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Converting Plasmonic Light Scattering to Confined Light Absorption and Creating Plexcitons by Coupling a Gold Nano-pyramid Array onto a Silica-Gold Film

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Abstract

This report presents a facile microfabrication-compatible approach to fabricate a large area of plasmonic nano-pyramid array-based antennas and demonstrates effective light management by tailoring the architecture. First, a long-range ordered gold nano-pyramid array is fabricated, which exhibits strong light scattering. The maximum electric field enhancement ($|\mathbf{E}|/|\mathbf{E}_0|$) of 271 is achieved at the corner but decays rapidly away from the pyramid bottom. After the gold nanopyramid array is coupled to a gold film, strong light scattering is converted into strong light absorption due to the excitation of a spectrally tunable plasmonic gap mode, where an intense electric field enhancement of 233 and a strong magnetic field enhancement ($|\mathbf{H}|/|\mathbf{H}_0|$) of 25 are simultaneously excited for a 10 nm silica gap. The electric field decays much slower away from the pyramid bottom while the magnetic field keeps almost constant. In addition, both experiments and finite-difference time-domain (FDTD) simulation have confirmed that strong plasmon-exciton coupling between the plasmonic gap mode and the J-aggregates can take place when the quantum emitters such as J-aggregates are embedded in the gap, creating plexcitons. This can overcome the problems of high energy loss and weak nonlinearity, which are typically associated with surface plasmon polariton (SPP) supported on plasmonic metallic nanostructures. The coherent plasmon-exciton coupling (plexciton) generated by the film-coupled nano-pyramid nanostructure is expected to find promising applications in light-emitting devices, photodetectors, photovoltaics and photoelectrochemical cells.

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ASSOCIATED CONTENT

Supporting Information. Figures S1-S8. This material is available free of charge.

Graphical Abstract

Keywords

localized surface-plasmon resonance; surface plasmon polariton; gold nanopyramid array; quantum emitters

Plasmonic nanostructures are promising antennas because they have strong ability to harvest light due to their large absorption cross-sections; and the incident light can be managed to transmit, scatter or absorb by controlling chemical composition, size, shape and coupling of nanostructures. Therefore, plasmonic antennas find extensive applications in photosynthesis, photovoltaics, photo-detection, optical biosensing, therapeutics and super-resolution microscopy¹⁻⁴ Plasmonic antennas fall into two categories, that is, free-standing nanoparticles and chip-based nanostructures. Large-area ordered nanostructure array patterns on chips are of particular interest. However, it remains a significant challenge to fabricate the chip-based plasmonic antennas to realize light management in a controlled manner (light reflection versus absorption versus transmission, resonance band position and spatial distribution). It is difficult to achieve nanoscale resolution for conventional photolithography techniques due to the diffraction limit of light. Although focused-ion beam (FIB) and electron-beam lithography (EBL) can reach nanoscale resolution but suffer from low throughput, impeding massive production. In contrast, nanosphere lithography (NSL) is a simple, inexpensive, and high-throughput method for manufacturing periodic nanostructure arrays. In our previous work,⁵ we have developed a method to create a large-area, well-ordered and close-packed polystyrene sphere monolayer template, which enables the fabrication of large-area ordered nanostructure array patterns such as nanotriangle arrays and nanohole arrays with NSL. By taking this advantage, herein we fabricate a large-area of ordered nano-pyramid array pattern. The reason for selecting pyramids not spheres is that pyramids exhibit much larger electromagnetic (EM) field enhancement at the corners and edges as compared to round-shaped nanoparticles. Our results demonstrate that the resulting nano-pyramid array pattern show large electric field enhancement ($|\mathbf{E}|/|\mathbf{E}_0|$ up to 271) and strong light reflection/scattering. That is, light scattering is dominant in the total extinction spectra while light absorption is small for the array of Au nano-pyramids (179 nm in base edge length and 200 nm in height for individual pyramids). To further improve the EM

enhancement near pyramids, the ideal way is to reduce the in-plane gap between adjacent pyramids less than 10 nm in order to enable in-plane (X-Y direction) plasmonic field coupling, which is difficult to achieved due to the fabrication limit. To convert the light scattering to the confined light absorption, the effect way is to reduce the size of individual pyramids down to 15 nm. But it will reduce the total area/volume of chip for harvesting incident light.

