Strong coupling between few molecular excitons and Fano-like cavity plasmon in two-layered dielectric-metal core-shell resonators

WENYANG WU,1 MINGJIE WAN,1 PING GU,1 ZHUO CHEN,1,2,* AND ZHENLING WANG1,2,3

1School of Physics and National Laboratory of Solid State Microstructures, Nanjing University, 22 Hankou Road, Nanjing 210093, China
2Collaborative Innovation Center of Advanced Microstructures, Nanjing University, 22 Hankou Road, Nanjing 210093, China
3zwang@nju.edu.cn
*zchen@nju.edu.cn

Abstract: We theoretically investigate the coupling between molecular excitons and dipolar Fano-like cavity plasmon resonance in two-layered core-shell resonators consisting of a dielectric core with high refractive index and a thin metal outer shell gapped by a low refractive index thin dielectric layer containing molecules. We demonstrate that associated with the excitation of the dipolar Fano-like cavity plasmon, the electric fields can be highly localized within the dielectric gap shell, leading to very small mode volumes. By using the three-oscillator temporal coupled model to describe the proposed plasmon-exciton system, we are able to demonstrate that the coupling between molecular excitons and cavity plasmon resonance can reach the strong coupling regime. Furthermore, we also demonstrate that reducing the thickness or the refractive index of the dielectric gap shell layer can result in further compression of the mode volumes, and consequently decrease the minimum number of the coupled excitons that are required to fulfill the criteria for strong coupling.

©2017 Optical Society of America

OCIS codes: (250.5403) Plasmonics; (230.4555) Coupled resonators; (290.4020) Mie theory.

References and links


36. C. F. Bohren and D. R. Huffman, Absorption and Scattering of Light by Small Particles (Wiley New York, 1983).
1. Introduction

Strong light-matter interactions that can generate new quasi-particles possessing both characteristics of light and matter have attracted a lot of interest in recent years. From the view of fundamental physics, the achievements of strong light-matter interactions can result in many novel phenomena, such as Bose Einstein Condensation of exciton polariton [1,2], quantum vortices [3], entangled photon pairs [4], and polariton bistability [5]. On the other hand, they also show great potential in the applications of quantum cryptography [6], quantum networks [7], single atom lasers [8], spin-optronic devices [9], and ultrafast single photon switches [10], etc. Optical microcavities including distributed Bragg reflector (DBR) based planar cavities [11], photonic bandgap cavities [12,13], micropillars [14], and microdisk cavities [15] have been widely exploited to provide well confined photons, and thus facilitating the strong interactions between light and excitons, such as atoms [16], quantum dots [14], quantum wells [1,17,18], semiconductor materials [19,20], organic layers [21,22] and two-dimensional materials [23]. Recently, instead of using these traditional microcavities with sizes being much larger than the wavelength of the incident light, metallic nanostructures have been employed as a platform to investigate light-matter interactions in the strong coupling regime [24–32], mainly due to their ability to support surface plasmon resonances (SPRs) and concentrate light into nanoscale volumes even when the nanostructure sizes are much smaller than the resonance wavelengths. For example, strong plasmon-exciton interactions have been demonstrated with different types of plasmonic systems, such as propagating SPRs in planar metal films [27], localized SPRs in metallic nanoparticles [24], and plasmonic Fano resonances in nanoparticle arrays or assemblies [32]. The emphasis in most of the aforementioned studies has been largely on the optical cavity or plasmon modes coupled to a large number of excitons and the realization of giant Rabi splitting, while relatively little attention has been given to achieving few molecule- or exciton-level strong coupling [33–35].

In this paper, we demonstrate that plasmonic core-shell resonators (CSRs), consisting of a high refractive index (HRI) dielectric core and a thin metal shell gapped by a low refractive index (LRI) dielectric shell layer, can support Fano-like cavity plasmon resonances with the electric fields being highly localized within the LRI dielectric gap layer and hence the small mode volumes. By introducing J-aggregate molecules into the LRI dielectric gap shell layer, we show that the plasmonic Fano resonance can be coupled to the molecular excitons, which lead to the observation of a Rabi splitting of 109 meV in the extinction spectrum. By using the three-oscillator temporal coupled model to describe the proposed plasmon-exciton system, we are able to confirm that such a coupling can reach the strong coupling regime. Furthermore, by investigating the effect of the shell thickness and refractive index of the dielectric gap layer, and the concentration of the molecules on the coupling strength, we also demonstrate that...
reducing the thickness or the refractive index of the dielectric gap shell layer can result in further compression of the mode volumes, and consequently decrease the minimum number of the coupled excitons that are required to fulfill the criteria for strong coupling.

