Anomalous spectral shift of near- and far-field plasmonic resonances in nano-gaps

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Supplementary information

POWER STUDY

Dark field scattering spectra are recorded in the very same experimental configuration before and after SERS measurements for each investigated gold nanoparticle. A comparison between optical spectra before and after laser irradiation does not show any changes (Fig.S1), proving that the laser power (<1μW) adopted in our measurements did not damage the particle nor its local environment.

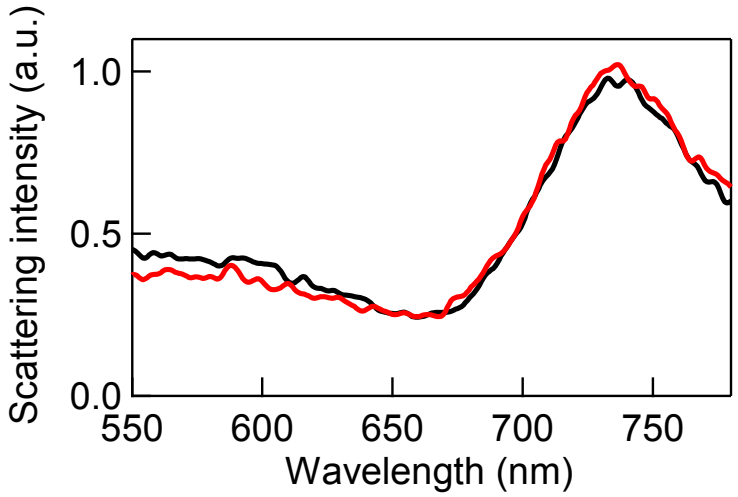

Figure S1: Scattering spectra from a single 60nm gold nanoparticle on mirror with TPT before (black) and after (red) laser irradiation. Laser excitation wavelength is tuned between 550nm and 700nm, the power always being kept < 1μW.

ABSORPTION AND RAMAN MEASUREMENT ON TPT POWDERS

We realize a series of tuneable Raman measurements on bulk TPT powder of known density ($\sim 10^{17}$mol/mm^2). The laser wavelength was scanned across a 500-640nm spectral window in 20nm steps (Fig. S2a).

The absorption of TPT was measured by depositing a thin film onto a gold substrate. To do so TPT was dissolved in THF and dried down on a gold film. The reflectivity of the TPT film was probed using an Olympus BX51 microscope (X100 objective, N.A. = 0.8) with a cold white LED light source (Thorlabs MCWHL5-C1). The reflected light was measured with a fibre coupled to a cooled Ocean Optics QE65000 spectrometer (integration time 18ms). The reflectivity on bare gold was used as a reference. A maximum absorption at 440nm was determined (Fig. S2b).

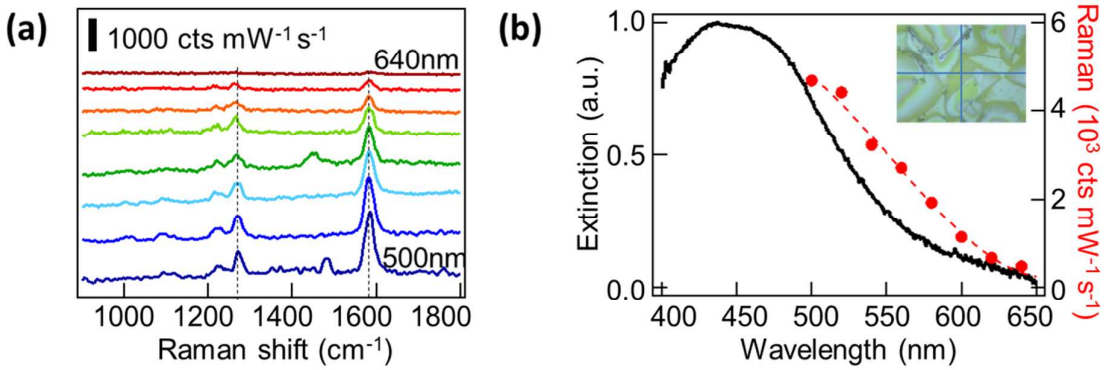

Figure S2: (a) Raman spectra from bulk TPT powder tuning the excitation from 500-640nm in 20nm steps. (b) Absorption spectrum of a TPT thin film deposited on a gold substrate (black line) and evolution of SERS intensity of TPT vibrational mode at 1585cm^{-1} (red circles) *vs* excitation wavelength. Inset: bright field image of the sample showing TPT crystal patterns created during the drying process on the gold film.

