Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Surface plasmon resonance of silver and gold nanoparticles in proximity of graphene studied with the discrete dipole approximation method

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Figure S1. Optical constants of Ag **(a)**, Au **(b)** and graphene in case of electric field polarized in transversal **(c)** and longitudinal **(d)** direction to the bidimensional crystal. Real (ε') and Imaginary (ε") parts are reported, respectively, in black and in red. The source for Ag and Au data is P. B. Johnson and R. W. Christy, Phys. Rev. B, 1972, 6, 4370-4379, while for graphene is V. Kravets, A. Grigorenko, R. Nair, P. Blake, S. Anissimova, K. Novoselov and A. Geim, Phys. Rev. B, 2010, 81, 155413.

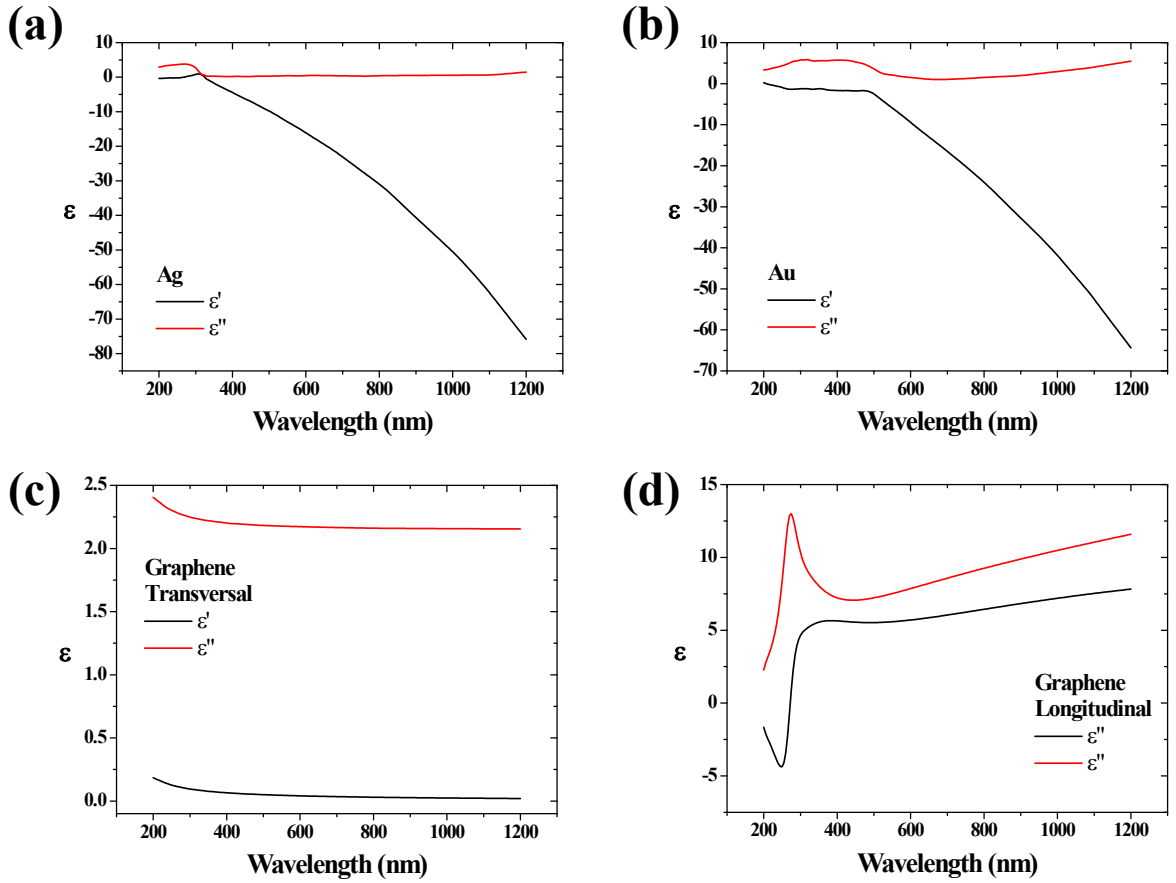

Table S1. Parameters for size correction of metal optical constant and of ω_p expressed according to

$$\omega_p = \sqrt{\frac{n_e e^2}{m_{eff}\varepsilon_0}}$$

where e is the electron charge and ε_0 vacuum permittivity (source: U. Kreibig and M. Vollmer, *Optical Properties of Metal Clusters*, Springer, Berlin, 1995 and M. Ashcroft, *Solid State Physics*, College ed.; Saunders College Publishing: Philadelphia, PA, 1976).

