Supporting Information

Nanoporous gold metamaterials for high sensitivity plasmonic sensing

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Supporting Note #1

In order to evaluate empirically the sensitivity obtained in our system we consider a well know system comprising a gold grating with the parametric dimension as reported in Figure S1. This system has been deeply investigated by J. Homola et al. [1] and here we calculate, by means of numerical simulations, the expected sensitivity when the plasmonic resonance is optimized at 1500 nm.

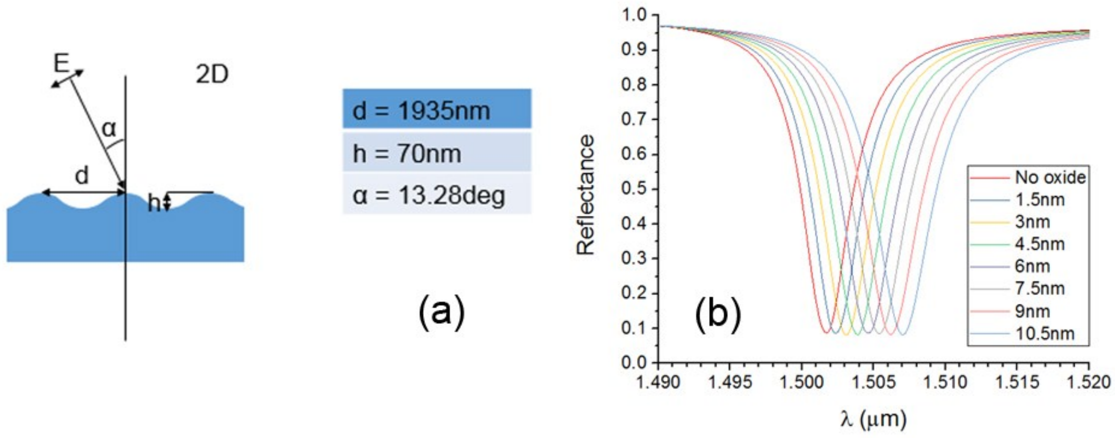

Figure S1. (a) Geometrical parameters of the simulated optimized gold grating with a plasmonic resonance at 1500nm. [1]; (b) The reflectance of the gold grating against the thickness of SiO_2.

The following table illustrates the numerical simulations results. The obtained sensitivity, expressed in nm/RIU results about 1495 nm/RIU.

$n_1 = 1.0$	$n_2 = 1.025$	$n_3 = 1.035$	$n_4 = 1.050$
$\lambda_1 = 1500$nm	$\lambda_2 = 1537$nm	$\lambda_3 = 1552$nm	$\lambda_4 = 1575$nm

Case 1: $S_{G\lambda} = (\lambda_2 - \lambda_1)/(n_2 - n_1) = 1480$ **nm/RIU**

Case 2: $S_{G\lambda} = (\lambda_3 - \lambda_1)/(n_3 - n_1) = 1485$ **nm/RIU**

Case 3: $S_{G\lambda} = (\lambda_4 - \lambda_1)/(n_4 - n_1) = 1500$ **nm/RIU**

Similar values can be obtained using the well-known grating equation for the Rayleigh anomaly resonance[2][3]:

$$\lambda_R^{(m)} = \frac{dn(-\sin\alpha \pm 1)}{m}, m = \pm 1, \pm 2, \dots,$$

$n_1 = 1.0$	$n_2 = 1.025$	$n_3 = 1.035$	$n_4 = 1.050$
$\lambda_1 = 1474$nm	$\lambda_2 = 1511$nm	$\lambda_3 = 1526$nm	$\lambda_4 = 1548$nm
Case 1: $S_{G\lambda} = (\lambda_2 - \lambda_1)/(n_2 - n_1) = 1480$ **nm/RIU** **Case 2:** $S_{G\lambda} = (\lambda_3 - \lambda_1)/(n_3 - n_1) = 1485$ **nm/RIU** **Case 3:** $S_{G\lambda} = (\lambda_4 - \lambda_1)/(n_4 - n_1) = 1480$ **nm/RIU**			

In the main manuscript we used this system to evaluate the spectral shifts after successive deposition of SiO_2 with the same thickness used in our NPG sensing experiment.

Supporting Note #2

A PDMS microfluidic chamber that enable in liquid IR spectroscopy has been developed following criteria recently reported[7]. A CaF_2 window is necessary to ensure the transparency to IR radiation, while a 10 μm thick channel ensures that the absorbance of H_2O does not saturate the intensity of the collected spectrum. Figure S2 illustrates the layout of the used chamber. Important to note, the top part can be opened and closed after every measurement. This allows to access the sample for a cleaning procedure.

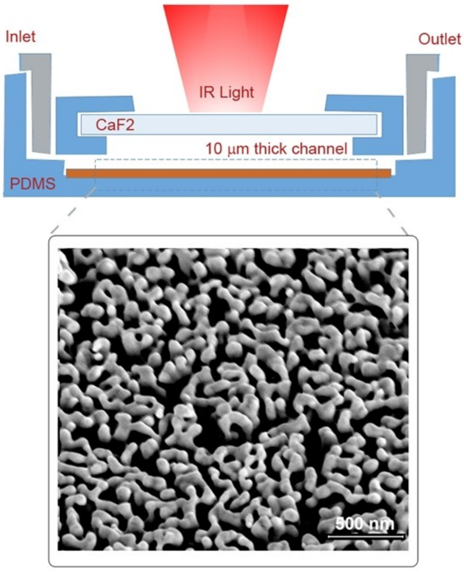

Figure S2. Layout of the used microfluidic chamber.

