Experimental investigation of energy transfer between CdSe/ZnS quantum dots and different-sized gold nanoparticles

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Abstract: Hybrid nanostructures of quantum dots(QDs) and metallic nanostructure are attractive for future use in a variety of optoelectronic devices. For photodetection applications, it is important that the photoluminescence (PL) of QDs is quenched by the metallic nanostructures. Here, the quenching efficiency of CdSe/ZnS core-shell quantum dots (QDs) with different sized gold nanoparticles (NPs) films through energy transfer is investigated by measuring the PL intensity of the hybrid nanostructures. In our research, the gold NPs films are formed by the post-annealing of the deposited Au films on the quartz substrate. We find that the energy transfer from the QDs to the Au NPs strongly depends on the sizes of the Au NPs. For CdSe/ZnS QDs direct contact with the Au NPs films, the largest energy transfer efficiency are detected when the resonance absorption peak of the Au NPs is nearest to the emission peak of the CdSe/ZnS QDs. However, when there is a PMMA spacer between the QDs layer and the Au NPs films, firstly, we find that the energy transfer efficiency is weakened, and the largest energy transfer efficiency is obtained when the resonant absorption peak of the Au NPs is farthest to the emission peak wavelength of CdSe/ZnS QDs. These results will be useful for the potential design of the high efficiency QDs optoelectronic devices.

Keywords: energy transfer, quantum dots, nanoparticles, surface plasmon resonance, photoluminescence

1. Introduction

Due to the outstanding optical properties and quantum size effect, quantum dots (QDs) have been applied in various aspects including sensing [1], biomedical imaging [2] and light emitting[3-5], which are based on the optical-to-optical or electrical-to-optical energy conversion, as well as photovoltaic converting and photodetecting [6-9], which are based on the optical-to-electrical energy conversion. In order to improve the optical-to-optical conversion efficiency of QDs, numerous methods have been adopted including in combination with designed metallic nanostructures [10-12]. The plasmonic properties of the designed metallic nanostructures could lead to the enhancement or the quenching of the fluorophore emission of QDs [13,14]. Contrary to QDs-based optical-to-optical conversion devices, in the QD-based photoelectric conversion devices, it is not necessary to enhance the photoluminescence intensity, however, it is more important to quench the photoluminescence intensity by forster resonance energy transfer (FRET) the excited energy of QDs to the acceptors as much as possible [15,16]. Although there have been a lot of investigations about the impact factors for FRET efficiency, most of the donors and acceptors are both organic molecules or inorganic QDs. Besides, even with other kinds of acceptors, for example gold NPs, the composite nanostructure is in solution [17,18], which is not suitable for solid state photoelectronic conversion applications. So in order to apply the gold NPs/QDs systems very effectively in photovoltaic devices and photodetectors, we should further understand the energy transfer mechanism in solid state QDs and metallic nanostructure film composite systems.

Current available method for the fabrication of metallic nanostructure films include electron-beam lithography [19], which can completely control the formation and shape of the

nanostructures for the design of metallic films with unique LSPR spectra but are too expensive for larger scale practical applications. Mask-assisted deposition [20] and nanoimprintation [21] are also useful in the construction of regular nanostructure arrays using metallic strips or nanospheres, but it is difficult to create elemental components with a gap distance of a few nanometers as occurs in aggregates. A completely different inexpensive, mask-less method consists of the self-assembly of colloidal particles to produce large-area metallic films was also adopted in our previous studies. However, self-assembled metallic films are usually fabricated by using surface-modified substrates after complex modification processes [22].

In this work, we experimentally present the energy transfer between three plasmonic samples of different sized Au NPs with shifted plasmonic resonance random gold nanoparticles (Au-NPs), created by a simple rapid thermal annealing(RTA) process, and a spin-coating colloidal CdSe/ZnS QDs. The influence of the Au NPs size on the energy transfer between CdSe/ZnS and the gold NPs is carefully investigated. The effect of the separation layer between CdSe/ZnS QDs and the gold NPs on the energy transfer efficiency is also discussed.

