Electronic Supplementary Information

Coupling of Plasmonic Nanoparticles on a Semiconductor Substrate via a Modified Discrete Dipole Approximation Method

Diogo F. Carvalho, *[a] Manuel A. Martins, [b] Paulo A. Fernandes [acd] and M. Rosário P. Correia [a]

[a] *i3N, Department of Physics, University of Aveiro, 3810-193 Aveiro, Portugal*

[b] *CICECO, Department of Materials and Ceramic Engineering, University of Aveiro, 3810-193 Aveiro, Portugal*

[c] *INL - International Iberian Nanotechnology Laboratory, 4715-330 Braga, Portugal*

[d] *CIETI, Department of Physics, ISEP - Porto School of Engineering, 4200-072 Porto, Portugal*

*E-mail: diogocarvalho@ua.pt

Table of Contents

1. SUPPORTING FIGURES

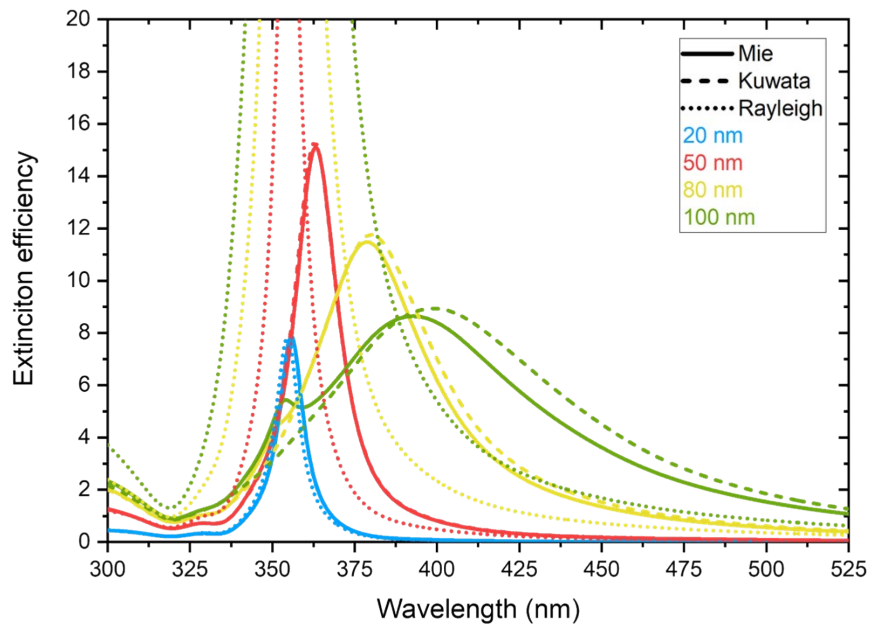

Figure S1.1. Q_{ext} calculated from the Mie theory, Kuwata model and Rayleigh approximation for spherical Ag NPs, with different diameters: 20, 50, 80, 100 nm. The resonance peaks obtained by Rayleigh approximation for the 100, 80 and 50 nm reach an efficiency of ~232.7, ~109.8, and ~30.9, respectively.

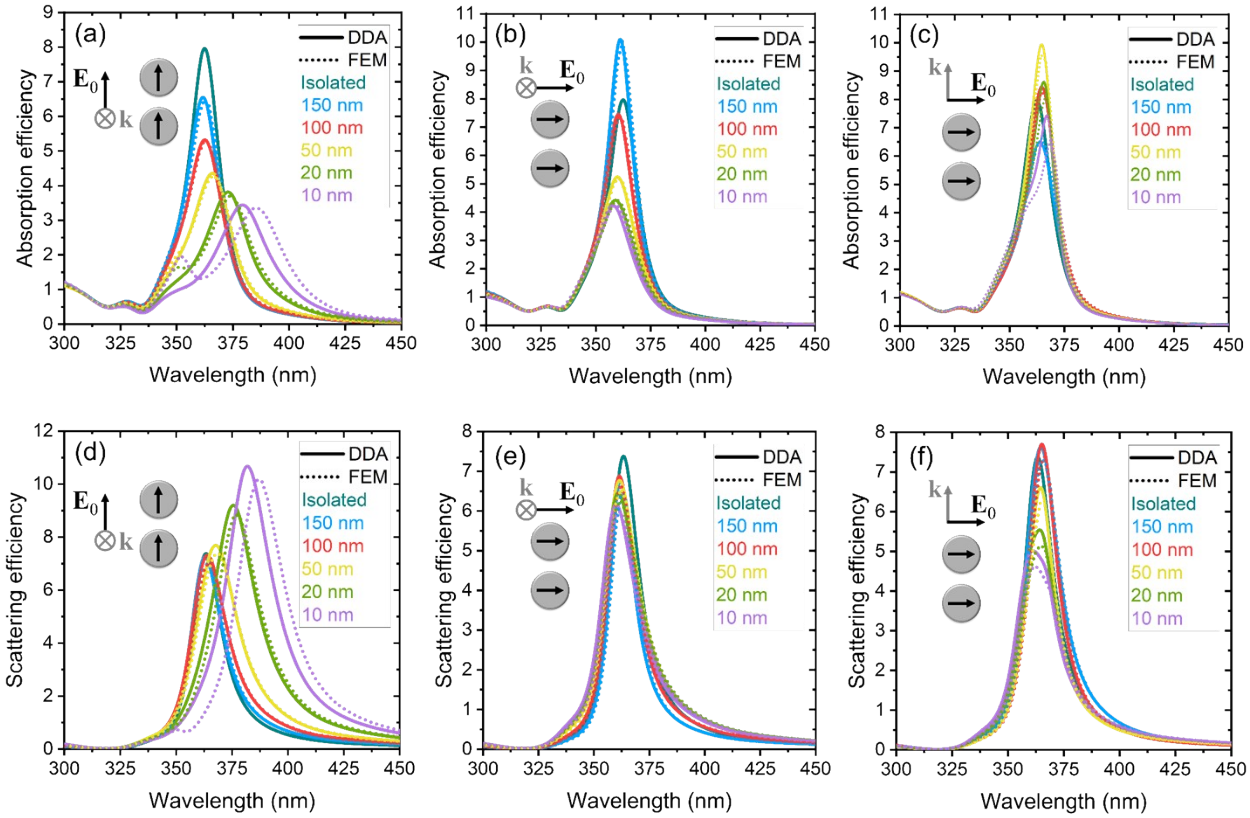

Figure S1.2. Q_{abs} (a-c) and Q_{sca} (d-f) spectra for 50 nm Ag NP dimers, for different gaps and geometries of incidence, obtained from DDA (solid lines) and FEM (dotted lines) calculations. (a, d) E_0 ∥ to the alignment axis, (b, e) E_0 and k ⊥ to the alignment axis, and (c, f) E_0 ⊥ and k ∥ to the alignment axis. Q_{abs} and Q_{sca} for an isolated NP are also represented.