	Ag	**Au**
n_e	5.86 10^{28} m^{-3}	5.90 10^{28} m^{-3}
m_{eff}	1.00203 10^{-30} kg	1.00203 10^{-30} kg
Γ_∞	2.4919 10^{13} Hz	3.4014 10^{13} Hz
v_f	1.39 10^{6} m/s	1.40 10^{6} m/s
A	1	1

Figure S2. Magnification of the SPR region of Figures 1b, c, e, f. **(a)** From Figure 1b: σ_{ext} of the nanohybrid for Ag NPs with size d = 10 nm, calculated for electric field polarized parallel to the NPs - flake axis (PI) at different gap values (black: 0.335 nm, red: 1 nm, green: 2.7 nm, blue: 5 nm). In all cases, the σ_{ext} are overlapped and no difference is appreciable. The σ_{ext} of the isolated 10 nm Ag NP (dashed red line) and of the graphene flake (dashed black line) are also shown for sake of comparison, and the sum of these two σ_{ext}, corresponding to the σ_{ext} of a nanohybrid with infinite distance between graphene and the Ag NS, is reported in grey. **(b)** From Figure 1c: same as in (a) but considering the electric field with transversal incidence (TI) to the NPs - flake axis. In this case, the decrease of the SPR band is observed by decreasing the gap. **(c)** From Figure 1e: same as in (b) but considering a d = 5 nm Ag NS. **(d)** From Figure 1f: same as in (b) but considering a d = 15 nm Ag NS.

