Available online at www.sciencedirect.com
SCIENCE DIRECT®
Mendeleev Commun., 2007, **17**, 1–3
Mendeleev Communications

Structural and optical properties of titania photonic crystal films prepared by a sol–gel method

Alexander S. Sinitskii,*[a] Vera V. Abramova[a] and Yuri D. Tretyakov[a,b]

[a] *Department of Materials Science, M. V. Lomonosov Moscow State University, 119992 Moscow, Russian Federation. Fax: +7 495 939 0998; e-mail: sinitsky@inorg.chem.msu.ru*
[b] *Department of Chemistry, M. V. Lomonosov Moscow State University, 119992 Moscow, Russian Federation*

DOI: 10.1016/j.mencom.2007.01.001

Photonic crystals based on titania with interconnected spherical voids were synthesised by replicating polystyrene microsphere templates to study their structural and optical properties.

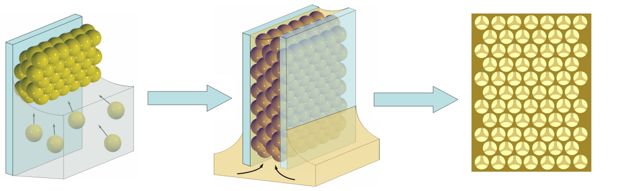
Photonic crystals (PCs) are of considerable interest due to unique possibilities that they offer in having control over photons.[1] PCs are predicted to exhibit a photonic band gap (PBG), for which light within a certain frequency range cannot propagate in any direction (full PBG) or some directions (stop-band) inside the crystals, causing the unique properties of PCs, such as the localization of light and the control of spontaneous emission. Many applications of PCs have been proposed, ranging from low-threshold lasers and high-efficient light emitting diodes to perfect dielectric mirrors and planar waveguides.[2]

From the standpoint of materials science, PCs are dielectric composites with a highly periodic structure, in which the refractive index varies on the scale of visible light wavelength. The key to making PCs is the requirement to synthesise an ordered dielectric lattice of materials with a high refractive index contrast n_2/n_1, where n_2 and n_1 refer to the high and low refractive indices in the structure.[1] For this reason, PCs made of ordered spherical voids in titania are of great interest since TiO_2 possesses both a high refractive index (~2.5–2.9, depending on the crystalline phase[3]) and low absorption in the visible region. Moreover, according to theoretical calculations for PCs consisted of close-packed air spheres in a high dielectric material, full PBG should appear at a refractive index contrast, which is very close to that in titania PCs.[4] Even though the full PBG was not experimentally demonstrated for titania PCs, their optical properties were successfully used, for instance, for controlling the dynamics of spontaneous emission from quantum dots[5] and increasing the conversation efficiency of photoelectrochemical cells.[6]

Apart from several promising techniques, such as co-sedimentation of latex microspheres and ultrafine titania colloidal particles,[7] atomic layer deposition[8] and X-ray lithography,[9] a sol–gel method is usually considered as the simplest route towards titania PCs.[6,10–18] In this method, a colloidal crystal composed of silica or latex monodisperse microspheres is used as a template; interstitial voids between the spheres are infiltrated with alkoxide precursors of TiO_2[11–16] or a titania sol;[17,18] after gelation, the initial spheres are selectively removed by an appropriate method. Here we report the preparation and optical study of PC films based on titania; angular transmission measurements allowed the estimation of the effective refractive index of PCs and the refractive index of a titania framework.

Titania PCs were prepared using a templating technique similar to that described previously[19] for the synthesis of PCs made of ordered spherical voids in silica (Figure 1). For template preparation, monodisperse polystyrene microspheres with an average diameter of 440 nm and relative standard deviation less than 5% were synthesised by the emulsifier-free emulsion polymerization of styrene using potassium persulfate as an initiator.[20] Colloids were centrifuged and re-dispersed in distilled water by ultrasonication. Colloidal crystal films made of polystyrene microspheres were prepared by the vertical deposition method.[21] Glass microslides were thoroughly cleaned and immersed in a ~1 vol% aqueous suspension of microspheres; the temperature of film growth was 45 °C [Figure 1(*a*)]. The samples were left undisturbed until the growth of films was completed. Finally, colloidal crystal films were annealed at 110 °C for 10 min to improve their mechanical stability. A scanning electron microscopy (SEM) image (LEO Supra VP 50 instru-ment) of the film reveals the close-packed arrangement of polystyrene colloids (Figure 2).

