Nanoparticle-Based One-Dimensional Photonic Crystals

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Herein we present a fast, reliable method for building nanoparticle-based 1D photonic crystals in which a periodic modulation of the refractive index is built by alternating different types of nanoparticles and by controlling the level of porosity of each layer. The versatility of the method is further confirmed by building up optically doped photonic crystals in which the opening of transmission windows due to the creation of defect states in the gap is demonstrated. The potential of this new type of structure as a sensing material is illustrated by analyzing the specific color changes induced by the infiltration of solvents of different refractive indexes.

Optical coatings made of several alternate layers of two different dielectric materials present brightly colored reflections arising from the interference of coherently scattered light waves. The frequency and width of the reflection is determined by the refractive index and the thickness of the layers in the film. Such structures, also known as Bragg reflectors or 1D photonic crystals, are commonly used in all branches of optics as precise frequency-selective filters or as antireflective coatings. The materials that the layers are usually made of are metal oxides with a large refractive index contrast between them, so an intense, wide reflectivity peak is attained just with a few alternate layers in the stack. SiO_2 and TiO_2 are two of the preferred materials for building these structures because they present very different dielectric constants and can be grown as highly uniform thin films using a wide variety of techniques such as pulsed laser deposition, reactive sputtering, or different types of chemical vapor deposition techniques.[1] Also, sol−gel methods combined with dip coating[2−4] or spin coating[5−7] have been employed because they allow one to obtain thin films with a large variety of compositions over wide area substrates in a simple and inexpensive way. In all of these examples, dense non-hygroscopic phases of the deposited coatings are sought after because performance stability under variable ambient conditions is usually desired. However, building multilayer structures whose optical response depends on the type of compound present in the environment might give rise to novel, interesting applications of such Bragg reflectors in the field of chemical sensing and detection. Unfortunately, the controlled response of a bulk material is difficult to attain unless precise control over both the composition and the mesostructure is achieved.

The first realization of such structures has recently been achieved by the alternate stacking of thin mesoporous films of organically templated SiO_2 and TiO_2.[8,9] Strict control over the ordered mesophase is mandatory to ensure its reproducibility. The high specific surface area arising from the presence of pores allows one to tune the color of the mesoporous Bragg reflector

