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

V. M. Sánchez, E. D. Martínez, M. L. Martínez Ricci, H. Troiani and G. J. A. Soler-Illia*  

Abstract

Gold nanoparticles (NP) were synthesized inside ordered mesoporous TiO₂ thin films (MTTF) by stepwise reduction of AuCl₄⁻ with NaBH₄. This leads to an optical material (Au@TiO₂) of interest for plasmonic applications. The films (pure titania or gold-titania nanocomposites) were thoroughly characterized by UV-Visible and ellipsometry spectroscopies. The dielectric function...
of the MTTF, considered as the dielectric environment in which the NP are embedded, was acquired by ellipsometry and rationalized by the asymmetric Bruggeman model as an effective medium formed by the mixture of dense TiO$_2$ and air. Nanocomposite Au@TiO$_2$ systems present an isotropic dispersion of Au NP in the 5-8 nm range. The UV-visible spectra obtained with a low nanoparticle filling fraction of the pore volume ($f_{NP} < 2\%$) are accurately reproduced by both Maxwell-Garnett (MG) and Mie theories. Accurate and coincident values of $f_{NP}$ and NP size are obtained by this method. The dielectric function of Au NP used in this work was studied in detail; in particular, the interface damping parameter related to the NP/MTTF interface was determined by comparison with TEM microscopy. The potential of the ellipsometry technique to determine the material plasmonic response, and its correspondence with the UV-Visible spectra, are discussed. This spectroscopy technique opens the possibility to study the plasmon response of the material to changes in the environment due to the presence of vapors, and other in-situ experiments, as well as to provide nanostructural information of metallic nanoparticles (NP size, interparticle distance, number of NP) with well-defined spatial localization in a multilayered system.

**Keywords:** Ellipsometry, Plasmonics, Effective Medium Approximation, Nanocomposites, Dielectric Function.

**Introduction**

Mesoporous thin films are established as a growing field in nanochemistry due to the high control attainable in the pore size, and the organization of the porous framework on the mesoscopic scale, and the possibility to control its accessibility. Those aspects are of paramount importance in the design of advanced catalysts, sensors, selective membranes and other devices exploiting related surface chemistry phenomena. The special case of TiO$_2$ nanostructures and
surfaces has been reviewed several times\textsuperscript{1,2} and recently it has been the exclusive subject of a special issue\textsuperscript{3} showing the relevance of this material in photochemistry applications like photovoltaics\textsuperscript{4} and photocatalysis\textsuperscript{5}.

Independently, noble metal nanoparticles, mainly made of silver and gold, possess unique optical properties arising from the excitation of Localized Surface Plasmon Resonance (LSPR) that takes place at optical frequencies. Several applications regarding the dependence of the plasmon frequency with its dielectric environment are of interest in technological developments of optical-based sensors\textsuperscript{6–10} and SERS substrates\textsuperscript{11–15}. The ability to locate NP in a solid matrix avoiding their aggregation and without affecting the accessibility of analytes of interest, is fully satisfied by the use of the mesoporous framework as a host material for their inclusion with NP, which can be done either by infiltrating the mesostructure with preformed NP,\textsuperscript{16} by controlling their nucleation and growth from the adsorption of soluble precursors,\textsuperscript{17} by electrodeposition\textsuperscript{18} or by photocatalytic-assisted deposition.\textsuperscript{19} Recently, gold NP of controlled shapes covered by a mesoporous film were produced,\textsuperscript{20} and the possibility of \textit{in-situ} monitoring solvent evaporation in a sensitive way was demonstrated.\textsuperscript{21} In particular, Au@TiO\textsubscript{2} nanocomposites have been proven to account for light driven charge transfer processes both from the NPs to the oxide and viceversa. The first mechanism can enhance the photocatalytic performance by accumulating and discharging electrons under On-Off cycles of UV light exposure\textsuperscript{22}; in the second case, plasmon excitation induce electron transfer from the NPs to the TiO\textsubscript{2} resulting in a visible light driven photoanode able to oxidize H\textsubscript{2}O in water splitting reaction\textsuperscript{23}. Solar cells involving plasmonic components have also been pursued\textsuperscript{24,25}. Surface-Enhanced Raman Scattering (SERS) effect has also been proven to take place in thin films nanostructures composed of Au NP and TiO\textsubscript{2} nanotubes\textsuperscript{26}. In addition, Au nanoparticles embedded into MTTF have proven to be highly active
for the water gas shift reaction in an idealized reaction gas mixture, presenting a remarkable
stability. The photocatalytic performance of MTTF loaded with Au NP have also been reported
for the oxidation of phenol and the reduction of chromium cations.

In all these cases, the characterization and interpretation of the optical properties is an essential
issue for the tailored design of this nanocomposite material. Optical properties give a sound
information about the size and the nanoparticle loading of a film, which is an essential issue for
Surface Plasmon Resonance (SPR), Surface-Enhanced Raman Scattering (SERS) or catalytic
applications. UV-Visible spectrophotometry and spectroscopic ellipsometry have been
extensively used as a basic characterization tool of NP embedded within sol-gel derived thin
films. In the case of mesoporous thin films, the plasmon band position and intensity are usually
interpreted as a consequence of the actual particle sizes and mesoporous matrix refractive index,
with no further interpretation. Therefore, there is a need for the development of simple
theories that permit to extract structural information of the NP and the mesoporous matrix
properties from the nanocomposite spectra. In addition, this theory should be able to reconcile
and exploit the information obtained by UV-Vis spectroscopy and ellipsometry. These aspects
have not been extensively treated, to the best of our knowledge, in the current literature.

The aim of this work is to formulate a formal description of the origin and interpretation of the
data obtained by each technique and to propose a mechanism by which this dual characterization
can provide valuable information about the particle size and the volume filling fraction of the
metal phase in the composite material. For this purpose, a reference system based on Pluronics
F127 templated TiO$_2$ mesoporous thin films loaded with gold NP will be described as a
collection of particles in a dielectric environment for which Mie theory can be applied, and also
by an effective medium theory, namely Maxwell-Garnett, whose calculation provides an
effective dielectric function that can be directly measure by ellipsometry. It is important to remark that the effective medium that surrounds metallic NP is experimentally determined through ellipsometer measurements and is not taken as a wavelength independent value, extracted from tabulated data, or inferred from the plasmon peak position as it is usually reported\textsuperscript{38,39}. This procedure permits a thorough yet simple modeling of the optical parameters of these nanocomposites.