On the other hand, our research interest is triggered by coupling nanoparticles to a metal film to form a metal-insulate-metal (MIM) sandwich structure. It has been reported that MIM structures are characteristic of the out-of-plane plasmonic field coupling (plasmonic gap mode) between the top-surface metal nanoparticles and the underneath metal film, which can be modulated by the thickness of the sandwiched space layer.^{6–11} The plasmonic gap mode is able to have the harvested light be absorbed in the space layer between the metal nanoparticle layer and the underneath metal film, and to create “hot spots” in the out-of-plane direction (Z direction). By taking the advantages of the MIM structure, the nano-pyramid array is herein coupled to the silica-gold double-layer to form a metal-insulate-metal (MIM) sandwich structure in order to expand the space of enhanced electric and magnetic fields and to convert the light scattering to the light absorption.

Furthermore, efficient tuning the light-matter interactions is essential for a variety of applications. However, it is difficult to control the light-matter interactions. For example, there exist fundamental mismatch between the diffraction-limited spatial confinement of visible-light and the size of quantum emitters (QEs).¹² The diffraction limit, however, can be broken by surface plasmon polaritons (SPPs), which are light-coupled propagating electromagnetic (EM) waves of coherent electron oscillations on metallic surfaces.¹³ SPPs comes with two prominent features.^{14–15} First, it belongs to bosons, leading to strong transportability of the EM energy. Second, it has the most harmonic behavior known in nature. Unfortunately, the plasmonic cavity, which supports SPPs, lacks essential functionalities in modern optoelectronic devices due to very weak nonlinear response and a high metal loss.^{16–17} Coincidentally, QEs are highly nonlinear in nature despite a low transportability.¹⁸ They are extensively exploited to realize optical gain in lasers and other optoelectronic devices.^{19–23} The integrated SPPs-QEs system can thus well balance and compensate the nonlinearity and transportability of the two counterparts except that a strong damping from the metal loss persists.

One promising approach to overcome the metal loss is to make conditions for the interaction of the SPPs-QEs system to take place in the strong-coupling regime.^{24–32} Realizing strong coupling demands an intense interaction between the transition dipole μ of QEs and the plasmonic cavity: $g \propto \mu\sqrt{N/V}$, where V is the effective mode volume of the plasmonic cavity in which the EM energy is confined and N is the number of QEs in V .^{12, 17, 33} The diffraction-unlimited nature of SPPs allows light to be confined in a significantly smaller plasmonic cavity than the photonic counterpart until the emergence of charge transfer plasmons due to quantum tunneling or nonlocal effects at a gap below 1 nm.^{34–37} Such extraordinarily small plasmonic cavities have been demonstrated on nanoparticle-on-mirror geometry, bowtie antennas, patch antenna, et al.^{24, 38–39} Minimizing the effective mode volume, however, is also at the expense of reducing the number of QEs participating light-

matter interactions, which compromises the coupling strength. Moreover, it is also a technique challenge to fabricate ultra-small plasmonic cavity. Therefore, from a practical point of view, modern optoelectronic devices working in the strong-coupling regime require a delicate balance between fabrication and performance.

In this work, the Au nanopyramid array-silica-Au film structure is predicted to enable SPP-QE systems into the strong plasmon-exciton coupling regime. First, the plasmonic gap mode of such a MIM sandwich structure is tunable both spectrally and in terms of the effective mode volume. Second, if QEs are incorporated into the spacer layer, they exactly fall into the effective mode volume, which ensures the largest coupling strength to achieve possibly. Third, it can be fabricated massively on a large area by the well-established and cost-effective NSL technique.⁴⁰ The spacer layer can be easily replaced with any other QEs of interest to realize different functionalities. Fourth, the long-range order of the nano-array structure ensures the robustness and reproducibility of fabrication. In addition, the two-dimensional nanostructure makes it practically easy to be integrated into optoelectronic devices. Therefore, in this study, the ability of the Au nanopyramid array-silica/QE-Au film structure to manipulate light-matter interactions is studied with finite-difference time-domain (FDTD) simulation when achieving strong coupling between the plasmonic gap mode and the QEs.