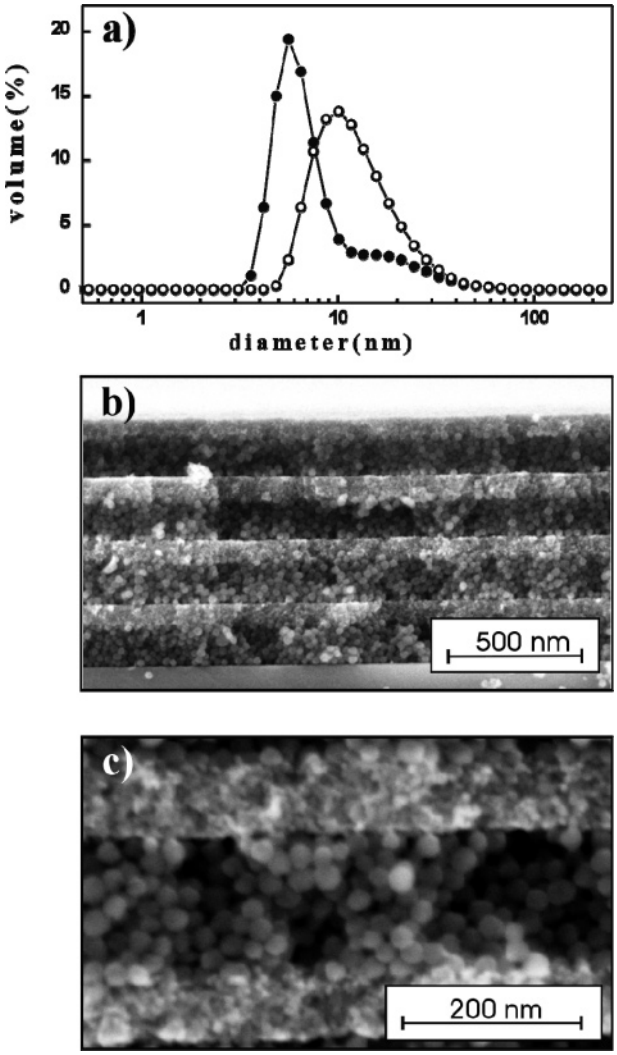

Figure 1. (a) Size distribution (vol %) of the suspensions employed to build a multilayer structure formed by packed nanoparticles of silica (white filled circles) and titania (black filled circles). (b and c) FESEM images of the cross section of an eight-layer Bragg reflector made of silica and titania nanoparticles deposited alternately on the substrate. The concentration employed in both suspensions is 5 wt %, and the rotational speed is set at 100 rps.

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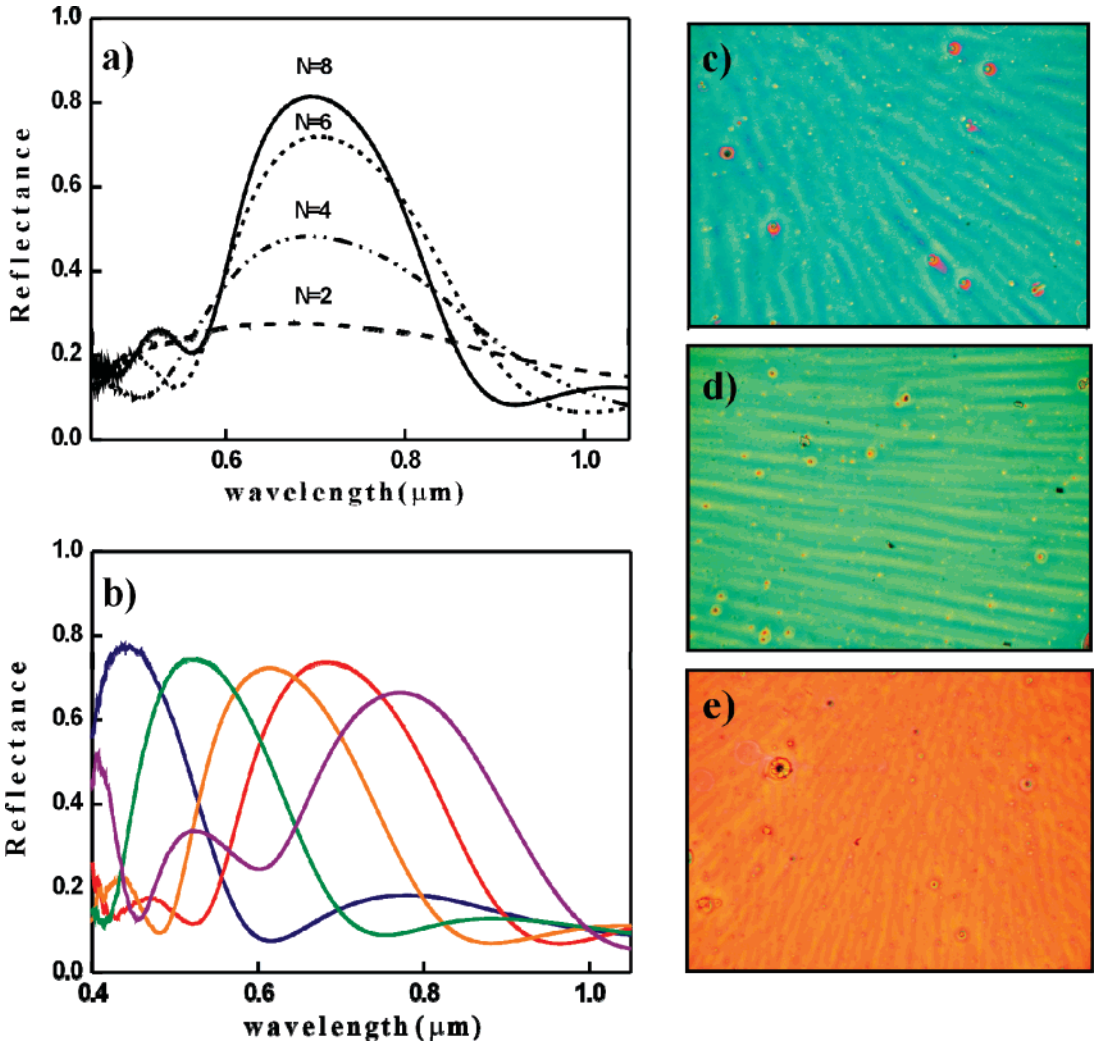

