Ultrafast Photophysics

DOI: 10.1002/ange.201101699

Hybrid-State Dynamics of Gold Nanorods/Dye J-Aggregates under Strong Coupling**

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Much attention has been paid to the study of interactions between surface plasmon (SP) and molecules, not only because of a fundamental interest but also their potential applications for ultrasensitive fluorescence detection, light-energy conversion,[1] photolithography, and data storage on the nanoscale.[2] Various plasmon/molecule hybrids were realized with periodically structured metal/molecule surfaces or by self-assembling metallic nanoparticles/molecules. The interactions between surface plasmons and molecules greatly affect the excited-state properties of molecules, such as energy pathway,[3] electron transfer,[4] spin relaxation,[5] and radiation.[6] The interactions often appear as two opposite cases, namely weak and strong couplings. In the weak coupling regime, wavefunctions of molecules and SP modes of plasmons are considered to be unperturbed. The strong coupling or coherent coupling occurs when resonant exciton–plasmon interactions modify molecular wavefunctions and SP modes, whereby the excitation energy is shared and oscillates between the plasmonic and molecular systems (Rabi oscillations), leading to vacuum Rabi splitting of energy levels at the resonance frequency. This is similar to behaviors of polaritons in an optical microcavity.[7]

In recent years, considerable progress has been made to observe the strong coupling in various SP–molecule hybrid systems. Rabi splitting was observed on a silver film with a concentrated cyanine dye in a polymer matrix.[8] The strong coupling effect between dye molecules and SPP has also been reported on many nanostructures.[9] Meanwhile, an absorption dip in the extinction spectra of metal nanoparticles coated with J-aggregates was observed.[10] This phenomenon may have resulted from coherent coupling between molecular excitons and the dipolar responses of metal nanorods.[11] These ideas were later extended to gold nanorods with different surfactants.[12] However, most work focuses on steady-state observations, and the intrinsic photophysics of these hybrid states and dynamics are still far from being understood. Recently, the Ebbesen group[13] studied a silver hole array and J-aggregate hybrid structure using a 150 fs pump-probe laser setup. Later, the Lienau group[14] reported the transient experiments of gold nanoslits and J-aggregates. However, these experiments were all performed under non-resonant excitation conditions. If the experiments were performed under resonance, intrinsic photophysics of the hybrid states would be understood more in detail. In this work, we investigate the dynamics of hybrid states in another kind of SP–molecule structure by self-assembling gold nanorods with dye molecules under resonant excitation for the first time. The intrinsic photophysics is only apparent under this excitation. In contrast, under nonresonant excitation, the dynamics is dominated by the thermal effect of the SPs, but not by the coherent coupling process.

Gold nanorods were synthesized using a slight modification of the previously reported seed-mediated growth method.[15] The as-prepared gold nanorods are positively charged owing to the encapsulation of the cationic surfactant, hexadecyltrimethylammonium bromide (CTAB), and the peaks of the transverse and longitudinal SP resonance are at 513 nm and 653 nm, respectively. The dye used in the current experiments was 3,3′-disulfopropy1-5,5′-dichloro-9-ethylthiacarbocyanine triethylammonium salt (Thia; Hayashibara Biochemical Laboratories, Inc.), which has a strong absorption peak at 623 nm upon J-aggregation (Figure 1 a). Molecule–nanorod hybrid structures were prepared using the procedure described by a previous report.[10] Briefly, 20 mL each gold nanorod sample was centrifuged twice at 9300 g for 10 min to remove the excess surfactant in solution. The precipitate was resuspended in water and the concentration of the colloidal solution was adjusted so that the optical density at 650 nm reached 0.55. Finally, the hybrid nanostructures were prepared by mixing the resuspended colloidal solution and Thia aqueous solution with 1 mM NaCl.

Figure 1 a shows the absorption spectra of the hybrid structure consisting of gold nanorods and J-aggregates. As can be clearly seen, the plasmon band splits into two distinct peaks at 620 nm and 685 nm owing to the strong coupling of

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[**] This work has been funded by Natural Science Foundation, China under Grants No. 20973081 and 10904049, and by the Ministry of Education, Culture, Sports, Science, and Technology of Japan: KAKENHI Grant-in-Aid for Scientific Research on the Priority Area “Strong Photon-Molecule Coupling Fields” (No. 470 (No. 19049001)).

