Stimuli-responsive two-dimensional photonic crystals based on polyelectrolyte hydrogel for optically encoded sensing

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The development of sensing techniques is driven by the ever increasing demand for miniaturized sensing platforms with fast response in areas such as bioassays, environmental monitoring and disease diagnostics.[1] Photonic crystals (PCs) are periodically structured materials where the refractive index is periodically modulated on a length scale comparable to the light wavelength of interest, which make them promising as signal transducers for sensitive optical detections in a non-destructive and label-free way. PCs based on hydrogels are of particular interest for sensing as they can be tailor-made to respond to various stimuli and show substantial volume changes upon recognition of analytes by swelling which enhances the optical readout.[2] However, existing motifs such as polymerized colloidal crystal arrays and hydrogel inverse opals suffer from slow response times when it comes to the sensing of analytes, such as pH or small molecules, because their thick hydrogel structure leads to slow diffusion of solutes and therefore slow sensor response.

We have developed a versatile sensing motif, namely stimuli-responsive two-dimensional (2D) PCs in the form of a monolayer inverse opal. A remarkable feature of this detection platform is its tunable photonic properties despite its sub-micron thickness, which enables an ultrafast optical response.[3]

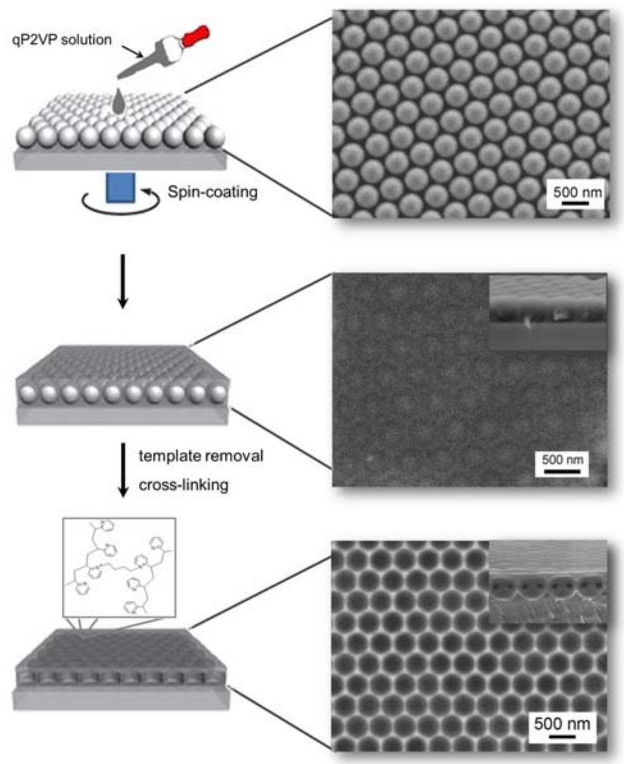

Figure 1: Schematic illustration (left) and the corresponding scanning electronic microscope (SEM) images (right) of the preparation of 2DPC-polyelectrolyte gels (PGs). The molecular structure of the cross-linked P2VP gel is indicated at the bottom-left panel. The top SEM image shows a monolayer array composed of PS spheres with a uniform diameter of 470 ± 20 nm. The middle SEM image outlines the composite film of qP2VP and PS spheres formed by spin-coating a qP2VP containing solution, and the inset shows the corresponding cross-sectional structure. The bottom SEM image depicts the as-prepared 2DPC-PG formed after the removal of PS spheres and the inset shows the corresponding cross-sectional structure.

As a proof of concept, we have developed 2D PCs made from poly-(2-vinyl pyridine) (P2VP), a pH-responsive polyelectrolyte gel (PG), by using a monolayer colloidal crystal as template. The P2VP-based PCs show tunable optical properties as well as prompt and reversible response to various pH conditions, which can be readily read out from the changes of either their optical spectra or interference colors. As outlined in Fig. 1, a solution of quaternized P2VP (qP2VP) is first spin-coated at a desired spin speed onto a monolayer of a polystyrene (PS) colloidal array that was assembled on a piece of glass or silicon substrate prior to spin-coating. The PS monolayer is then selectively removed by dissolving in toluene. Finally, a mechanically stable 2D PC of P2VP gel (2DPC-PG) is obtained after thermal cross-linking at 120 °C. The as-prepared 2DPC-PG replicates well the hexagonal order of the PS monolayer and the smallest distance between two sphere centers corresponds to the diameter of the template PS spheres. The void array is covered by a thin layer which owing to its small thickness appears almost transparent to the electron beam. The small holes in the walls of the voids are formed due to the close packing and, therefore, necking of the original

PS spheres, indicating that the voids are interconnected. The structural parameters of the 2DPC-PG, i.e. its overall thickness and the lattice parameter can be readily tuned with the presented method by adjusting the spin-coating speed and by using PS spheres of various diameters, respectively. Moreover, the thickness and lattice parameter can be tuned separately, which enables us to study experimentally the relationship between structural parameters and optical properties of 2DPC-PGs.

