Competition between surface trapping and nonradiative energy transfer to gold nanofilm

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Nonradiative resonant energy transfer from CdSeS quantum dot to gold nanofilm was investigated by taking nanosecond and picosecond time resolved photoluminescence measurements. Surface plasma resonant absorption peak of gold nanofilm was adjusted to meet the near resonant conditions with the fluorescence peak of quantum dot by changing the thickness. Surface trapping state was proved to be the origin of the long lifetime component by comparing fresh and eight months aged quantum dot. It was observed that the excitonic state lifetime of the quantum dots was reduced by nonradiative resonant energy transfer to gold nanofilm. Nonradiative resonant energy transfer time, which was comparable with the surface trapping time, was calculated based on the data of picosecond photoluminescence measurements. No nonradiative energy transfer from surface trapping state to gold nanofilm, thus the lifetime of surface trapping state was not affected obviously. It is suggested that in the assembly combined with quantum dot and gold nanostructure, nonradiative energy transfer will occur after the population of excitonic state, and compete with surface trapping process. The interactions between surface trapping state and gold nanofilm were not exhibited. © 2010 American Institute of Physics. [doi:[10.1063/1.3503518](https://doi.org/10.1063/1.3503518)]

I. INTRODUCTION

There has been a growing interest in the investigation of noble metal nanostructures (MNSs) in recent years because of their unique optical, electrical, and chemical properties,¹⁻³ which can be extensively used in metal enhancement and quenching fluorescence,^{2,4} surface-enhanced Raman scattering,⁵ and resonance energy transfer.^{2,6} More recent works have shown that the optical property is due to the collective oscillation of the electrons in the conduction band, known as surface plasmon oscillation. The oscillation frequency is usually in the visible region for gold and silver resulting in the strong surface plasmon resonant absorption. The resonant condition is determined from absorption and scattering spectroscopy and is suggested to depend on the size, shape, and dielectric constants of both the metal and the surrounding material. Semiconductor quantum dots (QDs) has been much accounted of in biological imaging⁷ and single photon sources⁸ because of the size- and shape-dependent optical and electronic properties.⁹ All these properties come from the quantum confinement of the electrons. As the particle size decreases below Bohr radius of the semiconductor material, the electron becomes more confined in the particle, which leads to an increase in the band gap energy and quantizes the valence and conduction bands. One important concern in the study of QDs is the radiative lifetime. Compared with the typical 1 ns radiative lifetime in bulk materials, the radiative lifetime of semiconductor QDs usually ranges from several to tens of nanoseconds,^{8,10} and an interesting feature of the photoluminescence (PL) decay of colloidal QDs is the almost universal occurrence of a biexponential time distribution in the radiative lifetime. The fast

lifetime can be attributed to the intrinsic recombination of initially populated core state,^{10,11} and it has been believed that the surface of QDs plays very important roles in carrier relaxation and recombination processes^{10,11} since it has large surface-to-volume ratio. Surface trapping state can be proved to be the origin of the slow lifetime component through changing the surface property of semiconductor QDs.^{12,13} Carrier relaxation and recombination processes with surface trapping state involved can be depicted as follows: carriers are first populated on the initial core state, which is referred to as excitonic state in this paper. The exciton state has two relaxation paths, emitting photons through carrier recombination to the ground state with few nanoseconds lifetime and surface trapping with tens picoseconds lifetime.^{10,14} Surface trapping state depopulates through emitting photons.

Modern nanotechnology gives opportunity to combine solid-state nanocrystals and biomaterials in one superstructure.¹⁵ This kind of superstructure represents new physical and chemical properties, which arise from the interactions between building blocks.¹⁶ In superstructures consist of semiconductor QDs and MNS, Coulomb interactions between carriers of QDs, and metal plasmons can result in emission enhancement or quenching and radiative lifetime shortening.⁶ And it is common to change the surface properties of QDs (Refs. 12 and 17) with biolinkers or dielectric materials^{16,18} while building up these assemblies. As depicted above, surface property plays very important roles in QDs' carrier relaxation and recombination processes, therefore, it is necessary to investigate whether the interactions between MNS and the surface of QDs exist or not.

In the present work, nanofilms deposited by gold nanoparticles were prepared by vacuum evaporation, and the surface plasmon resonant peak was adjusted by changing the

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thickness of the film to meet the near resonant condition with QDs' emission peak. Nanosecond and picosecond time resolved PL measurements were taken to investigate the lifetime of QDs free in solution and in the assembly. A biexponential time distribution in the radiative lifetime of QDs was revealed and surface trapping state was proved to be the origin of the slow lifetime component. It was observed that the lifetime and proportion of the excitonic state were changed by gold nanofilm but the lifetime of the surface trapping state was not affected obviously. Nonradiative resonant energy transfer (NRET) from the excitonic state to gold nanofilm occurred, and the transfer time was calculated based on the data of picosecond PL measurements. The NRET time was comparable with the surface trapping time. No NRET from surface trapping state to gold nanofilm occurred. It is suggested that in the assembly combined with QD and gold nanostructure, NRET will occur after the completion of excitonic state population, and compete with surface trapping process. No other interactions between surface trapping state and gold nanofilm exists.

