Plasmon-exciton polaritonics shed light on quantum dot dark-state dynamics

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Abstract

The strong coupling of quantum emitters to plasmonic cavities has emerged as an exciting frontier in quantum plasmonics and optics. Here we report an extensive set of measurements of plasmonic cavities hosting one to a few semiconductor quantum dots (QDs). Scattering spectra demonstrate that these devices are at or close to the strong coupling regime. Using Hanbury Brown and Twiss (HBT) interferometry, we demonstrate non-classical emission from the QDs, allowing us to directly determine their number in each device. Surprisingly, PL spectra measured from QDs coupled to the plasmonic devices are narrower than scattering spectra and show smaller values of the apparent Rabi splitting. Using extended Jaynes-Cummings model simulations, we find that the involvement of a dark state of the QDs explains these experimental findings. Indeed, the coupling of the dark state to the plasmonic cavity makes its emission bright enough to appear as a strong separate peak in the PL spectrum. The calculations also show that a slow decay component in the HBT correlation curves can be attributed to the relaxation of the dark state. The coupling of quantum emitters to plasmonic cavities thus emerges as a means to probe and manipulate excited-state dynamics in an unconventional manner and expose complex relaxation pathways.
Introduction

Manipulating and controlling the interaction of photons with individual quantum emitters has been a major goal of quantum photonics in recent years (1-3). Such control can be realized by engineering the local photonic environment of the quantum emitter, e.g. by placing it inside an optical cavity (4). By coupling the excited state(s) of the emitter to the electromagnetic (EM) field of the cavity, one can achieve various exotic light-matter coupled states (1, 2), single-photon emission sources (5, 6), photonic switches (7, 8) and more. Furthermore, in recent years it has been shown that strong coupling to electromagnetic modes can be used to modify photophysics and chemical reaction dynamics (9, 10).

The ability of an optical cavity to couple to a quantum emitter can be quantified in terms of their coupling rate, $g$, which depends, among other factors, on the quality factor of the cavity ($Q$) and the effective volume of its EM mode ($V$). The coupling rate can be compared with the rates of loss, including the rate of photon escape from the cavity ($\kappa$) and the intrinsic emission rate of the quantum emitter ($\gamma$). This comparison leads to two interaction regimes. In the weak coupling regime, the spontaneous emission of an emitter gets enhanced by the cavity, but the states of the emitter and the cavity do not change (11, 12). In contrast, in the strong coupling regime, these states combine, forming new hybrid states (1, 2). These so-called polaritons are separated energetically by essentially twice the coupling rate, manifested in optical spectra as the Rabi splitting. Achieving strong coupling at the limit of a single quantum emitter is essential for the observation of many quantum effects and is of great importance for optical applications such as quantum information processing (13-17) and quantum communication (18, 19).

Plasmonic cavities formed by metallic surfaces offer unique possibilities to achieve strong coupling with single quantum emitter even at room temperature, as they can focus light to deep sub-wavelength regimes (20). Although the $Q$ of plasmonic cavities is relatively low due to the ultrafast relaxation of surface plasmons (21), the mode volume is sufficiently small to reach the strong coupling limit with single emitters. This situation was realized in the last couple of years in our lab and others’ (22-25). In particular, we demonstrated strong coupling between individual semiconductor nanocrystals (quantum dots, QDs) and plasmonic bowtie antennas, which we observed as vacuum Rabi splitting in scattering spectra of the coupled systems (22). Two additional recent studies have also demonstrated the strong coupling of individual QDs and plasmonic cavities (23, 24).
To further understand the physics of strong coupling in plasmonic devices, we performed an extensive set of measurements of QDs within plasmonic cavities at or close to the strong coupling regime. Using Hanbury Brown and Twiss (HBT) interferometry, we directly demonstrated non-classical emission from one to three QDs within our devices. By comparison of spectra and HBT correlation functions to simulations based on an extended Jaynes-Cummings model, we inferred the unanticipated involvement of a dark state of the QDs in the relaxation dynamics of the coupled nanosystem.

Results

Scattering and Photoluminescence (PL) spectra of individual coupled plasmonic devices. We constructed plasmonic bowties with semiconductor QDs in their gaps. We used electron-beam lithography to fabricate silver bowties on 18 nm SiO₂ membranes. CdSe/ZnS quantum dots (QDs) were positioned into the gap region of bowties using interfacial capillary forces (22) (Figure 1a). Scattering spectra of individual QD-bowtie hybrids were measured using dark-field (DF) microspectrometry (22, 26), while PL spectra were measured from the same devices following excitation with a CW laser at 532 nm.

