Hybrid optical materials of plasmon-coupled CdSe/ZnS coreshells for photonic applications

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Abstract

A hybrid optical nanostructure of plasmon-coupled SQDs was developed for photonic applications. The coupling distances between the mono-layers of Au nanoparticles with a surface concentration of \(9.18 \times 10^{-4}\) nm\(^{-2}\) and CdSe/ZnS SQDs with that of \(3.7 \times 10^{-3}\) nm\(^{-2}\) were controlled by PMMA plasma etching. Time-resolved spectroscopy of plasmon-coupled SQDs revealed a strong shortening of the longest lifetime and ~9-fold PL enhancement. Polarization-resolved PL spectroscopy displayed linear polarization and depolarization at near- and far-field plasmon-coupling, respectively. The physical origin of PL enhancement could be attributable to both the large local field enhancement and the fast resonant energy transfer.

1. Introduction

Hybrid optical materials consisting of semiconductor quantum dots (SQDs) and plasmonic metal nanoparticles are of great interest for photonic and biomedical applications [1–4]. The SQDs of cadmium and lead chalcogenide (Te, Se, and S) have been extensively studied because of their high internal quantum efficiencies and wide optical tunability of absorption and emission spectra in the visible and near-infrared spectral region with quantum confinements at sizes near their Bohr radii [5,6]. Although the colloidal SQDs in solution exhibit high internal quantum efficiencies [7], their luminescence efficiencies considerably drop when the SQDs are casted into the thin films for photonic applications [8]. However, the internal quantum efficiency of SQDs in the proximity of plasmonic nanoparticles significantly changes when excitons and plasmons coherently interact via the Coulomb force. The changes in PL enhancement and quenching are closely related to the coupling distance. Therefore large changes in the optical properties of SQDs in the proximity of plasmonic nanoparticles are anticipated to be achieved by controlling the coupling distance [9].
The origin of coupling in hybrid optical nanomaterials is the Coulomb interaction between plasmonic nanoparticles and SQDs. When the applied oscillating electric field excites simultaneously both SQDs via the interband transition and plasmonic nanoparticles via the intraband transition, both dipoles of excitons and plasmons interact with each other. Excitons at the excited state relax to the ground energy state with radiative and non-radiative transitions. If the plasmon-exciton coupling rate is faster than the radiative and non-radiative transitions of excitons, then the energy is transferred from exciton to plasmon by dipole interactions. The oscillating collective dipoles of plasmons with strongly localized electric field re-excite the excitons within the plasmon penetration depth. The plasmonic multipole interaction is also anticipated, which is dependent upon the particle morphology and the coupling distances. The plasmon-exciton coupling distance is an important component for the reduction of non-radiative and radiative decay rates of excitons by their fast coupling rate. It is also scales the re-excitation density of the strongly localized plasmonic field to the excitons. Therefore, the modification of exciton lifetime is expected by the change of radiative and non-radiative decay rates. The quenching or enhancement of fluorescence intensity is also anticipated from the plasmon and exciton coupling density and the localized electric field enhancement. The internal quantum efficiency of plasmon-coupled SQDs can be explained with the Purcell enhancement factor [10].

Recently, the fluorescence enhancement and quenching of the ensemble plasmon-coupled SQDs have been extensively reported for photonic applications, such as light emitting devices, solar cells, and light amplifications. Early reports on the SQD luminescence enhancement through exciton and plasmon coupling include CdSe/ZnS coreshells on Ag islands [11], CdSe/ZnS on Au colloidal [12], CdSe/ZnS on nanoporous Ag arrays fabricated by electron-beam lithography [13], CdSe on Au layers by thermal evaporation [14], and CdSe/ZnS coreshells on rough Au surfaces [15]. The emission enhancement may depend on local field enhancement, coupling distance, coupling rate faster than nonradiative rate, coherent coupling, emission materials, concentration of emission materials, and PL efficiency of emission materials without plasmon coupling. Also, the fluorescence rate and temporal dynamics of a single SQD using confocal fluorescence microscopy have been quantitatively studied by controlling the plasmon coupling distance using an atomic force microscope (AFM) tip attachment or manipulation [16,17].

In this article, a hybrid optical nanostructure of plasmon-coupled semiconductor quantum dots is presented for photonic applications of LEDs and optical displays. The hybrid optical nanostructure consists of a mono layer of ensemble semiconductor quantum dots in the proximity of a single layer of ensemble plasmonic metal nanoparticles. The optical properties of hybrid nanostructure for different coupling distance conditions between two layers are studied with both a time-resolved confocal optical microscopy and polarization-resolved static optical spectroscopy. The coupling distance denotes the distance approximation between the center of Au nanoparticle layer and the center of SQD layer. On the basis of the time- and polarization-resolved spectroscopic results, the plasmon-exciton coupling dynamics and the origin of fluorescence enhancement are discussed.