Figure 2. Evolution of the specular reflectance spectra with (a) the number of deposited layers (*N*) in the stack for a multilayer structure achieved by employing 5 wt % suspensions and (b) the concentration of the nanoparticle suspensions comprising the layers. In all cases presented herein, the multilayer structure has been achieved by the alternate stacking of three layers of silica (concentrations in the precursor solution ranging from 2 to 6 wt %) and three layers of titania (5 wt % concentration in the precursor solution). (c−e) Pictures showing the different colors of 1D photonic crystals with different lattice constants.

by the condensation of different compounds within the pores because it changes the refractive index of the pores.[8] Furthermore, it was proven that the functionalization of the pores[9] gives rise to a selective response to a specific compound in the environment. Even more recently, other methods of producing mesoporous Bragg stacks have been developed by using a layer-by-layer approach involving the sequential adsorption of nanoparticles and polymers.[10]

In this work, we present a method to create mesostructured Bragg reflectors in which the building blocks are nanoparticles of different sort. The material that we have built possesses a multilayer structure in which each layer is formed by packed nanoparticles of different composition uniformly deposited by spin coating colloidal suspensions of a controlled aggregation state. To confirm the versatility of the method, we have also built optical cavities within the structure, which give rise to allowed states within the photonic band gap whose number and position can be controlled through the thickness of the cavity. These structures behave as 1D photonic crystals of high quality and also possess a large, highly accessible interconnected mesoscopic porosity that provides a clear optical response to the environment, as we confirm by studying their response versus different solvent infiltration.

The starting materials are suspensions of nanoparticles of SiO_2 and TiO_2. SiO_2 colloids were purchased from Dupont (Ludox TMA, Aldrich), and TiO_2 crystallites (nc-TiO_2) were synthesized using a procedure based on the hydrolysis of titanium isopropoxide (TTIP 97%, Aldrich), followed by growth under hydrothermal conditions.[11] Titanium alkoxide precursor (20 mL) was added to 36 mL of Milli-Q water and stirred for 1 h. The resultant white solid was filtered by employing 1.2 μm RTTP Millipore sieves and then was washed several times with distilled water and placed in a Teflon reactor containing 3.9 mL of 0.6 M tetramethylammonium hydroxide (TMAOH 25%, Fluka). Peptization takes place by heating in a furnace at 120 °C for 3 h. After this, a colloidal suspension of anatase crystallites is attained. Later, centrifugation at 14 000 rpm for 10 min allows the elimination of large aggregates from the dispersion. A sizable parameter to achieving uniform optical quality thin films made of these colloids is control over particle size and aggregation, as pointed out by Thomas et al.[12] This was checked using photocorrelation

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spectroscopy, with monomodal distributions of TiO_2 nanocrystals and SiO_2 colloids being attained as shown in Figure 1a.

