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Optically induced crossover from weak to strong coupling regime between surface plasmon polaritons and photochromic molecules

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Abstract: We demonstrate optically induced crossover from a weak to a strong coupling regime in a single photonic system consisting of propagating surface plasmon polaritons (SPPs) on a planar silver film and ultraviolet (UV)-switchable photochromic molecules. A gradual increase is observed in the vacuum Rabi splitting upon increasing UV exposure, along with intriguing behavior, where the reflectivity initially decreases due to increased losses at the weak coupling regime, and then increases due to the emergence of strongly coupled modes and the associated band gap formation at the resonance frequency of the uncoupled states. This work explicitly demonstrates the optical tunability of the degree of hybridization of the SPP and exciton modes, spanning the range from weak to intermediate and finally to the strong coupling regime.

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1. Introduction

Control over light-matter interactions forms the basis for many modern-day technologies [1,2]. The field of plasmonics focuses on optical modes, where the collective motion of charge carriers in a metal or a highly doped semiconductor is driven with light. These modes can also be found in subwavelength structures that allow confining and manipulating light down to nm³ mode volumes [3]. The field confinement to subwavelength length scales results in stronger light-matter interactions in the reduced mode volume, making it possible, for example, to create efficient sensors [4] and fast optoelectronic modulators for integrated optics [5]. Field confinement in plasmonic structures has also enabled the observation of the interactions between dye molecules and optical fields in the weak, strong, [6] and even ultrastrong [7,8] coupling regimes.

In the strong coupling regime, a coherent exchange of energy between plasmons and dye molecules results in new hybrid modes that are coherent superpositions of a plasmon excitation and excitations in the dye molecules. Various systems supporting localized surface plasmon resonances (SPRs) or propagating surface plasmon polaritons (SPPs) have been shown to strongly couple with both organic [9–11] and inorganic [12] materials as well as to influence chemical reactions [13]. Recently, strong coupling between a single emitter and a plasmonic cavity was demonstrated at room temperature [14]. Theoretically, one of the requirements to observe strong coupling is that the oscillators (SPPs and dye molecules) should have sufficiently narrow linewidths compared to the strength of the coupling [6]. However, Rabi splitting has been experimentally demonstrated for various systems with broad linewidths [7,15–17], indicating that strong coupling is not only limited to narrow-linewidth dyes such as J-aggregates [9]. The advantage of using organic dyes in strong coupling is their small size, providing numerous
oscillators in the small mode volume of the SPP modes (the coupling strength scales with the square root of the number of molecules [6]). In addition to providing easy control over the number density, organic molecules display unique features beneficial for controlling light-matter interactions. Photochromic molecules [18], in particular, allow for optical control over the molecular conformation, enabling reversible photoswitching between at least two (meta)stable states with different properties. When incorporated into materials, the photochromic switches enable all-optical control over a multitude of parameters, such as color, optical properties, dielectric properties, and surface characteristics [19]. Over the years, many different types of photochromic molecular switches have been developed, with the most popular ones being diarylethenes [20], azobenzenes, [21] and spiropyans (SPs) [22]. In plasmonic applications, SP molecules have been used as optically controlled switches to control the propagation of SPPs [23], to tune the plasmonic resonances of nanoantennas [24,25], and for strong coupling with nanostructured metal resonators [7,16,17]. This diversity of applications highlights the possibility of using photochromic molecules as a tuning tool for active plasmonics [26] and for tunable photonics in general. Active plasmonics, in particular, is an important development, as reversible adjustment of the resonances in a system helps to alleviate fabrication challenges and facilitates studies where the resonances are continuously tuned across a range of values.

Here, we experimentally demonstrate a mechanism for optical tuning from a weak to a strong coupling regime in a system consisting of a planar Ag film and photochromic SP molecules. We continuously increase the number of optically active molecules (and therefore the coupling strength) in the system by exposing the photochromic molecules to UV radiation. The experimental results match with the predictions from transfer matrix calculations and a simple coupled oscillator model.

