catalyst. The reaction was allowed to proceed in a 40 °C water bath for 6 h. The modified GCCA was then washed and exchanged into pure water.

Diffraction Measurements: The optical properties of GCCA film were studied utilizing an Ocean Optics PC 2000 fiber optic spectrometer. Spectra were collected between the wavelengths of 400 to 900 nm. During measurements, the GCCA samples were oriented normal to the incident light beam.

To characterize the response of the functionalized GCCA to Ni^{2+}, the hydrogel was equilibrated in pure water. $NiCl_2$ stock solutions were prepared by dissolving $NiCl_2{\cdot}6H_2O$ (1.1886 g, 5.00 mmol, Sinopharm Chemical Reagent Co., Ltd) in 100 mL of sodium acetate buffered saline. The pH was adjusted to 7.4 by addition of 20% aqueous NaOH. Lower Ni^{2+} concentrations were prepared by successive dilution.

The functionalized GCCA was titrated dropwise with 20 mmol L^{-1} HCl solution in the presence of 150 mmol L^{-1}NaCl. The GCCA was allowed to equilibrate after each addition of acid, while the pH was monitored and spectrum was recorded.

Table S1. The optical characteristics of the PVA GCCA composite.

band-stop (nm)	560	553	548	534	524	505	492	462
d_{111} (nm)	199.9	197.4	195.7	190.7	187.1	180.3	175.7	165.0
a_c (nm)	346.3	342.0	338.9	330.2	324.0	312.3	304.3	285.7
a (nm)	244.9	241.8	239.6	233.5	229.1	220.8	215.1	202.0
FWHM (nm)	18.8	18.2	25.6	25.1	37.5	33.0	27.7	18.2

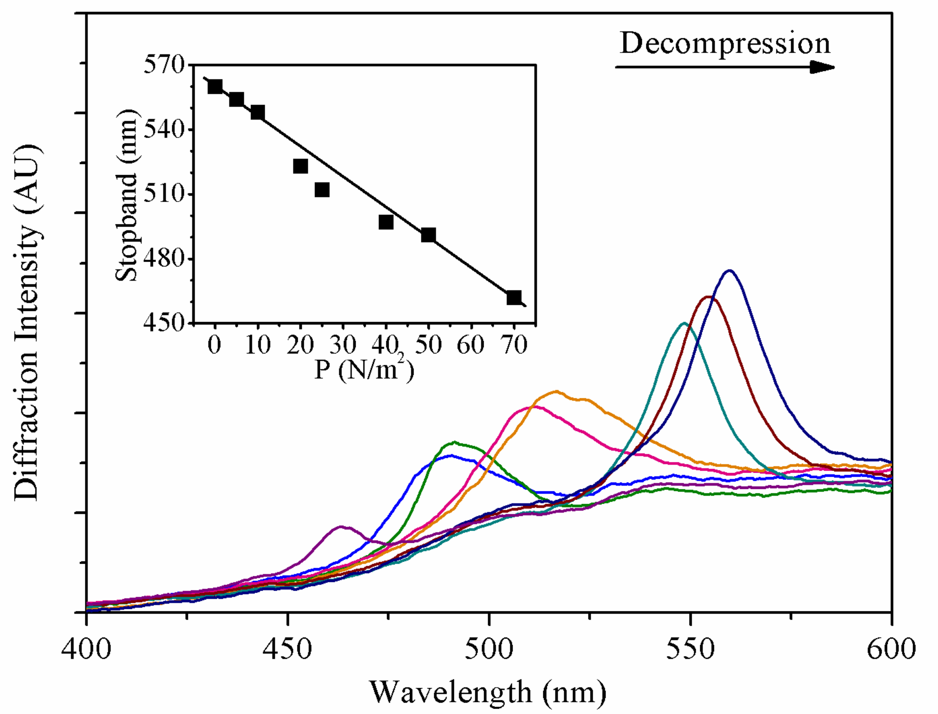

Fig S1 Diffraction wavelength shifting of a GCCA film with decreasing pressive strain. The insert shows a linear stop-band shifting with the decreased pressure. This result reveals that the compress-decompress process is also reversible.

References:

S1 C. E. Reese, C. D. Guerrero, J. M. Weissman, K. Lee and S. A. Asher, *J. Colloid. Interf. Sci.*, 2000, **232**, 76.

S2 C. Chen, Y. H. Zhu, H. Bao, P. Zhao, H. L. Jiang, L. M. Peng, X. L. Yang and C. Z. Li, *Soft Matter*, 2011, **7**, 915.