Supporting Information

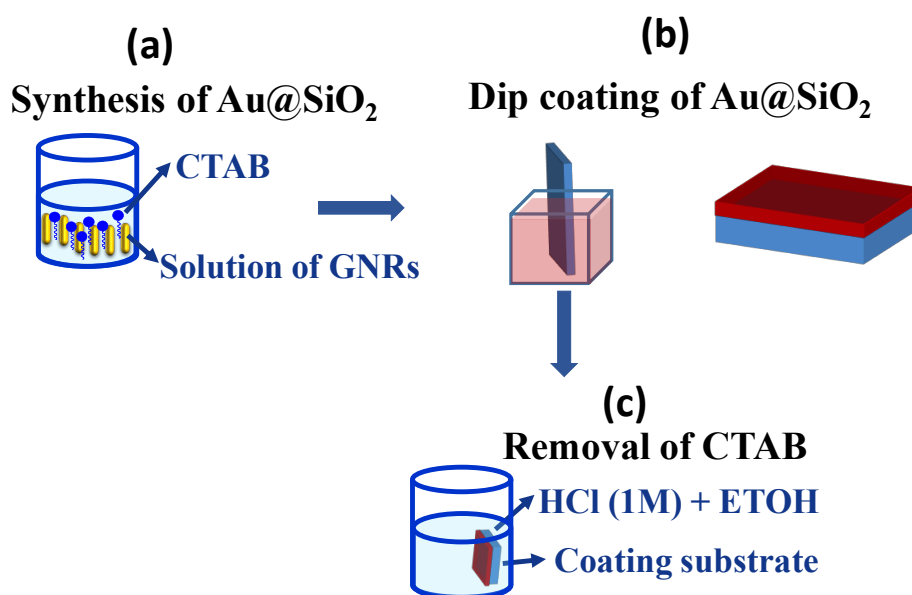# *Nanoconfined Water Vapor as Probe to Evaluate Plasmonic Heating*

Zeinab Chehadi[1], Cédric Boissière[1], Corinne Chanéac[1] and Marco Faustini [1]*

[1]*Sorbonne Université, UPMC Univ Paris 06, CNRS, Collège de France, Chimie de la Matière Condensée de Paris, 75005 Paris, France.*

1   Preparation of colloidal film of Au@mesoporous SiO$_2$

We use the methodology represented in Fig. S1 to fabricate the nanocomposite film of Au@SiO$_2$. First, we synthesize colloidal particles of Au@SiO$_2$. Then we deposited them on the glass substrate and finally we removed the CTAB by washing the samples with a solution of HCl (1M) in ethanol (1).

(a)
Synthesis of Au@SiO$_2$
CTAB
Solution of GNRs

(b)
Dip coating of Au@SiO$_2$

(c)
Removal of CTAB
HCl (1M) + ETOH
Coating substrate

***Fig. S1* :The methodology used to fabricate the film of Au@SiO$_2$.**

2   Characterization of GNRs and Au@mesporous SiO$_2$

The GNRs were characterized using the transmission electron microscopy (CM-12 Philips) to get access to the morphology and size of our gold nanoparticles. Fig. S2 show TEM image of a collection of monodisperse GNRs synthesized having an average aspect ratio of 4. The extinction coefficient obtained by Vis/NIR spectroscopy shows the L-LSRP and T-LSPR are located at 850 nm and 550 nm respectively. After the formation of SiO$_2$ shell, the L-LSRP of GNRs solution red shifts with increasing local refractive index.

(a)

