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Plasmon resonances of Ag capped Si nanopillars fabricated using mask-less lithography

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Abstract: Localized surface plasmon resonances (LSPR) and plasmon couplings in Ag capped Si Nanopillar (Ag NP) structures are studied using 3D FEM simulations and dark-field scattering microscopy. Simulations show that a standalone Ag NP supports two LSPR modes, i.e. the particle mode and the cavity mode. The LSPR peak position of the particle mode can be tuned by changing the size of the Ag cap, and can be hybridized by leaning of pillars. The resonance position of the cavity resonance mode can be tuned primarily via the diameter of the Si pillar, and cannot be tuned via leaning of Ag NPs. The presence of a substrate dramatically changes the intensity of these two LSPR modes by introducing constructive and destructive interference patterns with incident and reflected fields. Experimental scattering spectra can be interpreted using theoretical simulations. The Ag NP substrate displays a broad plasmonic resonance band due to the contribution from both the hybridized particle LSPR and the cavity LSPR modes.

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References and links

1. Introduction

Plasmonic nanostructures [1,2] are the key components for extensive applications such as surface-enhanced Raman Scattering (SERS) [3–5], refractive index sensing [6–8], surface-enhanced infrared absorption (SEIRA) [9,10], plasmonic optical devices [11,12] and thermal sensing [13], due to their ability to controllably confine light energy at the nanoscale. For sensing applications based on localized surface plasmon resonance (LSPR), emphasis has been drawn on the development of nanostructures exhibiting high and uniform field enhancement factors (EF), wide range and controllable plasmonic tunability, suitableness for mass-production, and reproducibility. Typical examples include nanoshells [14, 15], highly faceted nanoparticles [16, 17], nanopillars [18–20], and structured substrates [21–23].
Recently, a new class of Si pillar based nanoplasmonic structures fabricated using mask-less reactive ion etching has been developed [24, 25]. It consists of free standing Si nanopillars capped by Ag or Au films, as shown in Fig. 1(c). Such SERS substrates exhibit high and uniform EF and can effectively trap analyte molecules near the electromagnetic hot-spots via leaning of pillars. Substrate application examples include detection of TAMRA-labeled vasopressin molecules in ultra-low concentrations, and characterization of biologically relevant diphenylalanine nanotube-folic acid conjugates, revealing its potential for bioanalytical quantifications of complex biological samples [26, 27]. Most importantly, the fabrication of such substrates is extremely simple, quick, cost-effective and is suitable for mass production. The fabrication process can be completed in 15 minutes. Mask-less reactive ion etching (RIE) is used to form Si pillars with controllable height and density over an entire 4 inch wafer, and then Ag or Au caps can be deposited onto the Si pillars by e-beam evaporation. Despite the reported substrate applications, to the best of our knowledge there are no previous theoretical or experimental reports that address the LSPR behavior of Au/Ag nanopillars fabricated using mask-less lithography. In order to open new possibilities for optimizing the substrate towards a multifunctional plasmonic sensing platform that fulfills all the requirements of an ideal LSPR substrate, optical properties of isolated and interacting Au/Ag nanopillars need to be systematically investigated. To carry out such a study, a major challenge is that the geometry of the fabricated nanopillars varies from pillar to pillar significantly. This is due to the mask-less Si RIE process which cannot be precisely controlled to obtain Si nanopillar structures with a sub-10 nanometer resolution. In order to simulate experimentally observed optical properties of such nanopillar structures, representative pillar geometries observed by scanning electron microscopy (SEM) should be carefully selected. Due to similarities in the pillar geometry, a single pillar or a dimer of pillars can be modeled using the aforementioned method. Although we acknowledge that it is an approximate approach, a valuable theoretical insight into otherwise a quite complicated nanopillar structure can be obtained.

