

Enhanced solar light absorption in inverse opals via higher-order photonic modes and angular tuning

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Higher-order photonic modes have the potential to achieve superior absorption enhancement in inverse opal photocatalysts, beyond conventional blue or red edge slow light modes. This study reports a finite element method, numerical investigation of TiO_2 inverse opals with an ultrathin material skeleton and varying diameters of interconnected pores, at different angle of incidence. Both diameter and angle variations are used to tune slow light modes to the TiO_2 electronic band edge in the near-UV. In the case of air-filled pores, relevant to gas-phase photocatalysis, for a pore diameter of 240 nm, at normal incidence, the absorption enhancement factor reached a maximum value of $\alpha = 2.07$ thanks to tuning of the fifth allowed mode of the band structure. By contrast, for pore diameters corresponding to red (blue) edge tuning, an enhancement factor of only $\alpha = 1.18$ ($\alpha = 1.97$) could be achieved at normal incidence. Tighter confinement of the fifth mode into the skeleton is responsible for this enhanced performance. At 45° oblique incidence, tuning of that mode leads to even further enhancement ($\alpha = 2.42$) due to better coupling and light trapping caused by the nonzero in-plane component of the wave vector. In the case of water-filled pores, relevant to liquid-phase photocatalysis, for a pore diameter of 280 nm at normal incidence, the enhancement factor ($\alpha = 2.39$) greatly outperforms blue edge tuning ($\alpha = 1.62$) thanks to the tuning of the allowed modes from ninth to 15th of the band structure. We believe our study will offer additional insights into exploiting slow light effects in inverse opals for photocatalysis, and more generally, solar energy conversion applications.

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I. INTRODUCTION

In the early 1970s, Fujishima and Honda highlighted the environmental potential of photocatalysis for the conversion of photon energy into chemical energy [1]. Since then, it has been applied to diverse applications including hydrogen production [2], sewage water treatment [3], and air purification [4]. Nevertheless, the fraction of solar energy absorbed by semiconductors often hinders the practical use of photocatalysis. Among photoactive materials, the anatase titanium dioxide (TiO_2) indirect band-gap semiconductor has been extensively studied, thanks to its low cost, high efficiency, nontoxicity, and structural stability [5]. However, its activity is confined to the near-UV region due to its relatively wide electronic band gap (~ 3.2 eV). Recently, structural effects in photonic crystals have emerged as a promising strategy to enhance absorption, in synergy with other strategies aiming to extend absorption into the visible region through doping [6], heterostructures [7], disorder incorporation [8], and plasmonic resonances [9,10].

Among structural effects, the so-called slow photon effect has attracted growing interest. The vanishing group velocity that occurs at the edges of the fundamental photonic band gap (PBG), where photonic bands are flat, is exploited to enhance light-matter interaction as a result of photon harvesting [11]. The slow photon effect can be easily implemented in inverse opal (IO) photonic crystals, which combine further advantages for photocatalysis such as a high specific surface area and the antireflective effect [12,13]. To date, the optimization of the slow photon effect in IO structures has been confined to tuning the lower (red) and upper (blue) edges of the fundamental PBG. By aligning those nearly flat band edges with the electronic band gap of TiO_2 (around 385 nm) absorption can be resonantly enhanced. Tuning is typically performed by adjusting either the IO pore diameter or light incidence angle [14–16]. More recently, accessing to higher-order photonic bands (i.e., above the blue edge frequency) through the increase of pore diameter has shown potential to further enhance absorption [17,18]. Nevertheless, this strategy requires deeper investigation to fully exploit its potential for future solar energy harvesting applications.

Numerical methods are convenient to optimize inverse opal structures, providing insights that are not always accessible experimentally while overcoming the cost and time limitations associated with experimental essays [19]. The finite-difference time-domain (FDTD) method has been recently used to study the PBG properties of IO [20]. The rigorous coupled wave analysis (RCWA) method has been complementary applied to investigate the slow light effect

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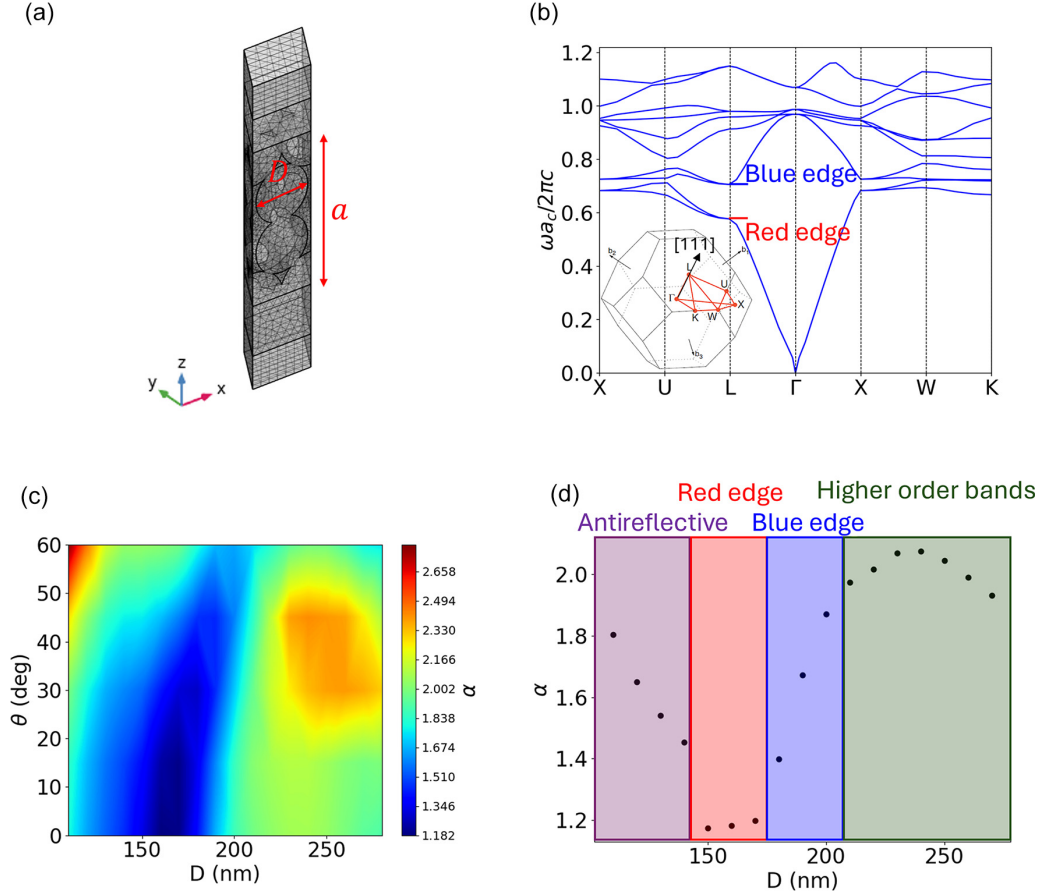


FIG. 1. (a) FEM model and mesh of one UC for an IO structure with pores of diameter $D = 200$ nm. From top to bottom, the model includes a perfectly matched layer (PML), the incident medium, the IO structure itself, the emergence medium, and another PML. (b) Photonic band diagram of an air-filled IO ($n_{\text{air}} = 1$) with a filling factor $f = 0.12$ and a refractive index of the dielectric skeleton ($n_{\text{TiO}_2} = 3.068$). Inset: Brillouin zone. (c) Map of enhancement factor (α) as a function of pore diameter D and incidence polar angle θ . (d) Variation of α with D at $\theta = 0^\circ$, highlighting the main effects responsible for absorption enhancement.

[16,21]. In this article, we use the finite-element method (FEM) to model three-dimensional propagation of light in IO slabs of different pore diameters at varying incidence angle, with the aim to optimize solar light absorption in the active near-UV TiO_2 region. The results highlight distinct absorption enhancement mechanisms. While absorption enhancement can be obtained at normal incidence by tuning the red or blue edges, as frequently reported [15,16,21,22], neither configuration leads to optimal results. In fact, further enhancement is achieved by tuning higher-order photonic modes. Furthermore, FEM implementation in *comsol MULTIPHYSICS®* allows us to provide detailed insights into light propagation and localization within the IO structure, which helps the interpretation of the underlying enhancing mechanisms. Our analysis of angular dependence reveals structural mechanisms driving further enhancement at oblique incidence.

