Research article

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Strong coupling with directional absorption features of Ag@Au hollow nanoshell/J-aggregate heterostructures

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Abstract: Tunable plasmon-exciton coupling is demonstrated at room temperature in hybrid systems consisting of Ag@Au hollow nanoshells (HNSs) and J-aggregates. The strong coupling depends on the exciton binding energy and the localized surface plasmon resonance strength, which can be tuned by changing the thickness of the Ag@Au HNS. An evident anticrossing dispersion curve in the coupled energy diagram of the hybrid system was observed based on the absorption spectra obtained at room temperature. In this paper, strong coupling was observed twice (first at lower wavelength and then also at a higher wavelength) via a single preparation process of the Ag@Au HNS system. The first Rabi splitting energy ($\hbar\Omega$) is 225 meV. Then, the extinction spectra of the bare Ag@Au HNS and the Ag@Au HNS-J-aggregate hybrid system were reproduced by numerical simulations using the finite-difference time domain method, which were in good agreement with the experimental observations. We attributed the strong coupling of the new shell hybrid system to the reduced local surface plasmon (LSP) mode volume of the Ag@Au HNS. This volume is about 1021.6 nm³. The features of the Ag@Au HNS nanostructure with a small LSP mode volume enabled strong light-matter interactions to be achieved in single open plasmonic nanocavities. These findings may pave the way toward nanophotonic devices operating at room temperature.

1 Introduction

Studies on strong light-matter interactions are interesting. Strong light-matter interactions, which are a focal issue for nanotechnology and modern nanophotonic devices, can be described by cavity quantum electrodynamics (cQED) [1, 2]. cQED lays the foundation for the studies on fundamental quantum science such as quantum information processing [3, 4], quantum networks [5], single-atom lasers [6, 7], and modern nanophotonic devices [8]. The interaction of surface plasmons with quantum emitters is the basis of most of the above light-matter interactions phenomena. These interactions can be classified into two principal regimes [3, 9–13]: the weak and strong coupling (SC) regimes. In the weak coupling regime where incoherent dissipation dominates, the spontaneous emission rate of the emitter is associated with the Purcell effect [14], leading to a phenomenon known as plasmon-enhanced fluorescence [15–17]. When the light-matter interaction cannot be considered as a perturbation, the system is in the SC regime, in which a reversible exchange of energy occurs faster than the electronic relaxation of the excitations, manifested as distinct hybrid modes. Then, the phenomenon of Rabi splitting in frequency domain arises between the near electromagnetic fields and the quantum emitter. Generally, two types of systems are employed to realize strong light-matter interactions: traditional cavity quantum electrodynamics systems (including various optical microcavities) and plasmonic nanocavity systems. Initial efforts to study these quantum optical phenomena have employed various optical Fabry-Perot microcavity systems, which involve considerable experimental challenges, such as ultrahigh vacuum, cryogenic temperatures, and fabrication issues [18–20]. However, the practical utility of these systems has not been explored due

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to the complexity involved in the design of cavity-based systems. These harsh conditions can be solved by using noble metal nanoparticles because plasmonic modes can be confined into volumes far below the diffraction limit [21, 22]. Confining the light field to small effective volumes in this way enables stronger coupling with the emitter [23, 24]. The interaction between plasmonic resonances and the nearby excitonic transition of emitters gives rise to so-called plexcitonic coupling (or plexcitons) [1, 25–32].