2. Results and discussions

As schematically shown in Fig. 1(a), the proposed two-layered plasmonic CSR is composed of a HRI dielectric core (radius: \(r_{\text{in}}\)) surrounded successively by a LRI dielectric shell layer (thickness: \(d\)) and a thin metal shell (thickness: \(t\)). Throughout this paper, the problem of scattering (extinction) of a plane wave by the spherical concentric core-shell particles is solved analytically using Mie theory [36]. In the calculations, the metal is assumed to be silver and its permittivity is taken from the experimental data of Johnson and Christy [37]. The radius and refractive index of the HRI dielectric core are fixed to \(r_{\text{in}} = 45\) nm and \(n_{\text{core}} = 3.4\). Figure 1(b) shows the extinction spectrum calculated for a two-layered plasmonic CSR, in which the silver shell thickness is \(t = 14.5\) nm, the thickness and refractive index of the LRI dielectric gap shell layer are \(d = 6\) nm and \(n_d = 1.5\), respectively. A distinct extinction peak with a Fano line-shape is clearly observed around the energy of \(E = 1.79\) eV. In order to interpret the origin of the observed Fano resonance, the spatial distribution of the electric field magnitude (\(|E|\)) is calculated and plotted in Fig. 1(c). It is clearly seen from Fig. 1(c) that most of the electric fields are confined within the cavity formed by the silver shell, and a small portion of the fields are distributed outside the silver shell. In particular, the outside and inside field distributions are found to have the same two-fold symmetry, confirming that the occurrence of the interactions between the dipolar cavity and sphere plasmons is the origin of the observed Fano resonance. In remarkable contrast to our previously reported single-layered plasmonic CSRs with a homogenous dielectric core, where the electric fields are distributed within almost the whole cavity [38], the electric fields in the proposed two-layered CSRs are found to be concentrated into the LRI thin dielectric gap layer [Fig. 1(c)]. The mode volume of the Fano-like cavity plasmon resonance, which can be calculated according to the equation of

\[
V_m = \frac{1}{\max \{W(r)\}} \iiint W(r) d^3r
\]

with \(W(r)\) being the energy density, is found to be as small as \(V_m = 1.26 \times 10^5\) nm\(^3\).
Fig. 2. (a) Extinction spectra of the plasmonic CSRs without (top panel) and with molecules (middle panel), and absorption spectra of the CSRs with molecules (bottom panel). The dielectric shell thickness is fixed to $d = 6$ nm. Horizontal dashed line indicates the transition of molecular excitons. Vertical dashed line indicates the silver shell thickness of $t = 14.5$ nm where the CSR reaches the on-resonance condition. (b) Extinction and absorption spectra of the molecule-doped CSR with the particular parameters of $d = 6$ nm and $t = 14.5$ nm.

In the following, we demonstrate that the Fano-like dipolar cavity plasmon can be coupled to the molecular excitons. Since the electric fields are mostly confined within the LRI dielectric gap shell [Fig. 1(c)], the J-aggregate molecules are introduced into the LRI dielectric layer to take full use of the enhanced fields. In this case, the dielectric function of the dielectric gap shell layer doped with J-aggregate molecules is described by Lorentz oscillator model

$$
\epsilon_f(\omega) = \epsilon_\infty + \frac{f \omega_e^2}{\omega_e^2 - \omega^2 - i\gamma_e \omega},
$$

where $\epsilon_\infty = n_i^2 = 2.25$ is the dielectric constant of the dielectric matrix, $f = 0.03$ is the reduced oscillator strength of the molecular excitons, $\omega_e = 1.79$ eV and $\gamma_e = 52$ meV are the transition energy and the damping rate of the exciton, respectively [24].

