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Suppression of the Plasmon Resonance in Au/CdS Colloidal Nanocomposites

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ABSTRACT: The nature of exciton—plasmon interactions in Au-tipped CdS nanorods has been investigated using femtosecond transient absorption spectroscopy. The study demonstrates that the key optoelectronic properties of composite heterostructures comprising electrically coupled metal and semiconductor domains are substantially different from those observed in systems with weak interdomain coupling. In particular, strongly coupled nanocomposites promote mixing of electronic states at semiconductor—metal domain interfaces, which causes a significant suppression of both plasmon and exciton excitations of carriers.

KEYWORDS: Plasmonics, photovoltaics, nanocrystals, quantum dots, nanorods

Bulk heterojunctions of metal and semiconductor materials have long been of interest to fundamental science and device engineering due to the unique interaction of respective domains through the formation of the space-charge region,1 which gives rise to numerous technological applications including Schottky barrier solar cells,2 solid state lasers,3 light-emitting diodes,4 and field effect transistors.5 Recently, the growing ability to fabricate metal—semiconductor (M-S) composites on a nanoscale has opened up new opportunities for designing multifunctional materials with properties that cannot be obtained in the bulk phase. Over the past decade, a wide variety of nanocomposite morphologies, including metal-core/semiconductor-shell heterostructures,6–8 metal-tipped semiconductor nanocrystals (NCs),9–17 and organically and nonepitaxially coupled metal—semiconductor composites have all been proposed for manipulating energy at nanoscale with potential utilization of these nanomaterials in areas of photovoltaics and solar fuel production,18 lasers,19 and Schottky detectors.20

Of a particular interest is a fundamental interaction between semiconductor excitons and surface plasmons (SP) of metal nanoparticles, which results from the modification of the exciton dipole moment due to local electromagnetic modes of SP.23,24 This interaction is enabled by the nanoscopic nature of both material domains and has a unique effect on optoelectronic properties of a composite M-S system, which has been shown to dramatically alter the energy flow that occurs across M-S junctions. For instance, the presence of plasmon radiative field in metals, caused by resonant oscillations of low-energy conduction electrons, can strongly affect the dynamics of excitons in S NCs via two distinct interaction mechanisms, including plasmon—exciton energy transfer and modification of the local radiation field in S domains.

Multiple studies have explored the nature of exciton—plasmon interactions in a weak coupling regime, characterized by the presence of a substantial potential barrier at the interface of S and M components, which was achieved experimentally by using spacer molecules or nonepitaxial domain coupling. For these composites, the emission intensity in S domains was increased25–32 due to the plasmon-induced enhancement of S radiative rates,33,34 and was subsequently explored toward improving the process of light amplification in lasers.35–38 Likewise, the plasmon-induced enhancement of the electric field in S domains has been demonstrated to increase the absorption cross section of S nanocrystals,39,40 thus promoting the development of light-concentrating nanocomposites to aid the energy harvesting mechanism in photovoltaic and photocatalytic applications.41–44 In addition to intensity enhancement, spectral modulation of the S emission in S-M composites has also been utilized for sensing target proteins attached to the linker moiety in Au-CdTe assemblies.41 Finally a weak exciton—plasmon interaction, achieved through nonepitaxial coupling of M and S domains using a core/shell morphology, has been employed for controlling the spin of Au nanoparticles,18 with potential utilization of this phenomenon in quantum information and spintronics.42–44

When metal and semiconductor components are coupled directly, without using a spacer moiety, the potential barrier for charges residing in adjacent domains may become sufficiently small to allow interdomain charge transfer and associated mixing of electronic states at the M-S interface. In addition, the enhanced
Temporal changes in the absorbance of CdS NRs induced by 340 nm excitation pulses. The negative signal around 1S(e)1S3/2(h) transitions, while a smaller negative signal at λ ≈ 410 nm corresponds to the formation of 1P(e)1P3/2(h) excitons.