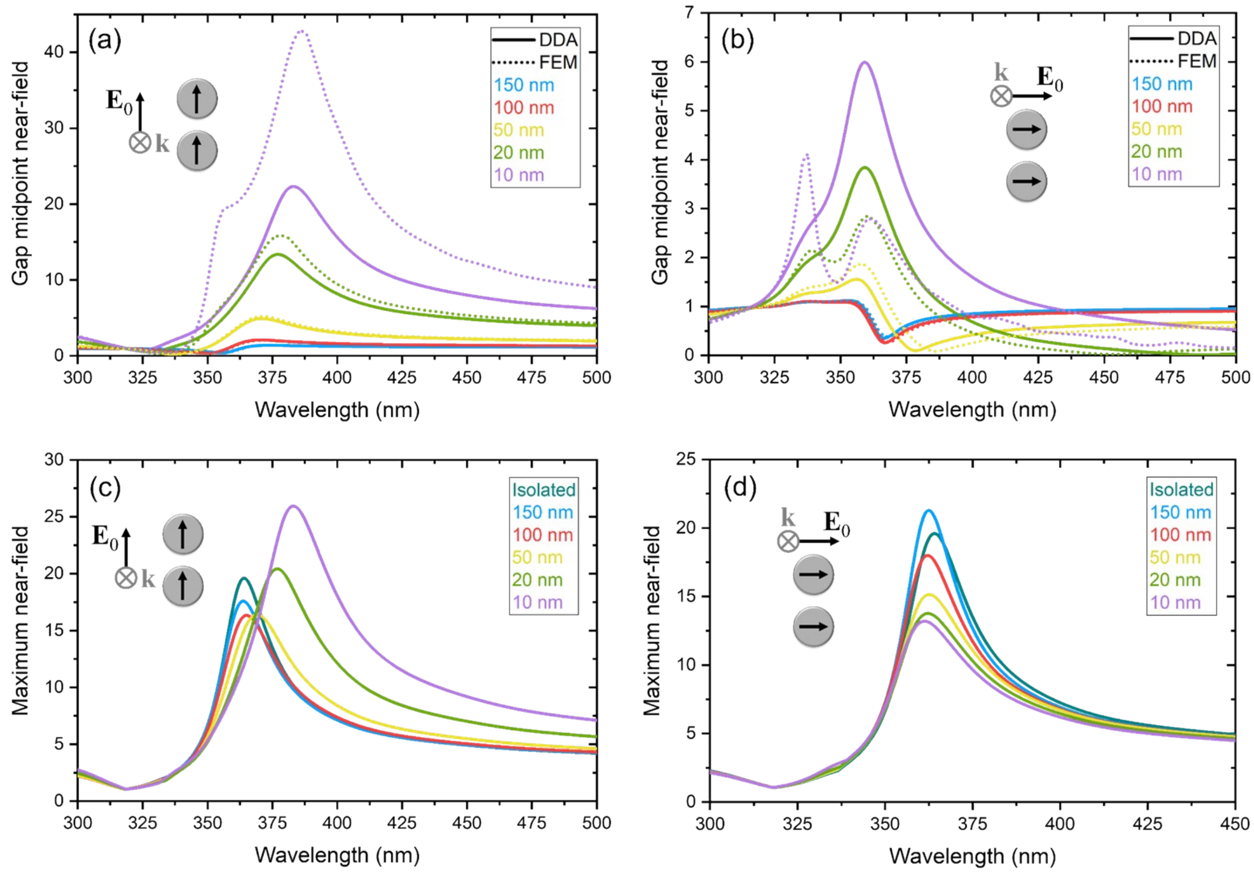

Figure S1.3. $Q_{NF,m}$ (a, b) and $Q_{NF,max}$ (c, d) spectra of 50 nm Ag NP dimers for different gaps, obtained from DDA (solid lines) and FEM (dotted lines) calculations. (a, c) E_0 ∥ to the alignment axis, and (b, d) E_0 and k ⊥ to the alignment axis. $Q_{NF,max}$ spectra obtained from FEM is not represented, due to the field oscillations on the NP surface in numerical calculations.

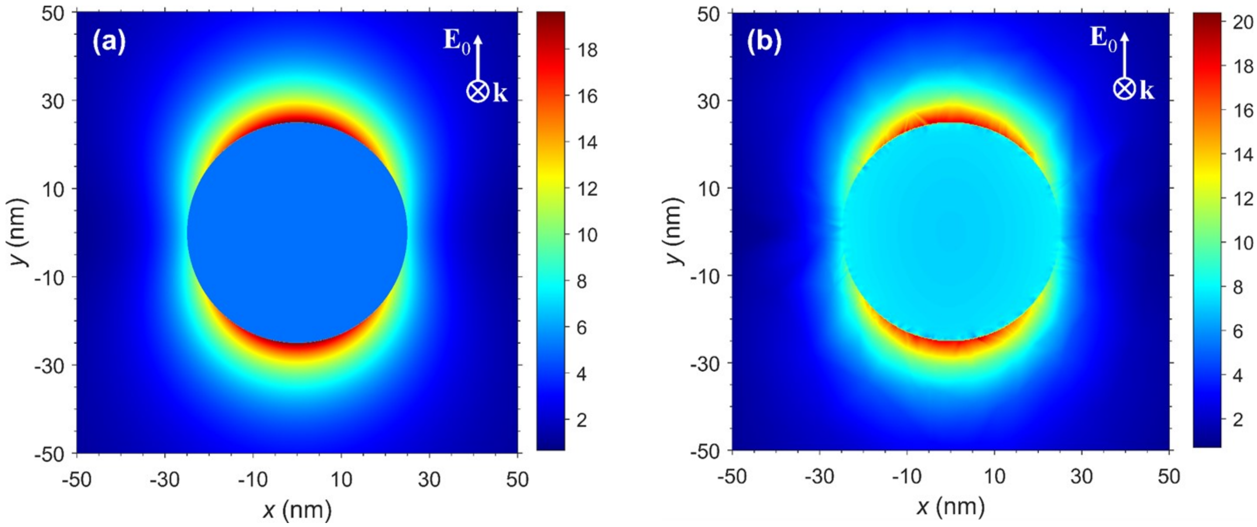

Figure S1.4. Electric field distributions for a 50 nm spherical Ag NP, for 364 nm light, calculated by (a) the single dipole DDA model, and (b) FEM numerical simulation.