2. Experiment

2.1 sample fabrication

Quartz slides ($15 \times 15 \text{ mm}^2$) were rinsed with acetone, ethanol, and deionized water, in an ultrasonic bath for 15 min and dried under a nitrogen stream. Gold was evaporated from a tungsten boat at around $7.0 \times 10^{-4} \text{ Pa}$ in a high vacuum thermal evaporator. Three samples

are chosen and grouped into S1, S2 and S3, and the thickness of the samples are 3 nm, 6 nm, 9 nm, respectively. Thermal treatment of the ultrathin gold film coated on quartz substrates was carried out in air by laying samples in a muffle furnace at 400 ° C for one hour and retracted to cool down in air to room temperature before any measurements.

CdSe/ZnS QDs were prepared by a single-step synthesis with chemical composition gradients method [23], dispersed in toluene (10mg/mL, the quantum yield is 85%), and then spin-coated on the quartz substrates with the designed Au NPs films. As a reference, the same CdSe/ZnS QDs are spin-coated on a bare quartz substrate. In order to investigate the influences of the spacing between CdSe/ZnS QDs and Au NPs on the substrate, CdSe/ZnS QDs is dispersed in PMMA solution (WM:350,00, wt : 0.3%) and then also spin-coated on the quartz substrates with different sized Au NPs and reference quartz substrate (See Fig.1). The TEM picture of the QDs is shown in Fig.1c, the absorption and PL spectra of the CdSe/ZnS QDs is shown in the Fig.1d. It is very important to note that we dropped the same amount of CdSe/ZnS QDs solution on each sample. The CdSe/ZnS QDs are homogeneously distributed onto all the samples.

2.2 Morphology and spectra characterization

In our experiments, scan electron microscope (SEM, Quanta 200 FEI) and atom force microscope (AFM,) is employed to characterize the gold NPs, Shimadzu UV-3600 spectrophotometer is used to detect the absorption spectra of the samples. The photoluminescence intensity spectra and time resolved photoluminescence spectra (TRPL) of the grouped samples are measured with the fluorescence spectrophotometer (Edinburgh Instruments, FLS 920).

Fig. 1. (a) The schematic of QDs dispersed in PMMA coated on the Au NP films. (b) The schematic of QDs directly dispersed on the Au NP films. (c) The TEM image of CdSe/ZnS QDs. (d) Normalized PL spectra (red line, the emission peak is located at 585nm) and absorption spectra (black line) of the CdSe/ZnS QDs dispersed in toluene.

3 Results and discussion

3.1 Morphology properties and optical absorption of Au NPs film

Fig. 2. SEM images of different sized Au NPs films (a) S1(26.1 ± 6.3 nm), (b) S2(40.5 ± 18.0 nm), (c) S3(71.6 ± 45.2 nm), AFM images of the Au NPs of (c)S1, (d)S2, (e)S3 samples as well as their depth profile(below)

Ultrathin island film prior to thermal treatment displays an irregular and complex shape formed during the high vacuum evaporation process in which the gold NPs are nucleated and coalesced on the quartz substrate to form a partially connected island film. Upon the thermal treatment, the island film experienced a drastic shape change varying with the heating temperature. The drastic shape change is caused by the thermal dewetting-induced morphological instability of the ultrathin gold film deposited on the nonwetted quartz substrate, as driven by the surface diffusion to reduce the surface area in order to minimize the total energy of the system. Fig.2 shows the SEM images and AFM images of the ultrathin gold film after RTA. Well dispersed Au NPs were obtained after the RTA process, with the size, the root mean square (RMS) roughness and the average height increased with the original thickness of the Au layer. The size of the Au NPs is increased from 26.1 ± 6.3 nm for

S1 to and 40.5 ± 18.0 nm for S2 and 71.6 ± 45.2 nm for S3. The RMS roughness is increased from 3.05 nm for S1 to 16.1 nm for S3 and the average height is also increased from 11.5 nm for S1 to 55.4 nm for S3, as shown at the lowest of Fig.2. Therefore, RTA process is a convenient method to obtain different sized metallic NPs by controlling the original film thickness, annealing time and temperature.

Fig. 3. Absorption spectra of the grouped samples before (a) and (b) after the rapid thermal annealing.