(b)
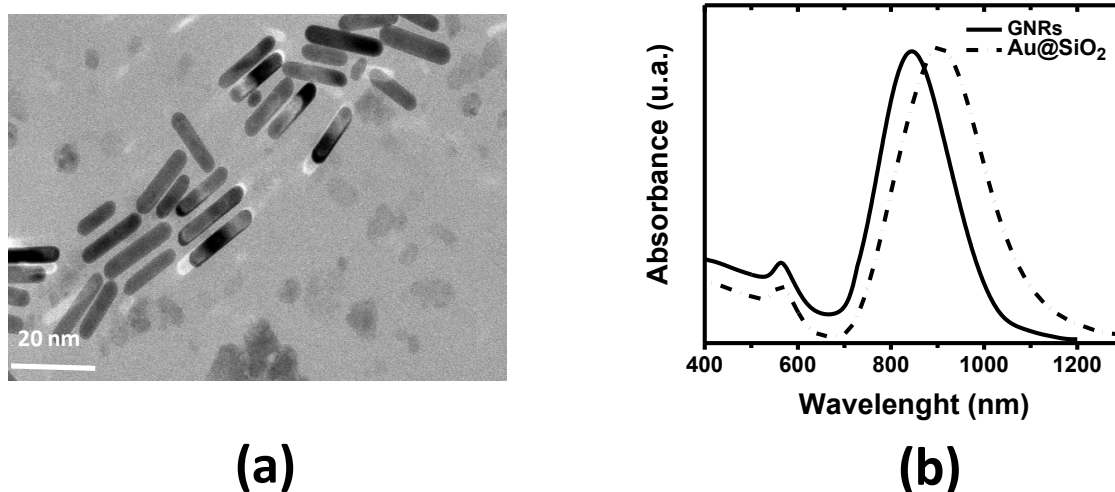
Fig. S2 : **(a) TEM image of GNRs synthesized (b) UV-Vis-NIR spectra of as-prepared GNRs (solid line) and core-shell Au@SiO$_2$ nanostructure (dash line).**

The Fig. S3 shows the influence of time of washing on the LSPR of GNRs.
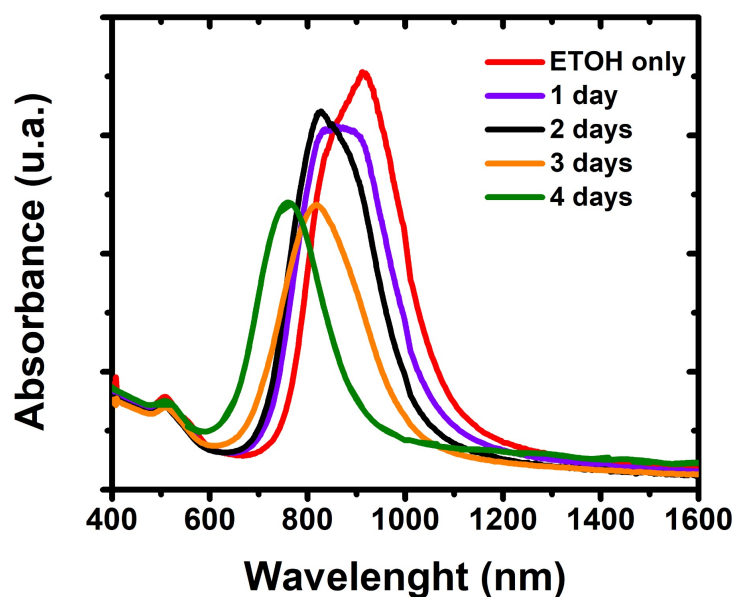
Fig. S3 : **UV-vis spectra of GNRs as a function of time of washing with a solution of HCl (1M) in ethanol.**

3   Preparation and characterization of film of colloidal particles of SiO₂

### 3.1   Preparation of colloidal particles of SiO₂

Mesoporous silica was prepared according to the stöber method. It was carried out as follows: 0.29 g of CTAB were dissolved in 125 ml of warm water. The solution was allowed to cool down to 20°C. Following this step 25 ml of NH₄OH (0.512 M), 0.55 g of Tetraethyl orthosilicate (TEOS) in 3 ml of Ethanol. Finally, the solution was placed at 20°C for 48h.

3.2   Preparation of colloidal film

After preparing the colloidal solution of SiO₂, the colloidal films were fabricated by dip coating on the glass substrate. Films were deposited at the withdrawal rate in the capillarity regime (0.005 mm/s) and at 60°C. Then, the CTAB was removed through washing the samples with a solution of HCl (1M) in ethanol.[1]

3.3 Characterization of colloidal film of SiO$_2$

The colloidal film of SiO$_2$ was characterized using the transmission electron microscopy (CM-12 Philips) to get access to the morphology and size of nanoparticles. SEM image of our film carried out using the scanning electron microscope (SEM-FEG Hitachi SU-70).

