## Supporting Information: Plasmonics of Supported Nanoparticles Reveals Adhesion at the Nanoscale: Implications for Metals on Dielectrics

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# SI Dielectric functions of materials

Figures S1 and S2 show the UV-visible range of dielectric functions, respectively, of all the metals and the substrates used in the present study. The loss functions of the two absorbing substrates ZnO and TiO<sub>2</sub> are displayed in Figure S3.

### SII Oscillator characteristics of spheroid resonances

As given in the text (Eq 6), the polarizability components of a full spheroid of volume V along its main axis:<sup>4-6</sup>

$$\alpha_{\parallel,\perp}(\omega) = \frac{\epsilon_a(\epsilon - \epsilon_a)V}{\epsilon_a + L_{\parallel,\perp}(\epsilon - \epsilon_a)}, \qquad (S1)$$

are functions of the depolarization factors  $L = L_{\parallel,\perp}$  defined along the directions perpendicular and parallel to the rotation axis of the spheroid.  $\epsilon$  and  $\epsilon_a$  are respectively the dielectric functions of the particle and ambient medium. After a demonstration of the oscillator behavior in the case of a Drude metal,  $L = L_{\parallel,\perp}$  are detailed in what follows, for free-standing and for supported spheroids in Conventional Dipole Approximation and in the more accurate Spheroid Dipole Approximation (SDA).

#### SII.1 Resonant frequency and oscillator strength

As mentioned in the main text, the dielectric function of a Drude metal with a plasma frequency  $\omega_D$  and a damping  $\Gamma_D$  is given by the following expression:

$$\epsilon(\omega) = \epsilon_D - \frac{\omega_D^2}{\omega^2 + i\omega\Gamma_D}.$$
 (S2)

Inserting Eq S2 in Eq S1, a straightforward algebra shows that Eq S1 can be recasted into the form of a damped oscillator:

$$\alpha(\omega) = \frac{2}{\pi} \frac{\omega_R F_R}{\omega_R^2 - \omega^2 - i\omega\Gamma_D},$$
 (S3)



Figure S1: Used dielectric functions  $\epsilon(\omega)$  of metals: (a) Ag, (b) Au, (c) Zn, (d) Cr, and (e) Ni. Left scale/blue squares: Re( $\epsilon$ ); Right scale/red circles: Im( $\epsilon$ ). Values are extracted from the compilation of Ref. 1 except for Zn (Ref. 2). For optically anisotropic media, the symmetry averaged values are used. Colored rectangles correspond to the estimated range, in which resonant modes parallel (green) and perpendicular (yellow) to the substrate are expected for particles with aspect ratio  $1 \leq A_r \leq 6$ .



Figure S2: Used dielectric functions of substrates: (a)  $Al_2O_3$ , (b)  $SiO_2$ , (c) KBr, (d) ZnO, and (e) TiO\_2. Same labels as in Figure S1. Data are extracted from Ref. 1 except for ZnO (Ref. 3).



Figure S3: Surface loss-functions  $\frac{1}{\epsilon(\omega)-1}$  of (a) ZnO and (b) TiO<sub>2</sub> obtained from Figure S2. Same color code as in Figure S1.

(i) when  $\omega$  is close to its resonant frequency  $\omega_R$  defined by  $\epsilon_R(\omega_R) = \epsilon_a(1 - 1/L)$  *i.e.*:

$$\omega_R = \omega_D \sqrt{\frac{L}{\epsilon_a + L(\epsilon_d - \epsilon_a)}}, \qquad (S4)$$

and (ii) when  $\Gamma_D \ll \omega_R < \omega_D$ . The oscillator strength  $F_R$  of the spheroid polarizability is given by:

$$F_R = \frac{\pi}{2} \frac{V\omega_D \sqrt{\epsilon_a}}{\sqrt{L} [1 + L(\epsilon_D/\epsilon_a - 1)]^{3/2}}.$$
 (S5)