In this paper, LSPR properties of Ag capped nanopillars (NPs) are studied using 3D FEM simulations, and the results are then verified experimentally. Following a step by step approach, LSPR modes of a standalone NP are first simulated and investigated. Two basic LSPR modes, the particle mode and the cavity mode are observed. The particle mode is the collective electron oscillations in the Ag cap. It can be distinguished by the enhanced localized fields around the center of the Ag cap. Its resonant wavelength can be red-shifted by increasing the Ag cap size or the Si pillar diameter, and by flattening the Si pillar tip. The cavity mode is the electron oscillations in the Ag cap coupled via the Si pillar. It can be distinguished from the enhanced and highly localized fields near the neck of the Ag cap. Its wavelength is dominant by the diameter of the Si pillar. The influence of the substrate is also investigated. The substrate is shown to have a strong influence on the intensity of the LSP resonance of the NP, by introducing constructive or destructive interference to the excitation light; however, it has only minor effect on tuning of the LSPR modes. Then, leaning of the NPs are studied by simulating a NP dimer. Results show that the particle mode hybridizes when two NPs lean together, splitting into various LSPR modes, with increased EFs by ~3 - 4 times. Contrary to what happens to the particle mode, leaning of the NPs does not change the cavity LSPR wavelength at all. Finally, scattering measurements are performed on real samples. Experimental results can be interpreted in light of the conclusions drawn from the simulations. This proves the validity of the numerical approximations and analysis.

2. Simulation model

3D FEM simulations are performed using the commercial software COMSOL MULTIPHYSICS ver. 4.4a. Figures 1(a) and 1(b) show the geometry of a single NP in the model. Such geometry is established according to the NPs observed in the SEM images, as shown in Figs. 1(c) and 1(d). In the model, an ellipsoid with a rounded bottom (r = 5 nm) and a cone are used to approximate the metal cap and the tip of the Si pillar, respectively. Unless otherwise noted, the substrate is excluded from the simulation to reduce computation time.
not mentioned, default values of the geometric parameters described in the caption of Fig. 1 are used in the simulation. Ag, Au and Si are modeled by their complex refractive indices as functions of wavelength [28]. The medium surrounding the NP is set to vacuum. The excitation plane wave propagates along the –z direction, where the electrical field is polarized along the x-axis.

In all cases, we calculate the scattering cross-section of the NP(s) using Eq. (1),

\[ \sigma_{\text{sca}} = \frac{1}{I_0} \int \nabla \cdot \mathbf{S}_{\text{sc}} \, dS \]  

(1)

where \( I_0 \) is the excitation intensity, \( \mathbf{n} \) is the normal vector pointing outwards the closed surface of the NP, \( S_{\text{sc}} \) and \( \mathbf{S}_{\text{sc}} \) is the poynting vector of the scattered light. The electromagnetic field distribution is calculated by setting the excitation field as the background field followed by solving the scattered fields multiple times. A perfect matched layer with scattering boundary conditions on its outer boundaries is employed to eliminate non-physical reflections.

Fig. 1. (a), (b) A modeled single NP, (a) x-z cross-sectional view, (b) x-y top view. Yellow represents metal, while gray stands for silicon. An ellipsoid with a rounded bottom (r = 5 nm) and a cone are used to approximate the metal cap and the tip of the Si pillar, respectively. The substrate is modeled by a Si layer stacked by an Ag film with a hole (radius = a). Unless otherwise noted, the substrate area (surrounded by dotted lines) is excluded from the simulation to reduce computation time. Default values of the geometric parameters are \( a = 62 \) nm, \( c = 155 \) nm, \( h_t = 100 \) nm, \( h_p = 635 \) nm, \( d = 40 \) nm, \( D = 200 \) nm and \( L = 400 \) nm. These values are chosen referring to real NPs observed in (c) and (d). (c) A cross-sectional SEM image of the NPs. Si pillars are covered by Ag, and the Si substrate is covered by an Ag film with holes near the Si pillars. The deposition thickness of Ag is \( D_{\text{Ag}} = 200 \) nm. (d) A cross-sectional SEM image of the NPs. The Ag film and the Ag caps are lifted up to reveal the bare Si pillars.
3. Results and discussion

3.1 LSPR modes of a single NP

First, LSPR modes of a standalone NP are studied by 3D FEM simulation. Scattering spectra are calculated for both Ag@Si and Au@Si NPs. Results are shown in Fig. 2(a). It can be seen that two LSPR modes can be excited in a single NP. For an Ag@Si NP, the LSPR peaks appear at 650 nm and 800 nm, whereas they appear at 710 nm and 865 nm for the Au@Si case.

