Optofluidic Modulation of Self-Associated Nanostructural Units Forming Planar Bragg Microcavities

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ABSTRACT

Bragg microcavities (BMs) formed by the successive stacking of nanocolumnar porous SiO₂ and TiO₂ layers with slanted, zig-zag, chiral and vertical configurations are prepared by physical vapor deposition at oblique angles (PV-OAD) while azimuthally varying the substrate orientation during the multilayer growth. The slanted and zig-zag BMs act as wavelength selective optical retarders when they are illuminated with linearly polarized light, while no polarization dependence is observed for the chiral and vertical cavities. This distinct optical behavior is attributed to a self-nanostructuration mechanism involving a fence-bundling
association of nanocolumns as observed by Focused Ion Beam- Scanning electron Microscopy (FIB-SEM) in the slanted and zig-zag microcavities. The outstanding retarder response of the optically active BMs can be effectively modulated by dynamic infiltration of nano- and mesopores with liquids of different refraction indices acting as a switch of the polarization behavior. The unprecedented polarization and tunable optofluidic properties of these nanostructured photonic systems have been successfully simulated with a simple model that assumes a certain birefringence for the individual stacked layers and accounts for the light interference phenomena developed in the BMs. The possibilities of this type of self-arranged nanostructured and optically active BMs for liquid sensing and monitoring applications are discussed.

The last innovations in the field of optofluidics have led to the development of highly versatile optical systems with a wide range of applications both at the micro and macroscales and a high impact in fields such as energy, 1 photonics, 2 microfluidics, 3 or sensors and biosensors. 4 Outstanding examples relying on the light control by means of liquids flowing through devices include adaptive and tunable microlenses, 5,6 optofluidic dye lasers 7 or advanced optofluidic microscopes. 8 Light polarization by liquids containing chiral molecules or by anisotropic solids is a classical optical principle widely used in advanced technologies for chemical analysis, communications, displays and photonics that, except for very recent works using complex polymer particles, 9 has not been addressed merging in a single device optics with microfluidics or nanofluidics. 3 In the present work we report about the development of a series of nanostructured planar Bragg microcavities (BM) devices prepared by physical vapor oblique angle deposition (PV-OAD) where a singular association of individual nanostructural units in the form of long asymmetric ensembles confers outstanding optical properties and a peculiar
polarization activity that can be used for different applications including liquid monitoring. In particular, we have found that light polarization can be effectively controlled by liquid circulation and filling of the nano and mesopores existing in this type of structures. The liquid-mediated control of the activity of planar BMs constitutes a first case of polarizer thin films optofluidics with high impact prospects for the fabrication of polarization active systems, wavelength retarders, photonic sensors or liquid monitoring devices. In addition, the singular association of nanocolumns responsible for the peculiar polarization properties of these systems constitutes a prominent example of the interplay between structural effects at the nano-scale and their correlation in the form of new properties at the macroscale.

Thin films fabrication by PV-OAD, also known as Glancing Angle Deposition (GLAD),\textsuperscript{10,11} is a straightforward procedure to tailor film porosities while achieving a strict control over optical properties such as refraction index\textsuperscript{12,13} or optical anisotropy and birefringence.\textsuperscript{14,15} In the called “sculptured thin films”,\textsuperscript{16,17} a class of nanostructured GLAD materials, their singular topography, geometry and in-depth architecture permits an effective control of their refractive index and birefringence and the development of optically active photonic structures\textsuperscript{18–23} or helicoidally bi-anisotropic media acting for example as narrow band pass optical filters,\textsuperscript{24} selective circularly polarized light transmitters\textsuperscript{25} or selective linearly polarized transmitters.\textsuperscript{26} In this regard, although polarization inactive SiO\textsubscript{2}-TiO\textsubscript{2} one dimensional photonic crystals (1DPC)\textsuperscript{27,28} and Bragg microcavities (BM)\textsuperscript{29} have been also prepared by PVD-OAD, no polarization activity is known for such two-oxide layered systems.

Herein, we demonstrate for the first time that two-oxide BMs prepared by PVD-OAD can be manufactured as polarization active systems behaving as wavelength dependent retarders. We also show that this polarization activity can be systematically and continuously controlled
adjusting the refractive index of the liquids circulating through these porous layer nanostructures. To account for this behavior, we have developed a simple optical model where each particular layer in the stack is taken as birefringent in a degree that varies with the refraction index of the liquid filling the pores. Moreover, the analysis of the optical and optofluidic properties is sustained on a systematic study by Focus Ion Beam Scanning Electron Microscopy (FIB-SEM) of the nanostructural features and association mechanisms at the nanoscale responsible for the polarization activity of these porous BMs.