(a)   **(b)**
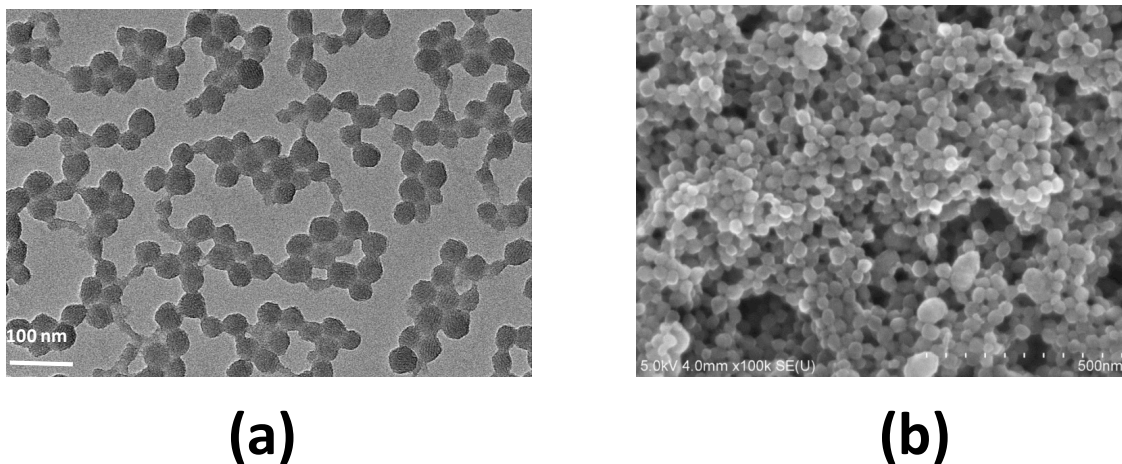
Fig. S4 : **(a) TEM image of colloïdal SiO$_2$ (b) SEM image of colloidal SiO$_2$.**

These images show clearly porous structure of silica particles, where the size of SiO$_2$ is about 40 nm.

4 Ellipsometric measurement of the optical properties of Au@SiO$_2$

The measured ellipsometry parameters profile (Ψ (λ) and Δ (λ)) were used to obtain the optical constants of our nanocomposite film through several fitting.

The model used to fit has been detailed in part 3.2.1 in the article. The table shows the detailed parameters of the Lorentz oscillators used to determine ε''.

Oscillator type	Amplitude	Breadth	Energy (eV)	Wavelength (nm)
Lorentz	1.977	0.6137	1.723	715
Lorentz	0.3625	0.4936	2.352	522
Lorentz	0.543	0.5727	2.771	447

5   Accuracy and methodology of the ellipsometric measurement

Ellipsometry is typically used for films whose thickness ranges from sub-nanometers to a few microns. The film thickness is determined by interference between light reflecting from the surface and light traveling through the film. The interference involves both amplitude and phase information. Compared other optical techniques, such as reflectivity, the phase information Δ in the ellipsometric measurement is very sensitive to films down to sub-monolayer thickness.[2] For this reason, ellispometry well suited to study ultrathin or even molecular monolayers.[3]

