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Plasmonic phase transition and phase retardation: Essential optical characteristics of localized surface plasmon resonance

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Modeling the LSPR of nanodots with TCMT

Equations for transmission and reflection

In this section, we present the modeling of the localized surface plasmon resonance (LSPR) of nanodots with temporal coupled-mode theory (TCMT) and the procedure for fitting the equations to the intensity and phase spectra for transmission and reflection. In TCMT, the LSPR can be viewed as a resonator coupled to two ports, which are the front side and the back side of the sample. The input wave at port 1, the output wave at port 1, and the output wave at port 2 are

denoted as s_{+1}, s_{-1}, and s_{-2}, respectively. The input wave is proportional to the incident electric field and can be expressed as

$$s_{+1} = \alpha_{+1} E_{\mathrm{i}} = \left(2\sqrt{\frac{\mu_{\mathrm{env}}}{\varepsilon_{\mathrm{env}}}} \right)^{-1/2} E_{\mathrm{i}} \tag{S1}$$

where $\varepsilon_{\mathrm{env}}$ and μ_{env} denote the permittivity and the permeability of the environment, respectively. The coefficient in front of E_{i} is used to normalize the magnitude of s_{+1} so that $|s_{+1}|^2$ is the energy flux of the incidence. In this case, the input at port 2 is closed. The output waves at port 1 and port 2 are proportional to the reflected and transmitted electric fields.

$$s_{-1} = \alpha_{-1} E_{\mathrm{r}} = \left(2\sqrt{\frac{\mu_{\mathrm{env}}}{\varepsilon_{\mathrm{env}}}} \right)^{-1/2} E_{\mathrm{r}} \tag{S2}$$

$$s_{-2} = \alpha_{-2} E_{\mathrm{t}} = \left(2\sqrt{\frac{\mu_{\mathrm{sub}}}{\varepsilon_{\mathrm{sub}}}} \right)^{-1/2} E_{\mathrm{t}} \tag{S3}$$

where $\varepsilon_{\mathrm{sub}}$ and μ_{sub} denote the permittivity and the permeability of the substrate, respectively. We employ the TCMT developed for Fano resonance in photonic crystals[1] and introduce internal dissipation into the theory. The dynamic equations for the amplitude a of the LSPR resonator is written as

$$\frac{\mathrm{d}a}{\mathrm{d}t} = \left(-\mathrm{i}\omega_0 - \frac{1}{\tau_0} - \frac{1}{\tau_{\mathrm{e}}} \right) a + \left(\langle \kappa | * \rangle \right) | s_+ \rangle \tag{S4}$$

$$| s_- \rangle = C | s_+ \rangle + a | d \rangle \tag{S5}$$

where a is the amplitude of the resonator, ω_0 is the center frequency, $1/\tau_0$ is the rate of internal dissipation, $1/\tau_e$ is the rate of decay caused by emission. From Equation S4 and S5, the scattering matrix S for the system is written as

$$\left|s_{-}\right\rangle \equiv S\left|s_{+}\right\rangle = \left(C + \frac{\left|d\right\rangle\left\langle\kappa\right|^{*}}{\mathrm{i}\left(\omega_0 - \omega\right) + 1/\tau_0 + 1/\tau_e} \right)\left|s_{+}\right\rangle \tag{S6}$$

The coefficients κ, d, and C are related by energy-conservation and time-reversal symmetry constraints, which are

$$\left\langle d\middle|d\right\rangle = \frac{2}{\tau_e} \tag{S7}$$

$$\left|\kappa\right\rangle = \left|d\right\rangle \tag{S8}$$

$$C\left|d\right\rangle^{*} = -\left|d\right\rangle \tag{S9}$$

The scattering matrix C is that for the direct transport process, in which the incidence directly transmits through the system.

$$C = \exp\left(\mathrm{i}\varphi\right)\begin{bmatrix} \mathrm{i}r & t \\ t & \mathrm{i}r \end{bmatrix} = \exp\left(\mathrm{i}\varphi\right)\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \tag{S10}$$

To simplify the equations, we consider the LSPR system to be mirror symmetric, and thus d_1=d_2. Using Equation S6–S10, the scattering matrix for LSPR of the nanodots is given by

$$S = \exp\left(\mathrm{i}\varphi\right)\left\{\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} - \frac{1/\tau_e}{\mathrm{i}\left(\omega_0 - \omega\right) + \left(1/\tau_0 + 1/\tau_e\right)}\begin{bmatrix} 1 & 1 \\ 1 & 1 \end{bmatrix}\right\} \tag{S11}$$