The extinction spectra of the plasmonic CSRs without molecules are plotted in the top panel of Fig. 2(a), in which the LRI dielectric shell thickness is fixed to $d = 6$ nm while the silver shell thickness is varied from $t = 8$ nm to $t = 20$ nm. It is clearly seen from the top panel of Fig. 2(a) that the cavity plasmon blue-shifts to the higher energy (shorter wavelength) with increasing the silver shell thickness. After J-aggregate molecules are introduced into the thin LRI dielectric gap layer, the extinction spectra presented in the middle panel of Fig. 2(a) show a distinct anti-crossing behavior as the energy of the cavity plasmon resonance is varied across the exciton transition of the molecules by changing the silver shell thickness. Such a splitting is also observed in the total absorption spectra of the plasmonic CSRs with molecules, as shown in the bottom panel of Fig. 2(a). For a two-layered CSR with a dielectric gap shell thickness of $d = 6$ nm, the Fano-like cavity plasmon resonance can be tuned to overlap with the exciton transition energy of $1.79$ eV [the horizontal dashed line in Fig. 2(a)] when the silver shell thickness is taken to $t = 14.5$ nm [the vertical dashed line in Fig. 2(a)]. Figure 2(b) shows the extinction spectrum (blue curve) of the molecule-doped CSR with the particular parameters of $d = 6$ nm and $t = 14.5$ nm, from which the vacuum Rabi splitting energy of $\hbar \Omega = 109$ meV can be directly obtained from the energy difference between the two plexciton modes. In addition, the total absorption spectrum (red curve) together with the individual contributions from the silver shell (dark-yellow curve) and molecules (green curve) are also shown in Fig. 2(b), which confirm that both constituents exhibit the splitting behavior. Therefore, the observation of
splitting not only in the extinction spectrum but also in the absorption spectrum reveals the occurrence of the strong coupling between exciton and cavity plasmon [39].

Usually, a two-oscillator coupled model is employed to fit the anti-crossing behavior on the energy diagram [40,41], which however is not suitable in our case because of the involvement of the plasmonic Fano resonance in the coupling. Hence, we propose a one-port assisted three-oscillator temporal coupled model to describe the coupling process. As already have been demonstrated above, the Fano resonance in the plasmonic CSRs is owing to the interference between the dipolar cavity plasmon and sphere plasmon modes. In the temporal coupled model, these two modes act as two bright oscillators, and the massive molecular excitons are viewed as a giant dark oscillator. For simplicity, the cavity plasmon mode is assumed to be lossless, and all loss is attributed to the sphere plasmon mode. The interaction among excitons is neglected due to the low concentration of J-aggregate molecules (the reduced oscillator strength, \( f = 0.03 \)). The molecular excitons are also assumed to have no interactions with the sphere plasmon mode and can be coupled only to the cavity plasmon mode. The whole system is assumed to have only one port for the incident and outgoing energy flux. Under these assumptions, the one-port assisted three-oscillator temporal coupled model can be expressed as,

\[
\begin{align*}
\frac{dP_{p1}}{dt} & = -j\omega_p P_{p1} + j\kappa_{le} P_e + j\kappa_{12} e^{j\phi} P_{p2} + \sqrt{\gamma_1} s_e, \\
\frac{dP_{p2}}{dt} & = -j\omega_p P_{p2} - \frac{\gamma_e}{2} P_{p2} + j\kappa_{1e} P_{p1}, \\
\frac{dP_e}{dt} & = -j\omega_e P_e - \frac{\gamma_e}{2} P_e + j\kappa_{1e} e^{j\phi} P_{p1} - j\sqrt{\gamma_2} s_e,
\end{align*}
\]

\[
s_+ = s_+ + \sqrt{\gamma_1} P_{p1} + j\sqrt{\gamma_2} P_{p2},
\]

\[
E_{\text{inner}} = |s_+|^2 - |s_-|^2
\]