Scattering and PL spectra were recorded from devices containing one or several QDs, and two examples are shown in Figure 1b-e. Scattering spectra showed dips indicative of vacuum Rabi splitting (22) (Figure 1c & e, green). The splitting values obtained from the scattering spectra in Figure 1 were 200 and 230 meV, respectively. Fits of the scattering spectra to a coupled-oscillator model (27, 28), presented in Figure S1, provided values for the coupling rate, g, which are 52.6±0.3 and 56.5±0.8 meV, respectively. The splitting was also observed in PL spectra (Figure 1c & e, red) recorded from the same cavities. However, scattering spectra looked significantly and consistently broader than PL spectra, even though it could have been expected that mixing of the QD and bowtie levels would yield similar spectral widths. This discrepancy was also manifested in the values of the splitting between peaks obtained from PL measurements, which were only 100 and 130 meV, respectively.

Overall, we measured scattering and PL spectra from 23 bowtie cavities loaded with QDs. (Additional spectra are shown in Figure S2.) Analysis of the whole ensemble of spectra is shown in Figure 2. Histograms of the splitting values obtained from scattering and PL spectra are shown in Figure 2a and Figure 2b, respectively. In DF scattering spectra, we observed splitting values (Ω₃F) as high as 350 meV, while in PL spectra the maximal splitting (Ω₃PL) observed was 160 meV. A correlation plot of Ω₃PL versus Ω₃DF is shown in Figure 2c. It is evident
that the correlation is very weak, suggesting that $\Omega_{\text{PL}}$ does not depend on various parameters like bowtie gap size, number of QDs etc., to the same extent as $\Omega_{DF}$.

**HBT interferometry.** To study the quantum properties of the light emitted by the coupled devices, we turned to HBT interferometry. We first measured the second-order photon correlation curves ($g^2(t)$) of light emitted from individual QDs on a glass substrate. An example of such a correlation curve is shown in Figure 3a. (Additional examples are presented in the SI, Figure S3.) The antibunching observed in the correlation curve at zero delay, with a value lower than 0.5, verifies that the measurement is indeed from a single QD. However, in some cases the number of QDs within the laser spot was larger than one. We therefore fitted the measured correlation curves with Eq. 1, in order to obtain both the lifetime of the emitting exciton and the number of QDs.

$$g^2(t) = A + B \left(1 - e^{-|t|/\tau}\right)$$

In this equation, A and B are constants and $\tau$ is the lifetime of the emitting exciton. The value of the second-order photon correlation curves at zero time delay, $g^2(0)$, should scale as $1-1/N$, where N is the number of QDs. However, background photons reduce slightly the zero time dip, which is given by the constant A obtained from the fit. The maximal possible N based on a particular $g^2(0)$ measurement is the largest integer smaller than $1/(1-A)$. We obtained 22 correlation curves of individual QDs on glass, and used these in order to plot the distribution of exciton lifetimes, which arises due to their non-uniform size distribution (Figure S3). The average exciton lifetime was found to be 24 ns, and the distribution was asymmetric with a standard deviation of 5.3 ns.

We then measured the second-order photon correlation curves of the PL from QDs within plasmonic cavities. Two examples are shown in Figure 3b & c. As in the case of QDs on glass, the correlation curves show clear evidence of antibunching, pointing to the non-classical nature of the emitted light. Fitting the correlation curves to eq. 1, we found that the probed devices contained one QD (Figure 3b) and three QDs (Figure 3c). The fits also provided the polariton lifetimes for the two devices: 5.6±0.3 ns and 3.5±0.2 ns, respectively. Overall, $g^2(t)$ functions were measured from 16 of the devices whose scattering and PL spectra showed a clear indication of splitting. More examples of $g^2(t)$ are given in Figure S4, and Figure S4d shows the distribution of lifetimes obtained from fits to the correlation curves, ranging from 3 ns to 12 ns. Surprisingly, there seems to be only a minor shortening of the lifetimes (by a factor of ~5) compared to QDs on glass. To verify this result, we also performed direct time-
resolved PL measurements of several devices, the results of which are shown in Figure S5. The lifetimes extracted from these measurements were also shortened by just a factor of ~5 from the lifetimes of bare QDs. This finding is highly unexpected, as the mixing of the QD exciton with the plasmon in the cavity should have opened a fast relaxation channel with a lifetime closer to that of the plasmon (29). A recent study of an ensemble of QDs deposited on a plasmonic hole array also reported only a modest shortening of the excited-state lifetime (30). Interestingly, Ebbesen and coworkers found a similar deviation from the expected shortening of the PL lifetime in a different system consisting of molecules coupled to a microcavity (31).

