

## Spin-Coating of Designed Functional Planar Defects in Opal Film: Generalized Synthesis

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Opals, or colloidal photonic crystals (CPCs), consist of close-packed spherical colloids with diameters ranging from nanometers to several micrometers. The resulting spatially periodic modulation in the dielectric constant between spheres and voids leads to photonic band gaps or stop bands that can suppress, slow, localize, or guide the propagation of electromagnetic radiation with a wavelength comparable to the periodicity.<sup>1,2</sup> These characteristics result in the dazzling colors reflected from opals and make CPCs promising candidates for optical chips, sensors, or laser microcavities.<sup>3–6</sup> In contrast to other types of photonic crystals, CPCs can be synthesized in a bottom-up self-assembly approach that requires only modest instrumentation, leads to large area samples, and allows for the integration of chemical diversity.<sup>7,8</sup> Analogously to the doping process of semiconductors, the functionality of photonic crystals can be enhanced by the controlled introduction of extrinsic defects, leading to optical states within the photonic band gaps or stop bands.<sup>9</sup> In this context, planar defect layers of different materials and functionality have been embedded within CPCs by several creative bottom-up approaches: A monolayer of spheres of an arbitrary diameter introduced into the bulk between two CPCs can be prepared with the Langmuir–Blodgett technique.<sup>10–12</sup> Chemical vapor deposition (CVD) has been used to sandwich a silica defect slab between two

inverted CPC layers.<sup>13,14</sup> Recently, we have developed a technique to incorporate chemically active polymer and biopolymer defects into CPCs.<sup>15–18</sup> A layer-by-layer (LbL) self-assembled polyelectrolyte multilayer is microcontact transfer printed onto a CPC and a second CPC is grown on top. The latter functional defect CPC heterostructures allows for switching of the defect wavelength by external stimuli (e.g., light, temperature, redox cycling) or can be used to optically monitor chemistry and biochemistry taking place in the functional thin film. Through shifts of the photonic intragap defect mode, DNA conformational changes and the enantioselective intercalation of a chiral anticancer drug can be optically monitored with femtomole sensitivity. In these cases, microcontact transfer printing was necessary to prevent the polymers from penetrating into the CPC voids, as would be the case with direct LbL self-assembly or spin-coating of polymer films onto the porous opal surface. However, the technique is limited to polymers, molecules, or particles that can be coated by LbL assembly onto a PDMS stamp and subsequently transferred onto the opal external surface. Consequently, in most of the cases, the LbL multilayer building blocks have to be charged and the solvent is aqueous. There has been a reported case of spin-coating of particle-based defect layers on CPCs, but this was only possible when the size of the spun particles (e.g., nanocrystalline aggregates) exceeded the size of the colloidal crystal entrance windows.<sup>19</sup>

In this report, we present a novel and universal method that allows for spin-coating of nanometer-scale CPC defect layers from a wide variety of polymers, doped polymers, or particles that are dissolved in hydrophobic solvents. Using this method, we have demonstrated fluorescent defects with strongly modulated light output and a mechanically tunable CPC incorporating an elastomeric planar defect.

The key to preventing infiltration of the cladding opal layer during the spin-coating process is filling the CPC voids with a suitable sacrificial material. Following spin-coating of the defect, the filling material is removed and the second CPC is grown on top to complete the structure (Figure 1). The use of a sacrificial substrate, such as silica, has been reported

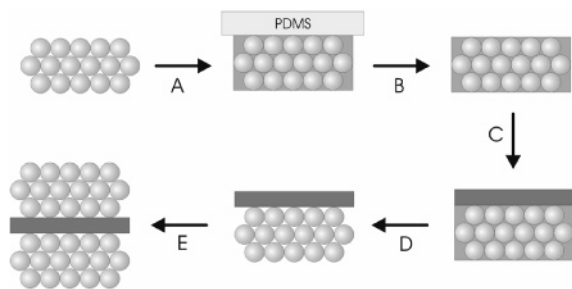
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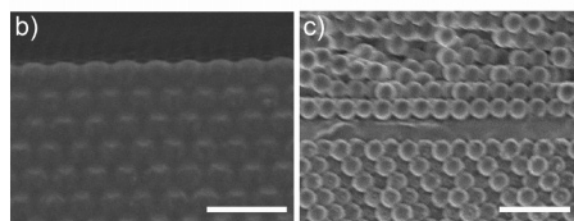
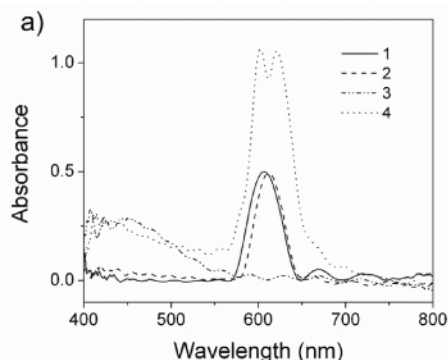
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**Figure 1.** Preparation of a CPC with spin-coated defect layer. (A) Sacrificial sugar filling is melted into the voids of a mechanically stabilized silica CPC. Top compression with a PDMS sheet prevents the formation of an overlayer. (B) PDMS sheet is carefully peeled off after complete infiltration and solidification of the sugar. (C) Spin-coating of various materials from hydrophobic solvents can be performed on top of the infiltrated CPC. (D) Sacrificial sugar filling is dissolved in water. (E) Second silica CPC is grown to complete the defect structure.