Strong plexcitonic coupling requires a high atomic cooperativity $C = g^2/\gamma\kappa$, where $g \propto \sqrt{1/V_{\text{eff}}}$ is the coupling strength and γ and κ are the dissipation rates of the emitters and plasmonic modes, respectively [33–35]. To achieve high atomic cooperativity C , a highly effective approach is to reduce the plasmonic mode volume V_{eff} . Recently, many efforts have been made to tailor the geometry of the metallic nanostructures such as gold nanobipyramids, nanorods, nanoprisms, nanocubes, and even the nanogaps between nanoparticles and mirrors to obtain smaller effective volumes [26–28, 36–42]. Among these metal nanostructures, hollow nanostructures of noble metals are particularly interesting because of their completely different plasmonic properties as compared to solid nanoparticles [43]. Especially for the Ag@Au hybrid nanoshell, the plasmonic properties can be tailored by adjusting their internal structure. We have demonstrated that the plasmon peak of the Ag@Au hybrid nanoshell could be tuned from 450 to 900 nm [44]. However, to the best of our knowledge, the strong light-matter interaction based on this plasmonic nanostructure has not been investigated. The role of various optical parameters dictating the plasmon-exciton interactions is less understood. To achieve strong plasmon-exciton coupling, the emitter must have a high oscillator strength and a high exciton binding energy, such as the electronic excitations (excitons) in quantum dots [45–47] and two-dimensional monolayer transition metal dichalcogenides [37, 39, 40, 48–50], for the realization of SC. The molecular excitation of J-aggregates represents an ideal platform for the formation of exciton polaritons because of their exceptionally high oscillator strength and narrow resonances even at room temperature and in the liquid phase [26, 27]. Herein, we use the J-aggregates as the quantum emitter to couple with the plasmonic modes.

In this paper, we realize light-matter interaction in the SC regime between plasmons confined within Ag@Au hollow nanoshells (HNS) and molecular excitons in J-aggregates in the solution phase. The bare Ag@Au HNS systems exhibit spectral tunability in a wide range from 450 nm to 700 nm, which overlaps with the J-aggregate exciton transition twice via redshifting and blueshifting

of the surface plasmon resonance (SPR) peaks. Thus, SC of plasmons and excitons occurs twice in the new HNS systems. The first experimentally measured SC Rabi splitting extracted from anticrossing curves of a series of Ag@Au HNSs with different shell thicknesses based on their absorption spectra reaches 225 meV. The spectra calculated by the finite-difference time domain (FDTD) method reproduce the experimental results very well, while the electric field distributions from the numerical simulations reveal that the spectrum modification is induced by the remarkable Rabi splitting. Furthermore, the effective local surface plasmon (LSP) mode volume of a Ag@Au HNS is estimated to be much smaller than that of a solid Ag or Au sphere with a similar radius.

2 Results and discussion

2.1 Strong coupling of plasmons and excitons based on experiments

We consider a hybrid fabricated by embedding an Ag@Au HNS into an ensemble of molecular J-aggregate. This nanoshell and J-aggregate plexcitonic hybrid structure is schematically shown at the top of Figure 1. The formation of polaritonic states (or Rabi splitting) can occur for this plexcitonic hybrid structure if the energy of the plasmon energetically matches the energy of the exciton. This matching leads to energy level splitting and the formation of upper (ω_+) and lower (ω_-) polariton modes separated by vacuum Rabi splitting. To experimentally study the plasmon and exciton coupling, Au@Ag HNSs were synthesized by chemical reduction (GRR, galvanic replacement reaction) using Ag nanoparticles as templates. Here the Au atoms newly formed via GRR tend to epitaxially deposit on the surface of the Ag nanoparticles. As the Ag particles continue to participate in the GRR, the holes in the shell region act as channels, which helps the formation of hollow Au nanostructures. The thickness of the shell constantly changes, while the inner part of the nanoparticle remains unchanged. We modified the synthesis method, and a more uniform Ag@Au hollow nanostructure was successfully prepared. In Figure 1 [44], the 15.6 nm shell thickness of the Ag@Au hollow nanostructure can be clearly observed. J-aggregates are covalently linked to the Ag@Au nanoshell with varying thickness (approximately 2 nm), and details on the synthesis of these nanohybrids are presented in section 4.1.2. By precisely controlling the Au shell thickness, the localized surface plasmon resonance (LSPR) wavelength λ_{LSPR}

Figure 1: Above, schematic diagram of the hybrid and related Rabi-splitting of an Ag@Au hollow nanoshell embedded in an ensemble of J-aggregate [the pristine monomer molecule is 1,1'-diethyl-2,2'-cyanine iodide (Cy^+)].

