Journal of Materials Chemistry

Cite this: DOI: 10.1039/c2jm33692h

www.rsc.org/materials

PAPER

Tuning the selectivity and sensitivity of mesoporous dielectric multilayers by modifiying the hydrophobic–hydrophilic balance of the silica layer†

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Received 8th June 2012, Accepted 7th September 2012
DOI: 10.1039/c2jm33692h

We investigate the possibility of tuning the selectivity and sensitivity of SiO_2/TiO_2 mesoporous dielectric multilayers for the adsorption of analytes with different chemical polarities. The hydrophilic–hydrophobic balance of the mesoporous SiO_2 layer was controlled by one-pot co-condensation of mixtures of methyltriethoxysilane (MTES) and tetraethyl orthosilicate (TEOS) in variable contents. Infrared spectroscopy analysis combined with water contact angle measurement confirmed the gradual increase of the hydrophobic behavior of the hybrid silica layer obtained by increasing the MTES content, without losing its porosity. Hybrid silica layers included into the dielectric multilayer material enabled controlling the surface properties of the Bragg stacks. UV-visible spectroscopy showed a Bragg peak red-shift. This shift depends on the affinity of the adsorbed molecule toward the functional groups present on the surface of the constituting materials. This procedure enabled the dramatic change of the adsorption properties of the mesoporous dielectric multilayer and correspondingly the optical response of the photonic crystal.

1. Introduction

Nanostructures in nature working as photonic bandgaps have been reported to be key components of coloured surfaces during interaction with light.[1] Natural photonic bandgap systems typically exhibit 1D, 2D and 3D architectures. Such structures are responsible for controlling light in butterfly wings,[1] cuticle surface of tropical beetles[2] or genus *Selaginella*[3] and provide the diverse fascinating color distributions known in these living beings. Some structures show an incredible ability to control the stop band *via* the change of the periodicity of the nanostructure[4] and/or by analyte uptake or migration in their structure.[2]

Inspired by nature, the design of 1D photonic crystals has attracted much more attention since the introduction of inclusions into the alternating materials. Building a mesoporous dielectric multilayer (MDM) by alternating two layers, which present a large refractive index contrast and a high accessible surface area, gives rise to new, interesting applications of such Bragg reflectors in the field of lasing[5] and chemical sensing.[6–8]

The MDM could constitute a promising alternative to porous silicon Bragg reflector sensing devices[9] since physical and chemical detections of target compounds can be combined. The optical properties of the MDM are sensitive to the refractive index change of the mesoporous film, induced by the capillary diffusion of analytes into the pores. This physical approach can be combined with a chemical one. The latter consists in changing the optical response by modifying the film's surface properties. Furthermore, it has been proved that changes in the thicknesses of the alternated layers,[6] the post-functionalization of the pores,[7] or the integration of clay films as chemically active sites[8] give rise to a selective response to a specific compound in the environment.

In this study, we show the change in the selectivity and sensitivity of MDM after the chemical introduction of a hydrophobic function on the silica surface *via* the one-pot self-assembly of a hybrid solution. The surface energy of the films is intimately related to the types of functional groups present on the surface of the composing materials. SiO_2 and TiO_2 are well known to contain surface –OH, providing them with a kind of hydrophilicity. For SiO_2, the modulation of this property is possible at its synthesis stage by using a one-pot co-condensation of methyltriethoxysilane and tetraethyl orthosilicate in variable ratios to introduce pendant methyl groups onto the silica surface at variable levels. Through a simple hydrolysis and condensation process, it is possible to dramatically change the adsorption properties of the mesoporous dielectric multilayer and then the optical response of the photonic crystal obtained by stacking these modified silica layers with titania ones.

2. Experimental section

All chemicals were of analytical grade and used without further purification: tetraethyl orthosilicate ($Si(OC_2H_5)_4$, TEOS,

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c2jm33692h

Aldrich), methyltriethoxysilane ($CH_3Si(OC_2H_5)_3$, MTES, Aldrich), titanium(IV) ethoxide ($Ti(OC_2H_5)_4$, TEOT 95% Aldrich), ethanol of absolute grade and hydrochloric acid (Aldrich, 37%). The triblock copolymer poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide), Pluronic F127 ($M_n \sim 12\,800$ g mol^{-1}, denoted as $EO_{99}PO_{69}EO_{99}$, Aldrich), and 1-hexadecyl trimethylammonium bromide (CTAB, $M_n \sim 364.4$, $(CH_3)_3N(CH_2)_{15}CH_3Br$, Alfa Aesar) were used as structuring agents. Soda lime glass (SLG) slides and indium tin oxide coated glass slides (ITO) were purchased from Aldrich.