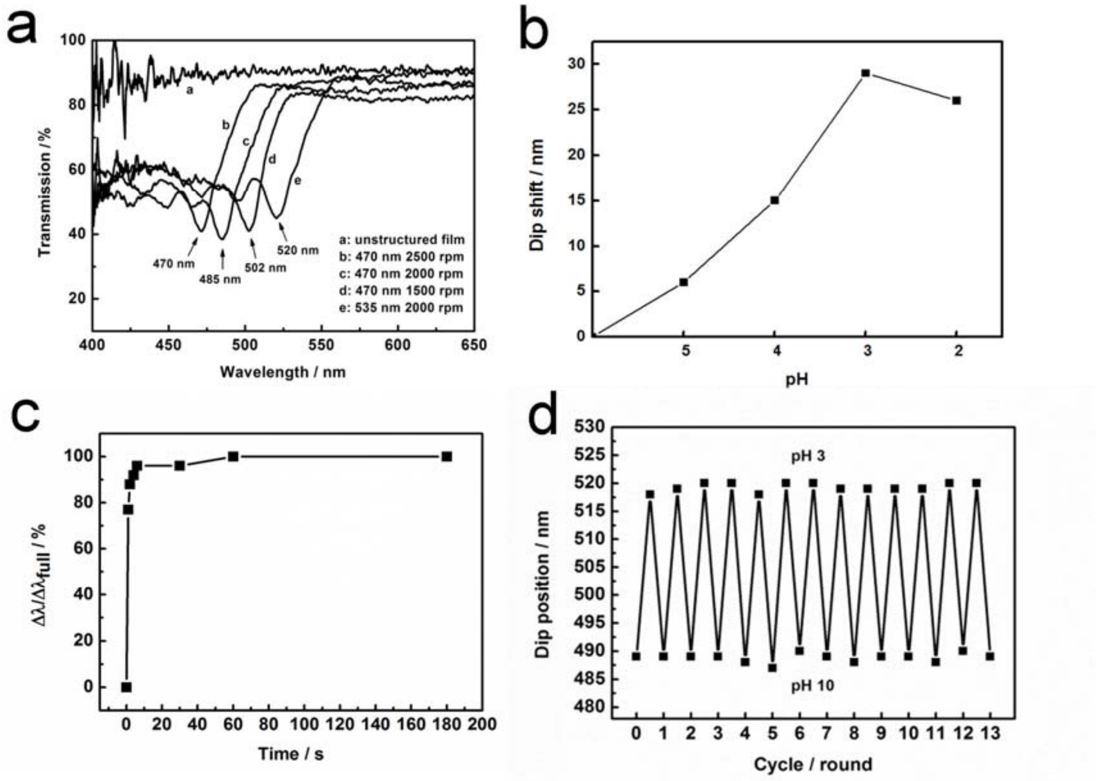

Figure 2: (a) Transmission spectra of an unstructured P2VP gel film and 2DPC-PGs prepared with varying PS sphere diameters and spin-coating speeds. (b) Wavelength shift of the transmission dip of a 2DPC-PG in response to varying pH conditions: pH 5, 4, 3 and 2. (c) Response kinetics of the transmission dip to pH 3. (d) Switch of the transmission-dip wavelength in response to alternating pH 3 and pH 10 conditions.

The 2DPC-PG demonstrates tunable optical properties associated with its structural parameters. As shown in Fig. 2a, while an unstructured, dense P2VP gel film prepared on a bare glass substrate is nearly transparent (a), the 2DPC-PG samples (b–e) all show a major, well-defined dip in their transmission spectrum. Such a transmission dip corresponds to an attenuation of the transmitted intensity as the incoming waves couple to the in-plane photonic modes provided by the periodic structure of the 2DPC-PG. The dip position of 2DPC-PG is experimentally shown to be both thickness- and lattice parameter-dependent. For samples b, c and d prepared with 470 nm PS spheres, the transmission dip red-shifts from 471, *via* 485 to 502 nm with a decrease in spin-coating speed from 2500, *via* 2000 to 1500 rpm (i.e. an increase in overall thickness) as a result of an increasing effective refractive index. With a fixed spin-coating speed of 2000 rpm and hence a constant thickness, the transmission dip of the samples c and e red-shifts from 485 to 520 nm as the template sphere diameter is increased from 470 to 535 nm.