Although the present study does not include experimental validation, which so far is lacking in the literature, our aim is to provide a robust numerical baseline for future experimental investigations. Interestingly, Habli *et al.* [23] modeled TiO_2 - BiVO_4 inverse opals based on experimental structures fabricated by Mandanu *et al.* [24]. The analysis already revealed higher-order mode trends consistent with the behaviors

identified here. These findings support the physical relevance of our predictions and position the present study as a quantitative framework to guide forthcoming experimental efforts.

II. NUMERICAL SIMULATIONS

A. Inverse opal model

IO structures consist of spherical voids (pores) arranged periodically in a solid skeleton, which serves as the active photocatalytic material. The numerical model considered in this study is a face-centered cubic (FCC) photonic crystal IO slab. The volume filling fraction (f) of the active material is set to 0.12, consistent with reported experimental values [14], resulting in interpenetrating spheres, whereas $f = 0.26$ would correspond to a close-packed FCC lattice (touching spheres). This configuration of interconnected pores is particularly relevant for photocatalytic reactions as it facilitates the diffusion of the reactants within the structure. The geometrical parameters of the IO slab are the following: pore diameter (D), FCC lattice constant (a_c), and number (N) of unit cells (UC) [Fig. 1(a)]. In this work, we consider a three-UC IO oriented such that the [111] crystallographic direction aligns with the z axis, perpendicular to the substrate, corresponding

to the typical orientation achieved during experimental formation of the opal template [22]. The lattice constant (a_c) and height of the unit cell (a) along the z direction are given by $a_c = D[3(1 - f)/2\pi]^{-1/3}$ and $a = a_c\sqrt{3}$, respectively.

We consider heterogeneous photocatalysis in both gas and liquid phases. Therefore, air ($n_{\text{air}} = 1$) and water ($n_{\text{water}} = 1.33$) are used as pore-filling media, respectively. The incident medium is always air ($n_{\text{air}} = 1$), while the substrate is assumed to be glass ($n_{\text{sub}} = 1.56$) [25]. The optical properties of anatase TiO_2 (i.e., the wavelength-dependent complex refractive index data) are taken from the literature [26]. Based on the wavelength dependence of the extinction coefficient k (i.e., the imaginary part of the refractive index), the TiO_2 absorption edge is estimated to be around 385 nm.

B. Computational methods

Light propagation in the IO structure was simulated using the FEM [27] implemented in comsol MULTIPHYSICS® software [28]. These simulations provide reflectance and absorptance spectra, as well as maps of key quantities such as electric-field intensity (V/m) and electromagnetic power dissipation density (W/m^3), a local indicator of absorption. In addition, the spatial distribution of Poynting vectors (W/m^2) was obtained, providing complementary insight into the propagation of electromagnetic energy within the IO structure. The group velocity v_g (in the following, expressed as a fraction of the speed of light in vacuum) was determined from the photonic band structure by evaluating the local slope of the bands ($v_g = d\omega/dk$) [29]. The concentration factor $\gamma = \int_{\text{TiO}_2} \epsilon(\mathbf{r})|E(\mathbf{r})|^2 d^3\mathbf{r} / \int \epsilon(\mathbf{r})|E(\mathbf{r})|^2 d^3\mathbf{r}$ enabled to quantify confinement of electric field in a dielectric skeleton of IO slabs [30]. In FEM, discretization of the structure into smaller elements resulted in a three-dimensional mesh [Fig. 1(a)]. The meshing of IO structures is particularly demanding due to their sphere-based architecture. In the present case, interconnected pores generate curved surfaces and narrow regions, which are difficult to discretize. To address this issue, key meshing parameters are carefully adjusted to maintain both numerical accuracy and computational feasibility. In comsol settings (parameter names in *italics*), the *maximum element size* within each domain was set to a fraction (1/6) of the wavelength in the medium. Beyond this choice, several parameters are tuned heuristically. The *element growth rate* is fixed at 8 in the dielectric skeleton and at 2 in the pore regions. These values account for the necessity to expand mesh elements rapidly in regions where wide and narrow parts coexist, with a higher growth rate for the skeleton to take into consideration sharper geometric transitions occurring within this domain. The *curvature factor* was set to 0.7 in both the skeleton and pores, a choice that allows slightly larger elements to be generated along curved surfaces to preserve mesh regularity at spherical interfaces, where geometrical transitions are otherwise abrupt. Finally, the *resolution of narrow regions* is selectively refined within the dielectric skeleton, where subwavelength regions are present. A value of 0.75 is retained, enabling the generation of finer elements in these critical areas. To verify numerical reliability, a mesh sensitivity analysis is performed on a representative geometry. Further mesh refinement leads to absorptance variations

$\leq 0.01\%$, confirming the robustness of the results. Our FEM model [Fig. 1(a)] was already benchmarked against rigorous coupled-wave analysis (RCWA), confirming its accuracy for simulating light propagation [31]. All simulations are performed for polarization aligned along the y axis (azimuthal angle ϕ equal to 0).

Another FEM tool developed by Mekawy [32] was employed to compute eigenmodes and their associated frequencies, enabling the construction of the photonic band diagram as well as maps of key physical quantities within the unit cell at the corresponding eigenfrequencies.

C. Enhancement factor

To evaluate the benefit of IO structure for light absorption enhancement, it is necessary to define both an appropriate figure of merit and a reference. The reference consists of a homogeneous TiO_2 slab of thickness $d_{\text{ref}} = Naf$ which ensures that comparisons are performed at constant active material volume. The incident medium is air ($n_{\text{air}} = 1$) for gas-phase photocatalysis and water ($n_{\text{water}} = 1.33$) for liquid-phase photocatalysis. The absorbed photon flux is calculated by $\phi = \frac{1}{hc} \int \lambda \eta A(\lambda) S(\lambda) d\lambda$ (h : Planck's constant, c : speed of light in vacuum, λ : incident wavelength, η : internal quantum efficiency, assumed equal to unity in this study [33], $A(\lambda)$: spectral absorptance, and $S(\lambda)$: reference AM1.5 solar spectrum [34]). It is important to note that the expression of ϕ accounts for both spectral dependencies: the solar spectrum and material absorption. The integral is evaluated over the wavelength range from approximately 280 nm (lower limit of the solar spectrum) to 385 nm (TiO_2 absorption edge). Finally, the absorption enhancement factor (α) is defined as the ratio between the absorbed photon flux of the IO structure and that of the homogeneous slab. A value $\alpha > 1$ thus indicates that the IO configuration provides a higher absorption efficiency than the reference.

III. RESULTS AND DISCUSSION

A. Air-filled pores

To determine the parameters that optimize light absorption in air-filled TiO_2 IO structures, a parametric study was carried out. This study focused on two key parameters: pore diameter (D) and angle of incidence (θ). Since the filling factor f is constant, changing D modifies the lattice constant a_c . The normalized frequencies $\omega a_c / 2\pi c$, in particular those associated with eigenmodes, depend directly on a_c . Consequently, increasing D increases a_c and shifts the eigenmodes toward lower frequencies (i.e., longer wavelengths). Since the azimuthal angle was set to $\phi = 0$, increasing θ (polar angle) from normal incidence (ΓL direction) corresponds to a wave-vector trajectory evolving towards the W point in the reciprocal space [Fig. 1(a)] and 1(b) [35]. At increasing oblique incidence, the PBG shifts to higher frequencies (i.e., shorter wavelengths) and its width decreases.