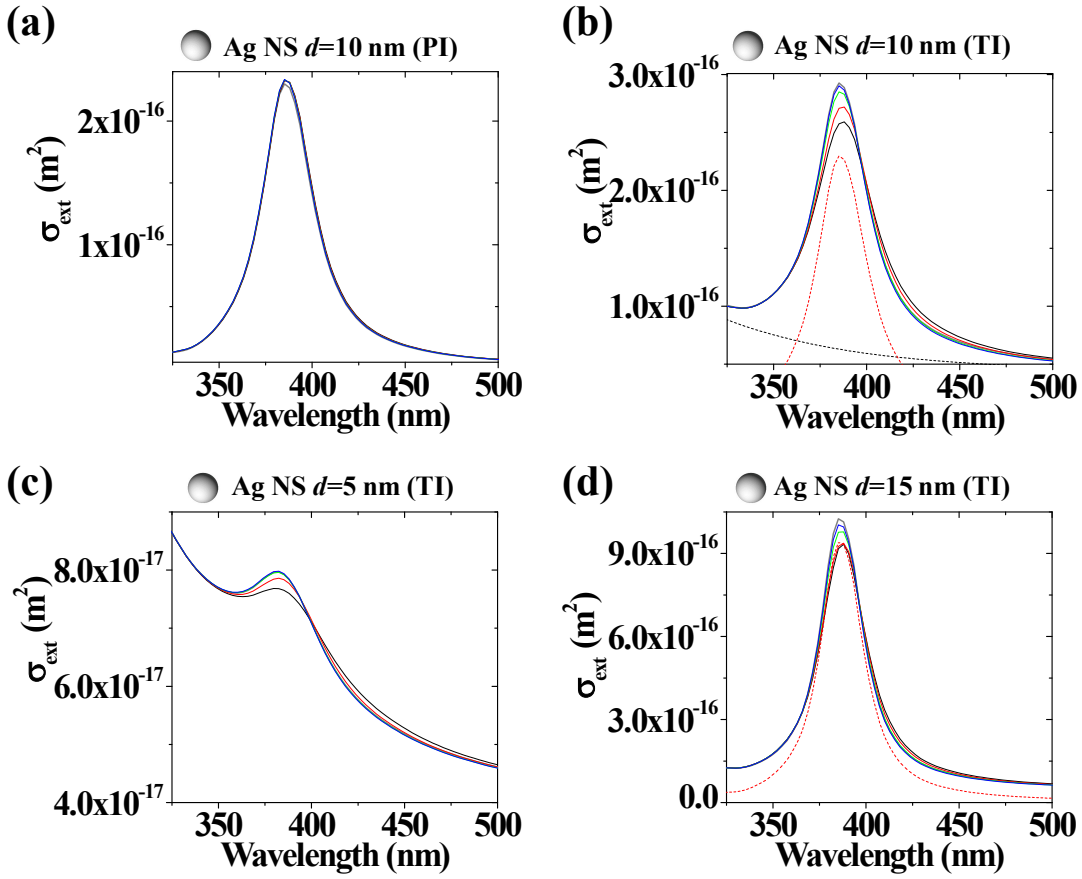

Figure S3. Magnification of the SPR region of Figures 2b, c, e, f. **(a)** From Figure 2b: σ_{ext} of the nanohybrid for a d = 10 nm Au NP, calculated for PI at different gap values (black: 0.335 nm, red: 1 nm, green: 2.7 nm, blue: 5 nm). In all cases, the σ_{ext} are overlapped and no difference is appreciable. The σ_{ext} of the isolated 10 nm Au NP (dashed red line) and of the graphene flake (dashed black line) are also shown for sake of comparison and the sum of these two σ_{ext}, corresponding to the σ_{ext} of a nanohybrid with infinite distance between graphene and the Au NS, is reported in grey. **(b)** From Figure 2c: same as in (a) but considering TI to the NPs - flake axis. **(c)** From Figure 2e: same as in (b) but considering a d = 5 nm Au NS. **(d)** From Figure 2f: same as in (b) but considering a d = 15 nm Au NS.

