



Supplementary Materials for

Plasmoelectric potentials in metal nanostructures

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This PDF file includes:

Materials and Methods

Supplementary Text

Figs. S1 to S9

References

Materials and Methods

Colloid Materials and Preparation:

60-nm-diameter Au colloids (BBI International, EM.GC60 Batch #15269, OD1.2) were used for optical and electrical measurements. Samples for electrical characterization were prepared on indium tin oxide (ITO) coated glass substrates (SPI brand, 30-60 Ω , 06430, ITO layer thickness: 100 nm) that were first ultrasonicated overnight in a solution containing an equal volume of acetone, methanol, toluene, and isopropyl alcohol and then dried with N_2 . Substrates were placed individually in glass scintillation vials (ITO-side up) with 600 μ L Au colloid diluted by 1.2 mL of deionized (DI) water; for control samples, DI water was used instead of the Au colloid solution. Then 60 μ L 0.1 M HCl was added, and the vials were immediately centrifuged at 2000 rpm (\sim 670 g-force) for 40 minutes. After centrifuging, the solution had become clear and the ITO film had a noticeable red color due to Au nanoparticles deposited on the surface. Subsequently, the substrates were rinsed thoroughly with DI water and heated to 290 $^{\circ}$ C by placing a heat gun 5 cm above the sample surface for 20 minutes. The scattering spectra of the deposited samples (as in Fig. 2A) were obtained using a Zeiss Axio Observer inverted microscope equipped with a 20 \times dark-field objective, with illumination from a halogen lamp.

Hole Array Fabrication

10 \times 10 micron sized hole arrays in 20 nm thick Au, with 100 nm hole diameter and pitch in the range of 150-300 nm, were fabricated on 1-mm-thick glass using electron-beam lithography. A three-layer process was used to fabricate a shadow mask for Au evaporation. First, 240 nm PMMA 35k300 was spincoated on a clean glass substrate, and baked at 180 $^{\circ}$ C for 15 min. Next, 25 nm of Ge was thermally evaporated (0.5 \AA /s) to make the substrate conductive and to protect the PMMA during further processing. Finally, 65 nm of hydrogen silsesquioxane (HSQ) negative tone resist (2 MIBK : 1 Fox 15 dilution) was spincoated and baked at 180 $^{\circ}$ C for 2 min. Proximity-corrected square arrays of disks were written in the HSQ (20 kV, 7.5 μ m aperture, 10.7 pA beam current) using area exposure with a dose of 200-500 pAs/cm² (depending on pitch). The HSQ was developed by submerging in MF-319 (Microposit developer) at 50 $^{\circ}$ C for 60 s, followed by thorough rinsing with dH₂O. The disk patterns were transferred into the PMMA by subsequent anisotropic reactive-ion etching of the Ge (using SF₆ and O₂) and PMMA (using O₂). Next, 20 \pm 2 nm of Au was thermally evaporated at 0.5 \AA /s. Finally, lift-off was performed by dissolving the PMMA in acetone at 50 $^{\circ}$ C for 3 hours, followed by 10 min of megasonification and 1 min of ultrasonification, both in acetone.

Hole Array Optical Characterization

Transmission and reflection spectra of the hole arrays were measured using a WiTec- α optical microscope. A fiber-coupled white light source (Ando AQ-4303B) in combination with a 9 μ m-core fiber was used to illuminate the hole arrays through a 60 \times objective (Nikon, NA=0.8, WD=0.3 mm), resulting in a 3-4 μ m diameter spot (unpolarized). The transmission was collected by a 50 \times objective (Nikon, CFI L-Plan EPI CR, NA=0.7, WD=3 mm corrected for substrate thickness). Both the transmitted and reflected light was coupled into a 100- μ m-core collection fiber and analyzed by a

spectrograph (Acton 300i) and Si CCD, which was cooled to -45 °C (Roper Scientific, model 7344-0001). Each spectrum is an average of 100 frames with 250 ms accumulation time each.

Supplementary Text

S1. Complex Dielectric Function of Ag and Au

To calculate the absorption cross section spectra of a Ag nanoparticle (Fig.1), we apply a 6th-order, multiple oscillator Lorenz-Drude model of the complex dielectric function of silver, fit to data from Palik (13). For the dielectric function of Au we use a Brendel–Bormann Gaussian oscillator model. We use the method outlined by Rakic and coworkers (14). These dielectric functions accurately reproduce the observed extinction spectra of spherical silver or gold nanoparticles when input into the exact analytic solutions to Maxwell’s equations provided by Mie theory (15). To introduce the explicit dependence on electron density, n , we assume that all terms in the dielectric function that depend on the bulk plasma frequency, ω_p^* , depend on electron density, n , according to a simple Drude model relation,

$$\omega_p^* = \left(\frac{n \cdot e^2}{\epsilon_o \cdot m_e^*} \right)^{1/2} \quad (S1)$$

where e is the electron charge, ϵ_o is the permittivity of free space, and m_e^* is the electron effective mass (16). This strategy is consistent with other work that examined carrier density-dependent plasmon shifts, for example in doped semiconductors, electrochemical cells, or at metal surfaces during ultrafast pump-probe measurements (17-20). Figure S1 shows the calculated relative change of the absorption cross section of a 20-nm-diameter Ag nanoparticle in vacuum, as a function of wavelength and electron density, n , compared with the absorption cross section for a neutral Ag silver particle with electron density n_{Ag} .

S2. Kelvin Probe Force Microscopy (KPFM) of Au Colloids on ITO/glass and Au Hole Arrays

For KPFM characterization of colloid particles on ITO/glass, the sample was measured at the limit of highest possible particle coverage, and it was anticipated that the measured region of ITO/glass adjacent to the Au particles was equipotential with the particles. Direct illumination of the AFM tip was avoided, and there was no dependence of the magnitude of signal based on the distance from the optical spot, within ~10’s of μm . A control measurement of ITO/glass free of Au colloids is shown in Fig S2 and shows no detectable wavelength-dependent signal. The absolute surface potential determined by the KPFM technique is always a convolution of the work function difference between the sample and a particular tip, and factors relating to the tip-sample geometry that define capacitance. Therefore, to emphasize wavelength-dependent changes of potential, the reported data (Fig. 2B) are plotted relative to the surface potential in the same spot measured in the dark before optical excitation.

For KPFM measurements of hole arrays, an optical spot encompassing the entire array was incident directly beneath the AFM tip. The plotted data (Fig. 4D) are the average response of the entire $10 \times 10 \mu\text{m}$ array integrated over ~20 min with a single

wavelength incident. This procedure allowed the sample to stabilize from any drift during the course of the measurement, and, by measuring a structure much larger than the tip, maximized the accuracy of the KPFM technique (21). Because the tip was illuminated, even control measurements of smooth Au films detected uniform changes in the KPFM signal based on whether the tip was illuminated or in the dark. This signal results from optical heating of the tip, while other contributions to the measured potential, such as photo-carrier generation in the tip, may also be manifest. The magnitude of the light vs. dark response, though independent of incident wavelength, was dependent on the incident power as well as the particular tip used. Therefore we could not employ the same simple subtraction procedure used to offset the data during the colloid measurements on ITO, as described above.