**Jaynes-Cummings simulations illuminate the experimental observations.** Three surprising observations emerge from the experiments reported above. First, PL spectra of QDs coupled to the plasmonic cavities are narrower than scattering spectra. Second, the splitting between peaks observed in PL spectra is only weakly (if at all) correlated with the splitting in scattering spectra. Finally, the PL lifetime seems to be only mildly shortened compared to that of QDs on glass. All three observations deviate from expectations for strongly or nearly-strongly coupled QD-plasmonic devices. Indeed, the formation of polaritonic states due to coupling should lead to scattering and PL spectra of similar width, to similar values of splitting seen in both spectra, and to PL lifetimes on the femtosecond time scale, close to the ultrafast decay times of the plasmonic cavities.

As a way to reconcile the experimental observations with our understanding of the physics of strong coupling, we hypothesized that a dark state of the QDs might be involved in the observed excited state dynamics of the coupled systems. Long-lived dark excitonic states of different origins have been demonstrated in QDs (32, 33). We assumed that the weak coupling of such a dark state to the plasmonic cavity might significantly alter the dynamics of the system and the PL spectra. To simulate such dynamics and examine their potential effect on the experimental observations, we turned to a quantum mechanical framework based on an extended Jaynes-Cummings Hamiltonian, with Lindblad terms to introduce incoherent pumping (for the PL spectra) and relaxation channels. The quantum emitter was modeled as an electronic system composed of three levels: a ground state, a level with a large decay rate, mimicking the lowest bright excitonic state, and another level, positioned slightly lower in energy and possessing a much smaller decay rate, mimicking the dark state. A scheme of the plasmon and quantum emitter energy levels used in this model is shown in Figure 4a, and the relevant parameters are given in Table 1. From dynamic simulations based on this model, we
calculated scattering and PL spectra as well as second-order photon correlation functions. A representative set of spectra and the associated correlation function are shown in Figure 4.

Importantly, simulated second-order photon correlation curves (Figures 4c and S6) were found to decay with two distinct lifetimes, a very fast one, on the femtosecond time scale, and a much slower one, on the nanosecond time scale. The fast lifetime is connected with the strong coupling regime, due to the involvement of the plasmonic decay channels, but is too short to be observed in our experiments. Hence, only the long-time component of the correlation curve is registered experimentally, and it can be attributed to the decay of the dark state into two possible channels. The first decay channel is due to population transfer to the bright excitonic mode of the QD, from which fast emission brings the system back to the ground state. The second decay channel involves enhanced emission due to weak coupling of the dark state to the plasmonic mode.

The calculated PL spectra are significantly narrower than the scattering spectra, and show a reduced spectral splitting between emission peaks, in qualitative agreement with the experimental observations. The PL spectrum is indeed composed of two peaks: the high-energy peak is a consequence of the emission from the bright exciton (strongly coupled to the plasmon), while the narrower low-energy peak is due to emission from the dark exciton (weakly coupled to the plasmon). This peak assignment was deduced from the emission spectra by exploring different coupling regimes for the excited states involved in our model. The spectral feature associated with the dark-exciton peak, for instance, completely disappeared when we set the coupling between the cavity and the dark exciton equal to zero (as shown in Figure S7).

The theoretical model thus clarifies the origin of the surprising observations in our measurements, attributing them to the involvement of a dark state in the excited-state dynamics. Indeed, while a minority of the experimental data sets showed spectra features that somewhat departed from the main trend, likely due to the intrinsic variability of the fabricated systems, most data sets were well explained by the model.