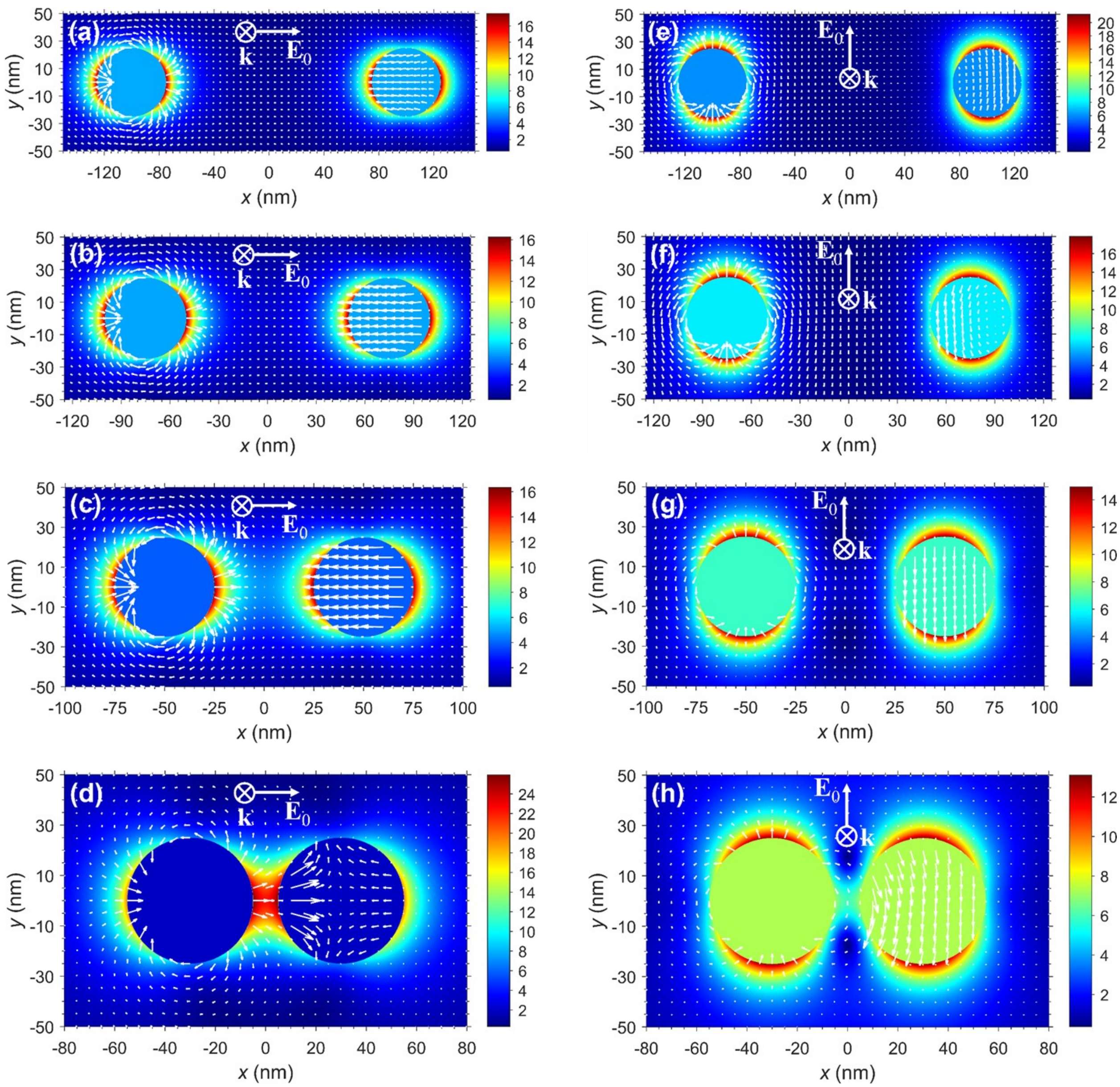

Figure S1.5. Electric field distributions of 50 nm Ag NP dimers, for l = 150 nm (a, e), 100 nm (b, f), 50 nm (c, g), and 10 nm (d, h), at the $Q_{\bar{N}F}$ peak wavelength, calculated from the single dipole DDA method. Geometries of incidence: (a-d) E_0 ∥ to the alignment axis, and (e-h) E_0 and k ⊥ to the alignment axis.

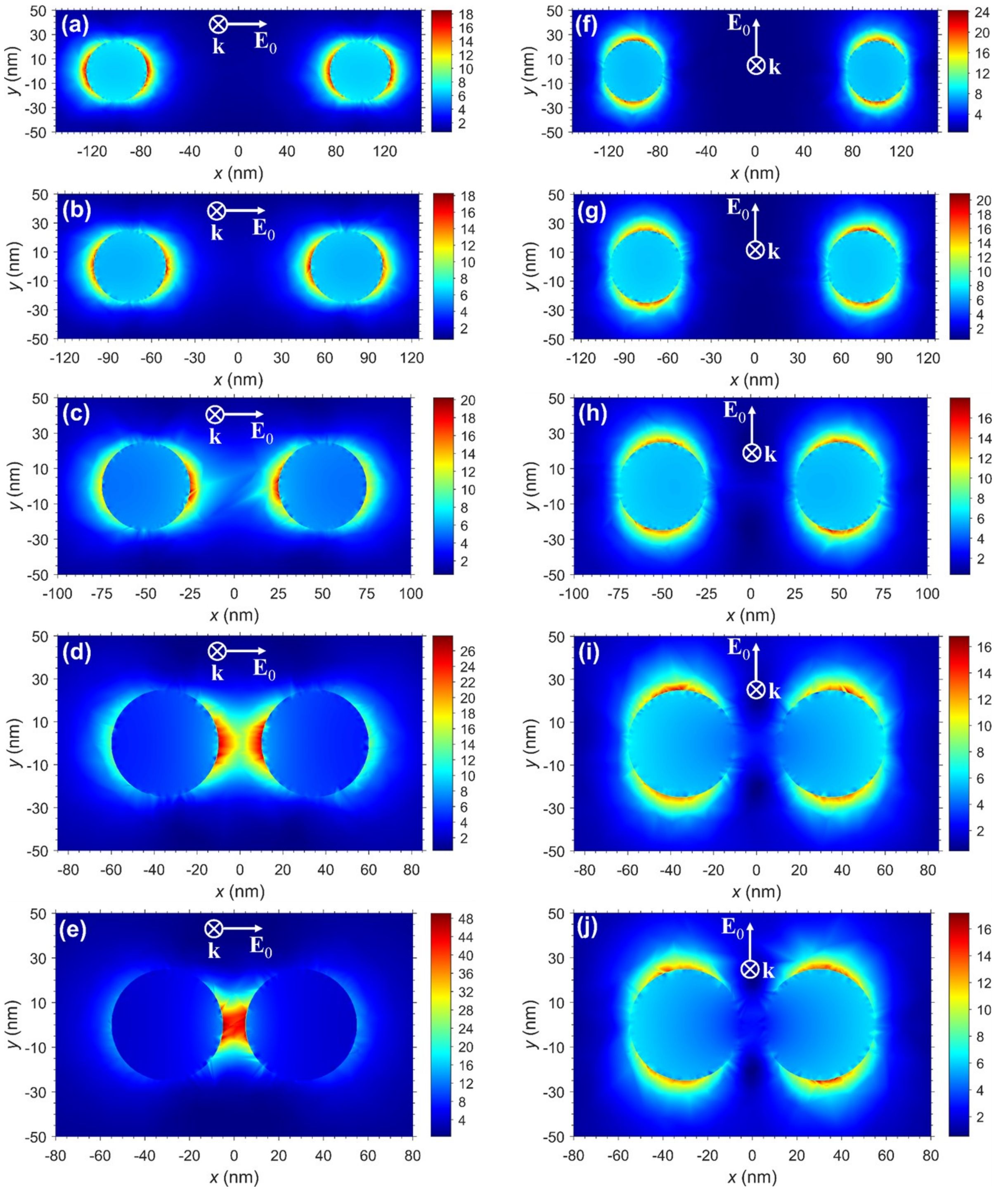

Figure S1.6. Electric field distributions of 50 nm Ag NP dimers, for l = 150 nm (a, f), 100 nm (b, g), 50 nm (c, h), 20 nm (d, i) and 10 nm (e, j), at the $Q_{\bar{N}F}$ peak wavelength, obtained from FEM. Geometries of incidence: (a-e) E_0 ∥ to the alignment axis, and (f-j) E_0 and k ⊥ to the alignment axis.