![Fig. 2. (a) Calculated scattering cross-section spectra for a single Ag@Si NP (grey line) and a single Au@Si NP (yellow dots). (b) EF distributions on the surface of an Ag@Si NP at resonant LSP wavelengths. (c) Calculated scattering cross-section spectra for an Ag@Si NP with substrate (red dash line) and a standalone Ag@Si NP (grey line). (d) Cross-sectional EF distributions of an Ag@Si NP with a substrate at its resonant LSP wavelengths. The maximum EFs in (b) and (d) are obtained based on the electric fields on the surfaces of those NPs.]

To classify the observed LSPR modes, electric field enhancement factor distributions at the resonance wavelengths are plotted for an Ag@Si NP, as shown in Fig. 2(b). At $\lambda = 650$ nm, intense and highly localized fields are observed around the Ag cap, due to the strong collective electron oscillations through the center part of the Ag cap. Obviously, such an EF distribution is similar to that of an Ag spherical particle on resonance. Therefore it is reasonable to define such a LSPR mode as the particle LSPR mode of the NP. At $\lambda = 800$ nm, strong EF is observed near the neck of the NP, i.e. near the bottom of the Ag cap. This resonance is caused by the collective electron oscillations inside the bottom part of the Ag cap. Since the diameter of the Si pillar is only 40 nm, which is much smaller than the excitation wavelength, strong coupling between Ag via the Si pillar can be expected. It can be predicted that the diameter of the Si pillar has a strong influence on the resonance wavelength of this mode. (The assumption will be assessed in section 3.2). Due to the plasmonic coupling...
via the Si pillar, we define such a resonance mode as the cavity LSPR mode of the NP. Note that the maximum EF of the cavity mode is 149, which is about 6 times higher than that of the particle mode. In addition, the enhanced electric field of the cavity mode is more localized than that of the particle mode, as observed in Fig. 2(b). The above discussion is also valid for a single Au@Si NP (field distributions not shown for the Au@Si NP). Its 710 nm and 865 nm peaks correspond to the particle mode and the cavity mode, respectively. The redshifts of the peaks for the Au@Si NP compared with those of the Ag@Si NP are due to the difference in the dielectric functions between Ag and Au. Such red-shifting behavior has been observed and studied extensively in other Ag and Au plasmonic structures [29–31].

Next, the influence of the substrate on the two LSPR modes of a single Ag@Si NP is investigated. The substrate is modeled by a 200 nm thick Si layer stacked by a 200 nm thick Ag film with a hole of radius $a = 62$ nm, referring to the SEM image in Fig. 1(c). The simulated scattering spectrum and the EF distributions at the scattering peaks are plotted in Figs. 2(c) and 2(d), respectively. It can be seen that with the presence of the substrate, the NP still has two LSPR modes, i.e. the particle mode and the cavity mode, but they are slightly blue-shifted (10 nm for the particle mode and 5 nm for the cavity mode) comparing to those of a standalone Ag@Si NP. Such blue-shifts are also observed in other plasmonic structures, e.g. crescents [32] and spheres [33] on substrates. Note that since the distance from the center of the Ag cap to the Ag film is 435 nm, which is larger than half of the excitation wavelength, the coupling between the LSP of the nanohole in the Ag film and that of the Ag cap is weak. This gives evidence for the weak LSPR tuning effect introduced by the substrate. However, from Fig. 2(c), it can be seen that introducing the substrate has a significant influence on the LSPR intensities. It strengthens the scattering cross-section by around 2.5 times for the particle mode, and weakens it by around 8 times for the cavity mode. The reason for this is that the substrate introduces constructive and destructive interference between the incident and the reflected excitation light, as can be seen from the EF patterns in Fig. 2(d). Compared with the maximum EFs of a single Ag@Si NP shown in Fig. 2(b), it can be seen from Fig. 2(d) that by introducing the substrate, at the resonant wavelength of the particle mode, constructive interference happens near the Ag cap region, causing an increase in the maximum EF from 25 to 45, while at the resonant wavelength of the cavity mode, destructive interference happens near the Ag cap region, causing a decrease in the maximum EF from 149 to 89.