Fig.3 shows the absorption spectra of the grouped sample before (Fig.3a) and after (Fig.3b) the rapid thermal annealing. From comparison of the spectra of the as-deposited and annealed samples, we can find that the annealed structures have qualitatively different shapes and lower absorbance. Both phenomena point at structural changes due to annealing. Besides, the absorption peak of annealed samples shifts from 560 nm to 650 nm with the increase of the size of Au NPs. The full width at half maximum (FWHM) of the absorption peaks also increases with the size of the particles, suggesting the size distribution of Au NPs increase with the film thickness, which can be demonstrated by the SEM images in Fig. 1.

3.2. Fluorescence emission of QD/Au NP composite

Fig. 4. (a) The PL intensity spectra of CdSe/ZnS QDs without/with different sized Au NPs. (b) The relationship among PL spectrum of CdSe/ZnS QDs, absorption spectra of different sized Au NPs films.

Fig. 4(a) shows the PL intensity spectra of CdSe/ZnS QDs without/with different sized Au NPs film. The fluorescence peaks are all located at the wavelength of 600 nm, which has a little red-shift compare with the CdSe/ZnS QDs in solution(585nm in Fig.1(d)) and maybe caused by the different dielectric environment. The PL intensity of QDs with Au NPs film is much smaller than that of the QDs on bare quartz, which means CdSe/ZnS QDs transfer partial absorbed energy to the Au NPs and cause the quenching. The PL intensity of the QDs on the different sized Au NPs are totally different and strongly depend on the Au NPs size. Specifically, the PL intensity of CdSe/ZnS QDs coupled with the samples (S1,S2,S3) is about 0.1, 0.06 and 0.17 of that of CdSe/ZnS QDs on bare quartz, respectively. As mentioned above, the quenching is related to the energy transfer from the CdSe/ZnS QDs to the Au NPs. To explore the energy transfer mechanism, the PL intensity spectra of bare CdSe/ZnS QDs and the absorption spectra of different sized Au NPs are shown in Fig.4(b). The absorption peak of sample S2 is just at the wavelength of 600 nm, where the peak of the PL intensity locates.

In this case, CdSe/ZnS QDs are directly contacted with the Au NPs, and we assume the spacing between the CdSe/ZnS QDs and three Au NPs films are nearly the same, so the spectra overlap between the PL spectra and the absorption spectra of Au NPs film is the main factor that influences the energy transfer efficiency between the CdSe/ZnS QDs and Au NPs films .

Fig.5. (a) The PL intensity spectra of CdSe/ZnS QDs diluted in PMMA solution without/with different sized Au NPs. (b) The relationship among PL spectrum of CdSe/ZnS QDs, absorption spectra of different sized Au NPs films with PMMA.

The spacing between the optical emitter and MNP is another important factor that controls the plasmonic interaction and consequently the fluorescence emission. In order to qualitatively investigate the influences of the spacing between the CdSe/ZnS QDs and Au NPs, we disperse CdSe/ZnS QDs in PMMA solution, and then spin-coat the materials on the quartz substrate with different sized Au NPs. In this case, there is PMMA spacer between CdSe/ZnS QDs and Au NPs films. Fig.5(a) shows the PL spectra of CdSe/ZnS QDs diluted in

PMMA solution without/with different sized Au NPs. Here, the quenching effect is obviously smaller than that of samples without PMMA, which means that the spacing distance have a big influence on the energy transfer efficiency. In this case, the PL intensity of CdSe/ZnS QDs with different sized Au NPs (S1,S2,S3) is about 0.75, 0.67 and 0.62 of that of bare CdSe/ZnS QDs on the quartz substrate. The PL emission spectrum of bare CdSe/ZnS QDs and the absorption spectra of Au NPs films are shown in Fig.5(b). Because of the PMMA barrier, the absorption peaks of all the samples shift to the large wavelength, compared with the spectra shown in Fig.4. Besides, contrary to the Fig.4, here the smallest PL intensity is not obtained for CdSe/ZnS QDs deposited on sample S1, of which the absorption peak is nearest to the PL emission peak of the QDs.