in the preparation of free-standing thin films;<sup>20</sup> in our case, a sacrificial CPC filling is crucial to confine the spin-coated defect material to the CPC surface and to block penetration into the opal voids. A free-standing film and consequently an overlayer of the sacrificial filling on the opal surface is not desired if we wish to obtain adhesion between the spin-coated defect layer and the bottom-CPC. For this purpose, we chose ribose, a low-melting-point sugar, which was melt-infiltrated under a vacuum into the voids of a silica CPC. The CPC was prepared by evaporation-induced self-assembly<sup>21</sup> of monodisperse silica spheres<sup>22</sup> and mechanically stabilized by CVD necking of the spheres.<sup>23</sup> To avoid the formation of a ribose overlayer on the CPC, we pressed a flat PDMS slab onto the surface of the ribose-CPC composite while heating at 180 °C under house-vacuum overnight, allowing any excess sugar to flow out the sides of the sample. After cooling to solidify the ribose, the PDMS was carefully peeled off. Spin-coating was performed on top of the ribose-infiltrated opal, followed by dissolving the sugar in water and growth of the top-CPC by self-assembly.

Using the described method, it was possible to synthesize doped polymer defect CPCs with a laser dye located exclusively in the defect layer. PMMA was used as defect material, 4-(dicyanomethylene)-2-methyl-6-(p-dimethyl-amino)styryl)-4H-pyran (DCM) as laser dye, and toluene as spin-coating solvent. In contrast, the LbL transfer-printing method cannot localize charged dyes such as rhodamine within the defect layer, because the dye molecules are washed out of the LbL film during the LbL rinsing steps or during evaporation-induced self-assembly of the top-CPC. Figure 2a shows the optical transmission spectra taken along the CPC [111]-axis during the preparation process. The Bragg diffraction peak of the bottom-CPC is red-shifted upon mechanical stabilization because of the formation of “necks” between the spheres and the increase in effective refractive index of the CPC. Ribose infiltration into the CPC voids



**Figure 2.** (a) Optical spectra of a silica CPC with spin-coated PMMA/DCM defect layer at different preparation steps: (1) bottom-CPC; (2) mechanically stabilized bottom-CPC; (3) sugar infiltrated bottom-CPC with spin-coated PMMA/DCM layer; (4) final structure. The spectra are taken in transmission along the CPC-[111]-axis. (b) Cross-sectional SEM image of a ribose infiltrated bottom-CPC. (c) Cross-sectional SEM image of a CPC with spin-coated DCM-doped PMMA defect layer. The scale bars represent 1  $\mu\text{m}$ .

leads to the expected disappearance of the Bragg peak caused by the large decrease in refractive index contrast. Additional absorbance between 400 and 550 nm after spin-coating is a result of the DCM-doped PMMA defect layer. After the ribose filling is dissolved and the top-CPC is crystallized, the Bragg peak reappears and shows a higher intensity (caused by the increasing number of sphere layers) as well as an intragap defect state. The position of the defect state in the Bragg peak depends on the thickness and refractive index of the defect layer. The defect layer thickness can be fine-tuned between 50 nm and 1  $\mu\text{m}$ . Cross-sectional SEM images of a ribose-infiltrated bottom-CPC as well as the complete structure of a CPC with a spin-coated DCM-doped PMMA defect layer are shown in images b and c of Figure 2. The images clearly prove that the formation of a ribose overlayer (Figure 2b) and the penetration of a spin-coated defect material into the bottom-CPC voids (Figure 2c) are successfully prevented. Slight distortions in the CPCs are caused by the cleavage of the samples.