The chirp-corrected transient absorption (TA) spectra (Figure 1d), resulting from the excitation of pure CdS NRs with 120 fs laser pulses (λ exc = 340 nm), show an expected bleach of 1S(e)−1S3/2(h) transitions, as well as smaller-amplitude bleach, explain the commonly observed suppression of FL emission in Au/CdS nanocomposites. Instead, present measurements indicate that the formation of excitons and corresponding band gap emission in CdS are suppressed as a result of ultrafast carrier trapping by the interfacial states. Finally, we propose that charging of gold domains under illumination effectively decreases the quantum confinement of CdS nanorods, which explains previously observed modification of CdS spectra in M-S nanocomposites.

Overall, the unique result revealed by ultrafast measurements is the demonstration of the spectroscopic evidence that optical signatures of isolated semiconductor (CdS) and metal (Au) domains are strongly modified in M-S systems exhibiting direct coupling of both domains. This is accompanied by the onset of new optical features, not present in weakly coupled M-S composites that include broad-range photoinduced absorption, plasmon damping, and delocalization of S excitations into Au domains, all of which may be important for the development of novel device technologies.

To better understand the nature of interaction between CdS and Au domains, we first re-examine the optical properties of isolated Au and CdS nanocrystals. Figure 1 shows the absorbance spectra of CdS nanorods fabricated via known seeded-type colloidal methods. The spatial confinement of optical excitations in the transverse direction of CdS rods gives rise to a characteristic excitonic edge around 465 nm, which corresponds to the lowest energy transition, 1S(e)−1S3/2(h), in these nanostructures. The sharpness of the absorption edge in Figure 1c confirms a narrow dispersion of nanorod widths, which agrees well with corresponding statistical distribution obtained from transmission electron microscopy (TEM) images of these structures (Figure 1a).

The chirp-corrected transient absorption (TA) spectra (Figure 1d), resulting from the excitation of pure CdS NRs with 120 fs laser pulses (λ exc = 340 nm), show an expected bleach of 1S(e)−1S3/2(h) transitions, as well as smaller-amplitude bleach,
corresponding to higher energy excitations of $1P(e) - 1P_{1/2}(h)$ excitons. Spectral distortion of TA traces associated with the Stark effect were not observed in these measurements due to fairly low excitation intensities, corresponding to linear power dependence regime (see Figure SFI in the Supporting Information). A negligible contribution of the Stark effect into the observed bleach dynamics is also consistent with the absence of a positive TA signal at early probe times ($\tau < 1$ ps). The observed changes in the absorption of CdS nanocrystals ($\Delta A$) are dominated by photoinduced electrons, as expected due to comparatively low effective masses of these carriers in bulk CdS and high degeneracy of hole states in CdS NCs. The recovery of $1S(e) - 1S_{1/2}(h)$ bleach is driven both via the radiative decay mechanism and trapping of excited carriers on nanorod surfaces, such that approximately half of the initial carrier population in the $1S(e)$ excited state is recovered after 300 ps, as was reported previously for isolated CdS NRs.

The absorption spectra of isolated Au nanoparticles are examined in Figure 2. Since the excitation of surface plasmons in metals is a resonant process, its frequency is dependent on the composition, size, and shape of metal nanoparticles, as well as their dielectric environment. To get a better understanding of how the size of Au nanoparticles affects the transient and steady-state absorption of SP, samples comprising three different Au nanoparticle diameters were compared. Furthermore, to facilitate a fair comparison, the range of Au nanoparticle diameters for these measurements was chosen to overlap with the size range of Au domains in investigated heteroepitaxial Au/CdS nanocomposites. According to Figure 2, the plasmon resonance is manifested in all three samples of isolated Au nanoparticles through the pronounced broad-range absorption peak in the steady-state spectra with corresponding maxima near 530 nm. A moderate variation in the spectral position of the plasmon resonance between the three measurements is consistent with the size-dependent trend of plasma oscillations according to Mie theory.

