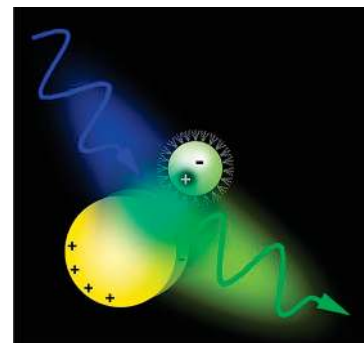


Exciton–Plasmon Interactions in Metal–Semiconductor Nanostructures

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ABSTRACT The complementary optical properties of metal and semiconductor nanostructures make them attractive components for many applications that require controlled flow of electromagnetic energy on the nanometer length scale. When combined into heterostructures, the nanometer-scale vicinity of the two material systems leads to interactions between quantum-confined electronic states in semiconductor nanostructures and dielectric-confined electromagnetic modes in the metal counterparts. Such exciton–plasmon interactions allow design of absorption and emission properties, control of nanoscale energy-transfer processes, creation of new excitations in the strong coupling regime, and increase of optical nonlinearities. With the advancement of novel fabrication techniques, the functionalities of metal–semiconductor nanostructures will be further increased for better control of optical properties and energy flows on nanometer length and femtosecond time scales.



The popularity of nanoscience has exploded within the last two decades, mainly because new nanofabrication processes have led to a wealth of novel, engineered nanostructures with tunable size and shape parameters, leaving researchers with unprecedented control over their electronic, optical, and mechanical properties. Some of the most prominent optical nanostructures include metal nanoparticles^{1,2} with controllable absorption and scattering resonances resulting from surface plasmon (SP) excitations and low-dimensional semiconductor nanostructures^{3,4} with engineered electronic levels that can give rise to tunable, highly efficient emission and absorption. The advantages of nanomaterials are not limited to controllable optical properties of single components but extend to the unique possibilities to combine different nanomaterials into composite structures. Such hybrid materials feature properties of two or more components and potentially synergistic properties caused by interactions between the nanoscale constituents. Interactions can be very strong as both the building blocks and the separation between the components have nanoscale dimensions. The number of possible hybrid materials that can be built from existing nanostructures is enormous; therefore, the potential for creating highly functional hybrid materials that enable, modify, and control energy processes and pathways is very promising.

Here, I will discuss the perspectives that are presented by interactions of optical excitations in metal–semiconductor nanostructures. Both material systems exhibit excitations at optical frequencies that can be designed to be resonant with each other. This opens up the possibility for coupled excitations that can act differently than the optical excitations of the individual components. Optical excitations in semiconductor nanostructures are defined by the electronic levels in the

conduction and valence bands. As a result of quantum confinement, the electronic levels are discrete in one or more dimensions and can be tuned by size and shape (Figure 1a).^{3,4} The fundamental optical excitations are transitions between these discrete levels in the conduction and valence bands that lead to the formation of bound electron–hole pairs or excitons. The equivalents in metal nanostructures are so-called surface plasmons that are collective oscillations of conduction band electrons.^{1,2} These SPs arise from the dielectric contrast between the metal nanostructure and the nonconductive environment, and the SP resonance frequency can be controlled by shape and size as well (Figure 1b).

Interactions between excitons and SPs occur when metal and semiconductor nanostructures are in close proximity. One often discerns two opposite cases of weak and strong coupling. In the weak coupling regime, wave functions and electromagnetic modes of excitons and plasmons are considered unperturbed, and exciton–plasmon interactions are often described by the coupling of the exciton dipole with the electromagnetic field of the SP. This model has been used to explain the original experiments by Drexhagen, who studied the change of the excitation decay rate of an emission dipole in the proximity of a plane metal surface.⁵ In general, well-known phenomena including enhanced absorption cross sections, increased radiative rates, and exciton–plasmon energy transfer are described in the weak coupling regime. The challenge remains to properly calculate the electromagnetic fields in the proximity of metal nanoparticles of nontrivial