3.2 LSPR wavelengths broadening of the NPs

Due to the mask-less etching method used, the geometry of the NPs varies, e.g. the diameter of the Si pillar =40 ± 16 nm, the tip shape of the Si pillar can be sharp or flat, and the shape of the metal caps are different from one to another. Some of these variations can tune the LSPR wavelengths of individual NPs, leading to inhomogeneous broadening of the LSPR peaks. In this section, we study those geometric LSPR tuning effects. First, the influence of the Si pillar diameter $d$ is studied. Figure 3(a) shows the calculated scattering cross-section of standalone Ag@Si NPs with different $d$. It can be seen that increasing $d$ causes substantial redshifts to the cavity mode. The mode shifts from 715 nm to 920 nm, when $d$ increases from 24 nm to 64 nm. Such redshifts are linear, as shown in Fig. 3(c), where increasing $d$ by 10 nm introduces a redshift of approximately 50 nm. Changing $d$ tunes the interaction intensity between the Ag on the two sides of the Si pillar near the NP neck. For example, a smaller $d$ strengthens the coupling intensity, leading to the increase of the LSPR energy and thus blue-shifts the cavity LSPR peak. In addition, $d$ affects the LSPR energy of the particle mode. Similarly to what happens to the cavity mode, increasing $d$ red-shifts the particle mode of the NP. Such a redshift is much gentler, compared with that of the cavity mode. Increasing $d$ from 24 nm to 64 nm only leads to a 50 nm redshift of the particle LSPR peak. This is due to the different electron oscillation paths between the particle mode and the cavity mode. Increasing $d$ dramatically changes the plasmonic coupling intensity via the Si pillar for the cavity mode, while it does not introduce big changes to the dielectric environments in the routes of electron oscillations of the particle mode. Moreover, other than the particle mode and the cavity mode,
a third LSPR mode emerges when $d$ is below 32 nm. This mode is marked by triangles in Fig. 3(a).

Since the sharpness of the Si pillar tips is different as shown in Fig. 1(d), their LSPR tuning effect must be studied. For simplicity, this is done by simulating two standalone Ag@Si NPs, one with a sharp Si pillar tip and the other with a flat one. The simulated scattering spectra are shown in Fig. 3(d). It can be seen that as the tip of the Si pillar changes from a sharp one to a flat one, a 10 nm redshift can be observed for the cavity mode, while the resulting redshift for the particle mode is about 35 nm. Similar to explaining the tuning effect of the Si pillar diameter $d$, the tuning effect of the sharpness of the Si pillar tip can also be explained by the changes in the dielectric environments of the electron oscillating paths and the LSP coupling routes. As the Si pillar tip becomes flatter, the dielectric environment near the NP neck does not change much, thus the resonance wavelength of the cavity mode stays at almost the same position. However, a flatter Si pillar tip dramatically increase the dielectric volume near the center of the Ag cap, where the electron oscillations of the particle mode pass through, therefore leading to a significant 35 nm redshift for the particle LSPR mode.

![Fig. 3.](image-url)
Finally, the tuning effect of the Ag cap shape is investigated. This is done by simulating additional three Ag@Si pillars including effects of the substrate. Their geometric parameters are extracted from the SEM images of NPs with different Ag deposition thicknesses: 125 nm, 150 nm and 225 nm. The values can be found in the caption of Fig. 3(e). The substrates are taken into account since the deposition thickness will also affect the distance between the Ag caps and the Ag film, resulting in variation of the interference pattern, which has been shown to have a significant influence on the LSPR intensity in section 3.1. The calculated scattering spectra are shown in Fig. 3(e). The particle LSPR mode red shifts from about 620 nm to 680 nm, when the thickness of the deposited Ag increases from 125 nm to 225 nm. In addition, as the deposited Ag thickness increases from 125 nm to 225 nm, it can be observed from Fig. 3(e) that the resonance wavelength of the cavity mode stays at around 800 nm. Therefore it can be concluded that the LSPR energy of the cavity mode is dominated by the cavity size, rather than the volume of the surrounding metallic structure. Similar results from the study of other cavity based LSP structures support this conclusion [34]. Furthermore, the intensity ratio between the cavity mode and the particle mode varies, when the deposited Ag thickness changes. This is due to the different light interference patterns for the different Ag deposition thicknesses. This effect will be discussed together with the experimental scattering measurements of the NPs in section 3.4.