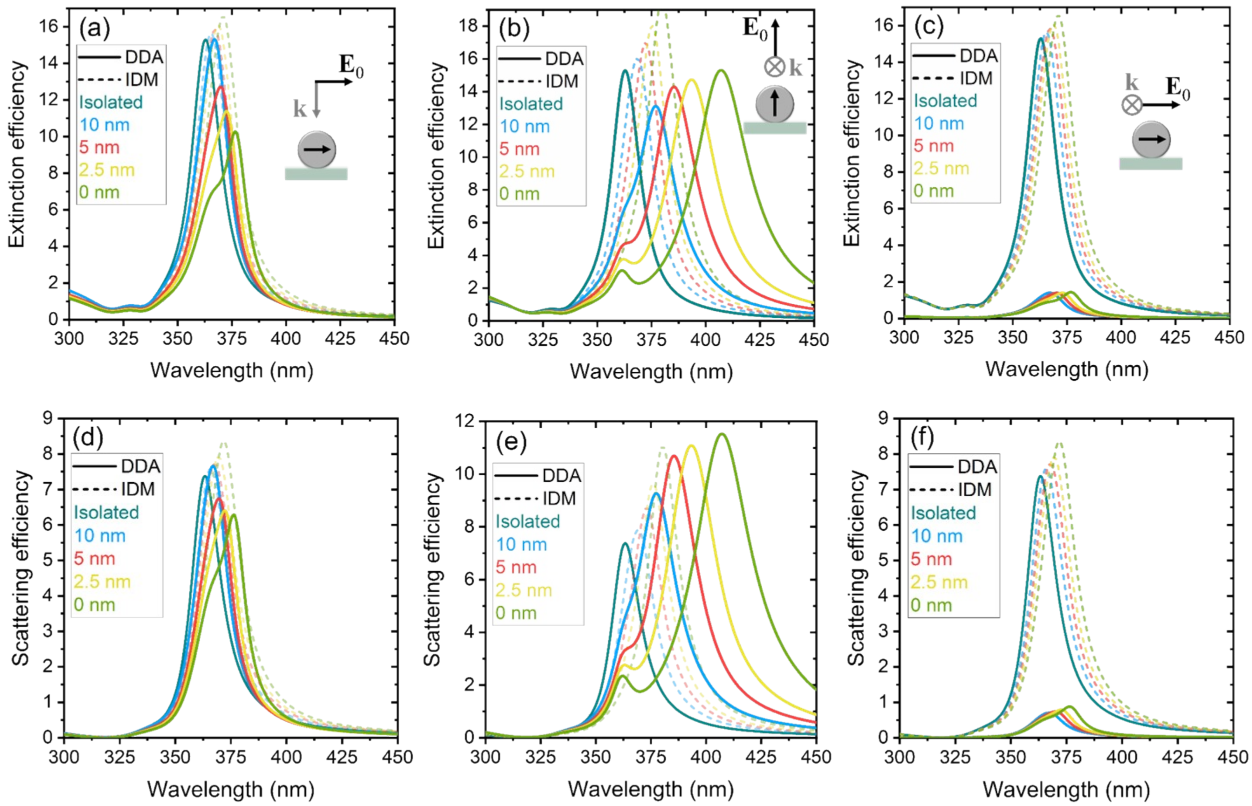

Figure S1.7. (a-c) Q_{ext} and (d-f) Q_{sca} spectra for a 50 nm Ag NP close to a GaN substrate, for different gaps and geometries of incidence, obtained from our DDA method (solid lines), and IDM (dashed lines). (a, d) k ⊥ to the substrate surface, (b, e) E_0 ⊥ and k ∥ to the substrate, and (c, f) E_0 ∥ and k ∥ to the substrate.