Below, TEM images of the Ag@Au hollow nanoshell-J-aggregate plexciton system at different magnifications, which corresponds to curves j in Figure 2B, are shown below. The corresponding LSP peak of the bare Ag@Au HNS is at 661 nm. The average diameter of the bare Ag@Au HNS is 80 nm; the diameter of the inner hollow cavity is 60 nm. (A) TEM images of the Ag@Au hollow nanoshell-J-aggregate plexciton system with scale bar 100 nm; (B) and (C) are enlargement of rectangle part shown in (A) with scale bars as 50 nm, 20 nm respectively; (D) and (E), (F) are enlargement of another rectangle part shown in (A) with scale bars as 50 nm, 20 nm, 10 nm respectively; Especially, J-aggregate and Au shell are clearly distinguished in (F).

of the Ag@Au HNS can be simultaneously tuned from 450 nm to 700 nm with an accuracy of 14 nm as shown in Figure 2A. This fine tuning is helpful for realizing Rabi splitting which originates from the high sensitivity of the LSPR modes to the precise Ag@Au shell thickness and the control of the hollow cavity.

From the onset of Ag@Au HNS formation, with decreasing thickness of the Ag@Au nanoshells, the SPR peaks first redshift from 436 to 670 nm as shown in Figure 2A curves a–q, then blueshift from 670 to 610 nm, as shown in Figure 2A curves q–y, and finally redshift again from 610 to a 657 nm, as shown in Figure 2A curves

Figure 2: (A) UV-visible absorption spectra of Au hollow nanostructures prepared by adding different amounts of $HAuCl_4$ solution from 70 μ l to 800 μ l to the Ag colloids every 10 min (black line a indicates pure Ag colloids; b–q correspond to the addition of $HAuCl_4$ solution at 90, 85, 80, 75, 70, 75, 80, 85, 90, 95, 100, and 150 μ l; q–y correspond to the addition of $HAuCl_4$ solution at 500, 400, 300, 500 μ l; y–d1 refer to the addition of 800 μ l of $HAuCl_4$ solution). (B) Typical experimental absorption spectra of HNSs doped with J-aggregate with different thicknesses of the Au shell corresponding to (A). (C) Absorption spectra of the HNS with LSPR at 575 nm strongly coupled to J-aggregates. (D) UV-visible absorption spectra of (I) a bare HNS with surface plasmon resonance at 576 nm, (II) pristine 1,1'-diethyl-2,2'-cyanine iodide (Cy^+), J-aggregates, and (III) HNS/J-aggregate ensembles. (D) Experimental dispersion curves of the hybrid state energies for the first SC are plotted as a function of their corresponding plasmon resonance. Anticrossing analysis of the plexciton with upper branch ω_+ (blue triangular symbol) and lower branch ω_- (pink triangular symbol); the circle and square patterns illustrate the exciton and plasmon, respectively. Here the Rabi splitting of the first SC is 225 meV, and that of the second SC is approximately 180 meV.

y–d1. These changes in the SPR peaks distinguish three dynamic growth stages of Ag@Au HNS [44]. Additionally, the voluminous void space in hollow structures could improve the radiation absorption efficiency through “light trapping” effects. Generally, solid core nanoparticles can only absorb a small fraction of the incident light, while in the case of hollow nanoparticles, multiple scattering events could occur within the internal cavity, which should improve the overall absorption efficiency of the cavity structure, enhancing the light harvesting efficiency [51, 52].

In the present study, we selected the pristine 1,1'-diethyl-2,2'-cyanine iodide (Cy^+) to form the excitonic system of the J-aggregate. Cyanine dyes exist in monomeric and aggregate forms with distinct spectral features. The monomeric forms of Cy^+ possess an absorption

maximum at 500 nm with a shoulder at 530 nm, while the J-aggregate possesses a sharp absorption band at 575 nm, as shown in Supporting Information Figure S1. Through the electrostatic interaction with the anionic chloride ion, the cationic dye is adsorbed on the surface of the Au@Ag HNS to form a J-aggregate exciton system. Then, the monomeric peak of Cy^+ at 530 nm undergoes a decrease in intensity with the concomitant formation of the share J-aggregate band at 575 nm.