**Experimental and Modeling**

1. **Synthesis**

*TiO\textsubscript{2} mesoporous thin films.* Mesoporous TiO\textsubscript{2} thin films were produced by combining a sol-gel chemistry route with self-assembly of surfactant templates, in the strategy known as Evaporation Induced Self Assembly (EISA)\textsuperscript{40,41}. In a typical synthesis, Pluronics F127 (Sigma, PEO\textsubscript{106}PPO\textsubscript{70}PEO\textsubscript{106}) was added to an ethanol solution of titanium tetrachloride (Merck, TiCl\textsubscript{4}). Water was subsequently added under strong agitation in order to dissolve the surfactant. The final molar relationships TiCl\textsubscript{4}:EtOH:F127:H\textsubscript{2}O were 1:40:0.005:10. Soda-lime glass slides were used as substrates for the deposition of the mesoporous films. The glass slides, previously washed with acetone, ethanol and water, and dried at 60 °C, were dipped into the sol heated up to 32 °C, and extracted at a constant withdrawal rate of 1 mm·s\textsuperscript{-1}. The relative humidity in the dip-coater chamber was set at 35%. After the dip-coating process was complete, the freshly deposited film was removed from the reverse side of the slides by gently rinsing with water and alcohol. Films were then placed in a closed chamber at 50% of controlled relative humidity (RH) at room temperature for 24 h to promote the stabilization of the mesostructure. Stabilized films were then submitted to a thermal treatment of 30 minutes at 60 °C, and 30 minutes at 130 °C, triggering Ti-O-Ti condensation, and finally calcined at 350 °C for 2 hours, for the removal of the polymeric
surfactant and further consolidation of the solid structure.\textsuperscript{42} The physical parameters of these films can be controlled with high accuracy and reproducibility and a narrow (approximately monodisperse) distribution of pore sizes can be achieved. Film thickness and porosity can be tuned by means of the withdrawal rate in the dip-coating process and the proper election of the templating agent respectively. Parameters like pore and neck size, accessible volume and thickness of the mesoporous films can be measured by ellipso-porosimetry (EP, see below).\textsuperscript{43}

Dense titania films were synthesized by the same sol-gel procedure from a sol of the same composition but in the absence of the templating agent. After deposition through dip-coating at 1 mm\cdot s\textsuperscript{-1} and submission to equal thermal treatment, the non-mesoporous TiO\textsubscript{2} films (TNM) result in thinner thickness compared to the mesoporous ones.

A bilayered mesoporous structure formed by a TiO\textsubscript{2} MTTF layer deposited over a preformed layer of mesoporous SiO\textsubscript{2} on a glass substrate, was synthesized as follows: a sol with molar fraction composition TEOS:EtOH:CTAB:HCl:H\textsubscript{2}O 1:20:0.1:0.004:5, where TEOS (tetraethyl orthosilicate) is the Si precursor and CTAB (cetyltrimethylammonium bromide, C\textsubscript{16}H\textsubscript{33}N(CH\textsubscript{3})\textsubscript{3}Br) acts as the templating agent, was dip-coated at 1 mm\cdot s\textsuperscript{-1} and stabilized at 200 °C for 24 h. After this, the deposition of TiO\textsubscript{2} from the described sol was performed as mentioned before. This bilayer preparation procedure was reproduced from previous works of the group.\textsuperscript{44}

**Formation of Gold NP.** The infiltration of MTTF with gold nanoparticles was achieved by an iterative two-step method that consists in the adsorption of a gold precursor on the mesopore surface, and its subsequent reduction with NaBH\textsubscript{4}. The film was immersed during one minute in a 1 mM solution of HAuCl\textsubscript{4}•3H\textsubscript{2}O (Sigma-Aldrich) at pH 4 for the adsorption of Au(III) species on the positively charged surface of TiO\textsubscript{2}. After that residence time, the film was removed and dried under air flow. The film was then immersed for another minute in a 1 mM NaBH\textsubscript{4} freshly
prepared solution for the reduction of the adsorbed AuCl$_4^-$ ion, and finally rinsed with water. This procedure, referred as a reduction step (RS), can be repeated as many times as desired increasing the filling fraction of the mesoporous framework (see Scheme 1). A pink color due to LSPR of gold nanoparticles arises after three steps of reduction.

**Scheme 1.** Synthesis of Au NP embedded in the MTTF by subsequent reduction steps.

### 2. Characterization

**UV-Vis spectrophotometry.** Optical absorption of the mesoporous films deposited on glass substrates was followed by conventional UV-Vis in an HP Agilent 8453 spectrophotometer in absorbance mode. The measurements were made by using as control or reference the same mesoporous film without the gold infiltration. Special attention was taken to provide a normal incidence of the light beam on the sample.

**Spectrometric ellipsometry and ellipsoporosimetry.** The mesoporous thin films without infiltration were first characterized by spectrometric ellipsometry (SE). This technique allows the determination of the thickness and optical constants, such as dielectric function and refractive index. In SE, the change in the polarization state of an impinging polarized light (with $s$ and $p$ components) -at off-normal incidence- over a film or surface is measured for a range of
wavelengths. For isotropic materials, the ratio between reflection coefficients for each polarization mode, $r_p$ and $r_s$, can be expressed as

$$\rho = \frac{r_p}{r_s} = \tan(\Psi)e^{-i\Delta}$$

Eq. 1.

The quantities $\Delta$ and $\Psi$ correspond to the phase difference and the amplitude ratio of the reflection coefficients, respectively. Since the change of these quantities depends on the dielectric constants of the materials involved, and film thickness for every wavelength, a model must be proposed to analyze the data and determine the complex dielectric function of the materials, $\varepsilon = \varepsilon_1 + i\varepsilon_2$. The refractive index ($n = n_r + i\kappa$) can be calculated by:

$$n_r = \sqrt{\frac{\varepsilon_1 + 1}{2\sqrt{\varepsilon_1^2 + \varepsilon_2^2}}}; \quad \kappa = \sqrt{\frac{-\varepsilon_1 + 1}{2\sqrt{\varepsilon_1^2 + \varepsilon_2^2}}};$$

Eq. 2

The Cauchy model was used to describe TiO$_2$ mesoporous thin films at wavelengths in which no absorption takes place. The localized surface plasmon resonance (LSPR) due to the presence of the nanoparticles is described by a Lorentz oscillator as following the works of Oates and Kürbitz.

The pore volume and pore size of the obtained films were assessed by ellipsoporesimetry (EP). This technique consists in performing SE measurements in a chamber of controlled water vapor pressure. By the use of a Lorentz-Lorenz effective medium theory, a water adsorption isotherm is obtained from which the total accessible volume can be extracted; the pore size distribution can be obtained from the adsorption isotherm through the Kelvin equation. The measurements were performed in a commercial SOPRA GES5-A multispectral ellipsometer in the microspot configuration and the data was analyzed by the use of the Winelli II software.

**Electron Microscopy.** Transmission electron microscopy (TEM) characterization was performed
in a Philips CM 200 electron microscope operating at 200 kV. The equipment works with a LaB₆ emission filament and is equipped with an ultra-thin objective lens. An EDS detector is attached to the microscope. The samples were prepared by scratching the thin films with a stainless steel chirurgical blade and depositing the scratched pieces over an ethanol drop placed on an ultrathin carbon film supported on a TEM Cu grid. Statistical counting of the particle size (on ca. 150-200 nanoparticles) was made on several micrographs to obtain the particle size distribution (PSD). It should be mentioned that this procedure, often reported in literature, gives an over estimated value of the mean particle size, since smaller particles are poorly defined and may be left aside in the counting. Field emission-scanning electron microscopy (FE-SEM) images were obtained with a ZEISS LEO 982 GEMINI field emission electron microscope in the secondary-electron mode, using an in-lens detector to improve resolution.