TUNEABLE SERS STUDY ON SINGLE NPoM USING DIFFERENT SPACERS AND DIFFERENT NANOPARTICLE SIZES

The validity of the adopted experimental method is proved over different samples, varying nanoparticle size and molecular spacer. As an example, we report tuneable SERS measurements realized on single gold 60nm and 40nm diameter NPoM with biphenyl-4-thiol molecular monolayers as the spacer (Fig.S3). In both case, dark field spectroscopy has been realized on the very same nanoparticles. Both SERS enhancement and background show the same wavelength-dependent evolution observed and discussed in the case of 60nm gold nanoparticle on TPT.

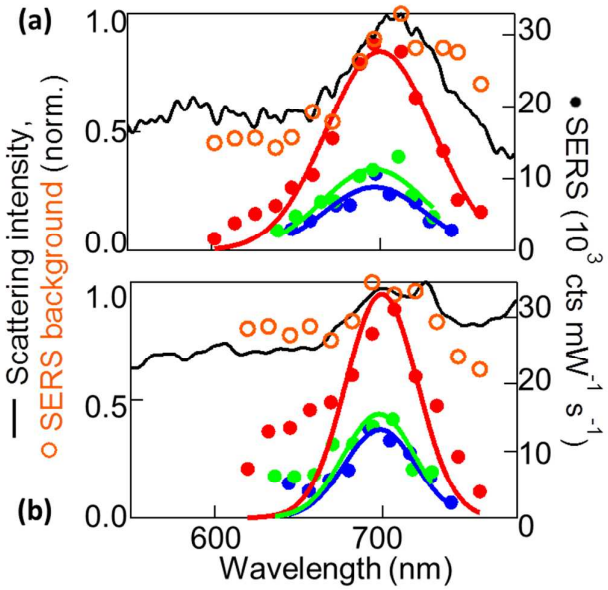

Figure S3: (a) Evolution of SERS intensity of BPT vibrational modes at 1585cm^{-1} (red), 1256cm^{-1} (green), and 1080cm^{-1} (blue) *vs* emitted Raman wavelength, compared to scattering spectra (black) for a 60nm gold NPoM (lines show Gaussian fits). Also shown is SERS background around 1585 cm^{-1} (orange). (b) Same as (a) for a 40nm gold NPoM.

DIMER SIMULATIONS

Scattering intensity and field enhancement in the proximity of a single gold dimer have been calculated by finite difference time domain (FDTD) calculations using Lumerical FDTD Solutions v8.9. The structure has been modelled as two gold spheres of 80nm diameter with a 1nm gap size separation. For the gold, we referred to the dielectric constants reported in Johnson and Christy.

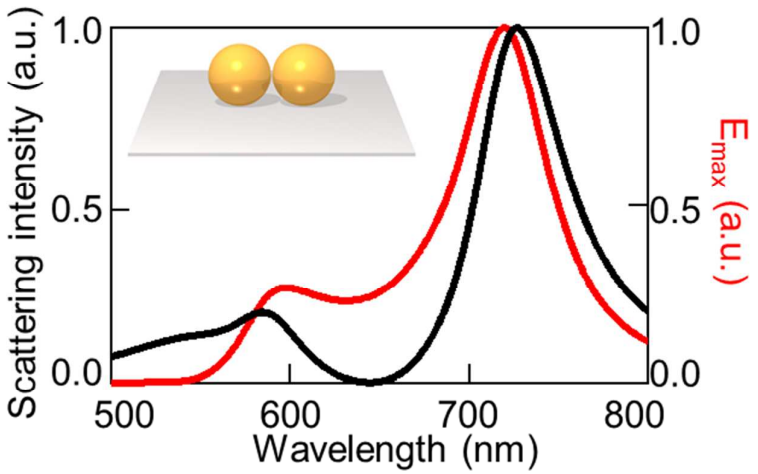

Figure S4: FDTD simulations of scattering and maximum near-field for a gold homodimer.

TRANSFORMATION OPTICS TECHNIQUE

We followed the transformation optics approach developed by Aubry et al.[1]. In this approach a conformal transformation is applied on a canonical system of a metal-insulator-metal, to reach a plasmonic structure made of a metal plate and a nanowire (see Fig.S5).