2. Optical materials preparation

2.1. CdSe/ZnS quantum dots and Au nanoparticles

The CdSe/ZnS coreshells were synthesized for preparing hybrid optical materials of plasmon-coupled SQDs. The CdSe spherical nanocrystal was the core material for CdSe/ZnS coreshells, which were prepared in the following literature procedures [18–21]. For preparing a stock solution, the mixture of CdO (4 mmol) and oleic acid (OA, 16 mmol) was heated at ~150 °C until the CdO is completely dissolved by the OA. Octadecene (ODE) solvent (~50 g) was added into the mixture of CdO and OA, and the mixture was heated to
280 °C. The solution of Se (~15 g) in trioctylphosphine (10%) was swiftly injected into this hot Cd solution to start the reaction. The temperature was then adjusted to 250 °C for the nanocrystal growth. The reaction was completed when the preferred size of CdSe nanocrystals (NCs) was synthesized. The product was precipitated by acetone, centrifuged, and re-dispersed in a suitable amount of toluene. This process was repeated a couple of times to get pure CdSe NCs in toluene. For growing ZnS shells on the CdSe core, a suitable amount of CdSe NCs in ODE was heated to 200 °C. Afterwards, solutions of Zn(OA)$_2$ and S in ODE were alternatively injected into the CdSe in ODE to grow a shell of ZnS. The reaction was terminated when three layers of ZnS were formed around the CdSe core NCs. The CdSe/ZnS coreshells were precipitated by acetone, centrifuged, and re-dispersed in the base solution of toluene or chloroform. For developing a surface functional group on the CdSe/ZnS coreshells, the CdSe/ZnS NCs in chloroform were mixed with poly(maleic anhydride-alt-1-octadecene) (PMAO, Mn = 30,000–50,000) at a molar ratio of 1:10 or higher, and then pure water was added into the solution. The chloroform in the mixture solution was slowly removed by slightly reducing pressure. When the chloroform was completely removed, the CdSe/ZnS NCs were dispersed in water. During this transfer, the functional group of maleic anhydride in PMAO was hydrolyzed. Eventually, the COOH functional group is formed on the surface of CdSe/ZnS coreshells. The excessive PMAO was completely removed through ultracentrifuge at 200,000 g-force for ~2 to 3 hours.

The plasmonic Au nanoparticles (NPs) were also prepared by sodium citrate reduction [22], for the production of hybrid nanomaterials of plasmon-coupled CdSe/ZnS coreshells. The solution of HAuCl$_4$ (1 mM) in the de-ionized water (550 ml) was refluxed with vigorous stirring for ~30 minutes. Sodium citrate (50 ml of 12-mM) was rapidly added and stirred for additional 30 minutes to prepare Au nanoparticles with diameter of ~32 nm. After the reaction solutions equilibrated the room temperature, the residual solutions were filtered through 0.45-μm polymer membrane filters.

The optical spectra of resulting colloidal CdSe/ZnS SQDs and Au nanoparticles were characterized by an UV-Vis spectrometer (Agilent 8453), and their morphologies were analyzed with transmission electron microscopes (FEI, Technai G2 F30 Super-Twin, 300 kV, and Hitachi, H-9000NAR, 300 kV). The average diameter of colloidal CdSe SQDs was estimated to be ~2.6 nm with the shell thickness of ZnS less than ~1 nm for the hybrid nanostructure preparation. The average diameter of Au nanoparticles was estimated to be ~32 nm. The concentrations of colloidal CdSe/ZnS SQDs were estimated using the Beer-Lambert’s law and the extinction coefficients given in the literature [18,21]. The concentrations of colloidal Au NPs were approximated with the Mie-scattering theory [23] and the Beer-Lambert’s law.

### 2.2. Preparation of hybrid nanostructure for plasmon-coupled SQDs

After preparing the colloidal nanoparticles of CdSe/ZnS and Au, the hybrid nanomaterials of Au-PMMA-CdSe/ZnS were assembled on quartz slides with a size of 10 × 10 mm$^2$. The quartz surface was hydroxylated using an oxygen plasma (Plasma System V15-G, Plasma Finish) with operation conditions of 30 Pa, oxygen 100 ml/min, and 100 watts for 300 sec. The hydroxylated quartz was silanized in ethanol containing 1 wt. % 3-aminopropyltriethoxysilane (APTES, Sigma-Aldrich, CAS#: 919-30-2) in order to form the amino (NH$_2$) functional group on the surface of the hydroxylated quartz. The amino functionalized quartz plate was washed with ethanol, and dried with nitrogen gas. Finally, the dried quartz was baked at 120 °C for 15 minutes. The amine reactivated-quartz was spotted with the high concentration Au nanoparticles for 12 hours at room temperature, and washed with de-ionized water, and dried with nitrogen gas. The schematic procedure of hydroxylation, amino functionalization, and Au nanoparticle deposition is depicted in the Fig. 1(a). The Au nanoparticle deposition images on the quartz plate were analyzed with an
atomic force microscope (AFM, Agilent, 5500AFM). The image indicated that the Au nanoparticles were well mounted on the quartz plate without multi-layers or aggregations.

For preparing a spacer with thickness from ~1 to ~50 nm between CdSe/ZnS SQDs and Au NPs, poly(methyl methacrylate) (PMMA, C2 950k) with a volume of 0.1 ml was casted on the Au NPs-attached quartz plate using a spin coater (SP-1, SPIN Programmer, ABLE Co.) at 5000 rpm for 30 sec. The PMMA/Au/quartz plate was subsequently baked at 120 °C for 2 min. The thickness of the PMMA spacer between Au NPs and CdSe SQDs was controlled by oxygen plasma etching with operation conditions of 30 Pa, oxygen 100 ml/min, and 100 watts for 7 min, 12 min, 17 min, 20 min, 25 min, 27 min, and 30 min, respectively. For the thickness of PMMA spacer from ~50 to ~100 nm between CdSe/ZnS SQDs and Au NPs, PMMA with a volume of 0.1 ml was casted on the Au-attached quartz plate using the same spin coater at 3500 rpm for 30 sec, and then the plate was baked at 120 °C for 2 min. The thickness of PMMA was controlled by plasma etching for 7 min, 12 min, 17 min, and 22 min, respectively. The plasma etching has been used to prepare a uniform morphology and stable surface [24,25], and it provided control of the PMMA thickness to within ~1 nm. In the plasma etching process, neutral and radical oxygen is produced by the reactions of \[ \text{O}_2 + \text{e}^- \rightarrow \text{O}_2^+ + \text{O} \] and \[ \text{O}_2^+ + \text{e}^- \rightarrow \text{O} + \text{O}. \] The radical oxygen attracts a hydrogen atom, and creates an OH and a hydrocarbon chain. The oxygen species breaks the polymer hydrocarbon chain into small pieces. In this procedure, the plasma etching simply bombards surfaces of PMMA with energetic particles that knock off surface particles.