Its damping is that of the Drude dielectric function  $\Gamma_D$ . The peculiar case  $\epsilon_a = \epsilon_D = 1$  is informative since  $\omega_R = \omega_D \sqrt{L}$  and  $F_R = \frac{\pi}{2} \frac{\omega_D}{\sqrt{L}}$ evolve in opposite directions with the depolarization factor. The resonance frequencies used in Figures 3-4 of the main text are normalized to the Drude frequency *i.e.*  $\frac{\omega_R}{\omega_D}$ . The corresponding normalized oscillator strengths are defined by  $\frac{2F_R}{\pi V \omega_D \sqrt{\epsilon_a}}$ .

#### SII.2 Depolarization factors of supported oblate/prolate spheroids

Oblate/prolate spheroids (Figure S4) are built through the rotation of an ellipse of focus aaround its small/large axis and are characterized by a flattening parameter  $\xi_0$ . The diam-



Figure S4: Used geometry of supported oblate/prolate full spheroid.  $\epsilon_a, \epsilon_s, \epsilon$  are the dielectric functions of the ambient medium, substrate and particle, respectively.

eters parallel  $D_{\parallel}$  and perpendicular  $D_{\perp}$  to the substrate surface, the aspect ratio  $A_r = D_{\parallel}/D_{\perp}$  and the volume V of the spheroid are given by:

$$D_{\parallel,o} = 2a\sqrt{\xi_0^2 + 1}; D_{\perp,o} = 2a\xi_0$$

$$V_o = \frac{4}{3}\pi a^3 \xi_0 (1 + \xi_0^2); A_{r,o} = \sqrt{1 + \frac{1}{\xi_0^2}}$$

$$D_{\parallel,p} = 2a\sqrt{\xi_0^2 - 1}; D_{\perp,p} = 2a\xi_0 \quad (S6)$$

$$V_p = \frac{4}{3}\pi a^3 \xi_0 (\xi_0^2 - 1); A_{r,p} = \sqrt{1 - \frac{1}{\xi_0^2}}$$

for oblate (o index) and prolate (p index) objects. Since  $0 < \xi_0 < +\infty$  for an oblate spheroid,  $1 < A_{r,o} < +\infty$ . For a prolate one,  $1 < \xi_0 < +\infty$  and  $0 < A_{r,p} < 1$ . The limit ( $\xi_0 \rightarrow +\infty, A_r \rightarrow 1$ ) corresponds to a full sphere, that of ( $\xi_0 \rightarrow 0; A_r \rightarrow \infty$ ) for an oblate spheroid to a flat disk and that of ( $\xi_0 \rightarrow 0; A_r \rightarrow 0$ ) for a prolate spheroid to a needle.

The depolarization factors of a free-standing oblate/prolate spheroid have been calculated in Refs. 5,7 as a function of the flattening parameter  $\xi_0$ :

$$L_{\perp,o}^{\infty} = (1+\xi_0^2) \left[ 1 - \xi_0 \arctan\left(\frac{1}{\xi_0}\right) \right]$$

$$L_{\parallel,o}^{\infty} = \frac{1}{2} (1+\xi_0^2) \left[ \xi_0 \arctan\left(\frac{1}{\xi_0}\right) - \frac{\xi_0^2}{1+\xi_0^2} \right]$$

$$L_{\perp,p}^{\infty} = (1-\xi_0^2) \left[ 1 - \frac{1}{2}\xi_0 \ln\left(\frac{\xi_0+1}{\xi_0-1}\right) \right] \quad (S7)$$

$$L_{\parallel,p}^{\infty} = \frac{1}{2} (1-\xi_0^2) \left[ \frac{\xi_0^2}{1+\xi_0^2} + \frac{1}{2}\xi_0 \ln\left(\frac{\xi_0+1}{\xi_0-1}\right) \right]$$

Notice that  $L_{\parallel} + 2L_{\perp} = 1$  and  $L_{\parallel} = L_{\perp} = 1/3$  for a sphere.

