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Thick and Crack-Free Nanocrystalline Mesoporous TiO_2 Films Obtained by Capillary Coating from Aqueous Solutions

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Organized mesoporous crystalline metal oxide coatings are a very active area of research as there are a vast array of potential applications, such as energy conversion and storage, catalysis, advanced analysis, or microelectronics.[1] The synthesis of such films by the evaporation induced self-assembly (EISA) approach, which combines chemical solution deposition (CSD), sol−gel chemistry, and block copolymer templating, appears to now be well-mastered.[2] However, important drawbacks are associated with this method. First, initial solutions are composed of organic solvents, whereas environmentally friendly processes require working in water. Second, final film thicknesses are usually limited to only several hundreds of nanometers[3,4] because cracks and delamination often develop during thermal treatment for thicker films. Finally, achieving a stable and reproducible ordered pore network necessitates precise control and time consumming repetitive coating;[1] however, there is a strong demand for facile methods to produce structured materials.[5] Among the reported mesoporous materials, TiO_2 is the second most studied system after silica, because of its interesting semiconduction properties, making it an important material for gas sensors,[6,7] photocatalysts,[8] dye-sensitized solar cells,[9,10] lithium ion batteries,[11] pseudocapacitors,[12] etc. Mesoporosity has a critical role in such materials since high surface area and nano-ordering promote a high density exiton generation and a low degree of charge recombination as recentely observed by Zhang et al.[10] With the goal of simplifying the existing preparation procedures to better meet industrial production requirements, the present communication reports an improved and easiest method to prepare mesoporous anatase TiO_2 films with the following accomplishments: (i) crack-free and very thick (several μm) films obtained; (ii) purely aqueous and inexpensive precursor solutions used; (iii) rapid and simple process. Besides the process could be extended to other crystalline oxide mesoporous films.

The films were prepared through a non conventional multilayer deposition process. Before going into detail about the experimental protocol, we will present the high degree of control provided by this process. A full structural characterization of a thick anatase TiO_2 layer is presented in Figure 1. First, ellipsometry investigations revealed that the film can be fitted using a crack-free and transparent single Cauchy layer model between 350 and 1000 nm in wavelength, as expected for a TiO_2 layer of high optical quality. Its physical thickness and refractive index were found to be 1800 nm and 1.65, respectively. A typical SEM-FEG micrograph for this material (Figure 1a) demonstrates that the surface of the film contains ordered perforations, with a periodical correlation distance of 11 nm. The GI-SAXS pattern in Figure 1b confirms this nanostructure. The two intense Bragg-diffraction points in the y-direction at $q_y = 0.58\ \text{nm}^{-1}$ are characteristic of diffracting planes with an interspacing distance of 10.8 nm, and that are perpendicular to the surface of the coating. The above results are typical of a gridlike structure formed through the thermally induced transformation of an initial [110] orientated Im3m mesostructure.[13]

Moreover mesoordering must be associated with a narrow pore size distribution, which is confirmed by the environmental ellipsometry porosimetry (EEP) experiment[16] in Figure 1c. The isotherm of water adsorption/desorption reveals that the material contains 50% pore volume, with a homogeneous pore size distribution centered around 9 nm in diameter (larger axis) throughout the whole thickness of the film[14] (spherical model). Experimental details concerning structural and microstructural characterization can be found in the Supporting Information.