Contrary to previous work on microcavities and hole arrays [7], the detailed study of the time evolution of a system at the uncoupled resonance wavelength reveals two distinct regimes: 1) a gradual decrease in reflectivity, and 2) a gradual increase in reflectivity upon continuous UV exposure. We associate the two regimes with increased losses at the weak coupling regime due to increasing absorption of the molecular film and decreased optical density of states due to vacuum Rabi splitting at the strong coupling regime. By employing a semiclassical coupled oscillator model, we calculate the relative weights of the hybrid modes and demonstrate optically tunable superposition of states in a single system. By using relatively low light intensities (below 12 W/m², similar to that in Ref. [15]), we ensure that the studies are performed within the vacuum Rabi splitting limit, where the system holds only 0 or 1 photons at any instant. In this case, a single photon interacts coherently with a (UV-tunable) number of optically active molecules, enabling the applicability of results in the field of quantum optics. Finally, we study the reversibility of the system by repetitive cycling between the absorbing and non-absorbing states. This study is particularly relevant for the field of plasmonics, where active tunability still remains one of the most prominent challenges.

2. Materials and methods

The samples were fabricated on 22 × 22 mm² borosilicate substrates with 0.175 mm thickness. The glass substrates were cleaned in an ultrasonic bath with acetone and isopropanol for 3 min each, followed by nitrogen blow drying at room temperature. Before metal deposition, the substrates were further cleaned by minute oxygen plasma treatment (1 min). A 50 nm-thick film of silver was then thermally evaporated on the substrate (see Supplement 1 Fig. S1 for a numerical study on the effect of the metal thickness on the strong coupling). On top of the metal layer, a 50 nm-thick SP-containing PMMA (950K, anisole solvent, Allresist) film was then deposited by spin coating. The SP derivative used was 1’,3’-dihydro-1’,3’,3’-trimethyl-6-nitrospiro[2H-1-benzopyran-2,2’-(2H)-indole] (Sigma Aldrich, 98 %). The concentration of
the SP molecules in the film was 70 mM. All chemicals were used as received without further purification.

The optically transparent closed-ring SP moiety is known to convert to a highly dipolar and metastable, open-ring merocyanine (MC) form upon UV irradiation [22], as shown in Fig. 1(a). Due to the planar structure and extended pi-conjugation of the MC form, the SP \( \rightarrow \) MC photoconversion gives rise to strong low-energy absorption, typically in the wavelength range of 550 - 600 nm. This is evident from Fig. 1(b), which displays the spectral changes in the SP-containing PMMA film on a glass substrate (without the silver film) in the visible range upon UV illumination (365 nm, 1 W). After 15 s irradiation, the initially transparent (black dashed line) film starts to absorb at 580 nm due to the SP \( \rightarrow \) MC photoconversion (magenta line) and within a few minutes, the absorption saturates to slightly below 0.2 (green line), indicating that the photostationary state has been reached. The conversion is reversible, and MC \( \rightarrow \) SP isomerization occurs either thermally or upon irradiation within the visible absorption band, providing means for reversible and cyclic control over the materials properties [22]. The photoswitching process can be extremely fast in solution at the picosecond time scale [27]. In a polymeric environment, the switching dynamics are greatly altered and the time to reach photostationary state typically ranges from seconds to minutes. The most likely limitation is the photon flux of the UV light source.

Kretschmann’s configuration [28], shown in Fig. 1(c), was used to characterize the composite system. The glass sides of the samples were attached to the flat side of a half-cylinder-shaped borosilicate prism with index-matching oil. A P-polarized white light source was collimated and spatially limited with an aperture to hit the silver film from the glass side at an angle \( \alpha \). The reflected light from the frustrated total internal reflection was collected with an optical fiber to a spectrometer (Avantes, AvaSpec 2048). The angle \( \alpha \) was varied to change the in-plane momentum of the incident light.

3. Results and discussion

To characterize the system dispersion, the wavelengths of the reflectivity minima with different angles of incidence were obtained for different UV exposure times. The mode dispersions were calculated as \( E = hc/\lambda \) and \( k_{SPP} = n \cdot \sin(\alpha) \cdot 2\pi/\lambda \), where \( n \) is the refractive index of the substrate. We observe either one or two minima in the modal dispersion data for each \( k_{SPP} \) as a function of energy. With a single minimum, the system is in the weak coupling regime. When there are two minima, we consider the system to be in the strong coupling regime when the coupling strength exceeds the linewidths of the modes [6]. We use the term "intermediate
coupling” whenever two minima can be distinguished from the spectra, but their separation does not exceed the linewidths of the uncoupled modes.