However, relative changes in the surface potential of the hole arrays that were dependent on the wavelength of illumination were stable and reproducible, and were independent of the tip employed or the tip distance from the sample, over a range of tip distances spanning ~ 1 to 100 nm. For this reason, the curves from different arrays in Fig. 3D are plotted to emphasize the comparison between wavelength-dependent changes, with zero set by the mid-point of the maximum and minimum surface potential measured from that array.

S3. Thermodynamic model for calculating plasmoelectric potentials

(A) Introduction

Our thermodynamic model posits that there is a well-defined, constant temperature, T , of a plasmonic nanoparticle during steady-state illumination at a single wavelength, λ , and intensity, I_λ . This constant T results from the requirement that the optical power absorbed and thermal power conducted away or radiated by the nanoparticle must be equivalent in a steady state. This temperature is a function of the absorption cross section, C_{abs} , of the nanostructure, which also depends on the electron density, n , due to the strong dependence on n in the complex dielectric function of the metal. Then, $T(n, \lambda)$ is the unique thermodynamic function of state that distinguishes an illuminated plasmonic absorber from one in the dark.

We assert that it is reasonable to define such a temperature for a resonantly heated particle, because electronic relaxation processes are fast and the electronic system and lattice are in equilibrium. We note that similar arguments are central to, for example, the detailed balance calculation of the limiting efficiency of a photovoltaic cell (22). This well-defined temperature describes a local thermal equilibrium in a thermodynamic system enclosing the particle, and motivates a thermodynamic equilibrium argument based on free energy minimization.

(B) Free Energy Minimization

We consider a nanoparticle under steady-state, monochromatic illumination at a wavelength near the plasmon resonance. The electron density of the particle can change via charge transfer through an electrical connection to a DC electrical conductor assumed to have no plasmonic response. We solve for the configuration of the nanoparticle where the free energy, F , of the particle is minimized with respect to free electron density, n , for a given irradiation wavelength λ and power density I_λ . That is, where

$$\frac{dF}{dn} = 0 \quad . \quad (S2)$$

For convenience, we convert between electron density, n , and the total number of unbound electrons in the particle, N , with the relation $N = nV$, where V is the (constant) volume of the nanoparticle. The total free energy of the nanoparticle, F_{tot} , is a function of N and temperature, T , the latter also depending on N and as outlined above. The differential quantity can be expanded:

$$\frac{\partial F_{tot}(N, T)}{\partial N} = \left(\frac{\partial F_{tot}(N, T)}{\partial N} \right)_T + \left(\frac{\partial F_{tot}(N, T)}{\partial T} \right)_N \frac{dT(N)}{dN} = 0 \quad (S3)$$

where the subscripts T or N indicate that that variable is held constant in the derivative. Note that both the intensity and wavelength are assumed to be constant, and are therefore not included in the partial derivative for simplicity. The electrochemical potential of the particle, μ , is by definition the quantity

$$\left(\frac{\partial F_{tot}(N, T)}{\partial N} \right)_T \equiv \mu(N, T) \quad . \quad (S4)$$

Additionally, the entropy of the particle, S , is by definition

$$-\left(\frac{\partial F_{tot}(N, T)}{\partial T} \right)_N \equiv S(N, T) \quad . \quad (S5)$$

Then, the free energy minimum corresponds to a configuration with a number of electrons, N , such that

$$\mu(N, T) = S(N, T) \frac{dT(N)}{dN} \quad . \quad (S6)$$

Expression (S6) is the central insight that predicts the plasmoelectric effect. It shows that an illuminated plasmonic particle adopts a non-zero electrochemical potential that is proportional to $dT(N)/dN$. The sign and magnitude of this potential is determined by how changes of charge density modify the absorption cross section, and hence the temperature of the nanoparticle, for the given incident wavelength.

(C) Calculation for the Configuration of Minimum Total Free Energy, F_{tot}

We determine the total free energy, F_{tot} , of the nanoparticle by considering the separate contributions from the electrons, F_e , and the phonons, F_p :

$$F_{tot}(N, T(N)) = F_e(N, T(N)) + F_p(T(N)) \quad . \quad (S7)$$

Note that for the optical power densities we consider, because of the fast electronic relaxation rate and electron-phonon coupling rate in a metal, the electron temperature and phonon temperature are equivalent (15):

$$T_{electron} \approx T_{phonon} = T(N) \quad . \quad (S8)$$

F_e is defined in terms of the chemical potential of the electrons, μ_e , and the electrostatic potential on the particle, ϕ , as

$$F_e(N, T(N)) = \int_0^N \mu_e(N', T(N')) dN' + \int_0^{N-N_0} \phi(N' - N_0) dN' \quad (S9)$$

where N_0 is the number unbound electrons on the neutral particle, and μ_e equals the Fermi function with a small ($< 0.1\%$) temperature correction (6)

$$\mu_e(N, V, T(N, \lambda)) = \epsilon_F(N, V) \left(1 - \frac{1}{3} \left(\frac{\pi k_b T(N, \lambda)}{2 \epsilon_F(N, V)} \right)^2 \right) \quad (S10)$$

with

$$\epsilon_F(N, V) = \frac{\hbar}{2m} \left(\frac{3\pi^2 N}{V} \right)^{2/3} \quad , \quad (S11)$$

and ϕ is the electrostatic potential for a conducting sphere:

$$\phi(N - N_0) = \frac{e^2(N - N_0)}{4\pi R \epsilon_0 \epsilon_m} \quad (S12)$$

with R the sphere radius, e the electron charge and ϵ_0 and ϵ_m the permittivity of free space and the relative permittivity of the surrounding medium, respectively.

F_p is defined in terms of the speed of sound in the particle, v_s , via the Debye temperature, θ , with (7, 23)

$$F_p(T(N)) = 3k_b T(N) A_0 \ln \left(\frac{\theta}{T(N)} \right) - k_b T(N) A_0 \quad (S13)$$

and

$$\theta = \frac{\hbar v_s}{k_b} \left(\frac{6\pi^2 A_0}{V} \right)^{1/3} \quad (S14)$$

where k_b is Boltzmann's constant, and A_0 the number of atoms in the particle which here is equal to N_0 . For Au, $\theta \approx 170$ K (6). Expression (S14) is the high-temperature limit of the quantum Debye model, valid for $T > \theta$.