Then, the output waves are

$$s_{-1} = -\exp(\mathrm{i}\varphi)\frac{1/\tau_e}{\mathrm{i}(\omega_0-\omega)+(1/\tau_0+1/\tau_e)}s_{+1} \tag{S12}$$

$$s_{-2} = \exp(\mathrm{i}\varphi)\frac{\mathrm{i}(\omega_0-\omega)+1/\tau_0}{\mathrm{i}(\omega_0-\omega)+(1/\tau_0+1/\tau_e)}s_{+1} \tag{S13}$$

If the materials of the environment and the substrate are different, the mirror symmetry of the nanodots is destroyed. We used a glass slide as the substrate and filled the environment with water. The refractive indices of the substrate and the environment are 1.45 and 1.33. In our results, the small difference between the refractive indices does not fail the applicability of the equations.

Fitting the TCMT equations to the transmission and the reflection

The procedure for fitting the TCMT equations to the spectra shown in Fig. 2 in the journal article is illustrated here. The parameters for fitting are ω_0, $1/\tau_0$, $1/\tau_e$, and φ. ω_0 is the angular frequency of the LSPR which is the spectral position of the reflection peak or transmission minimum. According to Equations S12 and S13, reflection and transmission are represented by

$$R(\omega) = \left|\frac{s_{-1}}{s_{+1}}\right|^2 = \frac{(1/\tau_e)^2}{(\omega_0-\omega)^2+(1/\tau_0+1/\tau_e)^2} \tag{S14}$$

$$T(\omega) = \left|\frac{s_{-2}}{s_{+1}}\right|^2 = \frac{(\omega_0-\omega)^2+(1/\tau_0)^2}{(\omega_0-\omega)^2+(1/\tau_0+1/\tau_e)^2} \tag{S15}$$

At $\omega=\omega_0$, the ratio of R and T is

$$\frac{R(\omega_0)}{T(\omega_0)} = \left(\frac{1/\tau_e}{1/\tau_0}\right)^2 \tag{S16}$$

The full width at half maximum (FWHM) for reflection is

$$\mathrm{FWHM} = 2\left(\frac{1}{\tau_0} + \frac{1}{\tau_e}\right) \tag{S17}$$

Substituting the reflection, transmission, and FWHM of the spectra of the nanodots into Equations S16 and S17, we obtain $1/\tau_0$ and $1/\tau_e$. From Equation S12, the phase φ can be obtained by

$$\varphi = \delta_r(\omega_0) + \pi \tag{S18}$$

where $\delta_r(\omega_0)$ is the phase of the reflected electric field at $\omega=\omega_0$. The results of the fit are shown in Fig. 2 in the journal article.

Slope of phase of transmission at the LSPR wavelength

The slope of the phase of transmission at the LSPR wavelength can be expressed as a function of $1/\tau_0$ and$1/\tau_e$. From Equation S13, the phase of transmission is

$$\delta_t(\omega) = \varphi + \alpha(\omega) - \beta(\omega) \tag{S19}$$

where

$$\tan(\alpha) = \frac{\omega_0 - \omega}{1/\tau_0} \tag{S20}$$

$$\tan(\beta) = \frac{\omega_0 - \omega}{1/\tau_0 + 1/\tau_e} \tag{S21}$$

The tangent of the difference between α and β is

$$\tan(\alpha-\beta)=\frac{1/\tau_e(\omega_0-\omega)}{1/\tau_0(1/\tau_0+1/\tau_e)+(\omega_0-\omega)^2} \tag{S22}$$

When ω is very close to ω_0, $\tan(\alpha-\beta)\approx\alpha-\beta$, and the phase of transmission becomes

$$\delta_t(\omega)=\varphi+\frac{1/\tau_e(\omega_0-\omega)}{1/\tau_0(1/\tau_0+1/\tau_e)+(\omega_0-\omega)^2} \tag{S23}$$

Then, the slope at $\omega=\omega_0$ is

$$\left.\frac{d\delta_t}{d\omega}\right|_{\omega=\omega_0}=\frac{-1/\tau_e}{1/\tau_0(1/\tau_0+1/\tau_e)} \tag{S24}$$

From this equation, the internal dissipation, $1/\tau_0$, should be lower to obtain a steeper slope.