Here, \( P_{p1}, P_{p2}, \text{ and } P_e \) are, respectively, the amplitudes of the cavity plasmon, sphere plasmon, and the exciton oscillators, \( \omega_{p1}, \omega_{p2}, \text{ and } \omega_e (\omega_e = 1.79 \text{ eV}) \) are their corresponding resonant frequencies, \( \gamma_{p2} \text{ and } \gamma_e (\gamma_e = 52 \text{ meV}) \) are the damping rates of the sphere plasmon and exciton oscillators, respectively. In the coupling between cavity and sphere plasmon oscillators, \( \kappa_{12} \) represents the coupling strength and \( \phi \) is the phase difference between these two plasmon oscillators. \( \kappa_{1e} \) represents the coupling strength of the coupling between the cavity plasmon and exciton oscillators. \( \gamma_{1s} \text{ and } \gamma_{2s} \) represent the coupling rates in the coupling of incident energy flux to the bright cavity and sphere plasmon oscillators, respectively. \( s_+ \) and \( s_- \) are the amplitudes of the incident and outgoing energy flux, respectively. It should be noted that the scattering contribution is excluded from the outgoing energy and virtually considered as a kind of absorption in the temporal coupled model. In this way, \( E_{\text{inner}} = |s_+|^2 - |s_-|^2 \) [Eq. (5)] represents the extinction of the system, because the extinction is the sum of the absorption and scattering [36].

It is obvious that for \( \kappa_{1e} = 0 \), the three-oscillator temporal coupled model is reduced to a two-oscillator model and actually describes the coupling between the cavity and sphere plasmon modes in the plasmonic two-layered CSRs without molecules. Therefore, all the parameters except for \( \kappa_{1e} \) in Eqs. (1)–(5) can be extracted from the temporal coupled model fitting to the extinction spectrum of the CSRs without molecules calculated using Mie theory. Consequently, with those obtained parameters, the coupling strength \( \kappa_{1e} \) can be extracted by fitting the extinction spectrum of the molecules-doped CSRs calculated using Mie theory with the temporal coupled model. As a representative example, Figs. 3(a) and 3(b) show the Mie theory calculation and the fitting results for the un-doped and doped plasmonic CSRs with the
silver shell thickness of $t = 14.5$ nm. The fitting results [solid lines in Figs. 3(a) and 3(b)] are found to be in excellent agreement with the calculated extinction spectra [open circles in Figs. 3(a) and 3(b)]. Such a two-step fitting process is then applied to the doped CSRs with the same dielectric gap shell thickness of $d = 6$ nm but different silver shell thicknesses. All the peak positions taken from the fitted and the theoretically calculated extinction spectra are plotted in Fig. 3(c) as a function of the silver shell thickness $t$, in which excellent agreement is obtained between the fit [solid line] and the theoretically calculated data [open circles], indicating that the proposed three-oscillator temporal coupled model with our assumptions can accurately describe the Fano resonance involved plasmon-exciton system. In addition, the extracted coupling strengths are summarized in Fig. 3(d). It has already been demonstrated in Fig. 2 that when the silver shell thickness is taken to $t = 14.5$ nm, the Fano-like cavity plasmon resonance energy for a two-layered CSR with a dielectric gap shell thickness of $d = 6$ nm can overlap with the molecule transition energy. As indicated by a vertical dashed line in Fig. 3(d), the coupling strength at the silver shell thickness of $t = 14.5$ nm is found to reach the value of $\kappa_{ic} = 57$ meV. The interactions between the exciton transition and optical resonances can be regarded as the strong coupling, when the coupling strength is larger than a critical value of $\kappa_s = \sqrt{\gamma_e^2 + \gamma_r^2}/8$, where $\gamma_e = 52$ meV is the exciton transition energy and $\gamma_r$ is the linewidth of the resonance. For the Fano resonance supported by the undoped CSR with $t = 14.5$ nm and $d = 6$ nm, its linewidth extracted from the Fano fitting [44] of the extinction spectrum calculated using Mie theory [Fig. 1(b)] is $\gamma_r = 88$ meV. Therefore, the critical coupling strength in this case is $\kappa_c = 39$ meV, which is smaller than the obtained coupling strength of $\kappa_{ic} = 57$ meV, demonstrating the system satisfies the strong coupling condition.
So far, we have only demonstrated that the achievement of the strong coupling in a two-layered plasmonic CSR with the silver shell and dielectric gap shell thicknesses being taken to $t = 14.5$ nm and $d = 6$ nm so that the Fano-like cavity plasmon energy overlaps with the exciton transition energy. Actually, for such a CSR even with the fixed core radius ($r_{in} = 45$ nm) and refractive index ($n_{core} = 3.4$), there are still three degrees of freedom including the silver shell thickness ($t$), the dielectric gap shell thickness ($d$) and refractive index ($n_d$). The extinction efficiency spectra are, respectively, calculated for the un-doped CSRs with the fixed dielectric gap shell refractive index of $n_d = 1.5$ and the fixed dielectric gap shell thickness of $d = 6$ nm, while varying the rest of the two parameters. The energies of the Fano-like plasmon resonances are collected from those spectra and plotted in Fig. 4(a) for the case of $n_d = 1.5$ as functions of $d$ and $t$, and in Fig. 4(b) for the case of $d = 6$ nm as functions of $n_d$ and $t$. By directly connecting points where the Fano-like cavity plasmon resonance appears at the same particular energy, for example, $E_{res} = 1.79$ eV, two dashed lines can be obtained in Figs. 4(a) and 4(b), which indicate that multiple choices of the parameters can make the CSRs support the Fano-like cavity plasmon resonance with the same energy. The mode volumes of the Fano resonances with the energy of 1.79 eV are further calculated for the CSRs at the points along the dashed lines shown in Figs. 4(a) and 4(b), and plotted in Fig. 4(c) as a function of $d$ and in Fig. 4(d) as a function of $n_d$, respectively, in which each $d$ and each $n_d$ is corresponding to a determined silver shell thickness $t$. It is seen that with reducing either the thickness ($d$) or the refractive index ($n_d$) of the dielectric gap shell layer, the Fano-like cavity plasmon resonances can exhibit gradually decreased mode volumes [red line with circles in Figs. 4(c) and 4(d)], which is highly desired to improve the coupling between the excitons and the Fano-like cavity plasmons. Meanwhile, the linewidths of the Fano resonances ($\gamma$) are also found to be increased and decreased with increasing the thickness ($d$) and the refractive index ($n_d$) of the dielectric gap shell layer, respectively [blue line with squares in Figs. 4(c) and 4(d)].