2.1.1 The first strong coupling

The combination of J-aggregates and the Ag@Au HNS provides opportunities to observe new optical phenomena based on strong plasmon-exciton coupling. To reach the

SC regime, the two uncoupled modes must exhibit spectral overlap, as shown in Figure 2C. Figure 2A shows the absorption spectra of the bare Ag@Au HNS with different shell thicknesses, which can be tuned by adding different amounts of HAuCl_4 solution from 70 μl to 800 μl to the Ag colloids. In the first growth state, the LSP redshifts (curves a to p). When the SPR mode positions of the Ag@Au HNS match the J-aggregate exciton peak (575 nm), the plasmon modes are hybridized with the excitons of the J-aggregates. The strongly coupled hybrids exhibit significant mode splitting into upper (ω_+) and lower (ω_-) plasmon-exciton polariton branches that are part light and part matter, as shown in Figure 2B. The peak positions and intensities of the upper ω_+ and lower ω_- plasmon-exciton polariton branches (in Figure 2B) systematically vary as a function of the separation between the two original resonance peaks. When the plasmon peak is far from the J-aggregate resonance band on either side, it splits into a strong peak that is shifted farther from the dye resonance band and a weak peak closer to the dye resonance band. When the plasmon is close to the dye resonance band, the two new peaks exhibit comparable intensities. Due to the strong influence of the monomeric form of the J-aggregate, the wavelengths of the split peaks were extracted by fitting the extinction spectra with Gaussian peaks. At resonance, the LSPR peak of the bare Ag@Au HNS is located at 575 nm (curve j in Figure 2A), while the two new polariton peaks of the corresponding plexciton system (Ag@Au HNS-aggregate) occur at 614 nm (ω_-) and 553 nm (ω_+) revealing that the Rabi splitting is 225 meV, as shown in Figure 2B.

To confirm that the coupled system is in the SC regime, the anticrossing of its hybrid resonances needs to be investigated. The preparation process of the bare Ag@Au HNS allows for tuning the LSPR position thus to probe the hybrid plexciton system with different plasmon-exciton detunings and thus reconstruct the anticrossing. The absorption spectra in Figure 2B clearly exhibit different plasmon-exciton detunings.

With increasing thickness of the Au shell, the intensities of the absorption peaks of the bare Ag@Au HNS first decrease and then increase. Additionally, the corresponding absorption peak frequencies are continuously redshifted. During the first redshift (curves a to j in Figure 2B) in the absorption spectra, the plasmon energy is greater than the exciton energy, and the absorption by the upper polariton (UP) is higher than that by the lower polariton (LP). At the resonance frequency (approximately 574 nm for LSP peak of the bare Ag@Au HNS, near the J band of the exciton at 575 nm), the LP and UP become almost identical in terms of absorption intensity

and spectral shape (Figure 2C III). When the plasmon energy is less than the exciton energy (<575 nm), the absorption by the UP is lower than that of the LP. A prominent anticrossing behavior between LP and UP occurs, which is a typical characteristic of SC, as shown in Figure 2D.

2.1.2 The second strong coupling

Furthermore, in addition to the occurrence of the first SC, we observed similar anticrossing behavior in the Ag@Au HNS-J-aggregate hybrid system as the LSP peaks blueshift. In the second growth stage, the LSP happened to blueshift (curves p to x of Figure 2A). The LSP peaks of the bare Ag@Au HNS blueshift back toward the resonance peak of the J-band, and then, a second SC occurs. Both the peaks of the LP and UP branches approach the position of the exciton peak (575 nm). The corresponding anticrossing behavior between LP and UP occurs again as shown in Supporting Information Figure S2 (in which the second Rabi splitting is approximately 180 meV). However, due to the limited blueshift of the peaks of the bare Ag@Au HNS, only part of the anticrossing curves reappeared.