The parametric study is performed for D values ranging from 110 nm to 280 nm in 10-nm increments, and θ values from 0° (normal incidence) to 60° (grazing incidence) in 15° steps. The absorption enhancement factor α is computed for each (D, θ) configuration. The absorptance of the reference

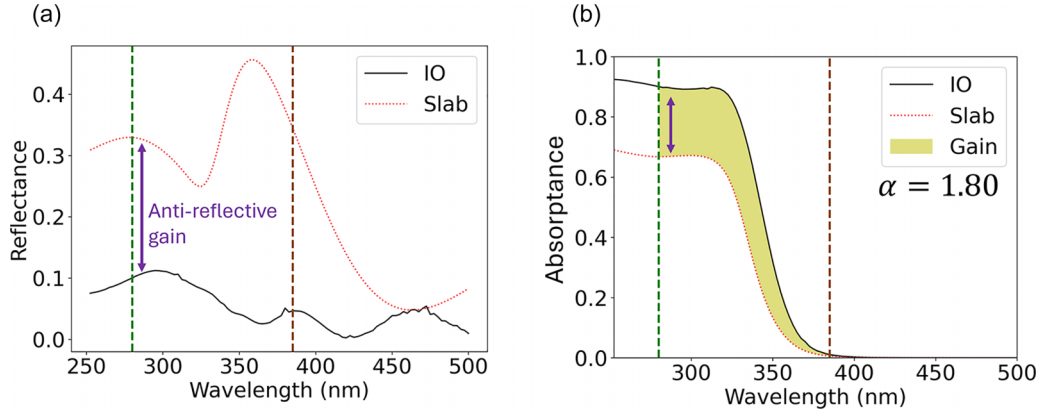


FIG. 2. (a) Reflectance and (b) absorbance spectra of an IO with air-filled pores of $D = 110$ nm and reference slab, at normal incidence. Vertical green and brown dashed lines indicate the lower limit of the solar spectrum and the TiO_2 absorption edge, respectively.

slab is evaluated at the same incidence angles. Figure 1(b) and 1(c) shows the map of α in (D, θ) parameter space. Figure 1(c) and 1(d) shows the evolution of α as a function of D at normal incidence ($\theta = 0^\circ$) where different physical mechanisms responsible for the absorption of enhancement are identified independently. However, in most configurations, multiple mechanisms coexist and this identification primarily serves to guide the following analysis. The first outcome of this parametric study is that structuring the active material into an IO leads to the enhancement of light absorption (i.e., $\alpha > 1$) across all investigated configurations. The following sections provide a detailed analysis of the underlying physical mechanisms responsible for this enhancement.

1. Antireflective effect

The antireflective effect in IOs arises from their macroporous surface which facilitates light penetration compared to a homogeneous slab [12]. The absorption enhancement observed for pore diameters smaller than 140 nm Fig. 1(d), appearing before slow light effects could take place, is due to the antireflective mechanism. This is confirmed by the significant reduction of reflectance observed in the IO compared to the reference slab [Fig. 2(a)] as well as a lower transmittance up to roughly $\lambda = 340$ nm. Correspondingly, a gain in absorbance is observed, yielding an enhancement factor of $\alpha = 1.80$ [Fig. 2(b)]. Another contribution to strengthened photon-matter interactions comes from multiple scattering within the macroporous IO geometry, which effectively increases the optical path ($d_{\text{IO}} = 763$ nm $\gg d_{\text{ref}} = 92$ nm). Both the antireflective effect and multiple scattering are intrinsic to the macroporous structure of IOs and are present across all pore diameters investigated. However, their contribution to absorption enhancement is particularly pronounced for smaller pores where they are not in competition with other effects discussed below.

2. Slow light effect at edges of fundamental photonic band gap

Increasing the pore diameter downshifts the fundamental PBG, with both its lower (red) and upper (blue) edges moving toward longer wavelengths. For instance, typically, an IO structure with $D = 160$ nm corresponds to red edge tuning [Fig. 1(d)] and yields to an enhancement factor of $\alpha = 1.18$

[Fig. 3(a)]. At $\lambda_r = 367.5$ nm, a resonant increase of absorbance by a factor of 2.44 is observed, due to the slow photon effect ($v_g = -0.012c$) at the red edge [see also corresponding reflectance spectrum in Appendix, Fig. 11(a)]. Increasing pore diameter, for example up to $D = 210$ nm, leads to blue edge tuning [Fig. 1(d)], yielding to an enhancement factor of $\alpha = 1.97$ [Fig. 3(b)]. At $\lambda_b = 372.5$ nm, absorbance is resonantly enhanced by a factor of 5.96 [see also in Appendix, Fig. 11(b)] due to the slow photon effect ($v_g = 0.009c$).

The stronger absorption enhancement by blue edge tuning in comparison with red edge tuning corroborates previous findings [21]. The explanation is as follows. According to the electromagnetic energy variational principle, the red edge eigenmode tends to be confined within the high refractive index regions (TiO_2) whereas the blue edge eigenmode tends to be localized in the low refractive index regions (pores) [30]. Since absorption originates solely from TiO_2 , one might expect the red edge tuning to be more favorable for absorption enhancement. However, the IO geometry reverses this intuitive prediction, making the blue edge more efficient [21]. First of all, in the red edge tuning the Bragg peak reflection strongly reduce wave penetration. Second, the IO ultrathin (subwavelength size) skeleton results in less tighter confinement in high refractive index regions for red edge eigenmodes ($\gamma_{\text{red}} = 0.52$ versus $\gamma_{\text{blue}} = 0.41$). This effect is reinforced here by a filling fraction significantly lower ($f = 0.12$) than the close packed value. Cross-section maps of the electric-field intensity and of the local absorption in the xy plane support this interpretation [Figs. 3(c) and 3(d)]. It is noteworthy that, at $\lambda = 335$ nm, the coupling of the fifth photonic mode [Fig. 1(b)] leads to near-perfect absorption ($A = 0.987$). Extremely slow light ($v_g = 0.003c$) combined with tighter confinement of the electromagnetic field ($\gamma = 0.68$) occurring at wavelengths for which absorption coefficient remains high ($k = 0.21$) explain this remarkable result.

3. Slow light effect from higher-order photonic bands

As the pore diameter is further increased, higher-order photonic modes (i.e., above the blue edge) become accessible to the studied wavelength range. For instance, at normal incidence, a pore diameter of 240 nm allows tuning the fifth mode [Fig. 1(d)] to $\lambda_5 = 351$ nm at the L point of the band structure