The reaction mixture for infiltrating colloidal crystals was prepared by diluting reagent-grade titanium(IV) butoxide (TBT) with absolute ethanol in a ratio from 1:10 to 1:2. Colloidal crystal films were vertically dipped into the reaction mixture so that the lower edge of the film was 1 or 2 mm beneath the surface of the liquid. Driven by capillary forces, the liquid filled the interstitial space of the film. When using a viscous reaction mixture with a high TBT content, the films were covered with



(*a*) (*b*) (*c*)

Figure 1 Schematic diagram for fabricating titania PCs. See the text for details.

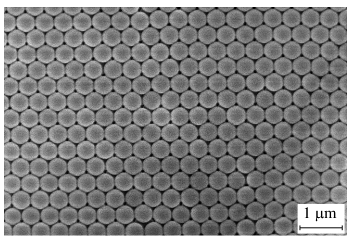


Figure 2 SEM image of a colloidal crystal film made of 410 nm polystyrene microspheres.

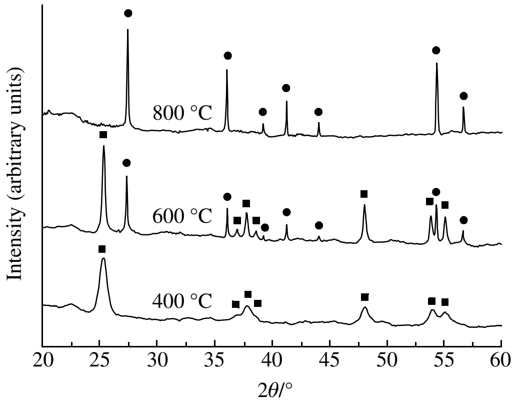


Figure 3 XRD patterns for titania synthesised by the hydrolysis of TBT and annealed at 400, 600 and 800 °C for 1 h. Squares and circles indicate anatase and rutile peaks, respectively.

glass microslides to facilitate the lift of the liquid [Figure 1(*b*)]. After that, the samples were dried in air for 24 h (the auxiliary microslide was carefully removed, if used), resulting in the hydrolysis of TBT by air moisture. Up to five infiltration–drying cycles were used to incorporate more material into the template voids.

In order to determine the optimal temperature for the heat treatment of the samples, a preliminary experiment on the annealing of hydrolysed TBT was performed. TBT was mixed with an excess of distilled water; the hydrated titania sol was paper-filtered and dried in air. Specimens of about 0.5 g were annealed in the temperature range 400–800 °C with a 100 °C step for 1 h. The phase composition was studied by X-ray powder diffraction (XRD) using a DRON-3M diffractometer with filtered CuKα radiation. Selected XRD spectra for titania annealed at 400, 600 and 800 °C are shown in Figure 3. The XRD spectrum of a sample annealed at 400 °C can be attributed to crystalline anatase, which persists at 500 °C. A polymorphic transformation from anatase to rutile is observable at 600 °C, since the corresponding XRD spectrum represents the peaks of both phases, and completed at 800 °C.

Based on these results, we heated the titania–polystyrene composite up to 500 °C at a rate of 1 K min^{-1} and annealed it for 1 h to remove the polystyrene template and thus obtain a porous anatase framework (Figure 1). Even though the refractive index of rutile is higher than that of anatase, we used the temperature of 500 °C because the ordering of a porous titania framework can be affected by recrystallization of TiO_2 at a higher temperature.[15]

The SEM observations demonstrate that better samples were obtained when using highly diluted solutions of TBT and a relatively small number of infiltration–drying cycles. The use of viscous reaction mixtures results in slow infiltration, despite the auxiliary glass microslide. The optimal number of infiltration cycles depends on TBT concentration in the reaction mixture. Further dipping of the titania–polystyrene composite into a reaction mixture results in the formation of an oxide film on the top surface of the colloidal crystal (Figure 4).

