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Large-scale control of enhancement and quenching of photoluminescence for ZnSe/ZnS quantum dots and Ag nanoparticles in aqueous solution*

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We investigated the optical properties of hybrid exciton–plasmon coupling ensembles composed of ZnSe/ZnS quantum dots and Ag nanoparticles in aqueous solution. We modulated their average interval by changing the ratio of quantum dots and Ag nanoparticles. The transition from dramatic PL enhancement to PL quenching state was experimentally observed, according to the continuous decrease of the PL lifetime. The PL enhancement rate exceeded 10, with the Purcell factor of 3.5. Meanwhile, the proportion of fast decay increased from 0.3 to 0.6, corresponding to the proportion of slow decay decreased from 0.7 to 0.4. Our experiment is important for the hybrid exciton–plasmon coupling system to be practicable in optoelectronic application.

Keywords: ZnSe/ZnS quantum dots, enhancement and quenching, localized surface plasmons, aqueous solution

PACS: 78.55.Et, 68.65.Hb, 73.20.Mf, 42.50.Pq **DOI:** 10.1088/1674-1056/28/5/057803

1. Introduction

Semiconductor quantum dots (QDs) are crystalline materials in which the electron wavefunction is confined in three-dimensions of space by the potential energy barriers and are known as "artificial atoms".[1,2] The particle size of QDs is generally between 1 nm and 10 nm. The continuous energy band structure is changed into a discrete energy level structure. Because of this characteristic, QDs possess attractive advantages such as high quantum yield, large oscillator strength, and excellent photostability. Due to these unique optical properties, QDs have been attracting much attention for optoelectronic applications including bio-imaging, bio-labeling, and QD-based lasers. Optical applications need efficient control of light emission processes. Photoluminescence (PL) enhancement and quenching are important factors to control the optical properties of semiconductor QDs. Engineering their local electromagnetic environment is the most effective and commonly used approach.[3,4] Optical microcavity and plasmonic metal nanoparticles (NPs) are two important structures that can modify the emission process. High-quality cavities are used to boost interaction time and enhance coupling strengths.[5,6] However, high-Q cavities of optical wavelength size are difficult to fabricate.

An alternative strategy is to use the plasmonic metal NPs system. In the metal NPs system, the optical energy can be trapped into spatial regions far smaller than the diffraction limit, quantized into plasmons. In this system, it is possible to transform far-field radiation into a strong localized electromagnetic field near the NPs, and therefore provide an excellent interface between light and matter.[7,8] On the other hand, localized surface plasmon modes display very fast relaxation times owing to losses in metals, which can be very helpful to ultrafast signal processing. The interaction of exciton–plasmon coupling and the conversion of exciton–plasmon–photon have been widely investigated experimentally and theoretically. In previous works, most studies focused on individual QD/NP interaction systems and manipulated light at the nanometer scale, which request advanced technology on the preparation of materials and impede their actual application.[9,10] In this paper, we choose ZnSe/ZnS core-shell QDs as the emitters and investigate their interaction with Ag-NPs in aqueous solution. We implement a simple and feasible way to control the enhancement and quenching of PL for ZnSe/ZnS quantum dots and Ag NPs at macro-scale level. Our results pave the way for practical applications of future biomarkers, color conversion, and optoelectronic devices based on the quantum dots and metal NPs system.