II. MATERIALS AND METHODS

The solution of CdSeS QDs in chloroform and n-hexane (1 mg/ml, emission centered at 555 nm) were purchased from Uraqd Ltd. in Tianjin, China. Gold powder (99.999%) was vaporized to glass slide substrates in 10^{-3} Pa vacuum chamber, with film thickness monitor monitoring the thickness. Surface images of the nanofilms were acquired by using the atomic force microscopy (Digital Instrument, Nanoscop III a) with contact mode. The assembly combined with CdSeS QDs and gold nanofilm was built up by adsorbing QDs to gold nanofilm in chloroform and n-hexane solutions.

A Ti:sapphire laser system (Spectra-Physics) are used to excite the steady-state and nanosecond time resolved PL. The excitation beam centered at 400 nm is acquired by Frequency doubling of the 800 nm laser beam through a BBO (beta-BaB₂O₄, barium metaborate) crystal. The emission is collected by a spectrometer (Bruker Optics 250 IS/SM) coupled with an intensified charge-coupled device (CCD) detector (IStar740, Andor). Nanosecond time resolved experiment is carried out by adjusting the delay time of the CCD shutter. Laser pulse gives a external trigger signal to open a 2 ns temporal gate of the intensified CCD through a digital delay/pulse generator (DG535), then the transient PL spectra at different decay time can be recorded by the CCD detector. Nanosecond time resolved PL decay curve is obtained by singling out the PL intensities of the specific wavelengths at different decay time. Figure 1 gives a schematic diagram of the experimental setup.

Picosecond time resolved PL decay was recorded with a time correlated single photon counting (TCSPC) (Becker & Hickl GmbH, SPC-130) fluorescence lifetime spectrometer. The excitation source was a pulsed laser diode (Becker & Hickl GmbH, BDL-375-SMC) centered at 375 nm with a 20 MHz repetition rate. The instrument response function (IRF) is about 60 ps.

FIG. 1. Experimental setup of nanosecond time resolved PL measurement.

III. RESULTS AND DISCUSSION

A. Preparation and characterization of gold nanofilm

There are two general strategies to obtain nanostructures. Bottom up method where the atoms are assembled to generate nanostructures, or top down method where material is removed from the bulk material, leaving only the desired nanostructures. The atoms in bottom up method can be produced from reduction in ions and evaporation from gold source. Top down techniques suffer from the waste of large amounts of material, while bottom up techniques suffer from poor monodispersity. In this work, vacuum evaporation was used to prepare gold nanofilm, and under low evaporation rate condition, gold nanofilms with good monodispersity were obtained. The glass slides used for gold nanofilm preparation were first cleaned by soaking them for overnight in 98% H₂SO₄. After washing rigorously with MilliQ deionized water, the glass slides were air-dried and placed in the top of the vacuum chamber, with the detector of the film thickness monitor underneath. Gold powder (99.999%) was put into a molybdenum boat connecting two electrodes. The vacuum degree was maintained at 10^{-3} Pa. The molybdenum boat was heated up by increasing the on-load voltage. The voltage was locked at 70 V to ensure that the deposition rate is 0.1 nm/min, and the current was 100 A. Under this condition, gold nanofilms with good monodispersity were obtained. The film thickness monitor displayed a 20 nm thickness, and the atomic force microscopy image (Fig. 2) exhibits that it is formed by accumulation of gold nanoparticles in 23 nm mean size. This gold nanofilm was used to adsorbed CdSeS QDs in chloroform, and the assembly was used to take nanosecond time resolved PL spectroscopy.

The on-load voltage of the molybdenum boat was increased to 75 V and the current is 110 A. It made 180 times increases in the deposition rate. The film is also formed by accumulation of gold nanoparticles (Fig. 3) but the monodispersity becomes poor and the mean size and the roughness increases. The thickness given by film thickness monitor was 15 nm. This gold nanofilm was used to adsorbed CdSeS QDs in n-hexane, and the assembly was used to take picosecond time resolved spectroscopy.

