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Photoluminescence enhancement and quenching in metal-semiconductor quantum dot hybrid arrays

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Hybrid monolayer arrays of metal and semiconductor quantum dots have been prepared to study the exciton-plasmon interaction. We observed crossover from strong quenching to enhancement in photoluminescence of the quantum dots as a function of the emission wavelength for fixed interparticle spacings. Remarkably, the enhancement is observed even for extremely short separation at which strong quenching has been observed and predicted earlier. A significant redshift in emission maxima is also observed for quantum dots with quenched emission. The possible role of collective phenomena as well as strong interactions in such ordered hybrid arrays in controlling the emission is discussed. © *2011 American Institute of Physics*. [doi:10.1063/1.3553766]

The possibility of creating materials with unique properties and emerging applications has driven the enormous growth in research on arrays and assemblies of nanoparticles (NPs).[1–4] Recent effort has been devoted to creation and study of multicomponent hybrid assemblies (binary) to exploit the characteristic physical properties of each component as well as to explore possibilities of unique emergent phenomena.[1,2,5–7] One such example of an emergent phenomena is the study of exciton-plasmon interaction in semiconductor-metal hybrid quantum dot (QD) assemblies.[8–19] Despite the lack of a clear understanding of the plasmon-mediated photoluminescence (PL) enhancement, it is now generally believed[6,8,14,15,17,18] that below a certain minimum interparticle separation, metal NPs, especially small ones, will always quench the PL emission, irrespective of the extent of spectral overlap between the QD PL and the metal NP absorption spectra. Although various methods can be applied for the creation of such arrays, self-assembly methods have emerged as the most efficient for this purpose.[1] Langmuir–Blodgett[13,20] (LB) monolayers of semiconductor-metal QD provide an ideal platform to study such interactions. Strong quenching of photoluminescence of cadmium selenide (CdSe) QD in the presence of gold nanoparticles (Au NP) in a close-packed hybrid LB monolayer of CdSe QD-Au NP was recently observed due to resonant energy transfer.[11] However systematic variations of exciton-plasmon coupling by controlling spectral overlap or interparticle spacing were not explored in this or any other work.

Here we show how both quenching and enhancement of CdSe QD PL can be obtained by tuning the spectral overlap between QD emission, the QD:Au NP ratio, and their mean interparticle separation in close-packed LB monolayer hybrid assemblies. We also obtain strong shifts in the PL emission of QDs in hybrid arrays whose magnitude depends on the extent of spectral overlap as well as the interparticle distance. Strong deviations in the observed variations of the PL emission from predictions based on exciton-plasmon interaction under dipole approximation are highlighted.

CdSe QDs used for the experiments were prepared according to the procedure reported earlier,[21] while the Au NPs were synthesized based on the method described previously.[22] CdSe QDs with average diameters D of (A) 4, (B) 5.8, and (C) 6.8 nm were used for the experiments, while the mean diameter of Au NPs was found to be ~8 nm. Thin films of CdSe QDs and QD:Au NP hybrids for different number ratios were prepared using an LB trough (KSV, Finland) as reported earlier.[13] For our optical measurements, we have transferred various monolayers on thin glass substrates at different surface densities Γ. Room temperature (295 K) PL measurements on our samples were performed with a confocal microscopy setup (WITec alpha SNOM) using 488 nm of an Ar-ion laser, as discussed earlier.[10] Figure 1(a) shows the ultraviolet-visible (UV-Vis) absorption spectra collected from toluene solution of CdSe QDs as well as Au NPs used for preparation of LB films. In Fig. 1(b), we also show the absorbance and PL spectra for monolayer of Au NP