Received Date: August 5, 2010

Accepted Date: September 7, 2010

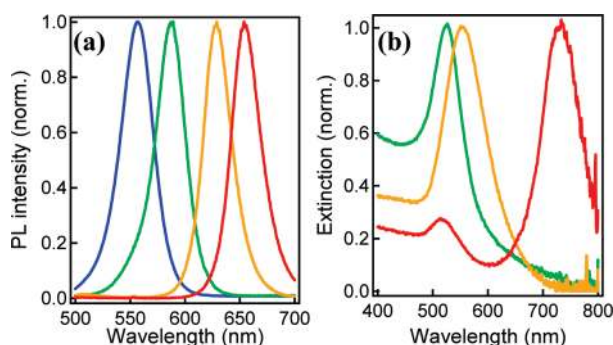


Figure 1. (a) Size-tunable emission spectra of CdSe/ZnS core/shell NCs. Spectra centered at longer wavelengths correspond to NCs with larger core diameters. (b) Size- and shape-tunable extinction spectra of gold nanoparticles, nanospheres with 30 and 90 nm diameters (green and orange line) and nanorods (red line).

shape and to take into account exciton wave functions beyond the point dipole approximation. The strong coupling regime is considered when resonant exciton–plasmon interactions modify exciton wave functions and SP modes and lead to changes of exciton and SP resonance energies that are larger than their natural line widths. In this regime, the excitation energy is shared and oscillates between the plasmonic and excitonic systems (Rabi oscillations), and a typical anticrossing and splitting of energy levels at the resonance frequency is observed. A thorough theoretical analysis is complicated, and one often uses a coupled oscillator model with a phenomenological interaction term that is related to the energy splitting at the resonance frequency.

A large variety of material systems has been used to study exciton–plasmon interactions. For the plasmonic part, gold and silver nanostructures are most often considered, although other metals offer interesting opportunities as well, such as aluminum with SP resonances in the ultraviolet (see ref 6 and references therein). Silver is advantageous for plasmonics because of low intrinsic losses that result in narrow SP resonances with high oscillator strengths and large optical field enhancements. The down side of silver is its reactivity in air with sulfur that corrodes the silver.⁷ Gold is a very inert metal but has higher intrinsic losses than silver, especially in the short wavelength range of the visible spectrum, where interband transitions occur.⁸ Intrinsic losses dampen SP oscillations and cause a broadening of SP resonances and lower quality factors. Therefore, plasmonic structures with target functionalities in the 400–530 nm wavelength range should be based on silver (or aluminum) nanostructures, while at longer wavelengths, gold structures are a good choice. The fabrication of metal nanostructures can be based on either lithography techniques or colloidal synthesis. In general, the former is well-suited for structures of 100 nm or larger, while the latter works well for sub-100 nm structures. Both approaches provide tunability over size and shape. Control over the location of metal nanostructures is straightforward with lithography techniques, and even large arrays with 100 nm feature sizes are possible to fabricate;⁹ for colloidal metal nanoparticles, it has been shown that self-assembly techniques provide a cost-effective way for arranging nanoparticles.^{10–13}

A broad range of semiconductors has been considered for exploring exciton–plasmon interactions. Silicon nanostructures have attracted a lot of attention since they can be integrated into existing chip technologies.¹⁴ Despite the indirect band gap, nanoscale Si structures are luminescent and have been combined with metal nanostructures to investigate exciton–plasmon interactions.¹⁵ However, semiconductors with a direct band gap are more commonly used in hybrid metal–semiconductor nanostructures. Generally speaking, there are two main fabrication procedures for semiconductor nanostructures, which are epitaxy and colloidal chemistry. The latter method allows synthesis of semiconductor nanocrystals (NCs) that are most widely used in the metal–semiconductor hybrid nanostructures discussed here.⁴ The preferences of colloidal over epitaxial techniques for studying exciton–plasmon interactions are wide tunability of NC optical properties (Figure 1a), strong NC nonlinearities, and compatibility with self-assembly techniques that allow the combination of NCs with metal nanostructures.