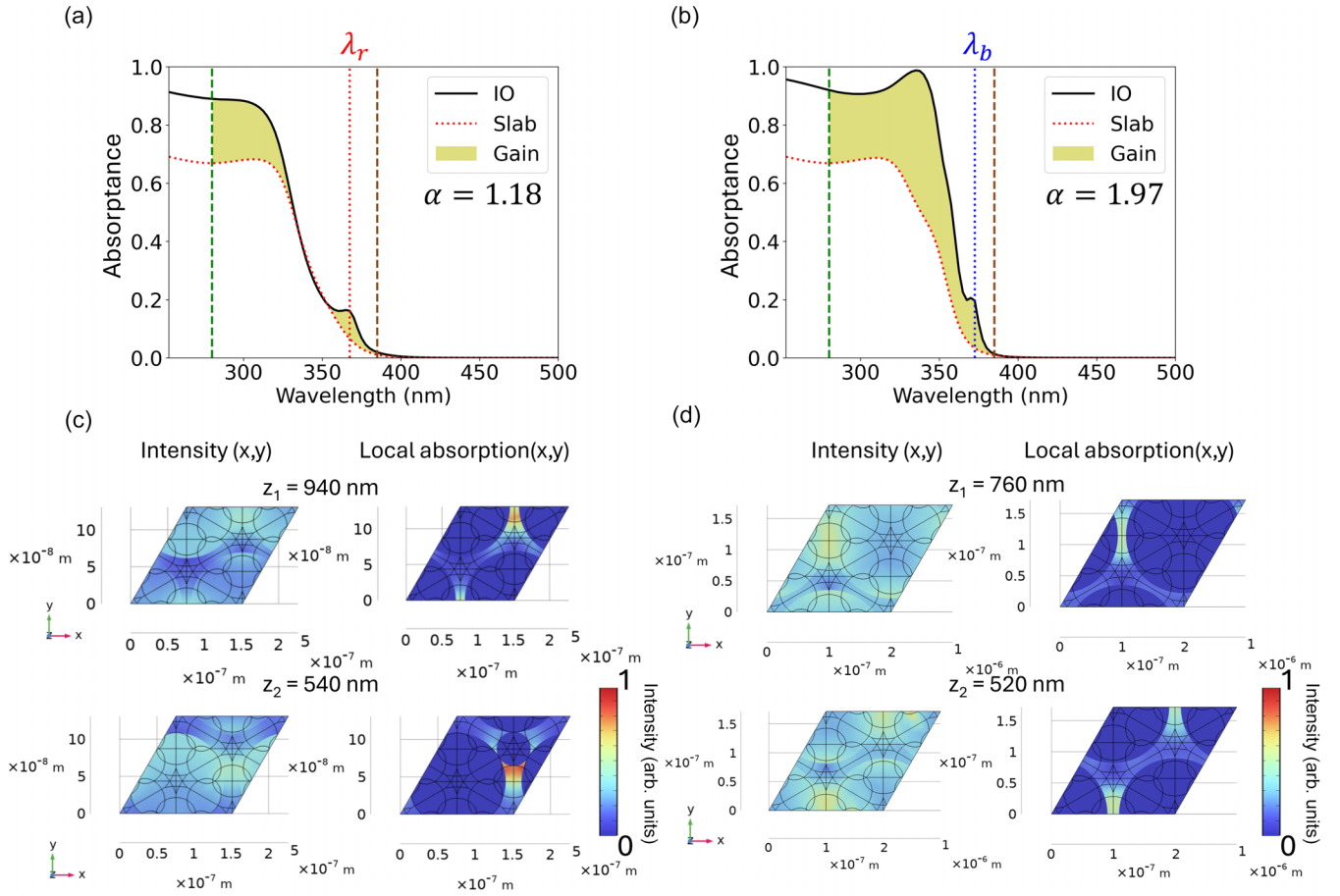


FIG. 3. (a), (b) Absorbance spectra of IOs with air-filled pores of (a) $D = 160$ nm (red edge tuning) and (b) $D = 210$ nm (blue edge tuning), at normal incidence. Vertical red (blue) dotted line marks the wavelength $\lambda_r = 367.5$ nm ($\lambda_b = 372.5$ nm) corresponding to the red (blue) slow light edge. (c), (d) From left to right: xy -plane cross sections of the electric field intensity and local electromagnetic power loss. (c) Results at $\lambda_r = 367.5$ nm for an IO structure with $D = 160$ nm air pores, illustrating red edge tuning. (d) Results at $\lambda_b = 372.5$ nm for an IO structure with $D = 210$ nm air pores, illustrating blue edge tuning.

[Fig. 4(a)]. This configuration yields a maximum absorption enhancement factor of $\alpha = 2.07$, which is slightly higher to the blue edge tuning value ($\alpha = 1.97$). The peak in the absorbance spectrum observed around $\lambda = 350$ nm [Fig. 4(b)] can be associated with the nearly flat fifth band ($v_g = 0.003c$). In the same narrow wavelength range, the modes of the third and fourth bands are also accessible. A high photonic density of states around the fifth band was found in the band structure of a close packed opal at nearly normal incidence ($\sim 5^\circ$) [35], a finding which is confirmed by our observations. The presence of numerous allowed higher-order modes enables more efficient light coupling to the crystal, explaining the reduced reflectance at $\lambda = 350$ nm [see Fig. 11(c)].

Another mechanism contributes significantly to the absorption enhancement. The confinement of higher-order modes within dielectric skeleton appears to be stronger compared to the red and blue edge modes [Fig. 4(c)]. A contribution to this enhancement arises from the relative size of the mode wavelength in the skeleton material. From normalized frequencies at L point, the fifth mode wavelength is found to be of the order of the lattice constant ($\lambda \sim a_c$) whereas the one of the red and blue edge modes is two times longer. In other words, the dielectric skeleton is relatively less narrow

for the fifth mode which tends to reduce the overlapping of the modes with the pores. As a result, a more efficient confinement of electromagnetic energy within TiO_2 ($\gamma = 0.71$) is achieved [Fig. 4(d)]. The potential of higher-order bands was previously highlighted by Zhang and John [17]. In their study, TiO_2 was assumed to have an absorption tail extending into the visible range (e.g., by doping) to highlight the benefits of higher-order modes for absorption enhancement. The present work confirms the relevance of higher-order modes in the case of undoped TiO_2 IOs.

Maximum absorption enhancement is obtained around $D = 240$ nm [Fig. 1(c)], beyond which the benefits of higher-order bands remain while being reduced. For instance, at $D = 270$ nm, the increased (reduced) absorbance (reflectance) associated with higher-order band modes is still observed but shifted to longer wavelengths (Fig. 5). According to the band structure [Fig. 5(a)], this value of the pore diameter allows propagation of modes of the third to eighth bands ($\lambda_{3-8} \sim 360$ nm). Most of these bands are nearly flat, indicating reduced group velocity, and hence, slow light ($|v_g| < 0.01c$). Notably, the existence of a partial photonic band gap along the ΓL direction explains the reflectance peak near $\lambda = 350$ nm and the associated decrease in absorption

