

Optical Properties of Au Nanoparticles Included in Mesoporous TiO₂ Thin Films: a Dual Experimental and Modeling Study

V. M. Sánchez,^{a,b} E. D. Martínez,^a M. L. Martínez Ricci,^c H. Troiani^d and G. J. A. A. Soler-Illia^{a,b}*

^a Gerencia Química, Comisión Nacional de Energía Atómica, Centro Atómico Constituyentes, Av. Gral. Paz 1499 (B1650KNA), San Martín, Buenos Aires, Argentina.

^b Departamento de Química Inorgánica, Analítica y Química Física, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Ciudad Universitaria, Pabellón 2, C1428EHA, Buenos Aires, Argentina.

^c INQUIMAE, CONICET, Ciudad Universitaria, Pabellón 2, C1428EHA, Buenos Aires, Argentina

^d Comisión Nacional de Energía Atómica, Centro Atómico Bariloche, and Instituto Balseiro, San Carlos de Bariloche, 8400, Argentina.

SUPPORTING INFORMATION

Porous volume fraction of the MTF could be acquired directly by means of ellipsoporosimetry as described in ref. S1.

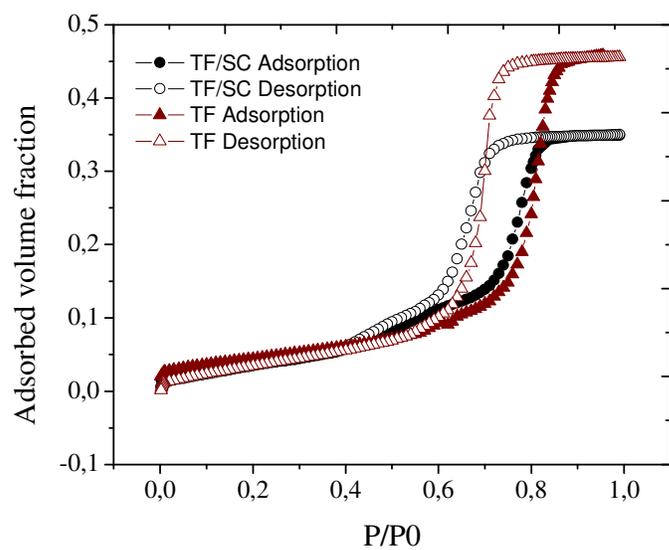


Figure S1. Water adsorption isotherms for monolayer TF (red) and bilayer TF/SC (black) on glass.

The complete characterization of the MTTF was performed through TEM and SAXS. The results of such techniques is displayed in figure S2.

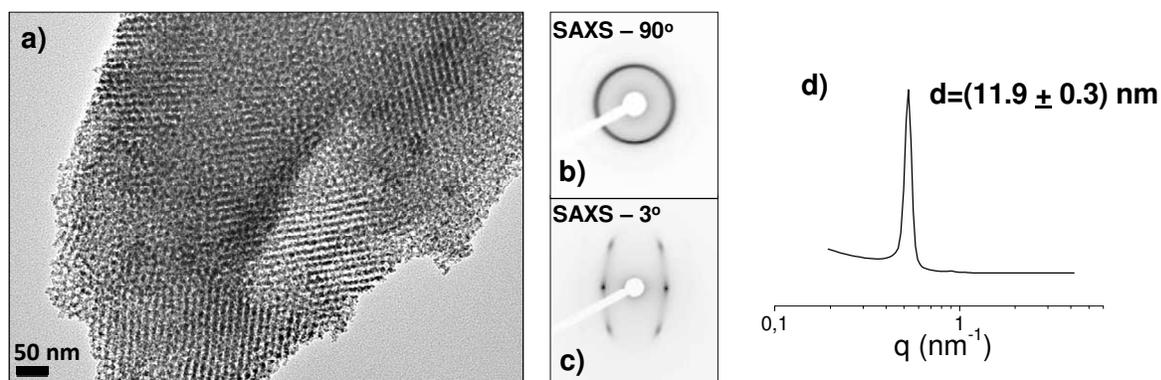


Figure S2. Characterization of the MTTF. In panel a) TEM image of the mesoporous framework. SAXS measurements were performed at normal incidence (b) and small angle

incidence (c). In figure d) it is shown the radial integration of the image b) from which the mean inter pore distance d can be calculated through $d=2\pi/q$.

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

$$F(\%) = \frac{r\delta_{TiO_2}M_{Au}(1-V_p)}{\delta_{Au}M_{TiO_2}V_p} \times 100$$

Eq. S1

where r is the Au:Ti atomic ratio and V_p is the accessible porous fraction (0.45 from Fig. S1), δ_{Au} and M_{Au} are respectively the bulk density and the molecular weight of gold (19.3 g cm^{-3} , $196.96 \text{ g mol}^{-1}$), 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 TF after five reduction steps (5RS), $r=0.0395$. Considering the errors involved in each technique, the application of the mentioned equation gives a $(1.9 \pm 0.1) \%$ of pore filling fraction.