Most often, metal and semiconductor nanostructures are first fabricated individually and then combined using techniques with different sophistication levels ranging from simple drop casting to controlled attachment procedures based on specific linker molecules. The assembly can be a key process for obtaining well-defined hybrid structures that are a prerequisite for a detailed study of exciton–plasmon interactions. Ideally, location, mutual orientation, and number of semiconductor and metal components should be well-defined and controllable. More recently, a new type of metal–semiconductor nanostructure has been developed based on colloidal chemistry that incorporates the metallic and semiconductor materials into a single unit that can have various architectures including core/shell,^{16,17} dumbbells, dot-on-rod,¹⁸ and so forth. This approach has great potential because the resulting hybrid nanostructures should be structurally very stable and exciton–plasmon interactions are enhanced because of the absence of spacer layers, such as linker molecules, between metal and semiconductor entities.¹⁹ It has to be noted though that for certain applications, for example, luminescence enhancement, dielectric spacer layers are required to omit unwanted nonradiative energy transfer.²⁰

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The attraction of combining metal and semiconductor nanostructures stems from their complementary optical properties, which are long-lived excitations in semiconductor nanostructures and localized electromagnetic modes in metal nanostructures. The former give rise to high emission yields

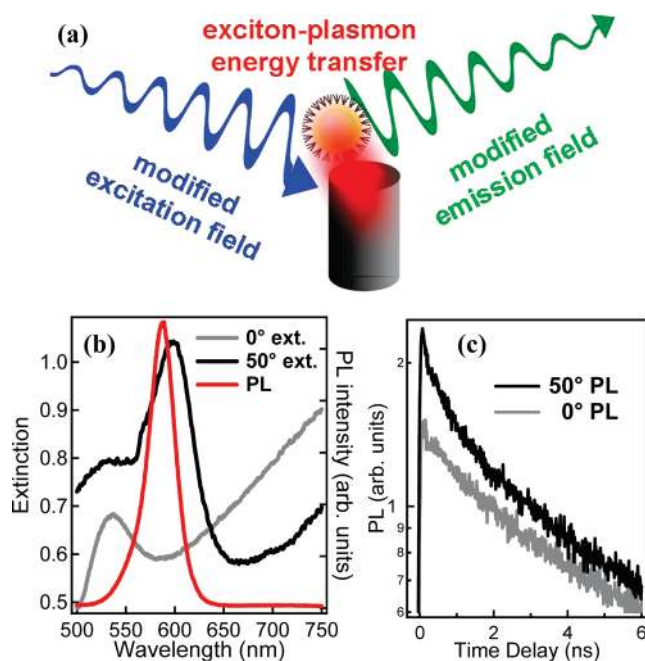


Figure 2. (a) Schematic of resonant exciton–plasmon interactions that can occur in metal–semiconductor nanostructures. (b) Emission spectrum of NCs (red line) and extinction spectra of Au disk arrays taken at 0° (gray line) and 50° (black line) incident angles. (c) p-Polarized emission detected at 0° (gray line) and 50° (black line) collection angles from NCs that were deposited onto the Au disk array. Adapted from ref 38.

and light-harvesting capabilities, while the latter enable the concentration of electromagnetic energy and enhance optical fields and nonlinearities. Therefore, the combination of the two material systems can provide attractive opportunities to modify and design specific optical properties and to observe new phenomena that are based on exciton–plasmon interactions (Figure 2a). Recent examples have been ubiquitous and can be roughly divided into three categories, which are modification and design of absorption and emission properties,^{20–40} energy transfer between excitonic and plasmonic systems,^{41–52} and strong coupling with coherent exciton–plasmon interactions.^{53,54} This partitioning should not be taken too rigorously because many of the observed phenomena are simply different facets of the same underlying physical process. Besides a fundamental interest in the properties of exciton–plasmon interactions, metal–semiconductor nanostructures have also attracted attention for their potential use in applications including optical sensing, light emitters, photovoltaic systems, and quantum information and communication applications.

The attraction of combining metal and semiconductor nanostructures stems from their complementary optical properties.