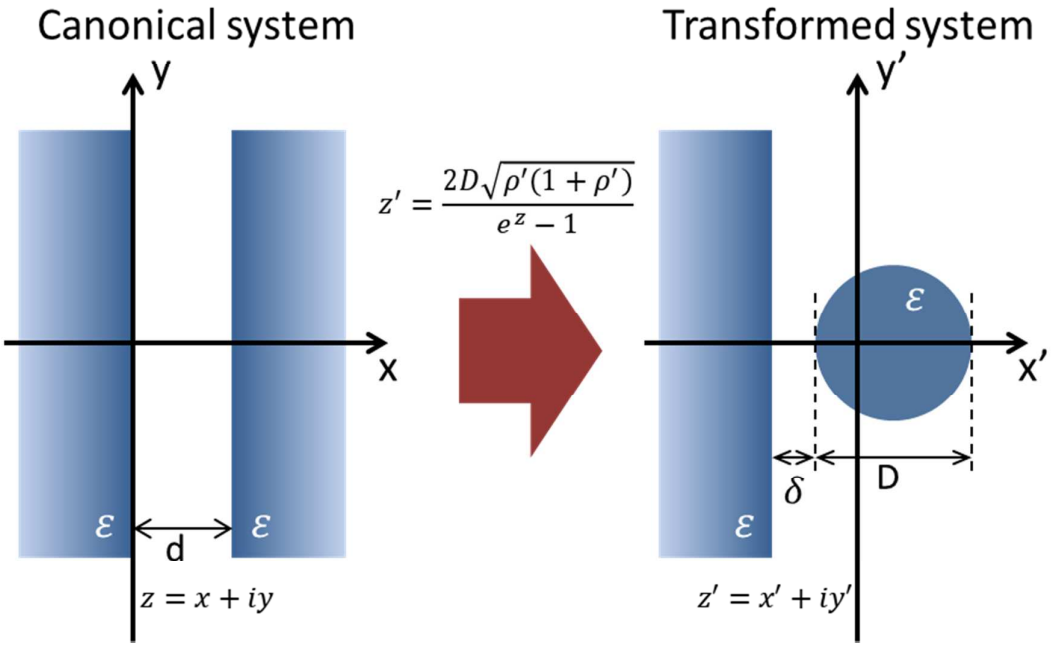

Figure S5: The transformation optics approach employed to calculate the fields for an nanowire at a close distance to a metal slab. Solutions are obtained for the canonical system, which are then expressed in the transformed system.

Using Laplace's equation, we find the electrostatic potential, ϕ, in the canonical system, which is preserved under the transformation. Hence the electric field in the transformed system is $E = \nabla \phi$, which leads to its decomposition to infinite sum of n modes as:

$$E = \sum_{n=1}^{\infty} \psi^n$$

where each mode ψ^n in the dielectric surrounding the nanoparticle is:

$$\psi_{x'}^{n} = 2E_0\rho'(1+\rho')D^2\frac{\varepsilon-1}{\varepsilon+1}\left(\frac{n}{\left(\sqrt{\rho'}+\sqrt{\rho'+1}\right)^{4n}-\left(\frac{\varepsilon-1}{\varepsilon+1}\right)^2}\right)\times$$
$$\times\left\{\frac{\varepsilon-1}{\varepsilon+1}\left[\frac{1}{z'^2}\left(1+\frac{2\sqrt{\rho'(1+\rho')}D}{z'}\right)^{-n-1}\right.\right.$$
$$\left.+\frac{1}{z'^{*2}}\left(1+\frac{2\sqrt{\rho'(1+\rho')}D}{z'^{*}}\right)^{-n-1}\right]$$
$$\left.+\left[\frac{1}{z'^2}\left(1+\frac{2\sqrt{\rho'(1+\rho')}D}{z'}\right)^{n-1}+\frac{1}{z'^{*2}}\left(1+\frac{2\sqrt{\rho'(1+\rho')}D}{z'^{*}}\right)^{n-1}\right]\right\}$$

