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Electronic Supplementary Information

Engineering Optical Defects in biopolymer photonic lattices

Elena Colusso, [a,e,*] *Fabio De Ferrari,* [a,b,*] *Paolo Minzioni,* [f] *Alessandro Martucci,* [e] *Yu Wang* [a] *and Fiorenzo G, Omenetto* [a,b,c,d,+]

[a]Silklab, Tufts University, 200 Boston Avenue, Suite 4875, Medford, MA 02155, USA

[b]Department of Biomedical Engineering, Tufts University, 4 Colby Street, Medford, MA 02155, USA

[c]Department of Physics, Tufts University, Medford, MA 02155, USA

[d]Department of Electrical Engineering, Tufts University, Medford, MA 02155, USA

[e]Università di Padova, Dipartimento di Ingegneria Industriale, Via Marzolo, 9, 35131 Padova, Italy

[f]Department of Electrical, Computer, and Biomedical Engineering, University of Pavia, Via Ferrata 5A, 27100 Pavia, Italy

*denotes equal contribution

+Email: fiorenzo.omenetto@tufts.edu

EXPERIMENTAL SECTION

Silk fibroin solution preparation

The silk fibroin solution used to infiltrate the opals was extracted from the silk cocoons of bombyx mori according to the protocol previously reported ([1]). The cocoons were cut in small pieces and boiled in a 0.02 M solution of sodium carbonate (Na_2CO_3) to remove the sericin. After rinsing with distilled water and drying, the fibers were dissolved in a 9.3 M aqueous solution of lithium bromide (LiBr) at 60°C for 4 hours. A water based silk solution was finally obtained after the removal of the salt by dialysis using a dialysis tube (Fisherbrand, MWCO 3.5K) for 3 days. The final concentration of fibroin in solution was 6-7% w/w.

SIO fabrication

The SIO was prepared by using large-scale close-packed PS sphere (modified by carboxylic acid group on the surface, Interfacial Dynamics Co.) arrays as template following the protocol previously reported ([2]). A suspension of 6% aqueous PS spheres was prepared in a mixture with an equal volume of ethanol. A few drops of the suspension were introduced to the water surface in a petri dish using a partially immersed Si wafer, which was pretreated by an O 2 plasma treatment to realize a hydrophilic surface. To help the direct crystallization process, a few drops of sodium hydroxide solution and sodium dodecyl sulfate (SDS) were added to the water phase before introducing PS spheres to adjust the surface tension of water. The formation of a large crystal layer by self-assembly was promoted by the addition of liquid medium. To prevent the formation of cracks during the transfer step, few drops of sodium dodecyl sulfate (SDS, $NaC1_2H_{25}SO_4$) were introduced. A silicon substrate was immersed into the subphase and elevated under a shallow angle to transfer the monolayer from the water surface to the substrate (scooping transfer). To facilitate the final detachment of the SIO, a layer of polymethylmethacrylate was

deposited on the wafer by spin-coating. After drying, the procedures were repeated for the fabrication of multilayer colloidal crystals, using a different size of beads for the defect layer. The silk solution was added to the colloidal crystals to fill the air voids after immersing the template in water for a few minutes to remove SDS. The sample was set to dry for 24 h (25 °C, 30% relative humidity) to form a free-standing silk/PS composite film. The PS spheres within the composite film were finally removed by immersing the film into toluene for 24 h.

Characterizations

Scanning electron micrograph (SEM) observations were performed with Zeiss Supra55VP microscope, after cleavage of the opal template and of the free-standing inverse opal films via cryofracture. The samples were sputtered with a 5nm thick layer of gold using an EMS 300T D Dual Head Sputter Coater.

The specular reflection spectrum was collected at normal incidence respect to the (111) crystallographic plane by using an optical spectrum analyzer (OSA, YokogawaAQ6370B, Yokogawa Corporation of America) in the wavelength range 650-1000 nm. The incident beam was provided by a Tungsten Halogen white light source (LS-1, Ocean Optics) connected to an optical fiber probe (R400-7-VIS-NIR, Ocean Optics) composed by 7 fibers with numerical aperture of 0.22 and core diameter of 400 µm. The 6 external cores of the probe are used to bring the while light illumination to the sample, while the central fiber is connected to the OSA. Before measuring the prepared sample, the system is calibrated by using as a reference a metallic mirror (PF10-03-P01 Protected Silver Mirror for the NIR, Thorlabs Inc.) guaranteeing a reflectivity on the whole analyzed wavelength range higher than 99%.