**X-Ray-based techniques.** Film density was obtained from the analysis of the critical angle of X-Ray Reflectometry (XRR) measurements that were performed at the D10A-XRD2 line of Laboratorio Nacional de Luz Sincrotron (LNLS), Campinas, SP, Brazil (λ=1.5498 Å). In order to obtain accurate density values, measurements were done under dry nitrogen flux to avoid atmospheric water condensation within the pores which would lead to an underestimation of mesoporosity.¹⁷ The same setup can be used to obtain a diffraction pattern in grazing incidence mode. Film mesostructure was analyzed using SAXS in transmission mode at the D11A-SAXS2 line of LNLS (λ=1.608 Å) at normal and 3° incidence on thin glass covers.

### 3. Modeling scheme

The modeling framework of the Au@MTTF optical properties will thoroughly presented and discussed in the next sections. Only a general sketch will be provided here. Effective Medium
Approximations (EMA) were applied to the complex dielectric functions determined by ellipsometry for MTTF or Au@MTTF. Mie Theory was applied to the Au NP absorbance spectra obtained by UV-Visible spectroscopy. From each independent model, the filling fraction \( f_{NP} \) and the NP radius \( a \) present in the NP@MTTF were calculated, as presented in Scheme 2. This procedure permits to obtain the pore filling fraction and the NP size by different models, and to evaluate their predictive power by confronting them to the crossed characterization techniques.

![Scheme 2. Summary of the modeling applied to NP@MTTF system](image)

**Results and discussion**

1. Synthesis and Characterization of MTTF and Au@MTTF nanocomposite films

*Mesoporous Thin Film Characterization.* The structure of MTTF deposited over soda-lime glass has been extensively characterized in several works\(^{41}\) using different techniques including X-ray diffraction and scattering from synchrotron radiation (XRD, SAXS, XANES), high
resolution TEM and dynamical thermo-ellipsometry characterization. After thermal treatment at 350 °C, the film gets contracted by c.a. 50% in the normal direction relative to the substrate, the oxide framework being mainly amorphous but containing a partially crystalline (c.a. 20%) anatase phase. Under the thermal treatment conditions employed in this work, highly ordered, mostly amorphous MTTF with similar pore size is obtained. The structure of the films can be described through their thickness, porous volume fraction, pore size, interpore distance, and the characteristic size of the channels or necks connecting adjacent pores. While the interpore distance calculated from SAXS at normal incidence was found to be (11.9 ± 0.3) nm for the systems analyzed in this work, the thickness was determined by both ellipsometry and XRR obtaining a coincident value of (120 ± 10) nm. EP measurements reveal a type IV adsorption isotherm with a H2 hysteresis loop, which is characteristic of a porous system composed of discrete pores with necks or restrictions. The total accessible volume reaches 45% and, from the adsorption and desorption branches respectively, a pore size of (10 ± 3) nm and a neck size of (6 ± 1) nm could be estimated. SAXS measurements at 3° incidence reveal that the titania films present a contracted mesophase with long-range pore order. Details of the characterization of the MTTF are shown in the Supplementary Information (SI).

Characterization of nanoparticles embedded in MTTF. Gold nanoparticles were grown into the MTTF pores as detailed in the Experimental Section. Fig. 1 shows the absorbance spectra obtained as the number of reduction steps (RS) was increased. It is possible to observe that the gold LSPR position keeps practically invariant for 1 to 10 reduction steps, while its peak position shifts slightly to higher wavelengths for a higher number of RS (Fig. 1, inset). This shift in the plasmon position might be due to interparticle interactions, due to the nucleation of new Au NP,
or to the growth of adjacent NP. It is known that for interparticle distances similar to the NP diameter, plasmons might interact with each other leading to a red shift in the LSPR\textsuperscript{52–54}. These interactions seem to take place for films submitted to more than 10 reduction steps. Therefore, under the conditions of synthesis presented in this work, only NP produced in less than 10 RS can be safely considered to be isolated from each other. Thus, in order to develop an appropriate description of the LSPR of gold NP infiltrated inside the MTTF neglecting the interparticle interactions, attention will be focused on films submitted to five reduction steps (5 RS). Fig. 2 shows TEM images of MTTF film before and after 5 RS. The use of TEM to determine NP distribution, sizes and the degree of interparticle connection is widely spread out in the literature\textsuperscript{33,34,55,56,57}. In our case, Fig. 2 shows that NP present mostly an isotropic shape, that could be in principle considered as spherical, and are sufficiently isolated to consider the absence of interactions among them. The occupied pore volume fraction was characterized by EDS and XRR techniques (see SI for details), resulting in a filling fraction of the porous volume of 1.9% and 2.2% respectively. Fig. 2d shows the NP size distribution analysis carried out over several TEM images, where it is possible to determine a distribution with an average radius $a = (2.9 \pm 0.5)$ nm.
**Figure 1.** FE-SEM images of the MTTF before (a) and after (b) gold infiltration. Panel c) absorption spectrum of the nanocomposite showing the evolution of the LSPR band after each reduction step of AuCl₄⁻. The shift in the LSPR peak position at increasing loadings is shown in the inset.
Figure 2. TEM images of mesoporous TiO$_2$ thin films before (a) and after (b, c) the infiltration with gold NP through five reduction steps (5 RS). In image (d), an example is shown of the particle statistical counting of image (c), displaying the PSD obtained by computing nanoparticle size from different TEM images in the inset.

2. Modeling framework

In order to model the optical response of NP@MTTF, it is first necessary to define how the NP and the MTTF are themselves represented. Then, the description of NP@MTTF and its subsequent comparison with experimental results can be attempted.

*Mesoporous Titania Thin Films (MTTF).* The modeling of MTTF is performed at optical frequencies, consequently the incident wavelength used (350-900 nm) is much larger than the pore size. Therefore the MTTF can be considered as an homogeneous effective medium. Several works describe porous materials through effective medium approximations (EMA) in which the material refractive index is expressed as an effective value, in this case: $n_{MTTF}$. This quantity can be calculated by using a mixing rule of the refractive indexes of the different components that
constitute the material. In particular, the MTTF effective medium is composed by the mixture of the refractive indexes of dense titania and of air-inside porosity.

A comparison between different EMA models to describe the dielectric function of highly ordered mesoporous thin films has been recently addressed by Hutchinson and coworkers \(^5\); they concluded that the employment of the Asymmetric Bruggeman \(^5\) (AB) model leads to the most accurate description. Based on this conclusion we applied the AB model given by the following expression:

\[
1 - f_p = \frac{\left(\frac{n_{MTTF}}{n_{ds}}\right)^2 - \left(\frac{n_{air}}{n_{ds}}\right)^2}{\left(\frac{n_{MTTF}}{n_{ds}}\right)^{1/3} \left(1 - \left(\frac{n_{air}}{n_{ds}}\right)^2\right)}
\]  
Eq. 3

where \(f_p\) denotes the volume porous fraction, \(n_{MTTF}\) the porous material effective refractive index, \(n_{air}\) the air refractive index (\(n_{air}=1\)) and \(n_{ds}\) the refractive index of the wall, \(i.e.,\) the dense solid, at a given wavelength.