3.3 LSP couplings in an Ag NP dimer

Leaning of the NPs have proved to be critical for applications such as SERS [24]. In this section, the leaning effect is investigated by simulation of a NP dimer with a minimum gap of 1 nm. Simulated scattering spectra of a NP dimer are shown in Fig. 4(a). Two perpendicular polarization directions are used in the calculation, and are labeled as px mode and py mode in Fig. 4(a). For the py mode, the peaks at 650 nm and 800 nm represent the particle mode and the cavity mode, respectively. For the px mode, plasmonic hybridization happens [35]. The results are the vanishing of the 650 nm particle mode peak and the generation of several new LSPR peaks. Some of them are blue shifted to 610 nm, 580 nm, 515 nm, and one is red shifted to 950 nm, compared with the original 650 nm peak of the particle mode in a standalone NP. However, for the cavity mode, its peak stays at 800 nm for both px and py polarization modes. The reason for this is that the two NPs in the model do not touch or form narrow gaps near their necks, thus plasmonic couplings and interactions are relatively much weaker for the cavity mode compared with those of the particle mode. EF distributions at
LSPR wavelengths for the px mode are plotted in Fig. 4(b). By comparing Fig. 4(b) with Fig. 2(b), it can be seen that leaning of two NPs can increase the EF of the particle and the cavity modes by around 1.5 – 4 times via plasmonic couplings and can introduce various new LSPR modes by plasmonic hybridization of the particle mode, enabling the pillars to have strong localized fields in a wide spectral range. Note that in the real case, a cluster of NPs can be dimers, trimers, or contain even more NPs. In addition, the angle of leaning for each NP is usually different. Therefore it is not feasible to simulate all the situations. However, it can be expected based on the simulation result of a NP dimer that for a NP cluster containing more NPs, the LSPR wavelength of the cavity mode does not change or changes very slightly, while the peak of the particle mode vanishes, accompanied by the emergence of various hybridized LSPR modes around 500 – 600 nm. Such an assumption will be proved experimentally in the next section.

3.4 Scattering measurements on NP substrates

Finally, scattering measurements are performed using a conventional dark-field setup on NPs before and after leaning. Four substrates with different Ag deposition thicknesses $D_{Ag}$: 125 nm, 150 nm, 200 nm, and 225 nm are used in the experiment. Cross-sectional view of these NPs are shown in the insets of Fig. 5(b) ($D_{Ag} = 125$ nm, 150 nm, 225 nm), Fig. 1(c) ($D_{Ag} = 200$ nm) and appendix, section 6. Top views of the leaning NPs are shown in Fig. 5(b). The measured scattering spectra are shown in Fig. 5(a).