Ellipsometric parameters of silver nanorods

When measuring the LSPR spectra by ellipsometry, the signal is a mix of the LSPR response to two polarizations. If the LSPR is suppressed in one polarization and is active in another, we can observe the phase transition phenomenon. The spectra of a nanorod array are shown in Fig. S1. The geometry is given in the inset of Fig. S1a. The materials of the nanorod and substrate are silver and glass, respectively. The refractive index of the environment is assumed to be 1.33, and the period of the rods is 500 nm. The edge lengths in the *x* and *y* directions are 100 nm and 250 nm, respectively. The thickness of the rod is 50 nm. The sample is under normal incidence. As shown in Fig. S1a and S1b, the *y* polarization presents a resonance minimum and a phase transition at approximately 1100 nm. However, the LSPR in the *x* polarization is tuned to the short-wavelength region. The transmission and the phase of the *x* polarization do not vary significantly at the LSPR wavelength of the *y* polarization. Using the phase of the *x* polarization as the baseline, the ellipsometric parameter Δ gives the phase transition of the *y* polarization without much distortion around the LSPR position (compare the phase spectra in Fig. S1b and S1c). The steep slope of Δ can also be applied to refractive index sensing at a fixed wavelength.

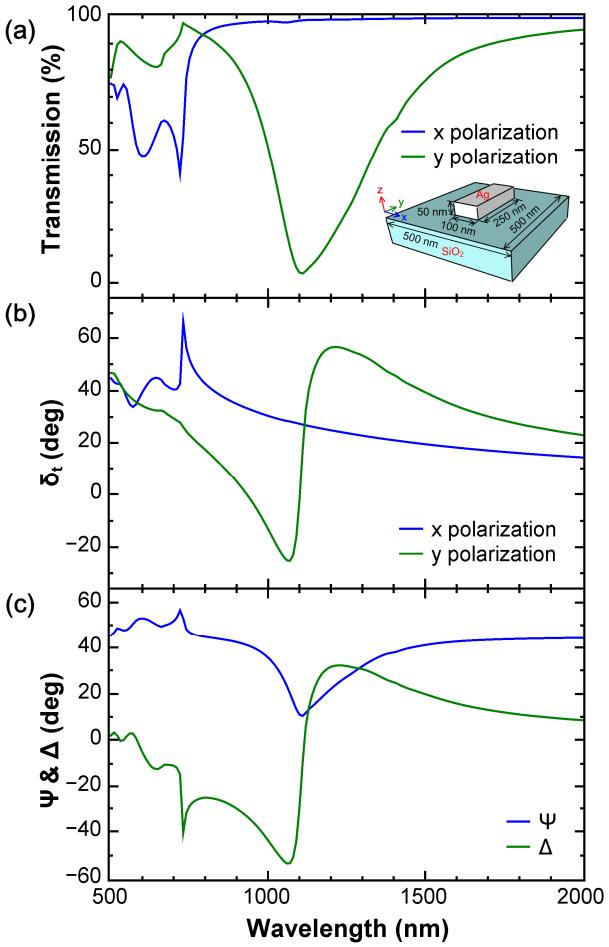

Fig. S1 Spectra of a nanorod array. The structure consists of silver nanorods on a glass substrate. The refractive index of the atmosphere is 1.33. The inset shows the geometry. (a) The transmission of the *x* and *y* polarizations. The LSPR minimum of the *y* polarization is evident, and the *x* polarization shows no resonance. (b) The transmission phases in the *x* and *y* polarizations. (c) The ellipsometric parameters Ψ and Δ, where Δ show the phase transition of the *y* polarization.

Fabrication of the nanodot array

The array of anisotropic dots is fabricated with the nanoimprint lithography and lift-off process. The first step is the fabrication of a silicon mold. A 300-nm layer of wet oxide is formed on a silicon wafer with a furnace. The resist is coated on the surface and is patterned with electron beam lithography. After the resist is developed, the pattern is transferred to the silicon oxide by dry etching; thus, the fabrication of the silicon mold is complete. Then, the pattern on the silicon mold is replicated on a perfluoropolyether (PFPE, Fluorolink MD 700, Solvay Specialty Polymers) mold for nanoimprinting. The schematic diagram of the subsequent fabrication steps is shown in Fig. S2. Approximately 120 nm of water-soluble polyvinyl alcohol (PVA) is spin coated onto a glass slide as a sacrificial layer. Approximately 120 nm of SU-8 (MicroChem Corp.) is coated on PVA as the resist layer. The PFPE mold is imprinted on the SU-8 under a pressure of 4 bar for 10 min. During the imprinting, the sample is heated to 80°C. After cooling and demolding, a hole structure is formed on the SU-8. Two reactive-ion etching steps are used to remove the residual SU-8 and the PVA underneath. The etching time for the PVA is carefully controlled to form an undercut structure. Then, 60 nm of silver is deposited on the sample by electron beam evaporation. The sample is soaked in water, and the silver dots remain on the substrate. The sample is very uniform under visual inspection. The scanning electron microscope (SEM) image in Fig. S3 shows the uniformity of the dot array.