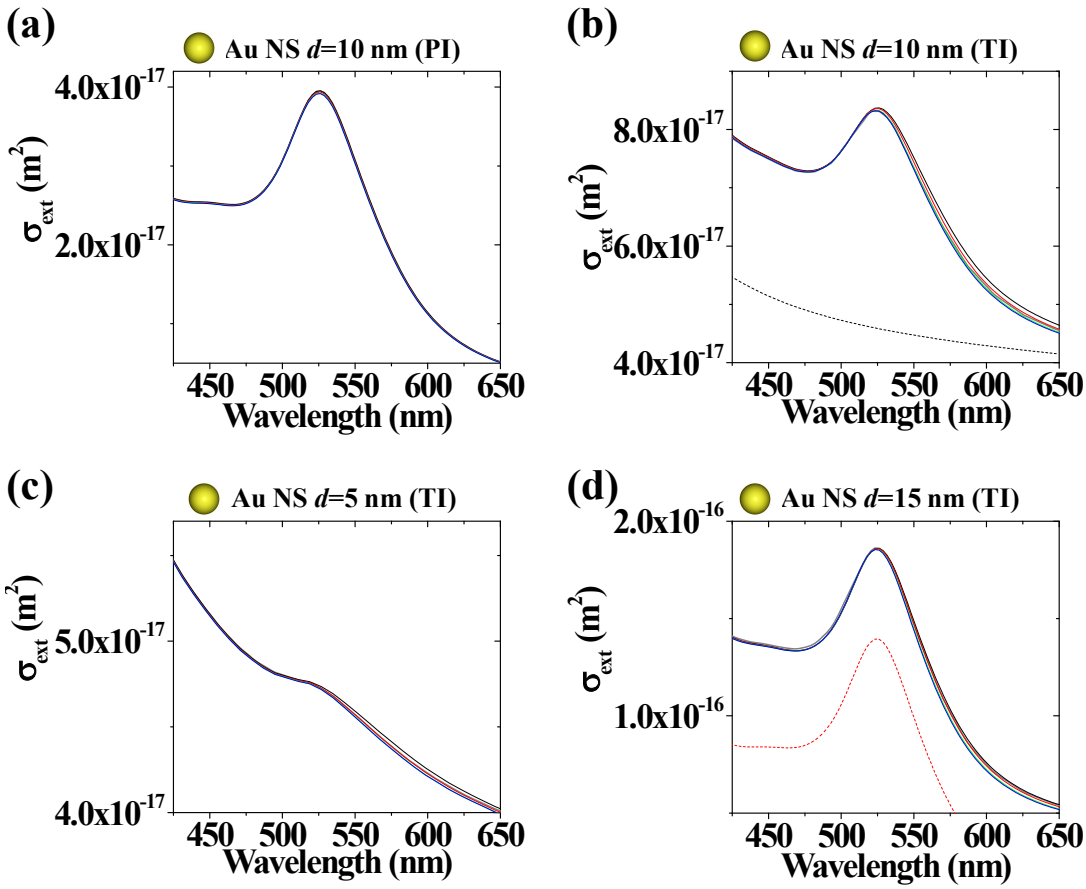

Figure S4. Plot of the absolute value of the quality factor of the SPR, proposed by Blaber et al. in Opt. Expr., 2009, 17, 3835-3847, as a function of wavelength for Ag (black line) and Au (red line).
In nanohybrids showing SPR quenching, the effect is clearly ascribed to the absorbance of graphene, which is larger at 400 nm (where the SPR of Ag nanospheres is located) than at 520 nm (where the SPR of Au nanospheres is located), as shown in Figure 1c (black dashed line).
However, to fully explain why SPR enhancement is observed only for specific nanohybrids containing Au nanoparticles, one must consider two additional factors:
1- When graphene approaches the metal nanoparticle, there is an increase of the "effective" real component of the optical permittivity in the surrounding of nanoparticles, with a consequent shift of the SPR towards longer wavelengths (i.e., red shift of the SPR).
2- The intensity of the plasmonic response of Ag and Au nanoparticles is a function of the wavelength, but the trend is different for Ag and Au. In particular, the intensity of the SPR increases slightly for Ag nanospheres and significantly for Au nanospheres, while increasing the wavelength.
Regarding point 2, the plasmonic response is well described by considering the plasmonic quality factor Q (equation 11 of the revised manuscript):

$$Q_{SPR} = -\frac{\varepsilon'}{\varepsilon''}$$

where ε' and ε" are, respectively, the real and imaginary (lossy) part of the metal optical constant.
In the figure below, dashed lines are centered at the same wavelength of SPR in Ag (black) and Au (red) nanospheres, and circles highlight the region of Q where the red shift in nanospheres occurs. In these regions, it is evident that Q significantly increases for Au, and remains almost unchanged for Ag.
Such a difference between Ag and Au is due to the different spectral location of interband transitions in the two metals, with respect to the SPR (see the plot of ε" in Figures S1a-b). In fact, interband transitions are responsible for the steep increase of ε", with consequent decrease of Q.

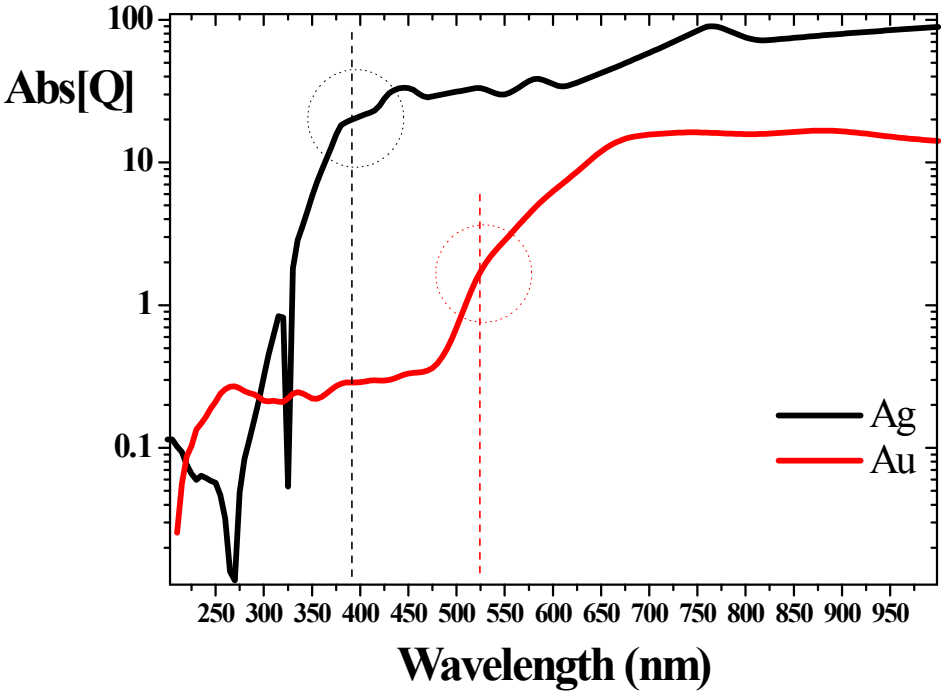

Figure S5. Magnification of the SPR region of Figures 3a, b, d, e. **(a)** From Figure 3a: σ_{ext} calculated for TI in case of a nanohybrid made of a spheroidal Ag NR, with short axis of 10 nm and long axis of 25 nm, and a graphene flake, with diameter of 50 nm. The gap between the two objects is varied in the 0.335 – 5 nm range (black: 0.335 nm, red: 1 nm, green: 2.7 nm, blue: 5 nm). The reference σ_{ext} of the graphene flake and the Ag NR for infinite gap is in grey. **(b)** From Figure 3b: same as in (a) but for an Au NR. **(c)** From Figure 3d: same as in (a) but for an Ag ND with diameter of 15 nm and height of 10 nm. **(d)** From Figure 3e: same as in (c) but for an Au ND.