![Fig. 4. The equi-energy plot of the Fano resonance for the case of $n_d = 1.5$ as functions of $d$ and $t$ (a), and for the case of $d = 6$ nm as functions of $n_d$ and $t$ (b). The dashed lines in (a) and (b) indicate the 1.79 eV contours. The mode volumes (red line with circles) and damping rates (blue line with squares) of the Fano resonances with the energy of 1.79 eV are plotted as a function of the LRI dielectric shell thickness of $d$ (c) and as a function of the LRI dielectric shell refractive index of $n_d$ (d).](image)

It has been demonstrated that the strength of the coupling between excitons and a resonance mode can also be described as

$$\kappa_{re} = \sqrt{N} \mu_j |E_{vac}|,$$

(6)
where \( N \) is the number of the excitons that are involved in the coupling, \( \mu_J \) is the dipole moment of excitons, and \( E_{\text{vac}} = \sqrt{\frac{\hbar \omega}{2 \varepsilon_0 V_m}} \) is the vacuum electric field with \( V_m \) being the mode volume [33, 42, 43]. Since the reduced oscillator strength \( f \) is proportional to the density of excitons (so the coupled excitons \( N \) [42] and the coupling strength is proportional to \( \sqrt{N} \) according to the Eq. (6), the coupling strength \( \kappa_{1e} \) is thus expected to be proportional to \( \sqrt{f} \). By using the same three-oscillator temporal coupled model based two-step fitting process described in Fig. 3, the coupling strengths \( (\kappa_{1e}) \) of the interactions between the excitons and the Fano-like cavity plasmon resonances having the same energy of 1.79 eV are extracted for the doped CSRs with the molecular excitons having different reduced oscillator strengths \( (f) \) and the specified parameters located in the dashed lines shown in Figs. 4(a) and 4(b), and are plotted as a function of \( \sqrt{f} \) in Figs. 5(a) and 5(b), respectively. As expected, in all cases the coupling strength \( \kappa_{1e} \) is linearly increasing with \( \sqrt{f} \) [Figs. 5(a) and 5(b)]. For a fixed reduced oscillator strength \( f \), it is seen from Fig. 5(a) that the coupling strength increases with increasing the gap shell thickness [Fig. 5(a)], mainly because the dielectric gap shell layer with larger physical volume can contain more molecular excitons. It is also found that the coupling strength decreases with increasing the gap shell refractive index [Fig. 5(b)], which could be attributed to the larger mode volume for the larger gap shell refractive index [Fig. 4(d)].

