

Electrical Conductivity in Patterned Silver-Mesoporous Titania Nanocomposite Thin Films: Towards Robust 3D Nano-Electrodes

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ELECTRONIC SUPPLEMENTARY INFORMATION

Titania Film Preparation. Titania mesoporous thin films were produced by dip-coating in hydroalcoholic solutions containing TiCl_4 and a polymeric template under controlled humidity and temperature. Solutions were prepared as follows: 0.01 mole TiCl_4 was weighed in a syringe and added dropwise to 20 mL ethanol cooled on an ice bath; subsequently, 1.8g H_2O was added under stirring. Nonionic Pluronics®F127 $(\text{EO})_{106}(\text{PO})_{70}(\text{EO})_{106}$ (M_w 13600, Aldrich) was used as a pore template. The final composition of the precursors solution was $\text{TiCl}_4\text{:EtOH:H}_2\text{O:F127}$ 1:40:10:0.005. Two dip-coating speeds were used: 0.6 and 2 mm s^{-1} .

After deposition, the films were placed in 50% RH chambers for 24 h, and were subjected to a stabilizing thermal treatment procedure consisting of two successive 24 h heat treatments at 60 and 130°C, and a final 2 h step at 350°C for template elimination, under a still air atmosphere in a tubular oven, leading to the formation of transparent crack-free mesoporous thin films with cubic $Im3m$ mesostructure.^I

Film Characterization. Film electronic density were determined from the analysis of critical angle by X-ray reflectometry (XRR) measurements, performed at the D10A-XRD2 line of Laboratório Nacional de Luz Síncrotron, Campinas, SP, Brazil ($\lambda = 1.5498$ Å).^{II} Film thickness was measured by ellipsometry using a SOPRA GES-5A apparatus, equipped with microspot optics. Measurements were carried out at 0 % RH to avoid the condensation of water within the pores. Water adsorption isotherms (at 298 K) were measured by ellipsometric porosimetry analysis (EPA) using the same equipment, according to the protocols developed by Boissiere *et. al.*^{III} A continuous flux of air containing a fixed partial water pressure was directly in contact with mesoporous film to be analyzed. Film thickness and reflective index values were obtained from the ellipsometric parameters ψ and Δ at each P/P_s (P_s being the saturation water pressure), which was varied from 0 to 1. Film porosity was evaluated by adjusting a three-medium (air, water, silica) Bruggeman effective medium approximation (BEMA). Typical results are shown in Figure S1.

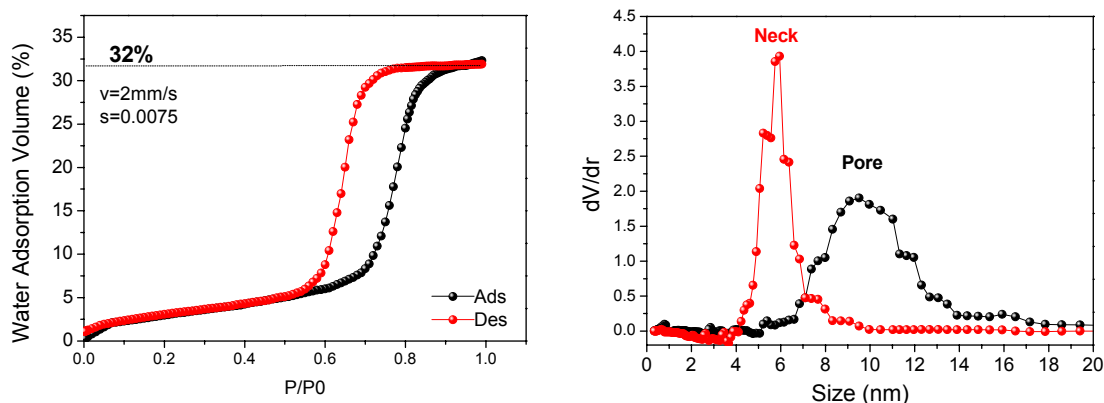


Figure S1: Typical EEP water adsorption-desorption isotherms (left) and size distribution (right) obtained from the mesoporous titania thin films used in this work, deposited on a silicon substrate.

