

Dynamics of Strong Coupling between J-Aggregates and Surface Plasmon Polaritons in Subwavelength Hole Arrays

Hai Wang, Hai-Yu Wang,* Angelo Bozzola, Andrea Toma, Simone Panaro, Waseem Raja, Alessandro Alabastri, Lei Wang, Qi-Dai Chen, Huai-Liang Xu, Francesco De Angelis, Hong-Bo Sun,* and Remo Proietti Zaccaria*

A prototypical hybrid system formed by strong coupled gold hole arrays and J-aggregate molecules is investigated by using both steady-state spectroscopic method and ultrafast pump-probe approach. In particular, the plasmonic response of the device has been tuned by modifying its periodicity thus to achieve the strongest possible coupling regime. It is found that in the transient absorption spectra, under upper band excitation, the bleaching signal from uncoupled J-aggregate molecules completely disappears. Instead, two distinctive period dependent bleaching bands are formed, clearly fingerprint of the hybrid exciton-plasmon state. The dynamics of these bands is also directly analyzed. A remarkable long lifetime is found especially for the upper band, corresponding to the presence of a trap state in its transient absorption spectra under resonance excitation. Such unique feature should provide a new approach to control quantum-mechanical states under coherent coupling.

It is indeed known that as molecules can interact one another through the exchange of electrons to form new molecular states, molecules can also interact with the electromagnetic field by the exchange of photons to realize the so called hybrid states. This phenomenon is known as strong coupling or coherent coupling. In particular, when molecules undergo strong coupling with SPPs, the molecular wavefunctions and the SPPs mode form coherent superpositions, leading to a new hybrid exciton-plasmon state. These states are defined by an upper and lower energy band, separated by the Rabi splitting energy.^[3–8] The exciton-plasmon interaction is indeed similar to light-matter coupling in microcavity structures.^[9–15]

Strong coupling dynamics has been investigated in J-aggregates,^[7,16–23] dye molecular systems,^[24–27] and quantum dots^[28,29] coupled to SPPs or light in microcavities. In particular, a unique strong coupling with individual sub-diffraction plasmonic nanostructure has been achieved.^[30,31] In these systems, hybrid states with Rabi-splitting values up to hundreds of meV have been demonstrated to have the potential for novel applications, such as electrically pumped LEDs,^[32,33] optical switches,^[34] and low-threshold polariton lasing.^[35–38]

Recently, the research on strong coupling of molecules with either SPPs or microcavities has made a lot of exciting progress.^[16,39–41] For example, Lienau and co-workers^[16] presented the first real-time observation of ultrafast Rabi oscillations on a 10 fs timescale for a strongly coupled SPP and J-aggregates system. Similarly, Ebbesen and co-workers^[39] demonstrated ultrastrong coupling by means of a microcavity resulting in a Rabi-splitting value exceeding 700 meV, which corresponds to 1/3 of the molecular transition energy. Furthermore, in SPP systems, the splitting was found of the order of 650 meV. In another interesting work the authors analyzed, by using wavelength-selective transient absorption technique, the dynamics of the strongly coupled J-aggregate-cavity system demonstrating that the intrinsic lifetime of the lower polariton branch can be much longer than the radiative lifetime of the cavity.^[41] This fundamental result opens new possibilities to control the dynamics of quantum-mechanical states under strong coupling regime.

With respect to cavity systems, SPPs have the strong advantage of being capable of confining the electromagnetic energy

1. Introduction

Strong interactions between surface plasmon polaritons (SPPs) and molecules are currently a subject of significant interest.^[1,2]

Dr. H. Wang, Dr. A. Bozzola, Prof. A. Toma, Dr. S. Panaro, Dr. W. Raja, Dr. A. Alabastri,^[†] Dr. F. De Angelis, Prof. R. Proietti Zaccaria
Istituto Italiano di Tecnologia
via Morego 30, 16163 Genoa, Italy
E-mail: remo.proietti@iit.it



Dr. H. Wang, Prof. H.-Y. Wang, Dr. L. Wang, Prof. Q.-D. Chen, Prof. H.-L. Xu, Prof. H.-B. Sun
State Key Laboratory on Integrated Optoelectronics
College of Electronic Science and Engineering
Jilin University
Changchun 130012, P.R. China
E-mail: haiyu_wang@jlu.edu.cn; hbsun@jlu.edu.cn

W. Raja
Università degli Studi di Genova
Via Balbi 5, 16126 Genoa, Italy

R. Proietti Zaccaria
Cixi Institute of Biomedical Engineering
Ningbo Institute of Materials Technology and Engineering
Chinese Academy of Sciences
Ningbo 315201, P.R. China

^[†]Present address: Laboratory for Nanophotonics, Smalley-Curl Institute, Rice University, Houston, TX 77005, USA

DOI: 10.1002/adfm.201601452

Similarly, in Figure 1f is illustrated the measured optical absorption for samples doped with J-aggregate, while the corresponding numerical calculations are reported in Figure 1g, hence confirming the full agreement between experiments and numerical calculations. In the figures, the upper and lower bands of the exciton–plasmon mixed states are reported with dashed lines. The energy corresponding to the absorption peak of the J-aggregate is also reported with a dashed horizontal white line. From Figure 1f,g it can be noted that the upper and lower branches experience a blue shift as the in-plane momentum is increased, together with the typical signature of strong coupling: anticrossing of energies.^[5,19] The resonance, characterized by the smallest splitting energy difference, occurs at the period of 310 nm, with a Rabi splitting energy value of 260 meV.