2.2 Strong coupling of plasmons and excitons via FDTD simulations

We performed FDTD simulations using the Lumerical FDTD Solutions 8.0 software to reproduce our experimental spectra results and obtain clearer insights onto how the features of the excitonic and the plasmonic systems influence the SC. A perfectly matched layer boundary condition was introduced to avoid reflection and backscattering of the electric field from the preselected boundary. The duration of all simulations was fixed at 500 fs to ensure full electric field convergence. The simulation mesh size was 0.1 nm. The J@NPS geometrical structures were modeled considering the average dimensions obtained from the transmission electron microscopy (TEM) analysis. The model was excited using a total field/scattered field wave with an electrical field amplitude of 1.0 V/m. Johnson and Christy dielectric data [53] were used for modeling the frequency dependence of the dielectric constant of Au, whereas the dielectric function from [54] was used for Ag. The hollow region was filled with a homogeneous air medium with a refractive index of 1. To account for the J-aggregate exciton, the dielectric permittivity was described with a classical one-oscillator Lorentzian model:

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

where f_L is the dimensionless Lorentzian oscillator strength, γ is the spectral width, ω_0 is the absorption maximum, and $\varepsilon(\infty)$ is the background permittivity. The J-aggregate absorption peak was set to 575 nm (2.156 eV) and was further simulated with $f_L=0.8$ and spectral width $\gamma=15$ meV. The parameter of $\varepsilon(\infty)$ used in the calculations was 1.77 which is a typical value for loose molecular layers. The model was placed along the x direction in the x - y plane. The extinction spectra were calculated for HNSs with the Ag shell thicknesses ranging from 10 to 0 nm and Au shell thicknesses ranging from 5 nm to 30 nm. The λ_{LSPR} of the HNS was calculated in the spectral

region of 450–700 nm with an accuracy of 4 nm. The result in Figure 3A demonstrates that the LSPR mode of the HNS exhibits a high sensitivity to the radius of the cavity, which is highly consistent with the experimental measurements in the same spectral region shown in Figure 2A. The dashed line in Figure 3A represents the absorption spectrum of the exciton model as a Lorentzian lineshape. In Figure 3A, the trends in the variations of the plexcitonic features are in very good agreement with the experimental results shown in Figure 2A, as is the anticrossing behavior of the molecular and plasmonic resonances shown in Figure 3B. Specifically, the calculated spectra exhibit a strong dip at the excitonic resonance frequency and two distinct plexcitonic resonances, namely, a higher energy mode on the blue side of

Figure 3: Simulation extinction spectra of HNSs with different thicknesses of the Au shell and exciton-HNS systems.

(A) Simulation extinction spectra of Ag@Au hollow nanoshell with various plasmon resonances obtained by FDTD method. The dashed curve e1 is the absorption spectrum of the exciton, with a Lorentzian lineshape. (B) Typical simulation extinction spectra of HNSs doped with J-aggregate with different thicknesses of the Au shell corresponding to (A). Extinction spectra of the HNS with LSPR at 575 nm strongly coupled to J-aggregates. (C) With various plasmon resonances obtained by FDTD method. The dashed curve e1 is the absorption spectrum of the exciton, with a Lorentzian lineshape. (D) Simulation dispersion curves of the hybrid state energies plotted as a function of their corresponding plasmon resonance. Anticrossing analysis of the plexciton with upper branch ω_+ (the solid blue triangular symbol) and lower branch ω_- (the solid pink triangular symbol); the circle and the square patterns illustrate the uncoupled exciton and plasmon, respectively. Here the Rabi splitting of the first SC is 248 meV, and that of the second SC is 210 meV.

Figure 4: Electric field enhancement distributions on the x-y plane center cross-section of the (I) bare Ag@Au HNS individual nanoparticle with SPR peak at 575 nm; (II) J-aggregate-doped Ag@Au HNS ensemble with SPR peak at the upper branch (ω_+) maximum; (III) J-aggregate-doped Ag@Au HNS ensemble with SPR peak at the minimum; and (IV) J-aggregate-doped Ag@Au HNS ensemble with SPR peak at the lower branch (ω_-) maximum. Here the three columns correspond to E_x , E_y , and E .

the exciton and a lower energy mode on the red side. The SC was realized twice via FDTD simulation. The second anticrossing behavior is clearly shown in Supporting Information Figure S3.