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2. Experiments and results

The ZnSe/ZnS core-shell QDs used in our experiment were prepared in accordance to the method published by Nikesh *et al.*[11] Larger band-gap inorganic shell materials (ZnS) around the ZnSe QDs were implemented to form the type-I core-shell system. In aqueous solution, a blue fluorescence of core-shell ZnSe/ZnS QDs was explored at the concentration of 1000 mg/L. The average size of the ZnSe cores was estimated at around 3.3 nm. The PL spectrum of the ZnSe/ZnS QDs (excited by 325 nm CW laser) was presented in Fig. 1(a). The peak wavelength and the full width at half-maximum (FWHM) of the PL spectrum were 386 nm and 15 nm, respectively. Ag-NPs with average diameter 30 nm were selected due to their absorbed energy very close to QDs emitting energy. 50 mg/L Ag-NPs were employed in this experiment. The absorption spectrum of the employed Ag-NPs is shown in Fig. 1(a) as well, with the peak wavelength centered at 395 nm. The exciton transition of the ZnSe/ZnS QDs is in close resonance with the plasmon excitation of the Ag-NPs. A 350 nm fs-laser was adopted to excite the system, which is close to the resonance energy level. Firstly, 5 mL of diluted QDs sample was put in a cuvette of 1.0 cm optical path. Then, various amounts (10–90 μL) of Ag-NPs were added into the ZnSe/ZnS QDs aqueous solution. These steps were carried out at room temperature. Figure 1(b) displays the sketch of this system and the internal process. After the excitation of the laser pulse, the system formed by the strong interactions of silver plasmons with nearby QD excitons coupled to the far field in the form of radiative dissipation, which is consistent with the observed PL signal. The time-resolved PL measurements were selected to explore the direct observation of this system.[12,13]

Time-resolved PL measurements were performed using a Ti: sapphire laser which can provide the frequency doubled output to excite the hybrid system from the side of the cuvette, and the time-correlated single photon counting (TCSPC) technique was employed. The pulse wavelength and repetition rate were set at 700 nm and 80 MHZ, respectively. The results are presented in Fig. 2. In Fig. 2, the transition of the typical PL spectra obtained from the ZnSe/ZnS QDs mixed with Ag-NPs is demonstrated. By increasing the content of Ag-NPs from 0 μL to 60 μL, the PL intensity enhanced from 5×10^3 to 5×10^4 (arb. units). Furthermore, the measured PL enhancement reached 1000% for the ZnSe/ZnS QDs with 60 μL Ag-NPs. On the other hand, with the increase of the content of Ag-NPs from 60 μL to 90 μL, the PL signal decreased. Thus, it can be demonstrated that the mixed Ag-NPs have great impact on the band gap emission of the ZnSe/ZnS QDs. That is to say, the enhancement of luminescence will diminish with the increasing inter-distance between the Ag-NPs and the ZnSe/ZnS QDs, as the increase of the Ag-NPs concentration can decrease the inter-particle spacing.[14–17]

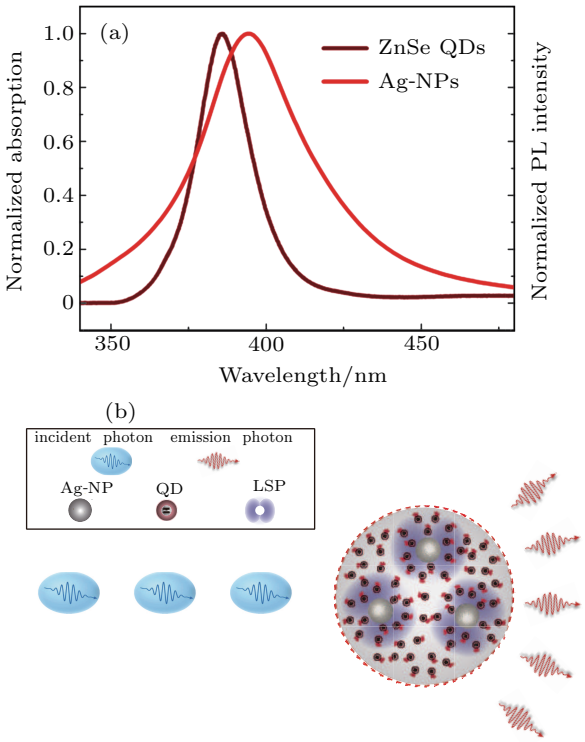


Fig. 1. (a) The photoluminescence spectra of the ZnSe/ZnS QDs (excited by 325 nm cw laser) and the absorption spectra of the employed Ag-NPs. (b) The schematic diagram of distribution and interaction for the ZnSe/ZnS QDs and Ag-NPs in aqueous solution.