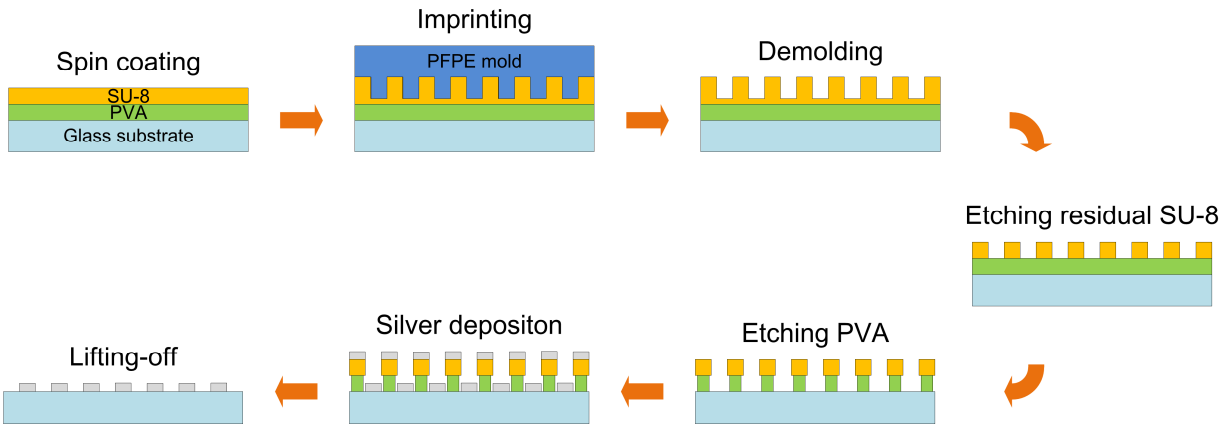

Fig. S2 Schematic diagram of the nanoimprint and lift-off processes.

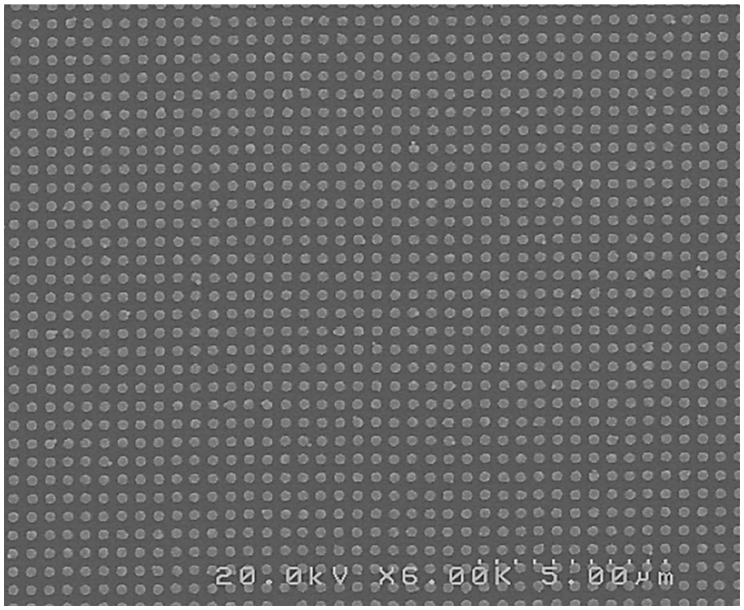

Fig. S3 SEM image of the silver dot array showing that the sample is very uniform.

Method of obtaining the experimental spectra

Here, the method of obtaining the transmission and phase spectra in Figs. 7d to 7e is explained. The spectra were measured with an ellipsometer (M-2000, J. A. Woollam Co., Lincoln, NE, USA) in transmission mode. The ellipsometry provides ellipsometric parameters Ψ and Δ and the average of transmissions of the *x* and *y* polarizations in one measurement. The phase spectra in Fig. 7e are the cosine values of the Δ. The transmission of the *x* polarization (I_x) and that of the *y* polarization (I_y) in Fig. 7d have to be calculated from the average transmission (I_{avg}) and the Ψ. It is obvious that

$$I_{avg} = \frac{1}{2}\left(I_x + I_y\right) \tag{S25}$$

From equation 7,

$$\tan^2\left(\Psi\right) = \frac{I_y}{I_x} \tag{S26}$$

Solving the two equations yields

$$I_x = 2\cos^2\left(\Psi\right) \times I_{avg} \tag{S27}$$

$$I_y = 2\sin^2\left(\Psi\right) \times I_{avg} \tag{S28}$$

Reference

1. S. H. Fan, W. Suh and J. D. Joannopoulos, *J. Opt. Soc. Am. A-Opt. Image Sci. Vis.*, 2003, **20**, 569-572.