**Discussion and conclusion**

We reported here a vast set of measurements of QDs embedded within plasmonic cavities, which allowed us to expose unique excited-state dynamics involving both polaritonic states
and dark states. Coupling values of \( \sim 75 \, \text{meV} \) were deduced from light-scattering spectra by fitting to a coupled-oscillator model (see histogram of \( g \) values in Figure S8). Based on two common conditions for strong coupling (34) (see Supplementary Text), our devices were found to be either at the strong coupling limit or close to it. In addition to scattering, we also obtained the PL spectrum of each device, and for most devices we also recorded the second-order photon correlation curves. The observation of antibunching in these correlation curves demonstrated unequivocally the non-classical nature of the light emitted by these devices, which emanated from either one or just a few QDs. Our measurements revealed several deviations from expectations based on the picture of a simple two-level quantum emitter coupled to a cavity level. Quantum simulations based on an extended Jaynes-Cummings model that explicitly took into account the presence of a dark state in the QD nicely reproduced all the intriguing features in the experiments. This success of the quantum model exposes the important role of the dark state in the dynamics observed in our experiments.

Theoretical and experimental studies of QDs have revealed different types of dark states. Exchange interactions lead to the splitting of the band-edge exciton with the appearance of a dark state as the lowest energy level and a bright state above it (32). Experimental work provided direct evidence for this splitting and showed that the dark and bright states are separated by less than 10 meV (35). This energy difference is too small to account for our observations. On the other hand, the occurrence of trapped surface states whose transitions are significantly red shifted compared to the bright exciton (33) can account for the hierarchy of energies used in our model. Therefore, it is reasonable to suggest that the low-energy narrow emission line in our PL spectra is due to a dark state that gets enhanced significantly through interaction with the plasmonic cavity. The theoretical simulations support this assertion; the interaction of the dark state with the plasmonic cavity is shown to enhance the dark state emission by at least a factor of \( \sim 1000 \).

Our findings, based on joint experimental and theoretical observations, demonstrate that it is possible to obtain strong coupling between one or just a few QDs and a plasmonic cavity at room temperature. Further, we find that coupling to the plasmonic cavity leads to unexpectedly rich excited-state dynamics and can allow a dark state to become bright enough to be readily observed in both PL spectra and second-order photon correlation curves. Our results pave the way for the manipulation of excitations within room-temperature strongly coupled devices, a necessary step for future applications such as the construction of quantum
devices operating under ambient conditions and the modulation of chemical reactivity at the single-molecule level.
Methods

Fabrication of silver bowties. SiN grids (TEM windows) were cleaned with plasma ($O_2 \sim 3.5$ sccm and $Ar \sim 1.5$ sccm) at 150 W. The cleaned grids were spin-coated with polymethylmethacrylate (PMMA) at 4000 r.p.m for 45 seconds to get a 60 nm thick layer of the polymer, followed by baking at 180 C for 90 seconds. The PMMA coated grids were then transferred to a Raith E_line Plus electron beam lithography chamber for electron beam exposure of PMMA in a series of pre-defined bowtie shapes, using an accelerating voltage of 30 kV and a current of 30 pA. The overall design of each fabricated grid involved matrices of bowties that were separated by 10 µm from each other to avoid any potential interaction between them. Each bowtie was composed of two 80 nm equilateral triangles, so that its plasmon resonance overlapped with the QD emission frequency (see Figure S9 for the scattering and PL spectra of an empty bowtie and a QD). The exposed PMMA was developed in a solution containing methyl isobutyl ketone and isopropyl (IPA) alcohol in 1:3 ratio for 30 seconds, followed by dipping in isopropyl alcohol (stopper) for 30 seconds and drying in a N$_2$ gas flow. Subsequently, 3 nm chromium was deposited as an adhesion layer, which was then followed by evaporation of a 20 nm silver layer within an electron-beam evaporator (Odem Scientific applications). Following metal deposition, a liftoff process was carried out using a REMOVER PG solvent stripper to obtain a set of silver bowties on the SiN grid.

Incorporation of QDs into the gap regions of bowties. The resist ZEP (a 1:1 copolymer of $\alpha$-chloromethacrylate and $\alpha$-methylstyrene) was spin-coated on the bowtie sample at 3000 r.p.m. for 45 seconds, and the sample was then baked for 180 seconds at 180 C. By using alignment marks, the electron beam was positioned at the bowtie gaps with an overlay accuracy of few nm to generate holes in the resist. The exposed regions were developed in amyl acetate and isopropanol. In order to drive QDs into the holes, we followed a method developed by Alivisatos and colleagues (36). The sample was placed vertically in an aqueous solution of QDs, and the solvent was allowed to evaporate slowly, exerting a capillary force along the receding line of contact, which drove the QDs into the holes. The number of QDs in the gap region could be partly controlled to be one, two or many by tuning the concentration of QD solution and diameter of the holes. A schematic of the bowtie fabrication and QD trapping process is shown in Figure 1a.