The total electrochemical potential μ and the entropy S can now be derived by applying Eqs. (S4) and (S5), respectively, to expression (S7) for the free energy. We find

$$\mu(N, T(N)) = \epsilon_F(N, V) - \frac{mk_b^2 T(N)^2}{6\hbar^2} \left(\frac{\pi V}{3N}\right)^{2/3} + \frac{e^2(N - N_0)}{4\pi R \epsilon_0 \epsilon_m} \quad (S15)$$

and

$$S(N, T(N)) = \int_0^N \frac{1}{3} \frac{\pi^2 k_b^2 T(N')}{2\epsilon_F(N')} dN' - 3k_b A_0 \ln\left(\frac{\theta}{T(N)}\right) + 4k_b A_0 \quad (S16)$$

The steady-state charge configuration (value of N) that corresponds to the minimum free energy can then be obtained by using eqs. (S15) and (S16) to solve Eq. (S6). This leads to

$$\begin{aligned} \epsilon_F(N) - \frac{mk_b^2 T(N)^2}{6\hbar^2} \left(\frac{\pi V}{3N}\right)^{2/3} + \frac{e^2(N - N_0)}{4\pi R \epsilon_0 \epsilon_m} - \int_0^N \frac{1}{3} \frac{\pi^2 k_b^2 T(N')}{2\epsilon_F(N')} dN' \frac{dT(N)}{dN} \\ + 3k_b A_0 \ln\left(\frac{\theta}{T(N)}\right) \frac{dT(N)}{dN} - 4k_b A_0 \frac{dT(N)}{dN} = 0. \end{aligned} \quad (S17)$$

This equation can be solved to find the steady-state value for N (for given λ and I_λ) using as input the function $dT(N)/dN$ which is determined by the plasmon resonance spectrum and the heat conducted or radiated away from the particle.

(D) Theoretical efficiency limit

This thermodynamics model shows that an excited plasmonic resonator behaves as a heat engine that can convert absorbed off-resonant optical power into a static electrochemical potential. In principle, optical-to-electrical energy conversion by this mechanism could be optimized to perform with an efficiency at the Carnot limit, as with any generalized heat engine (24).

S4. Temperature Calculations

(A) Ag nanoparticle in vacuum

To calculate the plasmoelectric potential for a Ag nanoparticle in vacuum we calculate the temperature of the nanoparticle, T , given the absorption cross section $C_{abs}(n, \lambda)$ from S1 and incident power density. Under steady state illumination, the power absorbed by the particle must equal the power going out:

$$P_{in} = P_{out} \quad (S18)$$

P_{in} constitutes the absorbed monochromatic optical radiation plus the absorbed thermal radiation from the ambient background (at $T_{amb} = 293$ K).

$$P_{in} = C_{abs}(n, \lambda)I_{\lambda} + \sigma A \varepsilon T_{amb}^4 \quad . \quad (S19)$$

Here, σ is the Stefan Boltzmann constant, A is the surface area of the nanoparticle, and ε is the emissivity. The nanoparticle emissivity $\varepsilon = 0.01$ was experimentally determined using FTIR absorption spectroscopy on gold colloids, assuming reciprocity of the absorption and emission in the 2-5 μm wavelength range of the measurement. This value is close to that of bulk gold and silver in the infrared, as reported elsewhere (8) and predicted by Mie theory. For Ag nanoparticles in vacuum the only loss channel for the power is thermal radiation, defining

$$P_{out} = \sigma A \varepsilon T^4 \quad . \quad (S20)$$

Solving eq. (S18) for the temperature of the particle then gives

$$T(n, \lambda) = \left(\frac{C_{abs}(n, \lambda)I_{\lambda} + \sigma A \varepsilon T_{amb}^4}{\sigma A \varepsilon} \right)^{1/4} \quad . \quad (S21)$$

Figure S3 shows the calculated temperature for a 20-nm-diameter Ag nanoparticle in vacuum as a function of illumination wavelength for an incident power densities of 1 mW/cm^2 ; it peaks at 400 K. The calculated temperature and its dependence on N , $dT(N)/dN$ (for a given λ and I_{λ}) are then used as input in solving Eqn. (S17) for the case of a Ag nanoparticle in vacuum (see S5).

(B) Au nanoparticles on ITO

To calculate the temperature of Au nanoparticles on ITO/glass we first calculate the absorption cross section spectrum $C_{abs}(n, \lambda)$ using finite-difference-time-domain (FDTD) full wave electromagnetic simulations. In the experiment, the exact dielectric surrounding of the nanoparticle is very complex. As shown in Fig. 2A, there are large variations in inter-particle spacing as well as clusters with different configurations, both inducing near-field coupling and thereby red-shifted resonance wavelengths. Furthermore, the KPFM experiments were performed in ambient conditions, such that adsorption of water to the particle-ITO interface is likely. Since the exact influence of such conditions on the plasmoelectric potential is beyond the scope of this paper, we simplified the geometry to a single 60 nm Au nanoparticle on an ITO substrate. We assumed a uniform background index of $n = 1.4$ to take into account the red-shift due to the dielectric surrounding described above, such that the modeled scattering spectrum represented the measured scattering spectrum. We then calculate the steady-state power balance to obtain the nanoparticle temperature. Heat flow into the substrate is modeled using a 1D heat transfer model, as sketched in Fig. S4, with the particle on a glass substrate with thickness $d = 1$ mm covered by a thin layer of ITO. We use the thermal heat conductivity for glass of $\sigma_T = 1.05 \text{ W m}^{-1}\text{K}^{-1}$ (25). The heat of the particle can be transferred from the particle (at T_{part}) through a cylinder of glass with cross sectional area equal to the contact area $A_{contact}$ between the glass and the particle, to the bottom of the substrate (at ambient temperature, $T_{amb} = 293$ K). The heat flow is given by (25)

$$P_{diff} = \sigma_T \frac{(T_{part} - T_{amb})}{d} A_{contact} \quad (S22)$$

Figure S4 shows the calculated temperature of the Au nanoparticle as a function of incident wavelength for the three different intensities used in Fig. 2B. In these calculations the parameter $A_{contact}$ is tuned such that the calculations of the surface potential (see S5) best match the experimentally observed surface potential for the largest power densities. The best fit for the contact area is 2.5 times the geometrical particle cross section, a reasonable value given the simple heat flow model. The same contact area is then used for the lower power densities to calculate the temperature profiles in Fig. S4 and the surface potentials in Fig. 2C. We find the same power-dependent trend for slightly more complicated 2D and 3D heat diffusion models, with the assumed contact area between the particle and ITO dominating the magnitude of the temperature. The maximum temperature calculated in Fig. S4 amounts to 308 K, 15 degrees above ambient temperature, which is a reasonable temperature to sustain for an Au nanoparticle on a substrate. Note that the increase of temperature due to the plasmoelectric effect compared with a neutral particle is only of order of up to 10s of mK, depending on geometry and illumination intensity. The calculated temperature and its dependence on N , $dT(N)/dN$ (for a given λ and I_λ) are used as input in solving Eqn. (S17) for the case of Au nanoparticles on ITO/glass (see S5).