After surface treatment of PMMA with oxygen plasma, casein (0.1 ml of 1% protein) in solution of 1×PBS (phosphate buffered saline) was spin-coated at 3,500 rpm for 30 sec on the PMMA/Au/quartz plate to reform the hydrophobic surface of PMMA to hydrophilic. Then, the CdSe/ZnS-COOH was properly bound on the hydrophilic PMMA. For developing hybrid plasmon-coupled SQDs, CdSe/ZnS SQDs with a volume of 0.1 ml of ~10 μM was casted on the plate at 3,500 rpm for 30 sec. The final layer of PMMA with a volume of 0.01 ml was coated to protect the SQDs from ambient environments. Also, both a PMMA/SQDs/PMMA/quartz plate without Au nanoparticles and a PMMA/Au/quartz plate without SQDs were prepared for comparison purposes.

### 2.3. Microscopic analysis

The resulting hybrid nanostructures of plasmon-coupled SQDs were analyzed with a field-emission scanning electron microscope (FE-SEM, FEI, Sirion) as shown in Fig. 2. The lateral images of PMMA/Au/quartz plate were produced by the FE-SEM with operation conditions of 10.0 KV as shown in Fig. 2(a) and 2(b). The samples for lateral view analyses with FE-SEM were coated by a platinum (Pt) layer with a thickness of less than ~10 nm to create clear images by reducing charge activities on the quartz plate due to the energetic electrons. The image of Fig. 2(a) displays the lateral view of a PMMA/Au/quartz plate at a slight angle without a sample cut. The image of the top surface in the Fig. 2(a) displays Au nanoparticle distribution under the PMMA film. The image of Fig. 2(b) exhibits a lateral view of the PMMA/Au/quartz plate after it was cut with a diamond knife (Ogura Jewel Industry Co., D-Point Pen). The rear side of sample (quartz) was scratched with the diamond knife, and cut in a uni-direction with ambient weak mechanical force. The image displays a single layer of Au nanoparticles with uniform and regular distribution through NH₂ functional group on the quartz plate.

The top view of QD/PMMA/Au/quartz plate was presented in Fig. 2(c). The image was also analyzed using a field-emission scanning electron microscope (FE-SEM, FEI, Sirion) with operation conditions of 10 KV. It was interesting to see the Au nanoparticles through the PMMA with a contrast image technique of FE-SEM. Even though the image did not display
the complete morphology of Au nanoparticles, the number density of nanoparticles was able to be estimated. The number density of Au nanoparticles (D~32 nm) was estimated to be \(-9.18 \times 10^{-4} \text{ nm}^{-2}\), which indicated ~9 particles in the area of \(100 \times 100 \text{ nm}^2\). The inset of Fig. 2(c) is a picture reformation with ~35% brightness and 35% contrast after the dark and bright images of Fig. 2(c) were inverted. The inset image in Fig. 2(c) displays Au nanoparticles and SQDs with large black dots and small dots, respectively. The number density of SQDs was roughly estimated to be \(-3.7 \times 10^{-3} \text{ nm}^{-2}\) by the inverted image of the Fig. 2(c).

To analyze the coupling distance from the layer of Au nanoparticles on the quartz plate to the layer SQDs on the surface of PMMA, the lateral view of QD/PMMA/Au/quartz plate with pt coating was also characterized with the FE-SEM (FEI) with operation conditions of 10 KV. The lateral views for estimating the coupling distance were taken from the sample as it was prepared without an additional cut. A typical image for estimating coupling distance from the center of Au layer to the center of QD layer is shown in Fig. 2(d). The layer distance was calculated to be ~45.5 nm after the radii of Au nanoparticles and SQDs were subtracted from the thickness between the top of the quartz and the top of the PMMA. The different sample thicknesses were prepared in various casting and plasma etching conditions which were described above for microscopic and optical analyses.