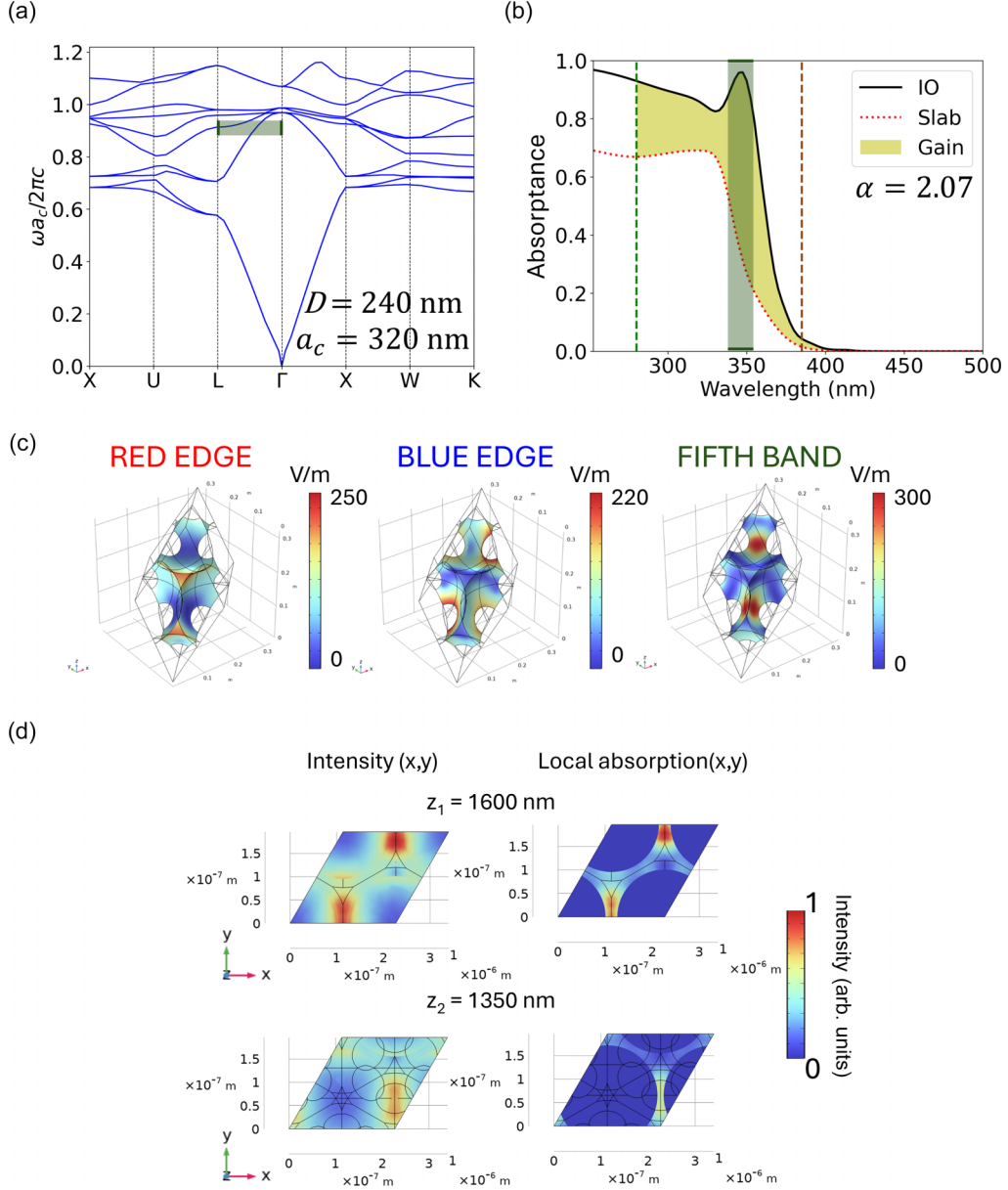


FIG. 4. (a) Photonic band diagram of an air-filled IO ($n_{\text{air}} = 1$) with a filling factor $f = 0.12$ and a refractive index of the dielectric skeleton $n_{\text{TiO}_2} = 3.068$. Band numbers correspond to the order of appearance from the lowest to highest eigenfrequencies. Specifically, at the L point, bands 1 and 2 correspond to the red edge, while bands 3 and 4 correspond to the blue edge. (b) Absorbance spectrum of an IO with air-filled pores of $D = 240$ nm, at normal incidence. Vertical green shaded band highlights the absorbance peak (reflectance dip) arising from the fifth photonic mode. (c) Electric-field intensity distribution of eigenmodes at the high symmetry point L within the UC, corresponding to, from left to right, bands 2 (red edge), 3 (blue edge), and 5. (d) From left to right: xy -plane cross sections of the electric field intensity and local electromagnetic power loss. Results obtained at $\lambda = 350$ nm.

enhancement [Fig. 5(b)]. However, this detrimental band-gap effect does not preclude the overall benefit of slow light associated with higher-order modes.

4. Angular dependence

The incidence polar angle plays a decisive role in the absorption enhancement mechanism since it governs reflections, scatterings, and the set of propagative modes allowed in the photonic crystal. Increasing the incidence angle (θ) leads to higher enhancement factors across all the configurations.

Two local maxima are identified [Fig. 1(b)]: $\alpha = 2.81$ for $D = 110$ nm at $\theta = 60^\circ$ and $\alpha = 2.42$ for $D = 240$ nm at $\theta = 45^\circ$. While such a behavior in inverse opals is usually attributed solely to the slow photon effects associated with angular shifts of the Bragg peak [24,36,37], our results indicate more complex mechanisms.

On one hand, the antireflective effect appears to account for the overall leverage of α with increasing θ , especially for small pore diameters, explaining the first local maximum [Fig. 1(b)], at ($D = 110$ nm, $\theta = 60^\circ$). Indeed, for

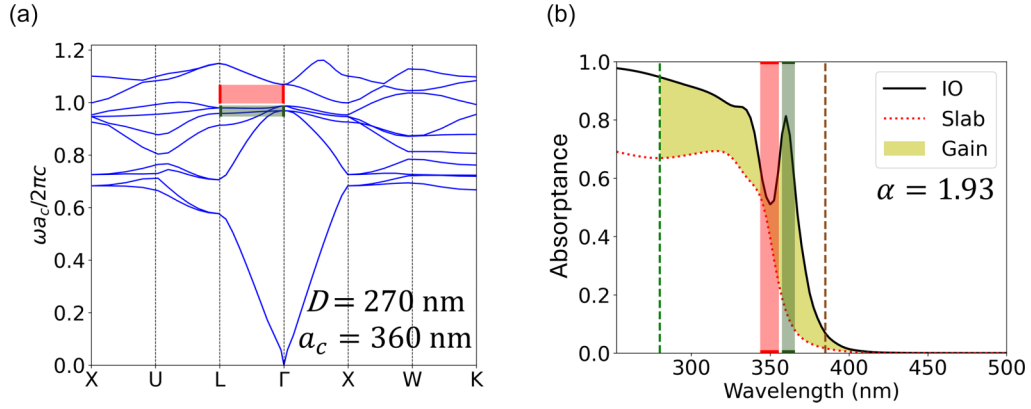


FIG. 5. (a) Photonic band diagram of an air-filled IO ($n_{\text{air}} = 1$) with a filling factor $f = 0.12$ and a refractive index of the dielectric skeleton $n_{\text{TiO}_2} = 3.068$. (b) Absorbance spectrum of an IO with air-filled pores of $D = 270$ nm, at normal incidence. Vertical green shaded band highlights the absorbance peak (reflectance dip) arising from higher order photonic modes while the red shaded region indicates the absorbance dip (reflectance peak) associated with the partial PBG between eighth and ninth bands.

this diameter, the reference slab reflectance increases more rapidly with θ than does the IO reflectance [Fig. 6(a)]. This effect results in a higher enhancement factor [Fig. 6(b)] $\alpha = 2.81$ (1.80) at $\theta = 60^\circ$ (0°).

On the other hand, coupling of slow light modes contributes to the angular dependence of α and, together with the antireflective effect, explains the second local maximum [Fig. 1(c)], at ($D = 240$ nm, $\theta = 45^\circ$). Increasing the incidence angle up to $\theta = 45^\circ$ results in the downshift of the Bragg peak wavelength until the blue edge tuning is achieved. In this situation, three wavelengths are of interest in the reflectance [Fig. 7(a)] and absorbance [Fig. 7(b)] spectra: $\lambda_\alpha = 352.5$ nm, $\lambda_\beta = 362.5$ nm, and $\lambda_b = 375$ nm. The wavelength of λ_b pertains to the blue edge tuning. Unlike at normal incidence, the field intensity is no longer concentrated at the center of the IO slab but instead in two separate sections along z axis where light trapping takes place as evidenced by the Poynting vector distribution [Fig. 8(a)]. This effect is further investigated in the Appendix through analysis of diffraction orders. The previously discussed less-tight confinement is further developed in this configuration thanks to light trapping ($\gamma_{\text{blue}, 45^\circ} = 0.58$ versus $\gamma_{\text{blue}, 0^\circ} = 0.41$).

The wavelength of λ_α can be associated with the fifth photonic band at the L point, whereas the wavelength of λ_β can be associated with the sixth and seventh photonic bands at the W point [Fig. 4(a)]. Indeed, at oblique incidence, the wave vector $\mathbf{k}$ has components $k_z = k \cos \theta$ and $k_x = k \sin \theta$ along the directions, respectively, perpendicular and parallel to the slab surface ($k_y = 0$ due to the choice of polarization). Hence the k_z component couples to the allowed modes along the ΓL direction, whereas the k_x component couples to the allowed modes along ΓW . In the following, we discuss the coupling of perpendicular (normal) and parallel (transverse) components of the modes at λ_α and λ_β , respectively. The reflectance peak around $\lambda_\beta = 362.5$ nm [Fig. 7(a)] arises from coupling with the sixth and seventh bands at the W point ($\lambda_6 = \lambda_7 = 367$ nm). The coupling with the allowed modes having $k_x = k \sin 45^\circ$ leads to the excitation of quasiguided modes [38] in the xy plane for which the electromagnetic energy is localized near the surface. Indeed, the spatial distribution of the Poynting vector confirms a propagation mostly along the lateral directions and reveals multiple reflections and scattering events underneath the surface [Fig. 8(c)]. Despite the high reflectance at λ_β , this in-plane coupling mechanism

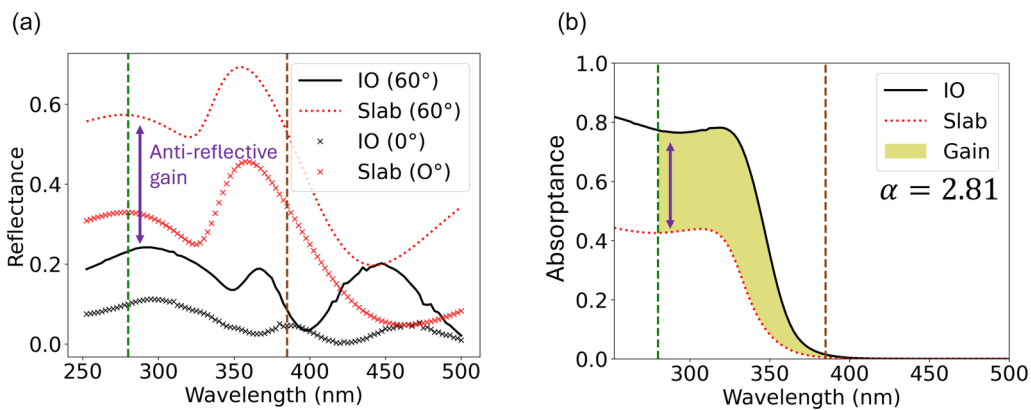


FIG. 6. (a) Comparison between reflectance spectra of an IO with air-filled pores of $D = 110$ nm (full and dotted lines) at grazing incidence ($\theta = 60^\circ$) and (crosses) at normal incidence ($\theta = 0^\circ$), for y -polarized light. Absorbance spectrum of an IO with air-filled pores of $D = 110$ nm at grazing incidence ($\theta = 60^\circ$), for y -polarized light.