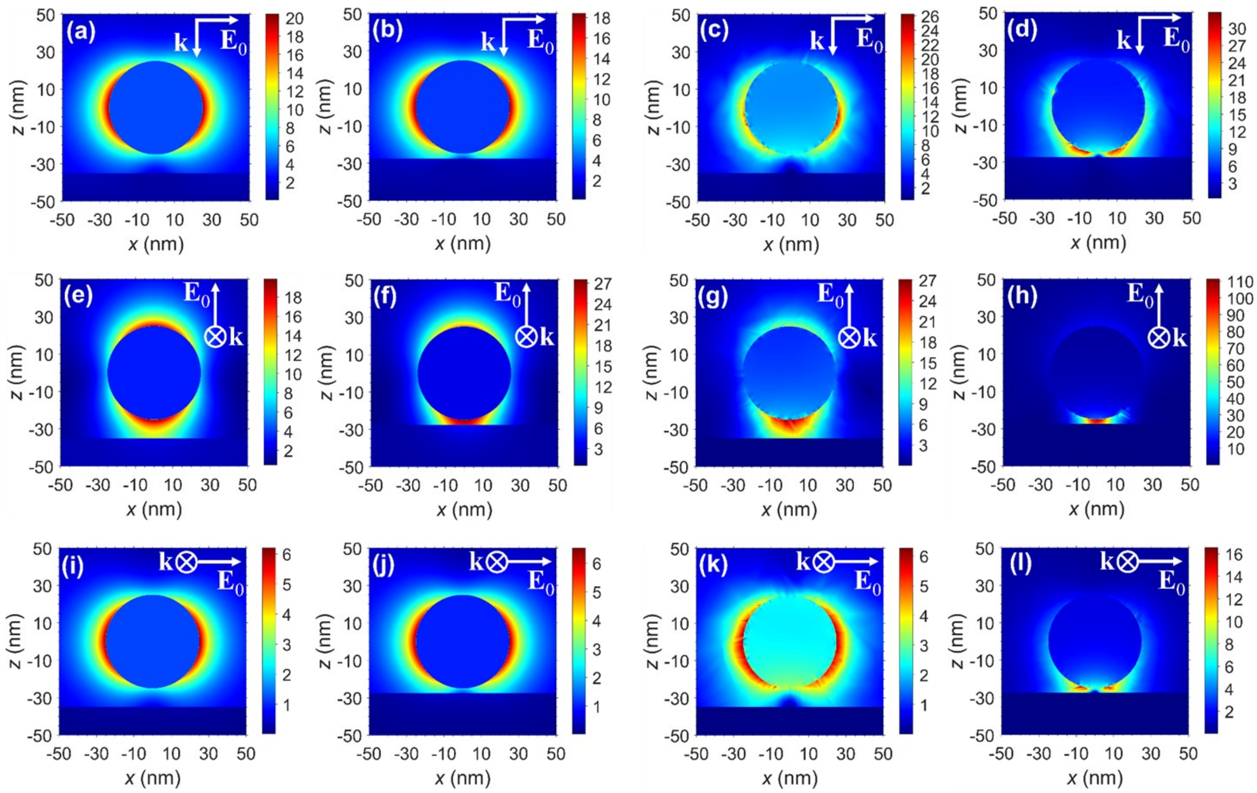

Figure S1.8. Electric field distributions of a 50 nm Ag NP close to a GaN substrate, at the Q_{NF} peak wavelength, for two gaps: 10 nm (a, c, e, g, i, k) and 2.5 nm (b, d, f, h, j, l), calculated from our DDA method (a, b, e, f, i, j) and FEM (c, d, g, h, k, l). Geometries of incidence: (a-d) $k \perp$ to the substrate surface, (e-h) $E_0 \perp$ and $k \parallel$ to the substrate, and (i-l) $E_0 \parallel$ and $k \parallel$ to the substrate.

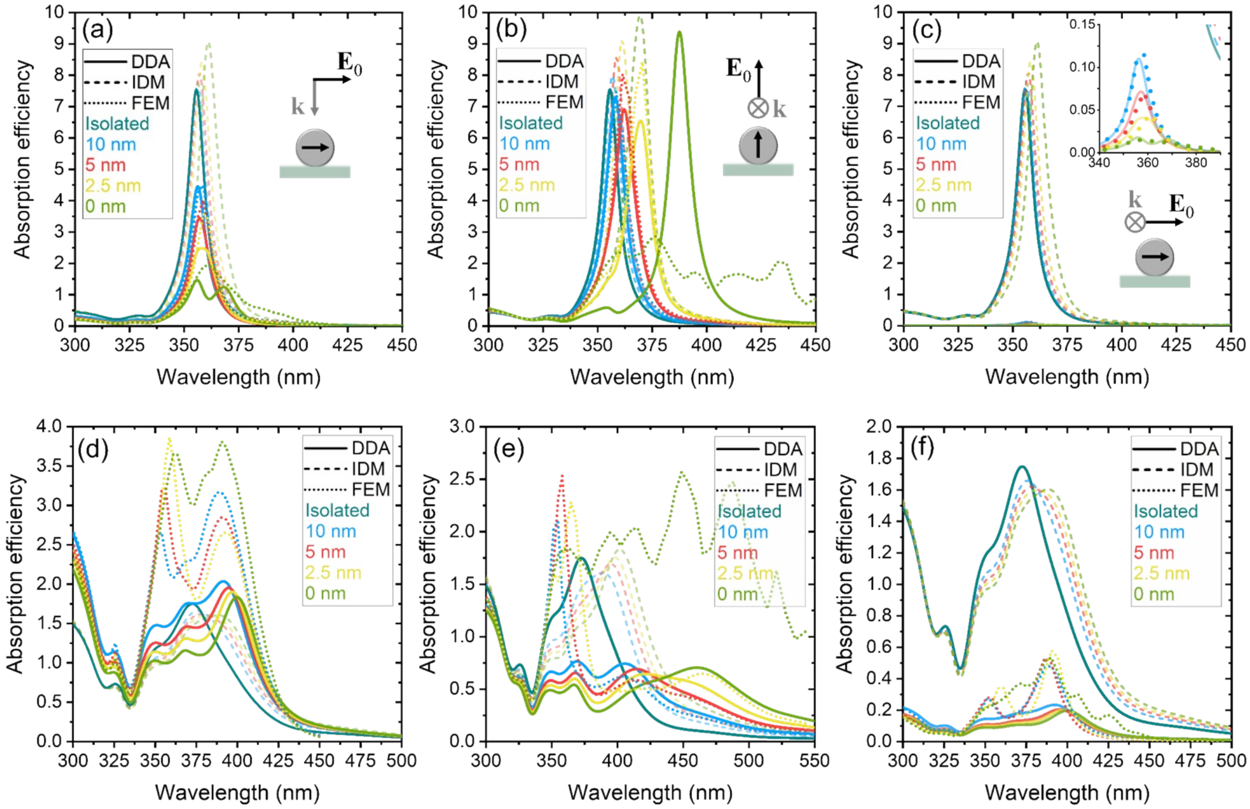

Figure S1.9. Q_{abs} spectra for a 20 nm (a-c) and 80 nm (d-f) Ag NP close to a GaN substrate, for different gaps and geometries of incidence, obtained from our DDA method (solid lines), IDM (dashed lines) and FEM (dotted lines). (a, d) k ⊥ to the substrate surface, (b, e) E_0 ⊥ and k ∥ to the substrate, and (c, f) E_0 ∥ and k ∥ to the substrate.

