Electronic Supplementary Information (ESI)

Stimuli-responsive 2D polyelectrolyte photonic crystals for optically encoded pH sensing

Cheng Li and Bettina V. Lotsch*

Max Planck Institute for Solid State Research, Heisenbergstrasse 1, 70569 Stuttgart, Germany, and Department of Chemistry and Center for Nanoscience, Ludwig-Maximilians-Universität München, Butenandtstr. 5-13, Haus D,81377 München, Germany. E-mail: b.lotsch@fkf.mpg.de

S1

Preparation of quaternized poly-(2-vinyl pyridine) (qP2VP) solution

The quaternization of P2VP was carried out following a procedure reported by Tokarev et al¹: 0.1 g of P2VP (molecular weight, $M_w = 159$ kg mol⁻¹, Fluka) and 0.1 mL of 1, 4-diiodobutane (DIB) (99 %, Alfa Aesar) was dissolved in a solvent mixture of 4 mL nitromethane (NM) and 1 mL tetrahydrofuran (THF) and kept at 60 °C with stirring to accelerate the quarternization reaction between P2VP and DIB. After 80 hours the reaction was cooled down to room temperature. In order to get rid of THF that would dissolve polystyrene (PS) monolayer templates during spin-coating and the residual DIB, qP2VP was isolated from the reaction solution by adding an excess amount of diethyl ether and centrifuging. Then the qP2VP was re-dissolved in 5 mL NM and formed a 2 wt % solution that was ready for subsequent spin-coating.

Preparation of 2DPC-PGs

A monolayer opal of polystyrene (PS) colloidal spheres (diameters 470 or 535 nm) was first assembled on a glass or silicon substrate following a reported procedure,² onto which the as-prepared 2 wt% NM solution of qP2VP was spin-coated at 1000, 1500, 2000, 2500, or 3000 rpm for 60 seconds. The PS monolayer opal was then selectively removed by dissolving it in toluene. Finally, mechanically stable 2DPC-PG was obtained after thermal cross-linking at 120°C for 48 hours.

Procedures for pH sensing

The 2DPC-PG was soaked in a solution with a certain pH adjusted by dilution series of 0.1 M hydrochloric acid or various buffer solutions (citrate/ hydrochloric acid/ phosphate) for 1 minute and then taken out and dried with N_2 . The swollen 2DPC-PG was recovered by soaking it in a pH 10 buffer solution (boric acid / potassium chloride / sodium hydroxide) for 2 seconds and then washed with deionized water and dried with N_2 .

General methods

Spin-coating was performed with a spin-coater (WS-650S-NPP-Lite, Laurell Technologies Corporation). SEM images were recorded with a scanning electron microscope (JMS6500F, JEOL), at 5 kV and the samples were coated with carbon. Film thickness was measured by a profilometer (Dektak150, Veeco). Optical spectra were measured with a fiber optic spectrometer (USB2000+, Ocean Optics) attached to a microscope (DM2500, Leica) with normal incidence and

the optical spectra are always taken at the same spot (1×1 Millimeter in area) of a 2DPC-PG by saving the pictures of the spot of the wafer to again identify the spot in the following experiments.

Effective refractive index (n_{eff}) of the 2DPC-PG

The effective refractive index of the 2DPC-PG can be estimated as

 $n_{eff} = (n_{P2VP}^2 f_{P2VP} + n_{air}^2 f_{air})^{1/2}$

where f stands for the filling fraction of each component.

Reference

- 1. I. Tokarev, M. Orlov and S. Minko, Adv. Mater., 2006, 18, 2458.
- 2. C. Li, G. Hong and L. Qi, Chem. Mater., 2010, 22, 476.



Fig. S1 Thickness changes of 2DPC-PG with the spin-coating speed.



Fig. S2 Cross-section SEM images of 2DPC-PGs prepared with 470 nm (left) and 535 nm (right) templates and a spin-coating speed of 2000 rpm. The scale bars correspond to 500 nm.

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Scheme S1 The incident light (I) is distributed among the reflected (R) and transmitted (T) light beam in the case of an unstructured P2VP gel (right), and additional index guided modes in a 2DPC-PG (left).



Fig. S3 Dip position shifts of a 2DPC-PG in response to alternate pH 3 and pH 10 solutions. The 2DPC-PG was prepared on a glass substrate by using a 470 nm PS opal monolayer as template and a spin-coating speed of 2000 rpm.



Fig. S4 Thickness changes of a 2DPC-PG upon exposure to different pH conditions. The 2DPC-PG was prepared by using a 470 nm PS monolayer template and a spin-coating speed of 2000 rpm. The thickness was measured at the same spot by monitoring with a microscope.



Fig. S5 Side-view SEM images of a 2DPC-PG before and after exposure to a pH 3 solution. The 2DPC-PG was prepared by using a 535 nm PS monolayer template and a spin-coating speed of 2000 rpm.



Fig. S6 Reflectance spectra of a 2DPC-PG: as-prepared (purple), upon exposure to pH 5 (blue), pH 4 (green), pH 3 (yellow) and pH 2 (dark yellow). The 2DPC-PG was prepared by using a 470 nm PS monolayer template and a spin-coating speed of 2000 rpm. The small dips in some of the reflectance spectra correspond to the waveguide-like modes in the 2DPC-PG.