Even though the illustrated results indicate that J-aggregate molecules can undergo strong coupling with SPPs, they can say very little about the nature of the hybrid exciton–plasmon state. In fact, under strong coupling condition, the excitonic and plasmonic characteristics coexist in the hybrid state whose lower and upper bands are populated transiently. However, due to the change of the local refractive index of the overall system caused by the strong absorption of the J-aggregate at high concentrations, extracting the absorption spectrum of the exciton–plasmon hybrid state from the static transmission of the bare nanohole arrays is extremely difficult. In this regard, transient absorption experiments can provide deeper insights about the dynamics of the overall system. In particular, transient absorption experiments can provide information, such as very small absorbance changes, otherwise difficult if not impossible to obtain with the more standard static approach.^[20]

The first series of transient absorption experiments were performed under nonresonant conditions by a 400 nm wavelength pulsed pump laser. In particular, we measured the variation of the optical density ΔOD , being it defined as $-\log(R_{\text{pump,probe}}/R_{\text{probe}})$. Here, $R_{\text{pump,probe}}$ describes the probe reflectivity right after the pump signal has hit the sample, namely, the sample reflection upon perturbation induced by the pump laser. Similarly, the R_{probe} describes the probe reflectivity in a condition far away from the pump excitation.

Figure 2a shows the transient absorption spectra of J-aggregate molecules on a flat gold film. The figure illustrates a narrow ground state bleaching signal at 623 nm and a positive signal around 600 nm due to the excited state absorption, both associated to the presence of J-aggregate. Figure 2b shows the corresponding spectra when a gold nanohole arrays with periodicity 310 nm is taken into account. Compared with the flat gold sample, the transient spectra change significantly. Under the nonresonant 400 nm excitation, the J-aggregate molecules manifest little absorption, therefore mainly the SPPs on the gold nanohole structures are excited.^[43] The excited electrons rapidly equilibrate via electron–electron scattering to create a hot electron distribution, which broadens the SPPs absorption bands and reduces the absorption intensity,^[44,45] leading to two positive signals on both sides of the SPPs band, at 561 and 656 nm. Hence, the observed spectra are dominated by the thermal effect of the SPPs, therefore the hybrid states cannot be clearly identified. In fact, similarly to many other ultrafast transient absorption experiments carried out with different

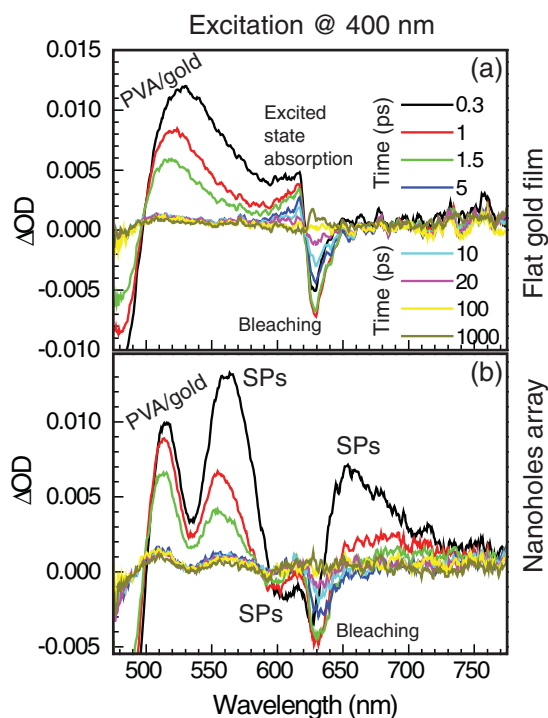


Figure 2. a) Transient absorption spectra of J-aggregates on a flat gold film, and b) on a gold hole arrays with 310 nm period. Nonresonant excitation at 400 nm was used. The spectra are recorded at 0.3, 1, 1.5, 5, 10, 20, 100, and 1000 ps. ΔOD : optical density variation.

kinds of metal nanostructures under nonresonant excitation,^[6] these experiments only reflect the thermal distribution, through electron–electron scattering and electron–phonon relaxation process.^[3,43,45] For this reason, they cannot provide information about the intrinsic photophysics of the hybrid state. Finally, for both flat and hole-patterned gold substrates, the signal below 550 nm does not change with or without J-aggregate (only PVA and gold are used; data not shown). Hence, this wavelength range cannot be considered as part of the coupling regime picture.

To better understand the nature of the hybrid exciton–plasmon state, transient absorption experiments were further performed under resonant excitation at 560 nm, which corresponds to the upper band of the hybrid state (see Figure 1c). For J-aggregate molecules on a flat gold film the result is shown in Figure 3. The plot is similar to the spectra obtained under excitation at 400 nm (Figure 2) illustrating a narrow bleaching signal at 623 nm and a positive excited state absorption signal around 600 nm. Noticeably, the minimum at 623 nm is about one order of magnitude higher than the corresponding peak in Figure 2 which can be ascribed to the resonant excitation condition.