Calculation of the pore filling fraction from XRR measurements. 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 described in ref. S2. We find a value of $(2.2 \pm 0.1) \%$ for the pore filling fraction of the sample loaded with 5 RS.

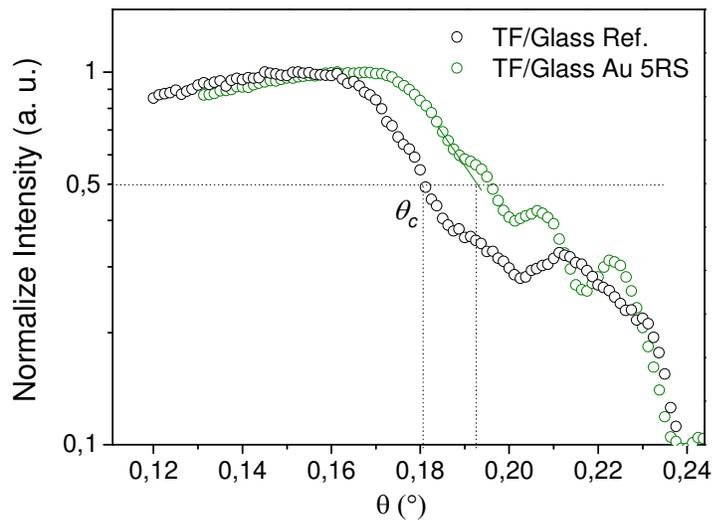


Figure S3. X-Ray reflectometry curves for the determination of the critical angle of reflectivity in empty TF and loaded with Au after 5 RS. Electron density and metal filling fraction are calculated from these values.

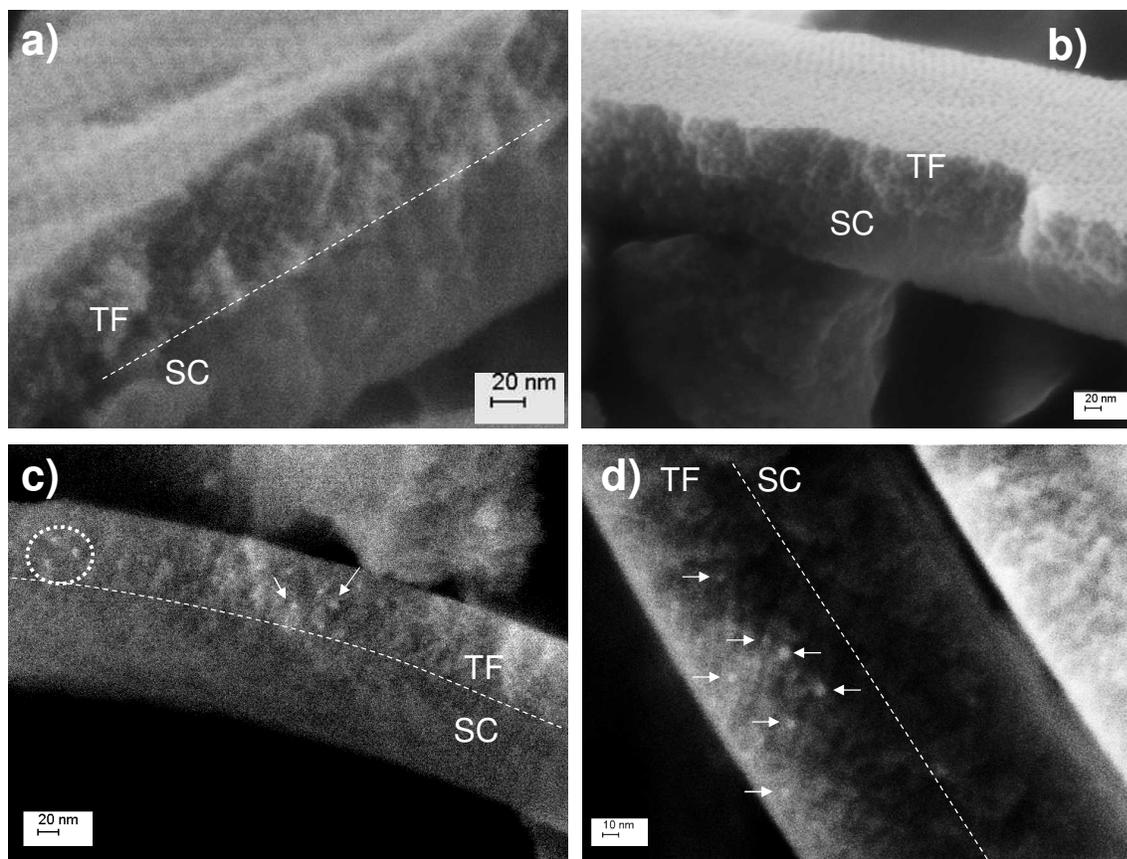


Figure S4. FE-SEM images of the bilayer system Au10RS-TF/SC. Panels a) and b) show the system before the gold infiltration; in c) and d) the same system after the gold infiltration. The presence of Au NPs is only clear in the TF layer distinguishable because of its larger pore size.