B. Steady-state absorption and PL spectroscopy

Figure 4 gives the steady-state absorption and PL spectrum of CdSeS QDs and gold nanofilms with different thicknesses. CdSeS QDs in chloroform and n-hexane have the

FIG. 2. (Color online) Atomic force microscopy imaging of 20 nm thickness gold nanofilm prepared under 0.1 nm/min deposition rate condition.

same absorption and PL peak position, thus only one set of QDs' absorption and PL spectrum are given in Fig. 4. The surface plasmon resonant condition of gold nanofilm depends on the thickness of the film, thus the surface plasmon resonant wavelength of 15 nm gold nanofilm prepared under fast deposition rate condition is shorter than that of 20 nm gold nanofilm prepared under slow deposition rate condition. Their normalized intensities were put into the same coordinates for comparison peak positions. As shown in Fig. 4, the emission peak of QDs is close to the surface plasma resonant peak of both gold nanofilms. NRET from QDs to gold nanofilms will occur under this near resonant condition.^{2,4,19}

C. Nanosecond time resolved PL lifetime measurement

The fresh and eight month aged CdSeS QDs in chloroform and the assembly combined 20 nm gold nanofilm with the fresh QDs were measured by nanosecond time resolved PL system. The semilogarithmic decay curves are shown in

FIG. 3. (Color online) Atomic force microscopy imaging of 15 nm thickness gold nanofilm prepared under 0.3 nm/s deposition rate condition.

FIG. 4. Normalized optical density of CdSeS QDs (solid), 15 nm gold nanofilm (dashed), and 20 nm gold nanofilm (dashed dotted), and normalized PL intensity of CdSeS QDs (dotted).

Fig. 5. Generally speaking, the population of the excited state can decay through two paths, radiative and nonradiative. The excited state population (A) is expressed by the following differential equation:

$$-\frac{dA}{dt} = (k_r + k_{nr})A, \quad (1)$$

where k_r and k_{nr} are radiative and nonradiative decay rate, respectively. Thus the PL intensity at delay time t , $I(t)$, can be depicted by:

$$I(t) = I_0 \exp(-t/\tau), \quad (2)$$

where I_0 is the PL intensity at the beginning of decay, τ is the lifetime of the excited state, and $1/\tau = k_r + k_{nr}$. The detected PL will exhibit a multiexponential decay process when it comes from several excited states. Figure 5 clearly reveals a biexponential decay process. The detected PL decay curve is the convolution of IRF and the real PL decay curve. The IRF can be produced through measuring the response of femtosecond laser pulse since the pulse is considered to be a δ

FIG. 5. Nanosecond time resolved PL decay kinetics and biexponential fit for aged (a) and fresh (b) CdSeS QDs and 20 nm gold nanofilm-fresh CdSeS QDs assembly (c).

TABLE I. Fitting parameters of nanosecond time resolved PL decay curves.

Sample	τ_1 (ns)	a_1 (%)	τ_2 (ns)	a_2 (%)
Fresh QDs	4.3	90	20.4	10
Aged QDs	6.2	53	25.9	47

function. The real PL decay curve here is described by:

$$I(t) = \sum_{i=1}^2 a_i \exp(-t/\tau_i), \quad (3)$$

where a_i and τ_i are the proportion and lifetime of the i th component. Least-squares fitting method was used to fit the experimental data, by using Eq. (3) and the measured IRF. Table I gives the fitting parameters of nanosecond time resolved experimental data, and the fitting curves are displayed in Fig. 5.

The fitting results of fresh prepared CdSeS QDs (Table I) exhibit a fast and a slow decay component, with lifetime of 4–6 ns and 20–25 ns. The proportions of the two components are 90% and 10%, respectively. As mentioned above, the fast one can be attributed to the excitonic states recombination.^{10,11} Since the long time aged QDs have more surface defects,¹⁴ 8 months aged CdSeS QDs were used to prove that the surface trapping state is the origin of the slow decay component. Fitting parameters of aged sample (Table I) reveal that the proportion of the slow decay component increased to 47%, with no obviously change in lifetime. It is implied that the slow decay component comes from the surface trapping state.^{12–14} Surface trapping state is located near the bottom of the conduction band, thus the steady-state PL spectrum do not exhibit two separated peak (Fig. 4), while the transient PL spectrum reveal a redshift slightly with increasing decay time.¹³

The decay kinetics of the assembly [Fig. 5(c)] also reveals two lifetime components. The fast one is shorter than the 2 ns temporal gate of the intensified CCD, thus the fitting method is not feasible. The slope of the semilogarithmic decay curve represents the decay rate $1/\tau$, and it can be clearly seen that the slow decay component of the assembly [Fig. 5(c)] almost parallels to that of the fresh QDs [Fig. 5(b)], thus it is indicated that the lifetime of slow decay component is not changed obviously, while that of the fast component is intensively reduced. MNS can intensively reduce the excited state lifetime of emitter nearby through NRET from emitter to MNS. The rate of NRET k_{NRET} should be more than tens, even hundreds of times of emitter's radiative decay rate k_r under the near resonant condition when the surface distance is appropriate.^{2,4,19} As exhibited in the steady-state spectrogram (Fig. 4), the emission peak of QDs is close to the plasma resonant peak of gold nanofilm, which enables NRET in the assemblies. NRET first comes from the excitonic state of QDs since the surface trapping time is about tens or hundreds of picoseconds.^{10,14} The decay rate of the excitonic state of QDs in the assembly $1/\tau_1^*$ can be expressed as