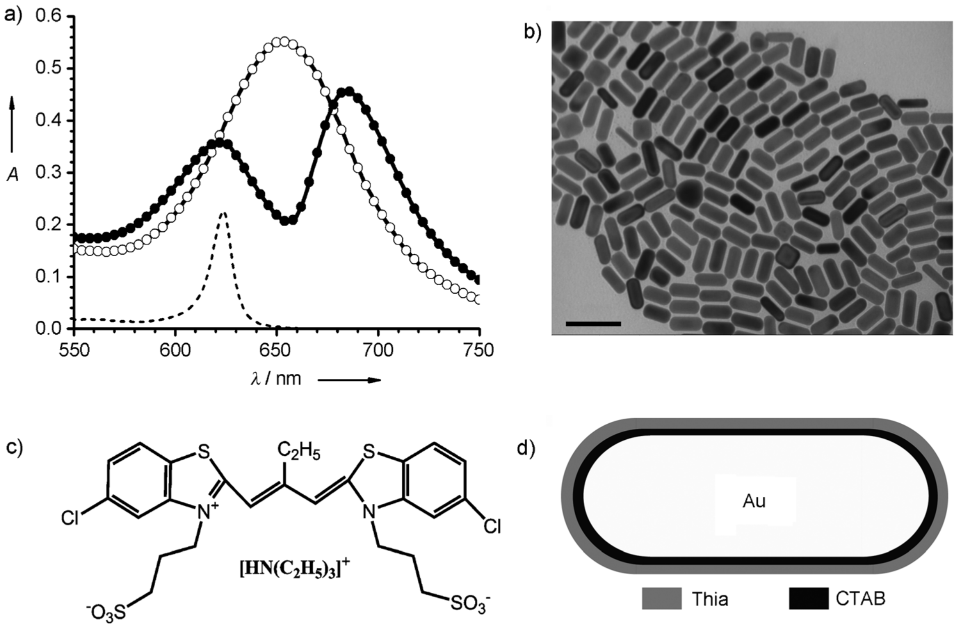

Figure 1. a) Static absorption spectra of a bare gold nanorod solution (○), hybrid structure solution (●), and Thia dye solution (-----). b) TEM image of bare gold nanorods. Scale bar: 100 nm. c) Structure of the Thia molecule. d) Representation of the Thia/Au nanorod hybrid structure.

the Thia molecules and the longitudinal SP mode. The Rabi splitting is about 190 meV, which is consistent with previous reports and close to maximum splitting value in similar hybrid structures. The static absorption spectrum indicates the existence of strong coupling, but we still cannot interpret the nature of these hybrid states. Under strong coupling, the hybrid states must have electronic and also plasmonic characteristics and they should be able to populate transiently. Nevertheless, extracting the absorption spectrum of the molecule-coated hybrid structure from the static absorption of the bare gold nanorods is extremely difficult. A great advantage of the transient absorption spectroscopy is its capability to measure small absorbance changes, by which the difference in the absorption spectra of the ground state and the excited states generated is distinguishable, and therefore robust information on the existence of hybrid states and dynamics would be provided.

Transient absorption spectra were taken with a 100 fs laser pump-probe setup.[15c] First, the hybrid structure was pumped under nonresonant conditions by 400 nm laser pulses. As Thia dye has almost no absorption at 400 nm, only gold nanorods are excited, which corresponds to the 5d→6sp interband transition of gold electrons. The excited electrons are thermalized to reach higher temperatures by electron–electron scattering, and the increase in the electronic temperature alters the dielectric function of gold nanorods, leading to the broadening of SP absorption bands and decreasing of the absorption intensity.[15c,16] These factors result in bleaching of both hybrid state absorption bands owing to new SP and dye coupling. Figure 2a shows the transient absorption spectra for hybrid structure solution. As expected, the transient spectra show two distinctive bleaching signatures at 610 nm and 675 nm, respectively, which is consistent with the steady-state result. However, the bleaching peaks clearly show a blue-shift to the steady-state peaks. This effect is because the steady-state spectra may contain the contribution from uncoupled dye and gold nanorod absorption. If the observed signals are indeed completely caused by the thermal effect of gold nanrods, the recovery of the bleaching signals will simply reflect the electron–phonon relaxation process of gold nanorods. The kinetics of the two hybrid bands and also bare gold nanorod bleaching under the same excitation power are shown in Figure 2b. As can be seen, the three kinetics processes are nearly the same. The excitation-power-dependent experimental results further support our hypothesis in which the kinetics gradually slow down owing to the slow electron–phonon relaxation rate versus the increasing pump power.[15c,16] Therefore, under nonresonant excitation, the transient absorption results can only tell us the existence of the hybrid states, but not the intrinsic photophysics of the hybrid states.