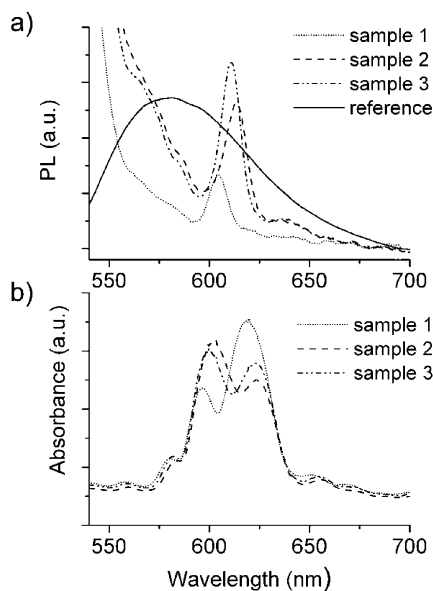
The influence of the photonic band structure and defect transmission state on the photoluminescence (PL) of the embedded dye was investigated. CPCs with DCM-doped PMMA defect layers showing defect transmission dips at 604, 611, and 615 nm, respectively, (Figure 3b) were excited at 532 nm with a frequency-doubled cw Nd:YAG laser. PL was detected in transmission. The resulting PL spectra as well as the PL reference spectrum of DCM in a nonphotonic organic polymer film are shown in Figure 3a. The emission of DCM in the defect layer of a CPC is strongly modified compared to the reference. Strong suppression of spontaneous emission at wavelengths of the photonic stopband is observed, and narrow luminescence peaks emerge at exactly

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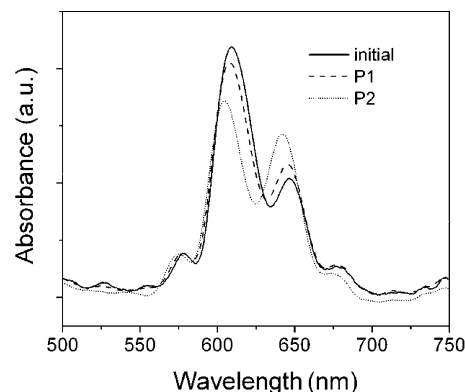
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**Figure 3.** (a) PL spectra of CPCs with DCM-doped PMMA defect layer (samples 1–3) and PL spectrum of DCM in a nonphotonic organic polymer film (reference). (b) Transmission spectra of samples 1–3 with defect states at 604, 611, and 615 nm, respectively.

the wavelengths of the defect transmission states. Because of slight inhomogeneities in the dye distribution within the defect layer and detection of scattered excitation light, quantitative comparisons of the modified and reference PL spectra were difficult.

Another structure enabled by this described spin-coating approach was a CPC bearing an elastomeric defect layer, allowing for active mechanical tuning of the defect wavelength. The thermoplastic elastomer Kraton G, a blockcopolymer with “hard” polystyrene domains (network junctions) in a “soft” polyethylene/polybutylene matrix, was used as defect material. Because of physical and not chemical cross-linking, the elastomer can be dissolved in a hydrophobic solvent (e.g., toluene) and processed into a thin film by spin-coating. The optical spectrum of the elastic defect CPC shows a defect transmission state that can be reversibly blue-shifted by applying mechanical pressure along the sample’s [111]-axis (Figure 4). Theoretical scalar wave approximation (SWA) simulations<sup>24</sup> of the experimental spectra show that the observed blue shift of the defect wavelength is caused by a 4 and 10% length compression



**Figure 4.** Transmission spectra of a CPC with spin-coated elastomeric defect layer. Initial spectrum and spectra when applying mechanical pressure ( $P_1 < P_2$ ) perpendicular to the sample surface.

of the defect layer along the [111]-axis. With a Young modulus of  $2.5 \times 10^5$  Pa determined by rheological measurements of Kraton G films, this corresponds to applied pressures on the CPC heterostructure between 0.1 and 0.25 bar.

In conclusion, we have developed a general and facile bottom-up method for the incorporation of planar defects in CPCs by spin-coating. A sacrificial sugar filling in the bottom-CPC prevents penetration of the defect material into the opal voids during the spin-coating process, and the sugar can be easily removed by aqueous dissolution to create the desired defect-CPC composite. This opens the door to the preparation of defect layers from a myriad of functional materials that could not be embedded into CPCs with any previously published procedures. The potential of this approach has been illustrated by the creation of CPCs with luminescent and elastic defects, interesting candidates for CPC-based lasers, pressure-tunable microcavities or color-based sensors.

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