2.3 Anticrossing behavior of plexcitonic states

The anticrossing of the hybrid plexcitonic states at the resonance wavelength of the plasmon and the exciton is another characteristic feature of SC. To further analyze the spectroscopic data of the coupled system in the SC regime, we employ the coupled oscillators model in the Hamiltonian representation:

$$\begin{pmatrix} \omega_{pl} - i\frac{\gamma}{2} & g \\ g & \omega_0 - i\frac{\kappa}{2} \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = \omega \begin{pmatrix} \alpha \\ \beta \end{pmatrix} \quad (2)$$

where ω_{pl} and ω_0 are the energies of the plasmon mode and emitter, respectively; κ is the decay rate of the plasmons; γ is the resonance width of the emitter; g is the coupling strength; and ω is the eigenenergy of the hybrid nanostructure. Parameters α and β are the coefficients of the linear combination of the plasmon and exciton. The eigenvalues of the above matrix correspond to the plexcitonic levels and are given by

$$\omega_{\pm} = \frac{\omega_{pl} + \omega_0}{2} \pm \sqrt{\left(\frac{\omega_{pl} - \omega_0}{2}\right)^2 + \left(g^2 + \frac{(\gamma - \kappa)^2}{4}\right)} \quad (3)$$

When $\gamma = \kappa$, the predicted upper and lower plasmon-exciton branches are in agreement with the famous quantum mechanical Jaynes-Cummings model [11, 27]:

$$\omega_{\pm} = \frac{\omega_{pl} + \omega_0}{2} \pm \frac{1}{2} \sqrt{g^2 + (\omega_{pl} - \omega_0)^2} \quad (4)$$

At resonance, $\hbar\Omega = \Delta\omega = 2\sqrt{g^2 - \frac{1}{16}(\gamma - \kappa)^2} = 225$ meV. This value must fulfill the following strict criterion for SC to occur:

$$\hbar\Omega \geq (\gamma + \kappa) / 2 \quad (5)$$

In our system, the plasmon linewidth of the HNS κ can be extracted to be 404 meV from Figure 2C. The γ of the J-aggregate is extracted to be 179 meV, and in Figure 2D,

Table 1: LSP mode volumes of an HNS and solid Au and Ag nanoparticles at 575 nm.

Structures	Wavelength (nm)	Mode volume (nm ³)
Ag@Au HNS	575	1021.6
Au solid nanosphere	575	32,985.3
Ag solid nanosphere	575	13,918.7

the Rabi splitting $\Omega = 2g = 225$ meV is observed, which satisfies the SC criterion.

2.4 Electric field distributions

Numerical analyses provide more insights into these phenomena. Specifically, we carried out FDTD simulations to determine the electric field distributions in undoped and J-aggregate-doped Ag@Au HNSs. The spatial profiles of the electromagnetic field modes can be redistributed when the HNS couples with J-aggregates. Figure 4(I) shows the x component E_x and y component E_y of the electric field observed on the x - y plane mid-cross-section of the HNS corresponding to the resonance at $\lambda = 575$ nm in the modeled spectrum of the bare HNS. As shown in Figure 4(III), when the HNS couples with J-aggregates, the electromagnetic field distribution of the J-aggregate-HNS system is in the dark mode. Figure 4(II) and (IV) show that the electromagnetic field distribution lies in the upper/lower branch of the splitting maximum. The electromagnetic field is clearly greatly changed in the hollow nanocavity. The results indicate that the hybrid plexcitonic modes possess very different electromagnetic spatial characteristics from those of the uncoupled cavities which would induce the E-field localization of the electric dipole mode and electric quadrupole mode.

The effective volumes of the LSPR modes supported by Ag@Au HNS were calculated by the method as in reference [55] according to the following formula:

$$V = \frac{\int \epsilon(r) |E(r)|^2 dV}{\max \|\epsilon(r) |E(r)|^2\|} \quad (6)$$

In a specific calculation, the electric field distributions inside and around the HNS were calculated at the exciton transition energy using the FDTD simulation. Subsequently, the mode volume used in our study at 575 nm was calculated to be about 1021.6 nm³, which is small enough for the SC in this study. A comparison of this value with those of solid Au and Ag nanoparticles with the same geometrical volume and 575 nm excitation wavelength

is shown in Table 1. The HNS clearly possesses a much smaller effective volume of the LSPR.