Calculation of pore filling fraction from EDS. Considering the values of the accessible porous fraction obtained by EPA and the Ag:Ti atomic ratio from EDS measurement it is possible to calculate the pore filling fraction by applying the following equation:

$$F(\%) = \frac{r \delta_{\text{TiO}_2} M_{\text{Ag}} (1 - V_p)}{\delta_{\text{Ag}} M_{\text{TiO}_2} V_p} \times 100$$

where r is the Ag:Ti atomic ratio and V_p is the accessible porous fraction, δ_{Ag} and M_{Ag} are the bulk density and the molecular weight of silver respectively (10.49 g cm^{-3} , $107.86 \text{ g mol}^{-1}$), δ_{TiO_2} is the bulk density (3.8985 g cm^{-3}) of anatase TiO_2 , which is the main crystallographic phase present in the films, and M_{TiO_2} is the molecular weight (79.89 g mol^{-1}). For the values obtained for sample BL after 90 minutes irradiation, $V_p=0.35$ and $r=0.59$, and considering the errors involved in each technique, the application of the mentioned equation gives a $(55 \pm 5)\%$ of pore filling fraction.

Calculation of pore filling fraction from XRR. From the X Ray Reflectometry curves it is possible to obtain the critical angle of reflection defined by the angle at which the reflected intensity is half of the maximum value. As the electronic density is proportional to the square of the critical angle it is possible to calculate the pore filling fraction by the methodology describe in ref. II.

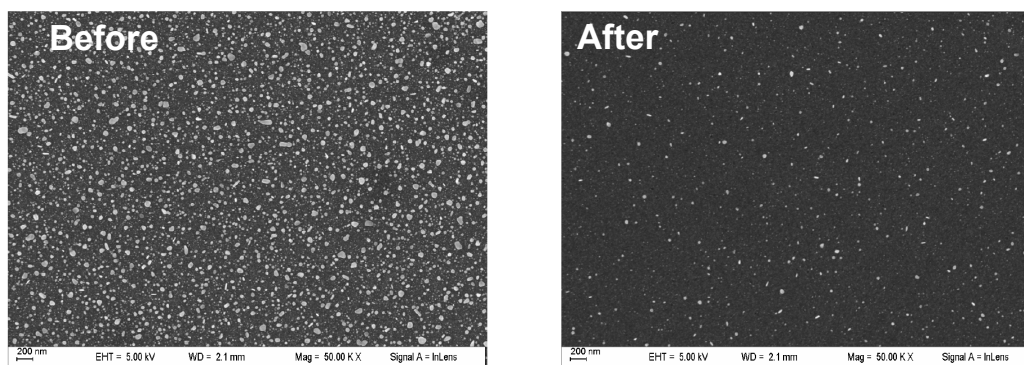


Figure S2: FE-SEM images of films surface before and after the cleaning process.