RESULTS AND DISCUSSION

Structure of plasmonic antenna.

Figure S1 and Figure 1 show the procedure for fabrication of the Au nanopyramid array pattern directly on a glass substrate, and the Au nanopyramid array-silica-Au film structure, respectively. The fabricated Au nanopyramid arrays with and without an underlying Au film looked similar to each other from the top-view SEM images as shown in Figures 2(a) and S2. The Au nanopyramids were 179 nm in base edge length and 200 nm high (Figure S3). The silica space layer was controlled to be from 35 nm to 130 nm. The overall lateral size of as-fabricated chips was typically comparable to that of a coin, as shown in the inset of Figure 2(a). This confirmed the strong capability of nanosphere lithography for long-range ordered nano-array nanofabrication. In contrast, it would take several days for e-beam lithography to produce such a large area of nanostructured patterns.

Strong light reflection by the Au nanopyramid array alone.

The fabricated Au nanopyramid array on the glass substrate displayed an intense reflection peak centered at 865 nm corresponding to the plasmonic corner mode, the orange solid curve as shown in Figure 2(b), which was consistent with the reflection peak at 850 nm calculated by FDTD, as shown with the olive dashed curve. The minor reflection peak at around 750 nm in the calculated reflection spectrum was ascribed to the edge mode, which was not clearly seen in the experimental data due to the rounded edge. The reflection peak contributed to strong light scattering of individual nanopyramids under excitation of the localized surface-plasmon resonance (LSPR) mode at the corner while light absorption by individual nanopyramids were small, as shown in Figure S4. It was not surprising because the size/volume of nanopyramids were quite large. For LSPR-associated total extinction

spectra of nanoparticles, both light absorption and scattering contribute to the total extinction.⁶ When the particle size is relatively small (typically less than 15 nm), light absorption is dominant. When the particle size increases, light scattering becomes dominant. In addition, the major reflection peak corresponding to the plasmonic corner mode red shifts with a decrease in the pyramid height, as shown in Figure S5. The FDTD simulation results show that the localized electric field enhancement took place primarily on the four corners, where surface polarization charges accumulate at the corners as shown in Figure S6. As a result, the plasmonic corner mode exhibits intense electric field enhancement. The calculated maximum electric field enhancement ($|\mathbf{E}|/|\mathbf{E}_0|$) at the corners was estimated to be 271, as shown in Figure S7.

Strong light absorption in the film-coupled gold nanopyramid array.

Although the top-view SEM images looked the same for the Au nanopyramid arrays with and without an underlying Au film, their optical properties were different significantly, as shown in Figure 2. After the Au nanopyramid array was coupled to a gold film with a silica film as the spacer layer, the strong reflection peak disappeared completely. Instead, the film-coupled Au nanopyramid array exhibited strong light absorption, which was featured as an intense dip in the reflection spectra, as shown in Figure 2(c). When the thickness of the silica spacer layer was reduced from 130 nm to 35 nm, the reflection dip underwent a red shift from 834 nm to 918 nm. This trend was also confirmed by FDTD simulation, as shown in Figure 2(d).

The observed intense reflection dip was ascribed to the plasmonic gap modes, which were induced in the spacer layer between the Au nanopyramid array and the underlying Au film. Since a transmission line type of resonances can be sustained at the gap,⁴¹ the incident light can thus be guided into the gap region and adjust themselves to satisfy boundary conditions. The impedance mismatch at the gap edge makes most of the incident light trapped inside the gap, and thus contributes to the strong absorption. This was confirmed by calculation of surface polarization charge distributions for a film-coupled Au nanopyramid array with a 10 nm thick silica spacer layer (Figure 3). This plasmonic antenna exhibited two dips at 1135 nm and 790 nm in the reflection spectrum, as shown in the green dash dotted curve in Figure 2(d). The primary plasmonic gap mode at 1135 nm showed a stronger reflection dip than the one at 790 nm, which can be interpreted by the fact that the positive and negative surface polarization charges were well separated from each other, as shown in the middle column in Figure 3. The higher-order plasmonic gap mode at 790 nm displayed a less intense reflection dip because its net dipole momentum was partially cancelled. By varying the thickness of the spacer layer, the plasmonic gap modes can be spectrally tuned (Figure 2(c) and 2(d)). Herein the study was focused on the primary plasmonic gap mode, which will be called plasmonic gap mode in the following sections.