Generally, the PL spectra of QDs coupled with metallic nanostructures have two trends including enhancement and quenching. They compete with each other and the total PL intensity of QDs is determined by the dominant. The enhancement is believed to be related to two mechanisms [24]. Firstly, if the wavelength of the excitation light is near to the localized surface plasmon resonance (LSPR) of metallic nanostructures, the strong localized electric field near the metallic nanostructures can incredibly enhance the absorption of the incident light, which can lead to a considerable increase of the absorption rate and the excitation rate of QDs(excitation enhancement). Secondly, if the emission wavelength of QDs is near to the LSPR wavelength, it will generate another effect, in this case, the PL enhancement is normally attributed to the enhancement of the local density of optical state, which is the key factor to determine the emission rate of QDs [25]. And the closer the plasmon resonance wavelength to the emission wavelength, the higher the PL enhancement. The radiative rate in

the QDs is significantly enhanced by the LSPR coupling of the metal NPs, which can be called as emission enhancement. The quenching is mainly caused by the energy transfer from the QDs to the metallic NPs, and the spacing and spectra overlap between the donor (CdSe/ZnS QDs here) and the acceptor (Au NPs here) is very important to the transfer efficiency.

When the original CdSe/ZnS QDs are spin-coated on the Au NPs films and directly contacted with the metallic NPs, energy transfer plays the dominant role in this nanostructure, and most of the energy of the excited CdSe/ZnS QDs transfer to the Au NPs. So, the PL intensity of CdSe/ZnS QDs with Au NPs is smaller than that of the referenced bare CdSe/ZnS QDs on the quartz substrate. Besides, as shown in Fig.4 (b), the absorption peak of the Au NPs film in the sample S2 is the nearest to the emission peak of CdSe/ZnS QDs, so the largest energy efficiency is got, which is in agreement with the conclusion that the largest energy transfer happened when the spectra overlap between the absorption spectra of Au NPs and the emission spectra of CdSe/ZnS QDs is the largest. So the CdSe/ZnS QDs with the Au NPs film in the sample S2 have the smallest PL intensity, while the CdSe/ZnS QDs with Au NPs film in the sample S3 have the largest PL intensity. Except the energy transfer from the CdSe/ZnS QDs to Au NPs, direct electron transfer (DET) from the CdSe/ZnS QDs to the Au NPs can also quench the fluorescence here [26]. But by observing the spectra, it is hard to prove whether the direct electron transfer mechanism is exist or not.

When CdSe/ZnS QDs is dispersed in the PMMA solution and then spin-coated on the Au NP films, there is one insulating layer between the Au NPs and the CdSe/ZnS QDs. According to SEM measurement, the thickness of PMMA is about 37.5 nm, due to the QDs is

dispersed uniformly in the PMMA film, the average distance between the QDs and the Au NPs is assumed to be about 19 nm. So the DET mechanism is excluded for the fluorescence quenching, and the only quenching mechanism is energy transfer. According to the FRET equation, due to the space between the Au NPs and CdSe/ZnS QDs is larger than that in the direct contact situation, the energy transfer efficiency of CdSe/ZnS QDs is weakened by the PMMA and only part of the energy of the excited CdSe/ZnS QDs transferred to the Au NPs. Besides, the enhancement caused by LSPR of Au NPs begins to have a bigger role in the fluorescence process, but the quenching effect is still dominant. So the PL intensity of CdSe/ZnS QDs with Au NPs is still smaller than that of the referenced CdSe/ZnS QDs, but energy transfer efficiency is smaller. Besides, the enhancement factors of different sized Au NPs are different. Because the resonant wavelength of the Au NPs films in the three samples is larger than the excited wavelength (375nm), it does not satisfy the first condition of enhancement mentioned above (absorption enhancement). Thus we attribute the different PL intensity enhancement to the second condition (emission enhancement). The largest PL intensity happened when the CdSe/ZnS QDs coupled with the Au NPs sample S1, whose absorption peak is nearest to the emission peak of CdSe/ZnS QDs as shown in Fig.5(b).