S5. Calculation of Steady-State Nanoparticle Surface Potential and Charge

Using the temperature and values for $dT(N)/dN$ described in S4 we solve Eqn. (S17) to determine the steady-state surface potential and corresponding charge on the nanoparticle as a function of irradiation wavelength. Figure S5 shows the calculated charge density $N-N_0$ for Au nanoparticles on ITO/glass, for the highest experimental power density of Fig. 2B ($I_\lambda=1000$ mW/cm²). The calculations use 6.67×10^6 Au atoms for a 60-nm-Au sphere. As can be seen, the excess electron number $N-N_0$ is modulated around a value of $N-N_0 = -104.69$ electrons, observed at the peak of the resonance (no plasmoelectric effect, $dN/dT=0$). This corresponds to the number of electrons for which the total electrostatic charging energy equals the Fermi energy for Au $E_F=5.02$ eV. In the dark, the offset between the Fermi level of the particle and the substrate will induce a compensating electrostatic charge on the particle, which is the usual condition for electrochemical equilibration between two dissimilar conductors. Note that the presence of the ITO substrate can be easily accounted for by subtracting the Fermi energy of the ITO substrate, such that the offset observed in Fig. S5 is in fact the difference in Fermi energy between the particle and the ITO. Correcting for this “dark” charge (right-hand scale in Fig. S5) we see that in the time-averaged situation, less than one electron on average is added or removed from the nanoparticle to generate the observed plasmoelectric potential. The data in Fig. S5 can be converted to surface potential, as shown in Fig. 2C. Additionally, we note that the thermoelectric effect (omitted in our analysis) induces only a minor contribution to the potential state of the particle, even for large temperature gradients between the substrate and particle, because of the small Seebeck coefficient of metals, $\sim \mu\text{V}/\Delta\text{K}$ (9).

S6. Charge Accumulation Shell Model

The calculations described above assume that any additional charge carriers that are transferred to the particle are uniformly distributed throughout the nanoparticle. However, electrostatic models require that any surplus charges reside on the surface of a metal object (less than 1 nm thickness), since no static electric fields can exist inside the metal (26). On the other hand, the surface plasmon resonance is a dynamic phenomenon, with electromagnetic fields that penetrate into the metal as defined by the electromagnetic skin-depth, which is $\sim 3\text{-}10$ nm for Ag and Au at optical frequencies, and an electron mean free path that is larger than the Fermi screening length. Additionally, the plasmon resonance frequency is predominately determined by the electron density of the very outer layer within the optical skin depth of the metal, as reported experimentally (27) and verified by us using FDTD simulations. Therefore, electrostatic arguments suggest that any additional charges will reside near the surface of the nanoparticle, and electrodynamic arguments suggest that only the electron density near the outer surface needs to be increased in order to blue-shift the plasmon resonance. If excess charge resides only near the surface, the plasmoelectric effect thus requires a smaller number of electrons to obtain the same frequency shift, and thereby $dT(N)/dN$ in eq. (S6) is larger.

To study the influence of non-uniform distributions of charge density in the particle, we consider a simplified shell model, in which we assume that all the additional charge carriers transferred due to the plasmoelectric effect reside in the outer shell with thickness δ (see inset of Fig. S6). To implement the shell in eq. (S17), one has to express the Fermi energy, temperature, and N and V in terms of the number of electrons in the shell and the shell volume rather than the whole particle. Eq. (S17) can then be solved for the number of electrons in the shell, assuming a certain shell thickness.

Figure S6 shows the plasmoelectric potential (a) and the relative increase in absorption (b) for a 20-nm-diameter Ag particle in vacuum, as a function of illumination wavelength (10 mW/cm^2), for different shell thicknesses. Figures S6 A and B clearly show the effect of a thinner shell: the transferred electrons induce a relatively larger increase in electron density and thereby a larger increase in absorption (Fig. S6 B). Note that for shell thicknesses larger than 1 nm, the magnitude of the potential rapidly converges to that obtained with uniform charge distribution ($\delta = 10$ nm, green curves). Uniform charge distribution is assumed for calculations throughout this manuscript. Further arguments for assuming a uniform distribution of charge include the fact that the area under the absorption spectrum of a dipolar plasmon mode should only scale with the total number of valence electrons in the metal, irrespective of their location inside the particle.

S7. Transmission and Reflection Experiments on Hole Arrays

The absorption spectra for the hole arrays in Au in Fig. 4 are derived from transmission and reflection spectra measured in an optical microscope. Light from a broadband light source (Ando AQ-4303B) was focused onto the $10\times 10\text{ }\mu\text{m}$ hole arrays to a $\sim 4\text{ }\mu\text{m}$ diameter spot using a 0.8 NA microscope objective. Transmitted and reflected light intensities were recorded using a fiber-coupled spectrometer equipped with a Si CCD array detector. To calibrate the measured transmitted and reflected intensity spectra, the transmission spectrum was measured for a bare region of the gold film, next to the hole arrays, and normalized this to the measured transmission of bare glass. Figure S7A

shows the resulting transmission spectrum for the bare Au film (dark blue). For comparison, the transmission obtained from Fresnel calculations of a air-Au-glass layer system (light blue) is shown, assuming a Au layer thickness of 18 nm and optical constants from Johnson and Christy (28). The calculated transmission was multiplied by a factor 0.96 to correct for the 4% reflection on the bottom interface in the experimental geometry. Figure S7A shows very good agreement between the measured and calculated spectra which provides further confidence in the normalization procedure for the transmission measurements.

Reflection measurements were normalized using the calculated reflection spectrum for the bare gold film, which is shown in Figure S7B, as a reference. This procedure does not take into account the small reflection from the bottom interface of the glass substrate. Therefore, derived reflectivities are slightly overestimated. The accuracy of all derived transmittance and reflectance spectra is within 5%.

Figure S7C,D shows measured transmission and reflection spectra for all hole arrays, with pitch ranging from 150 nm to 300 nm in steps of 25 nm. A clear dip is observed both in transmission and reflection spectra resulting from the resonant absorption in the hole array. The dips show a clear redshift with increasing pitch, as expected. The wavelength of the dip in transmission is significantly blueshifted with respect to the dip in reflection, which is due to interference between directly transmitted light and forward scattered light (Fano-effect) (29).