The spectra for samples with different hole array periods are reported in Figure 4 suggesting the formation of hybrid states. For a period equal to 280 nm, namely, low coupling strength, a negative signal, possibly corresponding to the lower hybrid band at 631 nm, can be observed; on the contrary, the associated upper hybrid band is nearly undetectable being it out from our spectral window. Even though the minimum of the lower

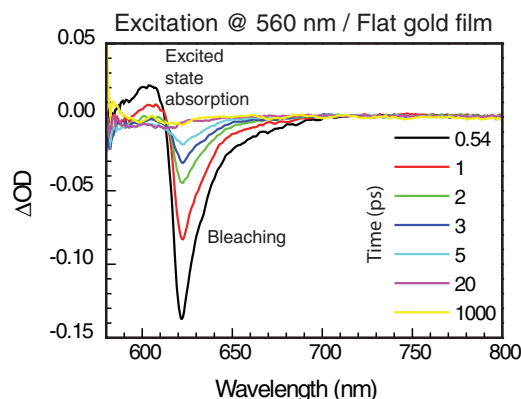


Figure 3. Transient absorption spectra of J-aggregate molecules on a flat gold film under 560 nm excitation (upper band excitation). The spectra are recorded at 0.54, 1, 2, 3, 5, 20, and 1000 ps.

hybrid band is very close to the transition of the J-aggregates (623 nm), it cannot be associated to the bleaching of the J-aggregate molecules. In fact, (i) the transient absorption spectra at $P = 280$ nm do not manifest any positive peak caused by the excited state absorption as in Figure 3; (ii) the dynamics from the bleaching band of the J-aggregates is substantially different from the dynamics of the lower hybrid state (see Figure 5).

For a period equal to 310 nm, the SPPs resonance overlaps the absorption peak associated to the J-aggregates (see Figure 1), thus maximizing the coupling intensity. Under this condition, the bleaching signal from the uncoupled J-aggregate molecules is completely absent, so that most of the molecules can interact with SPPs in a strong coupling regime. Instead, two distinctive bands, which can be interpreted as the bleaching of the hybrid SPPs/J-aggregate state, appear with similar intensity. As

the period further increases, the upper hybrid band becomes more apparent. Overall, the bleaching signal from uncoupled J-aggregate molecules is not detectable also for the 325 and 350 nm periods.

A general behavior of both the lower and upper hybrid bands, is their tendency of red shifting by period increase. Once again, the simultaneous shifting of both bands is consistent with the signature of strong coupling: anticrossing of energies. These results are clearly evidence that coherent exciton-plasmon hybrid states are formed in the patterned structures. It also worth noticing that in the strongest coupling regime ($P = 310$ nm) no positive signals are recorded. This behavior is related to the reduced SPPs excitation, in turn lack of thermal effects, with respect to the nonresonant excitation. Hence, under resonant excitation by 560 nm laser pulses, our experiments clearly identify the strong coupling conditions and they can directly analyze the SPPs-related nonthermal dynamics process.

The kinetics process associated to the lower hybrid band in the periods of 280, 310, and 325 nm are illustrated in Figure 5a. The plots show that the lifetimes of the lower hybrid band are indeed longer than the bleaching recovery of J-aggregates under the same pump power, for all considered periods. Similarly, in Figure 5b, is illustrated the bleaching kinetics of the upper band, always compared with the J-aggregates kinetics. In particular, the lifetimes of the upper band at 590 nm for periods of 310, 325, and 350 nm are recorded, finding them remarkably longer than the bleaching recovery of J-aggregates on a flat gold film. Indeed, the former reaches 1/e well after 10 ps, while the latter takes only 2 ps. In a conventional picture, the dynamics of hybrid states is simply determined by the fastest components. Due to the ultrafast damping of the SPPs mode, in the range of a few tens of fs,^[45] this longer hybrid bands lifetime might sound counter-intuitive. However, slowly decaying