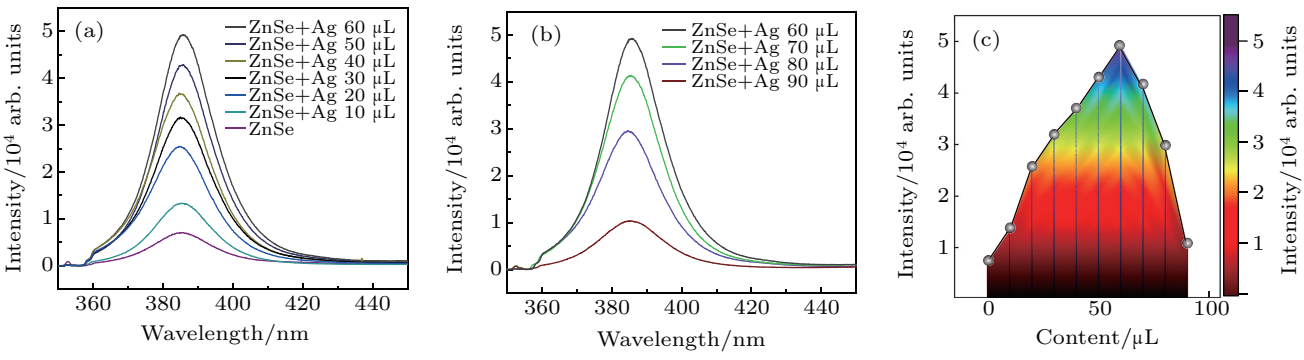


Fig. 2. (a) Typical PL spectra of ZnSe/ZnS QDs mixed with various amounts of Ag-NPs ((a) 0–60 μL, (b) 60–90 μL). (c) The trend of PL intensity of ZnSe/ZnS QDs mixed with various amounts of Ag-NPs from 0 μL to 90 μL.

Based on the above experimental phenomenon, the physical process of this period can be easily comprehended. The detected fluorescence intensity can be expressed as $F_e = E_{exc} Q k_{det}$. Here $E_{exc} = \left|(E_{lsp}p)/(E_{lsp}p)\right|^2$ is the enhancement factor of the exciting optical field which measures the enhancement effect of the local electromagnetic field when the molecule is in the vicinity of the metal structure.[18–20] k_{det} is the efficiency of the optical detection, and Q is the fluorescent quantum efficiency. In most cases, when the optical detection system and the experimental research system are selected, it can be approximated that the light detection efficiency k_{det} is determined. Therefore, the detected fluorescence intensity can be simplified as being determined by two factors: excitation gain $E_{exc} = \left|(E_{lsp}p)/(E_{lsp}p)\right|^2$ and quantum efficiency $Q = \Gamma_{rad}/(\Gamma_{rad} + \Gamma_{nonrad})$. Correspondingly, the two enhancement mechanisms are to enhance the incident excitation field and enhance the radiative recombination rate. When the silver nanoparticles were added to the ZnSe/ZnS quantum dot solution until the amount of silver nanoparticles reached 60 μL, the excitation electromagnetic field E_{lsp} became stronger and stronger, and the fluorescence intensity was enhanced continuously. However, as the amount of the silver nanoparticles exceeded the amount of the 70 μL, the excitation electromagnetic field E_{lsp} was still enhanced, at this time, as more energy would be transferred into the silver nanoparticles from the ZnSe/ZnS quantum dots in the form of non-radiative relaxation, the quantum yield of the ZnSe/ZnS quantum dots was greatly reduced to exceed the effect of the excitation light field gain, so the quenching of the fluorescence signal was expected at this time.[21–24]