The transient absorption spectra of isolated Au colloids ($\lambda_{\text{exc}} = 400$ nm) representing the same three nanoparticle diameters show a pronounced bleach, which spectral range overlaps the steady-state absorption maxima. This negative $\Delta A$ signal in TA spectra of isolated Au nanoparticle has been previously attributed to the excitation-induced broadening of the plasmon peak, which causes the TA spectra to form a characteristic "dip" at the plasmon wavelength sandwiched by the two positive wings. Such broadening of the plasmon absorbance results from non-dipolar plasma oscillations (quadruple) in Au nanoparticles induced by the excitation pulse. Notably, the central dip in the transient spectra is observed for all investigated gold samples, which further confirms the presence of resonant excited carrier oscillations in these nanoparticles.

To study the exciton-plasmon interaction in Au/CdS composites, gold domains were grown directly onto colloidal CdS NRs using a colloidal technique recently developed in our group, which relies on the temperature-controlled reduction of Au–oleate complexes on semiconductor surfaces. Arguably, this method could be used to enable an advanced control of Au/CdS morphology and is expected to increase the area of Au/CdS interfaces exhibiting epitaxial associations, as compared to previously reported protocols utilizing room-temperature deposition of Au tips onto cadmium chalcogenides in dodecylhexamethyleneammonium bromide/dodecylamine mixture. The details of synthetic procedures for fabrication of Au/CdS nanocomposites comprising three different Au diameters are provided in the Supporting Information. Typically, to grow small-diameter Au tips on CdS NRs, 20 mg of washed CdS NRs in hexane was injected into a mixture containing 11.3 mg of AuCl$_3$ and 3 mL of degassed oleylamine. Subsequently the temperature of the solution was increased to 115 °C at a rate of 2 deg/min. To synthesize large-diameter Au domains, the amount of gold precursor was increased to 20 mg and the heating was terminated at $T = 140$ °C. TEM images of Au/Cds nanocomposites for each of the three samples are shown as inserts in corresponding TA spectra.

The dynamics of exciton–plasmon interactions in epitaxially coupled Au/CdS composites was first investigated for heterostructures comprising large-diameter Au nanocrystals ($d = 15.4$ nm), grown on one end of a CdS nanorod via a "matchstick" composite morphology (see Figure 3). The existence of epitaxial relationships between gold and semiconductor domains, with the possibility of some interfacial defects was deduced from (i) X-ray powder diffraction (XRD) measurements exhibiting no evidence of lattice alloying (see Figure S2, Supporting Information) and (ii) high-resolution TEM images showing regular lattice fringes at the Au/CdS interface and crystallographic analysis revealing low-stress stoichiometric associations of the two crystals phases. To achieve an efficient excitation of carriers in both domains of the heterostructure, the wavelength of excitation pulses was set to 400 nm, whereby delivering sufficient photon energy for the simultaneous excitation 1S excitons in CdS ($\lambda = 465$ nm) and plasmons in Au domains ($\lambda = 530$ nm).

The TA spectra of Au/CdS matchsticks in Figure 3b shows spectrally broad bleaching of the absorption profile around $\lambda = 540$ nm, which corresponds to plasmon oscillations in Au domains (note that $x$ scales in (a) and (b) are different). The intensity of this bleach reaches its maximum in less than 500 fs, driven primarily by excitations of hot carriers and simultaneous fast cooling of the nonequilibrium carrier population via electron–electron interaction, and subsequently recovers to $\Delta A(\lambda) = 0$ in 500 ps. While the observed plasmon bleaching kinetics is in line with the TA spectra of isolated Au nanoparticles, surprisingly, there is no evidence of the
TA bleaching at 445 nm, corresponding to the formation of excitons in the CdS domain of the heterostructure. In contrast to the TA profile of pure CdS NRs, showing a well-defined 1S(e) bleach (ΔA/ΔA = 0.15), the TA amplitude of Au/CdS nanocomposites in the same wavelength range is positive (green arrow in Figure 3b). The absence of a distinct excitonic feature corresponding to 1S(e)−1S3/2(h) transitions in Au/CdS composites can explain the observed quenching of FL emission in S domains, which was also reported by other studies, wherein metal tips were grown directly onto the S component via colloidal routes. However, a generally accepted explanation attributing the FL quenching in S domains to the photoinduced transfer of 1S(e) electrons into Au does not seem to be compelling in light of the full suppression of the CdS bleach. Indeed, if an electron transfer was the dominant mechanism depleting the population of 1S(e) states in CdS, a significant portion of excited electrons would still be present in the 1S(e) state after 500 fs, since the transfer of carriers across nanoscale inorganic interfaces is generally slow enough to be observed using TA spectroscopy (τ(e) > 350 fs, τ(h) > 650 fs). Furthermore, an electron transfer process by itself, cannot account for an onset of a positive TA signal spanning a broad wavelength range from 400 to 520 nm, which was not present in the TA spectra of isolated Au and CdS domains. We note however, that decay of this positive TA feature can provide some clues regarding the origin of microscopic processes underpinning the carrier dynamics in Au/CdS nanocomposites, as its slow recovery (>100 ps) strongly suggests a contribution from the photoinduced absorption (PA) of excited carriers in either Au or CdS domains.