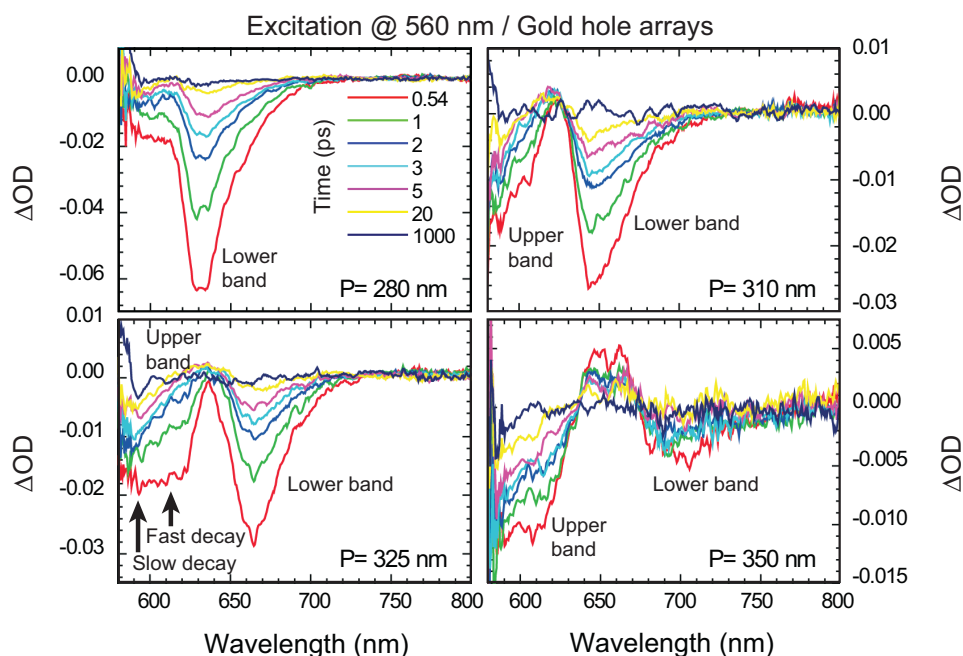


Figure 4. Transient absorption spectra of J-aggregates on different gold hole arrays with periods of 280, 310, 325, and 350 nm under 560 nm excitation (upper band excitation). The spectra are recorded at 0.54, 1, 2, 3, 5, 20, and 1000 ps.

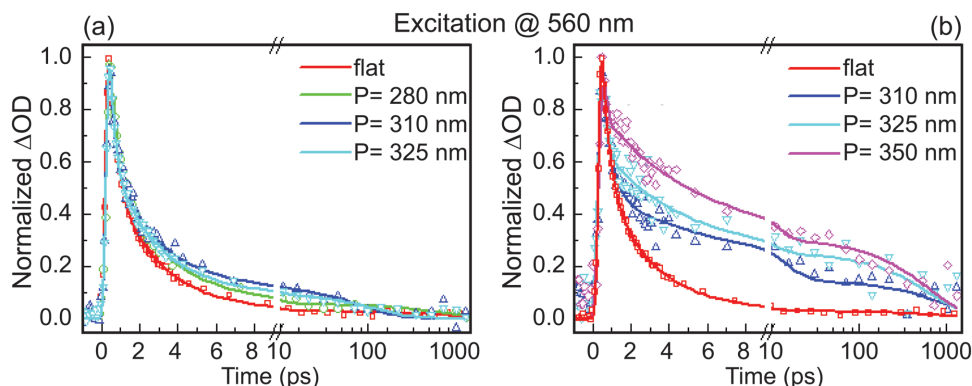


Figure 5. Comparison between normalized bleaching dynamics of J-aggregates deposited on a flat gold film at 623 nm with a) the peaks of the lower hybrid band, b) upper hybrid band at 590 nm. The solid lines represent the fitting results. For both cases the excitation source is taken equal to 560 nm (upper band excitation).

polaritons have also been studied in microcavity systems.^[41] In these cases the lifetime of the hybrid state can indeed be longer than the bleaching recovery of bare J-aggregates. One among the provided explanations is that the lifetime of the lower band is determined by vibrational relaxation phenomena, which are strongly affected by the large Rabi splitting. In fact, if the splitting is large enough, the lower band can be thought as a potential-minima quasi-bound state. Regardless the actual reason, further theoretical analysis, beyond the scopes of the present paper, will be necessary to understand the long lifetime of both lower and upper hybrid bands. In the following, we shall provide an alternative explanation based on the experimental observation of a trap state.

The next step is then to analyze the dynamics of the coupled system under lower hybrid band excitation, in contrast to the upper band excitation of Figure 4. In this regard **Figure 6** shows the transient response obtained at 670 nm laser pulses. The signal appears dominated by the thermal effect, which is similar

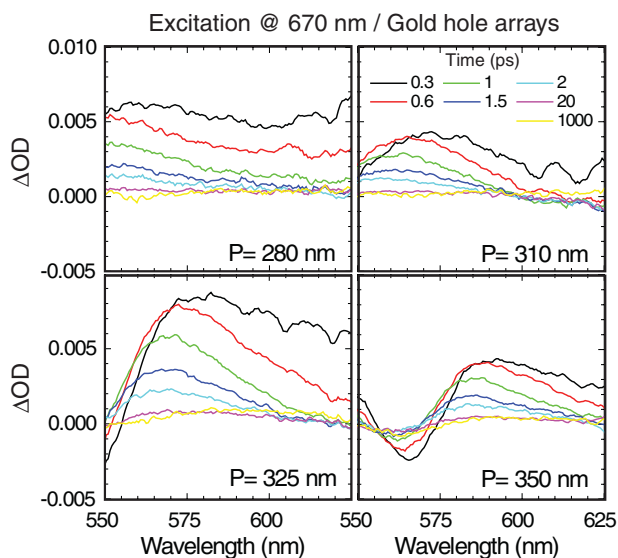


Figure 6. Transient absorption spectra of J-aggregate molecules deposited on gold hole arrays with periods of 280, 310, 325, and 350 nm under 670 nm excitation (lower band excitation). The spectra are recorded at 0.3, 0.6, 1, 1.5, 2, 20, and 1000 ps.