 Importantly, thickness measurements are not independent of the optical constants. Both n and k must be determined with the thickness to get the correct results from an optical measurement. Determination of the thickness and optical constants by ellipsometry is a multi-step process that can be summarized in the scheme hereafter :
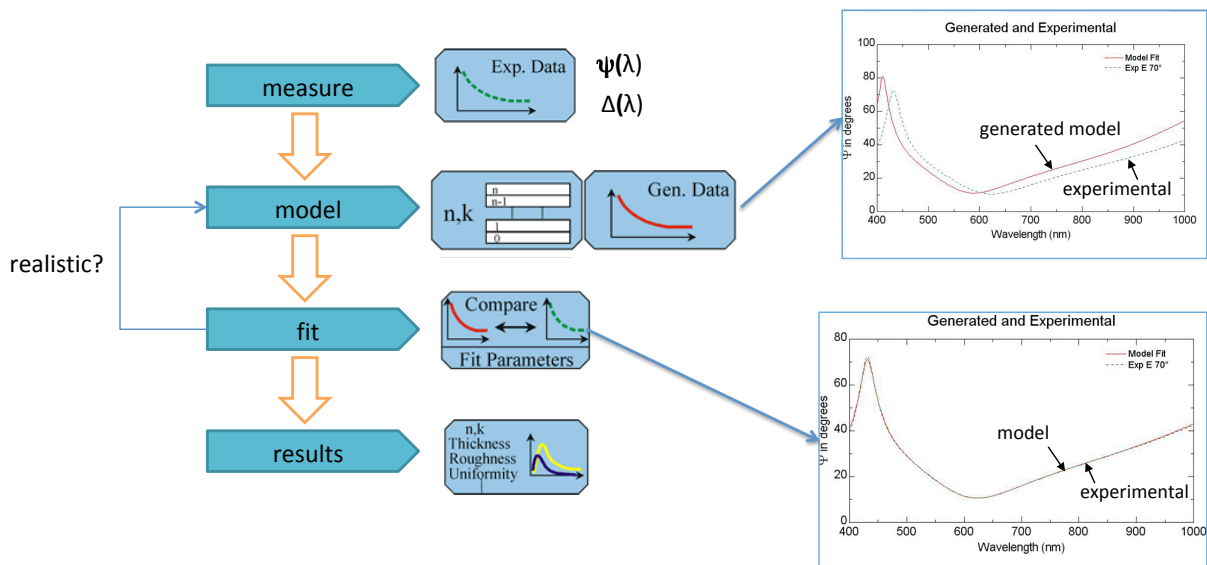

After measurement, a model is built to describe the layer. For transparent materials, the index is often described using the Cauchy such as in the case of the colloidal SiO_2 film. The

absorbing materials must account for both real and imaginary optical constants. Many models account oscillators (such as Lorentz) to describe absorption for various materials ; this is the case of plasmonic colloidal film in this work.

The model is used to calculate the predicted response from Fresnel's equations which describe the material with thickness and optical constants. If these values are not known, an assumption needs to be done : starting parameters (thickness estimation for instance) are entered for the purpose of the preliminary calculation (model). The calculated values are compared to experimental data. Any unknown material properties can then be varied to improve the match between experiment and calculation. Finding the best match between the model and the experiment is typically achieved through regression and fit. An estimator, like the Mean Squared Error (MSE), is used to quantify the difference between curves. The unknown parameters are allowed to vary until the minimum MSE is reached. The best results in terms of fit corresponds to the lowest MSE.[2]

5.1 Vapor adsoption/desoprtion of a rigid mesoporous films

As typical case, we first describe the ellipsometric porosimetry of a SiO_2 mesoporous coating template by CTAB (the same templating agent of the colloidal films). The fabrication of the film was carried out by dip-coating as described elsewhere (1).
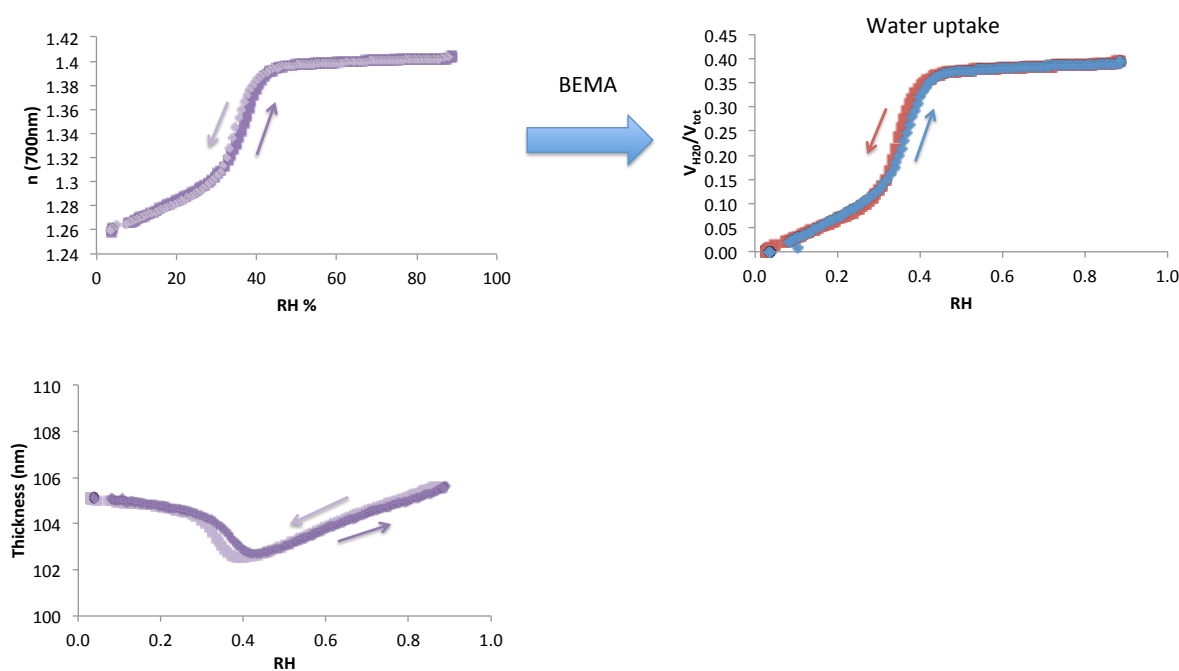
Fig. S5 Ellipsometric porosimetry of a rigid CTAB-templated mesoporous film