To understand the nature of SP and dye hybrid states, we performed transient absorption experiments under resonant excitation by 610 nm and 690 nm laser pulses, which correspond to the up and low hybrid bands, respectively. If the

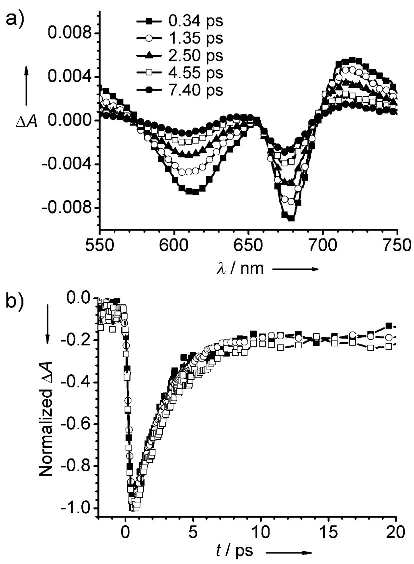

Figure 2. a) Transient absorption spectra for a hybrid structure solution under 400 nm excitation. b) Transient absorption kinetic traces for a bare gold nanorod solution at 635 nm (■) and a hybrid structure solution at 610 nm (○) and 675 nm (□).

interactions between Thia dye molecules and SP are indeed in the strong-coupling regime, both of them will be excited at the same time. The transient absorption spectra under 690 nm excitation are shown in Figure 3a. At early stages, the transient spectra of the hybrid structure shows significantly different features compared with those from 400 nm excitation (Figure 3b). Instead of two distinctive bleaching of hybrid states, the transient spectra show a negative bleaching band around 623 nm and a positive absorption band at 650 nm at the very beginning, which coincides with absorption peaks of uncoupling J-aggregates and SP, respectively. Within less than 1 ps, these new spectral features decay out and the transient spectra evolve back to the same shape as that under 400 nm excitation, which has two distinctive bleaching signatures at 610 nm and 675 nm, respectively.

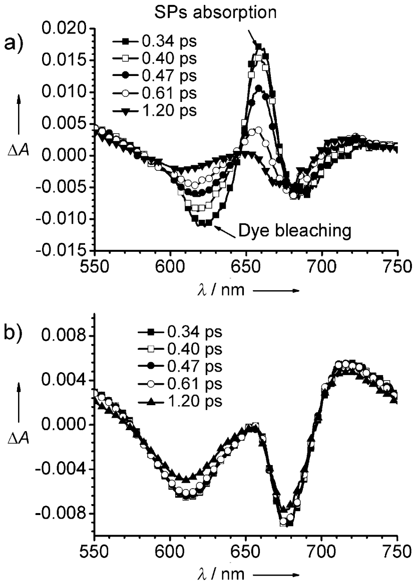

Figure 3. Transient absorption spectra for a hybrid structure solution using a) 690 nm and b) 400 nm excitation laser pulses.

To establish what this new spectral structure means, we should recall the concept of coherent coupling. In the case of coherent coupling, the strong interactions will modify both dye molecular wavefunctions and SP modes to form two new hybrid states. After the resonant pump, the excitation energy is shared and oscillates between the longitudinal SP mode of gold nanorods and the excited state of Thia J-aggregates with the Rabi frequency. It may be expected that a transient oscillation signal is observed between the bleaching of the J-aggregates and excited SP mode during the lifetime of hybrid states. Before assigning the new transient spectral features that are due to coherent coupling, three points still need to be clarified. First, in our case, the Rabi oscillation period of about 15 fs (Rabi splitting 190 meV) is too fast to be resolved by our 100 fs laser setup, so what we observe is an average result of this coherent oscillation. The transient spectra show both signal of the bleaching of J-aggregates and excited SP mode and decay with the same rate. Second, it is worth noting that SP absorption cannot be bleached and is barely changed after the excitation due to its intrinsic nature, so in transient experiments, nearly the same SP absorption as that in the steady state appears. Third, the observed spectrum in the transient experiments is a difference between the spectrum after the excitation and steady state. With all of these considerations, if the new transient spectral feature results from the coherent coupling, except the bleaching of J-aggregates, it will match the difference spectrum (A−B) by substracting absorption of bare gold nanorods (spectrum A) with that of hybrid structure (spectrum B). Figure 4a shows that the two spectra match very well in the SP absorption range, while the transient spectrum has additional bleaching part of J-aggregates. This gives unambiguous evidence for the existence of coherent coupling; that is, the dye molecule and SP coherently share the excitation. The lifetime of this coherent state is very short owing to the ultrafast damping of SP mode (Figure 4b, top). The fitting results give the same time constant of about 110 fs for both the SP absorption decay and the bleaching recovery of J-aggregates (the ps tail is due to electron–phonon relaxation). After the coherent states decay out, the excited electrons in the nanorod are thermalized to reach higher temperatures. Thus after 1 ps, the two distinctive bleaching bands result from the thermal effect of gold nanorods, just like the case under 400 nm excitation.

