Active Plasmonics

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An Unusual Marriage: Coupling Molecular Excitons to Surface Plasmon Polaritons in Metal Nanostructures**

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In a recent article, Salomon et al.[1] studied how molecules, and specifically J-aggregated molecules, interact with light confined to a periodic array of tiny cylindrical holes inside a silver film. They found that the excited-state lifetimes are slightly different from those of the bare molecules. What is then exciting about this feature, and why does it merit discussion?

When light impinges on metallic nanostructures, it interacts with a large density of mobile conduction electrons. This interaction gives rise to charge and current oscillations—surface plasmons—within the skin depth of the metal surface. In turn, these oscillating charges create an optical field near the surface that modifies the surrounding field acting on them. This mutual interaction results in the formation of combined resonant modes of the electron motion and the surface-bound evanescent electromagnetic field, which are known as surface plasmon polaritons (SPPs). Even though the optical properties of SPPs have been studied for many years,[2] there has been an upsurge of new interest in "plasmonics", that is, in SPP optics, during the last few years. This interest is so profound because the spatial extent of the SPP fields is dictated by the geometry of the metallic nanostructures rather than by the wavelength of the light. At visible frequencies, SPP fields can be spatially localized to dimensions of 10 nm or even less, thereby overcoming the diffraction limit of far-field optics. Moreover, the resulting SPP field strength can be much higher than that of the incident electromagnetic field. This unique combination of field localization and field enhancement in metallic nanostructures is of interest in a whole range of optoelectronic applications. Ultrasensitive nano- and biosensing applications using, for example, surface-enhanced Raman spectroscopy, have been well-known for quite some time. Recently, more controlled tip-enhanced Raman spectroscopy has promised chemical sensing of single molecules.[3] The strong-field localization also makes it interesting to explore metallic nanowires or chains of metallic nanoparticles as novel types of SPP waveguides that can transport light on the nanoscale.[4] Finally, the local field enhancement can give rise to greatly enhanced optical nonlinearites, which is of key importance for designing novel ultrahigh resolution optical microscopes[5] or even ultrafast tip-enhanced electron microscopes.[6]

So far, however, most of these promising applications suffer from the substantial SPP losses resulting from the finite conductivity of the metal and significant radiation damping by the metallic nanostructures. SPP excitations in metallic nanostructures typically live for only few tens or at most a few hundreds of femtoseconds until they decay either into heat or into far-field radiation.[7] Therefore, the propagation distances of SPP, which can travel at almost the speed of light, are mostly restricted to few tens of micrometers, thus limiting for example waveguide applications.

Consequently, quite a number of research groups are currently searching for ways to overcome these loss problems. A promising strategy, initially suggested by Bergman and Stockman,[8] is to couple metal nanostructures to active media, such as semiconductor nanostructures or molecular aggregates. Unlike metallic nanostructures, such active media can show pronounced nonlinear optical effects and can for example be optically or electrically excited to reach population inversion. The inverted active medium can then be utilized to achieve SPP amplification or lasing (Figure 1).

Such a SPP laser differs substantially from a regular laser in that it is based on the amplification of evanescent rather than propagating waves. A first prototype of a SPP laser consisting of a cadmium sulfide nanowire deposited on a silver film was demonstrated just a few months ago.[9] Hybrid metal/molecule or metal/semiconductor nanostructures are not only interesting for designing new nanolasers; the active medium can also be used to efficiently and rapidly switch the SPP field on and off, resulting in ultrafast SPP switches that may be important for implementing novel types of optical transistors operating at THz speed.