For an object standing at a distance  $d = a\xi_1$ from the substrate surface, the depolarization factors can be calculated within the Conventional Dipole Approximation (CDA)<sup>5,7,8</sup> which replaces the object by its equivalent dipole screened by the image field:

$$\begin{split} L^{cda}_{\perp,o} &= L^{\infty}_{\perp,o} + \frac{1}{12} \left(\frac{\epsilon_a - \epsilon_s}{\epsilon_a + \epsilon_s}\right) (1 + \xi_0^2) \frac{\xi_0}{\xi_1^3} \\ L^{cda}_{\parallel,o} &= L^{\infty}_{\parallel,o} + \frac{1}{24} \left(\frac{\epsilon_a - \epsilon_s}{\epsilon_a + \epsilon_s}\right) (1 + \xi_0^2) \frac{\xi_0}{\xi_1^3} \\ L^{cda}_{\perp,p} &= L^{\infty}_{\perp,p} - \frac{1}{12} \left(\frac{\epsilon_a - \epsilon_s}{\epsilon_a + \epsilon_s}\right) (1 - \xi_0^2) \frac{\xi_0}{\xi_1^3} \\ L^{cda}_{\parallel,p} &= L^{\infty}_{\parallel,p} - \frac{1}{24} \left(\frac{\epsilon_a - \epsilon_s}{\epsilon_a + \epsilon_s}\right) (1 - \xi_0^2) \frac{\xi_0}{\xi_1^3} \\ S8 \end{split}$$

where come into play the dielectric functions in the image term  $A = \frac{\epsilon_a - \epsilon_s}{\epsilon_a + \epsilon_s}$ . But more accurate expressions compared to multipolar calculations are given in the Spheroidal Dipole Approximation (SDA).<sup>5,7,9</sup> It consists in restricting to dipolar order the fulfillment of the boundary conditions of direct/image multipole potential expansion at the surface of the spheroid. The SDA depolarization factors read:

$$\begin{split} L_{\perp,o}^{sda} &= L_{\perp,o}^{\infty} - \left(\frac{\epsilon_a - \epsilon_s}{\epsilon_a + \epsilon_s}\right) (1 + \xi_0^2) \frac{\xi_0}{\xi_1} \left[ \left(\frac{3}{2} + \xi_1^2\right) \xi_1^2 \ln\left(1 + \frac{1}{\xi_1^2}\right) - \xi_1 \arctan\left(\frac{1}{\xi_1}\right) - \xi_1^2 \right] \\ L_{\parallel,o}^{sda} &= L_{\parallel,o}^{\infty} + \frac{1}{2} \left(\frac{\epsilon_a - \epsilon_s}{\epsilon_a + \epsilon_s}\right) (1 + \xi_0^2) \frac{\xi_0}{\xi_1} \left[ - \left(\frac{3}{2} + \xi_1^2\right) \xi_1^2 \ln\left(1 + \frac{1}{\xi_1^2}\right) + \xi_1 \arctan\left(\frac{1}{\xi_1}\right) + \xi_1^2 \right] \\ L_{\perp,p}^{sda} &= L_{\perp,p}^{\infty} + \left(\frac{\epsilon_a - \epsilon_s}{\epsilon_a + \epsilon_s}\right) (1 - \xi_0^2) \frac{\xi_0}{\xi_1} \left[ \left(\frac{3}{2} + \xi_1^2\right) \xi_1^2 \ln\left(1 - \frac{1}{\xi_1^2}\right) + \frac{1}{2} \xi_1 \ln\left(\frac{\xi_1 + 1}{\xi_1 - 1}\right) - \xi_1^2 \right] \\ L_{\parallel,p}^{sda} &= L_{\parallel,p}^{\infty} + \frac{1}{2} \left(\frac{\epsilon_a - \epsilon_s}{\epsilon_a + \epsilon_s}\right) (1 - \xi_0^2) \frac{\xi_0}{\xi_1} \left[ \left(\frac{3}{2} - \xi_1^2\right) \xi_1^2 \ln\left(1 - \frac{1}{\xi_1^2}\right) + \frac{1}{2} \xi_1 \ln\left(\frac{\xi_1 + 1}{\xi_1 - 1}\right) - \xi_1^2 \right] \end{split}$$