3. Optical characterizations

Figure 3 shows the normalized extinction spectra of Au (blue solid line), CdSe/ZnS (black solid line), and plasmon-coupled CdSe/ZnS (black dash line), and the normalized fluorescence spectra of CdSe/ZnS in water (olive solid line) PMMA-CdSe/ZnS-PMMA-quartz plate (green solid line), and PMMA-CdSe/ZnS-PMMA-Au-quartz plate (red solid line). The extinction spectra were collected using a UV-Vis spectrophotometer (Agilent 8453) with a 10-mm optical path for colloidal Au NPs and CdSe/ZnS SQDs in water, and with a mono layer of plasmon-coupled CdSe/ZnS on the quartz plate. The extinction spectral band with a peak at ~531 nm for Au nanoparticles is attributable to the localized surface plasmon resonance (LSPR) that is a result of transitions within the conduction band or intraband transitions [26]. The higher energy region relative to the LSPR band is assigned to the interband resonance transitions of 5d-6s of Au NPs. Both interband and intraband spectra of Au nanoparticles are extensively overlapped. The extinction spectrum of plasmon-coupled CdSe/ZnS exhibited two dominant peaks at ~546 nm and ~675 nm. It indicated different LSPR dynamic modes of Au NPs. The extinction spectrum of CdSe/ZnS could not be separately identified from the spectra of PMMA-CdSe/ZnS-PMMA-Au on the quartz plate. The dipolar plasmon mode of colloidal Au nanoparticles at ~531 nm was slightly red-shifted to ~546 nm after the Au NPs were mounted on the quartz plate. The second peak of LSPR mode was displayed at ~675 nm because of the LSPR modes of interparticle interaction between Au NPs [27]. It indicated the possible existence of hot spots between the Au NPs. The extinction spectrum of colloidal CdSe/ZnS in water displayed the first exciton absorption peak at ~517 nm and an optical bandedge at ~560 nm because of the quantum confinement effect within the dot boundary. The excitation source for static fluorescence measurement was a CW HeCd laser (Melles Griot, 45-MRM-803-120) operating wavelength at 442 nm. The average power of the excitation source was measured to be ~12.3 mW with a laser power meter (Coherent, PM3) and readout (Molelectron, Power MAX5200). The resulting fluorescence was collected through optical fibers (Ocean Optics, P600-2-VIS-NIR), a long wavelength pass filter at ~455 nm, and a spectrometer (Ocean Optics, USB4000) with a spectral resolution of ~1 nm. The fluorescence peak of colloidal SQDs in water was placed at ~546 nm with a stark shift of ~29 nm, which indicates the intrinsic quantum efficiency \((\eta_{\text{int}} = \frac{A_{\text{Abs}}}{A_{\text{Fl}}})\) of ~95%. The fluorescence peaks from SQD layer with and without plasmon coupling were exhibited at ~539.8 and ~539.3 nm,
respectively, without any major spectral changes. However, the fluorescence peaks from SQD layer on the PMMA with and without plasmon coupling displayed ~6.7 and ~6.2 nm blue shift, respectively, compared to the fluorescence peak of colloidal quantum dots. The colloidal SQDs in solutions exhibited a red shift of the exciton absorption peak with higher concentrations, and a blue shift with lower concentrations. The red shift was due to homo energy transfer from the higher energy of smaller SQDs to the lower energy of bigger SQDs for relatively high concentration. The blue shift was possibly because of the reduction of energy transfer between SQDs [28]. It implied that the SQDs on the PMMA were well distributed.

The time-resolved lifetime images of plasmon-coupled CdSe/ZnS were characterized with a confocal MicroTime 200 (PicoQuant GmbH) system and an Olympus IX71 microscope. The excitation source was a pulsed diode laser at ~470 nm (LDH-P-C470B, PicoQuant, GmbH) with a repetition rate of 20 MHz and an excitation power ~730 nW. The characteristic temporal pulse width of the laser system was known as less than ~90 ps for low-power operation condition at less than ~300 μW. The confocal microscope was utilized for the efficient elimination of out-of-focus fluorescence light and the practical fluorescence images from shallow depth of sample to remove potential contribution of background emission. The confocal technique was the conjugation of a focal point of the objective lens and an image at the spatial pinhole. The out-of-focus and deep-depth emissions could be any possible background emissions from polymers and/or gold nanoparticles if they exhibited significant emissions. The laser was focused by a 60x water immersion objective with numerical aperture (NA) 1.2 (MPLAPON, Olympus) to a diffraction-limited spot on the sample. A water immersion objective was used to reduce the refractive index difference between the objective and the coverslip through the air space, and the objective correction collar was adjusted for the thickness of the coverslip. In general, the NA affects both the spatial resolution and the magnifying power of the confocal microscope. The lateral spatial resolution of confocal microscope is determined by the Airy diffraction pattern. The diffraction pattern or minimum spot size in the focal plane was estimated to be around a half wavelength of laser excitation (Δγ = 1.22λ / 2NA ~ 239 nm). The axial spatial resolution along the optical axis of confocal microscope was estimated to be around twice of the Rayleigh length (Δb=2Zq=2πω02 / λ~763 nm). In order to measure the effective detection volume, sub-resolution fluorescent samples were scanned in the X-Z and X-Y directions. The fluorescent sample of nile red FluoroSphere (carboxylate-modified nanosphere beads, 20 nm in diameter) was purchased from Invitrogen (Eugene, OR). The beads were mixed into a 1% PVA solution and sonicated to break up aggregates. The beads were then spin coated onto a coverslip (#1, 20 × 20 mm2) from Menzel-Gläser (Braunschweig, Germany). Images of the beads were collected by scanning them in the X-Z direction along the optical axis and then the X-Y direction in the focal plane. Their fluorescent signal was broadened by diffraction, and this spot size was measured in all three dimensions. The intensity was first averaged along the X-axis for each position along the Z-axis, and this data was plotted on a graph of average intensity versus Z position. Then a Gaussian distribution was fitted to this data, with the full width at half maximum (FWHM) indicating the resolution limit along this axis. The procedure was repeated for the X and Y axes. The average intensity distributions of lateral and axial spatial directions were conservatively estimated to be ~250 nm and ~800 nm, respectively, from the measurement as shown in Fig. 4. The measurement was just ~5% off from the theoretical confocal volume of ~239 nm in the lateral direction of the focal plane and ~763 nm in the axial direction along the optical axis.