Dark-field and PL microspectrometry. Scattering spectra were measured using a home-built setup based on an inverted microscope and equipped with a 75 W Xenon lamp
(Olympus), a dark-field condenser, a 100x oil immersion objective of a tunable numerical aperture (from 0.9 to 1.3), a 150 mm spectrograph (SpectraPro-150, Acton) and an air-cooled CCD camera (Newton, Andor Technologies). A NA of 0.9 was typically used in these experiments. Photoluminescence measurements were performed on the same setup using a NA of 1.3. The excitation source was a 532 nm laser, whose polarization was selected to be parallel to the long axes of the bowties. All the spectra were smoothed with a Savitzky-Golay filter.

**Time-resolved PL measurements.** HBT interferometry and PL decay measurements were carried out using a Micro Time 200 (PicoQuant) single-molecule spectrometer. A 485 nm CW laser was used to excite the QDs through a 60X water-immersion objective. For these second-order correlation measurements emitted light from the sample was collected with the same objective and passed through a 50/50 beam splitter before being focused on two single-photon avalanche photodiodes (PerkinElmer, 50 ps time resolution). A band-pass filter was inserted in front of each detector to reduce the unwanted background signal. A single detector was used for time-resolved single-photon counting measurements with the same system. In both types of measurement we used a HydraHarp 400 time-interval analyzer (PicoQuant) for signal registration.

**Scanning transmission electron microscopy (STEM).** Plasmonic bowties and QDs were imaged using a Zeiss Gemini SEM microscope in a STEM mode, with an electron beam energy of 30 keV, a 20 μm aperture and a 5 mm working distance.

**Theoretical calculations. Model:** We assume that a quantum dot is composed of a ground state $|g\rangle$ of energy $E_g=0$ eV, a bright excitonic level, $|e_B\rangle$, of energy $E_B = E_g + \hbar \omega_B$, and a dark level, $|e_D\rangle$, of energy $E_D = E_g + \hbar \omega_D$. The Hamiltonian describing the QD, $H_{QD}$, can be expressed as:

$$H_{QD} = \hbar \omega_B |e_B\rangle \langle e_B| + \hbar \omega_D |e_D\rangle \langle e_D|$$

The QD is coupled to a single mode of a plasmonic cavity of energy $\hbar \omega_{pl}$, described via the Hamiltonian $H_{pl}$:

$$H_{pl} = \hbar \omega_{pl} a^\dagger a,$$

where $a$ ($a^\dagger$) is a bosonic annihilation (creation) operator. The plasmon-exciton coupling is included via the Jaynes-Cummings coupling term:

$$H_{pl-QD} = \hbar g_B (a^\dagger |g\rangle \langle e_B| + a |e_B\rangle \langle g|) + \hbar g_D (a^\dagger |g\rangle \langle e_D| + a |e_D\rangle \langle g|).$$
where $g_B$ ($g_D$) is the Jaynes-Cummings constant coupling the bright (dark) level to the plasmon.

The total Hamiltonian, $H$, of the system thus becomes

$$H = H_{QD} + H_{pl} + H_{pl-QD}. \quad (5)$$

To obtain the observables of the system, we solve the Liouville-von Neumann equation for the system’s density matrix, $\rho$:

$$\frac{d}{dt} \rho = -i[H, \rho] + \sum_i \gamma_{O_i} \mathcal{L}_{O_i} [\rho]. \quad (6)$$

which includes incoherent Lindblad operators, added to account for losses and pure dephasing. These operators take the following form:

$$\gamma_{O_i} \mathcal{L}_{O_i} [\rho] = \frac{\gamma_{O_i}}{2} \left( 2 O_i \rho O_i^\dagger - \{ O_i^\dagger O_i, \rho \} \right), \quad (7)$$

where $O_i$ is a generic system operator to be specified, and $\dagger$ stands for Hermitian conjugate. In particular, we add the following Lindblad terms:

$$\kappa \mathcal{L}_\alpha [\rho] \text{ (Plasmonic decay),} \quad (8)$$

$$\gamma_{GB} \mathcal{L}_{|e_B\rangle\langle e_B|} [\rho] \text{ (Decay of the bright excitonic level),} \quad (9)$$

$$\gamma_{GD} \mathcal{L}_{|e_D\rangle\langle e_D|} [\rho] \text{ (Decay of the dark excitonic level),} \quad (10)$$

$$\gamma_{BD} \mathcal{L}_{|e_B\rangle\langle e_D|} [\rho] \text{ (Population transfer from the dark level into the bright level),} \quad (11)$$

$$\gamma_{DB} \mathcal{L}_{|e_D\rangle\langle e_B|} [\rho] \text{ (Decay of the bright level into the dark level),} \quad (12)$$

$$\gamma_{DD} \mathcal{L}_{|e_D\rangle\langle e_D|} [\rho] \text{ (Pure dephasing of the dark level),} \quad (13)$$

$$\gamma_{BB} \mathcal{L}_{|e_B\rangle\langle e_B|} [\rho] \text{ (Pure dephasing of the bright level).} \quad (14)$$

Furthermore, we assume that the process of population transfer from the dark state to the bright state (and vice versa) is thermally activated and hence we get:

$$\gamma_{DB} = [1 + N_{th}(\hbar \omega_B - \hbar \omega_D; T)] \gamma^0_{DB}, \quad (15)$$

$$\gamma_{BD} = N_{th}(\hbar \omega_B - \hbar \omega_D; T) \gamma^0_{DB}, \quad (16)$$

where $N_{th}(E; T)$ is the Bose-Einstein Distribution at temperature $T$ (we assume $T = 300$ K) and energy $E$ and $\gamma^0_{DB}$ is the spontaneous decay rate of the bright state, $|e_B\rangle$, into the dark state, $|e_D\rangle$. 


We assume that the bright state, $|e_B\rangle$, as well as the dark state, $|e_D\rangle$, are incoherently pumped via terms $\gamma_B g |e_B\rangle \langle g|$ and $\gamma_D g |e_D\rangle \langle g|$, respectively. This accounts for pumping of the QD’s states via another higher-energy bright state that is directly excited by an incident monochromatic laser.

**Spectra:** We calculate the absorption, $S_{abs}(\omega)$, scattering, $S_{sca}(\omega)$, and emission, $S_{em}(\omega)$, spectra using the following formulas, valid close to the plasmonic resonance:

\[ S_{abs}(\omega) \propto \omega \text{Re} \left\{ \int_0^{\infty} \langle a(t) a^\dagger(0) \rangle e^{i\omega t} dt \right\} , \]  \hspace{1cm} (17)

\[ S_{sca}(\omega) \propto \omega^4 \left| \int_0^{\infty} \langle a(t) a^\dagger(0) \rangle e^{i\omega t} dt \right|^2 , \]  \hspace{1cm} (18)

\[ S_{em}(\omega) \propto \omega^4 \text{Re} \left\{ \int_0^{\infty} \langle a^\dagger(0)a(t) \rangle e^{i\omega t} dt \right\} . \]  \hspace{1cm} (19)

Here we assume that the system absorbs, scatters and emits light predominantly via the plasmonic cavity and neglect any direct absorption, scattering or emission of the quantum dot.

We evaluate the two-time correlation functions $\langle a(0)a^\dagger(t) \rangle$ and $\langle a(t)a^\dagger(0) \rangle$ using the quantum regression theorem (QRT) as described elsewhere (37).

**Second-order correlation function:** The second-order photon correlation function $g^2(t)$ is evaluated in the framework of cavity-quantum electrodynamics from the QRT as:

\[ g^2(t) = \frac{\langle a^\dagger(0)a^\dagger(t)a(t)a(0) \rangle}{\langle a^\dagger a \rangle^2} . \]  \hspace{1cm} (20)
Supplementary Materials

Supplementary Figures S1-S9.

Supplementary Text.