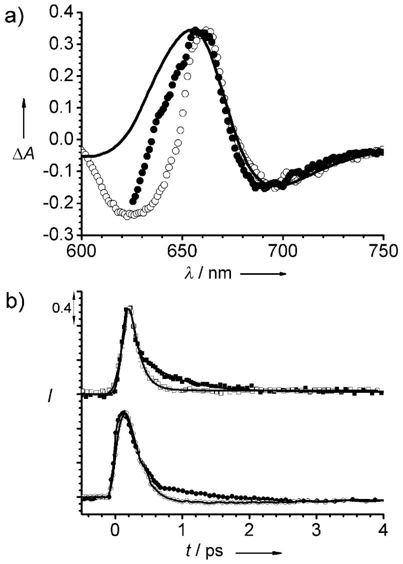

Figure 4. a) Comparison of a difference spectrum (——) to transient spectra using 610 nm (●) and 690 nm (○) excitation laser pulses. b) Top: kinetics traces of a hybrid structure solution at 625 nm (■) and 655 nm (□) using 690 nm excitation laser pulses. Bottom: kinetic traces of hybrid structure solution at 625 nm (●) and 655 nm (○) using 610 nm excitation laser pulses.

According to the nature of coherent coupling, the up and low hybrid states possess similar characteristics, which are the mixture of SP and exciton. In fact, under 610 nm excitation, the transient absorption spectra show nearly the same behavior as that under 690 nm excitation (Figure 4a), however the lifetime of the coherent state is longer, namely about 200 fs (Figure 4b, bottom). In our case, the coupling between

SP (650 nm) and exciton (623 nm) is not in perfect resonance, so the up hybrid band is more exciton-like and the low band is more like SP. Under different pump conditions (610 nm and 690 nm), the couplings contain different weights of the initial SP or exciton populations. As the decay of the coherent states is dominated by the damping of SP mode, excitation of the less-SP-like up-band certainly results a slower decay process. It should be noted that the lifetime of hybrid state remains the same as the pump power changes. Furthermore, we performed the same experiments on another hybrid sample in which the longitudinal SP resonance of the nanorod is found at 632 nm. In this case, SP mode and molecules are more close to resonant coupling. The transient results show similar spectral features, and hybrid state is found to be the present with nearly the same lifetime (150 fs) under the up- and low-state excitations (Figure 5).

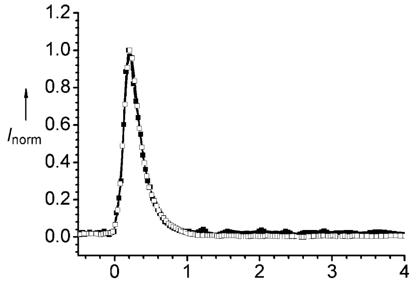

Figure 5. Kinetic traces under up- (□) and low-state (■) excitations using the nanorods with a longitudinal SP resonance at 632 nm.

The experiments under resonant excitation clearly release the coherent nature and dynamics of SP–exciton hybrid states. The photophysics is quite like the behavior of polaritons in optical microcavity,[7] where instead of a local SP mode, the strong coupling happens between the exciton and cavity photon, and the lifetime of polaritons is determined by the leakage rate of cavity photon. Finally, we should point out that transient SP absorption is hardly observed in bare metal nanoparticles owing to its nonbleachable nature. Large amounts of previous ultrafast transient results in various metal nanoparticles only reflecting the thermal effect, such as electron–electron scattering and electron–phonon relaxation process.[15c,16] Our experiments indicate that molecule-coated metal nanoparticles under strong coupling conditions offer a very interesting system to directly study real SP-related dynamics processes to gain further insight into the nature of SP.

In summary, we have constructed a molecule-coated gold nanorod hybrid structure and studied the photophysics of hybrid states using an ultrafast pump-probe approach. Under nonresonant excitation, the transient spectral features are simply caused by the thermal effect of gold nanrods, and the kinetics reflects the electron–phonon relaxation process of gold electrons. Under resonant pump, the transient results demonstrate that the excitation energy is indeed shared by the longitudinal SP mode of gold nanorods and the excited state of Thia J-aggregates, and the SP and exciton are found to decay with exactly same rate. This result gives a robust proof of coherent coupling between the exciton and SP mode. The coherent coupling is very short in duration (110–200 fs), and is dominated by the ultrafast damping of the SP mode. The photophysics has very similar behavior as the polaritons in the optical microcavity. Therefore, this work opens up a very good opportunity to realize the same function as expected from an optical microcavity, such as a polariton laser at nanoscale,[17] and also related quantum optical studies.[18]

Received: March 9, 2011

Keywords: photophysics · resonant excitation · strong coupling · surface plasmon · transient absorption

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