A typical fluorescence lifetime image of plasmon-coupled CdSe/ZnS quantum dots using a confocal optical microscope is shown in Fig. 5. The fluorescence lifetime imaging microscopy (FLIM) with a confocal optical microscope was utilized for creating the lifetime...
image in the exponential decay rates of fluorescence signal from the plasmon-coupled SQDs. The scanning area of the fluorescence lifetime image was 30 × 30 μm². The laser excitation power after the objective and before the sample was ~730 nW. The fluorescence photons from CdSe/ZnS with and without plasmon coupling for the lifetime measurement were collected by the same objective, separated from the laser scattering by two long pass filters at 488 (Semrock, BLP01-488R-25) and 495 nm (Semrock, FF495-DiO3), and guided to a silicon avalanche photodiode in the photon counting module (SPCM-AQR-14, PerkinElmer). The pulse width of instrument response function (IRF) collected from a glass plate was ~600 ps. The IRF estimated the response of scattering from the glass plate to the excitation source as seen by the instrument. The lifetime measurement was performed by the time-correlated single photon counting (TCSPC) module (PicoHarp300, PicoQuant GmbH), and was analyzed using the SymPhoTime software (5.2.4, PicoQuant GmbH) with a tail fitting or with a whole fitting with IRF deconvolution. All measurements were performed at near room temperature under ambient conditions. The lifetime analyses for three different local areas on the FLIM with scanning area of 30 × 30 μm² for the plasmon-coupled CdSe/ZnS SQDs were listed in the Table 1. The amplitude average lifetimes were ~9.21 to ~10.45 ns with a tail fitting. Two bright spots on the lifetime images suggest the existence of a QD cluster or multiple isolated SQDs in the prepared sample. The local lifetime variations of $\tau_1$ and $\tau_2$ may be due to different local conditions of the surrounding environments, interparticle interactions between CdSe/ZnS SQDs, or coupling conditions between SQDs and plasmon particles.

Figure 6 shows a typical fluorescence intensity decay characteristics of plasmon-coupled CdSe/ZnS with a coupling distance ~25 nm using the TCSPC system. The time-resolved plot comprises a multi-exponential decay and the excitation function or IRF of the TCSPC. The IRF shift was ~0.67 ns. The ensemble of QD fluorophores is charged with the excitation energy during the pulse. The excited fluorophores immediately started to emit and exhibit the characteristics of PL decays. The time-resolved fluorescence spectroscopy was utilized to extract the lifetime at the excited states of QD fluorophores which relaxed to the ground state by emitting a photon. The fluorescence lifetimes with a tail fitting were estimated to be ~2.78 ns and ~12.98 ns for the first and second decay components, respectively. The fluorescence lifetimes with a whole fitting with the IRF deconvolution were estimated to be ~2.079 ns and ~12.28 ns for the first and second decay components, respectively. The fluorescence lifetime with the whole fitting was estimated to be the faster decay time and the higher amplitude $\tau_1$ than that with the tail fitting. The amplitude and intensity averaged lifetimes with a tail fitting were 9.84 ns and 12.09 ns, and these lifetimes with a whole fitting were 7.67 ns and 11.03 ns, respectively. However, the problem with the average lifetimes is that it is not often clear which one is to be used to analyze hybrid materials like plasmon-coupled SQDs, because of the following reasons dependent upon the interest lifetime components.

The lifetime of plasmon-coupled SQDs were analyzed by fitting with the multi-exponential model of fluorescence intensity $I(\lambda, t)$ at the time $t$ and wavelength $\lambda$ [29,30],

$$I(\lambda, t)=I_o(\lambda, t=0)\sum a_ie^{-\frac{t}{\tau_i}},$$  

(1)

where $\tau_i$ represents the characteristic fluorescence lifetime of the $i$th decay component, $a_i$ is the corresponding decay amplitude fraction with total amplitude $\sum a_i=1$, and $I_o(\lambda)$ is the fluorescence intensity at time $t = 0$. This expression assumes the lifetime is independent of wavelength. The fluorescence intensity $I(\lambda, t)$ is the optical observation of the number of
excited SQDs, \( \rho(\lambda, t) = n_0 \sum a_i \exp(-t/\tau_i) \). The lifetime \( \tau \) is the inverse of the total decay rate, \( \tau = \gamma_{\text{tot}}^{-1} = (\gamma_r + \gamma_{\text{nr}})^{-1} \) for SQDs and \( \tau = \gamma_{\text{tot}}^{-1} = (\gamma_r + \gamma_{\text{nr}} + \gamma_{\text{ex-pl}})^{-1} \) for plasmon-coupled SQDs, where \( \gamma_r \), \( \gamma_{\text{nr}} \) and \( \gamma_{\text{ex-pl}} \) are the radiative and nonradiative decay rates of SQDs, and coupling decay rate with plasmon-exciton the hybrid nanostructure, respectively. The lifetime is a statistical average of the random emission decay-times. The intensity decay has been commonly analyzed with either intensity average lifetime or amplitude average lifetime [29–31]. The intensity average lifetime is average amount of time a fluorophore stays in the excited state, or average time of a collection of different excited state populations [29,30]. The intensity average lifetime is defined as

\[
\langle \tau \rangle_{\text{int}} = \frac{\sum a_i \tau_i^2}{\sum a_i \tau_i} = \sum f_i \tau_i \tag{2}
\]

where, \( f_i = a_i \tau_i / \sum a_i \tau_i \) is the fractional contribution of each decay components to the steady state intensity \( I_0(\lambda) \), the denominator \( \sum a_i \tau_i \) is over all amplitudes and decay times which is proportional to the total intensity. However, the intensity average lifetime is not true for more complex decay laws of multi- or non-exponential decays. In the case of multi-exponential decay, the amplitude average lifetime can be used as an approximation [29–31]:

\[
\langle \tau \rangle_{\text{amp}} = \frac{\sum a_i \tau_i}{\sum a_i} = \sum a_i \tau_i \tag{3}
\]

