Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information for

Adhesion Layer Influence on Controlling the Local Temperature in Plasmonic Gold Nanoholes

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This document contains the following supporting information:

S1. Linear relationship between thickness and infrared absorption

S2. Comparison between Cr and Ti adhesion layers of 6 nm thickness

S3. Fluorescence and infrared transmission time traces analysis

S1. Linear relationship between thickness and infrared absorption

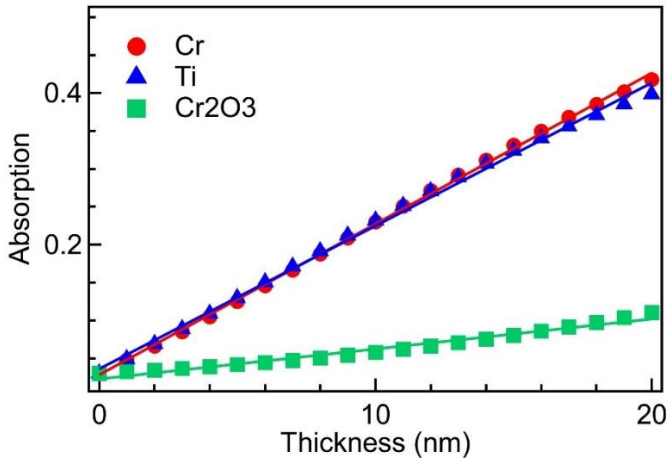

Figure S1. Analytical simulation of the 1064 nm infrared absorption as a function of the thickness of adhesion layers underneath a 100 nm thick gold film. The calculations are performed using Fresnel coefficients for multilayer systems. The simulation data of chromium (Cr, red), titanium (Ti, blue) and chromium oxide (Cr_2O_3, green) follow a quasi-linear dependence with the layer thickness for the thickness range below 20 nm. Additionally, the Cr and Ti films feature a similar IR absorption which leads to a comparable temperature increase for the same thickness.

S2. Comparison between Cr and Ti adhesion layers of 6 nm thickness

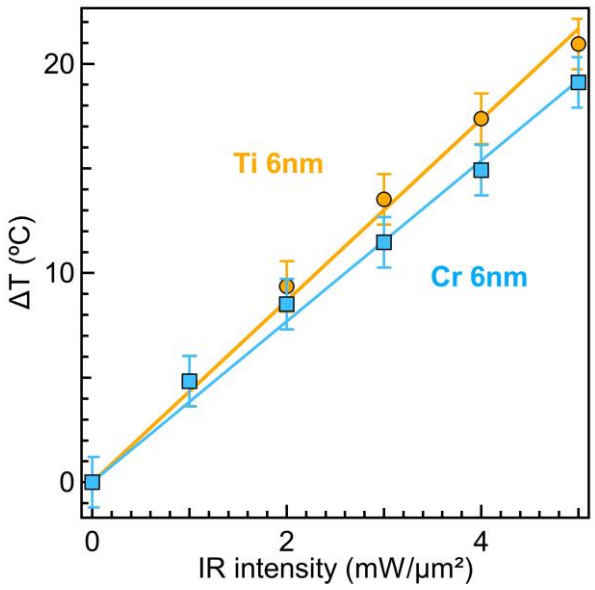

Figure S2. Temperature increase as a function of the infrared intensity at 1064 nm measured on a 300 nm diameter gold nanoaperture for chromium and titanium adhesion layers of similar 6 nm thickness. The experimental conditions are identical to Fig. 2 of the main document. Numerical simulations indicate that Cr and Ti films share a similar IR absorption (Fig. S1). Here our experimental data confirms that both Cr and Ti adhesion layers (of same thickness) lead to a comparable temperature increase within the experimental uncertainties.