**Results and Discussion**

*Morphology and fence-bundling association of nanocolumns*

To determine the nanostructural factors responsible for the polarization activity of the PV-OAD BMs, we have prepared and characterized four types of TiO$_2$-SiO$_2$ microcavities depicting different nanocolumn arrangements: i) *slanted*, prepared at constant azimuthal orientation of the substrate during deposition of successive layers; ii) *zig-zag* and iii) *chiral* obtained turning the substrate, respectively, by 180° and 90° for each layer of the stack; iv) *vertical*, deposited while continuously rotating the substrate around its azimuth. Surprisingly, the two first BMs present a strong polarization activity when interrogated with linearly polarized light, while the two latter are practically insensitive to the polarization state. Thanks to a thorough analysis by scanning electron microscopy (SEM) and a field ion beam (FIB) set-up we have been able to show that association of nanocolumns, a rather general phenomenon in OAD films known with the term *bundling*, $^{30,31}$ is the critical morphological feature responsible for the singular macroscopic behavior of the *slanted* and zig-zag BMs.
Figure 1 displays a series of cross section and normal micrographs taken for the TiO$_2$/SiO$_2$ BMs deposited on a silicon wafer. The cross section images and schemes in this figure show the characteristic nanocolumnar microstructure of the slanted (i), zig-zag (ii), vertical (iii) and chiral (iv) multilayer systems (the supporting information Scheme S1 illustrates the different nanostructural arrangements with a dynamic 360°-view scheme of the different microstructures).

**Figure 1.** Microstructure of planar BMs. i-iv) Cross section SE and BSE micrographs (left), and two scale normal SE micrographs (right) of the slanted, zig-zag, vertical and chiral BMs. The
inserted diagrams in the normal micrographs show the FTs calculated from these images. The red arrows indicate the vapour flux direction of arrival. The schemes at the right represent the ideal geometric arrangement of the nanocolumns in the successive stacked layers of the BM structures.

The normal images of the slanted and zig-zag and, to a minor extent, the chiral BMs also reveal a preferential arrangement of material along the direction perpendicular to the vapor flux, an anisotropy which is further supported by the 2-fold symmetry of their Fourier transforms (FT) as reported in the figure. Meanwhile, the highly symmetric FT shape of the vertical BMs clearly reflects an uncorrelated distribution of nanocolumn terminations at the surface of this sample.

Bundling association of nanocolumns is believed to extend along the whole thickness of single oxide OAD thin films, a feature that we have confirmed here by FIB-SEM analysis of the BMs. Figure 2 shows a series of cross section micrographs along the π (perpendicular to the film surface in a direction parallel to the bundling), Δ (perpendicular to the film surface in a direction perpendicular to the bundling), and Ω planes (close to the perpendicular to the nanocolumns direction) defined in the scheme of the slanted microstructure included in this figure. The layered distribution of brightness observed in the Back Scatter Electron (BSE) micrographs reflects the different atomic numbers of the SiO₂ and TiO₂ layers. In addition, the π-plane micrographs (i.e., panels (a) and (b)) of the slanted BM show that nanocolumns associate along the whole film thickness, i.e., association is not restricted to a single layer of the stack. We will call this nanocolumn association extending from one material layer to the next as fence-bundling, a specific microstructural feature that has not been previously reported in the literature. In the Δ-plane image (i.e., panel c), it is also apparent that large mesopores extends through the whole
material and that no disruption of nanocolumns morphology occurs when passing from one layer (e.g., TiO$_2$) to the next (e.g., SiO$_2$). Finally, the image taken along the Ω-plane (i.e., panel d)

![Image](image_url)

**Figure 2.** FIB-SEM cross section images of the BMs and scheme for a slanted structure showing the cross section planes used for the analysis and the resulting lateral surfaces in each case. a) to d) BSE images for the *slanted* BMs along the different analysis planes: a) micrograph taken for a cross section along plane π; b) the same as A in an enlarged scale; c) micrograph taken for a
cross section along plane Δ; d) micrograph taken for a cross section along plane Ω. The enlarged image at the right of micrographs a) is taken in SE mode to better visualize the lateral surface generated by the ion erosion. e) and f) BSE cross section micrographs taken for the zig-zag microstructure along planes π and Δ respectively. g) BSE cross section micrograph taken for the vertical BM along plane Δ. h) Ditto for a chiral BM.