SE characterization was carried out at 0% of relative humidity (RH) to determine the optical constants of MTTF and also of dense titania films prepared according to the protocols presented in the Experimental Section. With this information, Eq. 3 was used to calculate the MTTF effective refractive index (\(n_{MTTF}\)) and the porous volume fraction (\(f_p\)) employing \(n_{air} = 1\) and \(n_{ds}\) as the dense titania refractive index acquired by ellipsometry. The resulting values of \(n_{MTTF}\) were compared to the direct determination of the MTTF dielectric function through SE. According to the model, the \(n_{MTTF}\), a total porous volume \(f_p=0.42\) was calculated, which is in close agreement with the experimental value of \(f_p=0.45\) directly measured by ellipsoporosimetry (EP). With these results, we conclude that the use of asymmetric Bruggeman model is adequate to represent the MTTF medium as shown in Fig. 3. Consequently, the concept of MTTF as an effective medium
is valid and it is well characterized by both the ellipsometric measurement and the numerical calculus.

![Refractive index vs Wavelength](image)

**Figure 3.** Comparison of the dispersion relation of the refractive index achieved after the fitting of the ellipsometric data obtained directly from the measurement of the mesoporous thin film with the result of the asymmetric Bruggeman EMT calculation for the mixture of dense TiO$_2$ thin film and air in a volume fraction of 0.42.

**Nanoparticles.** The interaction of metallic NP with light leads to the appearance of Localized Surface Plasmon Resonance LSPR$^{60-65}$. LSPR depends on the metallic compound as well as on NP features such as morphology$^{66,67}$, size, interparticle interactions$^{11}$, and on the refractive index of the surrounding medium$^{38,52,65}$. In the context of Mie Theory, NP can either absorb or scatter light, defining the extinction coefficient ($c_{\text{extinction}} = c_{\text{absorption}} + c_{\text{scattering}}$).

For spherical NP below 10 nm in size, the *quasi-static approximation* is valid and the scattering coefficient is negligible in comparison with the absorption coefficient. It is also possible to account only for the dipolar mode *dipolar approximation* and consequently, the LSPR frequency does not depend on the NP size -for spherical NP between 2-10 nm$^{52,56,60,64,65}$. The optical properties observed for metallic compounds arise from the response of their electronic structure to the electromagnetic field -provided by light source. Although the dielectric
function of metallic NP cannot be measured directly, it is feasible to describe it considering the NPs electronic structure. Two types of electrons can be in principle distinguished in the simplest model: bonded and free – i.e. conduction-electrons. While free electrons provide the major response of the NP to the electromagnetic field, and are responsible for NP polarizability, bound electrons will also exert an influence:

\[ \varepsilon(\omega) = \varepsilon_{\text{bound}}(\omega) + \varepsilon_{\text{free}}(\omega) \]

Eq. 4

Several expressions for the dielectric function corrected to account for the reduce size of the particles are addressed in literature\textsuperscript{11,61,68–70}, being the dielectric function reported by Hövel et. al.\textsuperscript{71} the one employed in this work:

\[ \varepsilon(\omega, r, A) = \varepsilon_{\text{bulk}}(\omega) + \frac{\omega_p^2}{\omega^2 + i\omega \gamma_M} - \frac{\omega_p^2}{\omega^2 + i\omega(\gamma_M + \gamma(a, A))} \]

Eq. 5

We selected this function because it constitutes a fully description of the NP dielectric function where NP size, NP interface and also bound electrons are considered, as it is explained below.

In Eq. 5 Drude's model is employed to describe free electrons in a metal, where \( \omega_p \) is the plasma frequency (1.37·10\textsuperscript{16} s\textsuperscript{-1}) and \( \gamma_M \) (3.18·10\textsuperscript{13} s\textsuperscript{-1}) is a phenomenological parameter that represents the macroscopic damping constant due to the dispersion of the electrons by the ions of the bulk material. For NP with smaller size than the mean free path of conduction electrons\textsuperscript{57}, an additional term is added to the damping constant:

\[ \gamma(a, A) = \frac{\gamma_F}{a} \]

Eq. 6

This term accounts for interface dispersion damping - \( \gamma_F \) indicates the Fermi velocity (1.41·10\textsuperscript{16} m·s\textsuperscript{-1}) and \( a \) the NP radius-, it considers the effect of the NP/medium interface on the conduction electrons through the \( A \) parameter. The value of \( A \) depends on the theory employed to calculate it.
and it is usually around 1.\textsuperscript{70,72} As $A$ represents the effect of the interface characteristics into the
NP dielectric function, this value depends on the contact angle of the NP with the oxide walls of
the MTTF. According to Hilger et. al.\textsuperscript{73}, the $A$ parameter for silver NP varies from 0.6 to 1.8,
from NP in vacuum to NP totally immersed in a titania matrix. We expect similar values for Au
NP also immersed in titania.

Dielectric functions for bulk ($\varepsilon_{\text{bulk}}$) materials such as silver and gold have been reported in works
of Palik\textsuperscript{74} and Johnson & Christy.\textsuperscript{75} The use of each of the dielectric functions depends on the
spectral range in which calculations are carried out. For optical frequencies such as those studied
here, the Johnson and Christy data was found to be more accurate.

**Nanoparticles immersed in MTTF.** In the context of Mie theory, NP absorption coefficient
within the dipolar approximation is well defined for isolated particles of radius $a$ by\textsuperscript{76}:

$$C_{abs}(a, A, \omega) = 4\pi ka^3 \text{Im} \left[ \frac{\varepsilon_{\text{NP}}(a, A, \omega) - \varepsilon_{\text{MTTF}}(\omega)}{\varepsilon_{\text{NP}}(a, A, \omega) + 2\varepsilon_{\text{MTTF}}(\omega)} \right]$$

\textbf{Eq. 7}

Eq. 7 describes the absorption coefficient expression per NP, where $k = 2\pi/\lambda$, $\varepsilon_{\text{NP}}$ the NP
dielectric function and $\varepsilon_{\text{MTTF}}$ the medium dielectric function.

From Eq. 7, the absorbance can be obtained considering the number of NP per unit area ($N_{\text{NP}}$ )
present in the sample:

$$Abs(a, A, \omega) = \frac{N_{\text{NP}}C_{abs}(a, A, \omega)}{\ln(10)}$$

\textbf{Eq. 8}

where $Abs$ represents the absorbance measured in normal transmission mode in an UV-visible
spectroscopy experiment.

