Communication

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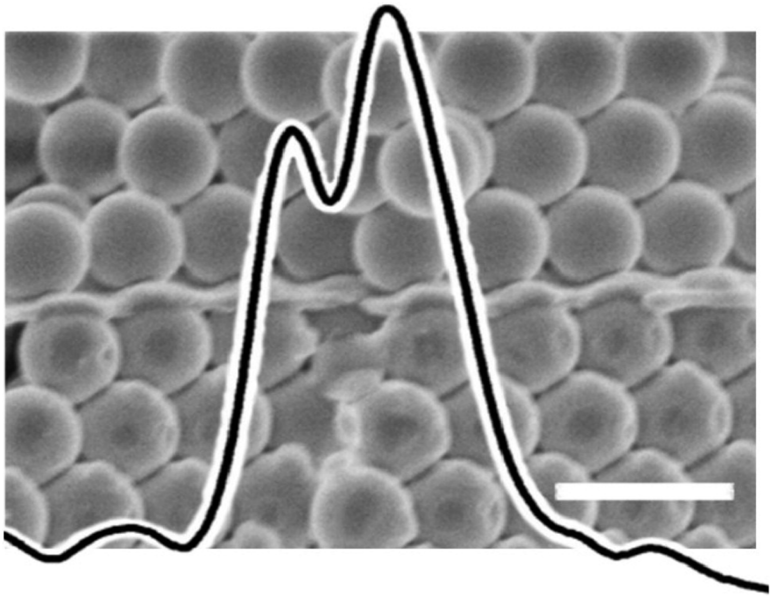

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# Photochemically and Thermally Tunable Planar Defects in Colloidal Photonic Crystals

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Photonic crystals (PCs) have attracted increasing attention as potential optoelectronic components for applications ranging from telecommunications to sensing, displays, lasing, and optical computing.[1−5] They are characterized by a periodic dielectric structure leading to photonic band gaps or stop bands with a depleted photonic density of states. At specific wavelength ranges, the propagation of electromagnetic radiation can be suppressed along certain lattice directions.[6,7] Colloidal photonic crystals (CPCs) are self-assembled from monodisperse silica or polymer spheres, a bottom-up approach which enables low-cost and large-scale fabrication.[8,9] Similar to the doping process of semiconductors, the functionality of PCs can only be truly harnessed by the controlled introduction of extrinsic defects in the crystal, leading to defect states within the photonic gaps.[10] Such defect states can serve as a platform for waveguiding,[11] highly efficient lasing,[12] and ultranarrow optical filters.[13] So far, proven methods for generating defects in 3D PCs include lithography,[14] two-photon writing[15] and polymerization,[16] laser writing,[17] as well as microrobotic manipulation.[18] While these top-down methods are precise and allow design flexibility, they are often time-consuming, limited to small areas, and possibly not applicable to mass-production. In addition, the introduced defects are mainly of a passive nature and cannot be actively tuned by an external stimulus. Tunable defects, actuated, for instance, by temperature and electrical fields, have only so far been realized in 1D and 2D PCs.[19,20] A bottom-up approach to passive planar defects in CPCs has been reported.[21,22] More recently, we demonstrated the preparation of a 3D CPC possessing a planar defect having refractive index and thickness tuned by exposure to different solvent vapor pressures.[23] In this paper, we present a new type of CPC with a "smart" polyelectrolyte (PE) planar defect that allows active tunability of a defect-state transmission window by UV-exposure as well as temperature changes.

The defect was prepared by transfer printing a PE multilayer,[24] grown layer-by-layer on a poly(dimethylsiloxane) (PDMS) stamp, onto the surface of a planar CPC consisting of silica spheres[25] ($d = 280$ nm) crystallized on a glass substrate[26] and mechanically stabilized by silica CVD.[27] A second CPC was then grown over the defect. Polydiallyldimethylammonium chloride (PDAC) and poly[1-[4-(3-carboxy-4-hydroxyphenyl)azobenzenesulfonamido]-1,2-ethanediyl, sodium salt] (PAZO) were used as commercially available PEs. The azo group in PAZO undergoes a well-known UV-induced trans-to-cis photoisomerization and partial thermal back isomerization.[28] SEM images of the CPCs with embedded active defects are shown in Figure 1. The thickness of the defect layer could be varied by the thickness of the PE multilayer stack, or by repeated printings. Such a planar layer gives rise to a narrow dip (transmission window) within the CPC's stop band frequency (Figures 2a,b and 3a) that is constant over the sample area (0.5−1 cm$^2$). Optical characterization was performed by transmission microspectroscopy to make spatially resolved optical measurements within the area of a CPC domain. The spectra were recorded along the CPC [111] direction using a fiberoptics spectrometer (Ocean Optics SD 2000) interfaced to an optical microscope (Olympus BX-41). Optical properties of the PE multilayer were independently determined by variable angle spectroscopic ellipsometry (SOPRA GES-5), which yielded a thickness of 4.6 nm per PAZO/PDAC bilayer with a refractive index of 1.58 in the wavelength range of the photonic stopgap.

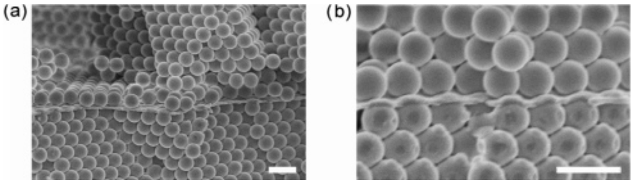

***Figure 1.*** SEM images (low and high magnification) of a silica CPC with embedded PAZO/PDAC defect layer. The scale bars represent 500 nm.