Precursor solutions were prepared by adapting a procedure described elsewhere.[10] The titanium precursor sol was obtained by mixing TEOT under highly acidic conditions (pH < 2, adjusted with hydrochloric acid). Under these conditions, the precursor was partly hydrolyzed without significant condensation. An additional mixture of ethanol and template (Pluronic F127) was added. The final molar ratios of the solution were TEOT/HCl/EtOH/F127 = $1 : 2 : 9 : 5 \times 10^{-3}$. The solution was subsequently aged with magnetic stirring at room temperature for 3 h.

Hybrid silica films were obtained by mixing TEOS with different proportions of MTES in the presence of an adequate amount of water in ethanol. The pH was adjusted to less than 2 with hydrochloric acid. The molar ratio of MTES/(MTES + TEOS) was varied from 0 to 0.6. Final molar ratios after CTAB addition were typically MTES/TEOS/H_2O/EtOH/CTAB = $x : y : 10 : 20 : 0.1$. Solutions were aged under magnetic stirring for 24 hours. The hybrid silica films were denoted as $SiC_{MTES/(MTES+TEOS)}$.

Mesoporous dielectric multilayers were fabricated *via* spin-coating the so-prepared hybrid solutions at 5000 rpm for 30 s on the substrates. The layers of SiO_2 and TiO_2 were alternatingly stacked up one by one (3 bilayers) and then dried in air at room temperature for 12 h. Subsequently, the films were subjected to a successive drying process consisting in gently heating them for 6 hours at 70 °C, 3 hours at 150 °C and 2 hours at 200 °C. The obtained consolidated layers were finally heated in air at 400 °C for 2 hours using a heating ramp of 1 °C min^{-1}. The above procedure ensures the cross-linking between the silica–titania interfaces and avoids cracks on the layers.[7] Prior to use, the substrate was ultrasonically cleaned in a detergent, distilled water, acetone, ethanol and finally in distilled water for 15 min each, and then dried at 150 °C.

The morphology and microstructure of the films were characterized by transmission electron microscopy (TEM) performed with a LEO922 electron microscope operating at 200 keV. The film was scratched off from the substrate, dispersed in ethanol and then deposited on copper grids coated with a porous carbon film. The solvent was evaporated in air before analysis.

In order to determine the porosity of the films, atmospheric ellipsometric porosimetry (A-EP) measurements were performed with equipment from Sopra (Model GES-5E, A-EP, Sopra, Paris, France) using the software package "WinElli2". The data were fitted in the range between 1.6 eV and 4.5 eV using a Cauchy-type material as a model layer to determine optical constants of the film. Refractive index values were given for a wavelength of 633 nm and the film thicknesses were obtained for each measurement. The samples were introduced into a vacuum cell for *in situ* measurements. The ellipsometer chamber was flushed with a variable humidity flow of 2.5 L of air per min. The humidity was adjusted using a mass flow controller such that the relative humidity increased until saturation in order to measure the adsorption branch and then decreased so that the desorption one could be obtained. The open porosity was measured from the change of the optical characteristics (n: refractive index, k: extinction coefficient). The pore size distribution (PSD) was determined from the isotherm using the modified Kelvin equation.[11]

Infrared spectra (200 scans were averaged with a resolution of 4 cm^{-1}) of the hybrid silica thin films coated on KBr substrates were obtained in transmittance mode on a Bruker EQUINOX 55 spectrometer in static air. The spectrum of a non-coated KBr substrate was used as the background. Measurements were performed by thermally treating the samples at different temperatures (70–400 °C) in air for 2 h and following identical successive and variable condensation–consolidation temperatures as detailed above.

Static water contact angles (θ_w) were measured at ambient temperature and humidity using the sessile drop method and image analysis of the drop profile. The instrument, consisting of a CCD camera and an image analysis processor, was purchased from Electronisch Ontwerpbureau De Boer (The Netherlands). The water (milli-Q, Millipore, Molsheim, France) droplet volume was 0.3 μL and the contact angle was measured 5 s after the drop was deposited onto the sample. For each sample, the reported value is the average of the results obtained on at least 5 droplets.

Scanning electron microscopic (SEM) analysis was performed with a LEO 983 GEMINI microscope equipped with a field emission electron gun working with an acceleration voltage of 1 kV and emission current of 70 μA. To obtain cross-sectional images, the coated SLG was broken and placed in the microscope without metallic coating.

Transmittance measurements in the range of 300 to 1100 nm were carried out using a UV-Vis-NIR spectrophotometer (Cary 5E) at normal angle of incidence. For UV-Vis-NIR analysis, the multilayer structures were deposited on SLG. The transmittance responses of the multilayers were obtained for the dried states after ethanol washing in a Soxhlet extractor for two hours followed by drying under nitrogen flow and then soaking with different analytes (water and hexane).

3. Results and discussion

3.1. Transmission electron microscopy

The films showed a mesoporous structure as revealed by TEM analysis in Fig. 1. The mesoporous titania and silica films (with only the TEOS precursor shown) were synthesized using, respectively, the nonionic Pluronic F127 and ionic CTAB surfactants as the templates. Indeed, the samples treated at 400 °C showed a distorted wormlike mesostructure as shown in Fig. 1a. The films exhibited pores differing in shape and size depending on the surfactant used. The titanium film showed irregular pore sizes (between 4 and 8 nm) and shapes, resulting from the crystalline growth of the channel walls.[12] On the contrary, the silica film exhibited a regular pore size (~3 nm) and shape. These observations are consistent with the hysteresis loop observed in H_2O sorption analysis for each sample (see Section 3.2).