The excitation of surface plasmons is a resonant process with a resonance frequency that is determined by composition, size, and shape of the metal nanoparticle and its dielectric environment. The coherent motion of conduction band electrons that is associated with SPs leads to strong electromagnetic fields that are localized at the surface of the metallic nanostructure. For simple shapes such as spheres and ellipsoids, the fields around small metal nanoparticles can be determined analytically. However, numerical simulations based on finite element methods have to be employed to calculate fields in the vicinity of more complicated, realistic shapes and nanoparticle assemblies. The field localization that is often in line with a field enhancement is one of the main drivers in plasmonics.^{55,56} In general, with a reduction of the size of the metal nanostructure, the field localization increases, but the absorption and scattering cross sections decrease. Since these cross sections follow different scaling laws, the optimal size and shape of the metal nanostructure depends on the applications that require either strong absorption or scattering effects.⁵⁷ In the context of exciton–plasmon interactions, these electromagnetic field enhancements have been utilized in photodetectors and photovoltaic devices.^{21–24} The metallic nanostructures localize the impinging light field that then is absorbed by an appropriate light harvester, such as organic molecules or semiconductor nanostructures, which is located in the proximity of the metal structure (Figure 2a). In this configuration, a large fraction of the light can be absorbed by the excitonic structure, and therefore, such exciton–plasmon interactions lead to an effective increase of the absorption cross section of the organic or inorganic semiconductor nanostructure. Hence, metal–semiconductor nanostructures can increase the performance of photovoltaic devices since they enable thinner absorption layers that reduce losses occurring in thicker layers due to short exciton diffusion lengths.^{22,24}

Exciton–plasmon interactions can also give rise to modified emission properties^{20,25–35} and enhanced device efficiencies of light emitters.^{36,37} In all-optical configurations when the emitters are optically excited, one has to distinguish between emission enhancements caused by an increase of the effective absorption cross section (see above) or by a change of the emission properties, such as the radiative lifetime or emission pattern (Figure 2a). As has been suggested by Purcell, the spontaneous decay rate of a transition can be modified by coupling it to a resonant system.^{58,59} Here, metal nanostructures provide the resonators that couple to the excitons through near-field interactions when spectral overlap between emitter and SP energies and precise positioning of the emitter in the vicinity of the metal nanostructure is achieved.^{20,25–32} Recently, we studied such exciton–plasmon interactions in hybrid systems comprised of CdSe NCs that were spin-coated on a gold nanodisk array.³⁸ Because of the nonspherical shape of the nanodisks, they exhibit two spectrally distinct SP resonances (in- and out-of-plane) that are excited with different polarizations and angles of incident light. Specifically, the out-of-plane SP resonance that spectrally overlaps with the NC emission can only be excited at off-normal angles (Figure 2b). We then showed that the emission decay of the optically excited NCs is accelerated

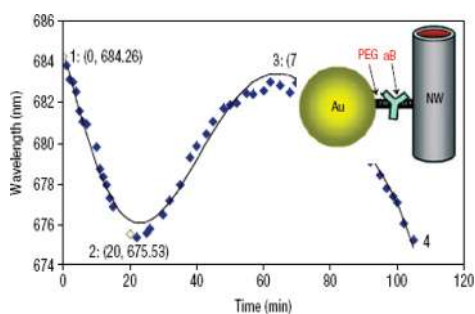


Figure 3. Reversible modulation of the emission wavelength of CdTe nanowires caused by a separation change between the nanowires and attached Au nanoparticles. Inset: Schematic of the CdTe nanowire with linker molecules that attach to Au nanoparticles. Reprinted by permission from Macmillan Publishers Ltd.: Nature Materials.⁴¹

when detected at a wavelength, angle, and polarization that correspond to a maximum in extinction measurements (Figure 2c). Because the extinction spectra are dominated by SP effects, the accelerated decay is attributed to NC–SP interactions and, more specifically, to an increased radiative rate caused by locally enhanced radiation fields in the vicinity of the gold nanodisks.⁵⁸ We determined a radiative rate enhancement of ~ 11 that is associated with an electric field enhancement of ~ 3.5 . The correspondence between measurements of extinction resonances and radiative rate enhancements under matching geometries can be explained by the generalized reciprocity between absorption and emission of homogeneous and evanescent waves and their angular components in the far and near field of local scatterers.⁶⁰ While radiative rate enhancements in hybrid exciton–plasmon structures have been widely reported, the opposite effect of a reduction in radiative rates has also been predicted.^{52,59} This effect could be beneficial for solar cell applications since a longer lifetime allows more time for charge separation to occur.