As seen in Figure S5 in which depolarization factors are represented as a function of the *ad hoc* variable  $S_r = 1/(1 + A_r)$ , where  $A_r$  is the aspect ratio, SDA strongly differs from CDA in the oblate case even for the modest image field of the chosen substrate ( $\epsilon_s = 3, A = -0.5$ ). The failure of CDA to describe image effects, clearly evidenced by the comparison to the calculation of exact polarizabilities at multipolar order, roots into the poor description of the boundary conditions of potential and displacement field at the surface of the spheroid.<sup>5,7,10,11</sup> Therefore, the modeling of the optical response of particles is herein restricted to SDA.

## SIII Renormalized polarizabilities in assemblies of supported particles

In assemblies of supported particles, the interparticle coupling leads to a renormalization of the polarizabilities of the isolated object  $\alpha_{\parallel}, \alpha_{\perp}$ . For particles organized in a regular lattice of period P, the renormalized polarizabilities at dipolar order read:<sup>5,7,8</sup>

$$\alpha_{\parallel}^{c}(\omega) \frac{\alpha_{\parallel}(\omega)}{1 + S_{20}^{+} \alpha_{\parallel}(\omega) / (\sqrt{20\pi}\epsilon_{a}P^{3})}$$
$$\alpha_{\perp}^{c}(\omega) \frac{\alpha_{\perp}(\omega)}{1 - 2S_{20}^{-} \alpha_{\perp}(\omega) / (\sqrt{20\pi}\epsilon_{a}P^{3})}, \quad (S9)$$

where

$$S_{20}^{\pm} = S_{20} \pm \frac{\epsilon_a - \epsilon_s}{\epsilon_a + \epsilon_s} S_{20}^r \qquad (S10)$$

are the direct and the image lattice sums that depend only on the ratio d/P of the distance of the dipole to the substrate to the lattice period. Their expressions can be found in Ref. 5. The dipolar approximation was proved to be satisfactory with respect to quadrupolar order up to a surface coverage of more than  $0.5^{12,13}$ while, above that limit, percolating films escape anyway the present truncated sphere/spheroid models. A square lattice, whose surface coverage is defined as  $\Theta = \pi D_{\parallel}^2/4P^2$ , is used hereafter to illustrate the case since no significant



Figure S5: Depolarization factors  $L_{\parallel}$  (red lines) and  $L_{\perp}$  (blue lines) of oblate/prolate spheroids calculated as a function of the *ad hoc* variable  $S_r = 1/(1 + A_r)$  for a spheroid touching the substrate. Several calculation frameworks are compared: (a) free-standing (thick lines), (b) Conventional Dipole Approximation (dotted lines), (c) Spheroidal Dipole Approximation (thin lines).  $0 < S_r \leq 1/2, 1 \leq A_r < +\infty$  $(1/2 < S_r < 1, 0 < A_r \leq 1$  respectively) corresponds to oblate (prolate) particles. Both objects have a revolution axis along the direction perpendicular to the substrate.

difference was found between lattice geometries (random, square, hexagonal).<sup>12</sup> Plugging Eq S1 for a spheroid in dipolar interaction with the substrate into Eq S9 yields the expressions of the depolarization factors that accounts for direct/image interaction with neighbors:

$$L_{\parallel}^{c} = L_{\parallel}^{\infty} + \frac{1}{2\sqrt{5\pi}} \mathcal{S}_{20}^{+} \frac{V}{P^{3}}$$
$$L_{\perp}^{c} = L_{\perp}^{\infty} - \frac{1}{2\sqrt{5\pi}} \mathcal{S}_{20}^{-} \frac{V}{P^{3}}$$
(S11)

where  $L^{\infty}_{\parallel,\perp}$  stand for corresponding expressions for the free-standing spheroid.