The evolution of refractive index and thickness as function of the relative humidity is reported in Figure S5 (left).

In rigid films (as opposed to flexible colloidal films), thickness contraction is induced by the capillary condensation of water in the mesopores during water adsorption and desorption.

Starting from refractive index evolution as function of the relative pressure the water uptaken (V_{H20}/V_{tot}) can be determined by Bruggemann Effective Medium approximation (BEMA) model:

$$f_{air}\frac{\varepsilon_{air}-\varepsilon}{\varepsilon_{air}-2\varepsilon} + f_{wall}\frac{\varepsilon_{wall}-\varepsilon}{\varepsilon_{wall}-2\varepsilon} + f_{water}\frac{\varepsilon_{water}-\varepsilon}{\varepsilon_{water}-2\varepsilon} = 0$$

in which ε_{air}, ε_{water} and ε_{wall} represent the dielectric constant of air, water and of the solid wall that is composed by SiO_2. Since air, SiO_2, and water do not absorb light in the considered range of wavelengths (400-1700 nm), the dielectric constants are taken to be the square of the refractive index values (real part of the dielectric constants).

## 5.2 Vapor adsoption/desorption of a colloidal mesoporous films
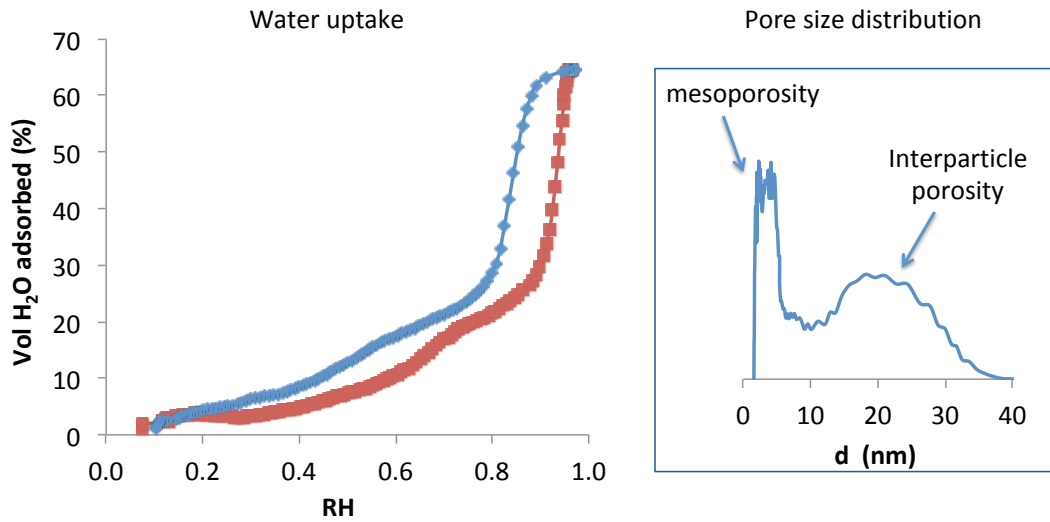
Fig. S6 Evolution of Water uptake as function of relative humidity for a colloidal mesoporous SiO₂ film ; inset : pore size distribution calculated by Kelvin equation