Depending on the UV exposure of the molecule film on top of the silver layer, the system can be tuned from weak to strong coupling. Figure 2(a) shows the measured absorption spectra for the intermediate and strong coupling cases as well as the obtained strong coupling spectrum from the model. Figure 2(b) displays the mode dispersions (locations of the observed reflection minima) for the weak, intermediate, and strong coupling regimes. In the weak coupling regime (black symbols), the molecules are in their native conformation (SP), with negligible absorbance at 580 nm, as seen in Fig. 1(b). Correspondingly, the dispersion is composed of a single branch. After 15 s of UV exposure (magenta symbols), band bending and anticrossing are observed at the energy corresponding to the absorption maximum of MC form. Both features are typical signatures of increased coupling. A Rabi splitting of 100 meV can be readily obtained for this case. A further increase in the UV exposure (300 s, green symbols) induces a larger splitting of 300 meV. Figure 2(c) shows the expected linear dependence of Rabi splitting with the square root of absorbance [6]. The angle-resolved modal dispersion and the reflectance spectra are presented as Figs. S2 and S3 in Supplement 1.

To model the reflectance spectrum of the system, a transfer matrix method based on Fresnel equations [29,30] for a multilayer stack was used. We calculated the reflectivity spectra as a function of the incident angle, and recorded the position of the dips. These are plotted for the weak, intermediate, and strong coupling cases in Fig. 2(b) using different oscillator strengths for the dye absorption transition.

For SP-doped PMMA, the complex dielectric permittivity was calculated as a function of frequency using the Drude-Lorentz approach [31], where electrons are considered as two damped harmonic oscillators:

\[ \epsilon(\omega) = \epsilon_s + \sum_{i=1}^{2} \frac{A_i \omega_0^2}{\omega_0^2 - \omega^2 - i\omega \gamma_i}, \]

Here, \( \epsilon_s = 1.88 \) is the background dielectric permittivity of PMMA, \( A_i \) is a dimensionless parameter that characterizes the oscillation strength at the resonance frequency \( \omega_0 \), and \( \gamma_i \) is the damping parameter. Note that due to the non-Gaussian absorption lineshape of the photochromic molecules, we model the lineshape with two oscillators (Table S1 in Supplement 1) for each of
We used experimental data from Johnson and Christie [32] for the dielectric permittivity of silver. There was a good agreement between the experimental results and the calculated curves, as shown in Figs. 2(a) and 2(b).

In the strong coupling regime, the excitations in the system become coherent superpositions of the uncoupled modes (SPPs and molecular excitations in the dye). In order to analyze the coupling strengths, we interpret the experimental data by solving the eigenvalue problem below [9,15,33]:

\[
\begin{pmatrix}
E_{\text{spp}}(k) - i\gamma_{\text{spp}} & \Omega \\
\Omega & E_{\text{EX}} - i\gamma_{\text{EX}}
\end{pmatrix}
\begin{pmatrix}
\alpha \\
\beta
\end{pmatrix}
= E_c
\begin{pmatrix}
\alpha \\
\beta
\end{pmatrix}
\]  

(2)

where the parameters \(E_{\text{spp}}\) and \(E_{\text{EX}} = 2.23\ eV\) are the energies of the SPP and the absorption maximum of the photochromic molecules, and \(\gamma_{\text{spp}} = 0.10\ eV\) and \(\gamma_{\text{EX}} = 0.12\ eV\) are the linewidths of the SPPs and the exciton, respectively. Only one transition is included for the dye in this model, as only a single avoided crossing is seen in the experimentally observed dispersions. The energy of the coupled state is given by \(E_c\), and \(\alpha, \beta\) are the coefficients for the SPP and molecular excitation in the coupled eigenstate, respectively. The coupling strength \(\Omega\) and linewidth for the molecular transition \(\gamma_{\text{EX}}\) were varied to obtain the best possible match between the model and the experimental data. The energy, linewidth, and wavevectors for the uncoupled SPP modes were obtained from the weak coupling transfer matrix method calculations described in the previous section [34,35].

The coupled modes can be described as a superposition of the SPP state with an amplitude \(|\alpha|^2\), and the molecular transition with an amplitude \(|\beta|^2\). These coefficients are normalized, i.e. \(|\alpha|^2 + |\beta|^2 = 1\). The amplitudes for the SPP and molecular excitations are shown in Fig. 3(a) for the weak, intermediate, and strong coupling cases. For each \(E_{\text{spp}}(k_{\text{spp}})\), one can find two solutions for Eq. (2), corresponding to the two branches seen in the dispersion plots. When \(|\alpha|^2 = |\beta|^2 = 0.5\) at the crossing point of the uncoupled resonances, the distance between the two branches in the dispersion is minimized and takes the value of \(\Omega\). The dispersions obtained from the coupled mode model are compared with the experimental results in Figs. 3(b) and 3(c), for the intermediate and strong coupling cases, respectively. For the intermediate coupling case, we find \(\Omega_{\text{int}} = 0.16\ eV\), and for the strong coupling case, we find \(\Omega_{\text{strong}} = 0.29\ eV\).