For the NPs before leaning, two peaks can be observed; one stays at around 800 nm, while the other red-shifts from near 600 nm to about 660 nm, when $D_{Ag}$ increases from 125 nm to 225 nm. The former peak corresponds to the cavity LSPR mode of the NPs, while the latter corresponds to the particle LSPR mode. The stability of the cavity LSPR peak and the red-shift of the particle LSPR peak when increasing $D_{Ag}$ have also been shown by the simulation results in Fig. 3(e), as discussed in section 3.2. Note that due to the uneven geometries of the fabricated NPs, the two observed scattering peaks are broad and overlapping. The broadening of the cavity mode peak is dominated by the uneven distribution of the Si pillar diameter, while the broadening of the particle mode is mainly due to the uneven geometries of the Ag caps and the Si pillar tips, according to the analysis in section 3.2 based on the simulated
results. The intensity ratio of the two peaks is related to the constructive and destructive interference of the excitation light caused by the substrate. It can be seen from Fig. 5(a) that for \( D_{Ag} = 125 \text{ nm} \) and 225 nm, the scattering intensity of the cavity mode is higher than that of the particle mode, while for \( D_{Ag} = 150 \text{ nm} \) and 200 nm, the scattering intensity of the two modes are similar. This is consistent to the simulation results shown in Fig. 3(e). When the NPs lean together, it can be seen from Fig. 5(a) that the particle LSPR mode dramatically weakens, accompanied by a very gentle bump in the spectra near 550 nm, indicating the generation of the hybridized modes. In addition, the cavity LSPR modes are shown to be stable at near 800 nm for all the four substrates regardless of leaning. The above results are in agreement with the conclusion in section 3.3, that when NPs form clusters, the LSPR wavelengths of the cavity mode are nearly unaffected, while the peak of the particle mode vanishes, and is accompanied by the emergence of various LSPR modes around 500 – 600 nm that represent the hybridized plasmonic modes. Further evidence of the existence of the cavity LSPR mode can be found in the appendix, in section 5, where we simulated the scattering spectra of a dimer of Ag NPs with and without Si cavities. We show that for such structures only the cavity LSPR mode can contribute to the experimentally observed LSPR peaks around 800 nm.

Furthermore, SERS measurements of 10 mM trans-1,2-bis (4-pyridyl) ethylene (BPE) in ethanol solution are performed on the \( D_{Ag} = 225 \text{ nm} \) sample under both 532 nm and 780 nm excitations. NPs are leaned when the analyte solution evaporates. The results are shown in Fig. 5(c). It can be seen that the SERS intensity ratio between 780 nm and 532 nm excitations is about 2, which is in agreement with the ratio observed in the scattering spectrum of the leaning NPs (\( D_{Ag} = 225 \text{ nm} \)) in Fig. 5(a). It can be deduced that the SERS signals under 780 nm excitation benefit most from the strong localized fields near the necks of the NPs generated by the cavity LSPR mode, while for the 532 nm case, the hot-spots in the gaps of the NPs generated by the hybridized particle modes contribute the most. Furthermore, the NP substrate exhibits a good SERS uniformity with a standard deviation of 5.2% of the average signal intensity over a length of 1 inch, as shown in the appendix. The result demonstrates the accuracy of the employed fabrication procedure.

4. Conclusion

Localized plasmon resonances and plasmon couplings in Ag capped Si nanopillar structures were studied by 3D FEM simulations and dark-field scattering measurements. The simulation results show that a standalone Ag@Si NP has two LSPR modes, the particle mode and the cavity mode. The particle mode can be distinguished by the enhanced localized fields near the center of the Ag cap. The cavity mode can be distinguished by the enhanced localized fields near the neck of the Ag cap, and its resonance position is dominated by the diameter of the Si pillar. The resonance energy of the particle mode is shown to be sensitive to the size of the Ag cap and can be hybridized by leaning of the pillars. The resonance energy of the cavity mode is however only dominated by the diameter of the Si pillar, and cannot be tuned via leaning of adjacent nanopillars. Furthermore, the presence of the substrate is shown to have little tuning effect on the two LSPR modes of the NP, but can dramatically change the intensity of the two modes by introducing constructive or destructive interferences of the excitation lights, depending on the distance from the substrate to the Ag cap. The scattering measurements support the conclusions drawn from the simulations. The measured scattering peaks are broad, due to the uneven geometries of the fabricated NPs. In addition, the ratio of the SERS intensities between 780 nm and 532 nm excitations for 10 mM BPE fits the ratio in the scattering measurement. These SERS spectra also prove that the NP substrate has a wide LSPR energy range due to the contribution of both the hybridized modes and the cavity modes, as shown in the scattering spectra, where each of them covers wide range LSPR energies. The results in this paper provide guidance for further optimization and development of such structures, to realize e.g. tuning of the LSPR wavelengths towards near- and mid-infrared for SEIRA applications and for further increases in EF to improve the SERS detection limits.
Appendix