The absorption spectra for the hole arrays in Fig. 4C were calculated from the measured spectra as $Abs = 1 - R - T$. This analysis slightly overestimates the actual absorption, as it neglects the small amount of light scattered in angles beyond the NA of the collection aperture. However, this fraction will be small, since no diffraction orders can occur in the visible spectral range for the used array pitch.

S8. FDTD Simulation Details

We performed full wave modeling using Lumerical finite-difference time-domain (FDTD) (30) simulations to determine the scattering and absorption spectra for Au particles on ITO and to simulate the transmission and reflection spectra for Au hole arrays. Optical constants for Au are as described in S1, taken from Johnson and Christy (28) for Fig. S7, and using the Brendel and Bohrmann model (14) for all other calculations. For ITO they were taken from spectroscopic ellipsometry measurements of sputtered ITO films.

For simulations of Au colloids on ITO, we modeled a 60-nm-diameter Au sphere on top of an ITO slab and a background index of $n = 1.4$ (see S4B). The simulations employed Perfectly Matching Layer (PML) boundary conditions on all boundaries. We used a Total Field Scattered Field (TFSF) source to launch and extinguish broadband plane waves ($\lambda = 460\text{--}650$ nm). The scattering and transmission due to the sphere were recorded and used to calculate the absorption and extinction spectra.

For the hole array geometry, we modeled a 20-nm-thin Au film on top of a glass substrate (index $n = 1.46$), and applied PML boundary conditions at the top and bottom interfaces of the simulation box to mimic semi-infinite media for both the glass substrate and air. A 100-nm-diameter hole is positioned in the center of the simulation box. The lateral size of the box is set equal to the desired pitch, and periodic boundary conditions are used to simulate an infinite array. A broad-band ($\lambda = 400\text{--}900$ nm) plane wave is

launched from the top. Power monitors above the source and 50 nm below the Au-SiO₂ interface are used to monitor the reflection and transmission respectively. Since the gold is the only absorbing material in the simulation box, the absorption of the hole array is calculated as $1 - R - T$. The mesh size is set to 10 nm, with a 1.0-2.5 nm refinement mesh around the hole.

S9. Mechanism of Resonant Absorption in Hole Arrays

Resonant absorption of light in the hole arrays results from the diffractive coupling of incident light to surface plasmon polaritons (SPP) propagating at the metal-dielectric interface (12, 31). For the thin (18 nm) Au films used, SPPs on the Au-air and the Au-glass interface are strongly coupled (32), giving rise to symmetric and anti-symmetric insulator-metal-insulator (IMI) SPP modes. Figure S8A shows the calculated mode profile of the in-plane magnetic field component of the anti-symmetric mode for the glass-Au-air layer geometry at a free-space wavelength $\lambda = 600$ nm. In the calculations, optical constants for Au were taken from the Brendel and Bormann model (14), which show good correspondence with data from Johnson and Christy (28). The index of glass was taken as $n = 1.46$. The dispersion for the anti-symmetric IMI SPP is shown in Figure S8B. For comparison, the light line in air and the dispersion of single-interface SPPs on a semi-infinite Au substrate are also shown. As can be seen, the strong coupling of SPPs across the Au films leads to large wave vectors compared to the free-space or single-interface SPPs.

Figure S8C shows the propagation length of the IMI SPP as a function of wavelength. Data for a semi-infinite Au substrate are also shown. Clearly, the IMI mode has a strongly reduced propagation length due to the strong absorption in the metal (32), the latter obviously a desired feature to achieve a strong plasmoelectric effect.

Incident light can couple to the IMI SPPs through diffractive coupling via $(\pm 1, 0)$, $(0, \pm 1)$, $(\pm 1, \pm 1)$ and higher order grating orders. To investigate which coupling order is dominant we performed FDTD simulations of the absorption in hole arrays (225 nm pitch) for angles of incidence $\theta = 0^\circ$ and $\theta = 25^\circ$ in a plane along the $(0, 1)$ axis of the array, for both s- and p-polarized light (data not shown). We find identical absorption spectra for the two angles for s-polarized light, whereas the spectra for p-polarized light differ significantly. From this we conclude that the in-plane component $k_0 \sin(\theta)$ of the incoming wave vector is orthogonal to k_{IMI} , which implies the incident light couples to the $(0, \pm 1)$ and $(\pm 1, 0)$ orders. The peak resonance wavelengths λ_{res} for the absorption spectra simulated by FDTD for different array pitch (Λ , indicated in the figure) are plotted in Figure S8B as $2\pi/\lambda_{res}$, with the x -coordinate given by $2\pi/\Lambda$, corresponding to coupling through $(\pm 1, 0)$ and $(0, \pm 1)$ orders (open circles). The data points lie quite close to the calculated dispersion curves indicating that absorption of incident light occurs through the $(\pm 1, 0)$ and $(0, \pm 1)$ orders, with good agreement observed for the wavelength at which the experiments were done ($\lambda = 600 - 700$ nm, $k_0 \sim 10 \mu\text{m}^{-1}$). Note that the large discrepancy for 150 - 175 nm pitch can be attributed to a second branch of the dispersion curve as described in (33-35), a detailed discussion of which goes beyond the scope of this paper (33, 34).

The dispersion data in Figure S8B provide guidelines for the design of the array pitch in order to achieve efficient diffractive coupling from the normal-incident light beam to the in-plane IMI SPPs for a given incident wavelength. Due to the strong

dispersion, the array pitches required to couple to the IMI SPP are much smaller than the free-space wavelength (e.g. 200 nm at $\lambda = 600$ nm) (31).

Next, we calculated the effect of a variation of the electron density in the Au film on the IMI SPP dispersion. Variations in carrier density n were included in the optical constants for Au as described in section S1. Figure S8B shows the dispersion curves for electron densities in the range of $n = 0.9 \times n_{Au}$ (red) to $n = 1.1 \times n_{Au}$ (blue). A decrease in electron density redshifts the dispersion curve, analogous to what is observed for the localized resonances in the colloidal nanoparticles. In the spectral range where the resonant absorption occurs, a 1% change in electron density gives rise to a spectral shift of ~ 1.5 nm. This matches well with the spectral shift observed in the FDTD simulated absorption spectra for the different electron densities (not shown here). It is this dependence of the dispersion on the electron density, that in turn modifies the absorption efficiency, that is the driving mechanism for the plasmoelectric effect in the hole arrays.

Note that the absorption mechanism described here is very similar to the phenomenon of extraordinary transmission (EOT) in sub-wavelength hole arrays in optically thick films (12, 36), the only difference being that for EOT the SPPs on the air-Au and glass-Au interface do not couple, such that the SPP absorption losses are minimized rather than maximized, as is desired for the plasmoelectric effect (32).