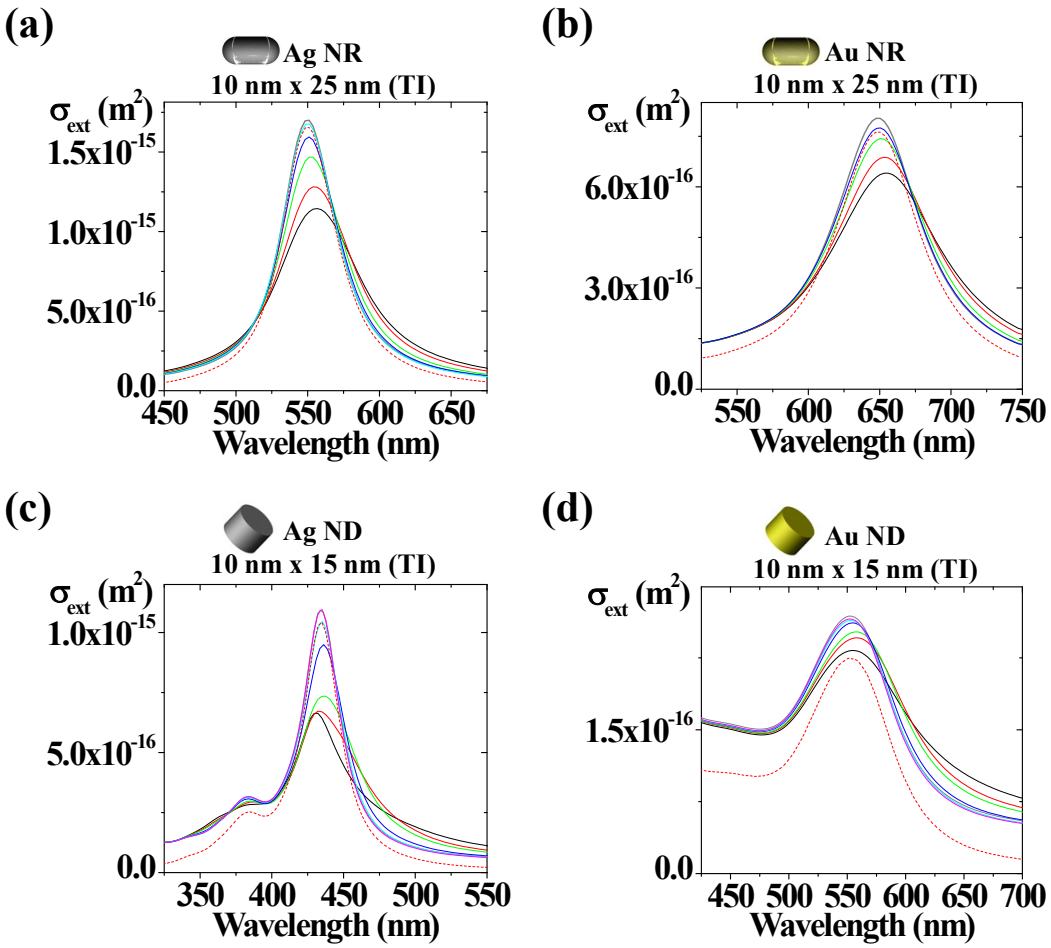

Figure S6. Magnification of the SPR region of Figures 7b, c. **(a)** From Figure 7b: σ_{ext} calculated for TI in case of Ag NS (black: a/d = 0.13, red: a/d = 0.30, green: a/d = 0.50, blue: a/d = 0.80, cyan: a/d = 0.93). The reference σ_{ext} of the graphene flake and the Ag NR for infinite gap is in grey, and the nanohybrid with 0.335 nm gap is the black dashed line. **(b)** From Figure 7c: same as in (b) but for an Au NS.