$$\psi_{y'}^{n} = i2E_0\rho'(1+\rho')D^2\frac{\varepsilon-1}{\varepsilon+1}\left(\frac{n}{\left(\sqrt{\rho'}+\sqrt{\rho'+1}\right)^{4n}-\left(\frac{\varepsilon-1}{\varepsilon+1}\right)^2}\right)\times$$
$$\times\left\{\frac{\varepsilon-1}{\varepsilon+1}\left[\frac{1}{z'^2}\left(1+\frac{2\sqrt{\rho'(1+\rho')}D}{z'}\right)^{-n-1}\right.\right.$$
$$\left.-\frac{1}{z'^{*2}}\left(1+\frac{2\sqrt{\rho'(1+\rho')}D}{z'^{*}}\right)^{-n-1}\right]$$
$$\left.+\left[\frac{1}{z'^2}\left(1+\frac{2\sqrt{\rho'(1+\rho')}D}{z'}\right)^{n-1}-\frac{1}{z'^{*2}}\left(1+\frac{2\sqrt{\rho'(1+\rho')}D}{z'^{*}}\right)^{n-1}\right]\right\}$$

The terms ρ', D are geometrical parameters of the system given by: $\rho' = \frac{\delta}{D} = \sinh^2\left(\frac{d}{2}\right)$ where δ is the separation between the nanoparticle and the mirror and D the diameter of the nanoparticle in the transformed system, and d the separation distance between the two metal layers in the canonical system. In this system, it is assumed that the nanoparticle and the mirror are surrounded by air and are made of the same metal with dielectric permittivity ε. The electric fields of $n = 1$ and $n = 2$ are plotted in Fig.S6, where it can be seen that the field enhancement occurs within the gap and that the two modes have opposite phase in the gap, but are in phase away from it.

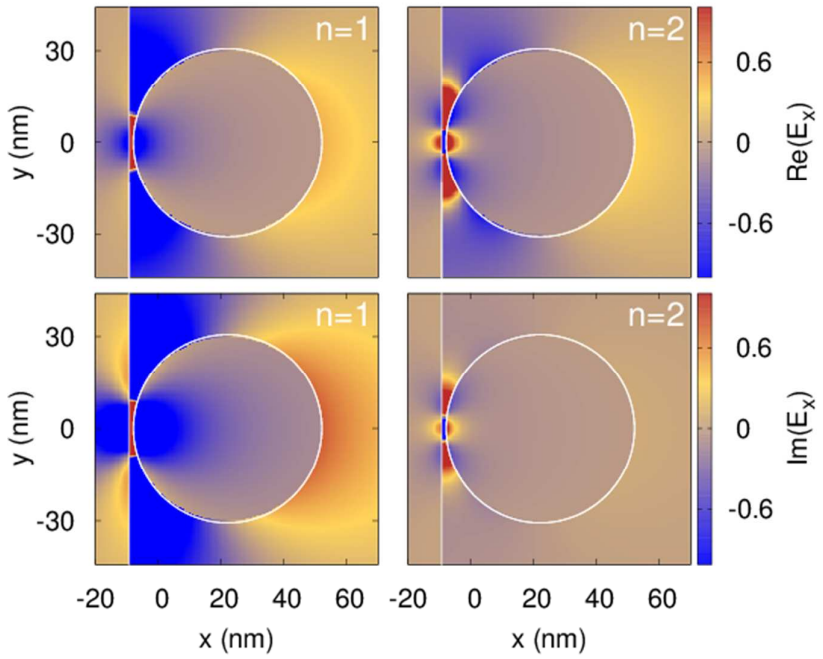

Figure S6: The E_x field distribution for the first two modes of the system.

Finally, the scattering cross-section can be obtained, given by:

$$\sigma_{scat} = -\left(\frac{8\pi k_0 \rho'(1+\rho')D^2}{\left|1 - i\pi D^2 \rho'(1+\rho')k_0^2 Re\left\{1+\frac{\varepsilon-1}{\varepsilon+1}\right\}(\beta^- + \beta^+)\right|^2}\right) \times \\ \times Re\left\{\pi D^2 \rho'(1+\rho')k_0^2 Re\left\{1+\frac{\varepsilon-1}{\varepsilon+1}\right\}|\beta^- + \beta^+|^2\right\}$$

where $\beta^- = \frac{\varepsilon-1}{\varepsilon+1}\sum_{n=1}^{\infty}\frac{n}{e^{2nd} - \left(\frac{\varepsilon-1}{\varepsilon+1}\right)\text{^}2}$ and $\beta^+ = \frac{\varepsilon-1}{\varepsilon+1}\beta^-$. It should be noted that the radiative losses are considered in this derivation[1,2], which makes the above approach valid for $\mathrm{D} < 100\mathrm{nm}$.