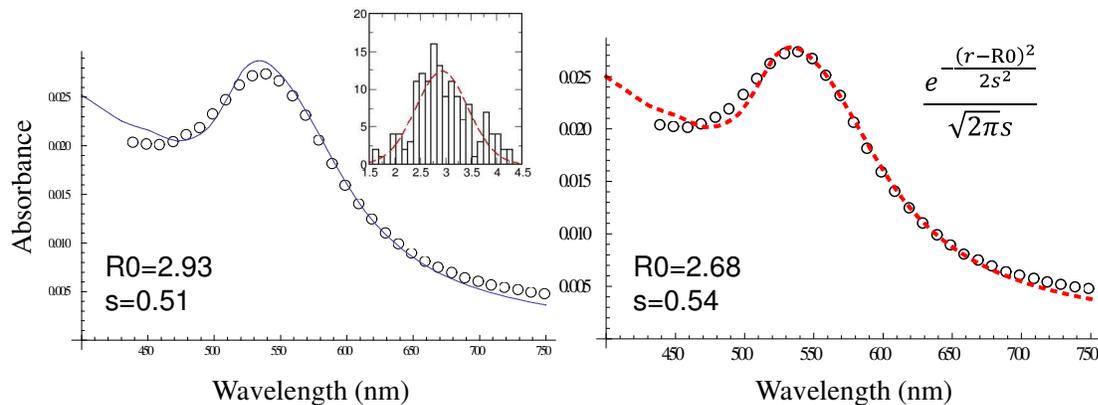


Figure S5. Calculated absorbance spectra using a Gaussian distribution function accounting for the polydispersity in particle size. On the left panel, the calculated spectra using the PSD extracted from TEM analysis; on the right, calculated spectra resulting from the fitting of the mean particle size (R_0) and standard deviation (s) using a fixed filling fraction of 1.77 %.

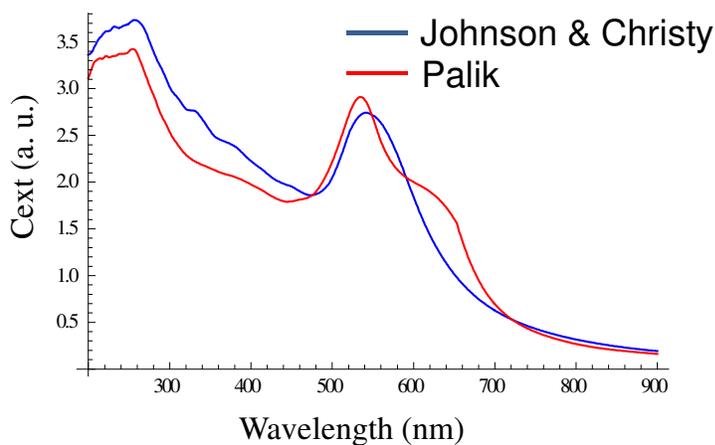


Figure S6. Comparison between the calculated C_{ext} spectra using gold bulk dielectric function from Palik^{S3} and Johnson & Christy^{S4} tabulated data.

Comparison between ellipsometry vs. UV-Vis spectra in dye loaded MTTF

In the case of the Au5RS-TF sample, the comparison of the spectra calculated from ellipsometric results with the direct spectra measured by spectrophotometry present an important difference in the amplitude of the LSPR, being the first one almost twice as intense as the latter. To clarify if this difference is an intrinsic characteristic of ellipsometry, an alternative system based on methylene blue (MB) adsorbed inside the porous framework of MTTF was characterized in the same way, both by spectrophotometry and ellipsometry. In this last case, two Lorentz functions were added to the dielectric description of the TF layer to account for the absorption bands of MB. After the fitting, the dielectric function obtained was transformed into the absorption spectra by means of Eq. 11-12. The comparison between both spectra is presented in Figure S7 showing an excellent agreement in its position, broadness and relative intensity of the two components.