To figure out the mechanism in this hybrid system, we measured a subset of ZnSe/ZnS QDs decay curves representative of Ag-NPs of various concentrations. As shown in Fig. 3(a), the purple curve shows the exponential curve for the ZnSe/ZnS QDs without the presence of the Ag-NPs used for reference. As the content of Ag-NPs increased, the decay curves of the ZnSe/ZnS QDs changed rapidly with the femtosecond pulsed laser excitation. The bi-exponential model functions that reproduced the data more adequately were used to obtain fast and slow components of the PL decay. The decay of the ZnSe/ZnS QDs in aqueous solution showed the time components of τ^0_{fast} =427 ps and τ^0_{slow} =3315 ps. When the Ag-NPs were added in the ZnSe/ZnS QDs, a significant decrease in the fluorescence lifetime was noticed, not only the fast component, but also the slow component.[25–27] This change in lifetime is consistent with the increase of the typical PL spectra (Fig. 2). However, the instrument response function (IRF) limited the observation of the fluorescence decay. As a result, the largest content of Ag-NPs was 90 μL with the time constants of τ^{90}_{fast} =122 ps and τ^{90}_{slow} =948 ps. In order to directly perceive the situation, the fast component and the slow component were extracted respectively, as can be seen in Fig. 3(b). The dominant fast components correspond to a Purcell enhancement can be related to ZnSe/ZnS QDs in solution of $F_p = \tau^0_{fast}/\tau^{90}_{fast}$ =3.5. The spontaneous emission rate enhancement (Purcell factor) means the strength of the coupling between the ZnSe/ZnS QDs is stronger than before.

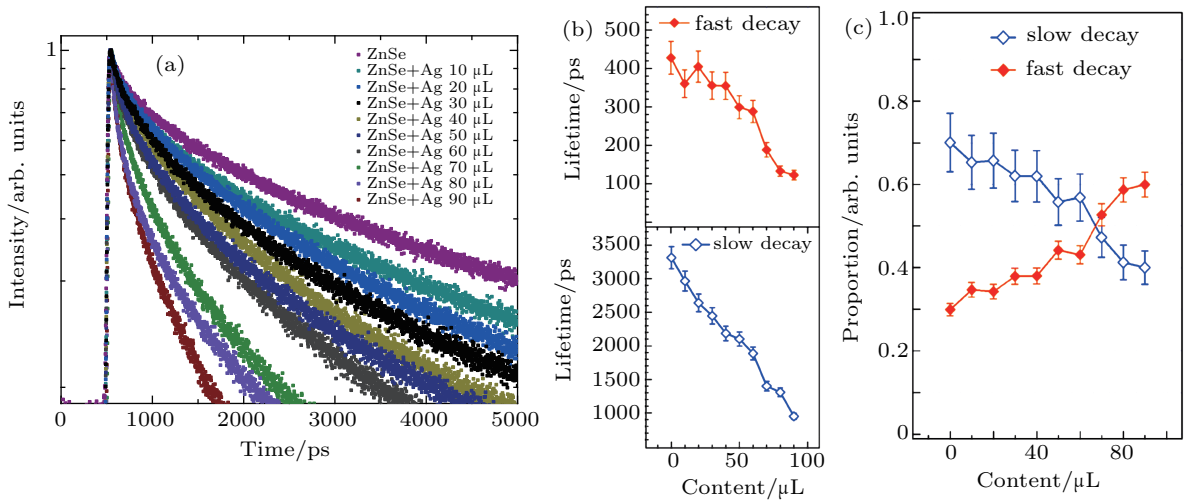


Fig. 3. (a) Typical time-resolved fluorescence of ZnSe/ZnS QDs mixed with various amounts of Ag-NPs; (b)–(d) the changes of the slow part and the fast part of the time constant with the Ag-NPs content varying from 0 μL to 90 μL.