From Eqs. 7-8 it is possible to observe that $Abs$ depends on the number $N_{\text{NP}}$, on NP size ($a$), on
NP/MTTF interface ($A$) and on the medium dielectric constant $\varepsilon_{\text{MTTF}}(\omega)$.
It is known that the Abs function can be directly compared with the UV-Visible spectrum of the sample in order to fit its function parameters. It is worth to mention that only two set of parameters can be determined together: $a$ and $N_{NP}$ or $A$ and $N_{NP}$, the $\varepsilon_{MTTF}(\omega)$ corresponds to the dielectric function determined through Eq. 2 by the $n_{MTTF}$ value acquired from the ellipsometric measurements (Eq. 3).

Taking this into account we firstly employed the absorbance spectrum of a sample with a well-known NP radius ($a$) acquired from TEM measurements -see Fig. 2- in order to obtain the $A$ and $N_{NP}$ by fitting the Abs function to the experimental spectrum. The $A$ parameter thus determined can then be employed to describe the effect of the interface between Au NP and MTTF.

Once the $A$ parameter is known, another sample can be taken and by fitting the Abs function to its UV-Visible spectrum, the NP radius ($a$) and the $N_{NP}$ can be determined.

Besides that, in a unit area, $N_{NP}$ can be related to the pore volume fraction occupied by the NP ($f_{NP}$), to the pore volume fraction ($f_p$) of the film, to the NP radius ($a$) and also to the film thickness ($d$) by,

$$N_{NP} = \frac{3f_{NP}f_p d}{4\pi a^3}$$  \hspace{1cm} \text{Eq. 9}

On the other hand, NP inside MTTF can be modeled through an EMA approach where $n_{eff}$ and $k_{eff}$ represent the NP@MTTF refractive index. This effective refractive index is obtained by combination of MTTF dielectric function -measured by ellipsometry- and metallic NP dielectric function -Eq. 5-. The Maxwell-Garnett (MG) model\textsuperscript{37} is an EMA that describes metallic spherical inclusions into an homogeneous matrix,

$$\frac{\varepsilon_{eff} - \varepsilon_{MTTF}}{\varepsilon_{eff} + 2\varepsilon_{MTTF}} = f_{NP}f_p \frac{\varepsilon_{NP} - \varepsilon_{MTTF}}{\varepsilon_{NP} + 2\varepsilon_{MTTF}}$$ \hspace{1cm} \text{Eq. 10}
where $\varepsilon_{\text{eff}}$ is the NP@MTTF dielectric function, $\varepsilon_{\text{MTTF}}$ the MTTF dielectric function, $\varepsilon_{\text{NP}}$ the NP dielectric function, $f_p$ the porous fraction and $f_{\text{NP}}$ the NP volume fraction. If NPs are spherical and do not interact with each other, MG and Mie theory should lead to the same results: $a$ and $f_{\text{NP}}$, considering that $A$ is known.

Besides the modeling through UV-Visible spectra, it is also possible to obtain the dielectric constant of the NP@MTTF system by ellipsometry. This function can be used to determine the absorption coefficient (see Eq. 2), from where the absorption constant ($\gamma_{\text{abs}}$) can be calculated:

$$\gamma_{\text{abs}}(a, A, \omega) = 4\pi k/\lambda$$

Eq. 11

which is an intrinsic optical property of the film that can be converted into its absorption spectra by

$$\text{Abs}(a, A, \omega) = \gamma_{\text{abs}} d/\ln(10)$$

Eq. 12

where $d$ denotes the film thickness.

From Eq. 2 and Eqs.11-12, the dielectric function can be transformed into the absorption spectra. In particular, we used this strategy to transform the $\varepsilon_{\text{eff}}$ obtained from MG theory to UV-Visible spectra and compare it with experiments and Mie's theory results. This can also be applied to convert $\varepsilon_{\text{eff}}$ measured by ellipsometry into UV-Visible spectrum. Fig. 4 displays $\alpha$ and $\beta$ angles (that are related to the $\Delta$ and $\Psi$ parameters of an SE measurement) with their corresponding fitting and the dielectric constant obtained for Au@TiO$_2$.

---

*They are related by: $\tan\Delta = \frac{\tan\theta}{\sqrt{1 - \kappa^2}} = \frac{\tan\Psi}{\sqrt{1 - \kappa^2}}$, where $A$ is the analyzer angle (45° in our case).
**Figure 4.** Ellipsometric functions Alpha (a) and Beta (b) for the TiO$_2$-Au5RS sample. The result of the fitting of the proposed model is presented superimposed (grey curve). In (c), the reconstruction of the dielectric function for both the real ($\varepsilon_1$) and imaginary ($\varepsilon_2$-dashed line) components is shown, obtained from the fitted parameters of the model.
**Au@TiO₂: comparison between modeling and experiments.** Two different samples of Au@TiO₂-5RS -obtained after 5 reduction steps- were considered. From the analysis of the TEM images, an average radius \( a \) of \((2.9 \pm 0.5) \) nm is extracted (Fig. 3), and employed in Eq. 8 to determine the Abs parameters \((A \text{ and } N_{NP})\) by fitting this function to the absorbance spectrum. As a result we calculated an \( A \) value of 1.5, which is representative for this kind of system: Au@MTTF. This result for \( A \) value could be expected in analogy to the increase in the \( A \) parameter with respect to the vacuum value reported for Ag NP in contact with TiO₂.⁷³

Once the \( A \) parameter was set up as 1.5, we determined on the other Au@TiO₂-5RS sample the radius \( a \) and the filling fraction \( f_{NP} \), by using Mie (Eq. 8-9) and MG (Eq. 2, 11-12) theories. Results are addressed in Fig. 5, with the corresponding correlation function for the adjustment with respect to the UV-Visible spectrum within the range of 440 to 750 nm. The Abs functions determined by both models are also displayed in Fig. 5, from which it can be observed an excellent coincidence between the experimental spectrum and the models.

![Absorbance](image)

**Figure 5.** Experimental (circles) and calculated absorbance spectra of Au5RS sample performed through Mie theory (red, dashed) and Maxwell-Garnett EMT (green, solid). Comparison with normalized spectra calculated from the parameterized effective dielectric function obtained from ellipsometry measurements (blue, dashed).
Table 1. Fitted parameters $a$ and $f_{NP}$ for MG and Mie theories with respect to UV-Visible spectra along with the correlation function $R^2$ obtained for each adjustment.

<table>
<thead>
<tr>
<th></th>
<th>$f_{NP}$ (%)</th>
<th>$a$ (nm)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mie vs. UV</td>
<td>1.77</td>
<td>2.88</td>
<td>0.99</td>
</tr>
<tr>
<td>MG vs. UV</td>
<td>1.76</td>
<td>2.89</td>
<td>0.99</td>
</tr>
<tr>
<td>MG vs. ellip. (corr)</td>
<td>1.78</td>
<td>2.87</td>
<td>0.99</td>
</tr>
</tbody>
</table>

The effective dielectric function ($\varepsilon_{eff}$) of Au@TiO$_2$-5RS was obtained not only by MG modeling (Eq.10) but also by ellipsometry (Fig. 4). Using Eq. 2 and Eqs. 11-12 it is was possible to determine the absorbance spectrum from the ellipsometry measurement. The LSPR peak position as well as the plasmon width can be reproduced by the ellipsometry data when it is converted to the absorbance spectrum. Regarding the LSPR intensity, which is related to the absolute absorbance value, in our case is overestimated -by a factor of 2- by this technique. For this reason, the corrected spectrum is shown in Fig. 5. A more detailed discussion about the excellent correspondence of these two techniques for adsorbed dye molecules can be found in the SI.