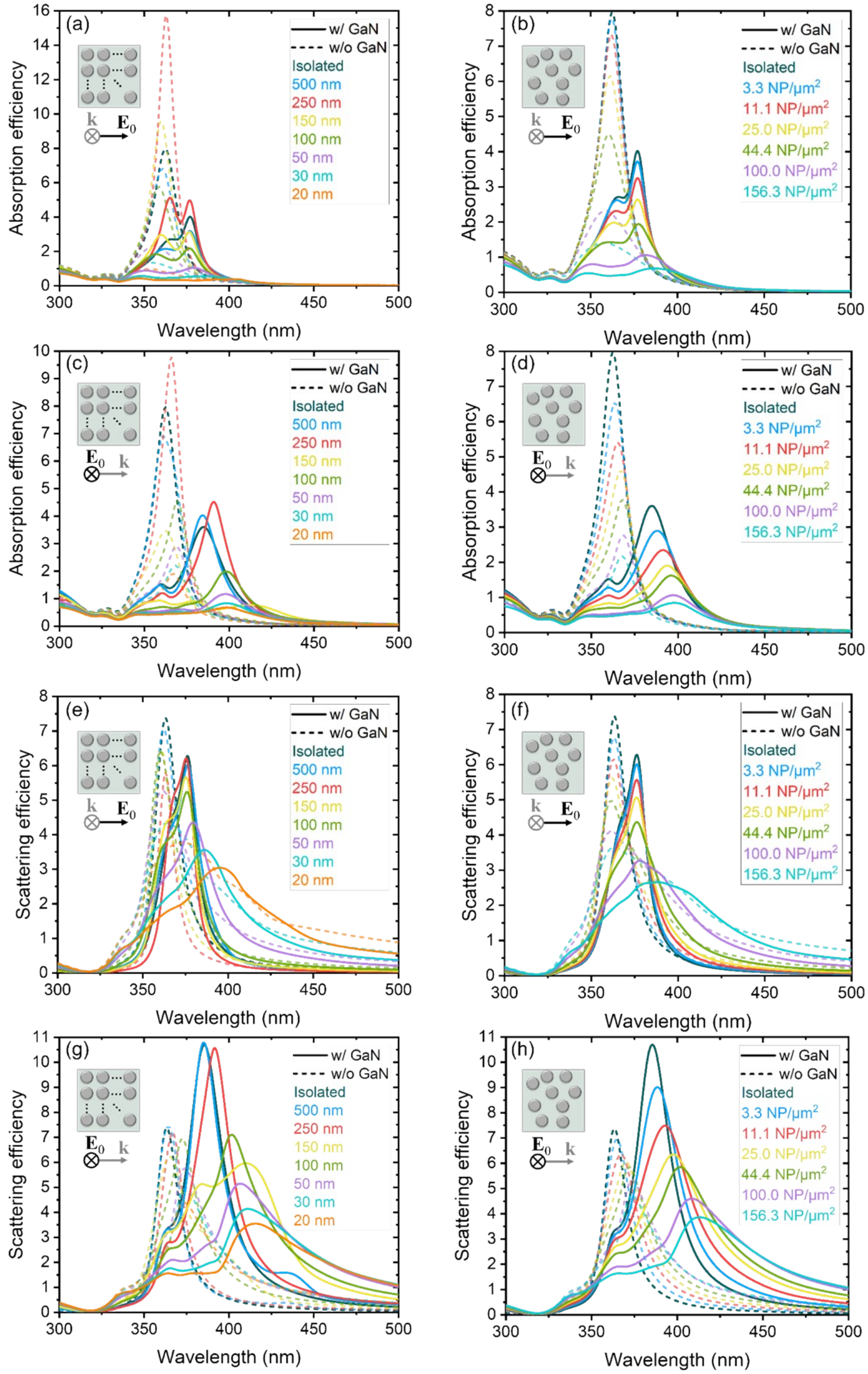

Figure S1.10. (a-d) Q_{abs} and (e-h) Q_{sca} spectra for (a, c, e, g) square and (b, d, f, h) random arrays of 100 Ag NPs of 50 nm close to a GaN substrate ((a, b, e, f) 0 nm gap, and (c, d, g, h) 5 nm gap), and without the substrate effect, for different interparticle gaps and surface densities. Geometries of incidence: (a, b, e, f) $k \perp$ to the substrate surface, and (c, d, g, h) $E_0 \perp$ to the substrate.

2. RAYLEIGH APPROXIMATION

The quasistatic approximation permits the study of the optical properties of small NPs compared to the wavelength of the incident light. Let us consider an isotropic sphere of radius r_p, with a complex permittivity $\tilde{\varepsilon}_m$, embedded in a medium with a real permittivity ε, in which there is a uniform electrostatic field E_0 in the z direction, i.e., $E_0 = E_0\hat{z}$.

The resulting electric fields inside, E_{in}, and outside, E_{out}, the sphere can be obtained through the electrical potentials inside and outside, Φ_{in} and Φ_{out}, respectively, through $E = -\nabla\Phi$. On the other hand, the electrical potentials can be calculated by solving the Laplace's equation: $\nabla^2\Phi = 0$. The general solution of this equation in spherical coordinates is given by:[1]

$$\Phi(r,\theta,\phi) = \sum_{l=0}^{\infty}\sum_{m=-l}^{l} R_{lm}(r)\,Y_{lm}(\theta,\phi) = \sum_{l=0}^{\infty}\sum_{m=-l}^{l}\left[A_{lm}r^{l} + B_{lm}r^{-(l+1)}\right]Y_{lm}(\theta,\phi) \qquad \text{(S1)}$$

where it is possible to distinguish a radial component, $R_{lm}(r) = A_{lm}r^{l} + B_{lm}r^{-(l+1)}$, and an angular component associated with the spherical harmonics, $Y_{lm}(\theta,\phi) = N\exp(im\phi)P_l^m(\cos\theta)$, where N is a normalization constant and $P_l^m(\cos\theta)$ are the associated Legendre functions of the first kind of degree l and order m. The parameters l and m are integers, such that $l \geq 0$ and $|m| \leq l$. The coefficients A_{lm} and B_{lm} are determined by the boundary conditions of the problem.

In the quasistatic approximation, we are interested in the dipolar solution of the problem, that occurs for $l = 1$ and $m = 0$. In this case, the spherical harmonic is given by:[1] $Y_{10} = (3/4\pi)^{1/2}\cos\theta$. Thus, the electrical potentials inside and outside the sphere are of the form:

$$\Phi(r,\theta,\phi) = \left(Ar + \frac{B}{r^2}\right)\cos\theta \qquad \text{(S2)}$$

with $A = (3/4\pi)^{1/2}A_{10}$ and $B = \sqrt{3/4\pi}B_{10}$. For Φ_{in}, the coefficient $B = 0$, so that the potential remains finite for $r = 0$.

In this problem, the potential must satisfy the following boundary conditions for the continuity of the potential and the normal component of the electric displacement at the boundary:[2]

$$\Phi_{in}(r = r_p) = \Phi_{out}(r = r_p); \qquad \tilde{\varepsilon}_m\frac{\partial\Phi_{in}(r = r_p)}{\partial r} = \varepsilon\frac{\partial\Phi_{out}(r = r_p)}{\partial r} \qquad \text{(S3)}$$

In addition to these conditions, it must still be defined that:[2]

$$\lim_{r\to\infty}\Phi_{out} = -E_0 z = -E_0 r\cos\theta \qquad \text{(S4)}$$

so that, at great distances from the sphere, the electric field is given by E_0. Through these conditions, the following electrical potentials are obtained inside and outside the sphere:

$$\Phi_{in} = -\frac{3\varepsilon}{\tilde{\varepsilon}_m + 2\varepsilon} E_0 r\cos\theta \tag{S5}$$

$$\Phi_{out} = -E_0 r\cos\theta + r_p^3 \frac{\tilde{\varepsilon}_m - \varepsilon}{\tilde{\varepsilon}_m + 2\varepsilon} \frac{E_0 \cos\theta}{r^2} \tag{S6}$$

Two charges q with opposite signs, separated by d, as shown in Fig. S2.1, give rise to an electric dipole, with an electric dipole moment $p = p\hat{z} = qd\hat{z}$. The potential due to the electric dipole, at an observation point P at a certain distance r, is given by:

$$\Phi = \frac{1}{4\pi\varepsilon}\left[\frac{q}{r_+} - \frac{q}{r_-}\right] = \frac{q}{4\pi\varepsilon}\frac{r_- - r_+}{r_- r_+} \overset{r \gg d}{\approx} \frac{q}{4\pi\varepsilon}\frac{d\cos\theta}{r^2} = \frac{p\cos\theta}{4\pi\varepsilon r^2} \tag{S7}$$

where r_+ and r_- correspond to the distances between the point P and the charges q and $-q$, respectively.