At present, however, it is rather challenging to design such novel plasmonic devices, because the optical properties of hybrid nanostructures are far from being understood. To date, most optical studies have focused on their linear optical properties in an attempt to demonstrate the formation of new

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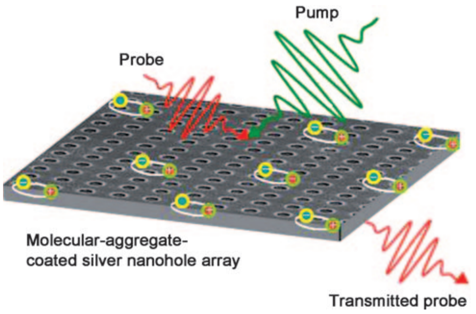

Figure 1. The experiment performed by Salomon et al.[1] A hybrid nanostructure is formed by spin-coating a thin layer of J-aggregated molecules onto a metallic nanostructure fabricated by perforating a 100 nm thick silver film with a hexagonal array of holes 230 nm in diameter. The dynamics of coupled exciton–SPP hybrid modes is studied in a transient absorption experiment. An ultrafast pump laser centered at a wavelength of 400 nm excites the hybrid structure. A spectrally broad-band probe laser transmitted through the array monitors the pump-induced transient changes of the optical transmission spectrum as a function of the time delay between both pulses.

hybrid states. Such hybrid states are formed if SPPs, the optical excitations of metal nanostructures, couple to excitons, the optical excitations of the active medium, by their optical near-field. The formation of such "excimons" (exciton–plasmon complexes) or "photoplexes", as Salomon et al. have labeled them, has now been established in a series of hybrid structures comprising both molecular[10] and semiconductor[11] active media. As in molecular spectroscopy, the energy splitting between coupled hybrid states has been analyzed, and Rabi splittings of up to several 100 meV have been found. Such large splittings show that the local enhancement of the near-field in these structures can result in very strong coupling effects.

Salomon et al.[1] find signatures of such a strong coupling between excitons and SPP in a hybrid structure comprised of a thin film of highly concentrated J aggregates of a phorphyrinoid (H_4TPPS; acidic form of tetraphenylporphyrintetrasulfonic acid) dissolved in polyvinyl alcohol. This film is spin-coated onto a silver film perforated with a periodic hexagonal array of nanometer-sized holes. Such J-aggregate films have high optical absorption coefficients, that is, large dipole moments, and narrow excitonic absorption resonances, which are important ingredients for large Rabi splittings. The optical properties of such hole arrays have recently been extensively studied because of their unusual transmission properties:[12] They show transmission peaks exceeding the filling fraction of the holes at certain resonance wavelengths. These peaks are related to the excitation of SPPs at both interfaces of the metal film. Transmission spectra of this hybrid structure indicate the formation of coupled exciton–SPP modes with Rabi splitting of about 200 meV.

Salomon et al.[1] now go one step beyond such linear optical measurements by probing the dynamics of these hybrid modes in a transient absorption experiment (Figure 1). Essentially they find indications for a reduction in lifetime of the coupled exciton–SPP states: The transient absorption resonance of the coupled state shows a fast decay component with a lifetime of 700 fs. In comparison, the corresponding S_2 exciton resonance of the bare J-aggregate film decays with a lifetime of only 2.5 ps. It is not yet very clear what the microscopic mechanisms underlying these modified relaxation dynamics are. Potentially, the formation of coupled states changes the relaxation pathways to lower-lying exciton states, as suggested in Figure 1 of Ref. [1]. It may also be expected that the coupling to SPP will modify the radiative damping of the excitons. To date, such Purcell effects have mostly been studied for weakly coupled hybrid structures. Independent of the exact origin of this effect, it is clear that the formation of exciton–plasmon complexes owing to electromagnetic interactions alters the dynamics of the optical excitations of the hybrid structures. This work is a step forward in unraveling the photophysical and optoelectronic properties of such hybrid complexes. However, much more still needs to be known to reveal their full potential for nanophotonic applications. Much like in the early days of molecular spectroscopy, many details about their wavefunctions, the relaxation dynamics and coherence properties of their excitations, and in particular about the microscopic interactions holding these complexes together need to be uncovered. The complex vectorial nature of the optical near-fields governing these interactions[13] poses not only substantial experimental but also theoretical challenges. More work along these lines will certainly follow in the near future.

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