confirms that both mesopores and nanocolumns arrange linearly along the surface bundling direction. Similarly, images taken along the π and Δ planes for the zig-zag microstructure (panels (e) and (f)) show the development of equivalent fence-bundling association extending through the whole BM. Lack of fence-bundling association in the vertical BM and only a negligible association in the individual layers in the chiral BM (i.e., panels g) and f) and Figure S2) are clear differences with respect to the two other photonic structures. The direct assessment of the topography evolution during ion etching of the slanted BMs reported as a video of SEM images, Video S3, confirms that this fence-bundling association extends through the whole BM thickness and that no boundary effects exists between stacked layers.

Polarization activity of planar BMs

The fence-bundling arrangement of nanocolumns in the slanted and zig-zag BMs has direct effects on the optical properties of these structures when examined with linearly polarized light. Figure 3 shows a series of optical transmittance spectra recorded around the resonant peak for the four studied BMs using linearly polarized light oriented with its polarization plane parallel (i.e. φ=0º) or perpendicular (i.e. φ=90º) to the surface bundling direction. Unlike the spectra of the vertical and chiral BMs which are almost unaffected by the orientation of polarized light, the
slanted and zig-zag BMs develop two different resonant peaks for \( \varphi \) equal to 0° and 90°, a double 

**Figure 3.** Transmission spectra recorded around the resonant peak for the indicated BMs with linearly polarized light oriented at 0°, 45° and 90° with respect to the perpendicular to the arrival flux direction.

peak structure for other orientations and an almost equivalent intensity of the two peaks when \( \varphi=45° \). The separation between the two resonant peaks is 18 nm (slanted) and 23 nm (zig-zag). The positions and Q factors of the resonant peaks summarized in Table 1 are practically identical for the two polarizations in the vertical BMs, but strongly differ for the titled and zig-zag structures and present slight changes for the chiral BM.
<table>
<thead>
<tr>
<th>Position (nm)</th>
<th>$\phi^\circ$</th>
<th>Slanted</th>
<th>Zig-zag</th>
<th>Vertical</th>
<th>Chiral</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>619.8</td>
<td>614.6</td>
<td>702.5</td>
<td>603.9</td>
</tr>
<tr>
<td>90</td>
<td>90</td>
<td>601.9</td>
<td>591.6</td>
<td>702.7</td>
<td>602.2</td>
</tr>
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<td>31.9</td>
<td>31.9</td>
<td>19.9</td>
<td>30.5</td>
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<td>90</td>
<td>90</td>
<td>26.5</td>
<td>28.4</td>
<td>19.7</td>
<td>26.8</td>
</tr>
</tbody>
</table>

The optical behavior depicted in Figure 3 can be simulated with an optical interference model where the SiO$_2$ or TiO$_2$ stacked layers of the BM are birefringent. For the slanted, zig-zag and chiral structures, the negative uniaxial anisotropy associated to each individual layer can be described by a fast optical axis (low refractive index) along a surface direction perpendicular to the fence-bundling ($n_p$) and a slow axis (high refractive index) along the fence-bundling direction at the surface plane ($n_b$). Figure 4 demonstrates that this simple model properly reproduces the transmittance spectra of the zig-zag BMs upon continuous $\phi$ rotation. This angular dependence supports the use of this BM to determine the orientation of the polarization plane of light. The birefringence (i.e. $\Delta n=n_p-n_b$) of the individual layers introduced in the model to properly reproduce the optical behavior of the zig-zag BM amounts to $\Delta n=-0.150$ and -0.043 for TiO$_2$ and SiO$_2$ layers, respectively. From a structural point of view, this optical anisotropy stands for a difference in void fraction of $\sim$20% between the more compact fence-bundling direction and the perpendicular to it. A similar analysis for the slanted structure, Figure S4, confirms the validity of this optical model to simulate the polarization response of the polarization active BMs.
Figure 4. Polarization angle dependence. Experimental a) and simulated b) spectra around the resonant peak of a zig-zag BM when recorded with linearly polarized light at the indicated angles formed between the polarization plane and the bundling direction (i.e., azimuthally rotating the sample by the indicated angles).