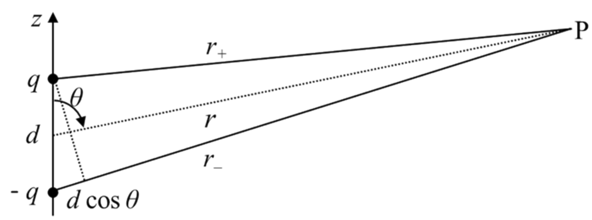

Figure S2.1. Schematic of an electric dipole.

Returning to the spherical particle problem, the potential in the outer region, given by eqn (S6), consists of a first term associated with the incident field and a second term associated with the generated electrical dipole. Comparing this second term with eqn (S7), the electric dipole moment is obtained:

$$p = 4\pi\varepsilon r_p^3 \frac{\tilde{\varepsilon}_m - \varepsilon}{\tilde{\varepsilon}_m + 2\varepsilon} E_0 = \varepsilon\alpha E_0 \tag{S8}$$

where

$$\alpha = 4\pi r_p^3 \frac{\tilde{\varepsilon}_m - \varepsilon}{\tilde{\varepsilon}_m + 2\varepsilon} \tag{S9}$$

where α is the polarizability of the sphere[2] in the medium of permittivity ε.

The resulting electric fields inside and outside the sphere, through eqn (S5), (S6), (S8) and (S9), are given by:

$$E_{in} = -\nabla\Phi_{in} = \frac{3\varepsilon}{\tilde{\varepsilon}_m + 2\varepsilon}E_0\hat{z} \quad \text{(S10)}$$

$$\begin{aligned} E_{out} &= -\nabla\Phi_{out} \\ &= \left(\frac{3\alpha}{4\pi}E_0 xzr^{-5}\right)\hat{x} + \left(\frac{3\alpha}{4\pi}E_0 yzr^{-5}\right)\hat{y} + \left(E_0 + \frac{\alpha}{4\pi}E_0\left[3z^2r^{-5} - r^{-3}\right]\right)\hat{z} \\ &= E_0 + \frac{3(p\cdot r)r - pr^2}{4\pi\varepsilon r^5} \end{aligned} \quad \text{(S11)}$$

where $r = r\hat{r} = x\hat{x} + y\hat{y} + z\hat{z}$.

3. KUWATA POLARIZABILITY

The quasistatic approximation is generally valid only for NPs up to a maximum diameter of ~20 nm. However, Kuwata *et al.*[3] proposed an empirical formula for the polarizability of an ellipsoid, which is valid for NPs with a maximum dimension up to ~80 nm:

$$\alpha = \frac{V}{\left(\frac{\varepsilon}{\tilde{\varepsilon}_m - \varepsilon} + L\right) + Ax^2 + Bx^4 - i\frac{4\pi^2}{3}\frac{V}{\lambda^3}} \quad \text{(S12)}$$

where V is the ellipsoid volume, L is a geometric factor related with the morphology of the particle (for the particular case of the sphere, $L = 1/3$), $x = kr_p$ is the size parameter, where k is the wavevector modulus in the surrounding medium; λ is the wavelength of light in the surrounding medium; and A and B are constants that were obtained by Kuwata *et al.* from the data obtained through numerical simulations for prolate ellipsoids. These constants are independent of the material, depending only on the geometric factor L: $A(L) = -0.4865L - 1.046L^2 + 0.8481L^3$, and $B(L) = 0.01909L + 0.1999L^2 + 0.6077L^3$. In this model, the extinction cross section is calculated through the absorption cross section equation in the quasistatic approximation (in fact, in the quasistatic approximation, $\sigma_{ext} \cong \sigma_{abs}$).

4. EFFECT OF A FLAT SUBSTRATE IN THE VICINITY OF A NP

To study the interaction effect of a spherical NP with a substrate, let us consider again the quasistatic approximation, and a sphere of radius r_p with a complex permittivity $\tilde{\varepsilon}_m$, in a medium with a real permittivity ε, with the centre at a distance d from the surface of a substrate with a complex permittivity $\tilde{\varepsilon}_s$. The charges generated on the substrate surface will change the polarizability of the sphere and, consequently, the resulting electric field applied to the sphere.

To study this problem, the image charge method is the simplest approach, usually used to obtain the electrical potential of a charge close to a substrate.[1,4] In the quasistatic approximation, the sphere can be represented by a dipole moment $p = \varepsilon\alpha E_{ef}$, located in the center of the sphere (origin of the referential), where α is the polarizability of the sphere and E_{ef} corresponds to the effective electric field that will act on the sphere, which is given by the incident electric field E_0 plus a term associated with the influence of the substrate. In this model, the charges induced on the substrate surface can be represented by a new dipole moment p', which corresponds to the image of the dipole moment p inside the substrate, as shown in Fig. S4.1.

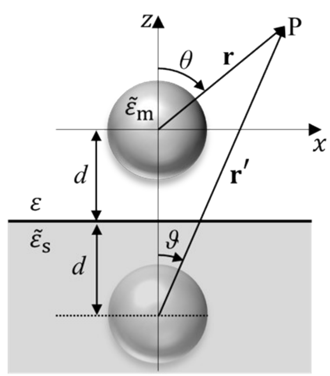

Figure S4.1. Image method applied to a sphere in the vicinity of a substrate.

Two different cases will be analysed: the case in which E_0 is perpendicular to the substrate surface, and the case in which it is parallel. In both cases, we will assume that the incident wave propagates only in the medium in which the particle is found.

Let us start by assuming that it is applied a uniform electrostatic field perpendicular to the surface of the substrate, in the z direction, i.e, $E_0 = E_0\hat{z}$. In this case, the dipolar component of the electrical potential in the region $z > -d$ (with permittivity ε), $\Phi_{\perp m}$, in the image method, is given by:

$$\Phi_{\perp m} = \frac{1}{4\pi\varepsilon}\left(\frac{p\cos\theta}{r^2} + \frac{p_2\cos\vartheta}{r'^2}\right) = \frac{1}{4\pi\varepsilon}\left(\frac{pz}{r^3} + \frac{p'(z+2d)}{r'^3}\right) \tag{S13}$$

where r corresponds to the distance between the dipole p and an observation point P, r' corresponds to the distance between the dipole p' and P, θ and ϑ correspond to the angles between the z axis and the vector position r and r', respectively. The first term of eqn (S13) is related to the dipole moment p induced in the sphere by E_{ef} and the second term with the dipole moment p' induced in the substrate.