Overall, the observed TA spectra of Au/CdS composites comprising a large-diameter gold domain (Figure 3) are qualitatively different from those of isolated Au and CdS nanoparticles, as manifested both by the absence of bleaching signal in the semiconductor component, photoinduced absorption, and by the relatively weak bleaching of the SP feature in Au. To get a deeper insight into the origin of this complex carrier dynamics, Au/CdS heterostructures comprising smaller size Au domains were examined next.

Figure 4 shows the TA spectra of Au/CdS heterostructures comprising 5.3 nm Au nanoparticles. For these nanocomposites, bleaching of the SP resonance in Au domains is no longer distinguishable, which strongly contrasts the TA dynamics of isolated nanoparticles (see Figure 1) exhibiting an apparent plasmon bleach at λ = 530 nm. The SP peak is also missing from the steady-state absorption spectrum of Au/CdS nanocomposites, even though this feature is clearly present in the absorption profile of isolated Au nanoparticles, indicating that the nature of excited electron oscillations in Au domains is modified due to direct coupling of CdS NCs. In addition to the suppressed SP feature, TA spectra in Figure 4 reveal a broad positive signal, which, in comparison with a TA trend of 15.4 nm Au/CdS heterostructures, extends across the entire spectral window of the probe pulse. The recovery of this feature is too slow to be classified as a nonlinear modification of the spectral profile due to local fields and, similar to the case of 15.4 nm Au/CdS heterostructures, was attributed to the photoinduced absorption of excited carriers occupying electronic states within CdS band gap. Interestingly, decreasing the size of gold domains from 15.4 to 5.3 nm results in the appearance of an S excitonic feature, which is manifested by a characteristic dip at λ < 450 nm, corresponding to the excitation of ground-state excitons, 1S(e)−1S3/2(h). Notably, the observed excitonic bleach is substantially weaker than that of pure CdS NRs and is offset by the positive background of the broad photoinduced absorption.

To uncover further experimental facts promoting the explanation of the observed plasmon suppression and photoinduced absorption in Au/CdS nanocomposites, we turn to the next structural morphology of Au/CdS composites, for which the size of Au domains is only 2.7 nm (Figure 5). These heterostructures were chosen as a transitional system spanning the link between optical properties of pure CdS nanorods and those of 5.3 nm Au/CdS nanocomposites, which exhibit several “unusual” trends, including suppression of the plasmon bleach, suppression of excitonic features in CdS, and spectrally broad photoinduced absorption.
Similar to 5.3 nm Au/CdS heterostructures, transient absorption spectra of Au/CdS nanocomposites comprising 2.7 nm Au tips (Figure 5b) do not reveal any evidence of spectral bleaching in the \( \lambda = 530 \text{ nm} \) range, corresponding to the excitation-induced broadening of the SP peak. Just as in the case of nanocomposites with larger tip sizes, the suppression of SP in 2.7 nm Au/CdS heterostructures contrasts the carrier dynamics observed for the control sample of isolated 2.7 nm Au nanoparticles (Figure 2), for which the presence of the plasmon resonance was manifested both through steady-state and time-resolved absorption measurements.