1. Fabrication of NP substrates

The Ag NP substrates are fabricated using a four-step nanofabrication process. First, maskless Si RIE is used to form Si pillars over an entire 4 inch Si wafer. 4 inch p-type single-side polished (100) wafers are used. Etching is conducted in an Advanced Silicon Etcher (Surface Technology Systems MESC Multiplex ICP) at a SF$_6$:O$_2$ flow ratio of 1.12, platen power of 120 W and a chamber pressure of 36 mTorr. The Si NPs are formed at a rate of ~3 nm/s. The Si NP density is ~20 pillars/µm$^2$. Subsequently, an oxygen plasma process of 1 minute is applied to remove Si RIE byproducts from the Si surface. Here, an Advanced Silicon Etcher (Surface Technology Systems MESC Multiplex ICP) is used at an O$_2$ flow of 45 sccm, a platen power of 20 W, a coil power of 800 W and a chamber pressure of 10 mTorr. Lastly, a continuous Ag metal film is deposited over the whole wafer using e-beam evaporation. Alcatel SCM 600 is used at a pressure of 2 x 10$^{-6}$ mbar for the deposition. The deposition rate is 10 Å/s for the Ag evaporation.

2. Scattering measurements

Scattering spectra of Ag NPs are acquired using a dark-field microscopy system. A schematic of the setup is shown in Fig. 6. First, light from a halogen lamp (Instrument Systems, Model: DLS 500) is coupled into a cleaved optical fiber for uniform irradiation of the Ag NP sample. The incident angle is 30 degrees. Then, the scattered light is collected by a 10x objective lens and recorded by a spectrometer (Instrument Systems, Model: Spectro 320-141). Finally, the recorded scattering intensity is normalized with the lamp spectrum.

![Fig. 6. A schematic of the dark-field scattering measurements.](image)

3. SERS measurements

The SERS experiments are conducted using a Thermo Scientific Raman DXR microscope. The signal collection time is 1s and is averaged 3 times. A 25 µm slit is used. The laser spot is about 3.1 µm in diameter. The microscope was coupled to a single grating spectrometer with a 5 cm$^{-1}$ FWHM spectral resolution and ± 2 wavenumber accuracy. All SERS spectra were collected at 0.1 mW laser power, using a 10x objective. The target molecule is 10 mM trans-1,2-bis (4-pyridyl) ethylene (BPE) dissolved in ethanol. Droplets of BPE were deposited on the NPs and left for drying during which the NPs lean together, forming clusters.

4. LSPR contribution of the nanoholes

To prove the validity of eliminating the LSPR effects of the nanoholes on the substrate, scattering and SERS measurements are performed on a substrate, where the NPs are peeled off by tape, as shown in Fig. 7(b). For comparison, measurements are also conducted on a sample with normal standing NPs. The measured scattering and SERS spectra are shown in Fig. 7(a) and Fig. 7(c), respectively. It can be seen from Fig. 7(a) that the contribution to the scattering signal by the nanoholes is negligible. This is reasonable since the sizes and shapes of the nanoholes are highly uneven, thus there are no specific resonance wavelengths for the

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nanoholes. It can also be seen from Fig. 7(c) that the localized fields around the nanoholes are very weak, since the SERS signal decreases by 200 times when the NPs are peeled off. In conclusion, the nanoholes on the Ag film above the Si wafer do not have a specific LSPR energy, and their LSPR resonance and the resulting localized fields are negligible compared with those produced by the NPs.

Fig. 7. (a) Measured scattering spectra using a conventional dark-field setup on an Ag@Si NP substrate and an Ag@Si NP substrate with NPs peeled off. The Ag deposition thickness is $D_{Ag} = 200$ nm. (b) Upper and lower left: Top view SEM images of the two substrates used for the scattering measurements in (a). Upper and lower right: Top view SEM images of the samples used in the SERS measurements in (c). The NPs are leaned during the evaporation of the target molecule solution, as seen in the upper right image. (c) SERS spectra of 10mM BPE in ethanol obtained using the substrates shown in (b) under 780 nm excitation. A 10x lens is used to focus and collect the light and the laser power is 0.1 mW.