Irradiating the sample with UV light (Xe-lamp, 180 W) at constant temperature leads to a small but reproducible blue shift of the defect state due to trans/cis isomerization of the PAZO molecules (Figure 2a). The stopband edges remain constant, implying that the CPC cladding layers are not affected by UV irradiation. The defect state position dependence on the UV irradiation time is plotted in Figure 2c and is best fitted using an exponential decay curve. After 120 min, a stationary state is reached. This is in agreement with Stroeve et al., who investigated the kinetics of photoisomerization of PAZO multilayer films.[28] Ellipsometry measurements show that the UV-induced trans/cis isomerization causes a 10% decrease in thickness and a 5% increase in the refractive index of PAZO/PDAC multilayer films. These parameters were used to simulate the observed optical spectra using a scalar-wave approximation (SWA) model;[29] the theoretically calculated defect shift was found to be in perfect agreement with experimental observations. Leaving the PAZO/PDAC-opal heterostructure in the dark leads to partial back isomerization of the azo component (∼50% based on wavelength shift) and, consequently, to a red shift of the defect state toward the original position (Figure 2b). The defect position versus the back isomerization time is plotted in Figure 2d and compares well to previous studies of the PAZO alone.[28]

Additionally, we found that tuning the defect state could also be achieved by thermal cycling of the PAZO/PDAC−CPC com-

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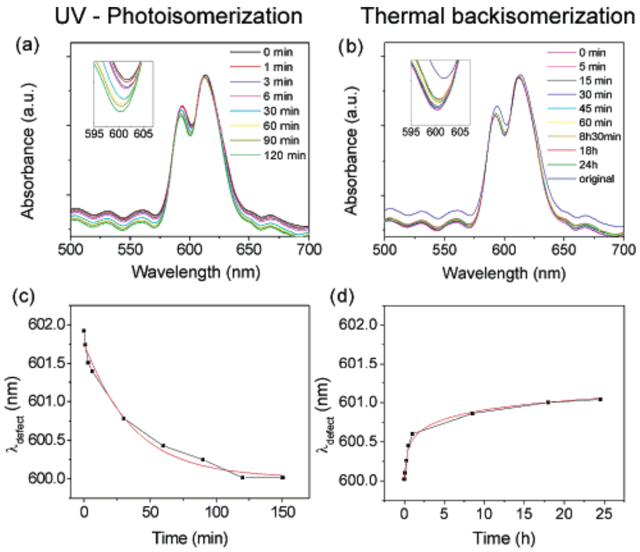

***Figure 2.*** Top: Transmission spectra of a PAZO/PDAC defect CPC at different (a) UV irradiation and (b) back isomerization times. The insets show a magnification of the defect state positions. Bottom: Dependence of defect state wavelength on (c) UV irradiation and (d) back isomerization time. Exponential and logarithmic fits are applied.

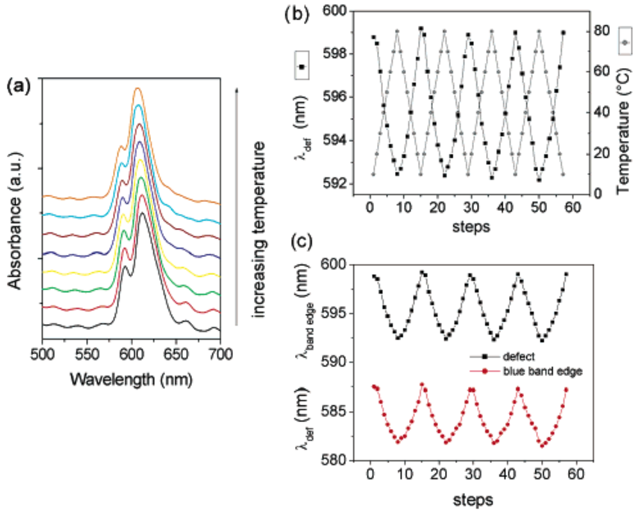

***Figure 3.*** (a) Transmission spectra of a PAZO/PDAC defect CPC at temperatures between 10 and 80 °C (10 °C increments). (b) Dependence of defect state wavelength on temperature during heating and cooling cycles. (c) Changes in defect state and blue band edge wavelength during the applied heating and cooling steps.

posite PCs. By heating and cooling the sample between 10 and 80 °C, completely reversible shifts of the photonic defect state and the stopband edges could be observed after 5−7 "conditioning" cycles (Figure 3). The sample was kept on a thermoelectric Peltier element, and transmission spectra were taken in temperature increments of 10 °C at a rate of 10 °C/min. The blue shift of the defect state with increasing temperature is due to the evaporation of water trapped in the planar defect as well as in the voids of the CPCs. The water loss leads to both a decreasing thickness of the planar defect and a decreasing effective refractive index of the opal. Upon cooling the sample, ambient humidity condenses back into the hydrophilic voids of the CPCs and into the PE defect, red shifting the defect state and band edges. Using the SWA model, the observed behavior could be simulated by taking into account a 10 and 20 vol % water loading in the CPC voids and defect state, respectively, at 10 °C, and a near-zero humidity level when the temperature was increased to 80 °C. Thermal gravimetric analysis shows the water content to be 9.14 and 18.1 vol %, respectively. These thermal experiments support the claim that the UV-induced defect state tuning is dominated by trans/cis isomerization, and not photothermal effects.

In conclusion, we have developed a bottom-up approach to create embedded active planar defects in large-area colloidal photonic crystal films. These defects can be photochemically tuned with partial reversibility or thermally tuned with full reversibility. Our method is easy and reproducible and can be adapted to a multitude of PE species, implying that it could find applications in large-scale optical components, such as chemically tunable filters, sensors, and laser sources.

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