Plasmon Induced Fluorescence Quenching of CdSe-CdS/ZnS Quantum Dot

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Abstract

Gold nanoparticles (AuNR) are known as efficient quenchers for semiconductor quantum dots (QD). The mechanism behind this phenomenon is still in debate. Usually people attribute it to energy transfer between excited quantum dots and metal particles but there is divergence in the energy transfer mechanism in reports. In this project, we investigated the quenching behavior of gold nanorod on high concentrated colloidal CdSe-CdS/ZnS multishell quantum dots. An excitation dependent quenching efficiency and a redshift in QDs fluorescence spectrum after injecting AuNR were observed, suggesting the existence of other static effect, e.g. stark effect, besides energy transfer. By studying the fluorescence lifetime change, we confirm the energy transfer between AuNR and QD along with the influence of a plasmon induced electric field.
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Chapter 1

Introduction

1.1 Overview

Thanks to the booming development in nanotechnology, nanoparticles with dimensions between atomic scale and bulk have attracted considerable interest in the past few decades. These nano-objects usually show different properties with their bulk material, for instance, the optical properties of nano-objects depend on their chemical structure, size shape and local environment. Depending on the synthesis methods, nanoparticles with different size and shape with tunable optical properties can be obtained. There are plenty of research papers investigating the physical properties of nanoparticles and their response to surrounding environment, which pave the way for scientific and technological applications of nanoparticles. For example, the efficiency of solar cells can be improved by depositing silver nanoparticles because of their strong scattering properties originating from surface plasmons [1]. Semiconductor nanocrystals providing much more photostable signal than organic molecules under similar conditions can serve as good microscopic single-photon sources [2–5]. Functionalized gold nanoparticles (AuNPs) are considered to be excellent tools for optical sensing and imaging, because their surface plasmon dependent optical properties are very sensitive to changes in the local environment [6–9]. Besides, gold nanoparticles can be utilized in drug delivery and targeted labelling since they are chemical stable, biocompatible and less toxic than some other alternatives, for instance quantum dots [10, 12–14, 65]. With the improvement of characterization and synthesis techniques on the nanometer scale, the number of research on nanoparticle is increasing rapidly every year, driving the application potential of nanoparticles in everyday life. Nanoparticles, no doubt, is an area of great promise and
1.2 Optical properties of nanoparticles

The definition of nanoparticles originates from their sizes, usually range from one to several hundred nanometers. In addition to size, there is a variety in particle shape. Besides common types as nanosphere and nanorod, particles with specific shapes like tetrahedron [15], decahedron [16], bipyramid [17] are synthesized and reported. Furthermore, the composition of nanoparticles is also playing an important role in tuning their optical properties. Some typical materials are semiconductor, metal, graphene and so on. In this thesis, experiments based on gold nanorods (AuNR) and cadmium selenide (CdSe) quantum dots (QD) are performed and discussed.

1.2.1 Quantum dot

Colloidal semiconductor quantum dots have attained extensive popularity due to their remarkable optical properties including narrow and size-tunable emission band, broad absorption band ranging from UV to visible wavelength, and controllable surface modification. Their unique optical properties are attributed to quantum confinement of electrons and holes at nanometer scales [18]. The size of QD is usually manufactured to be smaller than the average physical distance of conduction electrons and valence holes (excitons), known as Exciton Bohr Radius, leading to a strong quantum confinement [19]. Smaller quantum dot possess larger band gap between the conduction band and valence band. Thus, the emission peak blue shifts as the size of QDs decrease, and vice versa, offering a size-dependent color, as shown in Figure 1.1.

CdSe quantum dots, because of their tunable photoluminescence (PL) distributing throughout the visible region of spectrum, are widely applied in scientific researches, especially in biology [20]. To improve the luminescence efficiency and colloidal stability of the particles, core-shell nanostructure is often applied in QD fabrication. This core-shell system not only helps to prevent surface trap states and protects the core, but also provide extra pathway for the electron-hole recombination [21, 22]. In the case of CdSe nanocrystals, CdS [22] and ZnS [34] are popular choices to establish a core-shell system because they possess a higher band gap than the core material (CdSe), giving rise to a confinement of the photogenerated electrons and holes inside the CdSe, resulting in a photoluminescence
1.2 Optical properties of nanoparticles

![Figure 1.1: size-dependent QDs photoluminescence observed under UV light](image)

Figure 1.1: size-dependent QDs photoluminescence observed under UV light

Quantum yield as high as 50-80% [22, 34, 35].