5. Further evidence proving the existence of the cavity LSPR mode

We have measured optical properties (dark-field scattering spectra) of some Ag NP structures with different Ag NP cap sizes in order to evaluate LSPR peak positions, as shown in Figs. 5(a) and 5(b) in the main text. Here, we further evaluate and demonstrate the existence of the Ag cap cavity resonance mode using FEM calculations. For simplicity, we consider a dimer of Ag NPs with and without Ag cavities.

Fig. 8. (a) Calculated scattering spectra for a dimer of standard Ag@Si NPs without Si cavities (the Si inside the Ag caps are replaced by Ag) under different polarization directions. The polarization directions used in the calculation are shown in the insets. Insets: electric field enhancement maps plotted for the strongest resonance peaks under different polarization directions. (b) Same as (a), but for the case that the NPs contain Si cavities inside their Ag caps.

In Fig. 8(a), we define Ag NPs as Ag ellipsoid positioned on top of a Si nanopillar. We otherwise use the same parameters as shown in Fig. 4. The calculated scattering spectra in Fig. 8(a) for both incident field polarizations are dramatically different compared to those of
the Ag NP dimer with Si cavities, shown in Fig. 8(b). All LSPR peaks in Fig. 8(a) are at around 600 nm, and the spectra are quite different from the experimental ones shown in Fig. 5(a), since no LSPR peaks can be found near 800 nm in Fig. 8(a). In Fig. 8(b) we define the Ag NP dimer including Ag cap cavities. In this case, the LSPR peaks caused by the plasmon couplings via the Ag NP cap cavities are found at around 800 nm. Their position is close to those in the experimentally observed spectra shown in Fig. 5(a). We believe these results provide further evidence that proves the existence of the cavity LSPR mode whose resonance position is very stable regardless of leaning, and such cavity LSPR mode contributes to the experimentally observed LSPR peaks at around 800 nm, that are also stable regardless NP leaning.

6. Geometric changing of the NP substrate when increasing the Ag deposition thickness

![Cross-sectional SEM images of the NP substrates with different Ag deposition thicknesses D_{Ag} = 125 nm, 150 nm, 200 nm and 225 nm. Si pillars are covered by Ag, and the Si substrate is covered by an Ag film with holes near the Si pillars. For all the samples, Si pillars are made by the same etching recipe described in the appendix, section 1 with the same etching time of 4 minutes. All samples are tilted by 5° during the SEM measurements.](image)

As can be seen from Fig. 9, when the Ag deposition thickness D_{Ag} increases from 125 nm to 225 nm, the average size of the Ag caps increases both laterally and vertically. In addition, the average thickness of the Ag film on the Si substrate increases. Furthermore, the average distance between the bottom of the Ag caps and the Ag film decreases when increasing D_{Ag} from 125 nm to 225 nm.

7. SERS uniformity of the NP substrate

As shown in Fig. 10, the NPs exhibit high SERS uniformity over the 1 inch mapping line. The standard deviation for the 1641 cm\(^{-1}\) BPE Raman peak is 5.2% of the average signal intensity. Such a result indicates that the fabrication procedure of the NP substrate is quite accurate, i.e., NPs with a large-scale uniformity are fabricated.

![Mapped SERS spectra of 10 mM BPE in ethanol solution obtained using the NP sample of D_{Ag} = 225 nm under a 780 nm excitation. (a) 2-D view. (b) 3-D view. The mapping distance was 1 inch. The step size was 50 um. A 10x objective lens was used to focus and collect the light and the laser power was 0.1 mW. The diameter of the laser spot was 3.1 um. Droplets of BPE were deposited on the NPs and left for drying during which the NPs lean](image)
together, forming clusters. The standard deviation for the 1641 cm$^{-1}$ BPE Raman peak is 5.2% of the average signal intensity.

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