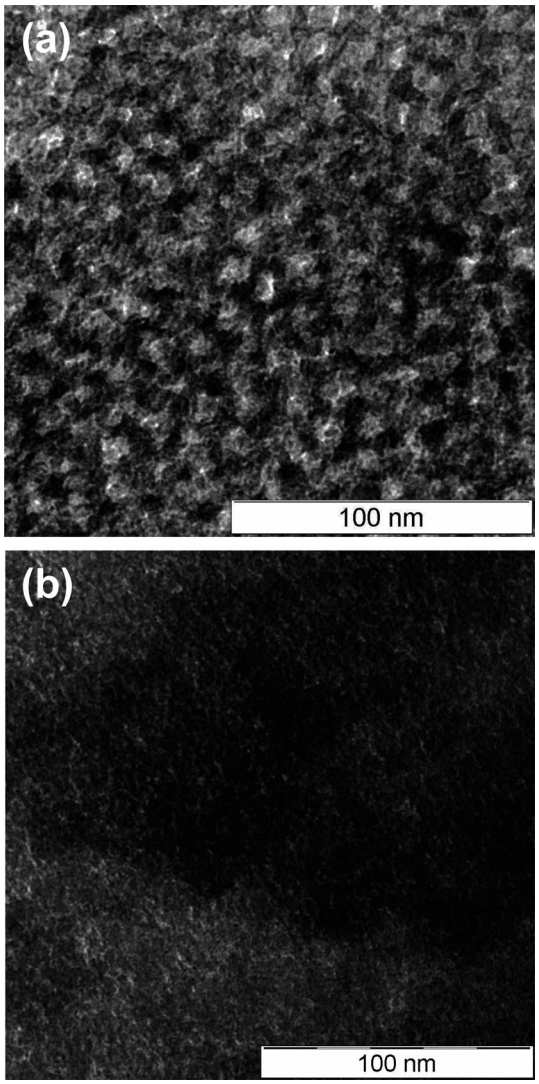

Fig. 1 TEM images of mesoporous titania, TiO_2 (a) and silica, SiO_2 (b) films.

3.2. Atmospheric ellipsometric porosimetry

Fig. 2a and b show the pore size distribution calculated from the isotherm curves by using the Kelvin equation modified for interconnected pores,[11] and the evolution of the refractive index for titania and silica films when the sample was exposed to increasing and decreasing relative vapor pressure ($0 < P/P_0 < 1$). Pore diameters were broadly distributed around ~6 nm in the TiO_2 film whereas the SiO_2 film presented pores of diameters around 3 nm. Such a finding was in agreement with the TEM results where pores of various dimensions were observed for the titania film and a narrow size distribution for the silica film. The adsorption branch (inset of Fig. 2a) shows a saturation above 80% which is consistent with the water condensation into the pore. The desorption branch (inset of Fig. 2a) shows a sudden decrease of the refractive index below 70% that corresponds to water decondensation. Based on the existence of such hysteresis loops due to capillary condensation (inset of Fig. 2a), the isotherm was a reversible type IV for the TiO_2 film according to the IUPAC adsorption isotherm classification indicating a

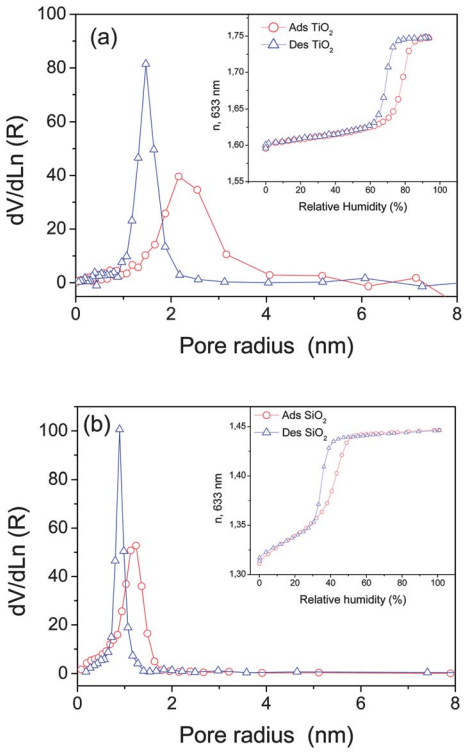

Fig. 2 Pore size distribution calculated using the Kelvin equation applied to the water adsorption–desorption isotherms for TiO_2 (a) and SiO_2 (b). In the inset, the evolution of the optical index n for each layer as a function of relative humidity of two subsequent adsorption–desorption cycles is shown.