**BM thin films as wave retarders**

Zig-zag and slanted BMs behave as optical retarders or wave-plates \(^{34}\) and are characterized by resolving a linearly polarized beam into two orthogonal components separated by a wavelength dependent phase shift. Figure 5 shows a scheme of the polarization state of light (Figure 5a) and the transmittance spectra recorded through the zig-zag BM placed between two polarizers either in crossed (Figure 5b) or aligned (Figure 5d) configurations. The function of the first polarizer is to generate linearly polarized light, while the transmitted spectra in the figure are recorded as a function of the angles \(\varphi_1, \varphi_2\) formed by the bundling direction of sample and the first and second polarizer planes, respectively. Selected results of similar experiments conducted with the slanted, vertical and chiral BMs show that, as expected, only the former presents a similar retarder behavior (see Figure S5).
It is apparent in Figure 5 that for the cross-polarizer configuration and the BM bundling direction aligned along the polarization plane of light (i.e. $\varphi_1=90^\circ$ and $\varphi_2=0^\circ$) (Figure 5b), no light passes through the system. Meanwhile, progressively more intense spectra are recorded when azimuthally rotating the BM (i.e., $\varphi_1<90^\circ$ and $\varphi_2=90^\circ-\varphi_1$) up to reach a maximum intensity for $\varphi_1=\varphi_2=45^\circ$, an optical response that could be successfully reproduced by simulation (c.f. Figure 5c). When the BM is placed between two aligned polarizers at $\varphi_1=\varphi_2=0^\circ$ (see Figure 5d and simulated spectra in Figure 5e), the transmittance spectrum results identical to that recorded in the absence of the second polarizer (i.e., identical to that reported in Figure 4 for $\varphi=0^\circ$). The transmittance spectra drastically changes for other azimuthal orientations of the sample with respect to the aligned polarizers (i.e., for $\varphi_1-\varphi_2\neq0^\circ$), indicating that the BM modifies the polarization state of light. Thus, for $\varphi_1=\varphi_2>0^\circ$, there is a progressive transfer of intensity from the high to the short wavelength resonant peak. Then, these two peaks depict a similar intensity for $\varphi_1=\varphi_2=45^\circ$, experience a reversal in intensity ratio for $\varphi_1=\varphi_2>45^\circ$ and finally reach a maximum intensity/complete neglect at $\varphi_1=\varphi_2=90^\circ$.

The pure retarder behavior of the BM is confirmed verifying that the sum of the crossed and parallel polarizers spectra in Figure 5 matches the spectra in Figure 4 obtained with linear polarized light (see Figure S5). Further insights in this polarization activity, in particular into the light ellipticity as a function of wavelength and azimuthal orientation of sample, could be retrieved calculating the intensity ratio between signals measured with cross and parallel polarizers. Selected wavelength dependences of this ellipticity are reported in Figure S6, being worth noting that when equivalent transmitted intensities are measured for the cross and parallel configurations, the BM acts as a perfect quarter-wave plate.  

$^{34}$
Figure 5. Polarization angle dependence through a second polarizer. (a) Scheme of the two polarizers set up and light polarization behavior with the polarization active BM placed in-between and perpendicular to the direction of light. This particular representation corresponds to the cross polarizer configuration. b, c) Evolution of experimental (b) and simulated (c) spectra around the resonant peak of a zig-zag BM when recorded through two cross polarizers by
azimuthally rotating the BM as indicated. e) Evolution of experimental (d) and simulated (e) spectra of the resonant peak of a zig-zag BM when recorded through two parallel polarizers by azimuthally rotating the BM as indicated.

The singular wavelength retarder behavior of the optically active BMs evidenced in Figures 5 and S5 stems from interferences within the multilayer structure, whereby each layer behaves as an individual retarder inducing a retardance $\delta = \Delta n * t / \lambda$, where $t$ is the thickness of the birefringent medium (i.e., layer thickness), $\lambda$ the wavelength of light and $\Delta n$ the difference between extraordinary and the ordinary refractive indices of the layer, $\Delta n = n_p - n_b$.