S10. Spectral Broadening and Red-shift in Measured Spectra

Figure 4D shows that the wavelength of the zero-crossing in the KPFM spectrum is slightly blue-shifted with respect to the measured absorption maximum in Fig. 4C. This blueshift is more pronounced for hole arrays of smaller pitch. Based on the absorption mechanism described above, this discrepancy can readily be explained by the difference in numerical aperture (NA) of the objectives used for the two measurements. Transmission and reflection experiments were made using an NA=0.8, corresponding to a wide range of angles of incidence up to 53° . This gives rise to a large spread in the in-plane component of the wave vector of the incoming light, which translates into a large spread in spectral position along the dispersion curve. KPFM measurements were made using a lens with NA=0.25, giving rise to much sharper absorption peaks.

To quantify the effect of angular spread on the absorption spectra we performed FDTD simulations for a hole array (225 nm pitch), for different angles of incidence. Single-wavelength simulations were performed in the spectral range of $\lambda = 500 - 700$ nm, in steps of 5 nm. A plane-wave source was launched with an angle of incidence θ , p-polarized along one of the axis of the hole array. Bloch boundary conditions were used in the lateral direction of propagation.

Figure S9A shows the simulated absorption for $0^\circ \leq \theta \leq 14^\circ$ (blue to red), corresponding to the angles of incidence for NA=0.25 for the KPFM measurement. Also shown is the calculated absorption spectrum for normal incidence (solid black line) and the absorption averaged over all angles (dashed black line). Figure S9A shows only a small effect of angular spread for the NA=0.25 lens. Figure S9B shows the absorption spectra for an angular range ($0^\circ \leq \theta \leq 53^\circ$) corresponding to the NA=0.8 objective used in the transmission and reflection experiments. A pronounced redshift is observed for larger angles of incidence. Figures S9A,B also show the angle-averaged absorption spectrum, for the NA=0.8 geometry it shows a strong redshift compared to the absorption for normal incidence, as well as significant spectral broadening. The observation of a

redshifts indicates light couple to the (-1,0) order, consistent with what was observed by Braun et al. in absorption measurements on Au hole arrays (32). Note that to calculate a properly angle-weighted absorption spectrum the intensity profile on the back focal plane of the objective, and the transfer function of the objective must be taken into account. Nonetheless, the data in Figure S9 explain that the resonant absorption manifest in the KPFM signal in Fig. 4D is blueshifted and spectrally narrower compared with the measured absorption spectra in Fig. 4C. Finally, we note that for unpolarized light, variations in incident angle will lead to a further broadening of the absorption spectrum due to the different coupling conditions for different polarizations at different incident angles.

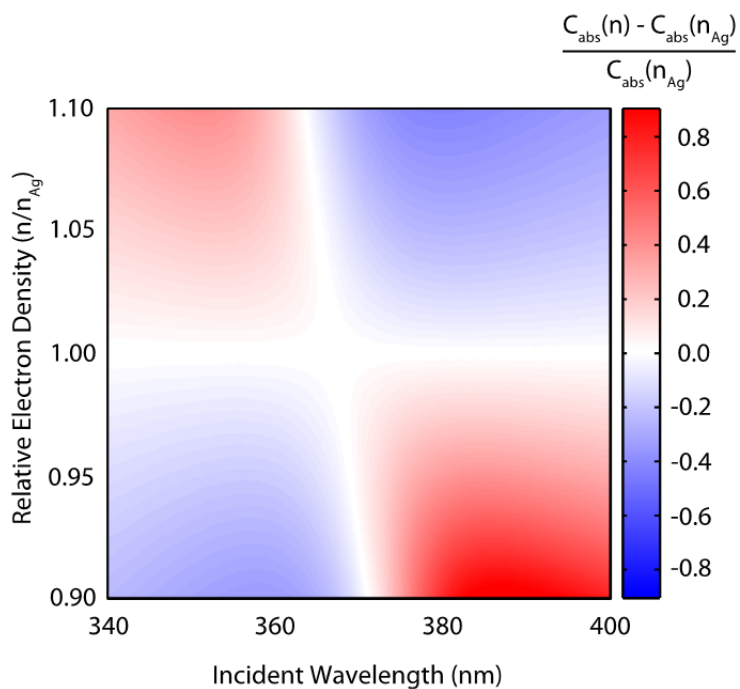


Fig. S1.

Relative change of the absorption cross section, $C_{abs}(n, \lambda)$, (color scale) of a 20-nm-diameter Ag nanoparticle in vacuum, as a function of wavelength and electron density, n , compared with the absorption cross section for a neutral Ag silver particle with electron density n_{Ag} .

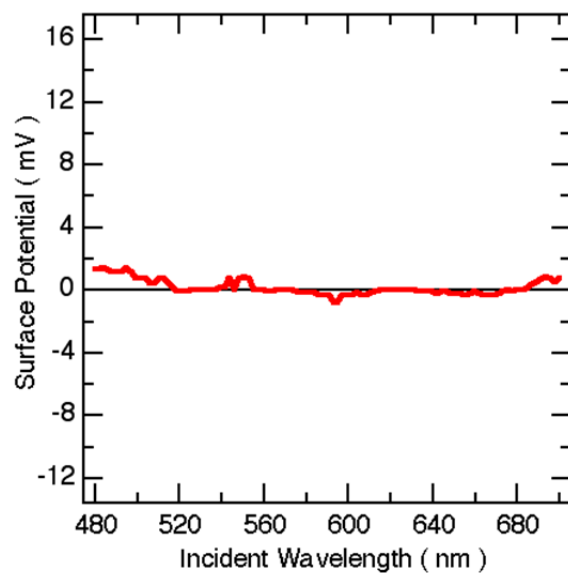


Fig. S2

KPFM-measured surface potential from a control experiment of bare ITO/glass under $1\text{W}/\text{cm}^2$ scanned monochromatic illumination, plotted on the same scale as Fig. 2B.

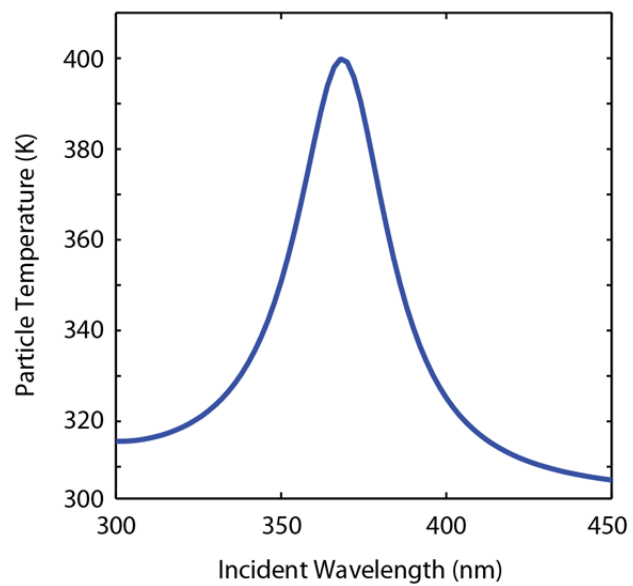


Fig. S3

Calculated temperature for a 20-nm-diameter Ag particle in vacuum as a function of illumination wavelength (1 mW/cm^2).