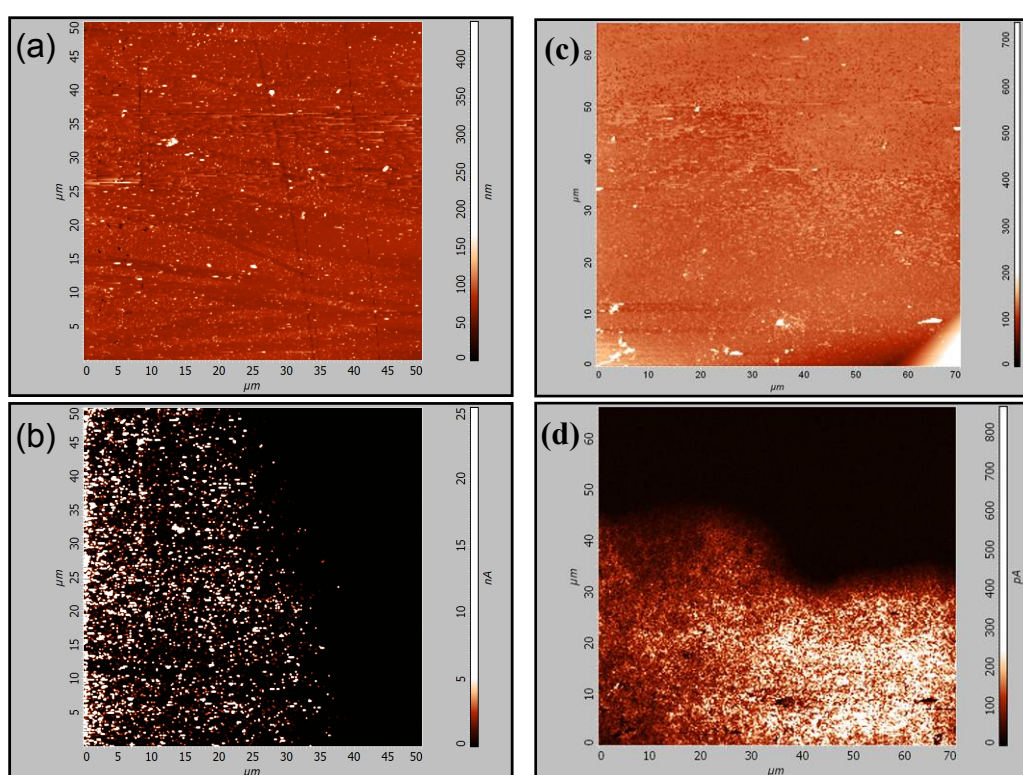


Fig. S3. CAFM images after 90 minutes of photoreduction time. Sample E_V on left (vertical conduction) and sample C_L (lateral conduction). (a, c) contact mode topography scanning and (b, d) current scanning at $V_0 = 10$ V.

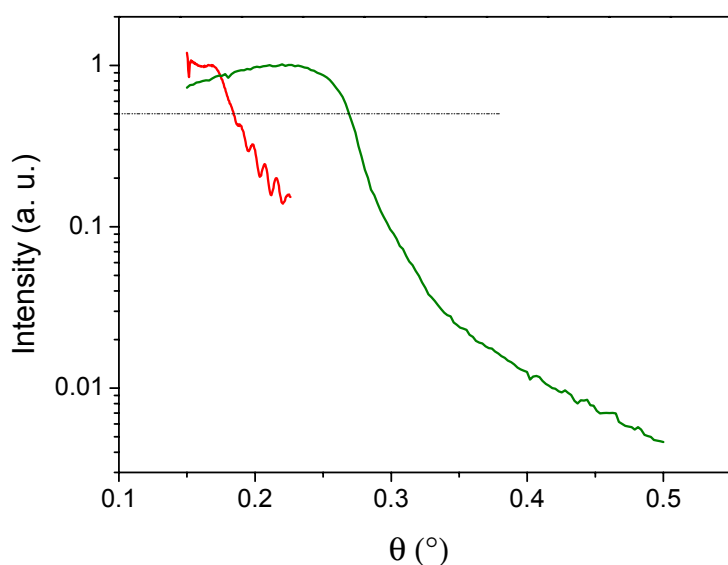


Fig. S4. XRR analysis of pristine (red curve) and Ag loaded after 90 minutes of photoreduction time (green curve) of sample B_L.

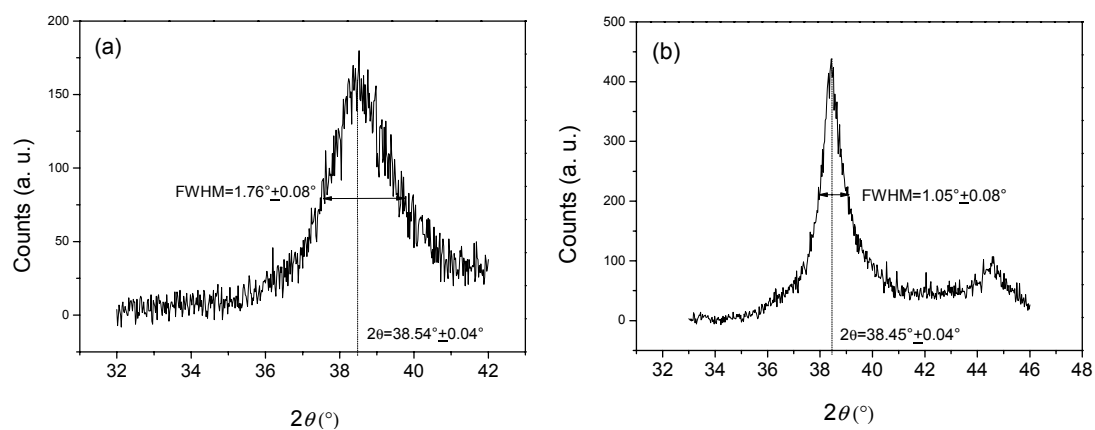


Fig. S5. CAFM images of sample E_V (vertical conduction) after 90 minutes of photoreduction time. (a) contact mode topography scanning and (b) current scanning at $V_0 = 10$ V.

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

^{II} M. C. Fuertes, M. Marchena, M. C. Marchi, A. Wolosiuk, and G. J. A. A. Soler-Illia, *Small* 2009, **5**, 272.

^{III} C. Boissière, D. Grosso, S. Lepoutre, L. Nicole, A. Brunet-Bruneau, C. Sanchez, *Langmuir* 2005, **21**, 12362.