The emission enhancement caused by exciton–plasmon interactions, as discussed above, has been promoted among other applications in the context of increasing the sensitivity of fluorescence-based sensors. A different approach in using exciton–plasmon interactions for sensor applications has been presented by Jaebeom Lee et al.⁴¹ In their work, they used assemblies of gold nanoparticles and CdTe nanowires to demonstrate that the CdTe emission wavelength depends on the separation of the Au–CdTe hybrid nanostructures (Figure 3a). When target proteins attach to antibodies that are incorporated in linker molecules between the gold nanoparticles and the semiconductor nanowires, the separation changes, which results in a modification of the energy-transfer efficiency between the semiconductor and metal nanostructures and, as a result, in a change of the emission wavelength.⁴¹ More specifically, emission occurs from a higher (lower) energy level when the Au–CdTe separation is small (large) and the semiconductor–metal energy transfer is fast (slow). This effect must not be confused with a change of the electronic energy levels that happens in the strong coupling regime. Because spectral modifications are easier to record than emission intensity changes, the proposed concept is

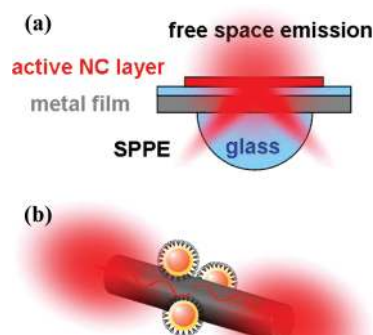


Figure 4. Typical configurations of metal–semiconductor nanostructures that lead to exciton–SP energy transfer. (a) Excited semiconductor NCs that are deposited on a metal film release their energy into free space emission or excite SPPs on the metal surface that then can decay radiatively and generate SPP emission (SPPE). A dielectric spacer layer prevents close contact between metal and semiconductor components and avoids NC emission quenching caused by coupling to lossy surface waves. (b) NCs attached to a metal nanorod can excite single SPPs that propagate along the metal wire, enabling nanoscale energy transport and localization. Since the propagating SPPs rapidly remove the energy from the location of the NCs, energy back transfer is unlikely.

more robust toward fluctuations in the optical conditions of the samples and, therefore, well-suited for optical sensing applications.

The possibility of exchanging energy between the excitonic and the plasmonic system has been exploited in many situations,^{42–46} including SP amplification and lasing.^{47–52} In general, when an optical dipole is located in the vicinity of a metal structure and spectrally resonant with SPs, energy transfer between the two systems occurs. In the case of weak exciton–plasmon coupling, the energy transfer can be considered unidirectional. The energy is transferred to the metal or semiconductor subsystem that either spatially removes the energy from the interaction zone (examples shown in Figure 4) or rapidly relaxes the energy to lower energy levels, thereby omitting resonant back transfer. In a simple model system consisting of NCs in the proximity of a thin metal film, energy transfer occurs from the excitonic system to surface plasmon polaritons (SPPs) that propagate on the metal surface. The coupled energy can then be released into photons and generate surface plasmon polariton coupled emission, as schematically shown in Figure 4a,^{42,45} or it can be used to amplify SPPs.^{49,50} Semiconductor nanocrystals are particularly well-suited for this task due to their high optical gain that arises from multiexcitons that can couple to surface plasmon polaritons.⁴⁶ When nanocrystals couple with metallic nanorods (Figure 4b), the energy is guided, locally concentrated, and released by SPs.^{44,45} In such nanoscale energy transport, the transferred energy maintains the quantized character of the excitonic source and can lead to single SP excitations.⁴⁵