The reflection spectrum was also collected at normal incidence and at different angles with respect to the (111) crystallographic plane by using an Extended Range Spectrometer for UV-NIR applications (USB2000+XR1-ES, Ocean Optics) in the wavelength range 350-850 nm. The same setup as previously described was adopted. Specular reflection was also evaluated considering different incidence angles

(i.e. the angle formed between the propagation direction of the incident light and the normal to the SIO surface) ranging from 20° to 45° . The incident white-light was brought to the sample by using the 6 external cores of a 7-fibers optical fiber probe (R200-7-VIS-NIR, Ocean Optics) , while the central core of another probe (R400-7-VIS-NIR, Ocean Optics) was used to collect the reflected light. For each angle, the system was calibrated using the reference metallic mirror. In case of normal incidence a single probe was used.

FIGURES

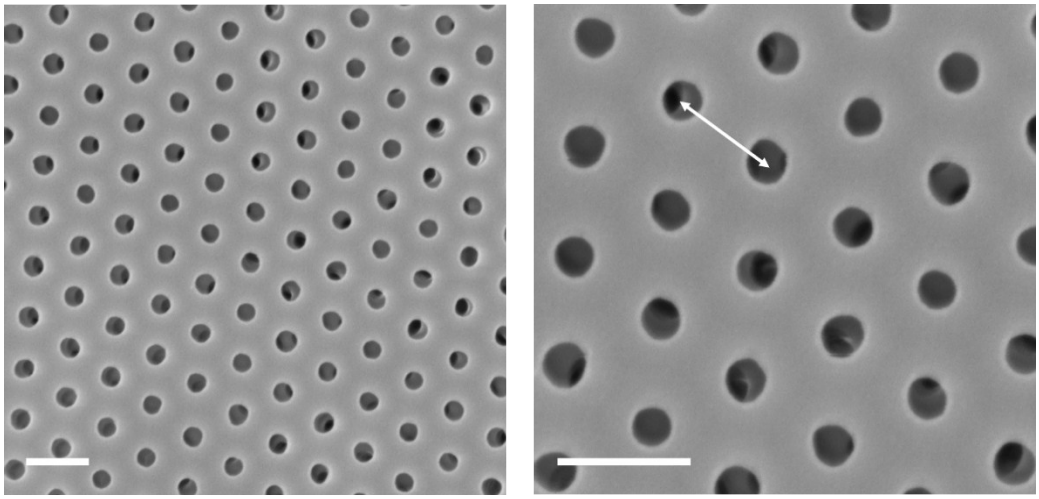

Figure S1. SEM images of the surface of the inverse opal structure made with 420 nm beads. The scale bars are 500 nm. The nanopores are stacked in a hexagonally arrangement highly ordered on a large-scale. The arrow indicates the center-to-center distance between two neighboring air cavities, which represents the lattice constant and it is equal to 420nm (the same of the diameter of PS spheres used).

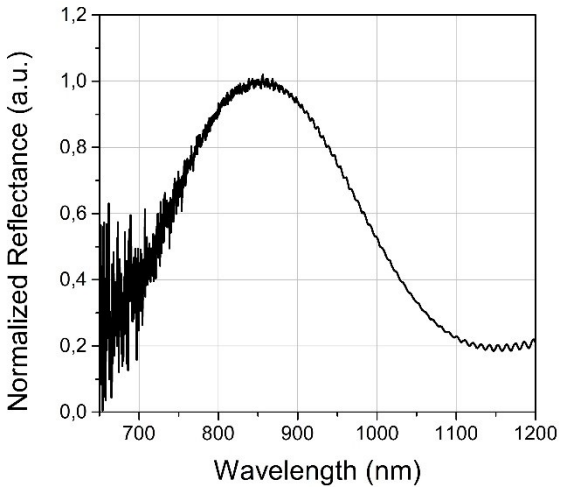

Figure S2. Reflectance spectrum of a simple 3 layer silk inverse opal obtained by replica of an opal template made with 420nm beads without a defect layer.

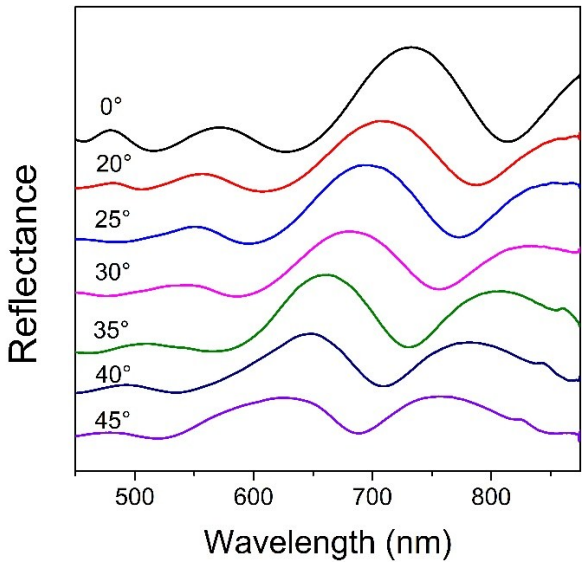

Figure S3. Experimental reflectance spectra of a SIO structure including a defect-layer measured from θ = 0° (top) to θ = 45° (bottom) in steps of 5° (angles between 5° and 15° could not be reported due to limitations of the experimental setup). The shift of the reflection-dip wavelength matches with what could be calculated by using the Bragg-Snell law.