In the intermediate coupling case with the short-duration (15 s) UV exposure, the lower energy branch is very SPP-like at low \(k_{\text{spp}}\) values, as shown with a solid magenta line in Fig. 3(a). At approximately \(k_{\text{spp}} = 1.4 \times 10^7\ 1/m\), the mode even exhibits 50-50 distribution, and becomes increasingly exciton-like at high \(k_{\text{spp}}\) values. Expectedly, the higher energy mode (dashed magenta line) behaves in the opposite manner, starting out as very exciton-like at low \(k_{\text{spp}}\) values and turning into very SPP-like at high \(k_{\text{spp}}\) values. By increasing the UV exposure time to 300 s, however, the sample behaviour changes. Both, lower and higher energy modes, become strongly hybridized for a broad range of \(k_{\text{spp}}\) values. To our knowledge, our results constitute the first demonstration of an optically tunable degree of hybridization in a single nanophotonic system. By controlling the UV exposure time, we can gradually increase the coupling strength, allowing optical control over the system response. This kind of gradual introduction of strong coupling in as simple a system as ours offers unique possibilities to study, for instance, how the time dynamics of strong coupling [36] change as a function of the coupling strength. Utilizing a single sample that can be optically tuned avoids the uncertainties associated with manufacturing separate structures for each coupling strength. Next, we will discuss the evolution of the system as a function of the UV exposure time.

To study the time evolution of a system, we conducted white light reflectivity measurements under continuous UV light exposure. Figure 4(a) (darkest blue line) shows the reflectance...
spectrum prior to any UV exposure, i.e., when the molecules are in their SP form, and the system is in the weak coupling regime. The angle $\alpha$ is maintained constant and chosen such that the incident light is resonant with the (uncoupled) SPPs at 580 nm. Note that this is the same wavelength where the absorption of the molecules at the MC form is at a maximum (Fig. 1(b)). The molecules are then exposed to UV light, while continuously monitoring the reflectivity spectra. Notably, the reflectivity first decreases with increasing UV exposure. We associate this with conformational change of the molecules to the MC form, resulting in increasing absorbance at 580 nm. After approximately 40 seconds, however, the reflectivity at 580 nm starts increasing again, which is accompanied by a gradual increase in the linewidth, and eventually, the emergence of two separate dips on both sides of 580 nm.

In Fig. 4(c), the time evolution of the reflectivity at 580 nm is shown with black symbols. The time-dependent enhancement in reflectivity at 580 nm, calculated as $(R(t = 0) - R(t))/R(t = 0)$, reveals a transition point at approximately 40 s and demonstrates the non-monotonic behaviour of the reflectance with increasing UV exposure. This behaviour is notably different from that in similar studies employing microcavities and hole arrays in metallic films [7]. In these studies, transmittance is typically measured, and a monotonic increase in the transmittance is observed with increasing molecular absorption. Our study constitutes an interesting case, where at a certain wavelength, the gradual increase in losses first decreases the light output (at the weak coupling regime), and then starts to increase the light output when the system enters the intermediate and strong coupling regimes.

We fit two Gaussians to each reflectivity curve exhibiting two distinct minima in Fig. 4(a) and plot their energy separation $\Delta E$ as a function of the exposure time in Fig. 4(c). Note that the first
Evolution of the SPP resonance dips in reflection with increasing UV exposure (a) Measured reflectivity spectra and (b) Calculated reflectivity spectra for different dye film absorbances. In (b) the different colors correspond to the amplitude of the main absorption feature in Eq. 1. Corresponding reflectivity enhancement at 580 nm \(\left(\frac{R(t = 0) - R(t)}{R(t = 0)}\right)\) and the energy difference between the resonance dips as a function of UV exposure time (c) from measured reflectivity spectra (a) and (d) from calculated reflectivity spectra (b).

Three measurement points (with the lowest UV exposure times) exhibit only a single minimum, in which case we interpret \(\Delta E = 0\). This plot reveals a transition point at approximately 40 s, where the energy separation of Gaussian peaks becomes larger than their width, indicating the onset of the intermediate coupling regime. Notably, this transition point corresponds to the transition point in the reflectivity. The results are qualitatively confirmed by our numerical model based on the transfer matrix method, showing similar non-monotonic behavior with increasing absorbance, (Figs. 4(b) and 4(d)).