It is noted that the plasmonic gap modes generated in the film-coupled nanopyramid structure in this work is different from that of the film-coupled nanosphere reported previously.^{42–45} For the film-coupled nanosphere structure, the plasmonic gap modes result from hybridization of plasmonic resonances, which lead to the symmetric and the anti-symmetric resonances. The symmetric resonance is featured by a horizontal electric dipole

in the nanosphere and an induced electric dipole in the film, which cancel each other. The anti-symmetric resonance is characterized by a vertical electric dipole in the nanosphere and an induced electric dipole in the film, which add up and produce an even larger vertical electric dipole. Therefore, the anti-symmetric resonance is responsible for coupling to the free space with a doughnut-like far-field emission profile. The spectral tunability of the film-coupled nanosphere structure is limited by the gap size because of the electric dipole nature. In contrast, for the film-coupled nanopyramid structure, the plasmonic gap modes are generated due to the Fabry-Perot-like resonance after the incident light gets trapped inside the gap through multiple reflections at the gap edges. Simultaneous to the formation of plasmonic gap modes, opposite charges are induced on the opposite sides of the gap, as shown in Figure 3, generating fictitious current density. This forms a large horizontal magnetic dipole that is absent in the film-coupled nanosphere structure. In short, the plasmonic gap mode in the film-coupled nanopyramid structure is coupled to the free space primarily through the magnetic dipole with a vertical far-field emission profile. Owing to the magnetic dipole nature, large spectral tunability can be achieved by tuning either the dimension of the pyramidal bottom plane or the gap size, which provide more flexibility than the film-coupled nanosphere structure.

Electromagnetic field enhancement by plasmonic gap mode.

A prominent feature of the plasmonic gap mode was that the charges with opposite signs were induced on the opposite sides of the gap. These charges resulted in an intense EM field localized inside the gap (Figure 4). Since the surface polarization charges are accumulated at the corner for individual Au pyramids on the glass substrate, the maximum electric field enhancement ($|\mathbf{E}|/|\mathbf{E}_0|$) of 271 was achieved at the corner (Figure S7). Likewise, the maximum electric field enhancement of 233 was achieved at the gap for the film-coupled Au nanopyramid array with a 10 nm thick silica spacer layer (Figure 4(b)). It is worth noting that the film-coupled Au nanopyramid array had a few unique features as compared to the Au nanopyramid array on the glass. First, not only the electric field, but also an intense magnetic field (an enhancement factor $|\mathbf{H}|/|\mathbf{H}_0|$ of 25) was supported in the gap (Figure 4(c)), whereas the magnetic field enhancement was negligible for the Au nanopyramid array on the glass. Second, the electric field was confined within the gap for the film-coupled Au pyramid array while the radial electrical field appeared at the corners for the Au nanopyramid array alone. Third, the magnetic field was kept almost constant in the gap for the film-coupled Au pyramid array and the electric field underwent only a small decay with an increase in the distance away from the pyramid bottom along the cross section (Figure 4(b) and 4(c)). In stark contrast, the electric field from the corner mode of the Au pyramid array alone decayed exponentially away with an increase in the distance away from the pyramid bottom (Figure S7(b)). Thanks to these unique features, the localized EM energy oscillated back and forth between the electric and magnetic counterparts inside the gap; and it only got damped either because of metal loss or by coupling to the free space. The gap which confines the spatially oscillating EM energy thus defines a spectrally tunable plasmonic cavity mode with an effective mode volume approximately the physical size of the gap. This feature provides an excellent configuration to enable the maximum interaction between SPPs and the spacer layer in the gap.