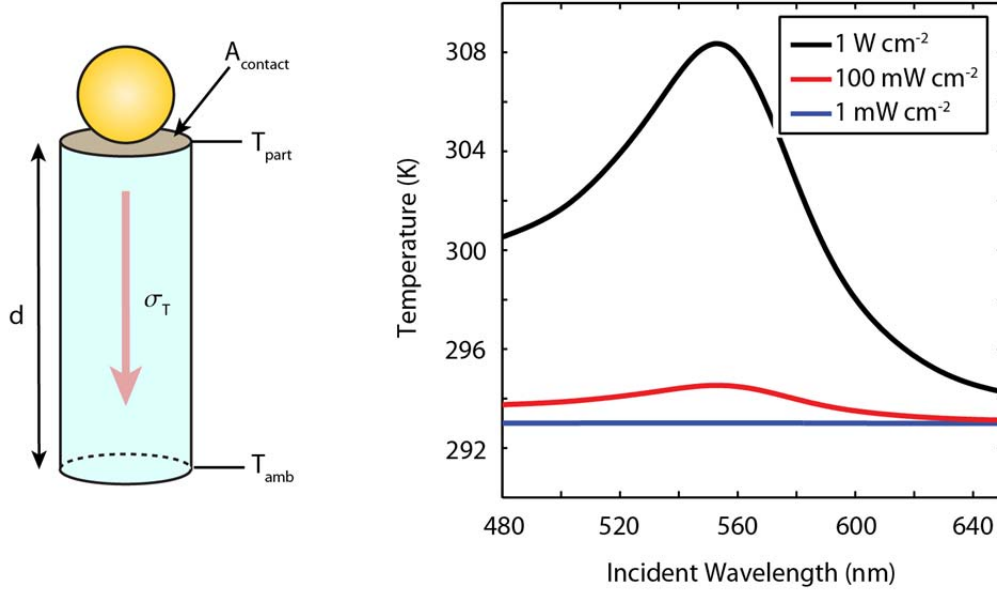


Fig. S4

(Left) Sketch of 1D heat diffusion model (left) for a Au nanoparticle on ITO/glass. (Right) Au nanoparticle temperature as a function of illumination wavelength, corresponding to the experiments in Fig. 2B.

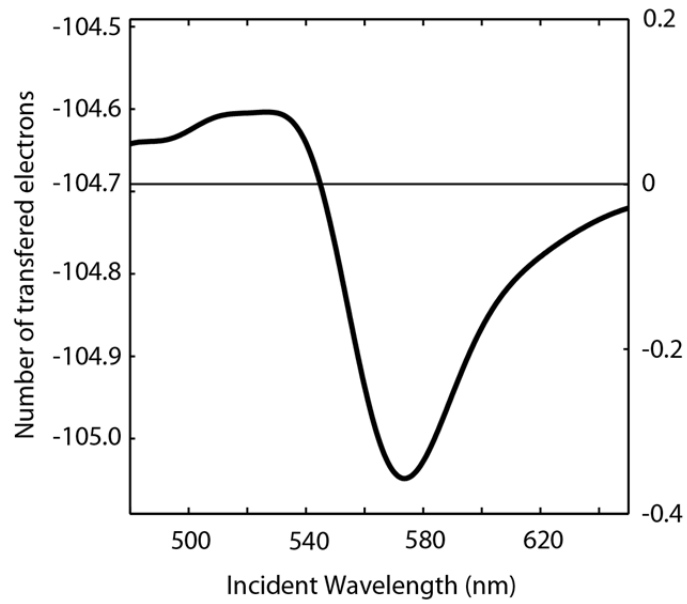


Fig. S5

Calculated excess electron number $N-N_0$ (left-hand scale) for a 60-nm-diameter Au particle on ITO/glass as a function of illumination wavelength (1000 mW/cm^2). The average number of electrons generating the plasmoelectric effect is shown by the right-hand scale.

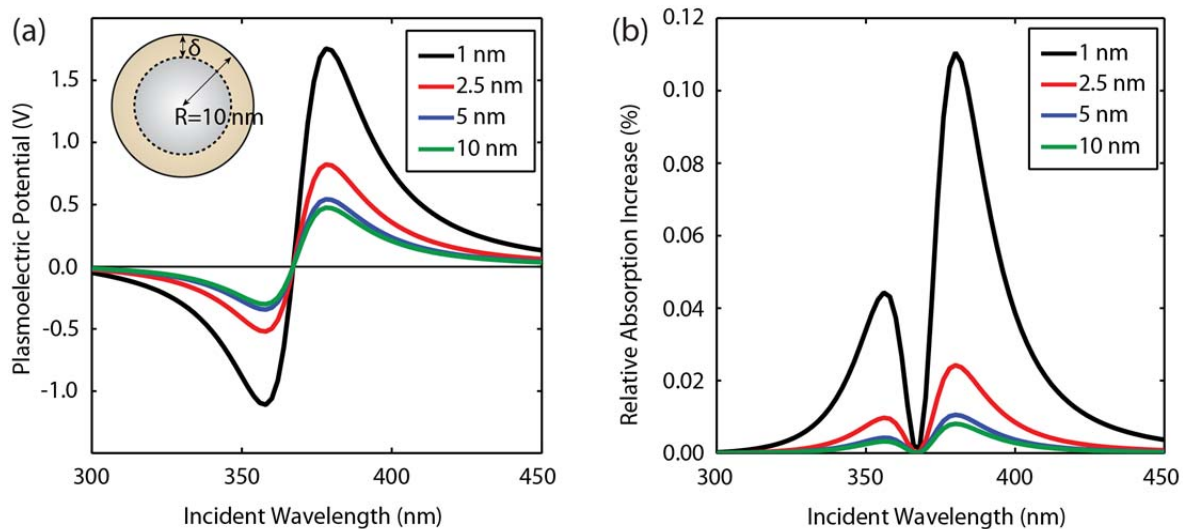


Fig. S6.

Calculated induced potential (A) and relative increase in absorption compared with a neutral particle (B) for a 20-nm-diameter Ag nanoparticle in vacuum as a function of illumination wavelength for shell thicknesses of 1.0, 2.5, 5.0 and 10 nm (black, red, blue and green trace respectively). The illumination power density is 10 mW cm^{-2} .