While in most of the discussion above, the exciton–plasmon interaction is in the weak coupling regime, strong exciton–plasmon coupling with typical anticrossing between coupled oscillator energies has been observed as well.^{53,54} In the strong coupling regime, the energy is stored in both systems and oscillates back and forth between excitons and

SPs (Rabi oscillations). The difficulty of achieving strong coupling is due to the decoherence time of SPs that is on the femtosecond time scale and often shorter than the time required for Rabi oscillations. Interband absorption and scattering due to surface roughness are two effects that can cause substantial losses and reduce the SP decoherence time significantly. Nevertheless, various groups have demonstrated strong exciton–SP coupling with organic⁶¹ and epitaxial⁵³ and colloidal⁵⁴ semiconductor nanostructures. Another coherent phenomenon has been demonstrated by the Ouyang group using Au/CdSe core/shell nanostructures.¹⁹ The exciton–plasmon interaction amplifies optical nonlinearities and leads to an enhanced optical Stark effect that is a change of energy levels in the presence of an optical light field. With circular polarized, subresonant light, the enhanced optical Stark effect can induce a spin splitting of electrons that then allows spin manipulation in the CdSe component of the hybrid nanostructures.¹⁹ Hence, these metal–semiconductor nanostructures are attractive for quantum information applications that require spin manipulation as one of the key processes. Ouyang's work demonstrates nicely the promising perspectives of using metal–semiconductor nanostructures for enhancing optical nonlinearities and ultrafast control of light–matter interactions.

In conclusion, exciton–plasmon interactions in metal–semiconductor nanostructures offer a wide range of opportunities to control light–matter interactions and electromagnetic energy flows on nanometer length scales. While many linear optical properties have been well studied and utilized in application-relevant settings, metal–semiconductor nanostructure hold great promise for controlling nonlinear optical properties. Specifically, the enhancement of usually weak optical nonlinearities can be utilized for optical switching, amplification, and coherent control of light–matter interactions. Moreover, SP resonances are intrinsically broad-band and well-suited for ultrafast operation.^{62,63} Therefore, femtosecond studies of exciton–plasmon interactions^{19,64} will promote the design of metal–semiconductor nanostructures with ultrafast functionalities. All of these phenomena and applications of exciton–plasmon interactions rely on carefully designed material systems that should be both well-controlled and producible in an easy and cost-effective manner. Self-assembly techniques are particularly well-suited for fulfilling these requirements and, therefore, most promising for future metal–semiconductor composite nanostructures that exhibit interesting exciton–plasmon interactions. While the field as a whole is well-advanced, challenges remain in both experimental and theoretical aspects. The functionality of many metal–semiconductor systems is still hampered by losses. New concepts need to be developed that either reduce intrinsic losses directly (e.g., by reducing the metal component of the heterostructures) or compensate them with additional gain structures. At the same time, SP resonance and exciton dipole strengths need to be maintained high for efficient exciton–plasmon interactions. Surface roughness in metal–semiconductor heterostructures can be another source of losses. However, it can also be the origin of strong exciton–plasmon interactions through field concentrations on irregularities and, therefore, dominate experimental findings.

Hence, control over surface properties is essential for a systematic evaluation of exciton–plasmon interactions and for comparing experiments with numerical simulations that are often challenged by the different length scales involved between the wavelength of light and nanometer-scale structural features.

Metal–semiconductor nanostructure hold great promise for controlling nonlinear optical properties

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Marc Achermann received his Ph.D. on ultrafast optical spectroscopy of nanomaterials from ETH Zurich in 2001. Afterwards, he joined the Los Alamos National Laboratory as a postdoctoral researcher and staff member. In 2006, he became Assistant Professor at the University of Massachusetts Amherst, working on time-resolved optical spectroscopy of nanoscale structures and assemblies, and in 2010, he moved to the Lucerne University of Applied Sciences and Arts. For more information, see: <http://www.people.umass.edu/acherman/>.

ACKNOWLEDGMENT The author would like to acknowledge support from the National Science Foundation under Grant ECCS-0725609.

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