Compared to previous work on metal-insulator-metal structure,^{46–47} the film-coupled Au nanopyramid array reported in this work can be easily fabricated over a large area using cost-effective nanosphere lithography, as shown in Figures 1 and 2(a). The plasmonic gap mode supported is thus highly tunable and controllable, as shown in Figures 2(c) and 2(d). Compared to cubic and spherical planes, the reduced degree of symmetry for the triangular pyramidal bottom plane partially lifts the degeneracy and allows higher-order plasmonic gap modes to be easily resolved, as shown in Figures 2(d) and 3. The three-dimensional pyramidal geometry also makes the film-coupled Au nanopyramid array more sensitive to the incident radiation and more efficiently confine incident light as EM energy at the gap, as shown in Figure 4. This paves the way for the plasmonic gap mode to strongly interact with quantum emitters embedded at the gap.

Strong coupling between quantum emitter and plasmon.

As mentioned above, surface plasmon polariton (SPP) supported on plasmonic metallic nanostructures suffers from high energy loss and weak nonlinearity. One promising approach to overcome the metal loss is to make the interaction of SPP with QEs to take place in the strong-coupling regime.^{24–32} The coupling strength g is characterized by Rabi frequency Ω_R ($\Omega_R = 2g$), which quantifies the rate of energy exchange between the plasmonic cavity and QEs.³³ In the strong-coupling regime, the coupling strength is strong enough to compensate the damping rate κ of the plasmonic cavity and the spontaneous decay rate τ_0 of QEs, *i.e.*, $g > \kappa, \tau_0$. The extraordinary coupling strength facilitates an extremely rapid, coherent and reversible energy exchange between the plasmonic cavity and QEs, leading to two newly formed hybridized states called upper and lower plexcitons, which are half-light, half-matter, and are split by Rabi frequency.^{12, 17, 33, 48} Given the dependence of the hybridized plexciton states on the coupling strength, the strongly-coupled SPPs-QEs system has strong implications in state-of-the-art optoelectronic devices such as ultrafast switching, all-optical control, *et al.*^{49–51} In comparison, in the weak-coupling regime where the damping rate of the plasmonic cavity outcompetes the spontaneous decay rate of QEs and the coupling strength, *i.e.* $\kappa > \tau_0, g$, the interaction is incoherent and irreversible.^{12, 17, 33} The energy extracted from QEs is unidirectionally transferred to the cavity with the spontaneous decay rate enhanced by the cavity-dependent Purcell factor.

The film-coupled Au nanopyramid array structure provides an excellent platform for achieving strong coupling between the QEs and the plasmonic cavity mode, as schematically shown in Figure S8. For example, J-aggregates are typical QEs. In this work, J-aggregates are taken as the spacer layer to test the possibility of strong coupling by a combination of experimental measurements and FDTD simulations, as shown in Figure 5. The experimentally measured reflection spectrum for the plasmonic gap mode and the absorption spectrum for J-aggregates are shown in Figure 5(a). To sandwich J-aggregates in the gap, they were first mixed with polyvinyl alcohol (PVA) and then spin-coated on the Au film followed by fabrication of Au nanopyramid arrays (See Methods for detailed experimental procedures). The plasmonic gap mode was found to split into two new modes separated by 218 meV, which was the Rabi frequency. One new mode was blue-shifted from the plasmonic gap mode and the other red-shifted from the absorption peak of J-aggregates. To verify whether coherent coupling can be achieved between the plasmonic gap mode and the

exciton of J-aggregates, FDTD simulations were conducted. In FDTD simulations, the permittivity of J-aggregates is assumed to follow the Lorentz Model, which is given by²⁸

$$\varepsilon(\omega) = \varepsilon_{\infty} + \frac{f_0 \omega_0^2}{\omega_0^2 - \omega^2 - i\gamma_0 \omega} \quad (1)$$

The absorption peak of J-aggregates is assumed at 861 nm ($\omega_0 = 1.44$ eV); the damping rate is assumed as $\gamma_0 = 50$ meV; the high-frequency permittivity ε_{∞} and Lorentz permittivity f_0 are set as 1.45 and 50 meV, respectively.