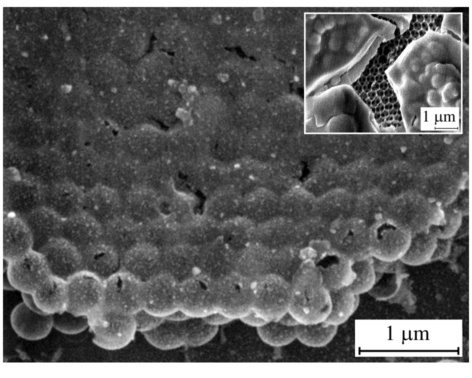


Figure 4 SEM images of porous titania frameworks covered with a solid oxide film. The samples were obtained from 1:5 TBT/ethanol reaction mixtures using three and five (in the inset) infiltration–drying cycles.

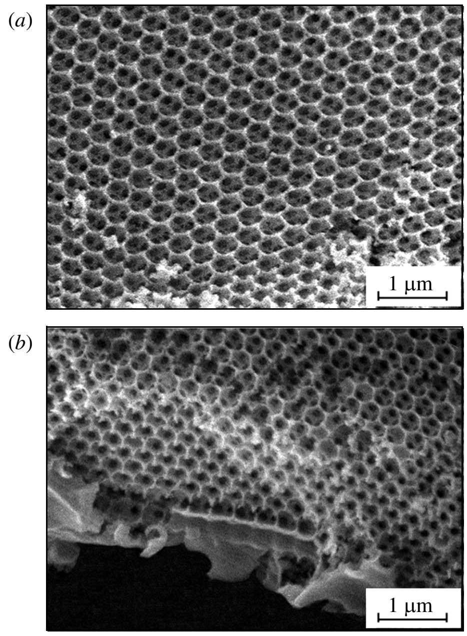


Figure 5 SEM images of a titania PC film: (*a*) top surface and (*b*) cross-section.

The SEM images of the porous titania sample (TBT/ethanol ratio of 1:5; two infiltration–drying cycles) are shown in Figure 5. The image of the top surface demonstrates that the spherical voids in the oxide framework have a hexagonal arrangement, inherited from the colloidal crystal [Figure 5(*a*)]. The average center-to-center distance between the spherical voids is 370 nm. Since the average size of polystyrene microspheres used for the template preparation was 440 nm, the sample shrinkage due to the removal of volatile components (mainly water and carbon oxides) can be estimated as 16%. The cross-sectional SEM image was taken to show that the film consisted of about 10 close-packed layers of spherical voids [Figure 5(*b*)].

According to Zakhidov *et al.*,[21] two situations are possible when templating a colloidal crystal. The complete filling of the voids with a reaction mixture was referred to as volume templating, while partial filling, when the liquid precursor covers only the surface of colloidal spheres, was termed as surface templating. The latter results in the formation of a porous framework, which can be interpreted as a system of interconnected hollow spheres.[21] Such hollow anatase spheres can be observed in the SEM pictures of disordered regions of titania

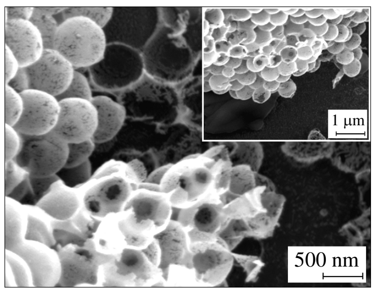


Figure 6 SEM images of hollow titania microspheres at different magnifications.