Despite the quite different arrangement of nanocolumns in the zig-zag and slanted BMs, their equivalent retarder behavior (see Figure 5a and Figure S5) points to that the fence-bundling association of nanocolumns is the common microstructural feature inducing the single layer birefringence responsible for the wave retarder response of the whole device. The lack of fence-bundling association in the vertical BMs discards such a single-layer birefringence and consequently prevents any wave retarder function for the whole structure (see Figure 5a and Figure S5 b and c). For the chiral BM, besides the limited fence-bundling association observed in its microstructure (c.f., Figure 2 f)), the 90° change in the tilting orientation of nanocolumns in successive layers precludes a common reference orientation for the slow and fast optical axis in different layers and, therefore, any significant polarization activity for the whole device.

Optofluidic behavior of polarization active BMs and fence-bundling association of nanocolumns

An outstanding characteristic of PV-OAD single or stacked multilayer photonic crystals or BMs, is their high porosity and the possibility that their optical response can be altered by liquid
infiltration.\textsuperscript{28,29} In previous studies on the liquid infiltration of 1DPC and chiral BMs (i.e., polarization inactive) we found a pore fraction of \textit{ca.} 50\% that were filled with liquids in its practical totality. A similar value is expected for the polarization-active BMs studied here. Figure 6 shows a series of transmittance spectra recorded for the polarization active zig-zag BM successively infiltrated with water (n: 1.333), ethanol (n: 1.362) and toluene (n: 1.496). It is apparent that, besides a shift in the resonant peak positions, the magnitude of wavelength splitting between the resonant peaks recorded with unpolarized light decreases from 23 nm in the originally empty zig-zag device to 8, 7 and 5 nm, when infiltrated with these liquids. The well-matched simulated spectra in Figure S8 sustains that filling the pores of the structure with these liquids produces a decrease in the birefringence of the individual layers from $\Delta n_{TiO_2} = -0.150$ and $\Delta n_{SiO_2} = -0.043$ when the BM is empty (i.e., filled with air) to $\Delta n_{TiO_2} = -0.112$ and $\Delta n_{SiO_2} = -0.011$ (water); $\Delta n_{TiO_2} = -0.109$ and $\Delta n_{SiO_2} = -0.009$ (ethanol); or $\Delta n_{TiO_2} = -0.094$ and $\Delta n_{SiO_2} = 0.004$ (toluene).
Figure 6. Optofluidic modulation of polarization behavior. Experimental spectra for a zig-zag BM recorded with unpolarised and 0° and 90° linearly polarized light for the as-prepared (i.e. air filled) (a) and water (b), ethanol (c) and toluene (d) infiltrated structure.

Furthermore, it is possible to verify that the retarder function of the active BMs can be modulated by liquid infiltration. Thus, although liquid infiltration attenuates the optical activity of the BMs (see Video S9), this is accompanied by changes in shape and intensity of the resonant peaks which constitute the basis of the outstanding optofluidic effects of these devices. Figure 7 shows the spectra recorded with the cross and parallel polarizers configurations and a $\phi_1=\phi_2=45^\circ$ azimuthal orientation of the zig-zag BM filled with air (taken as a reference), water, ethanol and
toluene. As expected, increasing the refractive index of the liquid produces a shift to longer wavelengths in the position of the resonant peaks. In addition, their intensities increase/decrease for the cross and parallel configurations as the refraction index of the infiltration liquid increases. An outstanding result of this experiment is that, after calibration, the intensity ratio between the two resonant peaks is a direct measurement of the refraction index of the infiltration liquid. The potential of this behavior for analytical applications with solutions (the refraction index directly correlates with solute concentrations) is quite obvious particularly because, even if the actual two resonant peak intensities would be proportional to the excitation beam flux, their ratio would be independent of malfunctions or time instabilities of the light source.

From a microstructural point of view, the reported optofluidic response of the polarization active zig-zag and slanted BMs depends on the development of a fence-bundling association between nanocolumns. Bundling association of nanostructures in PV-OAD thin films has been known since the earliest investigations with this deposition procedure, although this microstructural feature has been scarcely used for the development of optical devices.
Figure 7.- Optofluidic modulation of polarization behavior. Transmittance spectra recorded through the zig-zag BM azimuthally oriented 45° with respect to the two polarisers either in cross (x) or parallel (II) configurations. Bottom) Spectra recorded for the BM pores filled with air. Top) Spectra recorded for the BM pores filled with liquids of different refraction indices as indicated.