We calculate pore radius r_m from Kelvin equation at the value of RH corresponding to capillary condensation:

$$RTln\frac{P}{P_0} = -\frac{\gamma V_L cos\theta G}{r_m}$$

γ is the surface tension, V_L is the molar volume of water, θ is the advancing contact angle and r_m is the curvature radius of the liquid/vapor interface. G is a geometric factor accounting for the pores shape, it has a value of 2 for a sphere and 1 for a cylinder, and it can be calculated for elliptic pores knowing their anisotropy factor. For our calculations we used G = 1.965 for CTAB templated materials, $\theta = 40°$, $V_L = 1.80 \cdot 10^{-5}$ m^3/mol, $\gamma = 0.072$ N/m. [1] P/P$_0$ is assumed equal to RH. The two porosities (2-3 nm mesoporosity and the larger interparticle porosity) can be identified by the pore size distribution in agreement with microscopy analysis and with the literature on similar systems. [4]
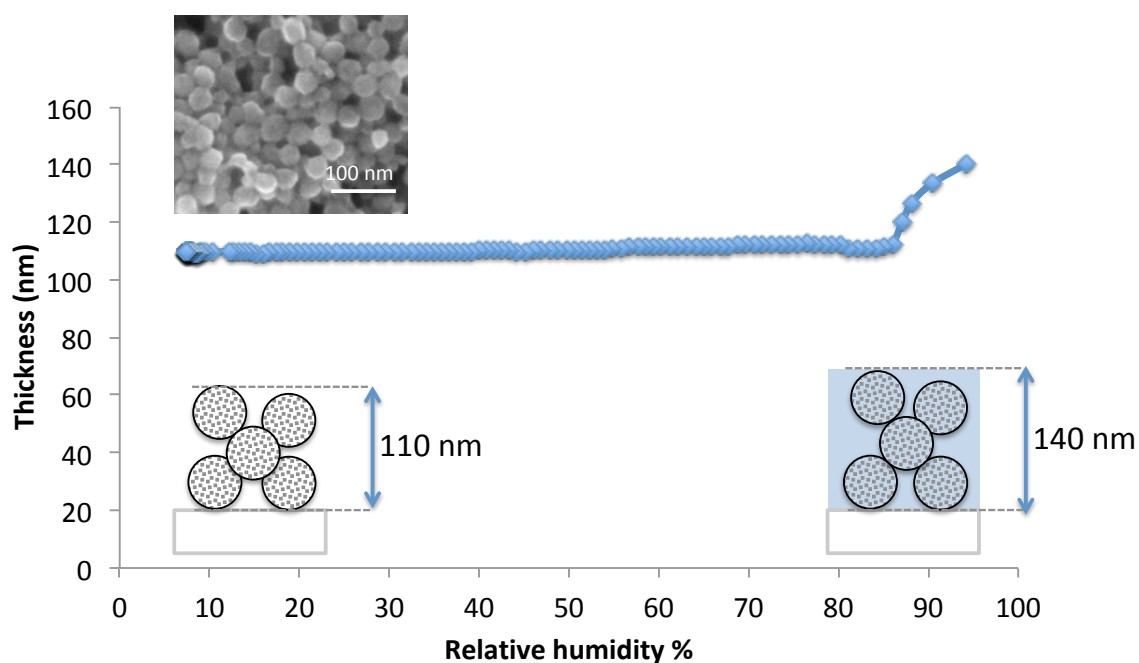
Fig. S7 Evolution of thickness as function of relative humidity (adsorption) for a colloidal mesoporous SiO$_2$ film
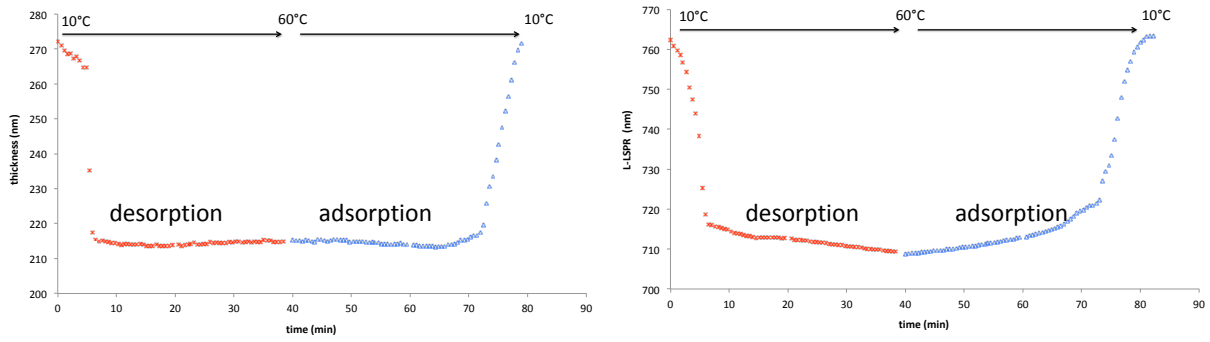
Fig. S8 Reversibility of the temperature triggered desorption and adsorption cycle.