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(1) Sanchez, C.; Boissière, C.; Grosso, D.; Laberty, C.; Nicole, L. *Chem. Mater*. **2008**, *20*, 682–737.
(2) Crepaldi, E. L.; De, A. A.; Soler-Illia, G. J.; Grosso, D.; Cagnol, F.; Ribot, F.; Sanchez, C. *J. Am. Chem. Soc*. **2003**, *125*, 9770–86.
(3) Bartl, M. H.; Boettcher, S. W.; Frindell, K. L.; Stucky, G. D. *Acc. Chem. Res*. **2005**, *38*, 263–71.
(4) Fuertes, M.; Colodrero, S.; Lozano, G.; Gonzalez-Elipe, A.; Grosso, D.; Boissiere, C.; Sanchez, C.; de, A. A.; Soler-Illia, G.; Miguez, H. *J. Phys. Chem. C* **2008**, *112*, 3157–3163.
(5) Drisko, G. L.; Zelcer, A.; Luca, V.; Caruso, R. A.; De, A. A.; Soler-Illia, G. J. *Chem. Mater*. **2010**, *22*, 4379–4385.
(6) Sokolov, S.; Ortel, E.; Kraehnert, R. *Mater. Res. Bull*. **2009**, *44*, 2222–2227.
(7) Strandwitz, N. C.; Nonoguchi, Y.; Boettcher, S. W.; Stucky, G. D. *Langmuir* **2010**, *26*, 5319–22.
(8) Yun, H.; Zhou, H.; Honma, I. *J. Inorg. Org. Polym. Mater*. **2006**, *16*, 169–173.
(9) Kim, Y. J.; Lee, Y. H.; Lee, M. H.; Kim, H. J.; Pan, J. H.; Lim, G. I.; Choi, Y. S.; Kim, K.; Park, N.; Lee, C.; Lee, W. I. *Langmuir* **2008**, *24*, 13225–30.
(10) Zhang, Y.; Xie, Z.; Wang, J. *ACS Applied Mater. Interfaces* **2009**, *1*, 2789–95.
(11) Dambournet, D.; Belharouak, I.; Amine, K. *Chem. Mater*. **2010**, *22*, 1173–1179.
(12) Brezesinski, T.; Wang, J.; Tolbert, S. H.; Dunn, B. J. Sol−Gel Sci. Technol. **2010**.
(13) Grosso, D.; De, A. A.; Soler-illia, G. J.; Crepaldi, E. L.; Cagnol, F.; Sinturel, C.; Bourgeois, A.; Brunet-bruneau, A.; Amenitsch, H.; Albouy, P. A.; Sanchez, C. *Chem. Mater*. **2003**, 4562–4570.
(14) Boissiere, C.; Grosso, D.; Lepoutre, S.; Nicole, L.; Bruneau, A. B.; Sanchez, C. *Langmuir* **2005**, *21*, 12362–71.

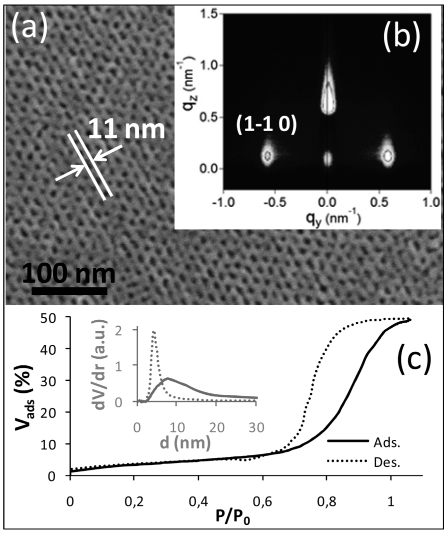

Figure 1. Microstructural characterization of 1.8 μm thick TiO_2 mesoporous film treated at 500 °C: (a) SEM image, (b) GI-SAXS pattern, (c) EEP sorption isotherm and (inset) the corresponding pore size distribution.

Two main pre-existing methodologies aimed at building up thick mesoporous films have been developed using successive deposition and thermal treatment of TiO_2 thin layers. In the first methodology, an intermediate treatment at a temperature allowing the decomposition of the organic template and the crystallization of the inorganic network is applied.[15-18] However, severe damage to the mesostructure has been observed after several cycles. They were likely attributed to the infiltration of inorganic precursors within the open pore volume and to the several repetitions of thermal treatment. The second method involves a long pretreatment at a moderate temperature between each deposition to prestabilize the inorganic network without removing the organic template, in order to prevent infiltration and to partially relax the lateral stresses upon each cycle.[4] A final treatment at higher temperature is then applied to remove the template and trigger the crystallization once the desired final thickness is achieved. This latter method often requires expensive templates with high thermal stability (e.g., PB-*b*-PEO or PS-*b*-PEO) that present the drawback of being poorly soluble in conventional solvents and absolutely insoluble in water. Because in conventional CSD processes, film thickness is directly proportional to solution concentration, only thin monolayers can be prepared per coating with these templates. A great number of cycles is therefore needed to reach a significant thickness. A maximum thickness of 4 μm was achieved by stacking up to 20 coatings.[4] This is definitely not appropriate to mass production.

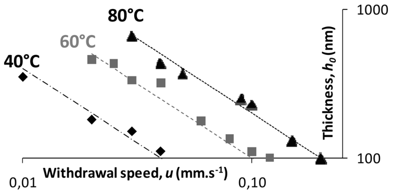

Figure 2. Plots of thickness versus withdrawal speed (log−log scale) and temperature for films calcined 5 min at 500 °C and prepared from an initial solution composed of (1 $TiCl_4$ + 60 H_2O + 5 × 10^{-3} F127 molar ratio).