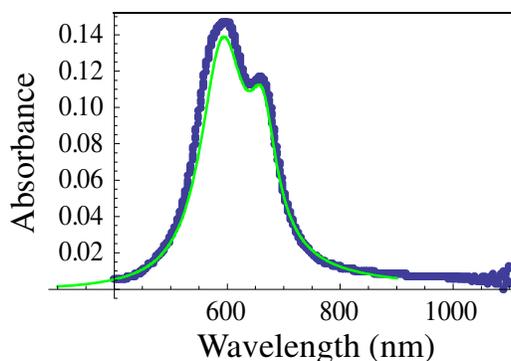


Figure S7. Comparison between experimental (blue) and calculated absorbance spectra of MB-TF obtained from ellipsometry measurements (green). Adsorption of MB was made from a 1.25 mM solution.

From this experiment it is concluded that ellipsometry provides a confident way to characterize optical materials involving dyes, however, the characterization of embedded NP must be taken

with care, in particular the LSPR intensity. The reason for this discrepancy is still not clear, although several possibilities were considered and discarded including inhomogeneous filling throughout the thickness, particles on the surface of the film and reflection losses. Taking into account the difference in the incident angle of both techniques a correction to the optical path length was considered. In this regard ellipsometry measurements were acquired for incident angles in the range of 65° - 72° . No significant difference was observed. Anisotropy of the samples was also considered. To explore this possibility, a linear polarizer was used to polarize the incident light of the spectrophotometer but no observable difference was obtained. Finally, also the sample was tilted at different angles with respect to the incident light. It was observed that only the baseline of the spectra was affected, probably due to a higher reflection, but not the intensity of the LSPR absorption band.

Additional TEM images

TEM images were performed to verify the results of the model in sample of MTTF of *c.a.* 145 nm in thickness, loaded with Au NP after 6 reduction steps as detailed in the main text under the section named Critical Aspects. Figure S8 shows the typical size of the NP and their dispersion inside the mesostructure. Panel b) shows a cross section view in which NP can be identified along the whole thickness of the film.

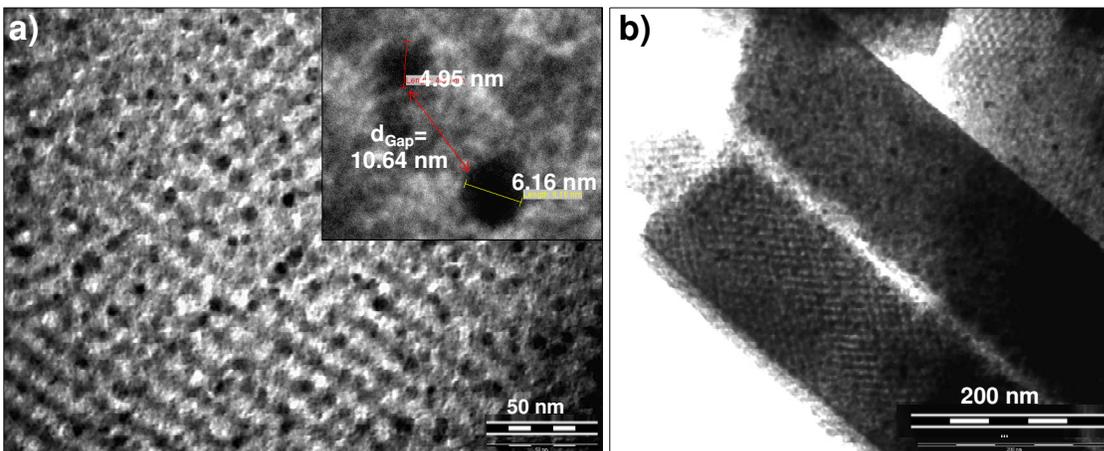


Figure S8. TEM images of sample TF/Glass 6 RS after the cleaning of the surface. Panel a) show the dispersion of NP in the highly ordered mesoporous structure; in b) a cross-section image of the film over a scratched fragment of the sample.

^{S1} Boissiere, C.; Grosso, D.; Lepoutre, S.; Nicole, L.; Bruneau, A. B.; Sanchez, C. Porosity and Mechanical Properties of Mesoporous Thin Films Assessed by Environmental Ellipsometric Porosimetry. *Langmuir* 2005, 21, 12362-12371.

^{S2} Fuertes, M.C.; Marchena, M.; Marchi, M.C.; Wolosiuk A.; Soler-Illia, G. J. A. A.; Controlled Deposition of Silver Nanoparticles in Mesoporous Single- or Multilayer Thin Films: From Tuned Pore Filling to Selective Spatial Location of Nanometric Objects. *Small*, 2009, 5, 2, 272-280.

^{S3} Palik, E. D. "Handbook of Optical Constant of Solids", Academic Press, 1998.

^{S4} Johnson, P. B.; Christy, R. W. Optical Constants of the Noble Metals. *Phys. Rev. B.*, 1972, 6, 4370-4379.