Fig. 5. (a) and (b) The dependencies of the coupling strengths of the interactions between the excitons and the Fano-like cavity plasmon resonances having the same energy of 1.79 eV supported by the CSRs with the specified parameters located in the dashed lines shown in Figs. 4(a) and 4(b) on \( \sqrt{f} \), respectively. The dashed lines are linear fit. (c) and (d) Strong coupling criteria \( \kappa_{1e}/\kappa_c \) on dependence of the numbers of coupled excitons \( N \) for different \( d \) and \( n_d \), respectively. The horizontal dashed lines indicate \( \kappa_{1e}/\kappa_c = 1 \).
Furthermore, according to the Eq. (6), the number of the excitons that contribute to the coupling in each case shown above can be calculated by 

\[ N = \frac{\kappa_{1e}^2 \epsilon e V_m}{\mu J^2 \hbar \omega} \]

where the dipole moment of excitons is assumed to be \( \mu_J = 20 \) Debye \[33\], the corresponding coupling strength \( \kappa_{1e} \) is taken from Figs. 5(a) and 5(b), and the mode volume \( V_m \) is taken from Figs. 4(c) and 4(d). Since the linewidths \( (\gamma_r) \) of the Fano-like cavity plasmon resonances with the same energy of 1.79 eV supported by the CSRs with different specified parameters are different [Figs. 4(c) and 4(d)], the critical coupling strength of \( \kappa_c = \sqrt{\left(\gamma_r^2 + \gamma_r^2\right)/8} \) in each case is thus different. In order to determine whether the system satisfies the strong coupling condition, the ratio \( (\kappa_{1e}/\kappa_c) \) of the obtained coupling strength to the critical coupling strength is calculated in each case and plotted in Figs. 5(c) and 5(d) as a function of the number of the excitons involved in the coupling \( (N) \), where \( \kappa_{1e}/\kappa_c > 1 \) represents the strong coupling regime. It is seen from Fig. 5(c) that the least number of the coupled excitons that are required to fulfill the criteria for strong coupling is decreased with decreasing the dielectric gap shell thickness. Such a least number is also found to be decreased with decreasing the dielectric gap shell refractive index [Fig. 5(d)]. For example, for a plasmonic two-layered CSR with \( n_d = 1.0 \) and \( d = 6 \) nm, the least number of the coupled exciton is estimated to be as small as \( N = 56 \) [red cross in Fig. 5(d)]. It is worth noting that the least number of the coupled excitons that are required to fulfill the criteria for strong coupling could become even smaller if the dielectric gap shell thickness is further reduced.

3. Conclusions

In conclusion, we demonstrate that the strong coupling to molecular excitons can benefit from the strongly enhanced electric fields that are localized in the gap layer of the proposed two-layered plasmonic CSRs at the Fano-like dipolar cavity plasmon mode. The splitting behavior is observed not only in the extinction spectrum but also in the absorption spectrum, which indicates that the coupling between molecular excitons and cavity plasmon resonance can reach the strong coupling regime. By further using the three-oscillator temporal coupled model to describe the coupling process, we demonstrate that reducing the thickness or the refractive index of the dielectric gap shell layer can decrease the minimum number of the coupled excitons that are required to fulfill the criteria for strong coupling. We suggest that the proposed CSRs could be practically implemented by using a fabrication procedure consisting of three steps: synthesis of silicon nanospheres (HRI dielectric cores) by trisilane thermolysis [45] or femtosecond laser ablation [46], coating of a polymer dielectric layer (LRI dielectric shell) containing molecules with a seeded emulsion polymerization approach [47], and wrapping of a silver shell on the outer surfaces of the as-prepared nanoparticles with physical deposition process [38, 44] or wet-chemistry method [48, 49]. Our proposed plasmonic CSRs can be operated individually without the need of the support of substrate and have a silver outer shell that can prevent the molecules within the gap layer from being influenced by the outer environment, which might be useful for many applications such as sensing and manipulation. We hope our study could promote the study of strong interactions between plasmon and excitons.

Funding

National Natural Science Foundation of China (NSFC) (11674168, 11474215, 91221206, 11274160, 51271092).