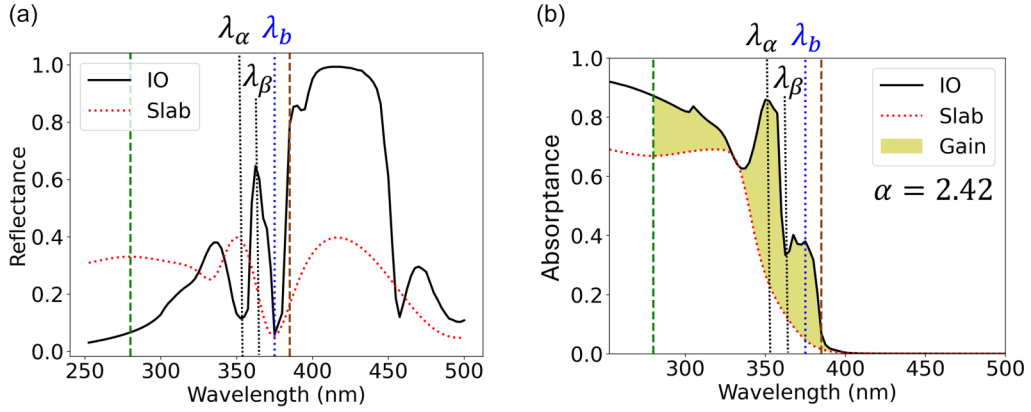


FIG. 7. (a) Reflectance and (b) absorptance spectra of IO with air-filled pores of $D = 240$ nm, at oblique incidence ($\theta = 45^\circ$) and for y -polarized light. Vertical blue dotted line marks the wavelength $\lambda_b = 375$ nm corresponding to the blue slow light edge.

strongly favors higher absorptance than expected [Fig. 7(c)]. A further confirmation is given by a reduced transmittance of the IO slab ($T_{IO} = 0.0147 \ll T_{ref} = 0.638$). The absorptance

peak around $\lambda_\alpha = 352.5$ nm [Fig. 7(b)] arises from coupling with the fifth band at the L point ($\lambda_5 = 351$ nm). Contrary to the previous case, coupling with an allowed mode having

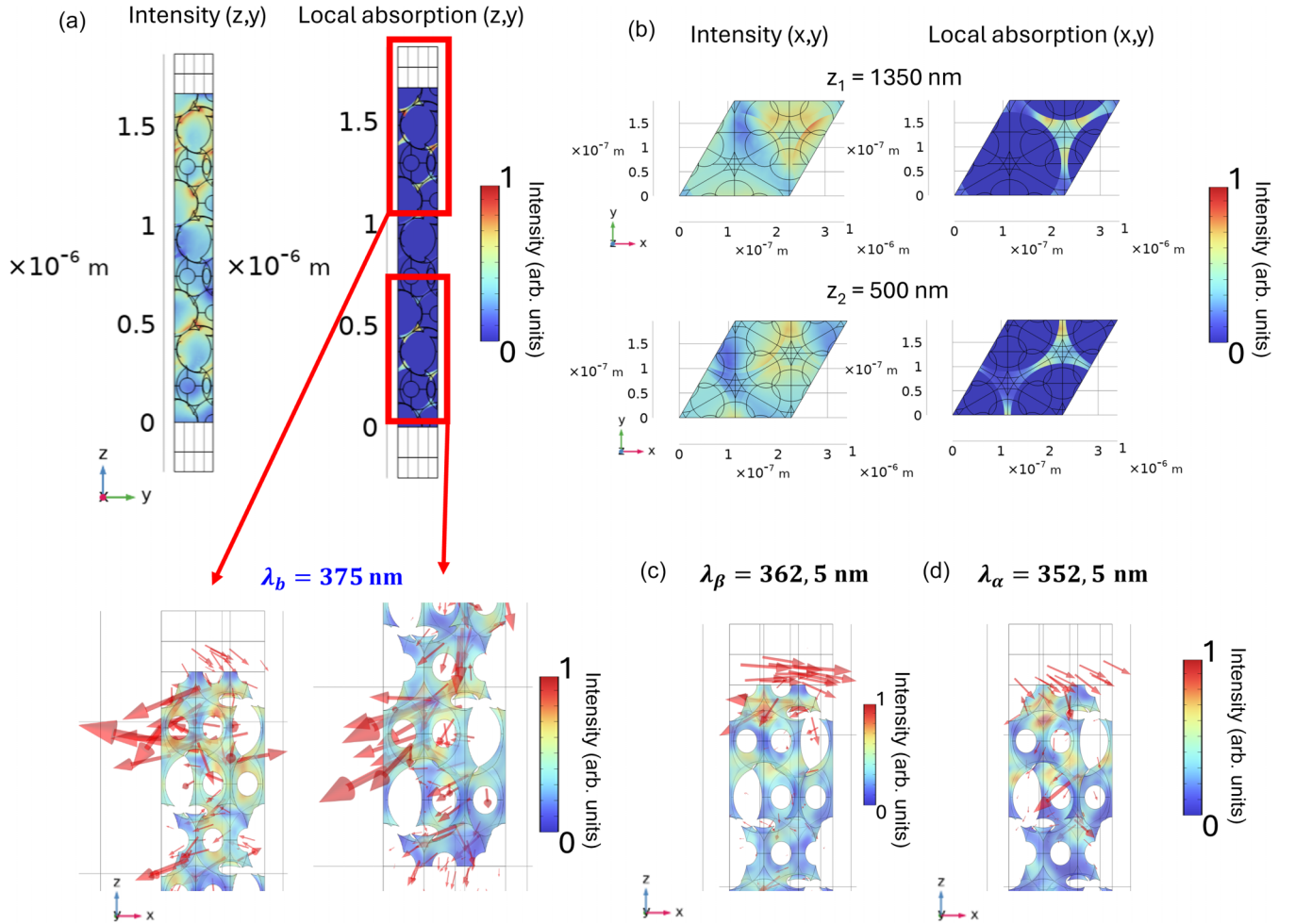


FIG. 8. IO with air-filled pores of $D = 240$ nm. (a) Top: From left to right, yz -plane cross sections of the electric field intensity and local electromagnetic power loss. Below: Poynting vector distribution (red arrows) in high absorption regions. Dielectric skeleton is represented with the electric field norm to help visualization. Arrow lengths are proportional to the Poynting vector norm. (b) Transverse xy -plane cross sections of the same physical quantities. (c), (d) Poynting vector distributions within the first few nanometers of the structure for (c) $\lambda_\beta = 362.5$ nm (reflectance peak) and (d) $\lambda_\alpha = 352.5$ nm (absorptance peak). Colors on the dielectric skeleton indicate the electric field norm to help visualization. Arrow lengths are proportional to the Poynting vector norm.