to the results obtained in Figure 2b in the range from 550 to 600 nm, where 400 nm excitation was considered. Differently from the results shown in Figure 4, no hybrid state bleaching signal is detected under lower band excitation, as clearly shown by Figure 6. This result was recently highlighted by George et al.,^[46] where they argue that the presence of a lower band does not imply its direct population, namely, transient absorption. This result also recalls similar responses involving cavity systems,^[40,41] where the transient behaviors are very different for lower and upper bands excitation. In particular, Schwartz and co-workers showed a very fast decay of the hybrid bands under lower band excitation. This fast decay is here responsible for the absence of any hybrid state signal, as shown in Figure 6, being them virtually undetectable by our apparatus. In the present case, the SPPs mode of 280 nm period sample is not expected to be efficiently excited under lower band excitation since the lower hybrid band, for low periods, shows mainly an excitonic nature, as seen by comparing Figure 1d,f. Furthermore, in Figure 6 the curves corresponding to the period equal to 280 nm, show a behavior somehow similar to the corresponding graphs measured for periods equal to 310, 325, and 350 nm. Hence, we suggest that at least in SPPs/J-aggregate strong coupling system, the intrinsic lifetime of the hybrid states is extremely short under lower band excitation (cannot be resolved by our setup), in contrast to the upper band excitation where we observe a life time of the hybrid states longer than the bare J-aggregate, as seen in Figure 5.

Finally, a last important result needs to be stressed: the upper hybrid band decays much slower than the lower hybrid band with respect to J-aggregates deposited on a flat gold film. This behavior is not readily understandable by a first look of the transient spectra of Figure 4, where both the bleaching of the upper and lower bands under resonant excitation are shown. In fact, considering that the two bands share the same common ground state, after the pump laser has emptied the population of the ground state, it is expected a bleaching from both of the two hybrid bands just as would occur in a molecule with S1 and S2 excited states. Hence, from this argument, no predictions can be done on the decay times of the two hybrid states. However, from a deeper analysis of Figure 4, some useful information in this regard can be extracted. In the early times of the transient spectra excited by 560 nm pump laser pulse,

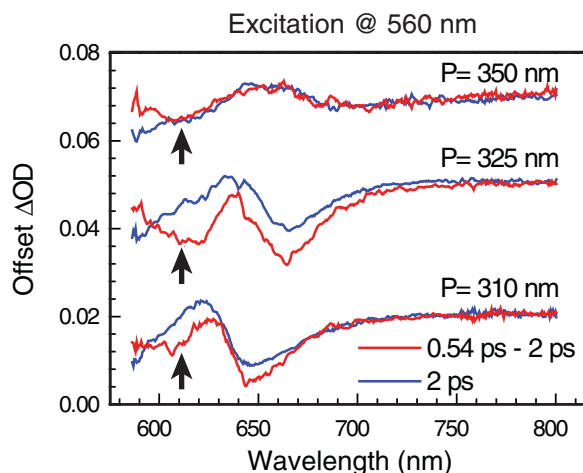


Figure 7. Transient absorption spectra of J-aggregate molecules deposited on gold hole arrays with periods of 310, 325, and 350 nm under 560 nm excitation (upper band excitation) and measured at 2 ps (blue line). Differential spectra between 2 and 0.54 ps (red line), together with the emerging peaks of the upper bands (pointed out by black arrows).

a fast decay behavior of the red side of the upper hybrid band is noticed (highlighted in Figure 4) for all considered periods. The spectra shape shows a distinctive difference between the initial $t = 0.54$ ps and the immediate subsequent times, while no appreciable change is observed for longer times. To visualize this feature, we subtracted the spectra measured at 2 ps from the initial spectra at 0.54 ps, thus finding a clear peak on the red side of the upper band for the three considered periodicities. This result is reported in Figure 7. Vice versa, the lower hybrid band spectra keeps the same shape for any considered time (see Figure 4).

We conjecture that this fast decaying portion of the peak characterizing the upper hybrid band can be associated to a trap state, namely, from the actual upper hybrid band the system decays in it, thus reflecting the initial relaxation process of the upper band. This process would determine a lifetime of the upper state surprisingly long (at least several hundred femtoseconds) as it is found in Figure 5. Importantly, this process reflects the decay of population from the upper hybrid band to the ground level. In fact, the alternative decay route from the upper to the lower hybrid band is precluded because, similarly to the upper hybrid band, also the lower hybrid band undergoes a bleach recovery at increasing times. After the occurring of the transition from the upper hybrid band into the trap state, a very long decay time is observed, even longer than the decay time characterizing the bare J-aggregate molecules (Figure 5). Vice-versa, we can conjecture that a trap state is absent in the lower hybrid band. Indeed, as seen in Figure 6, even under lower band excitation we cannot detect the formation of the hybrid bands due to the time-resolution capability of our set-up with respect to the hybrid state time decay. Considering all, further experiments (such as transient fluorescence) are needed to clarify this aspect.

Finally, we would like to stress that an alternative explanation of the unusual long lifetime of the upper band may be provided through the vibrational relaxation mechanisms suggested for microcavity systems. We can indeed assume that the transition

from the upper to the lower band is mediated by multivibrational modes relaxation which is strongly affected by the Rabi splitting. If the splitting is large enough, these vibrational relaxations will be blocked just as the phonon bottleneck effect.^[47,48] in the state filling of semiconductor quantum dots, which results in a long live upper band.