The pronounced dependence of the transmission dip of the 2DPC-PG on its structural parameters as shown above makes it promising for optically encoded sensing, as the swelling of the polyelectrolyte gel through external stimuli will lead to changes in the structural parameters that can be read out directly from the shift of the transmission dip. As P2VP is well known as a weak cationic polyelectrolyte that exhibits fast and substantial swelling under acidic conditions due to protonation of the pyridine group, a pH sensor based on 2DPC-PG is demonstrated in this report. Fig. 2b shows the wavelength red-shift of the transmission dip of a 2DPC-PG in response to pH 5, 4, 3 and 2, which is 6, 15, 29 and 26 nm as compared to its initial position, respectively. Therefore, the variation of pH conditions can be readily read out from the wavelength shift of the 2DPC-PG's transmission dip. Remarkably, the 2DPC-PG pH sensor exhibits a prompt optical response. As shown in Fig. 2c, within 6 seconds soaking in a solution of pH 3 the transmission dip shift already reaches 96% of the full response reached after 1 minute of soaking, indicating that equilibrium can be well established within seconds. Compared with the PC-based pH sensors designed so far, the 2DPC-PG presents the thinnest gel structure, resulting in the fastest response times. Besides, the swollen 2DPC-PGs can be entirely recovered by a quick wash with a basic solution or pure water. Accordingly, the optically encoded response of the 2DPC-PG upon pH changes is totally reversible and can be cycled more than 10 times without degradation (Fig. 2d).

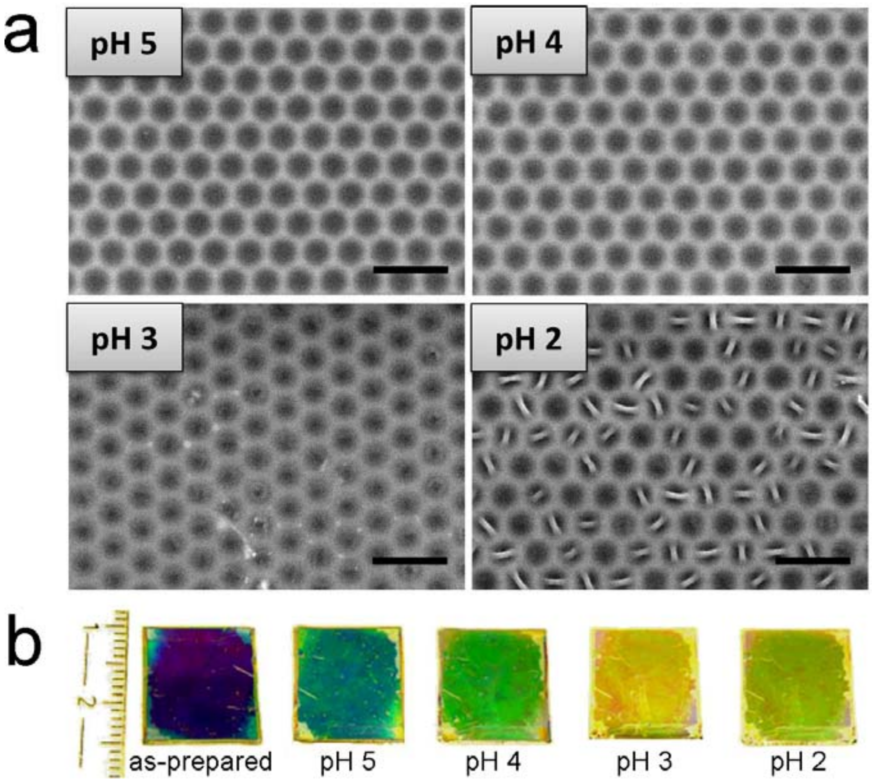

Figure 3: (a) SEM images of a 2DPC-PG after exposing it to different pH conditions of pH 5, 4, 3 and 2. (b) The 2DPC-PG prepared on a silicon substrate exhibits vivid color that varies in response to different pH conditions.

To explain the observed optical response, i.e. the transmission dip shift of the 2DPC-PG as a function of pH, its related morphological changes under different pH conditions was studied by SEM. As shown in Fig. 3a, from pH 5 *via* pH 4 to pH 3 the lattice parameter of the 2DPC-PG stays almost the same, although the inner voids gradually diminish. Notably, upon pH 2 the suspended part of the top layer of the 2DPC-PG exhibits significant wrinkling, which correlates well with the observed blue-shift of the transmission dip from pH 3 to pH 2.

Apart from the transmission dip arising from the in-plane waveguide-like mode and hence, the inherent PC properties of the membrane, the 2DPC-PG exhibits vivid color when prepared on highly reflecting substrates as a result of optical interference, which can also be exploited as a visibly perceptible indicator for sensing events. Fig. 3b shows in a row the photographs of the same 2DPC-PG on a silicon substrate before and after soaking in solutions of pH 5, 4, 3 and 2 and subsequent drying. The varying hues from purple, blue, green to yellow upon different pH conditions are noticeable to the naked eye. The present sensing motif based on 2D PCs can be easily extended to various sensing events besides pH sensing when coupled with tailor-made responsive materials.

References:

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