In most fabrication protocols, QDs are synthesized in organic solution and coated with hydrophobic organic ligands, e.g., ODA for our QDs, making them insoluble in water. In order to render semiconductor quantum dots more bio-compatible for biological and medical applications, it is critical to alter the QDs to be dispersible in aqueous solution. One of the most preferred approaches is to exchange the hydrophobic surfactant molecules with bifunctional molecules which are hydrophilic on one end with anchoring group on the other end to bind to the QDs surface. Commonly used ligand molecules include thiol (-SH) groups which bind strongly to the inorganic surface of QDs, replacing the weaker bound ligands coming from the nanoparticle synthesis process. At the same time, carboxyl (-COOH) group is a popular choice as the hydrophilic end because it can easily bind to multiple bio-molecules such as antibody, DNA [36–38]. In this project, 3-Mercaptopropionic acid (3-MPA) was utilized as the surface ligands of CdSe-Cds/ZnS core-multishell QDs, giving rise to negatively charged QDs.

1.2.2 Gold nanorod

Gold nanoparticles have been widely used for application in scientific research due to their unique optical properties. The electromagnetic resonance of the conduction electrons on the surface of gold nanoparticles, known as surface plasmon resonance, is one of the most fascinating properties of gold nanoparticles. The resonance happens when the frequency of photons matches the oscillation of surface electrons charged by electric field of the excitation. This feature results in a strong interaction with light, making gold nanoparticles very efficient absorbers and scatterers of light.

In order to utilize rational synthesis of gold nanoparticles for specific applications, great effort has been spent on investigating their optical prop-
properties depending on morphology, size and shape.

Nanosphere and nanorod are two common gold nanoparticle shapes used as a sensor in scientific research [39]. Compared with gold nanosphere, nanorod tends to have better sensing capability. The asymmetry of gold nanorod leads to an additional plasmon resonance, known as the longitudinal surface plasmon resonance. The wavelength of this resonance depends on the aspect ratio of gold nanorods and the corresponding change in the refractive index in the close environment. As shown in Figure 1.2, the extinction spectrum of nanorods exhibits dual peak while there is only one for nanospheres. The two peaks observed in the extinction spectrum of gold nanorods represent transverse and longitudinal surface plasmon resonances which are due to collective oscillation of conduction electrons along the short and along the long axis of the nanorod, respectively. The plasmon resonance observed at short wavelength in the extinction spectrum of gold nanorods consists of a contribution from transverse mode of plasmon resonance of gold nanorods and of the resonance of residual gold nanospheres. While the longitudinal surface plasmon resonance observed at long wavelength is the unique characteristic of the gold nanorods. It’s interesting that the longitudinal plasmon resonance can be tuned from visible (600nm) to near-infrared (850nm) by changing the aspect ratio of the nanorod from 2 to 4 [40, 41]. Furthermore, the optical signal depends on the relative orientation of the particle with respect to the polarization of the excitation light beam. When the nanorod is aligned parallel
1.3 Quantum dot-gold nanoparticle complex system

to the polarization of the excitation light, only the longitudinal absorption band is excited. When the nanorod is aligned perpendicular to the excitation polarization, only the weak transverse mode is excited [43]. This tunable and polarization dependent optical properties of individual gold nanorods make them good candidates as optical probes for optical imaging and sensing purposes [42].

Beside absorption and scattering, gold nanorods also exhibit fascinating photoluminescence property. Although there have been considerable efforts spent on investigating the PL in gold nanorods, its origin and mechanism are still in debate. Some explained the luminescence by the radiative recombination of electron-hole pairs, the process of which is very inefficient in metal (gold in this case), but can be greatly enhanced by local fields associated with the particle plasmon resonance [44–46]. While in some other studies, the luminescence from small gold nanoparticles was attributed to the radiative decay of the surface plasmon [47–50]. However, the mechanism of PL in gold nanorods remains an open question worthwhile to figure out.

1.3 Quantum dot-gold nanoparticle complex system

Gold nanoparticle based fluorescence quenching of luminescent semiconductor quantum dots and its applications have been studied in many groups [23–25, 51–53]. However, the mechanism behind this efficient quenching is still a subject of much recent debate.