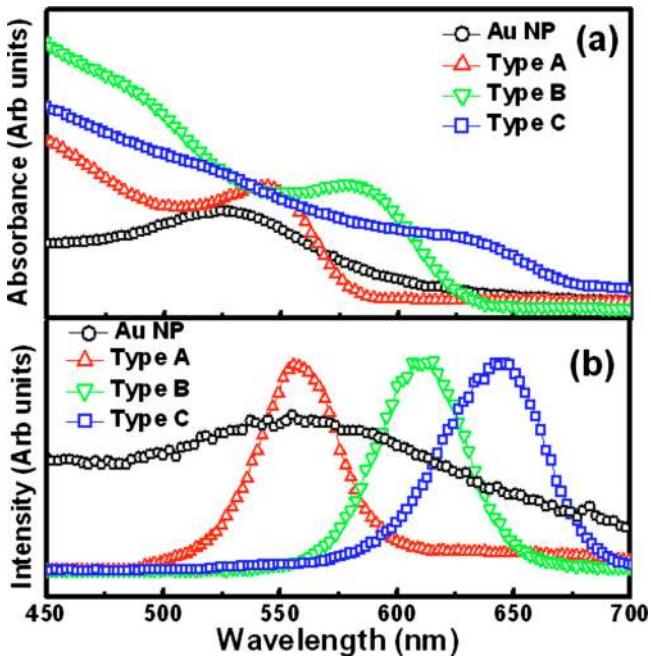

FIG. 1. (Color online) (a) UV-Vis absorption spectra for the Au NPs (○) and for CdSe QDs of types A (△), B (▽), and C (□) in toluene. (b) UV-visible absorption spectra collected from Au NP monolayer (○) and confocal PL emission spectra from isolated CdSe QDs dispersed in poly(methyl methacrylate) on glass substrates for the same QDs as in (a).

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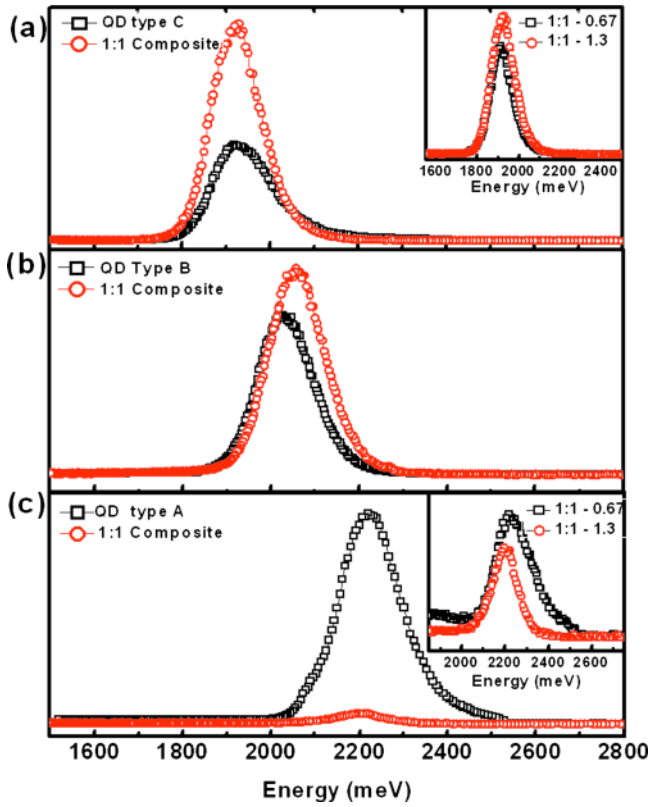

FIG. 2. (Color online) Typical PL spectra from hybrid films with CdSe QD to Au NP ratio 1:1 with $\Gamma = 1.3 \times 10^{-2}$ nm^{-2} (○) and QD (□) monolayer with $\Gamma = 1.3 \times 10^{-2}$ nm^{-2}, for type (a) A, (b) B, and (c) C QDs. Comparison of PL spectra at $\Gamma = 0.67 \times 10^{-2}$ nm^{-2} (△) and $\Gamma = 1.3 \times 10^{-2}$ nm^{-2} (○) for hybrid (1:1) monolayers of type A [inset (a)] and type C [inset (c)] QDs.