mesoporous structure. This is a characteristic of cylindrical pores, where the two extremities have identical diameters. The adsorption and desorption isotherms of the SiO_2 film were different. Indeed, the smaller observed hysteresis loop suggests "bottleneck" pores in the film, where a smaller aperture assures interconnection of the neighboring pores. The sudden increase and decrease of the refractive index could be attributed to the short pore size distribution, in fair agreement with the PSD results. The refractive index was found to vary from 1.59 to 1.74 for TiO_2 and from 1.31 to 1.44 for SiO_2 when exposed from 0 to 100% relative humidity, suggesting that approximately 32.6% and 36% of the porosity can be filled up with condensed water respectively for TiO_2 and SiO_2. These results prove that the optical properties of mesoporous silica and titania films can be tuned by the water filling the pores, in agreement with previous reports.[11,13]

3.3. FTIR spectroscopic analysis of hybrid silica films

Fig. 3a shows the FTIR spectra of a hybrid silica film deposited on KBr, prepared from a coating solution derived from a MTES/(MTES + TEOS) composition of 0.6 and thermally treated at increasing temperature (from 70 °C to 400 °C). The presence of hydroxyl groups at lower temperatures is revealed by the large absorption band ranging from 3000 to 3800 cm^{-1}. The band at 1640 cm^{-1} is assigned to the –OH deformation vibrational mode of adsorbed water molecules. A decrease of the hydroxyl group bonds was observed as the calcination

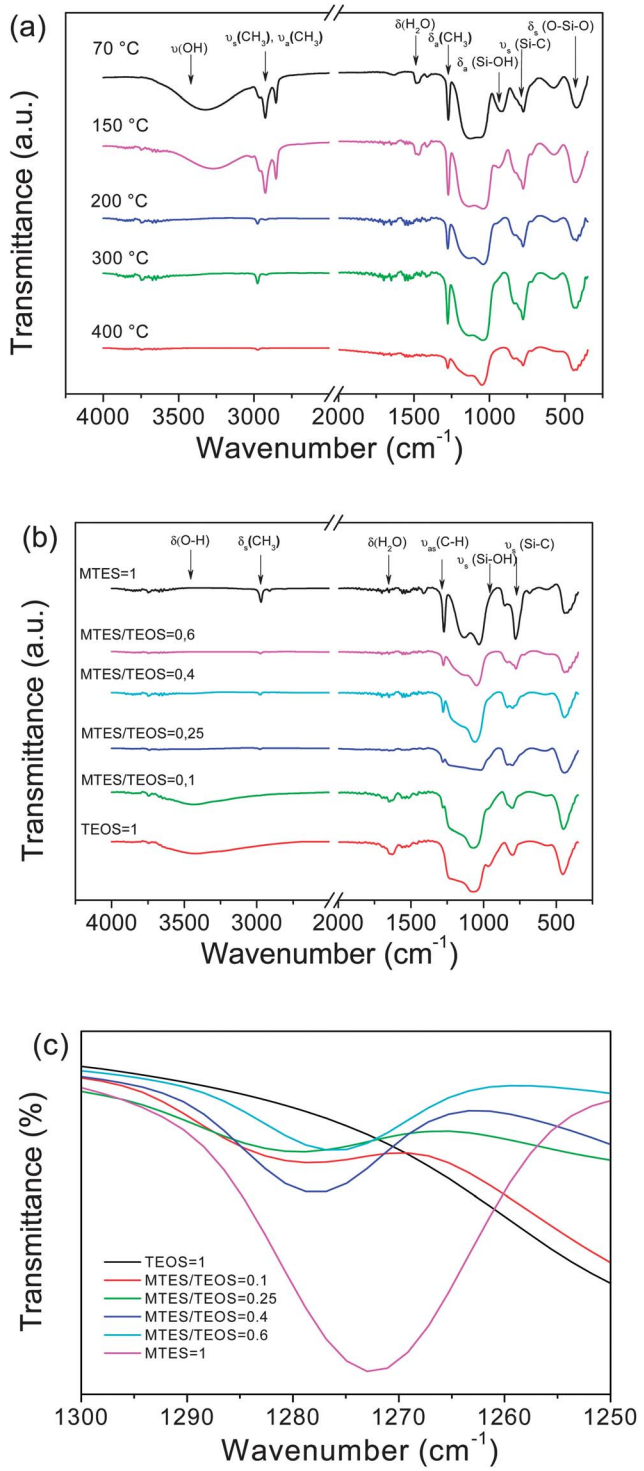

Fig. 3 FTIR spectra of (a) a hybrid silica layer with a MTES/TEOS ratio of 0.6 calcined at increasing temperatures, (b) variable MTES/TEOS ratio treated at 400 °C and (c) the bands due to the methyl groups on each material.