S3. Fluorescence and infrared transmission time traces analysis

Having established how to control the local temperature inside a SNH, we take a closer look at the fluorescence and IR transmission signals under conditions of large temperature gains up to +40°C. First, we confirm that the optical microscope setup is stable, leading to a steady fluorescence time trace where the noise fluctuations are dominated by shot noise (Fig. S3a). We also check that the transmitted IR signal is stable in the absence of gold structure (Fig. S3b). The situation becomes clearly different when a SNH is illuminated, leading to a temperature raise of +32°C (Fig. S3c,d). Additional fluctuations appear on top of the shot noise with a time scale of a few seconds, and are anti-correlated between the fluorescence and IR transmission signals. More time traces for increasing IR intensities are shown in Fig. S4.

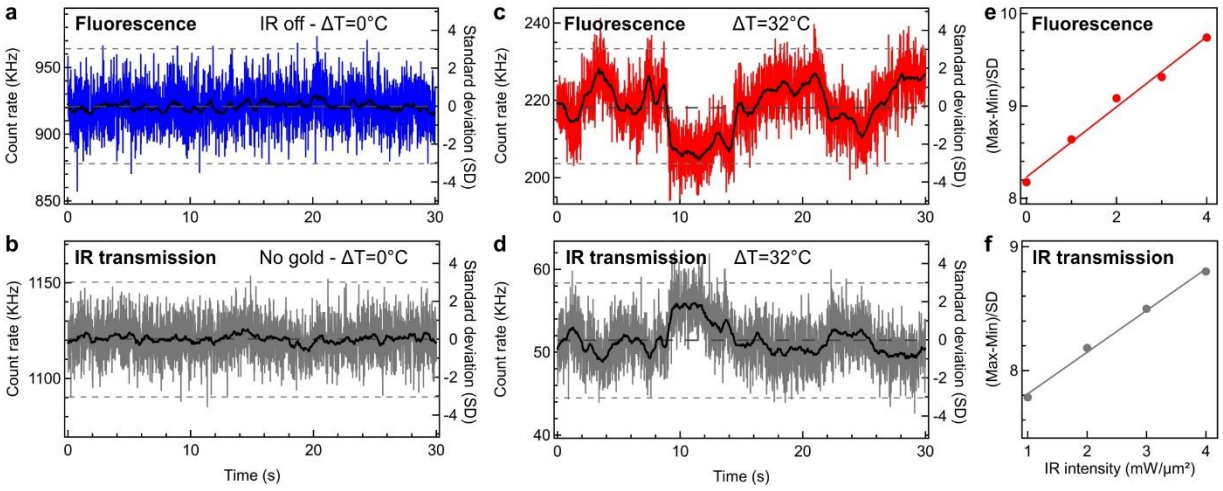

Figure S3. Time traces of fluorescence intensity and infrared transmission in a 300 nm diameter SNH with 13 nm Cr adhesion layer. (a) Alexa Fluor 647 fluorescence intensity on a SNH with no heating infrared beam: the signal is stable and within ±3 standard deviation (SD) as indicated by the horizontal dashed lines. The thin blue trace corresponds to a binning time of 10 ms while the thick black trace is smoothed over a 500 ms period. (b) Infrared transmission when no metal film is present, again the trace is stable and within ±3 SD. (c,d) Fluorescence and IR transmission when the SNH is illuminated at 4 $mW/\mu m^2$IR intensity, leading to an average temperature increase of +32°C. Additional fluctuations are clearly visible on top of the shot noise, and are anticorrelated between fluorescence and IR transmission. (e,f) Analysis of the fluctuation amplitude normalized by the standard deviation defined as (max-min)/SD for the fluorescence (e) and IR transmission (f) time traces as a function of the IR intensity.

We quantify the fluctuations amplitude by recording the peak-to-peak amplitude (defined as the difference between the maximum and minimum values found for a 60 s trace), and normalize it by the standard deviation (SD) calculated from the most stable (flat) parts within 2 s (200 points) in each time trace. For a shot-noise limited Gaussian statistical distribution, the peak-to-peak values should remain within 6 to 8 times the SD. However, our experimental observations clearly deviate from this range and increase with the IR power (Fig. S3e,f), indicating the presence of a supplementary source of fluctuations. Specific time intervals can be selected on the fluorescence time trace to estimate the fluorescence lifetime and local temperature during events corresponding to high or low amplitude fluctuations (Fig. S5). When the fluorescence intensity is clearly below the average level (Fig. S5a, red selected part), the fluorescence lifetime is shorter, indicating a higher temperature of +32.6°C. Reversely, when the fluorescence intensity is above the average level (Fig. S5a, blue selected part), the fluorescence lifetime is longer and the