and the three CdSe QDs (A)–(C), respectively, deposited on a glass substrate. The spectral overlap between the Au NP absorbance and the various QD PL emissions is clearly visible, and its relevance will be discussed later. We prepared close-packed hybrid Langmuir monolayers in the particle number ratio CdSe QD:Au NP of 1:1. Our aim was to study the role of Au NP:CdSe QD number ratio, their mean surface to surface separation Δ, and spectral overlap on PL enhancement properties as displayed in Fig. 1(b). The surface densities were changed by continuously compressing the monolayers, thus allowing continuous control of Δ between Au NPs and CdSe QDs. As a reference, we also transferred monolayers of CdSe QDs at identical surface density of CdSe as in the corresponding hybrid films, as well as that of Au NPs. The ordering and dispersion of the QDs and Au NPs in the hybrid monolayers were verified from the transmission electron microscope (TEM) image collected from monolayers transferred on grids.[23] The mean surface to surface separation, Δ, in the Au NP monolayers was found to be 2.2 nm, while this value was 1.5 nm for 1:1 hybrid monolayers at $\Gamma = 1.3 \times 10^{-2}$ nm^{-2}. The compactness of the monolayers was further verified by an atomic force microscope[23] (AFM), and we confirmed the formation of a monolayer of either QD or hybrid systems at the air-water interface as well their transfer on glass substrates. Representative confocal PL spectra from the three types of hybrid monolayers showing significant variations are shown in Fig. 2, while the PL spectra for the hybrid with type A QDs show strong quenching with respect to QD monolayer at identical Γ's (1.3×10^{-2} nm^{-2}), in the presence of Au NP. The hybrid monolayers of the type

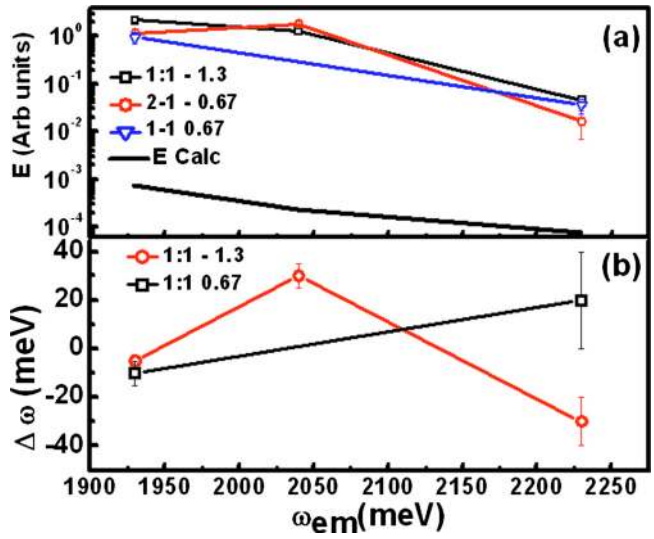

FIG. 3. (Color online) (a) Enhancement factor E for various hybrid array films at the indicated Au NP:QD (Γ) values. The solid line indicates calculation of E based on Eq. (1). (b) PL spectral shift $\Delta\omega$ for various hybrid array films at the indicated Au NP:QD (Γ) values.

C QD show strong enhancement at identical surface densities. Type B QDs also show PL enhancement which is intermediate between types A and C, pointing to systematic spectral dependence of enhancement ratio. It might be pointed out here that these variations are over and above the small variations in PL intensities for the various samples due to microscopic inhomogeneities of QD or Au NP densities in the respective monolayers.[23] Further control of the exciton-plasmon interaction in such hybrid monolayers is demonstrated through the variation of Γ or Δ. In the inset of Fig. 2, we show how the PL enhancement factor E increases (decreases) for type C (A) QD 1:1 hybrid monolayer with an increase (decrease) in Γ(Δ). The Δ values we have obtained vary from 2.1 to 1.4 nm. The key results of the confocal PL measurements on the array films are summarized in Fig. 3(a). It is clear that the PL enhancement factor E in hybrid monolayers with respect to the corresponding QD monolayer at the same Γ increases with an increase in the PL emission maxima ω_{em}. In addition, E also increases with an increase in Γ. How does our results compare with those available in the literature? In control experiments and theoretical calculations[8,9,14,17,18] of single QD or emitter near metal particles, it has been clearly demonstrated that quenching occurs if the QD-metal NP separation goes below a certain value (typically ~5 nm). Essentially in the near field regime, quenching is always expected due to nonradiative energy transfer for metal particles where extinction is dominated by absorption and not scattering. In order to quantify and compare our results, we have used recently proposed theoretical results for the prediction of plasmon-mediated enhancement/quenching regime in QDs. The PL enhancement factor E can be written as[8,9]