The different mode interference in the near-field and far-field can also be demonstrated by truncating to a mode N the infinite summation both in the near-field (i.e. $E = \sum_{n=1}^{N}\psi^n$) and the far-field (σ_{scat}), and observing their resonant wavelength (see Fig.S7). The far-field always red-shifts, while the near-field enhancement oscillates due to the destructive interference of consecutive modes.

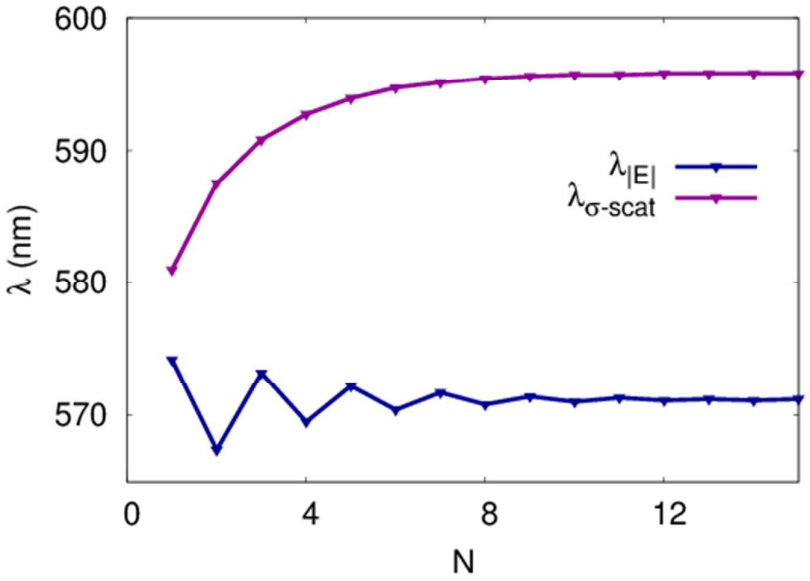

Figure S7: The resonance wavelength for both the near-field (i.e. $|E_{max}|$) and far-field (σ_{scat}) spectra, when the infinite summation of modes is truncated to a mode N. This illustrates the different interference of modes in the near- and far-field.

SCANNING ELECTRON MICROSCOPY CORRELATION

To make sure we optically address only isolated nanoparticles, we performed several correlated optical and scanning electron microscopy (SEM) experiments (Figure S8) before realizing tuneable SERS measurements.

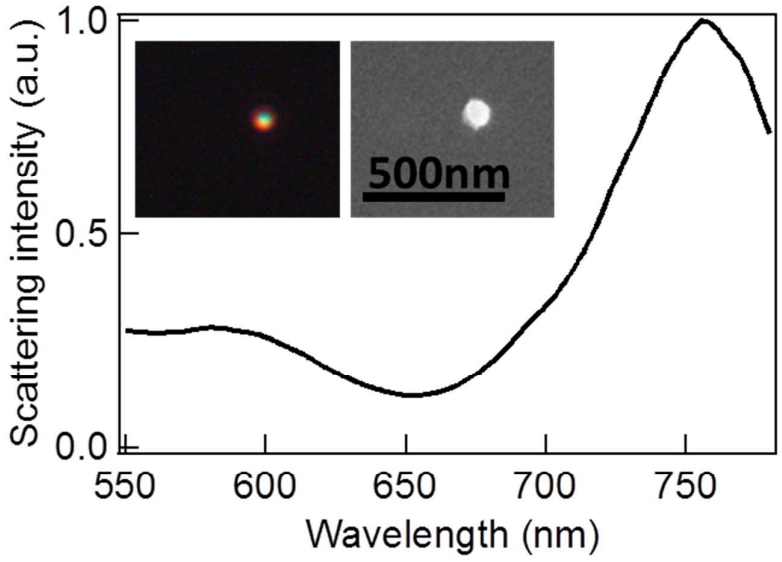

Figure S8: scattering optical spectrum of a single 60nm gold nanoparticle on a gold mirror. Inset: dark field optical image (left) and SEM image (right) of the same gold nanoparticle.

[1] A. Aubry, D. Lei, S. Maier, J.B. Pendry, Plasmonic Hybridization between Nanowires and a Metallic Surface: a Transformation Optics Approach*, ACS Nano*, **2011**, *5*, 3293-3308

[2] A. Aubry, D.Y. Lei, S. Maier,J.B. Pendry, Conformal Transformation Applied to Plasmonics Beyond the Quasistatic Limit, *Phys. Rev. B*, **2010**, *82*, 205109