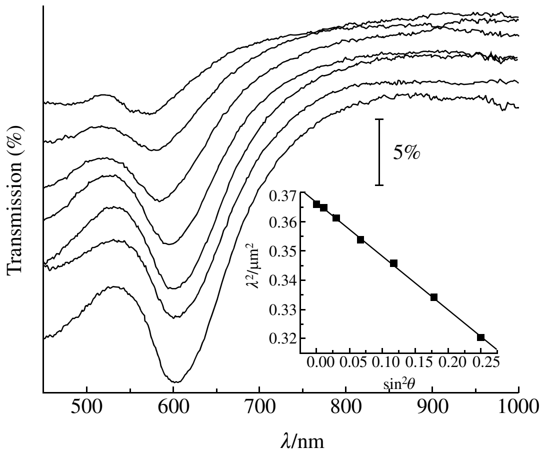


Figure 7 The transmission spectra of titania PC films measured at different angles of incidence θ; from bottom to top: θ = 0, 5, 10, 15, 20, 25 and 30°. Spectra have the same coordinate range and were shifted vertically for the sake of clarity. In the inset: the plot of λ^2 *vs.* $\sin^2\theta$ (where λ is the wavelength of the minimum of transmission and θ is the angle of incidence) and the linear fit to the experimental data.

PC films (Figure 6), suggesting that the filling of the template void volume with a reaction mixture was not complete.

Since the thickness of the titania PC films was only several micrometers, it was possible to characterise them by optical transmission spectroscopy. The spectra were measured in the wavelength range 200–1100 nm using a Perkin–Elmer Lambda 35 double-beam spectrophotometer. The transmission spectra recorded at different incident angles θ with respect to the normal to the sample are shown in Figure 7. Each spectrum represents a pronounced drop in transmission, corresponding to the stop-band in the <111> direction.[22–24] The position of this minimum shifts to shorter wavelengths with the incidence angle obeying the Bragg–Snell law

$$\lambda = 2d\sqrt{n_{\mathrm{eff}}^2 - \sin^2\theta},$$

where λ is the wavelength of radiation in a vacuum, d is the interplanar spacing and n_{eff} is the effective (average) refractive index of a titania–air medium. The effective refractive index can be determined from the λ^2 *vs.* $\sin^2\theta$ plot (see the inset in Figure 7) because a linear fit to the experimental data has a gradient of $-4d^2$ and an intercept equal to $4d^2n_{\mathrm{eff}}^2$. The calculated value of n_{eff} is about 1.40. The effective refractive index can also be expressed as

$$n_{\mathrm{eff}} = n_{\mathrm{air}}f_{\mathrm{air}} + n_{\mathrm{TiO_2}}(1 - f_{\mathrm{air}}),$$

where $n_{\mathrm{air}} \approx 1$ and $n_{\mathrm{TiO_2}}$ are the refractive indices of air and titania, respectively, and f_{air} is the volume fraction occupied by spherical voids in a PC structure. For an ideal close-packed structure, $f_{\mathrm{air}} \approx 0.74$ resulting in $n_{\mathrm{TiO_2}}$ equal to 2.54. This value is in a good agreement with the refractive index of anatase (2.48–2.56[3]), even though the actual value of f_{air} is higher than 0.74 because the titania framework is surface templated.

Thus, we reported the synthesis of titania PC films by a sol–gel method. The thickness of these films is less than 15 layers of close-packed spherical voids, which makes the samples transparent to light, but still allows exhibiting PBG properties. The titania PC films obtained are of potential interest for doping with various luminescent materials like quantum dots[5] and compounds of rare-earth elements.[25]

This work was supported by the Russian Foundation for Basic Research (grant nos. 05-03-32778 and 04-03-39010), the Programme for Fundamental Research of the Russian Academy of Sciences and the Federal Target Science and Engineering Programme (grant no. 02.434.11.2009). We are grateful to Dr. A. G. Veresov for the SEM study of samples.