**Conclusion**

The present study constitutes a first example of the interplay between nanostructure, light polarization and liquid-controlled properties of OAD layered materials that should serve to develop new applications in fields like sensing, optical device manufacturing and optofluidics.
We have demonstrated that the fence-bundling association of nanocolumns in multilayer thin films deposited by evaporation at oblique angles can be engineered to develop polarization active BMs acting as wavelength retarders. Filling the highly porous structure of these multilayers with liquids attenuates the optical activity and gives rise to quite striking optofluidic responses easily monitored by the position, shape and intensity of the resonant peak(s). In particular, we have shown that the liquid modulation of the retarder function of the BM can be used to detect the orientation of polarization plane of light or for the analysis of liquids when integrated in microfluidic devices. Taking into account the easy manufacturing procedure of these multilayer structures, its compatibility with any kind of substrates and the possibility of using masks, we anticipate a wide range of optofluidic applications for this type of planar BM systems characterized by the fence-bundling self-association of nanostructures.

**Materials and Methods**

*Fabrication of BMs and optofluidic devices.*

Uniform, mechanically stable, and highly porous BMs made of alternated layers of TiO$_2$ and SiO$_2$ have been prepared by oblique angle deposition (OAD) according to the procedure reported for single layer deposition. The investigated porous BMs were e-beam evaporated on glass plates of 1.2 × 2.5 cm$^2$ at a zenithal angle of 70° ($\alpha$). For electron microscopy characterization, samples were simultaneously deposited on a silicon wafer. Other experimental details can be found in this previous work. The BMs consisted of 2×7 individual layers with a thickness of approximately 85 nm, plus one SiO$_2$ middle layer of approximately 200 nm thickness. Four different types of BMs have been prepared depicting slanted (i), zig-zag (ii), chiral (iii) or vertical (iv) microstructures. These different morphologies were obtained by keeping fix the
substrate for the slanted BM or by azimuthally turning the substrate from one layer to the next in the zig-zag (180°) and chiral (90°) and continuously (40 rpm) in the vertical configuration.

For the optofluidic essays the BMs deposited on a glass plate were sandwiched with another glass plate as reported previously. 29 This simple microfluidic arrangement enabled handling the device as a plate substrate in front of the light beam of a spectrometer and to record spectra while replacing the circulating liquid by simple injection.

Characterization of BMs

Cross section and normal scanning electron microscopy (SEM) images were obtained in a Hitachi S4800 field emission microscope for samples deposited on a silicon wafer that were cleaved for cross-section analysis.

FIB-SEM analysis was performed using a FEI Helios Nanolab 660 tool. First, SEM images were acquired normal to the surface at 2keV primary beam energy using both Secondary Electrons (SE) for topographic and Back Scatter Electrons (BSE) for compositional information. Thereafter, an optional strip of Pt was deposited using electron beam and ion beam induced deposition in order to prevent ion damage to the surface. Subsequently 2 trenches were milled at 30keV Ga⁺ ion energy at 90° angle with one another and oriented parallel and orthogonal to the preference direction seen in the SEM images from the surface. After coarse milling, the side surfaces were polished using a 30keV, 80pA Ga⁺ ion beam. The cuts were then observed with the electron beam under 52° incidence in the same modes (SE and BSE) as mentioned before. In Figure 2 (b, c, d) the BSE images show a periodic contrast that we attribute to the different atomic numbers of the stacked TiO₂ (bright) and SiO₂ (dark) layers and other possible morphological effects.
UV–vis transmission spectra were recorded in normal incidence with a Cary 100 instrument. In order to analyze the optical activity with polarized light, a linear polarizer was placed before the sample. A second polarizer crossed or aligned with respect the first one was placed after the sample to assess the retarder behavior of the BMs and optofluidic devices upon azimuthal rotation.

**Simulation of the optical response and polarization dependence**

Simulation of the optical response of the optofluidic device was done using WVASE32 software [J. A. Woollan Co.] applied to a Bragg microcavity consisting of two Bragg reflectors separated by a “defect layer”. Each Bragg reflector has 7 layers, with a HLHLHLH structure, where H denotes high index material (i.e., TiO₂) and L low index material (i.e., SiO₂). The defect layer was a L material. The optical model relies on the assumption of a birefringent behavior of the stacked SiO₂ or TiO₂ individual layers in the slanted, zig-zag and, partially, chiral microstructures. The negative uniaxial anisotropic medium in each layer of the slanted and zig-zag BMs has been characterized by a fast optical axis (low refractive index, n_p) in the direction perpendicular to the fence-bundling association (see next section) and a slow axis (high refractive index, n_b) in the fence-bundling plane. For the chiral BM, each layer was taken as a positive uniaxial material, with an optical axis normal to the layer, along the nanocolumn direction.