temperature is lower with a value of +31.0°C. The 1.6°C temperature difference between the cases is moderate, but significantly above the experimental noise level. Let us also stress that the fluorescence lifetime measurement depends only on the arrival time of the fluorescence photons. This measurement is largely independent of the intensity of the fluorescence signal, therefore the fluctuations observed cannot be ascribed to mechanical drifts of the microscope focus. We have checked that the fluorescence properties of the molecules is not affected by the IR illumination alone up to values of 80 mW/µm².[S1] Currently, our observations indicate the occurrence of a change in IR transmission, leading to a modification of the local temperature and in turn an alteration of the fluorescence lifetime and intensity of Alexa Fluor 647 molecules. The nature and origin of the IR transmission fluctuations remain unclear. It should be noted than at 5 mW/µm² we are approaching the damage threshold for the gold film on a 13 nm Cr layer. When we performed experiments at values higher than this level, we could not retrieve the initial values anymore when the IR intensity was reduced. This indicates the occurrence of irreversible damage to the SNH structure, and sets an upper limit for the maximum temperature increase reachable. Therefore, we believe that the IR transmission fluctuations could be due to some thermally-induced expansion or collapse of the SNH aperture edges, which in turn induces the modifications of the local temperature and fluorescence properties. We have also checked that convection fluxes in the water medium do not play a significant role in our observations. Similar results were obtained with two different liquid heights above the SNH: one height of a few micrometers (where convection is prohibited) and one of several hundreds of micrometers (where convection may occur).