The calculated absorption spectrum of J-aggregates is derived from the imaginary part of the complex permittivity given by Equation (1) and was shown in Figure 5(b). In the meanwhile, the reflection spectra for the corresponding plasmonic gap modes were calculated using FDTD simulations by modelling the spacer layer as an insulator with a fixed refractive index of 1.25, roughly the mean value of the real part of the permittivity of J-aggregates.

Without coupling, the calculated dispersion of the plasmonic gap modes was found to be independent of the absorption line of J-aggregates, as shown in Figure 5(c), where the detuning is defined as the energy difference between the plasmonic gap mode and the absorption peak of J-aggregates. With a layer of 16 nm J-aggregates sandwiched into the spacer, the plasmonic gap mode and J-aggregates were spectrally mixed. Instead of being independent of each other, their spectral mixture led to the Rabi splitting of the plasmonic gap mode and generated two new hybridized plexciton modes at 795 nm and 912 nm, respectively, as shown in Figure 5(d). The mode splitting, however, does not necessarily guarantee that the strong-coupling regime is reached. As documented previously, the plasmonic coupling and Fano resonance could also cause similar features.^{52–53} A positive confirmation of strong coupling requires that the coupling strength far exceeds any other damping rates.

For the case with a layer of 16 nm J-aggregates sandwiched between the Au film and the gold nanopillar array pattern, the Rabi frequency was calculated as $\Omega_R = 200$ meV, comparable with the experimentally measured Rabi frequency. The coupling strength was found as $g = \frac{1}{2}\Omega_R = 100$ meV. The damping rate of SPPs was obtained by fitting the reflection dip with a Lorentzian function, which was given as $\kappa = 56$ meV. The fact that $g > \kappa$, γ_0 confirms that strong coupling was indeed achieved in this nanostructure. The two new hybridized modes are actually two newly formed plexciton states corresponding to upper plexciton (UP) and lower plexciton (LP), which are half-light, half matter. These entangled states are characteristic of strong coupling where SPPs and J-aggregates lose their own identities. The confined energy is rapidly and coherently exchanged between SPP and J-aggregates at a rate of the Rabi frequency. By varying the thickness of the J-aggregate layer, the anti-crossing behavior of the two plexciton states are observed, as shown in Figure 5(d), which would not occur in the weak-coupling regime.¹⁷

The anti-crossing region is of great fundamental significance. It has been predicted to give rise to numerous intriguing optical effects such as photon blockade, emission of correlated photons, nonclassical or squeezed state generation, super-radiant phase transitions and ultra-efficient light emission.^{17, 54} Furthermore, the problems of a high energy loss in metallic nanostructures can be effectively circumvented since the rates of any other damping channels are outcompeted by the overwhelmingly strong coupling rate in the strong-coupling region. The demonstration of reaching the strong-coupling regime by sandwiching a layer of excitonic material in the film-coupled gold nanopillar array has strong implications in designing state-of-the-art optoelectronic devices with new functionalities by fully utilizing the nonlinearity of QEs and the transportability of SPP.

CONCLUSIONS

In summary, a long-range ordered gold nanopillar array pattern was fabricated on the glass substrate by nanosphere lithography. The gold nanopillar array exhibited strong light scattering, displaying an intense reflection peak. The maximum electric field enhancement ($|\mathbf{E}|/|\mathbf{E}_0|$) was estimated to be 271 at the corners, which decayed exponentially away from the pillar bottom. After the gold nanopillar array was coupled to a gold film, a plasmonic gap mode was generated in the silica spacer layer, which led to strong light absorption confined in the space layer. In case of a 10 nm thick space layer, the maximum electric field enhancement ($|\mathbf{E}|/|\mathbf{E}_0|$) and the magnetic field enhancement ($|\mathbf{H}|/|\mathbf{H}_0|$) were estimated to be 233 and 25, respectively, which occurred at the gap edge. The magnetic field remained almost constant and the electric field decayed much slower with an increase in the distance away from the pillar bottom. Because of the induced charges on opposite sides of the gap, the confined EM energy was found to oscillate back and forth between the spatially separated electric and magnetic counterparts, which made the effective mode volume to be approximately the actual volume of the gap region. Filling the gap with J-aggregates, strong coupling between the plasmonic gap mode and J-aggregates occurred, creating two plexciton states. The demonstration of strong plasmon-exciton coupling on this two-dimensional metallic nanostructure not only effectively circumvents the unavoidable high loss on metals, but also makes it possible to fully utilize the nonlinearity of QEs and the high transportability of SPPs. It is worth noting that the coherent plasmon-exciton coupling (plexciton) is the most efficient way to transfer energy between plasmon and exciton, which will find promising applications in devices based on light-matter interactions.