References

1 J. D. Joannopoulos, R. D. Meade and J. N. Winn, *Photonic Crystals: Molding the Flow of Light*, Princeton University Press, New Jersey, 1995.
2 T. F. Krauss and R. M. De La Rue, *Prog. Quantum Electr.*, 1999, **23**, 51.
3 *CRC Handbook of Chemistry and Physics*, ed. D. R. Lide, CRC Press, Boca Raton, Florida, 1995–1996, vol. 76.
4 K. Busch and S. John, *Phys. Rev. E*, 1998, **58**, 3896.
5 P. Lodahl, A. F. Van Driel, I. S. Nikolaev, A. Irman, K. Overgaag, D. Vanmaekelbergh and W. L. Vos, *Nature*, 2004, **430**, 654.
6 L. I. Halaoui, N. M. Abrams and T. E. Mallouk, *J. Chem. Phys. B*, 2005, **109**, 6334.
7 G. Subramanian, V. N. Monoharan, J. D. Thorne and D. J. Pine, *Adv. Mater.*, 1999, **11**, 1261.
8 J. S. King, E. Graugnard and C. J. Summers, *Adv. Mater.*, 2005, **17** 1010.
9 K. Awazu, X. Wang, M. Fujimaki, T. Kuriyama, A. Sai, Y. Ohki and H. Imai, *J. Vac. Sci. Technol. B*, 2005, **23**, 934.
10 J. E. G. J. Wijnhoven and W. L. Vos, *Science*, 1998, **281**, 802.
11 B. T. Holland, C. F. Blanford and A. Stein, *Science*, 1998, **281**, 538.
12 B. T. Holland, C. F. Blanford, T. Do and A. Stein, *Chem. Mater.*, 1999, **11**, 795.
13 S. Nishimura, A. Shishido, N. Abrams and T. E. Mallouk, *Appl. Phys. Lett.*, 2002, **81**, 4532.
14 M. E. Turner, T. J. Trentler and V. L. Colvin, *Adv. Mater.*, 2001, **13**, 180.
15 J. E. G. J. Wijnhoven, L. Bechger and W. L. Vos, *Chem. Mater.*, 2001, **13**, 4486.
16 A. Richel, N. P. Johnson and D. W. McComb, *Appl. Phys. Lett.*, 2000, **76**, 1816.
17 S.-L. Kuai, V.-V. Troung, A. Hache and X.-F. Hu, *J. Appl. Phys.*, 2004, **96**, 5982.
18 S. Kuai, S. Badilescu, G. Bader, R. Bruning, X. Hu and V.-V. Truong, *Adv. Mater.*, 2003, **15**, 73.
19 P. E. Khokhlov, A. S. Sinitskii and Yu. D. Tretyakov, *Dokl. Akad. Nauk*, 2006, **408**, 59 [*Dokl. Chem.* (*Engl. Transl.*), 2006, **408**, 61].
20 P. Jiang, J. F. Bertone, K. S. Hwang and V. Colvin, *Chem. Mater.*, 1999, **11**, 2132.
21 A. A. Zakhidov, R. H. Baughman, Z. Iqbal, C. Cui, I. Khayrullin, S. O. Dantas, J. Marti and V. G. Ralchenko, *Science*, 1998, **282**, 897.
22 V. N. Astratov, V. N. Bogomolov, A. A. Kaplyanskii, A. V. Prokofiev, L. A. Samoilovich, S. M. Samoilovich and Yu. A. Vlasov, *Nuovo Cimento D*, 1995, **17**, 1349.
23 A. S. Sinitskii, A. V. Knotko and Yu. D. Tret'yakov, *Neorg. Mater.*, 2005, **41**, 1336 [*Inorg. Mater.* (*Engl. Transl.*), 2005, **41**, 1178].
24 A. S. Sinitskii, S. O. Klimonsky, A. V. Garshev, A. E. Primenko and Yu. D. Tretyakov, *Mendeleev Commun.*, 2004, 165.
25 A. S. Sinitskii, S. O. Klimonsky, Yu. D. Tretyakov, M. Li, J. Li and J. Zhou, *Proceedings of SPIE*, 2006, **6182**, pp. 571–577.

Received: 15th August 2006; Com. 06/2773