3 Conclusions

In conclusion, we have successfully demonstrated the SC in a Ag@Au HNS/J-aggregate hybrid system. The plasmon resonance of the HNS can be precisely tuned to match the exciton excitation of the J-aggregate. The LSPs of the bare HNS are very sensitive to changes in the shell thickness. Then, SC was realized twice through a single preparation process of the Ag@Au HNS by tuning the LSP position (first at lower wavelength and then also at a higher wavelength). The first Rabi splitting is 225 meV. Although the SC at a higher wavelength could only be evidenced by the partial anticrossing behavior, the HNS system may provide a new sensitive system for light-matter interactions. This SC obtained with one HNS system was reproduced by our FDTD simulation, as was the anticrossing behavior, consistent with our experimental results. Furthermore, to interpret our observations, we have calculated the plasmonic mode volume for the HNS system under study. This volume was compared with those of solid Ag and Au nanospheres. The plasmonic mode volume of the HNS is clearly much smaller than those of solid nanospheres with the same physical volume. Our FDTD simulations revealed the E-field spatial distribution both inside and around the HNS, which is a phenomenon that traditional investigations have not studied. These findings have enlarged our understanding of the physical nature of light-matter interactions and provide a novel platform to fabricate complex structures for optical applications.

4 Experimental section

4.1 Sample preparation

4.1.1 Ag@Au HNS synthesis

The Ag nanoparticles were prepared by chemical reduction method following reference [44]. The Ag nanoparticles were dispersed in 36 ml of 12 mM hexadecyltrimethyl ammonium bromide (CTAB) solution and 3 mM ascorbic acid (AA^+) solution (growth solution). Here, CTAB as a surfactants formed a soft micelle template that could be used to control the microscopic size and shape of the grown samples. Then, after every 10 min, different amounts of $HAuCl_4$ solution were added to the dropwise to the growth

solution which are described in the Figure 2 (A) caption in detail. Stirring was continued for 25 min until the growth solution color was stable. Finally, the solution was centrifuged with water to remove excess Cl^- , CTAB, and ascorbic acid (AA^+). The resulting sample in the form of a precipitate was then redispersed in water.

4.1.2 Ag@Au HNS/J-aggregate hybrid fabrication

To trigger the formation of J-aggregates of 1,1'-diethyl-2,2'-cyanine iodide (Cy^+), we utilized the electrostatic interaction between the anionic chloride ion and the cationic dye molecules Cy^+ . The addition of chloride ions is believed to promote the attachment of J-aggregates to Ag@Au HNSs. Before the HNS/J-aggregate hybrids were fabricated, J-aggregates were first prepared. Briefly, 292 mg of NaCl was dissolved in 1 ml of Cy^+ monomer solution (2.5×10^{-5} M) and kept at 85°C for 20 min, and then followed by a cooling process from 85°C to 20°C. In this cooling process J-aggregates gradually formed as demonstrated by the sharp absorption band located at 575 nm shown in Supporting Information Figure S1. The Ag@Au HNS sample and the J-aggregate were mixed in equal parts to obtain the Ag@Au HNS/J-aggregate structure through self-assembly of J-aggregate on the surface of Ag@Au HNSs.

4.2 Characterization

All absorption spectra were obtained using a Shimadzu UV 2401 PC instrument with a high spectral resolution of 0.1 nm. The ready-made solution of Ag@Au HNS and Ag@Au HNS-J-aggregate was placed in 1 ml quartz cells, which were then placed on the sample cell of a UV-visible spectrometer for measurements. High-resolution TEM images were carried in FEI 2.0 (FEI Inc., America) operated at 200 kV. The samples were prepared by drop casting 100 μ l of the solution (same solution as that used for spectroscopic investigations) onto a carbon-coated copper grid, and the solvent was allowed to evaporate.

4.3 Numerical simulations

The theoretical simulations in this paper were carried out using the FDTD method with the software Lumerical FDTD Solutions 8.0 [56].

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