While SP excitations are not distinguishable in the TA spectra of 2.7 nm Au/CdS heterostructures, bleaching of excitonic transitions in the S portion of composite nanoparticles is the most pronounced of all three investigated nanocomposite morphologies, with the observed \( \Delta A \) profile being nearly identical to that of pure CdS NRs. Notably, the decay of CdS excitons in 2.7 nm Au/CdS nanocomposites occurs at an order of magnitude faster than those in pure CdS NRs, as was estimated from the comparison of respective decay traces in Figure 6, and is attributed to the transfer of photoinduced carriers from CdS into Au domains. Such charge transfer kinetics is consistent with the previously measured interdomain carrier transfer dynamics in epitaxial nanocomposites of the two semiconductor domains, for which electron transition times of 350 fs\textsuperscript{54} were reported. A slower transfer of photoinduced carriers at the Au/CdS interface compared to those of semiconductor—semiconductor composites is expected due to stress-related interfacial defects and nonmatching electron momenta in adjacent crystal lattices. Finally, the amplitude of the photoinduced absorption (the positive portion of the TA signal) in 2.7 nm Au/CdS nanocomposites was found to be substantially weaker than in 5.3 nm Au/CdS heterostructures, as can be inferred from the relatively small area of the two PA cusps in Figure 5b. This positive \( \Delta A \) signal is yet distinctly different from the TA profile of pure CdS NRs, which does not contain positive "wings" (Figure 1d), or SP excitations in Au domains, which contribute a positive \( \Delta A \) only at substantially lower energies (Figure 2). Therefore, the PA signal of Au/CdS nanocomposites is believed to arise as a result of direct coupling between M and S domains that mutually create a modified distribution of electronic states, allowing for the excitation of low-energy conduction electrons contributing to PA.

The TA dynamics of investigated Au/CdS nanocomposite morphologies shows several important trends. First, the plasmon absorption in Au/CdS heterostructured is suppressed. This effect is particularly strong in heterostructures comprising small-diameter Au, for which any spectral features associated with SP oscillations are completely vanished from the TA spectra (Figure 7). Such suppression of Au/CdS plasmons is clearly conflicting the measurements of SP in isolated gold nanoparticles, which show both the transient and steady-state signatures of the SP resonance. Second, there is a strong suppression of excitonic features in CdS domains, with the magnitude of this effect exhibiting positive correlation with the size of the Au domain. As demonstrated above, this suppression cannot be explained in terms of photoinduced transfer of charges from CdS to Au domains. Third, TA spectra of all Au/CdS nanocomposites show strong photoinduced absorption, which is not present in the spectra of isolated CdS and Au components, as evident from kinetic traces in Figure 7.

To explain the observed suppression of SP oscillations in Au domains, we consider a "low-barrier" coupling between Au and CdS components, for which Au electrons with energies located above the Fermi level (plasmon band) are not sufficiently confined by the Au/CdS interface to exhibit resonant oscillations. The validity of this assumption is supported by the fact that the interface of the two nanosized domains consists of just a few monolayers and thus cannot form a substantial potential barrier and the fact that energies of conduction electrons in Au domains are raised relative to their respective positions in isolated Au nanoparticles due to charging. Indeed, the photoinduced transfer of excited electrons from CdS to Au (see Figure 6) leaves Au domains with an excess negative charge, which equalizes the energy difference between the conduction states in both domains. As a result, electronic wave functions of conduction carriers in S and charged M domains partly overlap, giving rise to mixing of electronic states at the interface and corresponding changes in the density of states in both materials (see Figure 8). For small-diameter Au nanoparticles, such mixing

Figure 6. Temporal evolution of 1S(e)−1S(h) excitons in "pure" CdS NRs (blue) and Au/CdS (red) heterostructures. A faster recovery of band edge excitons in Au/CdS \( \tau_{\text{Au/CdS}} = 11 \text{ ps} \) is attributed to the transfer of 1S electrons into gold domains.