TiO_2 nanocrystals and SiO_2 nanoparticles employed to obtain highly uniform oxide films were suspended in a mixture of water and methanol in order to be used as precursor dispersions for a spin-coating process. This alcohol is chosen because no coagulation is observed in the suspension when prepared in this way,[13] and at the same time, the medium is volatile enough to obtain liquid-free films in a few seconds. Drops (250 μL) of these suspensions, which were prepared by employing 79:21% volvol mixtures of MeOH/H_2O, were spread onto a previously treated square glass substrate (2.5 cm × 2.5 cm) and spun immediately at constant velocity using an SCI series Novocontrol GmbH spin coater operating at atmospheric pressure. The thickness of the deposited nanoparticle films was controlled by changing the concentration of the suspensions or the rotational speed of the substrate, which ranged from 1 to 6 wt % for both SiO_2 and TiO_2 suspensions. By doing so, we attained very thin (between 40 and 200 nm) uniform nanoparticle films. Once one film is deposited and without any further stabilization needed, a second layer made of a different type of nanoparticle was deposited. By repeating this cycle, we can grow nanoparticle multilayers with a nanostructure like that shown in Figure 1b,c. The stacks so prepared were thermally treated in a furnace at 450 °C in order to stabilize them mechanically, with no cracks or deterioration of the coatings being observed after cooling. Field-emission scanning electron microscopy (FESEM, Hitachi 5200 operating at 5 kV) images of a cross section of an eight-layer 1D photonic crystal made of silica and titania colloids deposited alternately on the substrate demonstrate the uniformity of the thickness of both types of layers and the different morphology of nanoparticles used, as shown in Figure 1b,c. The silica and titania concentrations employed in this case were 5 wt %, and the rotational speed was set at 100 rps for 1 min to deposit each type of layer. It should be remarked that every time a layer of the smaller (on average) TiO_2 particles is deposited onto an already formed layer of larger SiO_2 colloids, interpenetration of the former within the latter occurs. On the other side, when SiO_2 colloids are deposited onto a TiO_2 nanoparticle layer, the latter behaves as an impenetrable slab. Direct evidence of this is provided in the FESEM pictures shown in Figure S1a,b in Supporting Information. This does not significantly affect the fact that we can achieve a high dielectric contrast between neighboring layers, as the intense Bragg peak observed in the optical reflectance spectra and the refractive index values attained from the corresponding fittings demonstrate (Figure S1c in Supporting Information).

The quasi-normal incidence reflectance spectra of SiO_2−TiO_2 nanoparticle multilayers were obtained with a Bruker IFS-66 FTIR spectrophotometer attached to a microscope with a 4× objective with a 0.1 numerical aperture (light cone angle ±5.7°). The evolution of the optical properties with the number of layers (N) deposited is illustrated in Figure 2a. An intense (above 70% reflectance for stacks made of six or more alternate layers), wide Bragg reflection peak is observed, which is a direct consequence of the large refractive index contrast between the SiO_2 nanoparticle layers and the TiO_2 nanocrystal ones. It is observed, as expected, that the reflectance primary maximum becomes both narrower and more intense in time as the number of layers in the stack is increased. The spectral position of the Bragg peak can be tuned by changing the lattice parameter of the periodic structure, which is realized by varying the thickness of each type of layer

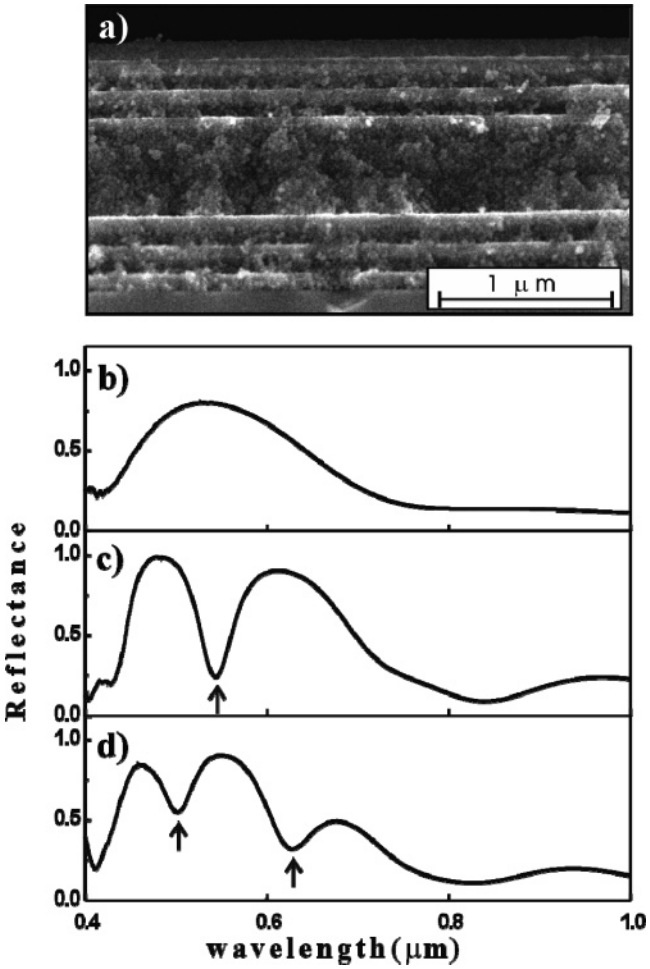

Figure 3. (a) FESEM image showing the cross section of a multilayer in which a SiO_2 nanoparticle defect layer almost 5 times thicker than those forming the periodic structure that surrounds it has been built. The optical cavity is built in the center of a stack made from silica (3 wt % precursor solution) and titania (5 wt % precursor solution) nanoparticles. (b) Specular reflectance spectrum corresponding to the six-layer Bragg reflector. (c and d) Optical response attained from doped multilayers containing defects of different thickness built within the structure shown in plot b.