temperature increases, and no –OH bands were detected above 200°C. The vibration of the C–H stretching shows a $–CH_3$ stretching band at 2957 cm^{-1}, and antisymmetric and symmetric stretching bands of $–CH_2$ at 2925 and 2854 cm^{-1}, respectively, corresponding to the template. The intensity of this band was considerably reduced at higher thermal calcination temperatures, which indicates the degradation of the template. The band of the terminal methyl groups was observed even after the degradation of the template. Indeed, the C bonds present are C–H (ν_a at 2973 cm^{-1} and δ_a at 1272 cm^{-1}) and C–Si (δ_a at 777 cm^{-1}), both of which are present in the $Si–CH_3$ organic component introduced by the MTES precursor. The $Si–CH_3$ is thermally stable up to 400 °C. The calcination of the films is accompanied by the usual decrease in the intensity of the Si–OH stretching band around 940 cm^{-1}, indicating the formation of Si–O–Si linkages observed at 1045 cm^{-1} in the hybrid network due to polycondensation.[14]

Hybrid silica films were also studied by FTIR spectroscopy for increasing MTES content. All spectra recorded for the films cured at 400 °C are shown in Fig. 3b. The silanol groups remain clearly stable at 400 °C for lower MTES/(MTES + TEOS) content (from 0 to 0.25), suggesting that the dehydration does not occur even at high temperatures for inorganic and hybrid silica films. The noticeable features are the decrease of the bands due to the hydroxyl vibration (at 3000–3800 cm^{-1} and 1640 cm^{-1}) and the increase of the bands due to the methyl groups (Fig. 3c, at 2972, 1272 and 777 cm^{-1}) with increasing MTES/(MTES + TEOS) content. The first band is due to the interaction of water molecules *via* hydrogen bonds with Si–OH groups inside the pores. The other samples, which contain less or no Si–OH groups (as is evident from the low intensity or absence of Si–OH peak at 940 cm^{-1}) show no bands corresponding to adsorbed water. With increasing organic content in the hybrid silica network, a shift of the main Si–O–Si vibration from 1074 to 1031 cm^{-1} was observed, indicating the loss of the Si–O–Si framework by the substitution of $Si–CH_3$.[15] This shift shows that the degree of cross-linking of the silica network changes if methyl groups are added to the system.[16] Furthermore, the intensity of the peaks due to the methyl groups ($–CH_3$ stretch at 2975 cm^{-1}, $–CH_3$ deformation at 1272 and $Si–CH_3$ at 777 cm^{-1} in Fig. 3c) gradually increases with increasing methyl content. This behavior suggests a gradual extension of the hydrophobic–hydrophilic balance of the hybrid silica surface.

3.4. Contact angle measurement

The water contact angle was measured in static mode on the surface of hybrid silica films coated on glass. The water contact angle results were presented *versus* the MTES/(MTES + TEOS) ratio in Fig. 4. The values show a trend of increase of the contact angle with the increase in the concentration of MTES in the starting solution. The coating prepared with a pure TEOS precursor shows a lower contact angle of 12° indicating a hydrophilic character and that with the higher MTES content shows a higher contact angle of 88° indicating a hydrophobic nature. The result obtained for the silica surface shows that the hydrophilic behavior becomes gradually hydrophobic by adding MTES to TEOS. This behavior is likely due to the presence of more and more pendant methyl groups, whose concentration increased with the MTES/TEOS ratio as revealed by FTIR measurement (Fig. 3c). Using a one-pot co-condensation of increasing contents of MTES and TEOS thus allows tuning gradually the hydrophobic–hydrophilic balance of the surface of

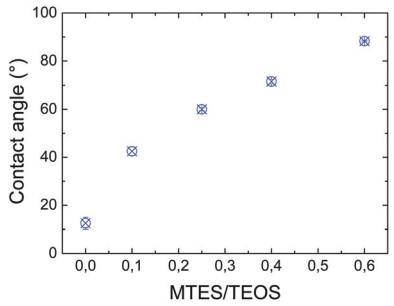

Fig. 4 Evolution of the water contact angle measured on the surface of the hybrid silica films as a function of the MTES/TEOS ratio.

the silica films. These results are consistent with the FTIR measurement that shows that the fraction of hydrophilic silanol groups decreases as the fraction of hydrophobic methyl groups increases.