The amplitude average lifetime is an average time of several lifetimes for the same steady-state intensity of a fluorophore. The lifetime is a statistical average of the random emission decay-times. Some fluorescence decays may be fast following the excitation, and some decays may be slower than the average lifetime. Each amplitude component of lifetime should be carefully analyzed for multi-exponential decays with a complex materials system. Therefore, the amplitude average lifetime was utilized for analyzing the optical dynamics of hybrid optical nanomaterials of plasmon-coupled SQDs.

The fitting of models to the experiment data should be the maximum probability of being correct. This is indeed the result of a least-squares fit, \( \chi^2 \). The least-square fit, \( \chi^2 \), serves as the maximum probability of being correct fitting, which is expected to be near 1.0 for a good fit [32]. The best fit in the least-squares sense minimizes the sum of squared residuals. The residuals being differences between observed values and fitted values provided by the multi-exponential decays were shown in Fig. 6(b) with a tail fitting and Fig. 6(d) with a whole fitting with the IRF deconvolution. The corresponding least-square-fit, \( \chi^2 \), for fitting of the multi-exponential models to the experiment data was estimated to be ~0.99 and 1.01 for a tail fitting and a whole fitting, respectively. For a large number of nanoscale QD fluorophores with hybrid coupling nanoparticles, the decay lifetimes are also dependent on size distribution, surrounding environments, and the interparticle distance of the nearest neighboring particles between the SQDs or between SQDs and Au nanoparticles. Figure 6(e) displayed a typical fluorescence lifetime distribution (\( \Delta \tau \sim 13 \text{ ns} \)) of plasmon-coupled QD ensemble (d~25 nm).

The decay time traces of CdSe/ZnS and plasmon-coupled CdSe/ZnS were shown in the Fig. 7, and the average lifetimes CdSe/ZnS with and without plasmon coupling were shown in the Table 2. The decay times of CdSe/ZnS between a PMMA film and a quartz substrate without plasmon coupling were analyzed into three components of \( \tau_1 \sim 2 \text{ ns} \), \( \tau_2 \sim 11 \text{ ns} \), and \( \tau_3 \sim 39 \text{ ns} \). The fast decay time component (\( \tau_1 \sim 2 \text{ ns} \)) was unchanged between the lifetimes of CdSe/ZnS and plasmon-coupled CdSe/ZnS. The fast lifetime component (\( \tau_1 \)) was
possibly because of the direct energy transfer from a nearest-neighbor CdSe/ZnS to CdSe/ZnS nanoparticles [33], rather than the possible contribution of a weak decay component of plasmonic Au nanoparticle emission in the green spectral region. The second decay component (~11.2 – ~13.7 ns) of amplitude average lifetime for CdSe/ZnS with plasmon coupling exhibited a small variations compared to that (~10.99 ns) of CdSe/ZnS without plasmon coupling. The second component lifetime of plasmon-coupled S Q D S was similar to the decay time of CdSe/ZnS in thin films or on the glass [15]. The lifetime quenching and the photoluminescence efficiency reduction have been observed when the SQDs were cast into the thin films [8], due to the increase of nonradiative rate. The longest decay time (τ₃ ~39 ns) was the exciton lifetime characteristic of an isolated CdSe/ZnS on the glass plate [17] or well-dispersed colloidal SQDs in base solutions. The exciton lifetime originated from radiative decay within CdSe/ZnS. The longest decay component of CdSe/ZnS was completely quenched when the SQDs were coupled with plasmonic Au nanoparticles. It is evidenced by the fact that the plasmon and exciton coupling rate in the presented hybrid nanostructure was faster than that of non-radiative decay rate, even though the lifetime for plasmon-exciton coupling rate was not clearly resolved within the experiment condition. The photoluminescence efficiency of semiconductor nanoparticles without plasmon coupling is given by

\[ \eta_{\text{in}} = \frac{\gamma_r}{\gamma_r + \gamma_{\text{nr}}} \quad (4) \]

where \( \gamma_r \) and \( \gamma_{\text{nr}} \) are the radiative and nonradiative decay rates, and \( \gamma_{\text{PL}} = \gamma_r + \gamma_{\text{nr}} \) is the PL decay rate of SQDs without plasmon coupling. The photoluminescence efficiency of hybrid plasmon-coupled semiconductor nanoparticles is given by

\[ \eta_{\text{in}}^* = \frac{\gamma_r + \gamma_{\text{ex-pl}}}{\gamma_r + \gamma_{\text{nr}} + \gamma_{\text{ex-pl}}} \quad (5) \]

where \( \gamma_{\text{ex-pl}} \) is the coupling decay rate with plasmon-exciton, and \( \gamma_{\text{ex-pl}}^* = \gamma_r + \gamma_{\text{nr}} + \gamma_{\text{ex-pl}} \) is the PL decay rate of the hybrid nanomaterials of plasmon-coupled SQDs. The nonradiative decay may include energy transfer between SQDs or possibly to impurities. If the coupling rate (\( \gamma_{\text{ex-pl}} \)) of hybrid optical materials of plasmon-coupled SQDs is much faster than radiative and nonradiative decays, the PL lifetime of plasmon-coupled SQDs