3. Conclusion

We have constructed a hybrid structure comprising a gold hole arrays and J-aggregate molecules to investigate the photophysics of hybrid states using an ultrafast pump-probe approach. Under resonant pump at 560 nm laser pulse, corresponding to upper band excitation, the bleaching signal associated to the uncoupled J-aggregates (623 nm) is found to be completely absent. On the other hand, it is observed the presence of two distinctive bleaching signals in the transient absorption spectra which were related to the existence of the hybrid exciton-plasmon state, hence providing unambiguous signatures of strong coupling. Furthermore, no positive signal in the transient absorption spectra was found hence ruling out any thermal effect in the strong coupling condition. Our experiments on the kinetics process time decay dynamics also showed a very long decay time both for the lower but especially for the upper hybrid band, even longer than the lifetime of bare J-aggregate molecules. Among the possible explanations we introduce the possibility that a trap state, observed in the red side of upper bands, can be responsible for such a behavior. When instead lower band excitation is considered, the intrinsic lifetime of the hybrid state results extremely short, to the extent to be undetectable by our set-up. We believe that this new piece of understanding on the dynamics of hybrid states in strong coupling regime should provide new approaches to design novel ultrafast plasmonic devices with coherent functionalities.^[49]

4. Experimental Section

Sample Fabrication: The scheme of the samples used in this work is shown in Figure 1a. A CaF_2 substrate is coated with a 200 nm thick gold film (with a 5 nm titanium adhesion layer) which is then milled with a focused ion beam (FEI/Helios Nanolab 650) to create a 2D array of circular nanoholes. A series of samples were made with different lattice periods between 275 and 375 nm, covering a total area of $200 \times 200 \mu\text{m}^2$. The hole period to diameter ratio is kept at ≈ 2.5 while the period is varied. The periodicity of the nanohole arrays provides the necessary momentum-matching condition in order to couple the incident light into SPPs.^[50] Finally, a 300 nm thick PVA film, both with and without J-aggregates, was spin-coated on the samples. The dye used in the experiments was 3,3'-disulfopropyl-5,5'-dichloro-9-ethylthiacarbocyanine triethylammonium salt (Thia; Hayashibara Biochemical Laboratories, Inc.), which was dissolved in water with a concentration as high as 8 mg mL. Afterward, the solution was dispersed in liquid PVA (50 mg mL⁻¹) and spin-coated onto a precleaned CaF_2 substrate with a speed of 2000 rpm. To determine the absorbance of the J-aggregates film, a sample with no gold layer was fabricated, whose absorbance spectrum is shown in Figure 1c (gray line). The Thia molecule was chosen owing to its large absorption coefficient which makes J-aggregates interesting candidates for studying exciton-plasmon interactions. To avoid degradation by oxygen, the sample was sealed by a quartz slide under

nitrogen environment in glove box with an oxygen concentration smaller than 0.1 ppm.

Transient Absorption Measurements: Femtosecond transient absorption spectra were recorded with a 100 fs laser pump-probe setup.^[51,52] A modelocked Ti:sapphire laser (Solstice, Spectra-Physics) was used and the output was amplified with a regenerative amplifier (RGA, Spitfire, Spectra Physics). The used amplifier can provide 800 nm fundamental pulses at a repetition rate of 250 Hz with energy of 1.5 mJ and a pulse width of 100 fs, which was split into two parts. The strongest part was used to pump a TOPAS system to generate excitation pulse at 560 nm or sent to a 1 mm thick BBO to get the double frequency of 400 nm excitation pulse. Then the pump light was sent into an optical delay line and modulated by a synchronized optical chopper (Newport Model 75160) with a frequency of 125 Hz as the pump beam to excite the sample. The remaining part of the RGA output (800 nm) was used to generate a white light continuum as probe beam by focusing the beam into a sapphire. The pump and probe beams were orthogonally collinearly recombined by a dichroic mirror and focused on the sample at normal incidence by a microscope objective (NA 0.75, magnification 10). Reflected light from the sample, collected by the same objective, was then transmitted through a beam splitter, spectrally filtered to reject the pump light, and focused on a highly sensitive spectrometer (Avantes AvaSpec-2048 × 14). Traces of the dynamics were obtained by controlling the relative delay between the pump and the probe pulses with a stepper-motor-driven optical delay line (Newport M-ILS250CC). The group velocity dispersion of the whole experimental system was compensated by a chirp program.

The multiexponential dynamics fits of the life-time studies were performed by using the software ASUFIT (<http://www.public.asu.edu/~laserweb/asufit/>) in MatLab, through a standard deconvolution procedure and nonlinear regression. The decay curves at a selected wavelength in the TA spectra were fit to a sum of exponentials

$$\Delta A(\lambda, t) = \sum_{i=1}^n A_i(\lambda) \exp(-t/\tau_i)$$

where $\Delta A(\lambda, t)$ is the observed absorption change at time delay t and n is the number of kinetic components used in the fitting. The pre-exponential factors A_i represent the amplitudes of each component, which has a lifetime of τ_i .

Importantly, due to far-field and near-field interactions originating from the periodicity and the short distance among the nanoholes, the transient spectrum of the hybrid state results angle sensitive.^[53,54] To solve this issue we set up a pump and probe system where pulses are collinearly recombined by a dichroic beam splitter and focused on the sample. In this way the probe signal can monitor the transient spectrum eliminating the effect of the angle of incidence.