The fluorescence spectral curve and the fluorescence lifetime decay curve obtained in the experiment showed that when the amount of silver nanoparticles in the solution of ZnSe/ZnS quantum dot was increased from 0 μL to 60 μL, the fluorescence signal of the ZnSe/ZnS quantum dot solution was gradually enhanced, while the fast and slow lifetime of the fluorescent lifetime decay curve became smaller and smaller. Hence, a negative correlation between the fluorescence intensity and lifetime can be identified. When the amount of silver nanoparticles in ZnSe/ZnS quantum dot solution reached 70 μL, the

fluorescence signal of the ZnSe/ZnS quantum dot solution gradually decreased until 90 μL, which was accompanied by the fast and slow lifetime of the fluorescence relaxation curve. This can demonstrate the positive correlation between the fluorescence intensity and lifetime.[28,29] The results were repeatable when the solution was preserved for more than a year, which demonstrates the stability of the system.

As shown in Fig. 4, with the combination of experimental phenomena obtained, it should be noted that there is one more relaxation tunnel to transfer the energy between the ZnSe/ZnS QDs and the silver nanoparticles, which is indicated by ES in the figure. Here GS refers to the ground state of ZnSe/ZnS QDs, ES represents the excited state of the ZnSe/ZnS QDs, and TS indicates the trap state of the ZnSe/ZnS QDs. g_1 represents the dipole interactions between QD to NP, γ_1 represents the energy dissipation from QD to NP, γ_2 represents the energy dissipation from QD to TS, and γ_3 represents the energy dissipation from NP to vacuum state. ω_1 represents the photon energy transition from ES to GS, and ω_2 represents the photon energy transition from TS to GS. The process of the electron relaxation from the excited state to the ground state is consistent to the fast lifetime of the fluorescence lifetime. The process of the electron's relaxation from the surface-defected state to the ground state is consistent to the slow lifetime of the fluorescence relaxation. The spontaneous emission rate enhancement (Purcell factor) means that the strength of the coupling between the ZnSe/ZnS QDs is stronger than before.

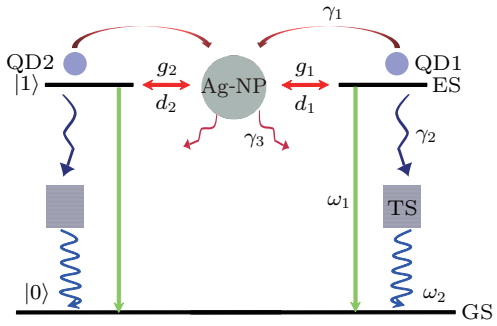


Fig. 4. Schematic presentation of various relaxation paths including energy transfer of ZnSe/ZnS QDs in the presence of Ag-NPs.

There exist two competition mechanisms in the process, which include the excitation field gain and the energy transfer between ZnSe/ZnS QDs and silver nanoparticle system simulated by the coupling between the ZnSe/ZnS QDs and silver nanoparticles. When the effect of excitation field gain is greater than the energy transferred between ZnSe/ZnS QDs and silver nanoparticles, the radiation recombination of exciton state and surface defect state will be greater than that of non-radiation recombination and energy transfer,[30,31] the fluorescence will be enhanced, and the fast lifetime and slow lifetime will be faster due to the recombination of radiation. However, when the effect of excitation field gain is less than the energy transferred between ZnSe/ZnS QDs and silver nanoparticles, the radiation recombination of exciton state and surface defect state can be weaker than that of non-radiation recombination and energy transfer, the fluorescence can be quenched, and the fast lifetime and slow lifetime can be shorter because the energy transfer process still speeds up more quickly. Therefore, the competition between the two mechanisms generates these experimental results.

3. Conclusion

We demonstrated a large-scale control of the enhancement and quenching of photoluminescence for ZnSe/ZnS quantum dots and Ag nanoparticles in aqueous solution. The ultrafast spontaneous emission modulation of ZnSe/ZnS quantum dots was discussed by means of PL spectra and time-resolved fluorescence spectrometry. It was identified by this research that the more silver nanoparticles there are, the more apparent is the modulation of the spontaneous emission rate for the ZnSe/ZnS quantum dots. And the fluorescence intensity of ZnSe/ZnS quantum dots was firstly enhanced and then quenched. This is the result of competition between the energy transfer and the radiation recombination process under conditions of different amounts of Ag-NPs.

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