\( \tau_{\text{pl}}^* = \frac{1}{(\gamma_r + \gamma_{\text{nr}} + \gamma_{\text{ex-pl}})} \)

will be significantly quenched compared to that of SQDs (\( \gamma_{\text{PL}} = \frac{1}{(\gamma_r + \gamma_{\text{nr}})} \)) without plasmon coupling. If the coupling rate (\( \gamma_{\text{ex-pl}} \)) is similar to the radiative decay rate (\( \gamma_r \)) or slower than nonradiative decay rates (\( \gamma_{\text{nr}} \)), the PL lifetime of plasmon-exciton coupling (\( \tau_{\text{pl}}^* \)) will not be quenched compared to that of SQDs (\( \gamma_{\text{PL}} \)). As the Table 3 listed, the longest lifetime (~38.8 ns) with 7% amplitude of SQDs without plasmon coupling was completely quenched when the SQDs were coupled with plasmonic Au nanoparticles. The amplitude \( a_2 \) for the second component lifetime of plasmon-coupled SQDs were increased ~15% – ~24% compared to that of SQDs without plasmon coupling. The increment was possibly because of the reduction of non-radiative decay in the hybrid nanomaterials of plasmon-coupled SQDs. Meanwhile, the total PL intensity of hybrid nanostructure was enhanced up to ~9-fold compared to that of CdSe/ZnS without plasmon coupling. It suggests that the PL enhancement is possibly originated from large local field enhancement and additional resonant energy transfer and re-excitation process. The PL intensity was weakly decreased as the interparticle distance was increased, but exhibited strong PL enhancement up to the coupling distance ~82 nm which was the largest distance for the hybrid optical material for this article.
Apart from the time-resolved photoluminescence characteristics with the interparticle distance, the polarization-resolved PL spectroscopy also indicated an evidence of the coupling between the CdSe/ZnS emission dipoles and dipolar plasmon modes in the hybrid nanostructure. The polarization-resolved PL properties of hybrid plasmon-coupled CdSe/ZnS were characterized as shown in Fig. 8. The excitation source was a CW HeCd laser (Melles Griot, 45-MRM-803-120) operating at 325 nm at 40 mW. The PL of the hybrid nanostructure was collected using an optical fiber (Ocean Optics, P600-2-VIS-NIR), a long wavelength pass filter at 455 nm, and a spectrometer (Ocean Optics USB4000, Resolution: 1 nm). The laser excitation polarization was kept in same direction for all PL polarization measurements. The PL of CdSe/ZnS was uniformly distributed without plasmon coupling as shown in Fig. 8(a). It was expected to observe that the normalized PL of plasmon-coupled CdSe/ZnS with the interparticle distance of ~25 nm was horizontally polarized as shown in Fig. 8(b) [34,35]. However, the PL of hybrid nanostructure with the interparticle distance of ~50 nm was depolarized. It was possibly due to the weakening of dipolar interactions. Therefore, both time- and polarization-resolved PL studies of plasmon-coupled SQDs implied that the PL enhancement of hybrid nanostructure is originated from large local field enhancement, fast resonant energy transfer, and re-excitation process.

4. Conclusion

A hybrid optical nanostructure of plasmon-coupled SQDs was prepared for photonic applications. Au plasmonic nanoparticles were attached on the amino functionalized quartz plate after it was hydroxylated with oxygen plasma etching. The aqueous CdSe/ZnS-COOH was attached on the hydrophilic PMMA after the thickness was controlled for various plasmon-exciton coupling conditions. The microscopy analysis revealed mono-layers of Au nanoparticles with a surface concentration of ~9.18 × 10⁻⁴ nm⁻² and SQDs with that of ~3.7 × 10⁻³ nm⁻². The optical spectroscopy for the hybrid optical nanostructure of plasmon-coupled SQDs exhibited two dominant LSPR peaks of Au nanoparticles at ~546 nm and ~675 nm, and blue-shifted (Δλ~6.7 nm) PL spectra of CdSe/ZnS nanoparticles. The LSPR at longer wavelength indicated the plasmonic coupling between the Au nanoparticles, and the blue shift of PL spectra implied the reduction of interparticle interaction between SQDs. The time-resolved spectroscopy of hybrid optical nanostructure revealed that the average lifetimes for major amplitude component were ~9.21 to ~10.45 ns throughout the scanning lifetime image areas without critical defects on the hybrid optical nanostructure. The decay times of CdSe/ZnS on the PMMA/quartz substrate without plasmon coupling were analyzed into three components of τ₁ ~2 ns, τ₂ ~11 ns, and τ₃ ~39 ns. However, the largest decay component of CdSe/ZnS was not displayed and the total PL intensity of hybrid nanostructure was enhanced up to ~9-fold when the SQDs were coupled with plasmonic Au nanoparticles. The polarization-resolved PL spectroscopy exhibited a uniform circular polarization of PL from the SQDs without plasmon coupling, a horizontal polarization at the shorter plasmon-coupling distance, and a de-polarization at the longer plasmon-coupling distance. Both time- and polarization-resolved PL studies of the hybrid optical nanostructure suggested that the PL enhancement of hybrid nanostructure was originated from large local field enhancement, fast resonant energy transfer, and re-excitation process. Therefore, the presented hybrid optical nanostructure of plasmon-coupled semiconductor quantum dots can be considered as a potential optical materials system for photonic applications.