Once the corrected spectrum is obtained from ellipsometry, we can determine by MG theory (Eq.2, 10-12) –as we did for UV-Visible spectrum- the NP size and $f_{NP}$. The results obtained from these two techniques are in accordance (see Table 1).

It is useful to remark that the ellipsometric $\varepsilon_{eff}$ of Au@TiO$_2$-5RS is constructed by Cauchy and Lorentz models within the range of 400-960 nm. The Lorentz model accounts for LSPR, leading to an adsorption coefficient that only corresponds to the LSPR. As no term is added to model the Au NP interband transitions, the spectrum obtained at shorter wavelengths -around 400 nm- is different than the ones determined by Mie and MG models as well as the one acquired by UV-Visible spectrophotometer. It can be seen –Fig. 5- that the Au interband transitions are far enough
of the LSPR. Therefore, its influence should be minor, and for this reason we believe it is not relevant to account for the interband transitions in the ellipsometric measurements.

For this case, the average gap distance \( d_{\text{gap}} \) can be estimated as:

\[
d_{\text{gap}} = \left( \frac{3f_p d}{4\pi N_{\text{NP}}} \right)^{1/3} - 2a \quad \text{Eq. 13}
\]

Considering the NP inside the porous volume fraction of the MTTF, an average value of gap distance \( d_{\text{gap}} = 12.0 \text{ nm} \) (defined between NP surfaces) is obtained for 5RS. This value, which is slightly higher than the interpore distance, supports the idea of non-interacting NP, individually located in the mesopores.

3. The effect of the Relative humidity

Due to the high surface area and the presence of mesopores, exposure to increasing vapor pressure of a solvent, such as water, leads to adsorption on the MTTF pore system. A gradual increase of the refractive index is observed for low relative humidity (RH) values since the onset of water capillary condensation takes place for RH values in the range 55-65% (see EP results in Fig. S1 in SI). Upon condensation of water inside the pores, a dramatic change in the effective refractive index is observed, if compared to the minor change (between 1.53 and 1.55) observed for values below the critical vapor pressure of condensation. This allows the employment of two components to describe the Au@MTTF system even though experiments are carried out in ambient conditions where RH<45%.

Since the pores and the NP present in the film are accessible to the humidity, capillary condensation of water leads to a plasmonic response.\textsuperscript{21,77} With the aim of studying this effect, we characterized the LSPR at 0% and 95% RH by SE, obtaining an excellent agreement between the proposed model and the measurements (Fig. 6). The plasmon position recorded for successive measurements under these two conditions show a reproducible and reversible 10 nm
bathochromic shift of the LSPR peak position, as shown in Fig. 6c. It is noteworthy to observe that the peak positions in “dry” and “wet” conditions do not suffer an appreciable shift or trend under the explored conditions (7 cycles), demonstrating the robustness of this nanocomposite system.

Figure 6. Ellipsometry measurements at different RH conditions. Figures a) and b) show the alpha values at 0% and 95% RH respectively. The shift in LPSR peak position upon exposure to
cycles of 0% and 95% RH is displayed on c).

4. Bilayer systems

In order to analyze the extension of the method proposed we synthesized a bilayer mesoporous system composed by two mesoporous thin films, SiO\(_2\)-CTAB (SC) and TiO\(_2\)-F127 (TF), as described in the experimental section. The sample consists of a CTAB-templated silica (SC) layer in contact with the substrate (glass) while the upper layer is an F127-templated titania (TF), as described in reference 44. For the ellipsometry measurements, each layer was adequately adjusted through a Cauchy model. This bilayer system was infiltrated with Au NP with 10 reduction steps (10RS) since the LSPR developed after each RS was found to be less intense than for the monolayer system. The sample was measured using micro-spot SE (<1mm beam diameter) in five different points separated several millimeters from each other. The measurements were analyzed proposing a model in which a Lorentz oscillator was added to the dielectric description of each layer to account for the LSPR. The starting parameters for this absorption component were exactly the same for both layers, i.e. the same filling fraction of Au NP was supposed as a starting point in the fitting procedure. The parameters describing the LSPR for the TF layer converged in all cases to similar values, while the ones corresponding to the SC layer were more erratic (Fig. 7); in particular, the amplitude of the Lorentz functions in this case were one order of magnitude less than for the TF layer, suggesting a significantly lower filling fraction for the SC layer. In fact, the fitting of a model that accounts for NP only in the TF layer (no Lorentz function added to SC dielectric function) was excellent (R\(^2\)=0.996). These results strongly suggest that the infiltration-reduction procedure is taking place mostly at the TF layer, and much less in the SC layer. This can be explained by considering the low adsorption of AuCl\(_4^-\) anions at pH 4 in SiO\(_2\), in which the isoelectric point (iep) is close to ~2, as previously
reported.\textsuperscript{78} On the contrary, the Au(III) precursor can be efficiently adsorbed within the titania mesopores, in which the \textit{iep} is in the \( \sim 5-7 \) range. Additionally, the selective reduction might be catalyzed by TiO\(_2\) as was reported to occur in bilayer mesoporous thin films for the case of silver NP.\textsuperscript{17}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure7.png}
\caption{Fitted parameters describing the amplitude, peak position and broadness of the Lorentz function of the LSPR for each layer in Au10RS-TF/SC/glass.}
\end{figure}

For the calculation of the particle size and the filling fraction, the porous volume fraction of the TF layer was determined through EP in the bilayer system; a value of 35\% pore volume was found.

As in the case of the monolayer TF sample, and using the previously discussed value of \( A=1.5 \), the fitting procedure of the Mie and Maxwell-Garnett calculated spectra was performed to the measured absorbance of the Au10RS-TF/SC sample. The results are displayed on Fig. 8, together with the corrected spectra calculated from the ellipsometry measurement. From the analysis of the spectra, a particle radius \( a = (2.8 \pm 0.1) \) nm and filling fraction \( f_{NP} = (3.8 \pm 0.1)\% \) of the porosity can be extracted.
Figure 8. Experimental (circles) and calculated absorbance spectra of Au10RS-TF/SC sample performed through Mie theory (red, dashed) and Maxwell-Garnett EMT (green, solid). Comparison with normalized spectra calculated from the parameterized effective dielectric function obtained from ellipsometry measurements (blue, dashed).