3.5. Optical properties of hybrid mesoporous dielectric multilayers

By alternating a multiple spin-coating of hybrid silica and titania precursor solutions on the glass substrate, we were able to build a hybrid mesoporous dielectric multilayer consisting of 3 bilayers. The material was fabricated with a good structural and optical quality over an area of 2.5 cm × 2.5 cm. The mesoporous dielectric multilayers were crack-free and did not present delamination during the coating procedure, thanks to the method employed for curing. It is important to point out that it was not possible to fabricate a multilayer from a hybrid solution with the MTES/(MTES + TEOS) content higher than 0.6. A likely explanation for this is that the presence of a very low amount of Si–OH groups at high MTES/(MTES + TEOS) content (over 0.6) would not provide sufficient ligands to bond the coating to the substrate. Indeed, the presence of hydrophilic ligands was a *sine qua non* condition for the hybrid silica coating solution to form uniform, continuous thin-film coatings on the inorganic substrate. The thickness of each layer is very uniform over a cross-sectional area as is shown for all 1D photonic crystals in Fig. 5. The high-density hybrid silica regions are much darker than the low density titania layers. The thicknesses of the titania layers were homogeneous whatever the system was, suggesting that hybrid silica layers did not affect their thicknesses. However, the hybrid silica layers present a decrease of the thickness for a MTES/TEOS ratio over 0.4 (ESI†). The optical properties of the hybrid mesoporous dielectric multilayers were measured between 250 and 1000 nm by UV-Vis-NIR spectroscopy. The spectra were obtained after rinsing the samples in ethanol (Soxhlet technique) and drying under a N_2 atmosphere. The absolute transmittance of the sample was determined by adequate calibration. All samples exhibit a deep drop in transmittance in the visible region, thanks to the suitable layer thicknesses. In Fig. 6a, the Bragg reflection peaks observed are a direct consequence of the large refractive index contrast between the SiO_2 layers and the TiO_2 ones. As shown in the transmittance spectra (Fig. 6a), changing the MTES/(MTES + TEOS) ratio, which induced a change in the hydrophilicity, also induces a shift of the Bragg peak positions at 461, 520, 571, and 626 nm,

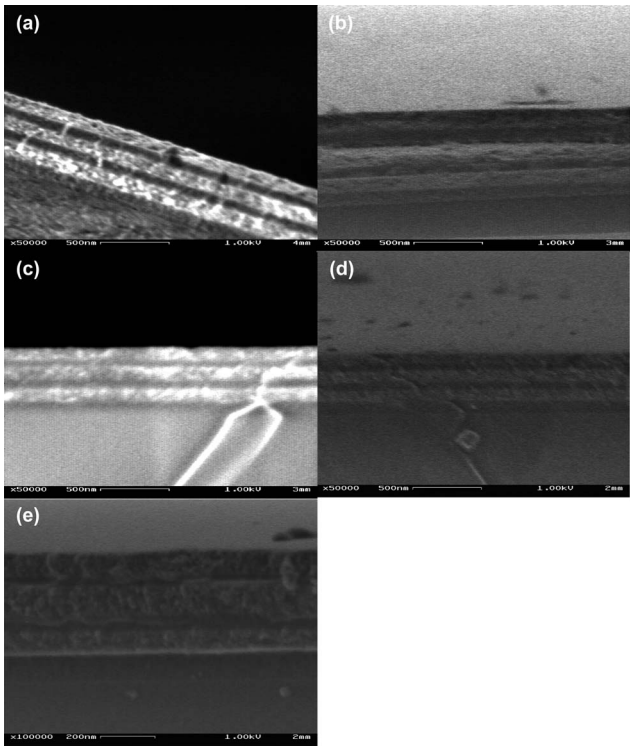

Fig. 5 SEM cross-sectional view of (a) 3 × SiO_2/TiO_2, (b) 3 × $SiC_{0.1}/TiO_2$, (c) 3 × $SiC_{0.25}/TiO_2$, (d) 3 × $SiC_{0.4}/TiO_2$, and (e) 3 × $SiC_{0.6}/TiO_2$ multilayer.

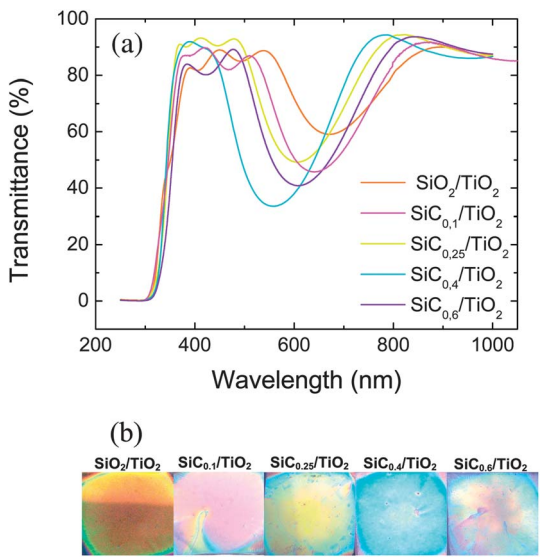

Fig. 6 (a) Experimental transmittance spectra of multilayers consisting of three layers with increasing MTES/TEOS ratio. (b) Photographs of the color variation of the multilayers with variable MTES/TEOS ratios.

respectively, as well as an increase in the dips of the transmittance bands. According to Bragg's law,[17] to explain the change of the Bragg peak intensity, the variation of the optical refractive index of silica layers must be considered, namely, lowering the refractive index of the silica layer by hybridization increases the dielectric contrast between the films. The refractive index of the silica layer was reported to be lower when silanols were replaced

by methyl groups.[18] The Si–CH_3 groups induce a less important shrinkage in the hybrid silica framework reducing the Si–O–Si linkage and forming a porous phase around the pendant methyl groups[19] since these cannot condense. These are known to lower the density of hybrid sol–gel matrices because of steric hindrance.[20]