FIG. 6. (Color online) Picosecond time resolved PL decay kinetics and biexponential fit (solid line) for free CdSeS QDs (+) and 15 nm gold nanofilm-CdSeS QDs assembly (○). Decay curves during a smaller temporal scale (solid inset) and IRF (dashed inset).

$$\frac{1}{\tau_1^*} = \frac{1}{\tau_1} + k_{\text{NRET}}, \quad (4)$$

where $1/\tau_1$ is the decay rate of the excitonic state of free QDs. As mentioned above, k_{NRET} may be much faster than $1/\tau_1$, τ_1^* should be heavily quenched as shown in Fig. 5(c). NRET to gold nanofilm and surface trapping process are two nonradiative decay processes of the excitonic state, and they compete in the excitonic state decay kinetics. NRET not only quenched the lifetime of the excitonic state but also reduced the population of the surface trapping state. However, no NRET from surface trapping state to gold nanofilm since the lifetime of surface trapping state was not reduced by gold.

D. Picosecond time resolved PL lifetime measurement

The analysis of nanosecond time resolved PL measurement cannot give NRET time, thus TCSPC fluorescence lifetime measurement with 60 ps time resolution was taken to determine the NRET time. The repetition rate of excitation source is 20 MHz, which makes a 50 ns time-interval between two adjacent excitation pulses. The recorded decay curve of the sample with long excited state lifetime will be distorted since the last fluorescence pulse tail impacts the following one. 12 months aged n-hexane solution of CdSeS QDs were tested, and it was found that this sample has appropriate lifetime and greater proportion of surface trapping state. Compared with the QDs in chloroform, this sample exhibits the same absorption and PL spectrum. The only difference between these two sample is surface ligand, which leads to the differences in lifetimes of the excitonic state and surface trapping state.^{10,14} Great proportion of surface trapping state makes it credible to reveal the changes in lifetime. The assembly was built up by adsorbing CdSeS QDs onto a 15 nm gold nanofilm in n-hexane. NRET can also take place since the steady-state spectrum meets the near resonant condition (Fig. 4).

Figure 6 displays the decay kinetics recorded by TCSPC. The IRF of this experimental setup is a Gaussian function. The duration time of IRF and the parameters of the biexponential decay formula [Eq. (3)] were fitted out at the same

TABLE II. Fitting parameters of picosecond time resolved PL decay curves.

Sample	τ_1 (ns)	a_1 (%)	τ_2 (ns)	a_2 (%)
Free QDs	1.48	29.3	7.60	70.7
QDs in assembly	0.13	47.4	5.27	52.6

time. The time resolution was calculated to be about 60 ps. It can be clearly seen from Fig. 6 that the lifetime of surface trapping state was not reduced by gold nanofilm but the lifetime of excitonic state was quenched. The decay curves during a smaller temporal scale are inseted in Fig. 6, to clearly represent the lineshape of IRF and decay process of the excitonic state of the QDs in the assembly. The time resolution of TCSPC is high enough for the excitonic state lifetime measurement.

The fitting parameters of free QDs (Table II) exhibit a 1.48 ns excitonic state lifetime and a 7.60 ns surface trapping state lifetime. However the excitonic state lifetime of QDs in the assembly was reduced to 130 ps. NRET time was calculated to be 140 ps by using Eq. (4). The carrier relaxation time from the excitonic state of QDs to the surface trapping state is about tens or hundreds of picoseconds.^{10,14} Thus NRET time to gold nanofilm and surface trapping are comparable. NRET competes with surface trapping, inducing a population decrease in surface trapping state, thereby the proportion of surface trapping state in the decay kinetics is reduced from 70.7% to 52.6%. As revealed by Fig. 6, the lifetime of surface trapping state is not obviously changed, which implies that there is no interaction between MNS and the surface trapping state of QDs.

IV. CONCLUSION

In conclusion, competition between surface trapping and NRET to gold nanofilm during the excitonic state decay process of semiconductor QDs was observed by taking nanosecond and picosecond time resolved PL measurements. Near resonant condition was realized by adjusting the thickness of gold nanofilm so that NRET can take place in the assembly. NRET time has the same order of magnitude as surface trapping time. They compete in the excitonic state decay kinetics, and decrease the excitonic state lifetime and surface trapping state proportion. No NRET from surface trapping state

to gold nanofilm was observed since the lifetime of surface trapping state was not quenched, implying that no interaction between MNS and the surface trapping state of QDs exists. The change in surface property during building up assemblies will not affect the interaction between building blocks.

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