6 Estimation of thermal gradients across the film

The correlation between the two experiments, temperature and light-induced desorption correlation is based on the hypothesis that the two heating modes lead to the similar local temperature into the film. This assumption can be verified by estimating that the thermal gradients across the film. This estimation is challenging since the composite film is made of Au, SiO_2 and air.

We then consider a more demanding hypothesis, being the film only composed of insulating mesoporous SiO_2. The temperature drop across a mesoporous silica layer is given by [5]:

$$\Delta T = q \frac{L}{\kappa A_s}.$$

with k= 10^{-1} $WK^{-1}m^{-1}$; A_s= $6.4*10^{-3}$ m^2 and q=1 W (we consider the full light power converted in heat)

Two configurations can be considered:

using L= 20^{-9} m (silica shell thickness) $\Delta T = 3.1\ 10^{-5}$ K

using L= 300^{-9} m (thickness of the entire layer) $\Delta T = 4.7\ 10^{-4}$ K

In both cases the thermal gradient values (in the most demanding conditions) are several orders of magnitude below the temperature difference estimated by ellipsometry. This is in agreement with a previous study concerning thermal fluxes in mesoporous layers [5]

7 Evaluation of the temperature
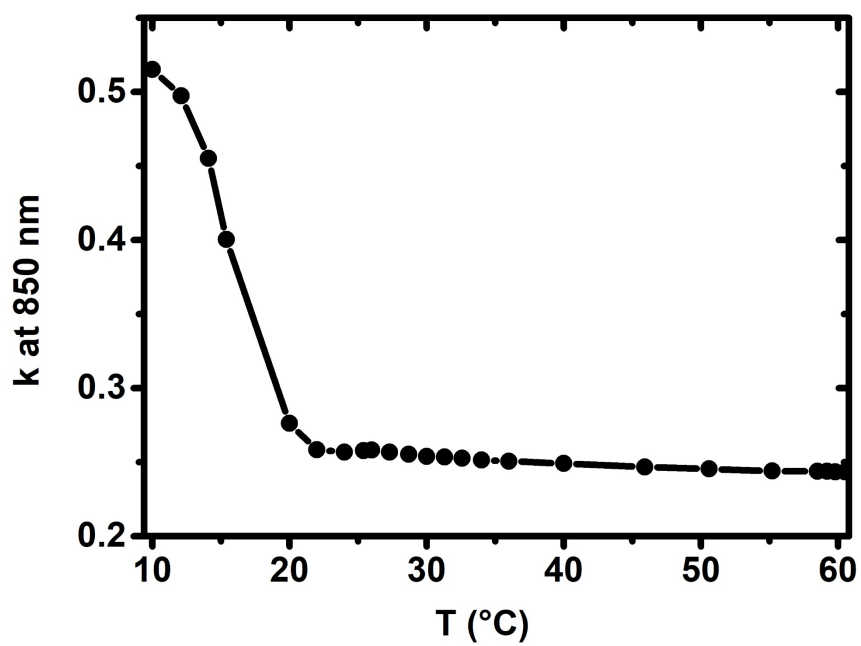
Fig. S*9* : **Effective k at 850 nm as function of the temperature for the plasmonic colloidal films in presence of 90% relative humidity**
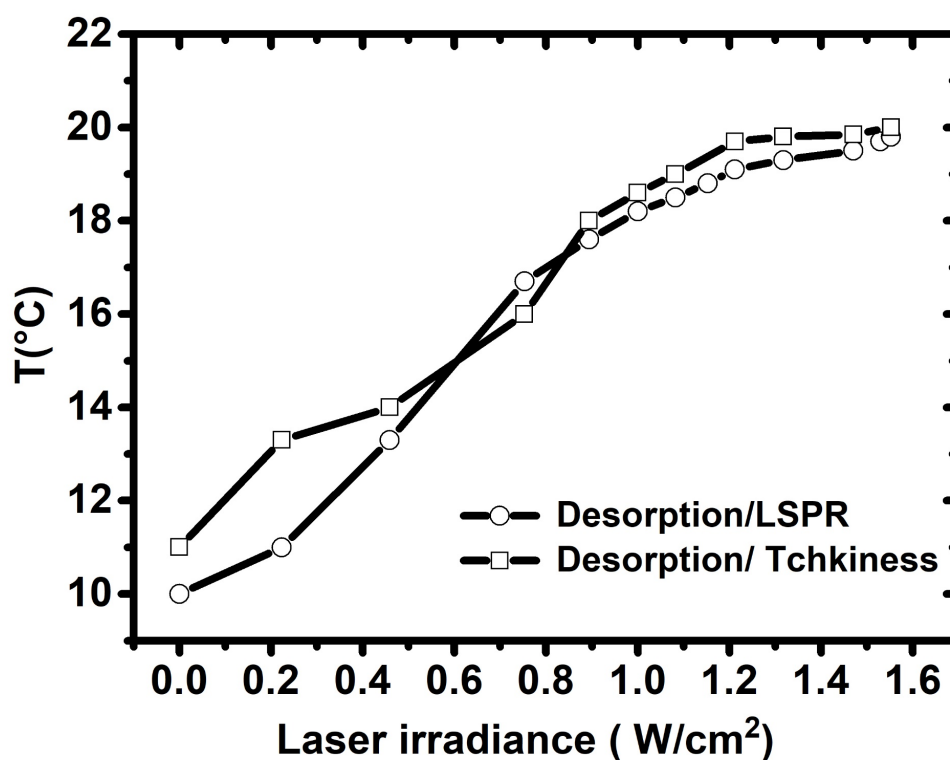
Fig. S10 : **Estimation of the local temperature as function of the laser irradiance determined from the variation of LSPR and thickness during vapor desorption.**

References

1. E. Bindini, Z. Chehadi, M. Faustini, P.-A. Albouy, D. Grosso, A. Cattoni, C. Chanéac, O. Azzaroni, C. Sanchez and C. Boissière, *ACS Applied Materials & Interfaces*, 2020, DOI: 10.1021/acsami.9b19956.
2. W. tutorial, https://http://www.jawoollam.com/resources/ellipsometry-tutorial/what-is-ellipsometry?gclid=EAIaIQobChMIsu3s_Ke56AIVElXTCh3NcAkZEAAYASAAEgL_XvD_BwE.
3. L. Hsiang-Lin, S. Chih-Chiang, S. Sheng-Han, H. Chang-Lung, L. Ming-Yang and L. Lain-Jong, *Applied Physics Letters*, 2014, 105, 201905.
4. P.-C. Liu, Y.-J. Yu, B. Peng, S.-Y. Ma, T.-Y. Ning, B.-Q. Shan, T.-Q. Yang, Q.-S. Xue, K. Zhang and P. Wu, *Green Chemistry*, 2017, 19, 5575-5581.
5. C. D. S. Brites, M. C. Fuertes, P. C. Angelomé, E. D. Martínez, P. P. Lima, G. J. A. A. Soler-Illia and L. D. Carlos, *Nano Letters*, 2017, 17, 4746-4752.