Refractive index measurements for hybrid silica and titania bilayers were performed under a N_2 atmosphere according to the literature. The models of bilayer stacks, the porous silica as well as the porous titania layers, are fitted using the Cauchy dispersion model for dielectric materials. Cauchy 1 represents the silica materials and Cauchy 2 stands for the titania layers. This model described the structure of titania and silica films.[21] The refractive index values of each layer were obtained from the best fit along its normal direction at a relative humidity of 0% (dry atmosphere). The results presented in Table 1, contrary to the literature, show that the refractive index of the hybrid silica layers remains relatively constant with a minimum for a MTES/TEOS content ratio of 0.4, however, that of the titania layers increases. The refractive index of the titania film increased until reaching a maximum at 1.82 for the $SiC_{0.6}/TiO_2$ system. This is consistent with the evolution of the contrast for the mesoporous dielectric multilayers. The variation of the refractive index of the titania layers as well as the variation of the thickness of the period of the films could explain the shift of the Bragg peak position to a lower wavelength.[7] The refractive index change could be attributed to the difference in the interfacial tension between the adjacent layers. The loss of the porosity of titania films grown on different silica layers is calculated by making a comparison of the total porosity for all films.[10] Regarding the refractive index of the titania films, measured by ellipsometric spectroscopy for the bilayer system, the porosity loss is 6.3% (for TiO_2 coated $SiC_{0.1}$), 1.8% (for TiO_2 coated $SiC_{0.25}$), 6.3% (for TiO_2 coated $SiC_{0.4}$) and 15% (for TiO_2 coated $SiC_{0.6}$) of the total porosity (in comparison with the total porosity of the titanium film grown on SiO_2). The total porosity of the titanium layer as well as the hydrophilic–hydrophobic balance of the silica layer decreases. However, the accessible porosity remains the most important parameter for the MDM system. Indeed, open porosity of titania and silica layers which compose the 1D photonic crystals enables the infiltration of molecules and then changes the Bragg resonance maximum. The adsorption–desorption isotherm was then determined by fitting the $n = F(\mathrm{RH})$ curve at each RH in order to determine open porosity of the water-saturated mesoporous films. The open porosity measured for titania films grown on silica layers which have a variable hydrophilic–hydrophobic balance (ESI†) shows an identical hysteresis loop for all titania samples. The open porosity of the films varies from 32.6% for TiO_2 grown on SiO_2 to 26.8% for $TiO_2/SiOC_{0.6}$. The open porosity remains close to ~30% when the MTES/TEOS ratio increases up to 0.25, and a slight decrease was observed over that value. The result suggests an identical mesostructure for all titania films whatever the MTES/TEOS ratio. This result suggests that no change in the mesostructure of the titania films occurred and they remained porous.

Table 1 Refractive indices of silica and titania films for bilayer systems[a]

Refractive index	SiO_2/TiO_2	$SiC_{0.1}/TiO_2$	$SiC_{0.25}/TiO_2$	$SiC_{0.4}/TiO_2$	$SiC_{0.6}/TiO_2$
n_1	1.31	1.29	1.29	1.18	1.29
n_2	1.59	1.69	1.62	1.69	1.82

[a] n_1 and n_2 are the refractive indices measured under a N_2 atmosphere for silica and titania layers, respectively, for bilayer systems.

The photographs taken of the mesoporous dielectric multilayers displayed uniform colors over a large area with minimal accidental striation due to the coating method (Fig. 6b). The colors of the mesoporous dielectric multilayers change from red to blue with the increase of the MTES/(MTES + TEOS) content ratio, in accordance with the shift of the Bragg peak position. By varying the MTES/(MTES + TEOS) content ratio of the hybrid silica layers, one is able to modulate the Bragg-peak position and hence the film color over the visible range. The MTES/(MTES + TEOS) content ratio could constitute an additional control parameter of the Bragg peak of the 1D photonic crystal, besides thickness[7,22] and porosity.[7]