3.3 Fluorescence decay lifetime measurements

The main signatures of non-radiative energy transfer in a system are decreases in the lifetime and the PL emission of the donor species. To further understand the energy transfer between the CdSe/ZnS QDs and the Au NPs, the lifetime of the QDs is therefore measured in a QD layer on the silica substrate (QDs only) and in the presence of different sized Au NPs. In the TRPL measurements, all the samples were excited with a 375 nm pulsed laser and

emitted photons were collected in the region from 595 to 605 nm. PL decays of these samples are shown in Figure 6a and 6b for the directed(without PMMA) and indirected (with PMMA) conditions, respectively. For both conditions there is a decrease in the QD lifetime in the presence of the Au NPs. This more obvious for the without PMMA condition in Fig.6a

Fig.6 TRPL spectra of (a)CdSe/ZnS QDs direct contact with the different sized Au NPs(without PMMA) and (b)CdSe/ZnS QDs indirect contact with the different sized Au NPs. The inset table shown fluorescence lifetime decay parameters (lifetimes^a, fractions, average lifetime^b,and energy transfer efficiency(ET)) for CdSe/ZnS QDs/Au NPs composite in directly(without PMMA) and indirectly contact condition(with PMMA). ^aIntensity decay equation: $I(t)=A_1\exp(-t/\tau_1)+A_2\exp(-t/\tau_2)$. the decay parameter τ_1 , τ_2 , A_1 and A_2 are the lifetimes and their corresponding amplitudes, ^baverage decay lifetime: $\tau_{av}=(A_1\tau_1+ A_2\tau_2)/(A_1+A_2)$,

In general, emission quenching and decay lifetime shortening are the main evidence for the occurrence of non-radiative energy transfer in the optical emitter. Our observations support these two characteristics in the CdSe/ZnS QDs/Au NPs composites. The emission lifetime measurement support the existence of distinctive states for CdSe/ZnS QDs/Au NPs

composites shown and summarized in Fig.6. As the CdSe/ZnS QDs contacted with the Au NPs, a subset of excited state CdSe/ZnS QDs transfer the excited energy to the Au NPs through non-radiative relaxation. The double exponential decay lifetime profile confirms two distinctive subsets of similar CdSe/ZnS QDs, corresponding to the fast and to the slow decay components, τ_1 and τ_2 , respectively. The slow component corresponds to radiative decay of the CdSe/ZnS QDs while the fast component corresponds to those CdSe/ZnS QDs that transfer their excited energy non-radiatively to Au NPs.

The energy transfer efficiency from CdSe/ZnS QDs to Au NPs is given by

$$E_D = 1 - \frac{\tau_{QD-Au}}{\tau_{QD}} \quad (1)$$

Where τ_{QD} is defined as the average lifetime of bare CdSe/ZnS QDs and τ_{QD-Au} is defined as the average lifetime of the CdSe/ZnS QDs-Au NPs composite. From the table in the inset of Fig.6, we can find that the energy transfer efficiency in the direct contact condition(without PMMA) is larger than that of indirect contact condition(with PMMA), which is according with the PL intensity measurement in Fig.4 and Fig.5

Besides, the PL lifetime of the CdSe/ZnS QDs is closely related with the Au NPs sizes. In the indirect contact condition(Fig.6b), it is interesting to find that the strongest reduction in fluorescence lifetime of the sample S3 is not where the maximum fluorescence intensity (S1) is observed. It indicates that the observed lifetime decay is not only caused by the increase of the radiative decay rate, but also the contribution of the increase in the non-radiative decay rate. As we known that only the increase of radiative decay rate can contribute to the fluorescence enhancement, so the reduction of fluorescence lifetime is a complex process here. Both the enhanced radiative decay and the non-radiative decay contribute to the

decreased fluorescence lifetime.

4. Conclusion

In conclusion, various sized Au NPs films are fabricated via the post-annealing. The PL intensity and energy transfer of CdSe/ZnS QDs direct and indirect contact with the different sized Au NPs is investigated. We find that the energy transfer efficiency (from QDs to Au NPs) is not only dependent on the overlap between the absorption spectra of Au NPs and the emission spectra of CdSe/ZnS QDs, but also dependent on the distance between them. When the QDs direct contact with the Au NPs, the largest energy transfer happened when the absorption peak of Au NPs is match with the emission peak of CdSe/ZnS QDs. But when there is PMMA separation layer between the CdSe/ZnS QDs and Au NPs, the energy transfer efficiency is totally smaller than that of direct contact condition, and the smallest energy transfer happened when the absorption peak of Au NPs is match with the emission peak of CdSe/ZnS QDs. So in the practical condition, in order to improve the energy transfer efficiency in the optoelectric devices, we should design the device structure reasonable and take the particle size and the distance between the QDs and NPs into consideration.

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