5. Analysis of NP growth

The model developed in this work can be applied to the first ten reduction steps in order to shed light into the infiltration mechanism. We determined NP radius and $f_{NP}$ for five different reduction steps (4 to 8 RS) through modeling their plasmonic response. From these results we calculated the number of NP per volume unit ($N_{NP}^v = N_{NP}/d$) and the interparticle gap distance ($d_{gap}$, Eq. 13). We observed that both $N_{NP}^v$ and NP size increase during the infiltration, but $N_{NP}^v$ reaches a plateau after the sixth reduction step, as shown in Fig. 9. In addition, the calculated $d_{gap}$ exhibits a decreasing trend for subsequent reduction steps.
Figure 9. Calculated values of a) filling fraction and particle radius, and b) average gap distance ($d_{gap}$) and particle density ($N_{NP}$) after successive reduction steps.

The observed behavior suggests that the mechanism of particle formation proceeds through nucleation and growth. A fast nucleation and growth of ca. 2 nm radius particles takes place in the first steps; subsequent exposure to Au(III) precursor and reducing agent can lead to concurrent nucleation and growth processes. After six reduction steps, however, while the NP filled pore volume and NP size keep growing (Fig. 9a), the total number of nanoparticles ($N_{NP}$) levels off, suggesting that nanoparticle growth dominates the scenario, and new nucleation is no longer significant. The NP radius increase is accompanied by a significant decrease in the interparticle gap distances (Fig. 9b).

It is interesting to note that calculated gap distances are smaller than the pore diameter, i.e., each pore contains one metallic nanoparticle at most, which is also consistent with the TEM observations. In the RS<10 regime, thus, the presented model of isolated spherical nanoparticles is valid, and useful information on nanoparticle size, separation and pore filling can be simultaneously extracted. Plus, this method permits to shed light into a crucial question: which should be the effect of the number of nuclei or NP size in the shape of the plasmon.
For further infiltration-reduction cycles, the situation is more complex. As observed in Figure 1C, a significant bathochromic plasmon shift takes place for RS>10. Fig. 10 shows TEM micrographs of MTTF exposed to 6, 12 and 16 RS. A higher number of larger size particles are obtained within the pore systems after successive RS. A thorough statistical analysis performed on top-view micrographs permitted to determine an increase in the NP horizontal section from ca. 5 nm to almost 9 nm while going from 6 to 16 RS. In the latter case, completely filled mesopores are observed, as well as patches of neighbouring nanoparticles of similar size.
Figure 10. TEM images of MTTF filled with Au NP after 6, 12 and 16 reduction steps, and statistical counting of several images (mean particle size ($D_0$) and standard deviation ($\sigma$) determined from Gaussian fits in each case).

The observed optical and structural properties can be due in principle to the combination of three effects that take place for $RS>10$:
a) Nanoparticle size growth
b) Development of nanoparticle asymmetry
c) Plasmon coupling between nanoparticles

In this context, we can advance that the mechanism of NP growth within the pore system is complex, and implies the steps a-c presented above. For low pore fillings, almost spherical nanoparticles grow and the model adequately describes them. For higher Au pore filling, nanoparticle growth is responsible of the increase in the plasmon absorption. Further growth can lead to full pore filling, leading to ellipsoidal nanoparticles and eventually to pore blocking.\textsuperscript{79} In the latter case, Au\textsuperscript{°} nucleation can take place at the TiO\textsubscript{2}-solution interface of an empty pore. In the high supersaturation conditions present in this reduction method, new nucleation is likely followed by very fast nanoparticle growth. This leads to a leveling off of the NP size which is ultimately templated by the pore size and shape. In addition, for RS>10, NP sizes begin to be comparable to gap distances (see Figures 9 and 10), implying optical interaction between NP, sustaining hypothesis c). In summary, the combined interplay of NP shape and interactions can explain the steep red shift in the spectra for RS>10 presented in Fig. 1.

The model framework presented here accounts for spherical NP between 2-10 nm without interactions, but could be extended to other shapes and sizes. It could be easily employed for ellipsoidal NP through the use of Gans theory as an extension of Mie’s and the EMA model given by Polder & Von Santen\textsuperscript{80}. For NP larger than 10 nm, the dipolar approximation is no more valid, and higher modes have to be considered for the extinction coefficient $C_{ext}$. Consequently, the model can be extended to these systems but at the expense of increasing the computing time.

It is worth to mention that this way of modeling the LSPR of gold NP included in MTTF can be extended either to other matrix systems, such silica and zirconia mesoporous thin films, or to
other metallic NP, such as Ag NP. As the $A$ parameter is intrinsic of each composite it has to be
determined for each case.

The main limitation, however, arises when interparticle distances become short enough for
electromagnetic interactions to take place. In such scenario, MG and Mie theories are no longer
valid, and more complex calculation methods should be applied\textsuperscript{11}, in particular García and
coworkers presented a simple way to account for the interactions by the addition of a single extra
parameter\textsuperscript{81}.

6. Critical aspects concerning reproducibility and predictive power

The model presented here permits to extract NP size, particle density, pore filling fractions and
mean gap distance for gold NP embedded within a mesoporous matrix from the analysis of LSPR
bands. This information also permits to understand the formation paths of such nanocomposite
systems, opening the possibility to design their optical properties.

The reproducibility of the reduction process that leads to NP generation is a very important issue.
We noticed that the spectra of independent experiments presented slight differences on the
maximum absorbance along the reduction steps. Consequently, we decided to compare these sets
by classifying them by their maximum absorbance, instead of considering the number of
reduction steps performed.

Fig. 11a shows the calculated filling fraction ($f_{\text{NP}}$, closed red symbols) and NP radius (open red
symbols) of a series of reduced samples presented in Fig. 9, replotted as a function of the
absorbance maximum. The increasing trend regarding both quantities along reduction is still
evident. An excellent agreement between the NP size and pore filling of this series extracted
from the modeling of the optical properties and the independently obtained sample discussed in
Section 2 is presented in Fig. 11a. This reinforces the confidence in the predictive capacity of the
model.

However, there are subtleties in the synthesis method that have to be taken into account in order to make a correct evaluation of the system properties obtained from the spectra. An independent experiment performed in slightly different conditions, named synthesis-2 (Fig. 11a, blue symbols) exhibits a similar filling fraction to synthesis-1, but a greater NP radius. The only difference between these two syntheses is the cleaning procedure of the film surface. On synthesis-1, the film surface was cleaned after each reduction step before measuring its spectrum, as was done in the film thoroughly discussed in Section 2. This cleaning step after each RS was not performed for synthesis-2. To study this effect on synthesis-2, we cleaned the film surface and measure its spectra immediately after (see Fig. 11b) and recalculated the filling fraction and radius, obtaining a substantial difference on the radius determined. The average NP radius obtained after cleaning the film surface was in very good agreement with TEM images of this sample (6±1nm diameter, Fig. S8 SI). Observing the slight difference between spectra –Fig. 11b- and the clear difference on the subsequent radius determined –Fig. 11a-, we observe that this modeling methodology detects subtle variances on the particle growth among sets of experiments that would be difficult to assess by other characterization techniques. We believe that the first infiltration-reduction steps are more sensitive to physicochemical conditions that affect the NP growth mechanism, including synthesis variables that were not systematically explored, such as temperature, film thickness and the aging of Au(III) and NaBH₄ solutions. As demonstrated above, the cleaning process before infiltration is also important. However, we have to remark that the modeling of the plasmon response developed in this work provides a very sensitive tool to observe and eventually correct the influence of these conditions in the actual synthesis.
Figure 11. a) Calculated values of filling fraction and particle radius for two different samples prepared in similar conditions. The inset shows the evolution of the spectra for synthesis 1. The point marked as 1 represents the monolayer sample discussed in section 2. The point marked as 2 corresponds to the particle radius and filling fraction calculated before and after cleaning the film surface. In panel b) spectra of sample referred as 2 before cleaning (BC) and after cleaning (AC) the film surface with their respective calculated radius.