Acknowledgements

The authors would like to acknowledge National Basic Research Program of China (973 Program, Grant No. 2014CB921300), Natural Science Foundation China (NSFC) under Grant Nos. 21273096 and 21473077 and Doctoral Fund Ministry of Education of China under Grant No. 20130061110048 for support. Furthermore, the authors would like to recognize the support from the 3315 Innovative Teams Program of Ningbo - China.

Received: March 21, 2016

Revised: May 2, 2016

Published online:

- [3] V. M. Agranovich, A. G. Malshukov, *Opt. Commun.* **1974**, *11*, 169.
- [4] I. Pockrand, A. Brillante, D. Mobius, *J. Chem. Phys.* **1982**, *77*, 6289.
- [5] J. Dintinger, S. Klein, F. Bustos, W. L. Barnes, T. W. Ebbesen, *Phys. Rev. B* **2005**, *71*, 035424.
- [6] A. Salomon, C. Genet, T. W. Ebbesen, *Angew. Chem.* **2009**, *121*, 8904.
- [7] P. Vasa, R. Pomraenke, G. Cirmi, E. De Re, W. Wang, S. Schwieger, D. Leipold, E. Runge, G. Cerullo, C. Lienau, *ACS Nano* **2010**, *4*, 7559.
- [8] W. Wang, P. Vasa, R. Pomraenke, R. Vogelgesang, A. De Sio, E. Sommer, M. Maiuri, C. Manzoni, G. Cerullo, C. Lienau, *ACS Nano* **2014**, *8*, 1056.
- [9] D. G. Lidzey, D. D. C. Bradley, M. S. Skolnick, T. Virgili, S. Walker, D. M. Whittaker, *Nature* **1998**, *395*, 53.
- [10] D. G. Lidzey, D. D. C. Bradley, A. Armitage, S. Walker, M. S. Skolnick, *Science* **2000**, *288*, 1620.
- [11] Y.-Y. Lai, Y.-P. Lan, T.-C. Lu, *Light Sci. Appl.* **2013**, *2*, e76.
- [12] A. Nazir, S. Panaro, R. P. Zaccaria, C. Liberale, F. De Angelis, A. Toma, *Nano Lett.* **2014**, *14*, 3166.
- [13] S. Panaro, A. Nazir, C. Liberale, G. Das, H. Wang, F. De Angelis, R. P. Zaccaria, E. Di Fabrizio, A. Toma, *ACS Photonics* **2014**, *1*, 310.
- [14] Z.-Y. Zhang, H.-Y. Wang, J.-L. Du, X.-L. Zhang, Y.-W. Hao, Q.-D. Chen, H.-B. Sun, *Appl. Phys. Lett.* **2014**, *105*, 191117.
- [15] D. M. Coles, P. Michetti, C. Clark, W. C. Tsoi, A. M. Adawi, J.-S. Kim, D. G. Lidzey, *Adv. Funct. Mater.* **2011**, *21*, 3691.
- [16] P. Vasa, W. Wang, R. Pomraenke, M. Lammers, M. Maiuri, C. Manzoni, G. Cerullo, C. Lienau, *Nat. Photonics* **2013**, *7*, 128.
- [17] J. Bellessa, C. Bonnard, J. C. Plenet, J. Mugnier, *Phys. Rev. Lett.* **2004**, *93*, 036404.
- [18] Y. Sugawara, T. A. Kelf, J. J. Baumberg, M. E. Abdelsalam, P. N. Bartlett, *Phys. Rev. Lett.* **2006**, *97*, 266808.
- [19] C. Symonds, C. Bonnard, J. C. Plenet, A. Bréhier, R. Parashkov, J. S. Lauret, E. Deleporte, J. Bellessa, *New J. Phys.* **2008**, *10*, 065017.
- [20] Y.-W. Hao, H.-Y. Wang, Y. Jiang, Q.-D. Chen, K. Ueno, W.-Q. Wang, H. Misawa, H.-B. Sun, *Angew. Chem.* **2011**, *123*, 7970.
- [21] D. M. Coles, N. Somaschi, P. Michetti, C. Clark, P. G. Lagoudakis, P. G. Savvidis, D. G. Lidzey, *Nat. Mater.* **2014**, *13*, 712.
- [22] S. Wang, T. Chervy, J. George, J. A. Hutchison, C. Genet, T. W. Ebbesen, *J. Phys. Chem. Lett.* **2014**, *5*, 1433.
- [23] X. Zhong, T. Chervy, S. Wang, J. George, A. Thomas, J. A. Hutchison, E. Devaux, C. Genet, T. W. Ebbesen, *Angew. Chem. Int. Ed.* **2016**, *55*, 1.
- [24] A. Berrier, R. Cools, C. Arnold, P. Offermans, M. Crego-Calama, S. H. Brongersma, J. Gómez-Rivas, *ACS Nano* **2011**, *5*, 6226.
- [25] A. Cacciola, O. Di Stefano, R. Stassi, R. Saija, S. Savasta, *ACS Nano* **2014**, *8*, 11483.
- [26] N. I. Cade, T. Ritman-Meer, D. Richards, *Phys. Rev. B* **2009**, *79*, 241404.
- [27] T. K. Hakala, J. J. Toppari, A. Kuzyk, M. Pettersson, H. Tikkänen, H. Kunttu, P. Törmä, *Phys. Rev. Lett.* **2009**, *103*, 053602.
- [28] D. E. Gómez, K. C. Vernon, P. Mulvaney, T. J. Davis, *Nano Lett.* **2009**, *10*, 274.
- [29] D. E. Gomez, K. C. Vernon, P. Mulvaney, T. J. Davis, *Appl. Phys. Lett.* **2010**, *96*, 073108.
- [30] A. E. Schlather, N. Large, A. S. Urban, P. Nordlander, N. J. Halas, *Nano Lett.* **2013**, *13*, 3281.
- [31] G. Zengin, M. Wersäll, S. Nilsson, T. J. Antosiewicz, M. Käll, T. Shegai, *Phys. Rev. Lett.* **2015**, *114*, 157401.
- [32] K. Okamoto, I. Niki, A. Shvartser, Y. Narukawa, T. Mukai, A. Scherer, *Nat. Mater.* **2004**, *3*, 601.
- [33] G. Lozano, D. J. Louwers, S. R. K. Rodriguez, S. Murai, O. T. A. Jansen, M. A. Verschuuren, J. G. Rivas, *Light Sci. Appl.* **2013**, *2*, e66.
- [34] T. Ming, L. Zhao, M. Xiao, J. Wang, *Small* **2010**, *6*, 2514.