$$E = E_{abs}(\omega_{ex}) E_{em}(\omega_{em}), \quad (1)$$

where E_{abs} is the absorption enhancement factor at excitation frequency ω_{ex}, and E_{em} is the emission enhancement factor at the emission frequency ω_{em}. Using Eq. (1) above[23] and the measured values of radiative coupling efficiency η_{rad} and absorption cross-section σ_a of the QDs, we have calculated the enhancement factor E. The calculated results are shown

as solid lines in Fig. 3(b), indicating strong quenching for all ω_{em}. Although the extent of quenching does decrease with decreasing ω_{em}, the observed crossover from quenching to enhancement regime in our experiments is not reproduced using the formalism described in Ref. 9. The enhancement regime is only attained in Ref. 9 for a critical metal nanoparticle radius of ~15–20 nm and a nanoparticle-QD separation of 5 nm or more, and in addition E increases with increasing (ω_{em}) (Fig. 15 in Ref. 9), whereas in our case it decreases with increasing (ω_{em}). It is clear that the trends in our data are remarkably different from those obtained from Eq. (1). It is to be noted that their theory is valid only in dipole approximation, and the authors[9] did indicate the unreliability of the formalism below $\Delta \sim 5$ nm, where strong quenching is expected due to nonradiative energy transfer to higher multipoles. Therefore our results for type B and C QD hybrids is quite remarkable and indicate the need to (a) go beyond the dipole approximation and (b) consider possible collective effects, as observed recently,[19] in understanding the effects of exciton-plasmon interaction in large scale hybrid assemblies. Such collective phenomena could lead to the observed strong deviation from the predicted behavior for PL enhancement on exciton-plasmon interaction under dipole approximation. For hybrid monolayers with a CdSe QD:Au NP number ratio of 1:2 for type A and C QDs, similar and consistent behavior is observed. In Fig. 3(b) we also depict the shift in the PL emission maxima, $\Delta\omega$ (>0 blueshift and <0 redshift), for the various LB transferred hybrid monolayers as compared to those of the QD monolayers at similar QD Γ values, while for the type A QDs we find that $\Delta\omega < 0$ for the 1:1 hybrid films at $\Gamma = 1.3 \times 10^{-2}$ nm^{-2} and $\Gamma = 0.67 \times 10^{-2}$ nm^{-2}, and $\Delta\omega$ increases with Γ. For type C QDs $\Delta\omega$ is smaller than that of type A or B QDs, and the variation with Γ is less. For the type B QDs we find the opposite behavior ($\Delta\omega > 0$), although the reason for this is not clear. The magnitude of $\Delta\omega$ is smaller than that for type A QD 1:1 hybrid monolayer at the same Γ (1.3×10^{-2} nm^{-2}). The presence of spectral shift has already been predicted[24] and observed[25] recently in experiments and has been attributed to the presence of strong exciton-plasmon interactions. The magnitude of this shift has also been shown to increase with inclusion of higher order multipoles. However, the magnitude of $\Delta\omega$, especially for type A QDs, is significantly larger than that which has been predicted[24] or observed[25] experimentally. It is also possible that this redshift in the PL emission could also originate from Dexter transfer which typically has been observed[26] to take place between QDs of certain size and also occurs when they are in close proximity. However, in our case since the shift is with respect to the close-packed QD monolayer, if such an effect is responsible for the observed shift, it would have to be mediated by plasmons which would be a very interesting possibility and has not been observed earlier.

In conclusion, we have studied the systematic variation of exciton-plasmon coupling in close-packed metal-semiconducting QD hybrid monolayers. We observed strong quenching of PL emission of QDs in the presence of Au NPs, at very small interparticle distances, provided the emission spectra overlap strongly with the Au NP plasmon band. Surprisingly, we also observe strong PL enhancement for QDs at similar interparticle distances, for which the spectral overlap with the plasmon band decreases.

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