7. Discussion

We understand that ellipsometry possesses several advantages in the task of characterizing the LSPR of an optical material such as NP@MTTF. SE opens the possibility to study the LSPR at different relative humidity (*i.e.* EP), as well as providing structural information such as the localization of the NP in a multilayer MTTF, or even in a more complex nanostructure involving both NP and adsorbed dyes (see Fig. S7 SI), which is applicable to dye-sensitized solar cells (DSSC). EP allows the evaluation of the plasmon response of the nanocomposite material to changes in environment vapor pressure, providing an additional tool in the research of these
materials acting as vapor sensors. For the bilayer system analyzed in this work, the nanostructural information regarding the localization of NP could be only achieved by more complex characterization techniques such as high resolution electron microscopy, (e.g. TEM in cross section mode), Rutherford back-scattering (RBS) or XRR. Ellipsometry, in this sense, provides a non-destructive optical option for this sort of studies. However, the limitation of the technique must also be considered both in the conditions of the measurement itself and on the accuracy of the resulting parameters after the fitting. The former issue involves: the ambient conditions in the surroundings of the sample, the angle of incidence which must be as close as possible to the Brewster angle, and the use, or not, of a micro-spot configuration. Since the use of a micro-spot reduces the area of measurement to a few hundreds of square microns, increasing the intensity of the signal, several points of the sample should be acquired in order to quantify its homogeneity and the statistical standard deviation of the fitted parameters. This analysis depends, of course, on the particular sample under study, but the inhomogeneity could possibly be the principal source of incertitude in the resulting values, regardless of the accuracy of the fitting. With respect to the fitting procedure, several topics emerge: on one side, the dielectric model proposed could only be applicable to a restricted range of the spectrum, as in this case, limiting the validity of the resulting dielectric functions outside the fitting range. On the other hand, once the model and the multilayer structure are selected, the fitting procedure is highly dependent on the starting parameters as the minimization has not a unique solution. For this reason, any previous information of the sample is valuable and careful must be taken for the analysis of unknown samples.

On the other hand, regardless of the simplicity of its operation, spectrophotometry provided direct and confident information about the absorbance spectrum for the sort of samples analyzed
in this work. Although non-transparent substrates could also be analyzed in a similar way in reflectance mode, it requires special accessories, like optical fiber systems or integration spheres, of less common accessibility. In any case, the spectrum acquired is insensitive to the details of the micro/nano-structure of the sample since it only relates the intensities of the incoming and outgoing light and no extra information is retrieved regarding the phase and polarization of light. As was shown in this work, the absorbance spectra obtained for the samples studied is sufficient to calculate both the volume filling fraction and the mean radius of the NP present in the MTTF, but it fails in providing additional information about the microstructure like the location of the NP in a mesoporous multilayer film.

We would like to remark that the employ of TEM images is decisive to determine the NP morphology and size. The feedback between TEM images and the optical techniques (UV-Vis spectroscopy, ellipsometry) permitted to determine the $A$ parameter for the Au@$\text{TiO}_2$-5RS system, allowing in turn the subsequent prediction of NP size and $f_{NP}$ for other filling fractions. This was employed for a more complex system such as the NP immersed in the titania layer of the bilayer system (Au10RS-TF/SC/glass).

**Conclusions**

Along this work, we set up the basis to model the plasmonic response of Au NP -without interactions- inside MTTF (TiO$_2$-F127). By experimental UV-Visible spectrophotometry we determine the LSPR of the system and the reduction steps that should be performed to consider isolated NP. We then conducted the modeling, analyzing each component -NP and MTTF- in detail. After this discussion we were able to model the NP@MTTF and to understand the appropriate way to describe it and compare it with experimental data. Spectrometric Ellipsometry measurements provide accurately the dielectric function of the
MTTF, that when used in the framework of Mie and Maxwell-Garnett theories leads to excellent agreement with UV-Visible spectra of the nanocomposite NP@MTTF (see Fig. 5 and Table 1). This technique also opens the possibility to acquire the full dielectric function of the nanocomposite systems, providing a precise result of the LSPR peak position, and thus enabling to study the response of the LSPR to the humidity present in the porosity. On the other hand, this technique supplies nanostructural information to determine the NP localization in a multilayer system and can be used to obtain the absorbance spectrum when a non-transparent substrate is used. We find out that this conversion gives exact results for dyes adsorbed in the MTTF, as detailed in the SI.

A valuable output of this modeling method is the excellent agreement between the proposed model and the actual experimental data. This permitted us to follow NP growth and assess NP size and filling fraction with a high degree of confidence. This has proven to be particularly interesting in understanding the role of synthesis variables in the reproducible production of NP@mesoporous oxide films, as well as proposing a plausible mechanism of formation of these nanocomposites.

Finally, and as a consequence of this work, it is worth to mention that this modeling strategy can be applied to other systems. In particular, we are investigating Ag@TiO$_2$ and Ag@SiO$_2$, where the modeling is more complex due to the reactivity of Ag NP that get usually oxidized in air conditions. These NP evolves to core-shell like structures Ag/Ag$_2$O NP$^{82}$ and constitute our current challenges to be modeled.

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Supporting information available

Detailed information regarding the film characterization is described including ellipsoporosimetry measurement, TEM and SAXS characterization of the MTTF and the calculation of pore filling fraction from EDS and from XRR measurements. FE-SEM images of the bilayer system Au10RS-TF/SC, calculated absorbance spectra using a Gaussian distribution function accounting for the polydispersity in particle size. Comparison between ellipsometry and UV-Vis spectra in dye loaded MTTF. Additional TEM images of Au nanoparticles embedded in MTTF. This information is available free of charge via the Internet at http://pubs.acs.org.

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References


17 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,


32 Losurdo, M.; Bergmair M.; Bruno, G.; Cattelan, D.; Cobet, C.; Martino, A.; Fleischer, K.; Dohcevic-Mitrovic, Z.; Esser, N.; Galliet, M.; et. al. Spectroscopic Ellipsometry and


9846-9853.


79 It is well known that these mesopores are of an ellipsoidal shape, due to uniaxial contraction.
Typical uniaxial shrinkages of the mesopore structure are in the order of 40-50%, the pore height being in the order of 5-6 nm.\cite{35} This supports the hypothesis b), i.e., that filled pores contain asymmetric particles. Interestingly, the spherical model explains very accurately the optical properties when NP are below 6 nm diameter.


**TOC Figure**