To considerably simplify the latter process and to reduce the number of iterative coatings, we used the recently reported capillary regime dip-coating method (at extremely low withdrawal speeds) that allows the deposition of thick films in one step from sol−gel solutions.[19] First, we found that this procedure was fully compatible with high surface tension solutions, such as those containing water as solvent. As a result, we decided to apply this method to ultra simple H_2O, F127 block copolymer and $TiCl_4$ solutions. Although the preparation of TiO_2 powders from aqueous solutions is well-known,[20,21] only a few publications report titania film formation from aqueous solutions,[8,21,22] but these exclusively describe very thin and dense coatings synthesis. To the best of our knowledge, only one work reports the synthesis of mesoporous titania films from aqueous solutions, however they are using titanium alkoxides whose hydrolysis generates EtOH, which represents 60 vol % in total solvent.[23] Figure 2 illustrates how the final film thickness, measured by ellipsometry, varies in the capillary regime as a function of both the withdrawal speed and the evaporation temperature from an initial solution that contains 1 $TiCl_4$ + 60 H_2O + 5 × 10^{-3} F127 (molar ratio), which has simply been stirred at room temperature to complete dissolution (~24 h). $TiCl_4$ was added in cold water as a very exothermic hydrolysis reaction takes place. Thicknesses have been measured on final films treated for 5 min at 500 °C straight after deposition without need of prestabilization. The plots confirm that the final film thickness is inversely proportional to the withdrawal speed and increases with higher temperatures due to faster evaporation rates, as already described for ethanolic solutions by eq 1.[19] Applying eq 1, where h_0 is the final thickness, k is the TiO_2 proportion constant characteristic of the solution concentration and the shrinkage due to final treatment, E is the evaporation rate, L is the substrate width, and u is the withdrawal speed, to our system, the slope of the regression curves gives E/L = 1.4×10^{-10}, 3.3×10^{-10}, and 6.4×10^{-10} m^2 s^{-1} for 40, 60, and 80 °C, respectively.

$$h_0 = \left(k\frac{E}{L}\right)\frac{1}{u} \qquad (1)$$

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(15) Zukalová, M.; Procházka, J.; Zukal, A.; Yum, J. H.; Kavan, L. *Inorg. Chim. Acta* **2008**, *361*, 656–662.

(16) Procházka, J.; Kavan, L.; Shklover, V.; Zukalová, M.; Frank, O.; Kalbáč, M.; Zukal, A.; Pelouchová, H.; Janda, P.; Mocek, K.; Klementová, M.; Carbone, D. *Chem. Mater.* **2008**, *20*, 2985–2993.

(17) Procházka, J.; Kavan, L.; Zukalová, M.; Frank, O.; Kalbáč, M.; Zukal, A.; Klementová, M.; Carbone, D.; Graetzel, M. *Chem. Mater.* **2009**, *21*, 1457–1464.

(18) Ostermann, R.; Sallard, S.; Smarsly, B. M. *Phys. Chem. Chem. Phys.* **2009**, *11*, 3648–3652.

(19) Faustini, M.; Louis, B.; Albouy, P. A.; Kuemmel, M.; Grosso, D. *J. Phys. Chem. C* **2010**, *114*, 7637–7645.

(20) Di Paola, A.; Bellardita, M.; Ceccato, R.; Palmisano, L.; Parrino, F. *J. Phys. Chem. C* **2009**, *113*, 15166–15174.

(21) Kim, K.; Benkstein, K. D.; van de Lagemaat, J.; Frank, A. J. *Chem. Mater.* **2002**, *14*, 1042–1047.

(22) Kambe, S.; Nakade, S.; Wada, Y.; Kitamura, T.; Yanagida, S. *J. Mater. Chem.* **2002**, *12*, 723–728.

(23) Kirmayer, S.; Neyshtadt, S.; Keller, A.; Okopnik, D.; Frey, G. L. *Chem. Mater.* **2009**, *21*, 4387–4396.