## SIV Spectral representation of truncated particle polarizabilities and absorption modes

The polarizability of a supported particle mainly depends on both the particle shape and the substrate-induced break of symmetry, namely the image effect.<sup>6,14,15</sup> The cases of supported truncated sphere and spheroid have been treated in great details.<sup>5,10,16</sup> Solving the underlying Laplace equation through a direct and image multipolar expansion of the potential leads to a linear system of equations 17,18whose first coefficients are proportional to the sought  $\alpha_{\parallel}, \alpha_{\perp}$  quantities. In the limit of poor damping, 19-21 an expansion to first order of the matrix system around each mode<sup>19,21,22</sup> leads to the approximate spectral representation of the polarizabilities in terms of damped oscillators which is given in the main text (Eq. 8):

$$\alpha(\omega) = \alpha_{bk}(\omega) + \sum_{i} \frac{2}{\pi} \frac{F_i \omega_i}{\omega_i^2 - \omega^2 - i\omega\Gamma_i}.$$
 (S12)

For truncated spheres or oblate spheroids  $(A_r > 1.5)$ , dipole-like modes (see Figure S6; modes  $A_{\parallel}, A_{\perp}$ ) dominate the polarizability along both directions and contribute to most of the line shape.<sup>11,19–21</sup> This overwhelming behavior, similar to the case of the full spheroid (Section SII) calls for a more detailed com-

parison to that case. Once the exact polarizabilities of the truncated object are calculated,<sup>5,10,16,23-25</sup> complex effective depolarization factors  $L_e$  can be deduced from Eq S1 corresponding to the equivalent free-standing spheroid. The effective  $L_e$  is plotted in Figure S6 for a Drude metal and for truncated particles with representative aspect ratios  $A_r = 0.5, 1, 2, 4$  and given values of  $t_r$  (truncation parameter defined in the main text). For the particle shape not too close to the full sphere  $(A_r > 1.5)$ ,  $\alpha$  is dominated by modes whose patterns of polarization charges are dipole-like. Their effective depolarization factor  $L_e$  being nearly constant close to the resonance (see dash-dotted vertical lines in Figure S6), they behave actually as oscillators.



Figure S6: Truncated particles: (a),(c),(e),(g) calculated  $\text{Im}(\alpha_{\parallel})/V$  (red line) and  $\text{Im}(\alpha_{\perp})/V$  (blue line) at multipolar order M = 16; (b),(d),(f),(h) corresponding effective complex depolarization factors  $L_{e,\parallel}$  (red) and  $L_{e,\perp}$  (blue) (real part/full lines/left scale and imaginary part/dotted line/right scale). Potential maps at the resonance frequencies of the main peaks of  $\alpha$  are plotted on the top. Hemi-spheroid with aspect ratios of  $A_r = 0.5, 2, 4$  ( $t_r=0$ ) and full sphere  $A_r = 1$  ( $t_r=1$ ) are compared (see drawings on top). Particles are made of Drude metal  $\epsilon_D = 1, \Gamma_D = 0.02\omega_D$  and are standing on a  $\epsilon_s = 3$  substrate ( $\epsilon_a = 1$ ).

## SV Absorbing and dispersive substrate



Figure S7: Evolution with aspect ratio of  $\int \operatorname{Re}[\alpha_{\parallel}]\operatorname{Im}\left[\frac{1}{\epsilon_{s}-\epsilon_{s}}\right]d\omega/\int \operatorname{Im}[\alpha_{\parallel}]\operatorname{Re}\left[\frac{1}{\epsilon_{s}-\epsilon_{s}}\right]d\omega$ over the 1.5-5 eV energy range for the indicated systems. For  $A_{r} < 2$  ( $A_{r} > 2$ , respectively) truncated spheres (truncated hemispheroids, respectively) are used to compute the polarizabilities at multipolar order M = 16.

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