[1] W. L. Barnes, A. Dereux, T. W. Ebbesen, *Nature* **2003**, *424*, 824.

[2] S. A. Maier, *Plasmonics: Fundamentals and Applications*, Springer Science & Business Media, New York, NY, USA, **2007**.

- [35] M. A. Noginov, G. Zhu, A. M. Belgrave, R. Bakker, V. M. Shalae, E. E. Narimanov, S. Stout, E. Herz, T. Suteewong, U. Wiesner, *Nature* **2009**, *460*, 1110.
- [36] R. F. Oulton, V. J. Sorger, T. Zentgraf, R.-M. Ma, C. Gladden, L. Dai, G. Bartal, X. Zhang, *Nature* **2009**, *461*, 629.
- [37] K. Ding, C. Z. Ning, *Light Sci. Appl.* **2012**, *1*, e20.
- [38] Y.-H. Chou, B.-T. Chou, C.-K. Chiang, Y.-Y. Lai, C.-T. Yang, H. Li, T.-R. Lin, C.-C. Lin, H.-C. Kuo, S.-C. Wang, T.-C. Lu, *ACS Nano* **2015**, *9*, 3978.
- [39] T. Schwartz, J. A. Hutchison, C. Genet, T. W. Ebbesen, *Phys. Rev. Lett.* **2011**, *106*, 196405.
- [40] J. A. Hutchison, T. Schwartz, C. Genet, E. Devaux, T. W. Ebbesen, *Angew. Chem. Int. Ed.* **2012**, *51*, 1592.
- [41] T. Schwartz, J. A. Hutchison, J. Léonard, C. Genet, S. Haacke, T. W. Ebbesen, *Chemphyschem* **2013**, *14*, 125.
- [42] Comsol Multiphysics Modeling Softward, <https://www.comsol.com/> 2016.
- [43] S. Link, M. A. El-Sayed, *Annu. Rev. Phys. Chem.* **2003**, *54*, 331.
- [44] M. Pelton, J. Aizpurua, G. Bryant, *Laser Photoics Rev.* **2008**, *2*, 136.
- [45] G. V. Hartland, *Chem. Rev.* **2011**, *111*, 3858.
- [46] J. George, S. Wang, T. Chervy, A. Canaguier-Durand, G. Schaeffer, J.-M. Lehn, J. A. Hutchison, C. Genet, T. W. Ebbesen, *Faraday Discuss.* **2015**, *178*, 281.
- [47] J. Urayama, T. B. Norris, J. Singh, P. Bhattacharya, *Phys. Rev. Lett.* **2001**, *86*, 4930.
- [48] Y. Yang, D. P. Ostrowski, R. M. France, K. Zhu, J. van de Lagemaat, J. M. Luther, M. C. Beard, *Nat. Photonics* **2016**, *10*, 53.
- [49] K. F. MacDonald, Z. L. Samson, M. I. Stockman, N. I. Zheludev, *Nat. Photonics* **2009**, *3*, 55.
- [50] C. Genet, T. W. Ebbesen, *Nature* **2007**, *445*, 39.
- [51] L. Wang, S.-J. Zhu, H.-Y. Wang, S.-N. Qu, Y.-L. Zhang, J.-H. Zhang, Q.-D. Chen, H.-L. Xu, W. Han, B. Yang, H.-B. Sun, *ACS Nano* **2014**, *8*, 2541.
- [52] H. Wang, H.-Y. Wang, B.-R. Gao, Y. Jiang, Z.-Y. Yang, Y.-W. Hao, Q.-D. Chen, X.-B. Du, H.-B. Sun, *Appl. Phys. Lett.* **2011**, *98*, 251501.
- [53] Y. B. Zheng, B. K. Juluri, L. L. Jensen, D. Ahmed, M. Lu, L. Jensen, T. J. Huang, *Adv. Mater.* **2010**, *22*, 3603.
- [54] L. Chen, Y. Zhu, X. Zang, B. Cai, Z. Li, L. Xie, S. Zhuang, *Light Sci. Appl.* **2013**, *2*, e60.