Photochromic molecules are appealing for nanophotonic applications owing to their nanoscale dimensions, the possibility of a high number density, large changes in the dipole moment or other physical properties, all-optical tunability, and reversibility [18,22,27]. Figure 5(a) shows the reversibility of the system with fixed angle reflectivity measurements. Similar to the case in Fig. 4, an angle of incidence is chosen such that the reflectivity minimum in the weak coupling case occurs at 580 nm, i.e., at the maximum absorption of the MC form. A gradual widening of the band gap is observed upon increasing UV exposure, indicative of the transition from the weak to strong coupling regime, which is followed by the reverse process induced by heating the sample to approximately 85 °C. Heating was conducted in-situ in the measurement setup using a hot air gun. Figures 5(b) and 5(c) shows the reflectivity spectra measured for several
cycles at 580 nm (Fig. 5(b)) and the energy separation of the two reflectance minima in the spectrum (Fig. 5(c)). In the first cycle, the reflectivity increases steadily to 70 % and the energy separation to 0.6 eV. A longer exposure time would likely yield an even higher reflectivity and energy separation, as the system has not quite reached saturation. Upon heating, the reflectivity reduces to approximately 20 % and the energy separation vanishes. The next two cycles show gradually reduced contrast between the SP and MC forms. While the switching is not completely reproducible, it nevertheless demonstrates the possibility of reversing the optically induced changes.

We note that although reversible light-induced switching was not studied in the present work, there is scope to explore all-optical, bidirectional control in active plasmonics. The possibilities toward this are enriched by the wealth of photochromic compounds available, SP derivatives being by far not the only choice. Diarylethene switches [19,20], for instance, are known for their excellent fatigue resistance and bistability, and hence the molecules of choice where stability and long-term (photo)reversibility are preferred over fast time dynamics.

In the system studied here, all changes are slow as they depend on the bulk refractive index of the SP-doped polymer. The high concentration of photochromic molecules and the potential steric hindrance from the polymer matrix limit the possibility of reaching the picosecond-scale switching speeds observed in solution for the SP molecules [27] in the studied system. We expect these drawbacks to be mitigated by the judicious design of plasmonic applications, either through minimizing the electric field volume [24] or by a utilizing liquid medium instead of polymer matrix.

Photochromic molecules could be, for instance, incorporated into systems consisting of a liquid gain medium for plasmonic nanoparticle lasers [37]. In this case, the degree of coupling, hybridization, and losses could be independently tuned by UV exposure, potentially in picosecond timescales. Extremely fast switching times could enable another interesting prospect, namely ultrafast switching among the weak, intermediate, and strong (and perhaps ultrastong [7]) coupling regimes. Yet another interesting prospect is the utilization of such molecules as ultrafast, optically tunable saturable absorbers in nanolasers. Extending the weak-to-strong coupling switching to sub-picosecond timescales would make the switching speed comparable to the Rabi oscillation period in these systems. This could enable entirely new dynamical behaviour [36].
4. Conclusion

To summarize, we have studied the optically tunable strong coupling between photochromic molecules and propagating SPPs. Rabi splittings up to 300 meV were achieved. The optical tunability of the coupling strength, as well as the tunability of the relative weights of the superposition states, were demonstrated. The time evolution of the system was studied by continuously measuring the reflectivity during UV illumination. In contrast to previous studies that conducted transmission measurements in optical microcavities and hole arrays, we observed a non-monotonic behaviour of the light output with increasing absorption of the system. We associate this behaviour with the two-fold role of molecular absorption: in the weak coupling regime, the increasing absorption merely increases the system losses, resulting in reduced reflectance. However, a further increase in the number of absorbing (MC form) molecules transits the system into the intermediate and strong coupling regimes, resulting a widened band gap at the resonance frequency and consequent increase in the reflectance. The experiments are performed at low light exposures, ensuring 0/1 photons in a system at any given time. Thus, our results are directly applicable to studies in the field of quantum optics. Our results may enable ultrafast switching between the weak and strong coupling regimes. Finally, in highly pumped systems (high photon number limit), the reported optical tunability could be utilized for tunable saturable absorbers and Q-switching in nanolasers.

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Disclosures

The authors declare no conflicts of interest.

See Supplement 1 for supporting content.

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