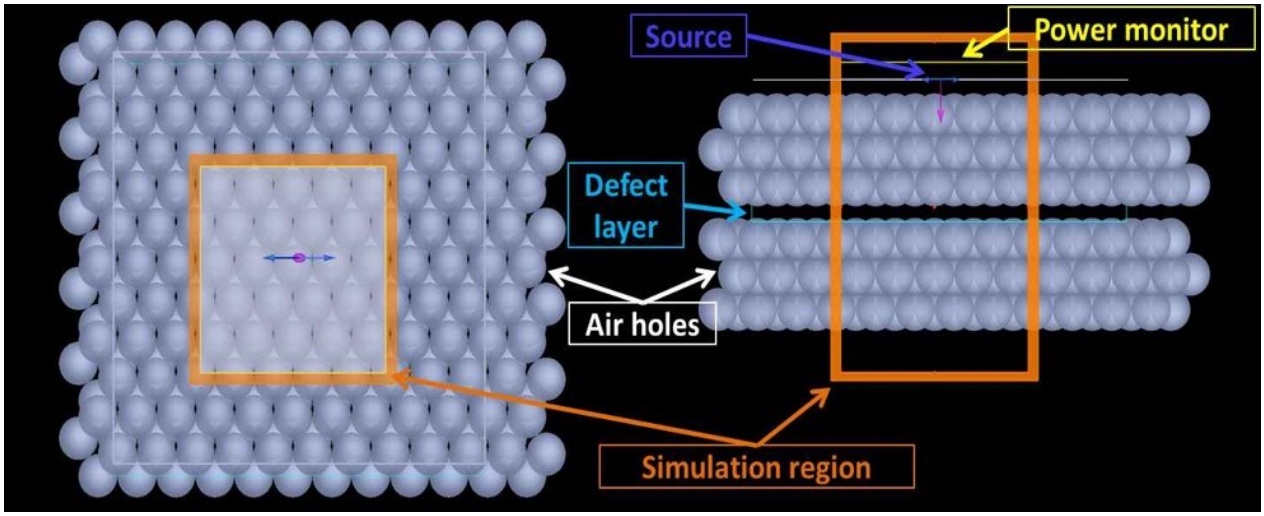

Figure S4. Schematic illustration of the structure used for the FDTD simulations. A plane-wave source was placed in close proximity of the opal surface (@ 135-nm distance) and reflectance was measured 235 nm away from the opal surface.

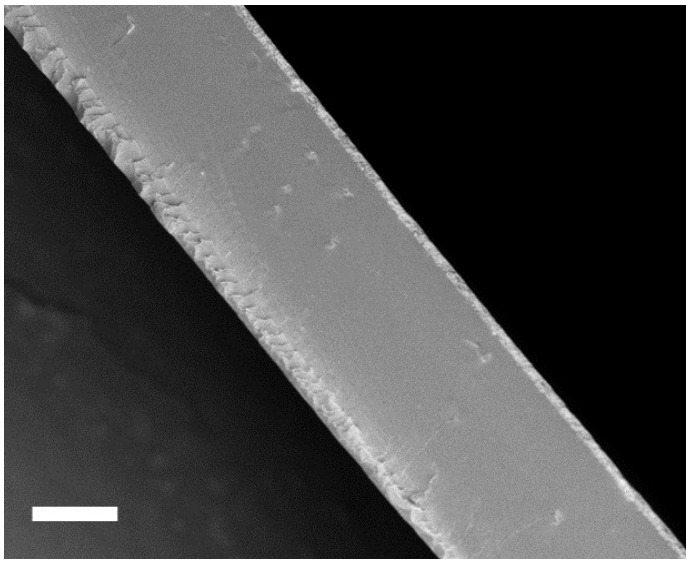

Figure S5. Cross-section SEM images of the free-standing SIO film (the scale bar is 20 μm).

REFERENCES

1 D. N. Rockwood, R. C. Preda, T. Yücel, X. Wang, M. L. Lovett and D. L. Kaplan, *Nat. Protoc.*, 2011, **6**, 1612–1631.

2 Y. Wang, D. Aurelio, W. Li, P. Tseng, Z. Zheng, M. Li, D. L. Kaplan, M. Liscidini and F. G. Omenetto, *Adv. Mater.*, 2017, 1702769.