in the structure. The thickness of each layer is determined by the concentration of nanoparticles in the precursor solution and the rotational speed of the substrate. Keeping constant the concentration of the TiO_2 nanocrystal precursor solution (5 wt %) and the substrate rotation speed (100 rps for 1 min), the SiO_2 nanoparticle suspension concentration was varied from 2 to 6 wt % in order to attain multilayers with different periodicity. Specular reflectance spectra from the different photonic crystals attained are shown in Figure 2b. It can be seen that the Bragg peak position can be tuned through the whole visible range. Optical microscope images are displayed in Figure 2c−e to show the different colors reflected by nanoparticle-based 1D photonic crystals with different lattice parameters. To illustrate further the control over film thickness achievable by spin coating, the dependence of the SiO_2 film thickness—the only one that we vary to change the lattice parameter of the structure—on the substrate rotational speed and on nanoparticle concentration is explicitly shown in Figure S2 in Supporting Information. Each thickness value was extracted by averaging measurements performed on FESEM pictures taken from cross sections of different films grown using similar conditions, confirming the reproducibility of the results. Some examples of the pictures employed are displayed in Figure S3 in Supporting Information. Radial color fluctuations observed in

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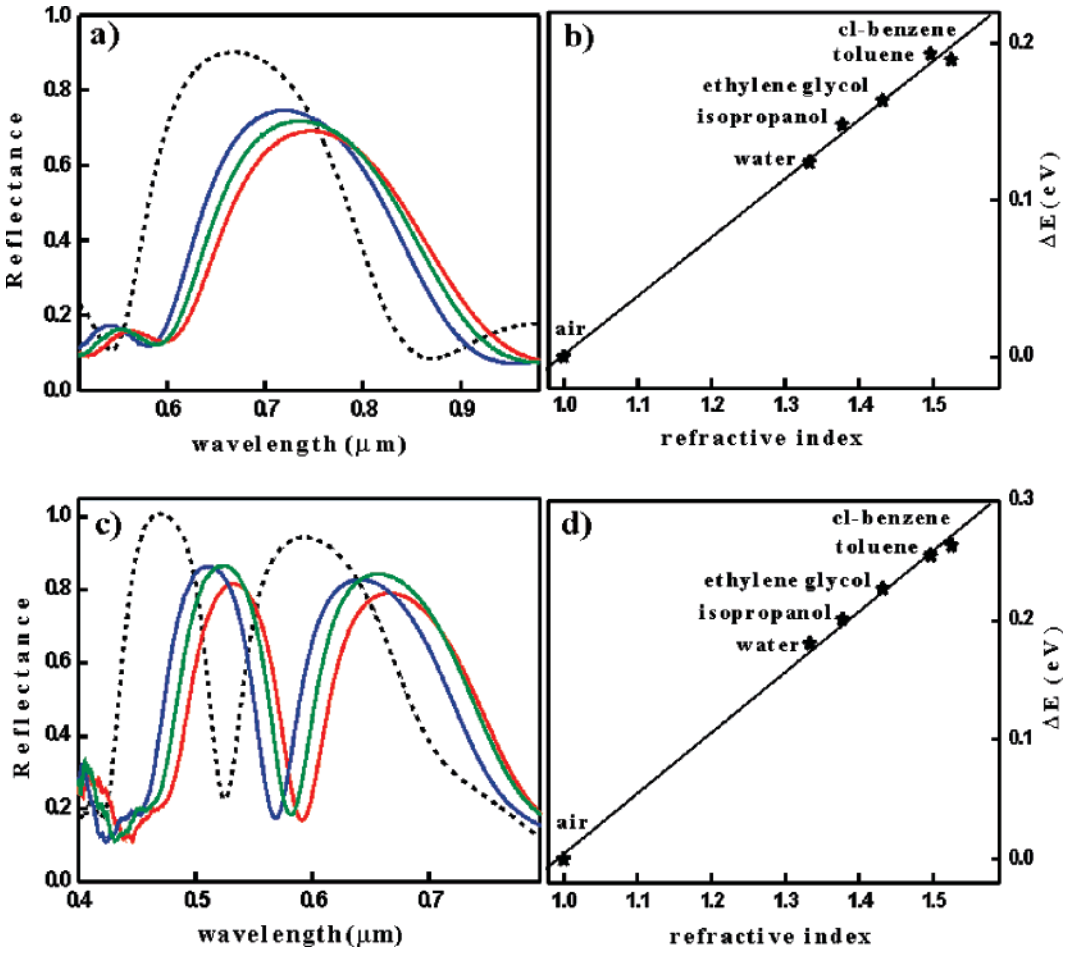