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Table 1. Set of parameters used to reproduce spectra and $g^2(t)$ functions, as shown in Fig. 4. The choice of parameters has been guided by the experimental results.

| Parameter          | Value               | Description                                      |
|--------------------|---------------------|--------------------------------------------------|
| $h \kappa$         | 400 meV             | Intrinsic plasmon decay rate                     |
| $h \gamma_{B}$     | 0.1 μeV             | Intrinsic decay rate of the bright exciton       |
| $h \gamma_{D}$     | 0.0325 μeV          | Intrinsic decay rate of the dark exciton         |
| $h \gamma_{DB}$    | 0.2 μeV             | Rate of energy transfer between the dark and the bright exciton |
| $h \gamma_{BB}$    | 130 meV             | Pure dephasing of the bright exciton             |
| $h \gamma_{DD}$    | 50 meV              | Pure dephasing of the dark exciton (Broadening of the dark-exciton line) |
| $h \gamma_{Bg}$    | 1 neV               | Incoherent pumping of the bright exciton         |
| $h \gamma_{Dg}$    | 5 neV               | Incoherent pumping of the dark exciton           |
| $h g_B$            | 100 meV             | Coupling between plasmon and the bright exciton  |
| $h g_D$            | 75 μeV              | Coupling between plasmon and the dark exciton    |
| $h \omega_{pl}$    | 1.93 eV             | Plasmon energy                                   |
| $h \omega_{D}$     | 1.95 eV             | Emission energy of the dark exciton              |
| $h \omega_{B}$     | 2.00 eV             | Emission energy of the bright exciton            |
Fig. 1: Spectroscopy of plasmonic cavities with QDs. (a) Schematic of the preparative process for trapping QDs within plasmonic bowties. (b,d) STEM images of a device with one QD (b) and two QDs (d). The scale bars represent 20 nm. The red arrows point to the QDs in the bowtie gaps. (c,e) Dark-field scattering spectra (green) and PL spectra (red) of the devices in b,d, respectively.
Fig. 2: Peak splittings in scattering and PL. (a, b) Histograms of peak splitting values obtained from dark-field scattering spectra, $\Omega_{\text{DF}}$ (a) and from PL spectra, $\Omega_{\text{PL}}$ (b). (c) Correlation between splitting values in PL and in scattering.
Fig. 3: Second-order photon correlation function ($g^2(t)$). (a) A bare QD on glass substrate. (b-c) QDs coupled to plasmonic cavities. The dip at zero delay is a manifestation of a single QD in (b) and three QDs in (c). Green- experimental results, orange- fits to equation 1.
Fig. 4: Quantum simulations of the plasmon-QD coupling dynamics. (a) Schematic level diagram describing the theoretical model. The plasmonic cavity is depicted on the left with an excited state of energy $\omega_{pl}$. The QD (right) is described as a three-level electronic system containing a ground state $|g\rangle$, a bright excitonic level, $|e_B\rangle$, and a dark excitonic level, $|e_D\rangle$. The bright (dark) excitonic transition occurs at energy $\omega_B$ ($\omega_D$). We assume that both the bright and the dark excitons are pumped incoherently. Plasmon-exciton coupling is described within the Jaynes-Cummings model with rates $g_B$ and $g_D$ (for coupling of the bright and dark exciton, respectively). The arrows mark incoherent transfer rates considered in the model. (b) Emission (red), scattering (green), and absorption (blue) spectra calculated theoretically for parameters shown in Table 1. The dashed line marks the energy of the dark exciton, $\hbar \omega_D$. (c) A simulated $g^2(t)$ features a double-exponential decay. Inset shows a zoom of the fast (fs) decay of the system excitations that is not resolved on the ns time scale.
**Supplementary Information**

**Supplementary Figures**

**Fig. S1: Coupled-oscillator model fits of scattering spectra:** STEM images (panels a&c) and dark-field scattering spectra (panels b&d) of two bowties containing QDs shown in Figure 1. The orange lines in panel b & e are fits to the coupled-oscillator model (27, 28):

\[ S(\omega) \propto \omega^4 \left| \frac{\omega^2 - \omega_e^2 - i\gamma_e\omega}{(\omega^2 - \omega_p^2 + i\gamma_p\omega)(\omega^2 - \omega_e^2 + i\gamma_e\omega) - 4\omega^2 g^2} \right|^2, \]