Supporting Note #3

As reported in the main text, we observed that the use of glycerol for the sensitivity tests presents some critical aspects. In particular, if the sample is not washed properly after every measurement, the results are not reproducible and different signals are collected from different zone of the NPG surface.

Figure S3 illustrates an example of a SEM micrograph obtained from a NPG sample after 15 minutes of measurement in Glycerol 10%. As can be seen a non-uniform organic layer is deposited over the surface, thus demonstrating the bad reproducibility observed.

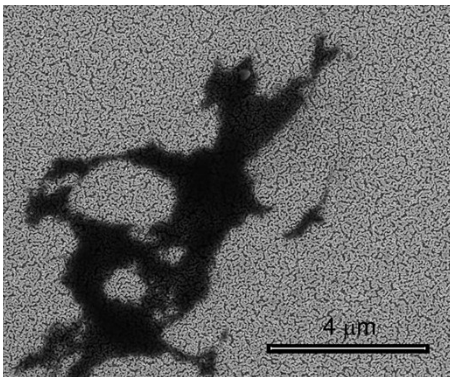

Figure S3. Typical residual layer of Glycerol on NPG surface after 15 minutes of incubation.

Supporting Note #4

The (3-Aminopropyl)triethoxysilane (APTES) monolayer has been deposited by using an ALD system (model FlexAl from Oxford Instruments). For our procedure APTES (Sigma-Aldrichbubbler PubChem Substance ID 24867571) was heated at 60°C and the precursor vapor was delivered into the chamber using 100 sccm of Argon. Precursor delivering lines were heated at 110°C, the chamber was at 120°C and substrate temperature was at 110°C.

Chamber pressure during the process was maintained at 200 torr with 100 sccm of Argon.

The process consisted of (n°40) cycles of 30" precursor exposure step followed by 30" of purging step using Argon as purging gas.

XPS analyses have been carried out using a Kratos Axis Ultra^{DLD} spectrometer equipped with a monochromatic Al Kα source operated at 20 mA and 15 kV. High resolution spectra have been acquired over the binding energy ranges typical for Au 4f peaks, with an analysis area of 300 x 700 microns and a pass energy of 10 eV. The Kratos charge neutralizer system was used on all specimens. Spectra have been charge corrected to the main line of the Au 4f spectrum set to 84 eV and analysed using CasaXPS software (version 2.3.17).

The data have been collected on two different samples, namely a bare Au substrate and a Au+APTES sample. The Au substrate have been cleaned in the vacuum chamber by Ar^+ ions sputtering (ions energy: 4 keV, sputtering time 30 s), in order to remove all possible environmental contaminations and provide a reliable reference for a clean gold surface.

The collected data are reported in figure S5.

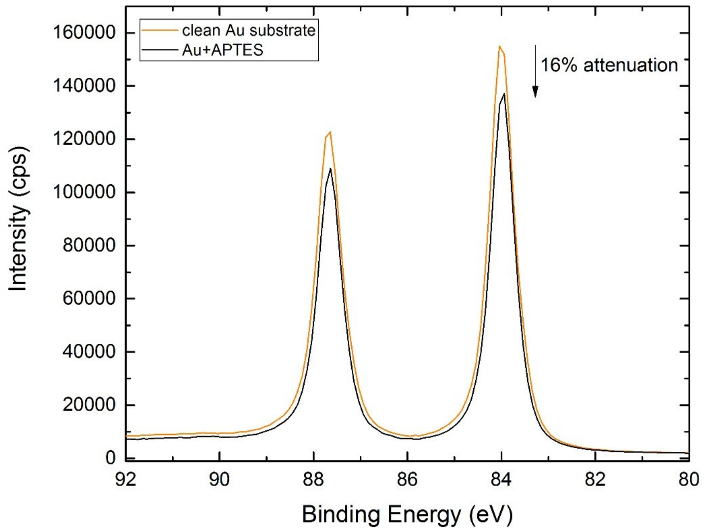

Figure S4. XPS analysis on APTS self-limiting ALD deposition.

The Au 4f signals collected on the APTES film show a reduced intensity with respect to those collected on the cleaned Au substrate. This attenuation, in the order of roughly 16%, is the typical signature of the presence of a film on top of a substrate and it can be used to determine the thickness of the film itself. In line with what reported in [5] and assuming an inelastic mean free path λ of 3.5 nm for electrons of kinetic energy of 1402 eV through the APTES organic layer (for reference, λ = 3.7 nm for polypropylene as calculated from the Tanuma, Powell, and Penn TPP2M formula [6], we therefore estimated the thickness of the APTES films, obtaining a value of (0.6±0.2) nm.

Supporting Note #5

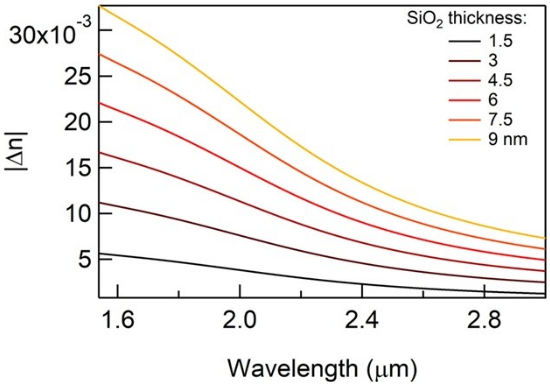

Figure S5. Δn as calculated in the method section of the main text.

Supporting References

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