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Fig. 1.
(a) Schematic procedure of hydroxylation, amino functionalization, and Au deposition, (b) TEM image of Au nanoparticles, and (c) AFM image (1 μm × 1 μm) of Au nanoparticle depositions on quartz plate.
Fig. 2.
SEM images of lateral views of PMMA/Au on a quartz plate (a) as it was prepared, and (b) after it was cut with a diamond knife. SEM images on (c) the top, and (d) the lateral views of QD/PMMA/Au on a quartz plate. The inset in fig. (c) was an inversion of bright and dark image.
Fig. 3. Extinction spectra of colloidal CdSe/ZnS SQDs (black solid line), Au NPs (blue solid line), and PMMA/SQDs/PMMA/Au NPs on the quartz plate (black dash line). Fluorescence spectra of CdSe/ZnS SQDs in water (olive solid line), and SQDs without (green solid line) and with (red solid line) plasmon coupling on the quartz plate.
Fig. 4. Fluorescence images (a) and (d) of the beads. The average fluorescence intensity in the X–Z directions (b) and (c), and the X–Y directions (e) and (f).
Fig. 5.
A typical fluorescence lifetime image of plasmon-coupled CdSe/ZnS (d~25 nm) using a confocal optical microscope. The scanning area of fluorescence lifetime image was 30 × 30 μm². The fluorescence average lifetime was encoded in a color scale from blue to red for 0–30 ns, and intensity was encoded in a color scale from black to white for 0–10 counts. Three red circles (top, bottom right, and bottom left) were the lifetime analysis areas as listed in the Table 1.
Fig. 6.
A typical fluorescence intensity decay of plasmon-coupled CdSe/ZnS (d~25 nm): (a) a tail fitting after the IRF and (c) a whole fitting with the IRF deconvolution, (b) and (d) residual trace as a measurement for the goodness of fit, and (e) average lifetime distribution.
Fig. 7.
Decay time traces of CdSe/ZnS and plasmon-coupled CdSe/ZnS. The scanning area of fluorescence lifetime image was $80 \times 80 \mu m^2$. 
Fig. 8.
Polarization-resolved photoluminescence of CdSe/ZnS (a) without, and (b, c) with plasmon coupling.
Table 1

Lifetime (unit in ns) analysis of plasmon-coupled CdSe/ZnS (d~25 nm) in different areas (red circles in Fig. 4).

| Area          | $a_1$(%) | $\tau_1$ | $a_2$(%) | $\tau_2$ | $\chi^2$ | $<t>_{\text{Top}}$ | $<t>_{\text{Bottom Right}}$ | $<t>_{\text{Bottom Left}}$ |
|---------------|----------|----------|----------|----------|----------|---------------------|-----------------------------|-----------------------------|
| Top           | 29       | 2.49     | 71       | 13.33    | 0.862    | 9.21                | 12.57                       |                             |
| Bottom Right  | 24       | 1.23     | 76       | 11.41    | 0.997    | 10.45               | 11.08                       |                             |
| Bottom Left   | 24       | 1.86     | 76       | 12.48    | 0.92     | 10.31               | 12.00                       |                             |
Table 2

Lifetime analysis of plasmon-coupled CdSe/ZnS (d~25 nm) with tail fitting after IRF and whole fitting with IRF deconvolution.

| Parameter  | a_1(%) | τ_1   | a_2(%) | τ_2   | χ^2  | <τ>_avg | <τ>_std |
|------------|--------|-------|--------|-------|------|----------|---------|
| Tail Fit   | 31     | 2.780 | 69     | 12.98 | 0.99 | 9.84     | 12.09   |
| Whole Fit  | 45     | 2.079 | 55     | 12.28 | 1.01 | 7.67     | 11.03   |
Table 3

Lifetime (unit in ns) analysis of CdSe/ZnS with and without plasmon coupling.

| Sample         | d(nm) | $a_1$(%) | $\tau_1$ | $a_2$(%) | $\tau_2$ | $a_3$(%) | $\tau_3$ | $\chi^2$ | $\Phi_{amp}$ | $\Phi_{tot}$ | $I$  |
|----------------|-------|----------|----------|----------|----------|----------|----------|----------|--------------|--------------|-----|
| CdSe/ZnS       | 43    | 2.2      | 50       | 10.9     | 7        | 38.8     | 0.97     | 9.09     | 18.47        | 1.0          |     |
| Au-CdSe/ZnS    | ~19   | 36       | 2.3      | 64       | 11.2     |          | 1.02     | 7.95     | 10.24        | 8.8          |     |
| Au-CdSe/ZnS    | ~25   | 36       | 2.1      | 64       | 12.3     |          | 1.01     | 8.60     | 11.38        | 6.2          |     |
| Au-CdSe/ZnS    | ~50   | 34       | 2.9      | 66       | 13.7     |          | 1.02     | 10.06    | 12.61        | 5.7          |     |
| Au-CdSe/ZnS    | ~82   | 41       | 2.3      | 59       | 13       |          | 0.98     | 8.62     | 11.86        | 5.1          |     |