Critical Aspects in the Production of Periodically Ordered Mesoporous Titania Thin Films

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Electronic Supplementary Information

Film preparation

MTTF were prepared by Evaporation Induced Self Assembly (EISA), under controlled deposition conditions (T, RH%), as previously reported.[i] Initial solutions were prepared by slowly adding $TiCl_4$ under stirring to an alcoholic solution containing the template (Nonionic triblock copolymer Pluronic F127 $[(EO)_{106}(PO)_{70}(EO)_{106}]$). Water ($h$=$[H_2O]/[Ti]$=10) was subsequently added under stirring. The final molar ratio in solution was Ti:F127:H_2O:EtOH 1:0.005:10:40. Clean glass or silicon wafers were used as substrates.

Films were produced by dip coating in a chamber under controlled humidity conditions (RH% 20-50%). Under these conditions, a body centered cubic (bcc or *Im3m*) titania-template mesophase is obtained.

2D SAXS experiments were performed at the D11A-SAXS line at the Laboratório Nacional de Luz Síncrotron, Campinas, SP, Brazil, using λ=1.608Å and a sample-detector distance of 650 mm; image plates or a CCD camera were used as detectors.

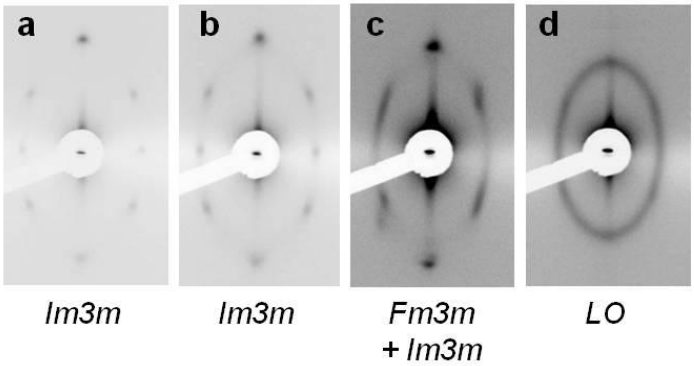

Figure ESI 1. 2D-SAXS patterns of titania samples dip-coated and treated for 24 h under controlled RH, followed by stabilization at 60, 120 and 200°C. Humidity in the dip-coating chamber and post-treatment was (a) 20%, (b) 50%, (c) 70%. Sample (d) was deposited at 25% RH, exposed to water vapours after dip-coating, then aged at 50% RH.

TEM images were collected using a Philips EM 301 transmission electron microscope (CMA, Universidad de Buenos Aires, Argentina) operated at 65 kV or Philips

CM 200 Super Twin (UAM, CAC, CNEA) operated at 200kV. Samples were obtained by scratching the films from the substrate and deposited on carbon-coated copper grids.

Field Emission-Scanning Electron Microscopy (FE-SEM) images were taken with a ZEISS LEO 982 GEMINI field emission electron microscope in the secondary-electron mode, using an in-lens detector to improve resolution.

***In-situ* ellipsometry analysis of as-prepared titania-template films:**

For the ageing experiments, a 4 cm^2 film of an as-made TiO_2 film produced on a silicon substrate as described above (template ratio s = [F127]/[Ti]= 0.005) was placed into an environmental chamber mounted into an ellipsometer, in which temperature and humidity were maintained constant. The variation of refractive index and thickness of this film was analysed with an EPA Spectroscopic ellipsometer from SOPRALAB in the spectral range 250-1000 nm. The relative humidity (RH) was fixed at 65%. Every three minutes, RH was decreased at 25% for 1 minute in order to monitor the shrinking –swelling behavior of the film. For optical dispersion modelling, a triple layer model consisting in a Silicon substrate previously fitted, a thin layer of SiO_2 issued from the reoxidation of the substrate, and a simple Cauchy model ($n(\lambda)=A+B/\lambda^2$) for the TiO_2 layer was used. The Cauchy three parameters (thickness, A and B) were adjusted in the spectral range of 450-1000 nm.

[i] E. L. Crepaldi, G.J.A.A. Soler-Illia, D. Grosso, F. Cagnol, F. Ribot, C. Sanchez, *J. Am. Chem. Soc.*, **2003**, *125*, 9770.