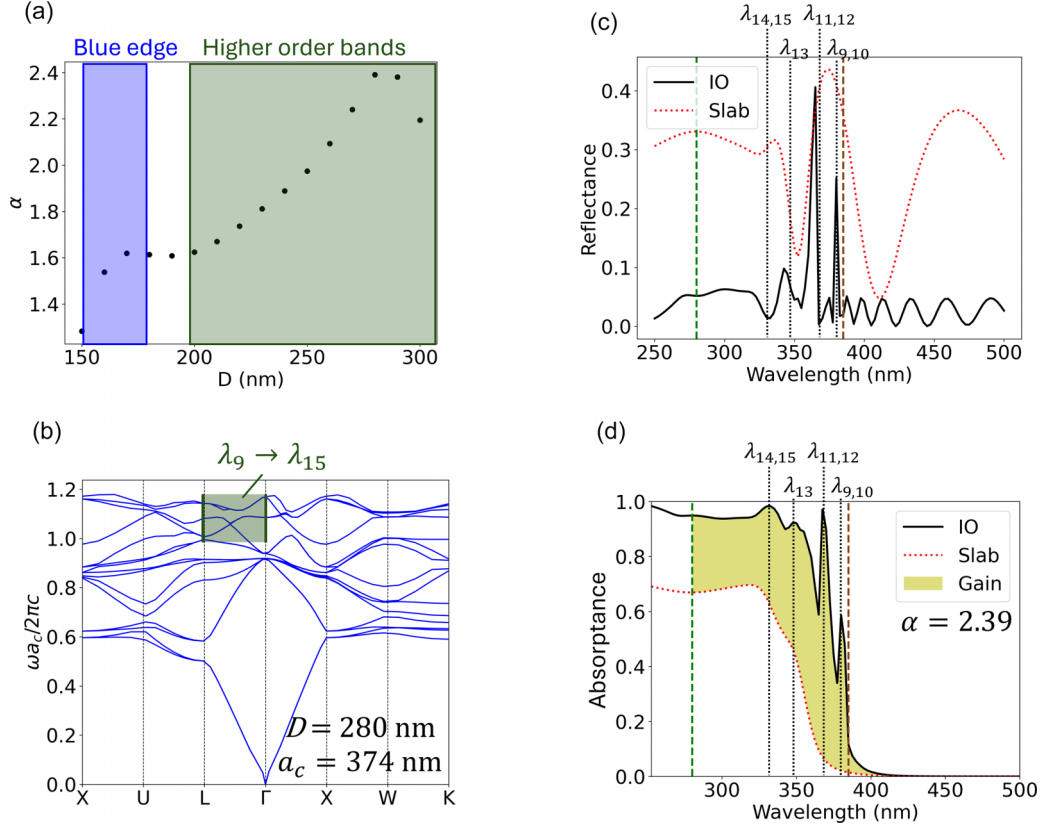


FIG. 9. (a) Enhancement factor (α) as a function of the pore diameter (D) for water-filled pores IOs. (b) Photonic band diagram of a water-filled IO ($n_{\text{water}} = 1.33$) with a filling factor $f = 0.12$ and a refractive index of the dielectric skeleton ($n_{\text{TiO}_2} = 3.068$). (c) Reflectance and (d) absorbance spectra of an IO with water-filled pores of $D = 280$ nm. Vertical green shaded band highlights the allowed modes of the higher order bands (i.e., bands 9 to 15) responsible of the multiple absorbance peaks.

$k_z = k \cos 45^\circ$ now leads to propagation primarily along the z direction. This mechanism is confirmed by the spatial distribution of Poynting vector distribution showing deeper light penetration compared to λ_β [Fig. 8(d)].

B. Liquid-filled pores

We verify that absorption enhancement also occurs with pores filled with liquid (water) by varying the pore diameter from 150 nm to 300 nm, at normal incidence [Fig. 9(a)]. Here again, accessing the higher-order modes enables a higher enhancement factor (up to $\alpha = 2.39$ at $D = 280$ nm) than with blue edge tuning ($\alpha = 1.62$ at $D = 170$ nm). Similarly to the case of air-filled pores, increasing D gives access to higher-order modes ranging from the ninth to 15th band number [Fig. 9(b)]. It is noteworthy that the red and blue edges no longer contribute to the absorption enhancement since the corresponding wavelengths ($\lambda_r = 693$ nm and $\lambda_b = 619$ nm, respectively) lie far above the TiO_2 absorption edge. In the wavelength region of interest, no PBG appears in the band diagram as opposed to the air-filled pores case. Consequently, the absorption enhancement is no longer spoiled by band-gap reflection. As a result, in comparison to the air-filled pores case, a broader range of allowed modes can be accessed by using larger pore diameters and higher absorption enhancement can be obtained eventually. At the L point, we identify seven allowed modes in the band diagram at $\lambda_9 = \lambda_{10} = 376$ nm,

$\lambda_{11} = \lambda_{12} = 371$ nm, $\lambda_{13} = 346$ nm, and $\lambda_{14} = \lambda_{15} = 328$ nm. To all these modes correspond absorbance peaks at 380 nm, 367.5 nm, 347.5 nm, and 332.5 nm (Fig. 9) in good agreement with the theoretical values. We discuss hereafter the pairs of degenerated modes $\lambda_9 = \lambda_{10}$ and $\lambda_{11} = \lambda_{12}$ which are closer to the band edge of TiO_2 .

The absorbance peak at $\lambda = 367.5$ nm is associated with a field intensity distribution that extends deeper into the IO structure [Fig. 10(a)]. The deeper penetration of the electromagnetic energy into the structure as well as the spatial distribution of the Poynting vector suggest strong light trapping in this configuration [Fig. 10(e)]. At fixed depth, in the cross sections, the degenerated modes ($\lambda_{11} = \lambda_{12}$) are preferentially localized in the triangular like parts of the skeleton [Fig. 10(c)]. Both light trapping and slow light ($v_g = -0.04c$) appear to drive the absorption enhancement.

The absorbance peak at $\lambda = 380.0$ nm is associated with a field intensity distribution that is concentrated in the near surface, where light trapping takes place [Figs. 10(b) and 10(f)]. At shallow depths, the slow light ($v_g = -0.004c$) degenerated modes ($\lambda_9 = \lambda_{10}$) are preferentially localized in the narrow connective parts of the skeleton [Fig. 10(d)], leading to tight confinement of the electromagnetic field ($\gamma = 0.64$). Near the surface, spatial distribution of the Poynting vector exhibits substantial back-scattering which explains the appearance of a reflectance peak ($R = 0.25$ at $\lambda = 380.0$ nm) [Fig. 9(c)]. Comparatively, the reflectance associated with previously