The electrical potential in the substrate region ($z < -d$), for an incident field perpendicular to the substrate, $\Phi_{\perp s}$, should not have any singularity, since the "real" dipole (associated with the NP) is defined only in the region $z > -d$. Thus, the simplest hypothesis is to consider that $\Phi_{\perp s}$ is given by the potential of a dipole, with a dipole moment p'', positioned in the same position as p (at $z = 0$):

$$\Phi_{\perp s} = \frac{1}{4\pi\tilde{\varepsilon}_s}\frac{p''\cos\theta}{r^2} = \frac{1}{4\pi\tilde{\varepsilon}_s}\frac{p''z}{r^3} \tag{S14}$$

For an incident field parallel to the substrate surface, in the x direction, i.e., $E_0 = E_0\hat{x}$, the field can propagate parallel ($\hat{y}$) or perpendicularly ($\hat{z}$) to the substrate surface. For now, let us just consider the case where the field propagates parallel ($\hat{y}$) to the substrate surface, because otherwise we would have to consider the reflected wave on the substrate surface. The electrical potentials for the dipolar component in the regions $z > -d$ ($\Phi_{\parallel m}$) and $z < -d$ ($\Phi_{\parallel s}$), for an incident field parallel to the substrate, are given by:

$$\Phi_{\parallel m} = \frac{1}{4\pi\varepsilon}\left(\frac{px}{r^3} + \frac{p'x}{r'^3}\right); \qquad \Phi_{\parallel s} = \frac{1}{4\pi\tilde{\varepsilon}_s}\frac{p''x}{r^3} \tag{S15}$$

The boundary conditions between the mediums with permittivities ε and $\tilde{\varepsilon}_s$ come:

$$\Phi_s(z = -d) = \Phi_m(z = -d); \qquad \tilde{\varepsilon}_s\frac{\partial\Phi_s(z = -d)}{\partial z} = \varepsilon\frac{\partial\Phi_m(z = -d)}{\partial z} \tag{S16}$$

where Φ_s can indicate $\Phi_{\perp s}$ or $\Phi_{\parallel s}$ and Φ_m can indicate $\Phi_{\perp m}$ or $\Phi_{\parallel m}$. The conditions are applied only to the dipolar component of the electrical potentials, since it is assumed that the incident field is defined only in the region $z > -d$. Applying the conditions (S16), the following relations between the dipole moments are obtained:

$$p'' = p + \gamma p' \tag{S17}$$

$$p' = \gamma p\frac{\tilde{\varepsilon}_s - \varepsilon}{\tilde{\varepsilon}_s + \varepsilon} \tag{S18}$$

where γ can take two different values depending on the direction of polarization of the incident field: $\gamma = 1$ for a polarization perpendicular to the substrate surface or $\gamma = -1$ for a polarization parallel to the substrate surface.

The electrical potentials can be rewritten through eqn (S17) and (S18), being:

$$\Phi_{\perp m} = \frac{p}{4\pi\varepsilon}\left(\frac{z}{r^3} + \frac{\tilde{\varepsilon}_s - \varepsilon}{\tilde{\varepsilon}_s + \varepsilon}\frac{z + 2d}{r'^3}\right); \qquad \Phi_{\perp s} = \frac{pz}{4\pi\tilde{\varepsilon}_s r^3}\left(1 + \frac{\tilde{\varepsilon}_s - \varepsilon}{\tilde{\varepsilon}_s + \varepsilon}\right) \tag{S19}$$

$$\Phi_{\parallel m} = \frac{p}{4\pi\varepsilon}\left(\frac{x}{r^3} - \frac{\tilde{\varepsilon}_s - \varepsilon}{\tilde{\varepsilon}_s + \varepsilon}\frac{x}{r'^3}\right); \qquad \Phi_{\parallel s} = \frac{px}{4\pi\tilde{\varepsilon}_s r^3}\left(1 + \frac{\tilde{\varepsilon}_s - \varepsilon}{\tilde{\varepsilon}_s + \varepsilon}\right) \tag{S20}$$

The electric fields associated with the dipolar component for $z > -d$, E_m, and for $z < -d$, E_s, from eqn (S19) and (S20), are given by:

$$E_m = -\nabla\Phi_m = \frac{3(p \cdot r)r - pr^2}{4\pi\varepsilon r^5} + \gamma\frac{\tilde{\varepsilon}_s - \varepsilon}{\tilde{\varepsilon}_s + \varepsilon}\frac{3(p \cdot r')r' - pr'^2}{4\pi\varepsilon r'^5} \tag{S21}$$

$$E_s = -\nabla\Phi_s = \frac{3(p \cdot r)r - pr^2}{4\pi\tilde{\varepsilon}_s r^5}\left(1 + \frac{\tilde{\varepsilon}_s - \varepsilon}{\tilde{\varepsilon}_s + \varepsilon}\right) \tag{S22}$$

where $r' = x\hat{x} + y\hat{y} + (z + 2d)\hat{z}$.

At this point, it is possible to calculate the effective electric field, E_{ef}, that will act on the sphere giving rise to the dipole p, which, as already mentioned, corresponds to the sum of E_0 and the electric field generated by the dipole moment p' at the dipole p position, at (0, 0, 0). This last component of the electric field can be calculated from the second term of the last expression of eqn (S21), for (0, 0, 0). Thus, E_{ef} is given by:

$$E_{ef} = E_0 + \frac{p}{C\pi\varepsilon d^3}\frac{\tilde{\varepsilon}_s - \varepsilon}{\tilde{\varepsilon}_s + \varepsilon} \tag{S23}$$

where C is a constant that depends on the direction of polarization of the incident field: $C = 16$ for a polarization perpendicular to the substrate surface, or $C = 32$ for a polarization parallel to the substrate surface.

As $p = \varepsilon\alpha E_{ef}$, eqn (S23) can be rewritten as:

$$E_{ef} = E_0\left(1 - \frac{\alpha}{C\pi d^3}\frac{\tilde{\varepsilon}_s - \varepsilon}{\tilde{\varepsilon}_s + \varepsilon}\right)^{-1} \tag{S24}$$

which allows to obtain the effective polarizability of the sphere, α_{ef}, assuming that the dipole moment p can be written as $p = \varepsilon\alpha_{ef}E_0$:

$$\alpha_{ef} = \alpha\left(1 - \frac{\alpha}{C\pi d^3}\frac{\tilde{\varepsilon}_s - \varepsilon}{\tilde{\varepsilon}_s + \varepsilon}\right)^{-1} \tag{S25}$$

This method can be generalized for NPs with other shapes, e.g. for ellipsoidal particles, considering the polarizability in the direction of each of the semi-axes of the ellipsoids.

REFERENCES

1 J. D. Jackson, *Classical Electrodynamics*, Wiley, New York, 1999.

2 C. F. Bohren and D. R. Huffman, *Absorption and Scattering of Light by Small Particles*, Wiley, 1998.

3 H. Kuwata, H. Tamaru, K. Esumi and K. Miyano, *Applied Physics Letters*, 2003, **83**, 4625–4627.

4 A. Pinchuk, A. Hilger, G. von Plessen and U. Kreibig, *Nanotechnology*, 2004, **15**, 1890–1896.