Figure 7. The kinetics of bleach recovery corresponding to exciton \( (\lambda = 540 \text{ nm}) \) and plasmon \( (\lambda = 540 \text{ nm}) \) excitations observed for (a) isolated gold nanoparticles, (b) 15.4 nm Au/CdS heterostructures, (c) 5.3 nm Au/CdS heterostructures, (d) 2.7 nm Au/CdS heterostructures, and (e) "pure" CdS nanorods.
results in the delocalization of the plasma electrons into CdS portion of nanocomposites, which has a substantially greater volume and therefore can significantly reduce the boundary effect in Au nanoparticles. Such delocalization-induced suppression of the plasmon resonance in Au NPs is further supported by steady-state absorption spectra of 2.7 and 5.3 nm Au/CdS nanocomposites through the absence of distinct plasmon features. These time-independent measurements rule out nonlinear excitation effects as a potential origin of plasmon suppression since excitation intensities used in steady-state absorption experiments are orders of magnitude below those used in ultrafast studies.

The proposed mixing of the electronic states at the interface of Au and CdS domains can also explain the existence of a positive TA signal observed for all investigated Au/CdS heterostructures. Indeed, due to strong coupling of S and M domains, carrier excitations in CdS can lead to the population of CdS-modified conduction states of Au, which will then serve the role of interfacial trap states (schematically shown in Figure 8). This process can occur on a time scale faster than the pulse duration, as can be expected from the general nature of excitation processes in nanocrystals, and will therefore contribute into the “instantaneous” photoinduced absorption of Au/CdS nanocomposites, manifested by the positive ΔA. A relatively large amplitude of this process is attributed to the fact that in addition to facet-localized Au tips, CdS NRs contain a range of smaller gold domains attached to NR walls that can create electron traps along the surface. Notably, for matchstick samples, exhibiting a relatively weakly coupled M-S systems. In addition to plasmon suppression, we also find that the formation of bound electron–hole pairs (excitons) in CdS portion of the structure is strongly hindered due to the presence of gold domains. This phenomenon is explained here in terms of the proposed mixing of conduction states at the boundary of M and S materials, which creates favorable conditions for valence electrons in CdS to be excited directly into interfacial states thus lowering the probability of band gap transitions. By using ultrafast spectroscopy, we demonstrate that it is the proposed interdomain mixing of electronic states and not the electron transfer process that leads to FL quenching in CdS domains.

In summary, femtosecond transient absorption spectroscopy was used to investigate the nature of exciton–plasmon interactions in epitaxially coupled Au/CdS nanocomposites. It was shown that mixing of conduction states at the interface of metal and semiconductor domains leads to the onset of unique optoelectronic properties, which are not observable in nonepitaxial metal–semiconductor heterostructures. One of these properties is the complete suppression of surface plasmon oscillations in Au domains, which is attributed to the delocalization of plasma electrons into CdS portion of the structure. Careful analyses of the transient kinetics as well as steady-state absorption data revealed that resonant plasmon oscillations are quenched in nanocomposites comprising small-diameter Au domains (<6 nm), which contrasts the plasmon dynamics in weakly coupled M-S systems. In addition to plasmon suppression, we also find that the formation of bound electron–hole pairs (excitons) in CdS portion of the structure is strongly hindered due to the presence of gold domains. This phenomenon is explained here in terms of the proposed mixing of conduction states at the boundary of M and S materials, which creates favorable conditions for valence electrons in CdS to be excited directly into interfacial states thus lowering the probability of band gap transitions. By using ultrafast spectroscopy, we demonstrate that it is the proposed interdomain mixing of electronic states and not the electron transfer process that leads to FL quenching in CdS domains.

Figure 8. Energy diagram showing the effect of strong interdomains coupling on electronic energies in Au/CdS heterostructures, which gives rise to the onset of new electronic states. First, the interface of Au and CdS materials can support the formation of trap states, whose energies are located between the Fermi level of Au nanoparticles and the conduction band of CdS NCs. Photoinduced filling of these states is manifested by the spectrally wide photoinduced absorption signal observed in TA measurements. Second, excitation bands of both Au and CdS domains are “bent” at the interface similar to those of bulk heterostructures to account for delocalization of carriers across interdomain boundary.