Figure 4. (a) Optical response of an eight-layer Bragg reflector such as the one shown in Figure 1b,c after being infiltrated with different refractive index solvents such as water (blue line), ethylene glycol (green line), and Cl-benzene (red line). The dotted line corresponds to the reflectance spectrum of the same multilayer structure in air. (b) Bragg peak position shift measured for the different solvent-infiltrated multilayers. (c) Optical response of the multilayer structure with a planar defect after being infiltrated with the same solvents. (d) Shift of the position of the reflectance dip corresponding to a defect state within the band gap for the different solvent-infiltrated multilayers.

the pictures are due to the phenomenon of striation that occurs while rotation takes place. This is a consequence of the presence of Marangoni convection flows caused by compositional inhomogeneities at the tens of micrometers length scale, which are almost unavoidable.[14] By fitting the optical reflectance spectra using a scalar wave approximation,[15,16] we estimated the refractive indexes of the TiO_2 and SiO_2 nanoparticle-based films to be $n_{TiO_2} = 1.74$ and $n_{SiO_2} = 1.24$, respectively, which implies that the pore volume fraction in the films, as calculated using the Bruggeman equation,[17] is 46% in both cases, assuming that bulk TiO_2 and SiO_2 have refractive indexes of 2.4 and 1.45, respectively. In fact, the refractive index may be varied in a controlled manner by changing the particle size distribution in the precursor suspensions, which will result in a different packing and thus porosity.

The optical response of multilayers can also be modified through the introduction of controlled defects that behave as optical dopants. A disruption of the periodicity leads to localized photonic states in the gap, that is, narrow ranges of frequencies within the forbidden band gap that are now allowed to propagate through the multilayer structure. For our 1D photonic crystals, the disruption of the periodicity can be achieved by depositing a layer of different thickness in the middle of the stack. An FESEM image of a SiO_2 nanoparticle defect built in the center of a TiO_2-SiO_2 multilayer structure is presented in Figure 3a. The number and position of allowed states can be controlled by modifying the thickness of the defect, which is achieved by repeating the deposition process several times for the same suspension. In Figure 3b, we show the reflectance spectrum of a six-layered Bragg reflector made of silica (3 wt %) and titania (5 wt %) and their corresponding optical responses for the same multilayer structures with different SiO_2 nanoparticle defects, which are about 3 and 5 times as thick as those forming the periodic structure, shown in Figure 3b,c, respectively. In these reflectance spectra, we can observe one or two sharp dips (i.e., regions of higher transmittance) within the forbidden band gap frequency range. These dips are the fingerprint of the defect states created by intentionally breaking the periodicity.

