Exploration and use of internal water in silica colloidal crystals

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Recently, it has been shown that silica artificial opals possess a PBG controlable by simple heating on a hot plate [1]. Submicrometer silica spheres easily form high-quality face-centered-cubic (fcc) structures displaying a Bragg peak (the lowest energy PBG) in the visible range. Given the hydrophilic character of silica, these opals inherently contain a substantial amount of molecular water (as much as 8 wt.% in as-grown samples) physisorbed on the silanol groups at the spheres surface. This water is partially placed between the spheres forming necks, leading to a nonclose-packed arrangement, so that the opal lattice parameter directly depends on the amount of water (Figure 1). Thus, controlled desorption of this water upon moderate opal heating induced large effects in the opal photonic properties, mostly due to shrinking of the lattice parameter in up to ~ 12 nm. Complete water removal (achieved at ~ 120 °C) leads to a pronounced blueshift of the Bragg peak of 25 nm. PBG changes are reversible upon cooling down to room temperature (RT) by virtue of spontaneous water re-adsorption. By *in situ* measuring PBG behavior with temperature one can extract relevant fundamental knowledge regarding water morphology and adsorption in silica colloidal systems [2], [3]. Further, this internal water plays an important role in Azo-Molecules photo-alignment [4] or in the mechanical properties of these systems [5].

Once the presence of water is characterized we are able to use it for different means. The amount of adsorbed water and its distribution can be controlled by modifying the chemistry of the silica surface, from hydrophilic to hydrophobic through thermal annealing. By doing this we can acquire deep knowledge on silica chemistry and use it to tune the structure photonic response. Further, although thermal effects regarding the whole structure (sample size around some square centimeters) are usually rather slow (seconds) we can bring this response to the millisecond range by inducing local heating [6]. The opal was photoirradiated with a focused 488-nm Ar^+-laser while measuring the opal reflectance spectrum in order to monitor *in situ* the PBG changes. Photoirradiation significantly affected the spectrum of the infiltrated opal in a reversible fashion (Figure 2a). Under light exposure the Bragg peak shifted to shorter wavelengths (up to 13 nm) within a few milliseconds and rapidly shifted back to the original position after turning the light off (Figure 2). Simultaneously, the bandgap width decreased (up to 5%) during irradiation, also reversibly. Thus, the photoinduced PBG changes were fast and, without external stimulus, fully reversible, and the shift distance directly depended on the irradiation intensity *I*. Additionally, the overall performance was reproducible over millions of cycles. All these issues are greatly relevant for switching applications demanding not only spontaneous reverse effect but also accurate response and fidelity in a fast fashion.

References

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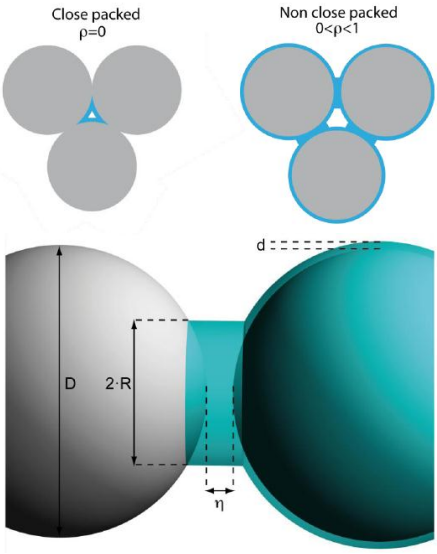

Figure 1: Proposed model for water distribution in as-grown silica opals at room temperature and about 35% humidity.

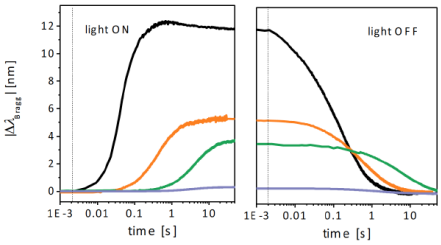

Figure 2: Temporal evolution of the Bragg peak position of infiltrated as-grown (black lines) and annealed (at 450, 525 and 600°C, orange, green and blue lines) opals. The laser was turned on/off 2 ms after beginning the measurement (denoted by the dashed lines). In all cases, the irradiated area S was 0.002 mm^2 and the laser intensity I was 30 W cm^{-2}.