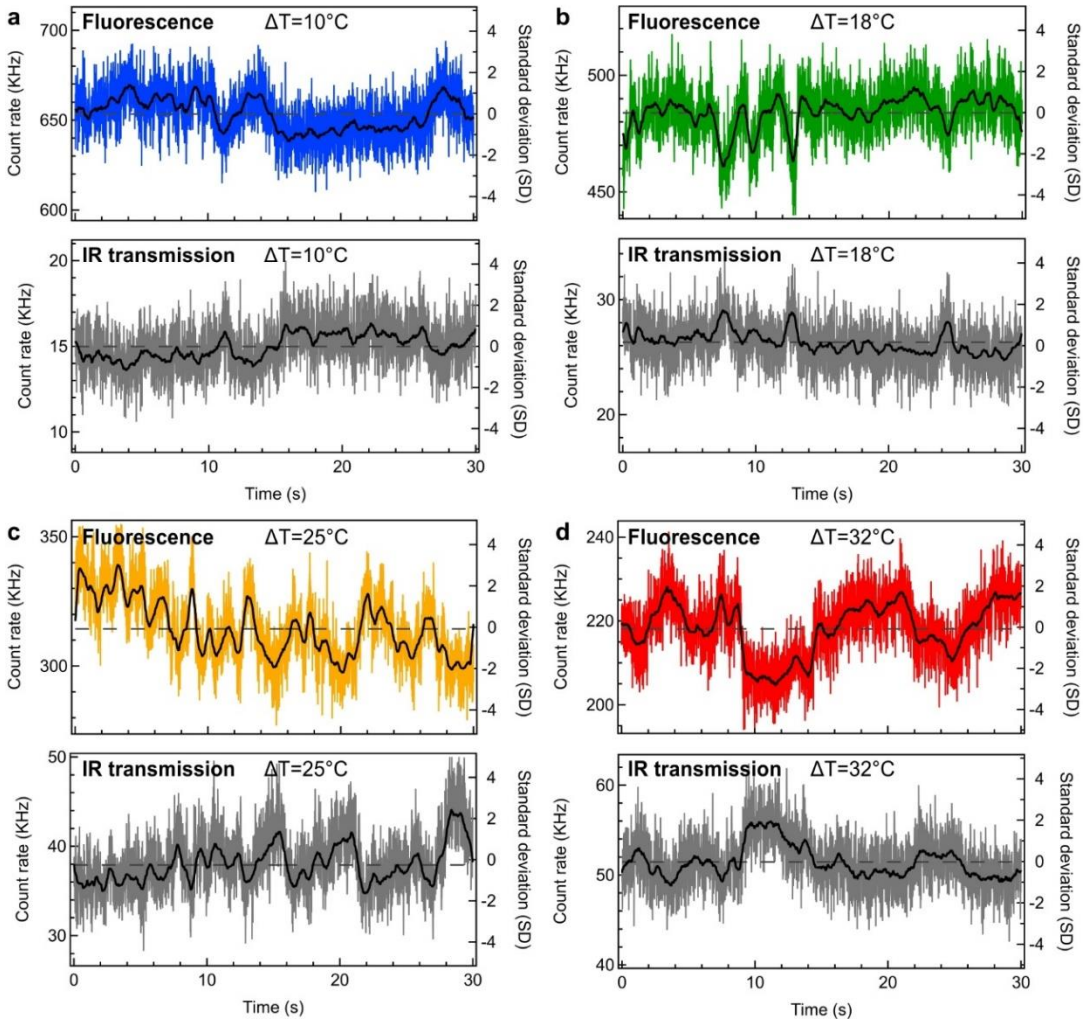

Figure S4. Time traces of fluorescence intensity and infrared transmission for a 300 nm diameter SNH with 13 nm Cr adhesion layer. Through (a-d) the IR intensity increases from 1 to 4 $mW/\mu m^2$. The temperature increase corresponds to +10°C, +18°C, +25°C and +32°C respectively. The thin color or gray traces correspond to a 10 ms binning time while the thick black traces are averaged over a 500 ms period. The dashed horizontal lines indicate the average value and the right vertical axis is normalized by the standard deviation for each trace.

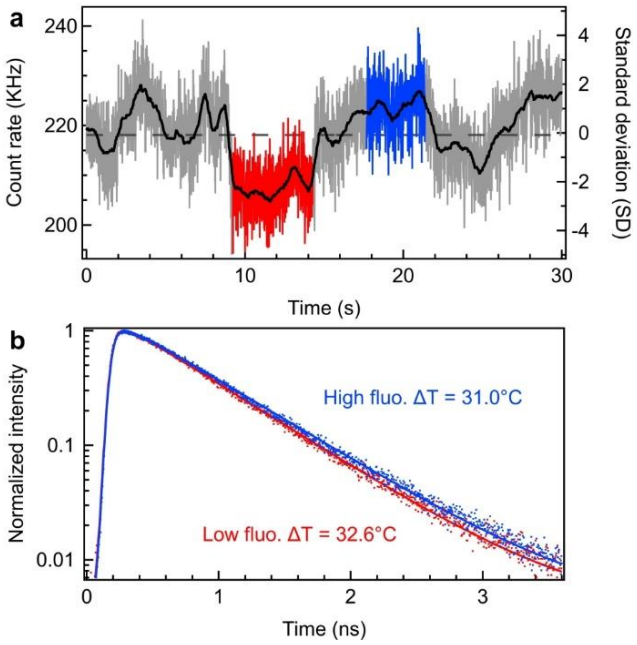

Figure S5. Fluorescence lifetime measured on a selected time interval corresponding to high/low fluctuations of the fluorescence intensity. (a) Fluorescence time trace (same as Fig. S2c). The lower (red) and higher fluorescence (blue) parts are selected for the partial lifetime measurement instead of the average of the overall time trace. (b) Normalized fluorescence decay curves of Alexa Fluor 647 solution corresponding to the red and blue parts in (a). The temperature gains extracted from the measured lifetimes are indicated on the graph.

Refererence

(S1) Q. Jiang, B. Rogez, J.-B. Claude, G. Baffou and J. Wenger, *ACS Photonics*, 2019, **6**, 1763–1773.