Besides the structural and optical characterization provided, we analyze the potential of the nanoparticle-based 1D photonic crystals as base materials for optical chemical sensing devices. The large, highly accessible interconnected porosity present in the multilayer stacks provides a quick, sensitive optical response to different environmental compounds. When an analyte is introduced into the pores of such structures, a variation in the effective refraction index of each layer is produced, which leads to a shift in the Bragg peak that causes a significant change in the color of the multilayer stack. In this case, we have studied

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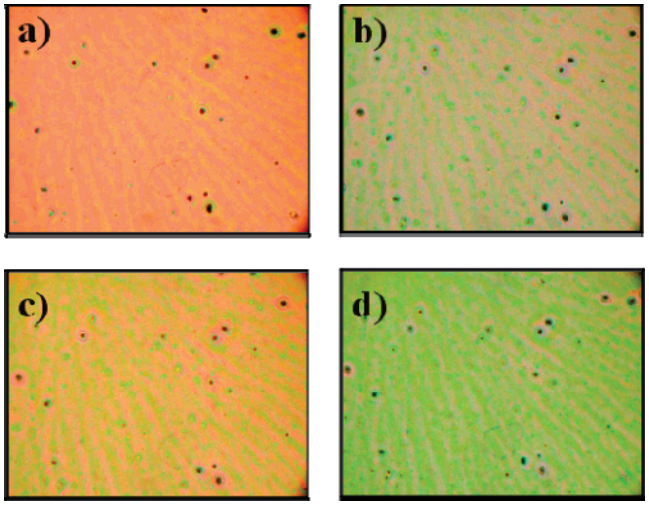

Figure 5. Optical microscope images of a multilayer structure containing an optical cavity (a) before and after being soaked in solvents with different refractive indexes: (b) isopropanol (n = 1.377), (c) ethylene glycol (n = 1.432), and (d) Cl-benzene (n = 1.525).

the reflectance peak shifts induced by infiltrating water, isopropanol, ethylene glycol, toluene, and Cl-benzene within an eight-layer TiO_2-SiO_2 Bragg reflector and also within a multilayer structure with an optical cavity of SiO_2 nanoparticles sandwiched between two four-layer TiO_2-SiO_2 photonic crystals. The refractive indexes at 20 °C of the above-mentioned analytes are 1.333, 1.377, 1.432, 1.497, and 1.525, respectively. Reflectance spectra were collected after soaking the photonic nanostructures in the different solvents, and we observe that the higher the refractive index of the guest, the larger the shift of the Bragg peak. We illustrate the type of changes observed in the optical response of the multilayers for some selected solvents in Figure 4a,c, namely, water (blue line), ethylene glycol (green line), and Cl-benzene (red line). In this Figure, the dotted line corresponds to reflectance spectra of the multilayer structures in air. The shift of the spectral position of the reflectance maxima of the multilayer is plotted as a function of the refractive index of the different analytes in Figure 4b. In Figure 4d, we show the shift of the spectral position of the reflectance dip caused by the presence of the thicker layer in the structure. An absolute energy scale is used. As seen in this Figure, the energy variation calculated for both structures exhibits a linear correlation with the refractive indexes of the solvents and is higher for that in which a defect is built, proving the higher sensitivity of the environment of the latter. Furthermore, color changes due to solvent infiltration are more easily perceived in the optically doped structures, as can be seen in the optical microscope pictures shown in Figure 5a–d. Besides, the sharper reflectance dip caused by the defect built within the stack provides better spectral resolution than in the case of the purely periodic multilayer.

To conclude, we have presented a fast, reliable method for building nanoparticle-based 1D photonic crystals in which a periodic modulation of the refractive index is built by alternating different types of nanoparticles and by controlling the level of porosity of each layer. The versatility of the method is further confirmed by building up optically doped photonic crystals in which the opening of transmission windows due to the creation of defect states in the gap is demonstrated. The potential of these new types of structures as sensing materials is illustrated by analyzing their specific color changes induced by the infiltration of solvents of different refractive indexes. We foresee that most of the potential applications that have been explored in the last years for 3D colloidal crystals, which have had a great impact in the field of photonic crystals, will be tested in these new materials whose performance is expected to be much better because they possess good optical quality, high mechanical robustness, and a porosity comparable to that of their 3D counterparts.

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Supporting Information Available: SEM images showing details of the cross section of a silica nanoparticle layer between two titania layers within a periodic stack. Example of one of the fittings realized of the optical reflectance spectra measured. Cross sections of titania–silica bilayers attained at different deposition conditions. Curves showing the evolution of the silica nanoparticle film thickness versus substrate spinning speed and particle concentration in the precursor suspension. This material is available free of charge via the Internet at http://pubs.acs.org.

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