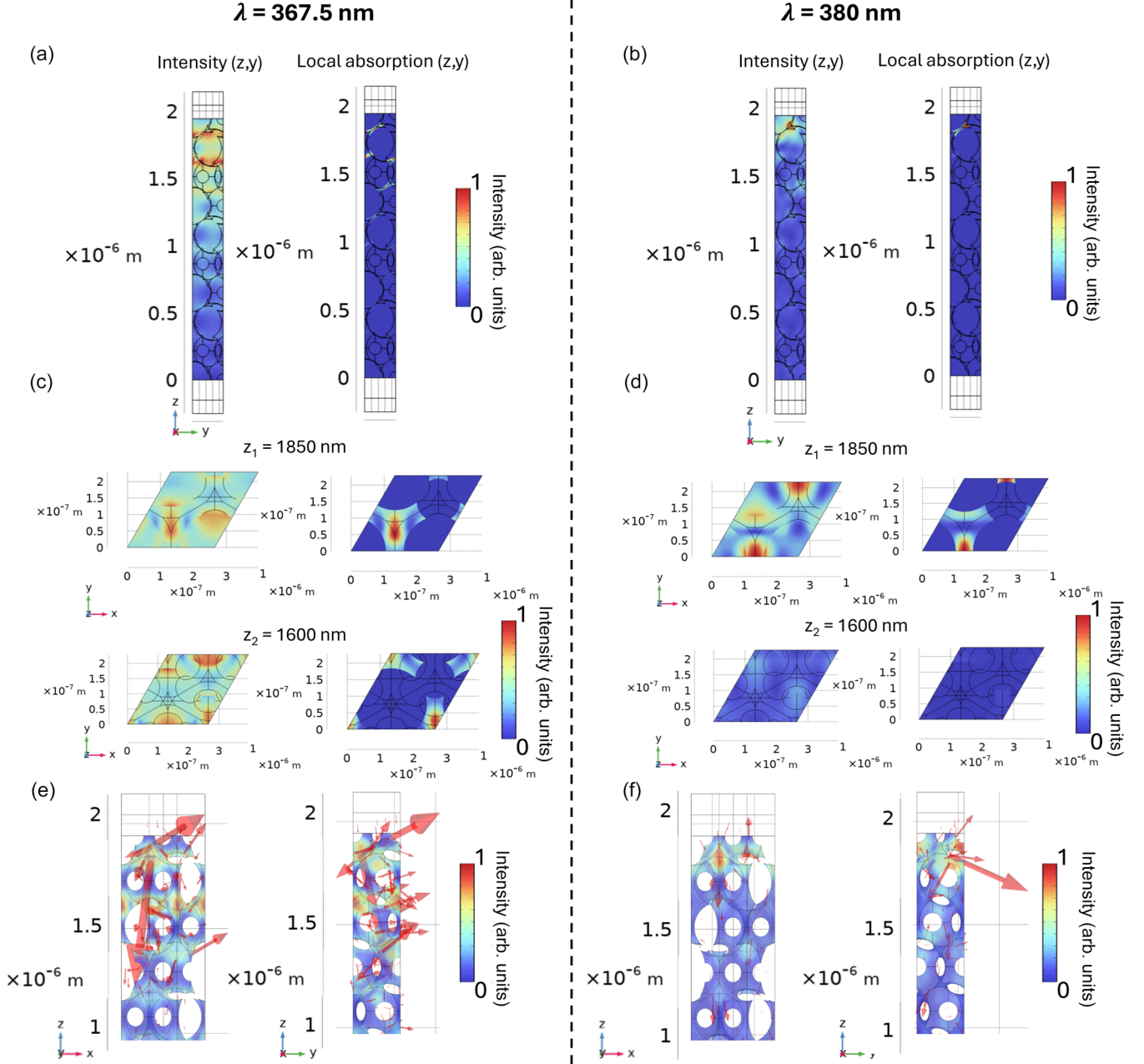


FIG. 10. IO with water-filled pores of $D = 280$ nm. (a), (b) From left to right: yz -plane cross sections of the electric field intensity and local electromagnetic power loss. (c), (d) From left to right: xy -plane cross sections of the same physical quantities. (e), (f) Poynting vector distributions (red arrows) in the first nanometers of the structure: left, xz plane and right, yz plane. The colors on the dielectric skeleton indicate the electric field norm to help visualization. Arrow length is proportional to Poynting vector norm. (a), (c), and (e) Results at $\lambda = 367.5$ nm. (b), (d), and (f) Results at $\lambda = 380$ nm.

discussed degenerated modes is much smaller ($R = 0.004$ at $\lambda = 367.5$ nm).

IV. CONCLUSION

This work brought additional insights into the potential of anatase TiO_2 inverse opals for photocatalysis in both gas and liquid phases, with particular emphasis on the slow light effects associated with higher-order photonic bands and their angular dependence. Significantly larger enhancement factors were achieved by increasing the pore diameter to

access higher-order modes (up to 15th band number) above the blue edge. At normal incidence, diameters of 240 nm (air-filled pores) and 280 nm (water-filled pores) yielded maximum absorption enhancement factors of $\alpha = 2.07$ and $\alpha = 2.39$, respectively. Moreover, near-perfect absorption ($A = 0.987$) could be achieved for air-filled pores of $D = 210$ nm at $\lambda = 335$ nm. The high density of modes from normalized frequency $\omega a_c / 2\pi c = 0.85$ to normalized frequency $\omega a_c / 2\pi c = 1.2$ greatly facilitated light coupling into the IO slab. Partly due to their higher normalized frequencies, those modes exhibited tighter confinement within the dielectric

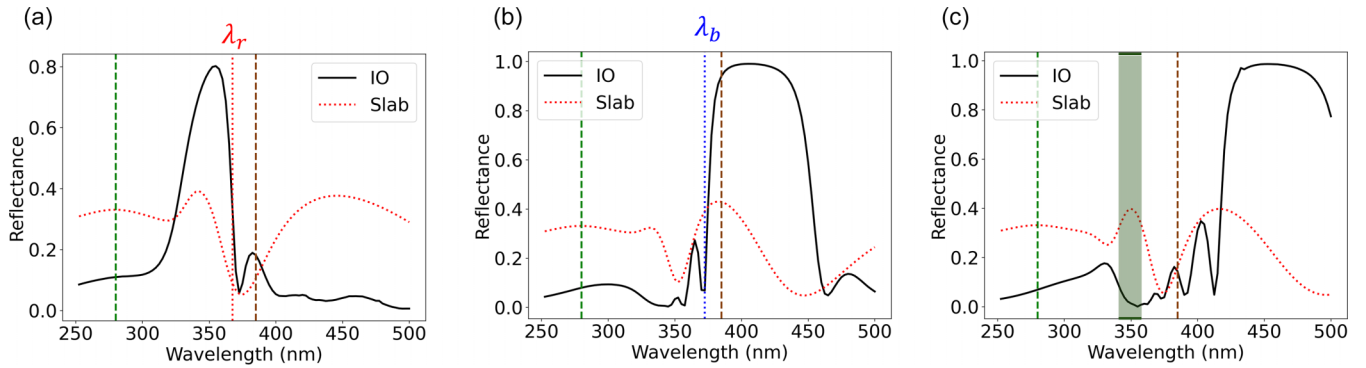


FIG. 11. Reflectance spectra of an IO with air-filled pores of diameters (a) $D = 160$ nm, (b) $D = 210$ nm, and (c) $D = 240$ nm, at normal incidence. Vertical green and brown dashed lines indicate the lower limit of the solar spectrum and the TiO_2 absorption edge, respectively.

skeleton compared to the red and blue edge modes. In the case of air-filled pores, however, a partial PBG had an adverse effect on α but did not compromise the benefits brought by higher-order modes. At oblique incidence, higher-order modes still played a significant role in absorption enhancement. The additional degree of freedom in the incident wave vector enabled more efficient coupling and light trapping in the skeleton. At 45° incidence, for a pore diameter of 240 nm (air-filled pores), the blue edge mode as well as the fifth, sixth, and seventh modes lead to further enhancement ($\alpha = 2.42$), in comparison with normal incidence. Our study highlighted the advantage of the finite-element method to accurately model IO structures with ultranarrow dielectric regions (TiO_2 filling factor lower than the close-pack value). Easy access to field intensity maps and Poynting vector spatial distribution enabled a detailed understanding of light trapping in the IO structures.

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DATA AVAILABILITY

The data that support the findings of this article are not publicly available. The data are available from the authors upon reasonable request.

APPENDIX

Additional reflectance spectra are provided below to offer complementary insights, for instance, Bragg peak

localization, for selected pore diameters ($D = 160$ nm, $D = 210$ nm, and $D = 240$ nm) (Fig. 11).

Light trapping which occurs at oblique incidence ($\theta = 45^\circ$) at $\lambda_b = 375$ nm for an IO with air-filled pores of $D = 240$ nm has been investigated through diffraction order analysis. No diffraction is observed for incidence angles below approximately 25° , while around 40° a significant increase in the transmittance of the $[0, -1]$ and $[-1, -1]$ diffraction orders arises, which leads to a marked rise in the absorbance (Fig. 12). This behavior indicates that light trapping at oblique incidence is governed by coupling into these diffraction orders.

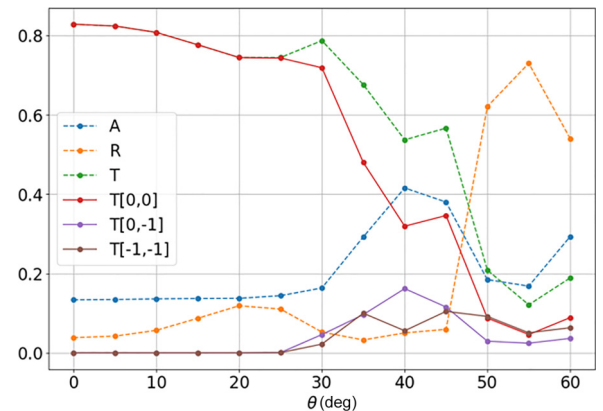


FIG. 12. Transmittance, reflectance and absorbance of IO with air-filled pores of $D = 240$ nm at $\lambda_b = 375$ nm as a function of the incidence angle (θ). The contributions of specific diffraction orders $[0,0]$, $[0, -1]$, and $[-1, -1]$ in transmittance are also shown, highlighting the coupling with diffraction modes around 40° and its correlation with the observed light-trapping enhancement.

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