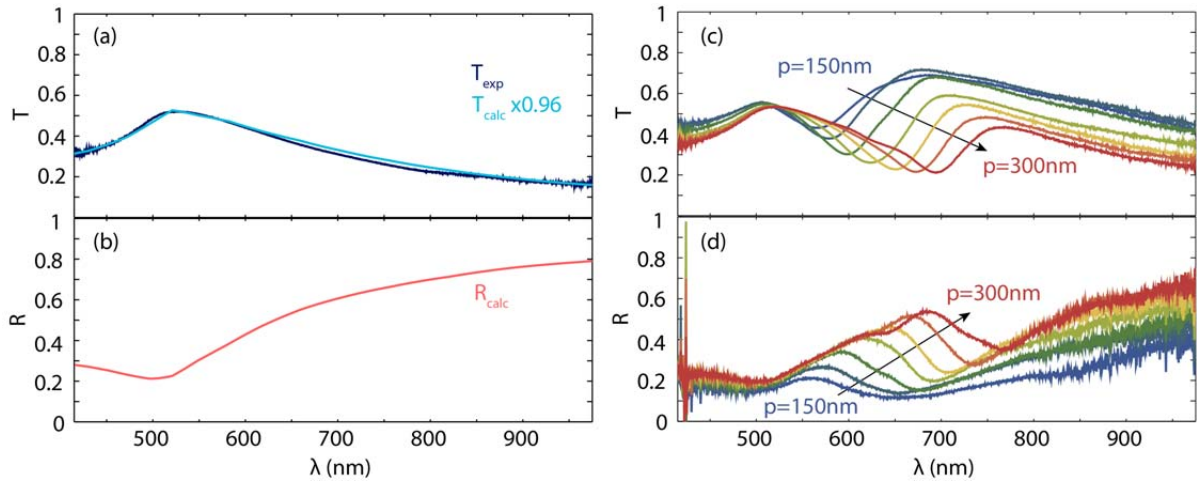


Fig. S7

(A) Measured (dark blue) and calculated (light blue) transmission spectrum for a 18 nm thick bare Au film on glass. (B) Calculated reflection spectrum for the same geometry. Measured transmission (C) and reflection spectra (D) of square arrays of 100 nm diameter holes in a Au film with pitch ranging from 150-300 nm, in 25 nm steps (blue to red).

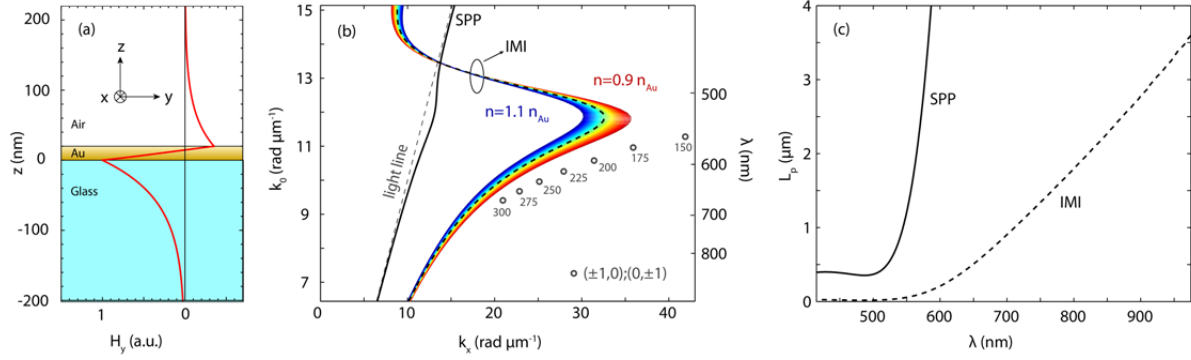


Fig. S8

(A) Field profile (in-plane magnetic field component) of the anti-symmetric IMI mode for a glass-Au-air layer geometry at a free-space wavelength $\lambda = 600$ nm. (B) Calculated dispersion for the anti-symmetric IMI SPP (black dashed line), and the SPP for a semi-infinite Au substrate (black solid line). Also shown is the light line in air (gray dashed). The colored lines show the calculated IMI dispersion curves for modified electron densities n in Au, ranging between 0.9-1.1 times the bulk density (red-blue). Also shown are the wavelengths of the peaks in the absorption spectra obtained from FDTD simulations plotted against wave vectors corresponding to $(\pm 1, 0)$ and $(0, \pm 1)$ grating orders (open dots). The numbers next to the dots refer to the pitch (in nm) of the arrays for which these numbers were determined. (C) SPP intensity propagation length of the IMI (dashed line) SPP and of the SPP mode on a semi-infinite substrate (solid line).

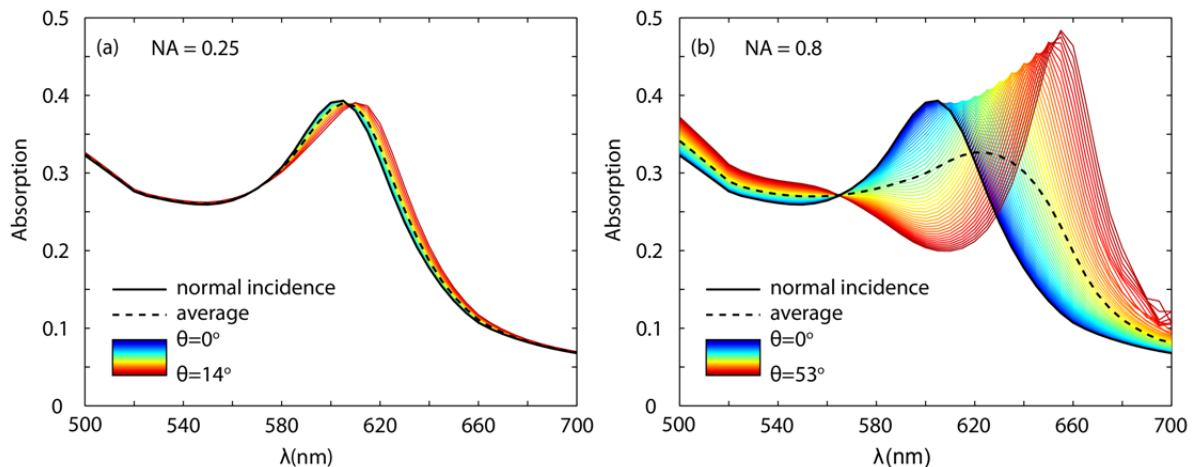


Fig. S9

Absorption spectra for a 225 nm pitched array, illuminated at different angles of incidence (colors) corresponding to the angles within the range of a NA=0.25 (A, used for KPFM measurements) and NA=0.8 (B, used for transmission and reflection experiments). A clear red-shift is observed for larger angles of incidence. The spectrum for normal incidence (solid black) and the average over all angles (dashed black) are also shown, clearly showing the effective redshift and broadening for the larger NA.

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