METHODS

Chemicals and materials.

Gold-coated glass slides were purchased from Fisher Scientific Inc. Polystyrene microspheres with a diameter of 600 nm were purchased from Thermo Scientific (Waltham, MA). XR1541 e-beam resist was purchased from Dow Corning. Acetone, methanol, and sulphuric acid (H_2SO_4) and hydrogen peroxide were purchased from Alfa Aesar (Haverhill, MA). Deionized (D.I.) water was produced by the Milli-Q Integral 3/5/10/15 system (18.2 M Ω cm, Millipore Corp., U.S.A.).

Nanosphere lithography fabrication.

Figure S1 shows the procedure for fabrication of Au nanopyramid array pattern on a glass substrate by NSL. Figure 1 reveals the procedure for fabrication of the Au nanopyramid array-silica-Au film structure. Specifically, a thin layer with varying thicknesses of silica was first coated on a commercially available Au-coated glass slide by spin coating a layer of silica precursor (XR-1541) at varying speeds and then conducting heat treatment at 400 °C for 1 hour. Subsequently, a monolayer of polystyrene beads with a diameter of 600 nm was patterned on the silica surface by dip-coating. After natural drying in air, a layer of 5 nm Ti film was deposited, followed by depositing a 200 nm thick Au film. After polystyrene beads were removed by ultrasonication, the film-coupled Au nanopyramid array was obtained. The entire fabrication process, which could be scaled up for mass production, was done in just one day in the cleanroom.

Fabrication of Au film-J-aggregates-Au nanopyramid structure.

5 mg/ml of J-aggregates in water were mixed with 25 mg/ml of Poly Vinyl Alcohol (PVA) in water, and then stirred for 3 h. The mixture was spin-coated on a cleaned 1 cm × 1 cm gold-coated glass chips at 4000 rpm for 60 s to form a J-aggregate polymer thin film. A 5 nm thick silica layer was then deposited on the top of J-aggregate polymer thin film for two reasons. Silica layer acted as a protective layer to prevent the J-aggregates from damaging when depositing the gold pyramids; and it also helped enabling a hydrophilic surface for dip-coating where J-aggregate polymer thin film was hydrophobic in nature. Later 500 nm sized polystyrene beads monolayer was dip-coated on the surface of silica. After drying in air, 5 nm thick Ti and 200 nm thick Au films were deposited successively on the monolayer. Finally, the chips were ultra-sonicated in methanol to remove polystyrene beads, leaving the Au nanopyramid array on the top surface.

Instrumentation.

E-beam evaporator (Kurt J. Lesker) was used to deposit gold. Spin coater (Laurel Technologies 600 spinner) was used to coat the silica precursor to make the silica films with different thickness. A Scanning Electron Microscope (JEOL-JSM-7600F) was used to characterize fabricated film-coupled gold nanopyramid array. Reflection spectra were acquired by an Ocean Optics USB 4000 spectrometer and DT-MINI-2-GS.

Finite-difference time-domain (FDTD) simulations.