3.6. Sensitivity and selectivity of the mesoporous dielectric multilayer

In this part, we explore the optical response of the mesoporous dielectric multilayer toward different analyte uptakes as a function of the hydrophobic–hydrophilic balance of the silica surface. First, the *dry* state was considered as that in which all accessible pores of the system are filled with air (Fig. 7a). The *wet* state was defined as that in which the molecules (water or hexane) are present in all the accessible pores of the system. The latter state was achieved after immersion of the samples into water or hexane solution. Then subsequent diffusion of the analytes into the accessible pores occurs. Pore size differences between layers, smaller pores in silica layers (diameter $d = 3$ nm) and larger pores in titania layers ($d = 6$ nm) enable capillary attraction in a liquid medium. Indeed, the pore size distribution in adjacent layers was reported to play a key role in liquid infiltration throughout the mesoporous dielectric structure.[13,23] The measurement was performed immediately after the removal of the sample from the analyte solution in order to minimize the evaporation from the system. Fig. 7a shows the spectral response of the mesoporous dielectric multilayer ($3 \times SiO_2/TiO_2$) immersed into water or hexane solutions. As illustrated in Fig. 7a, a red-shift of the Bragg reflection peak (both in intensity and wavelength) was observed between the *dry* state and the *wet* state, confirming the sensitivity of the porous multilayer system to the presence (dotted line)/absence (solid line) of analytes in the pores. This optical change was induced by changing the effective refractive index of the mesoporous system by filling pores with water or hexane. These results demonstrate that the prepared mesoporous dielectric multilayer has potential in chemical optical sensing of the change in the environment as reported by other groups.[6,7] The Bragg reflection peak was reported to be shifted to a higher wavelength that caused a color change of the multilayer when the pores of the system were filled by foreign compounds.[6] That shift was often correlated with the refractive index of the analytes filling the pores of the mesoporous system.[6,23] However, a correlation between the optical response and the refractive index of analytes adsorbed into the pore ($n_{H_2O} = 1.333$ and $n_{\mathrm{Hexane}} = 1.375$) was not obtained. In this case, the physical properties of

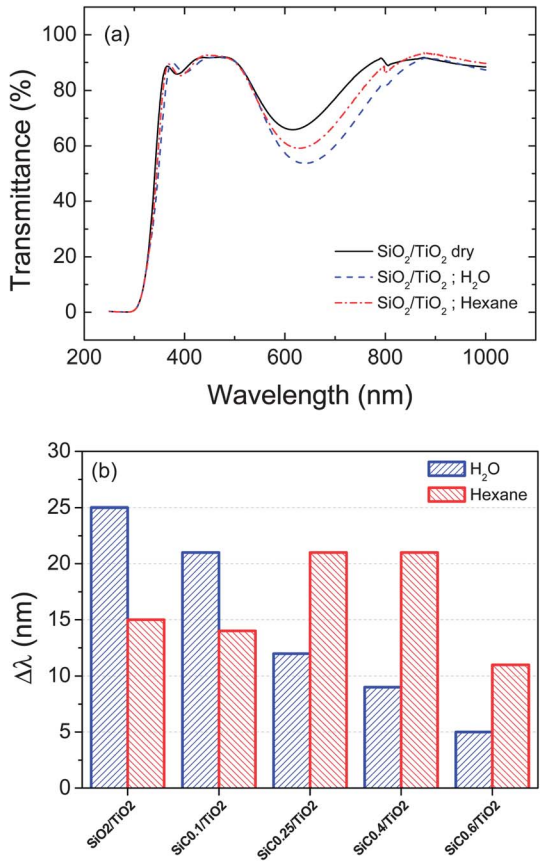

Fig. 7 (a) Optical response of the 3 bilayers of SiO_2/TiO_2 in the dry condition (black) and after soaking in H_2O (blue) and hexane (red). (b) Spectral shift of the Bragg resonance of the multilayers as a function of the MTES/TEOS ratio and the nature of the solution.

the silica and titania layers could play an important role during the analyte intrusion. Variable optical response was observed by tuning the hydrophobic–hydrophilic balance of the silica surface in the multilayer system. Fig. 7b shows the $\Delta\lambda$ (difference between the Bragg peak maximum measured in dry and wet states) obtained after soaking each system in water and hexane. The optical shift was larger for water than for hexane when the MTES/(MTES + TEOS) content was up to 0.25. Above this value, the spectral shift for hexane became higher than that observed for water. The spectral shift measured in the case of water decreases gradually with respect to the hydrophobic–hydrophilic balance. The water molecules are kept outside the silica layers due to the surface affinity which reduces their presence inside the structure channels, whereas hexane has more affinity to the hydrophobic silica pore surface and thus penetrates more easily. These results demonstrate that tuning the hydrophobic–hydrophilic balance of the silica layers allows modulation of the selectivity and the sensitivity of the mesoporous dielectric multilayer. This constitutes an alternative synthetic route to that previously reported[6,7] in order to tune the chemical surface compositions of the mesoporous Bragg reflector for sensing target molecules.

4. Conclusion

We have demonstrated that it is possible to tune-up the hydrophobic–hydrophilic balance of the hybrid mesoporous silica layer by varying the MTES/(MTES + TEOS) ratio used during the one-pot self-assembly inorganic–organic solution synthesis method. This was found to be related to an increase in the concentration of pendant methyl groups of the films. Alternation of the hybrid silica and mesoporous titania layers was easily achieved giving a Bragg reflection peak in the visible range. We show that tuning the hydrophobic–hydrophilic balance of the silica surface modifies the affinity of the mesoporous dielectric multilayer to the environment. The sensitivity and the selectivity of the mesoporous dielectric multilayer are highly dependent on the surface properties of the metal oxides.

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