The model interpreted the birefringence ∆n = n_p − n_b as resulting from the difference in porosity (meso- and nano-pores) along the-bundling direction and the perpendicular to it on the surface plane. The effect of porosity on the optical response was simulated according to Maxwell–Garnett effective medium approximation to describe a composite material formed by a
compact media (i.e., either compact TiO$_2$ or SiO$_2$) mixed with voids filled with either air or liquids with different refraction indices. For these calculations, it is assumed that both materials H and L have the same percentage of pore volume and the refractive index of the individual layers was described by a typical Cauchy wavelength dispersion.

**Supporting Information**

Dynamic scheme showing the arrangements of nanocolumnar elements, SEM micrograph of a *vertical* BM, video showing the evolution of nanostructures of a *slanted* BM by FIB-SEM during ion milling, experimental and simulated spectra around the resonant peak of a *slanted* BM recorded with linearly polarized light, experimental and simulated spectra for *slanted*, *vertical* and *chiral* BMs recorded with two cross polarizers, representation of the sum of spectra recorded with the parallel and crossed configurations and different azimuthal orientations of the *zig-zag* BM, degree of ellipticity of light for the *zig-zag* BM with parallel and cross polarizer configurations, simulated spectra recorded with unpolarized and linearly polarized light for a *zig-zag* BM as-prepared and fill with different liquids, video illustrating the attenuation of optical activity by infiltrating the BMs with a liquid. This material is available free of charge via the Internet at [http://pubs.acs.org](http://pubs.acs.org).

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References


Table of Content

TiO₂-SiO₂ nanostructured multilayers prepared by oblique angle deposition in a slanted and zig-zag configuration present a fence-bundling association of nanocolumns that confer them an outstanding optical retarder behavior when illuminated with linearly polarized light. The modulation of this response by infiltrating their porous structure with liquids of different refraction indices can be used for sensing and monitoring applications.
Supporting Information

Optofluidic Modulation of Self-Associated Nanostructural Units Forming Planar Bragg Microcavities

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**Scheme S1 (dynamic).**- Nanostructural arrangement of nanocolumns of the different architectures investigated in this work as illustrated with a 360°-view dynamic scheme.
**Figure S2.** Enlarge SEM micrograph of a *vertical* BM to show the lack of *fence-bundling* association. A sketch is including clarifying the FIB-SEM analysis.

**Video S3.** Video showing the evolution of the images taken from the surface of a *slanted* BM by FIB-SEM during the ion milling.

**Figure S4.** Experimental a) and simulated b) spectra around the resonant peak of a *slanted* BM when recorded with linearly polarized light at the indicated angles formed between the polarization plane and the *bundling* direction (i.e., azimuthally rotating the sample by the indicated angles).
Figure S5.- Experimental (left) and simulated (right) evolution of spectra and spectra for slanted (a), vertical (b) and chiral (c) BMs when recorded with two cross polarizers and the indicated azimuthal orientation of the sample according to the scheme of figure 5 in the main text.
Figure S6. Representation of the sum of the transmission spectra recorded with the parallel (II) and crossed (x) configurations and the indicated azimuthal orientations of the zig-zag BM.
Figure S7.- Degree of ellipticity of light determined as the indicated intensity ratios between the transmission spectra recorded for the zig-zag BM with parallel (II) and cross (x) polarizer configurations and 0°, 15°, 30° and 45° of azimuthal orientation. At the wavelengths at which the two lines interfere for $\phi_1 = 30^\circ$ and $45^\circ$ the light is circularly polarized (gray circles in the figure).
**Figure S8.** Simulated spectra for a zig-zag BM recorded with unpolarised and 0° and 90° linearly polarized light for the as-prepared (i.e. air filled) (a) and water (b), ethanol (c) and toluene (d) infiltrated structure.

**Figure S9.** Video illustrating the attenuation of optical activity by infiltrating the BMs with a liquid.