where \( \omega_e \) and \( \gamma_e \) are the emitter resonance frequency and decay rate respectively, \( \omega_p \) and \( \gamma_p \) are the plasmon frequency and plasmon decay rate, respectively and \( g \) is the coupling rate. The obtained values of \( g \) are 52.6±0.3 and 56.5±0.8 meV for panels b and d, respectively. In these fits, as well as the fits in Figure S2, we fixed the values of \( \gamma_e \) (132 meV) and \( \gamma_p \) (395 meV), based on the measured line widths of the individual QD PL and scattering spectra of the empty bowtie. A baseline parameter was used in the fitting in order to take care of a constant background signal.
**Fig. S2: Additional examples of the spectroscopy of devices loaded with QDs.** STEM images (panels a,d,g), dark-field scattering spectra (panels b,e,h) and PL spectra (panels c,f,i) of three bowties containing QDs. The orange lines in panels b,e & h are fits to the coupled-oscillator model described in the legend of Fig. S1. The obtained coupling strengths are $81.3 \pm 0.6$, $77.2 \pm 1.0$ and $54.4 \pm 0.5$ meV, respectively. Scale bars in panels a,d,g represent 20 nm.
**Fig. S3:** (a-c) Three additional examples of measured second-order photon correlation function ($g^2(t)$) of individual QDs on a glass substrate. (d) Distribution of the lifetimes of the excitons of 22 QDs on glass, obtained from analysis of $g^2(t)$ functions.
Fig. S4: (a-c) Three additional examples of second-order photon correlation functions ($g^2(t)$) measured from strongly coupled QDs. (d) Distribution of the lifetimes of 14 coupled plasmonic cavity-QD systems, obtained from analysis of $g^2(t)$ functions.
**Fig. S5**: **Time-resolved PL measurements of QDs.** (a) Measurement of QDs on a glass substrate. (b-d) Measurements of QDs coupled to plasmonic cavities. The solid red lines are bi-exponential fits to the experimental data. The average lifetime is given in each panel.
Fig. S6: (a,c,e,g) Emission, absorption, and scattering spectra and (b,d,f,h) $g^2(t)$ functions calculated from the theoretical model considering different ratios of incoherent pumping ($\gamma_{Bg}/\gamma_{Dg}$, with $\hbar \gamma_{Bg} = 1$ neV in all cases) and different values of the Jaynes-Cummings coupling constant of the dark exciton with plasmons, $g_D$. The values are given in the inset and apply to each pair [(a,b), (c,d), (e,f), and (g,h)] separately. All other parameters are listed in Table 1. The spectral response is almost identical in all cases, but the form of $g^2(t)$ very sensitively depends on both $\gamma_{Bg}/\gamma_{Dg}$ and $g_D$. The ratio $\gamma_{Bg}/\gamma_{Dg}$ controls the relative contribution of the fast component of the decay with respect to the slow one. On the other hand, large values of $g_D$ give rise to a Purcell effect that shortens the lifetime of the dark exciton, thus shortening the lifetime associated with the slow decay.
Fig. S7: PL spectral shape depends on dark-state coupling rate. Emission, absorption, and scattering spectra calculated from the theoretical model when the dark state is weakly coupled to the plasmonic cavity $g_D = 0.00035 g_B$ (a), and when it is not coupled at all $g_D = 0$ (b). In the latter case the PL spectrum features one broadened asymmetric peak arising from the onset of plasmon-bright-exciton strong coupling. The remaining model parameters used to generate the spectra in (a,b) are summarized in Table 1 of the main text.
Fig. S8: Coupling rate values. Histogram shows the distribution of the values of coupling rates, $g$, obtained from fits of the scattering spectra using the coupled-oscillator model.
**Fig. S9:** (a) PL spectrum of a bare QD on a glass substrate. (b) Dark-field scattering spectrum of an empty plasmonic bowtie.
Supplementary Text

Criteria for the strong coupling regime: The different regimes of coupling between a cavity and quantum emitters are distinguished based on the relationship between $g$, $\gamma$ and $\kappa$ (34). For the weak coupling regime, the condition is $g < \gamma \kappa$. For the transition from weak coupling to strong coupling, there are two widely used criteria. The first criterion, $g > (\kappa - \gamma)/4$, guarantees two real solutions in the coupled-oscillator model when the QD is resonantly tuned to the plasmon and may be seen as defining a lower bound for the strong-coupling regime. The second criterion, given by $g > (\kappa + \gamma)/4$, is more heuristic, and requires a larger $g$ to be fulfilled.