FDTD simulations were implemented throughout the paper to study the film-coupled gold nanopyramid array using commercially available software Lumerical FDTD Solutions. A mesh size of 2 nm was imposed in the simulation region. The permittivity of gold was from Johnson & Christy.⁵⁵ The refractive index of silica was set as 1.52. A plane wave was used as the input light source. Back reflection spectra, electromagnetic field enhancement, and surface polarization charges were calculated. Perfectly Matched Layer (PML) boundary conditions were imposed on all these simulations.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Conceptual Insights Statement

Strong light scattering of gold nanopyramid array have been demonstrated to be converted into strong light absorption by coupling it to an underlying gold film because of the excitation of the spectrally tunable plasmonic cavity mode. The film-coupled gold nanopyramid array exhibits unique features as compared to gold nanopyramid array alone. First, not only an intense electric field but also a strong magnetic field is supported. Second, the electric field is confined within the gap of the coupled nanostructure while it occurs at the corners for the gold nanopyramid array alone. Third, the magnetic field is almost constant in the gap and the electric field undergoes only a small decay across the gap. In stark contrast, the electric field from the corner mode for the gold nanopyramid array alone decays exponentially away from the corner. These unique features endow the film-coupled gold nanopyramid array with significant advantages over the gold nanopyramid array alone, which has implication in state-of-the-art optoelectronic devices. Our study confirms that strong coupling can be achieved between the plasmonic cavity mode and the quantum emitters embedded at the gap, which can overcome the problems of high energy loss and weak nonlinearity typically associated with surface plasmon polaritons.

Figure 1. Protocol of nanosphere lithography fabrication for film-coupled gold nanopyramid array. Polystyrene beads with a diameter of 600 nm were used. 200 nm of gold was deposited.

Figure 2.

(a) SEM image of fabricated film-coupled Au nanopyramid array (the inset shows the size comparison between a coin and the fabricated sample); (b) Experimental (orange solid curve) and FDTD-simulated (olive dashed curve) reflection spectra for Au nanopyramid array (179 nm in base edge length and 200 nm in height) on glass (the inset shows the schematic nanostructure with the same dimension as in 2(a)); (c) Experimental and (d) FDTD-simulated reflection spectra with various silica thicknesses (the inset shows the schematic nanostructure and the silica thickness was labelled besides the reflection dip).

Figure 3.

FDTD-simulated surface polarization charge distributions at the reflection dip wavelengths of 1135 nm and 790 nm for a silica thickness of 10 nm (the green curve in Figure 2(d)).

Left: scheme of different parts of the structure; Middle: the primary plasmonic gap mode at 1135 nm; Right: the higher-order plasmonic gap mode at 790 nm. The back arrow indicates the incident polarization direction.

Figure 4.

Electromagnetic field enhancement excited at 1135 nm on the film-coupled Au nanopyramid array (179 nm in base edge length and 200 nm in height) with a 10 nm thick silica space layer. (a) Scheme of the four planes on which the electromagnetic fields are extracted, where ii, iii, and iv are 2.5 nm, 5 nm, and 7.5 nm away from the pyramid bottom, respectively; (b) electric and (c) magnetic field enhancement at different planes. Arrows indicate the incident electric field polarization directions; (d) the distance-dependent electric field enhancement corresponding to the plasmonic gap mode in the film-coupled Au pyramid array system and to the plasmonic corner mode in Au pyramid array, respectively. Also, the distance-dependent magnetic field enhancement induced by the plasmonic gap mode is shown. The inserted orange lines and red scales in (b-iii) and (c-iii) are the line profiles for the electric and magnetic field enhancement.

Figure 5.

(a) Experimentally measured, and (b) FDTD-simulated spectral profiles of J-aggregates (absorption, olive curves), plasmonic gap modes (reflection, blue curves), and the hybridized upper (UP) and lower (LP) plexciton states (reflection, orange curves) when a layer of J-aggregates are in the gap; (c) Calculated dispersion of the plasmonic gap mode compared to the absorption line of J-aggregates when they are uncoupled; (d) Calculated dispersion of the hybridized plexciton states (UP and LP) generated from the strongly-coupled system where the anti-crossing energy region could be clearly seen. The detuning is defined as the energy difference between the resonance frequency of the plasmonic gap mode and the absorption peak wavelength of J-aggregates.