The evaporation rate of the solution, E/L, increases with the deposition temperature since at 80 °C deposition occurs 4 times faster than at 40 °C. Humidity is important as an atmosphere saturated in water would completely prevent evaporation and therefore inhibit deposition. The thickest ($\sim$0.6 μm) crack-free film was obtained under the conditions that prompted the fastest evaporation (T = 80 °C, u = 0.03 mm s^{-1}). This thickness is far greater than what was reported thus far. The method is not limited in terms of evaporation rate and withdrawal speed, but above this maximum thickness, films starts to delaminate and crack as already reported with multilayer systems. Let it be noted that all films had the same mesostructure and optical qualities as shown in Figure 1. The latter observation suggests that neither humidity control nor slow and careful thermal treatment were required to reach a high quality of organization. This suggests that using water as solvent and the capillary regime of deposition, allow spontaneous self-assembly into well-ordered $Im3m$ mesostructures. In addition, the intermediate inorganic network appears to be more robust toward thermal treatment. This is certainly due to the chemical nature of the titanium oxo-hydroxo species formed in these solution conditions, but more research is in progress to understand the origin of this stabilization.

The thickness obtained in one single deposition step is nevertheless below the 1.8 μm reported in Figure 1. To reach this value and avoid cracks, we propose a simple and fast method, derived from the multilayer stack approach, but implemented with an intermediate step that consists of filling the pore space with F127 between each sucessive deposition, as illustrated in Figure 3. Once the first TiO_2 anatase mesoporous film is crystallized and relaxed at 500 °C, the pores are refilled with block copolymer by dipping the film in a 2×10^{-3} M F127 in ethanol at 5 mm s^{-1}. Subsequently, the second mesoporous TiO_2 layer is deposited and treated, repeating the same protocol used for the first deposition. The linear evolution of the thickness as a function of the number of cycles (Figure 3a) constitutes the evidence of the efficiency of such method since close to 1800 nm thick homogeneous films have been prepared without cracks in 4 successive depositions of 450 nm layer (T = 80 °C, u = 0.05 mm s^{-1}). The latter 4-layer coating corresponds to that analyzed in Figure 1. The linear dependence with the number of cycles is consistent with no intermixing. The intermediate thermal treatment, above the temperature of crystallization, is necessary since it allows for most of the lateral stress to be relaxed during the reorganization of the atoms by nucleation and growth of anatase nanocrystals, considerably reducing the risk of cracking.

On the other hand, because this thermal treatment completely removes organic matter from the pores, impregnation with F127 is necessary to prevent the titania precursor from penetrating the pore space upon deposition of subsequent layers. F127 incorporation is nontargeted and so, it is likely that a thin layer of F127 may also exist at the surface upon the refilling step, but it spontaneously redissolves in water upon the next CSD step. This dissolution does not concern the polymer situated within the pores as a result of the confinement-induced stabilization. SEM image in Figure 3b shows no distinguishable boundary between the two successively deposited layers, whereas the surface remains fully ordered, confirming the high homogeneity already observed by SAXS and EEP (Figure 1).

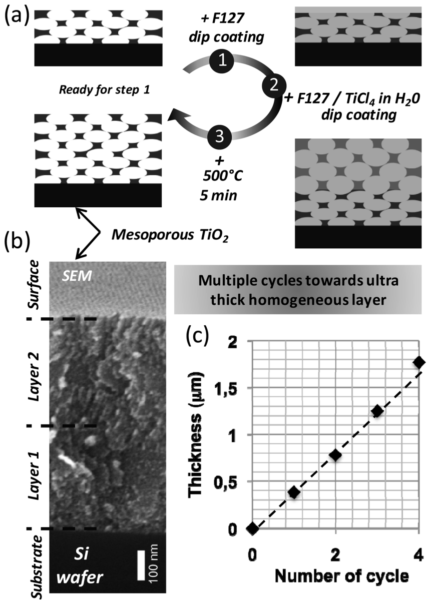

Figure 3. Preparation of thick films through multilayer stacking. (a) Scheme of one cycle for the three-step multidipping procedure. (b) Scanning electron micrograph of a 2-layer-coating profile showing surface, both layer and substrate. (c) Graph reporting the evolution of the thickness of the final film as function of the number of cycles.

In summary, we have shown a considerable advance over the cumbersome and complex pre-existing methods used to prepare mesoporous TiO_2 films. The method reported here used inexpensive reagents, water as the single solvent, and capillary regime dip-coating, making this a feasible procedure for industrial production. Additionally, much thicker films were prepared that were of extremely high homogeneity and optical quality. Advanced investigations will be performed to extend the protocol to other systems.

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Supporting Information Available: Experimental section and XRD pattern of the 4-layer sample PDF). This material is available free of charge via the Internet at http://pubs.acs.org.