In the early work by Nikoobakht et al. [23] who studied the quenching behavior of gold nanosphere and nanorod in CdSe quantum dots solution, the authors attributed the quenching mechanism to electron transfer between QDs and AuNPs and they excluded the possibility of energy transfer because of the observed decrease in quenching efficiency while the overlap between the emission of the donor and the absorption of the acceptor increased. However, Li [25] observed an opposite relation in the quenching efficiency and spectral overlap when studying CdSe-ZnS QDs and AuNRs complex and the efficiency followed inverse fourth power to their separation distance, indicating a dipole-surface energy transfer (SET) process. One may argue that the core-shell structure that confines the electrons in the core due to the large band offset between core and shell in the latter case could be an explanation for the diametrically opposite result, but how strong is the restriction of electrons in the QDs core-shell structure
under the prominently enhanced electric field raised by the longitudinal plasmon resonance remains a question mark. According to Gueroui et al. [52] who observed and analyzed CdSe-ZnS quantum dot and gold cluster pairs at single molecule scale, the quenching behavior obeys Förster resonance energy transfer (FRET) law, described by function $1 / [1 + (R/R_0)^6]$, where $R$ is the separation distance and $R_0$ is the Förster distance of this pair of donor and acceptor, the distance at which the energy transfer efficiency is 50%. On the other hand, in some ensemble measurements [53], it was found that small sized gold nanoparticles (3nm) which did not process strong plasmon resonance absorption quenched the QDs emission via SET mechanism, while larger particles followed FRET rule. Nevertheless, there are also some literature excluding FRET to be the mechanism of fluorescence quenching between QDs and AuNPs [24, 51].

In the project, we investigated the CTAB coated gold nanorod or plasmon induced fluorescence quenching behavior on 3-MPA coated CdSe-Cds/ZnS core-multishell QDs and explored the application potential of QD-AuNR complex as biosensors.
Chapter 2

Materials and Methods

2.1 Synthesis and characterization of nanoparticles

2.1.1 Quantum dot

The growing research interest in semiconductor quantum dot accelerates its synthesis technology, resulting in a variety of synthesis routes. Generally, these methods can be categorized either as a top-down or bottom-up approach [54].

Basically, top-down method is a process of decreasing the dimensions of bulk semiconductor. Some commonly used approaches are electron beam lithography, reactive-ion etching [55], and focused ion beam techniques [56]. In the approaches of bottom-up, the fabrication of QDs relays on self-assembly of nanostructures, with careful control of parameters for reaction solutions. By varying synthesis factors, such as temperature, stabilizers, concentration of precursors, QDs of different size, shape and composition can be achieved. Some popular methods are sol-gel process [57], microemulsion [58], and hot-solution decomposition [59, 60] which provides sufficient energy to anneal defects and generates mono-dispersed QDs.

In this project, our colloidal core-shell QDs are synthesized following the successive ion layer adhesion and reaction (SILAR) technique described in literature [61, 62] with a little modification. The synthesis process is composed of three steps: preparation of precursors, fabrication of CdSe core and coating CdSe core with shells. More specifically, five precursor were prepared in the first process by dissolving the chemicals at
Materials and Methods

Table 2.1: Chemicals and their amounts involved in the preparation of precursors. Components were mixed and stirred in a 50 mL three-neck flask, evacuated at a temperature lower than the dissolving point for several minutes, then filled with nitrogen and evacuated again. This process was repeated three times to eliminate the oxygen in the flask before dissolution. After that, the temperature was increased to the dissolving temperature and kept stirring until all the solids melted. (CdO: cadmium oxide; OA: oleic acid; ODE: 1-octadecene; ZnO: zinc oxide; S: sulfur; Se: selenium; TOP: trioctylphosphine)

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Components</th>
<th>Dissolving temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>CdO (71.2 mg); OA (1.37 g); ODE (4 mL)</td>
<td>240°C</td>
</tr>
<tr>
<td>Zn</td>
<td>ZnO (45.2 mg); OA (1.37 g); ODE (4 mL)</td>
<td>310°C</td>
</tr>
<tr>
<td>S</td>
<td>S (25.6 mg); ODE (8 mL)</td>
<td>100°C</td>
</tr>
<tr>
<td>CdZn</td>
<td>ZnO (22.6 mg); CdO (35.6 mg); OA (1.37 g); ODE (4 mL)</td>
<td>300°C</td>
</tr>
<tr>
<td>Se</td>
<td>Se (48 mg); TOP (1 mL)</td>
<td>100°C</td>
</tr>
</tbody>
</table>

 high temperature under constant nitrogen flow. The amount of chemicals and dissolving temperature in each precursor are listed in table 2.1. After dissolution, all the precursors were sealed with nitrogen in glass bottles and ready for use.

To synthesize CdSe core, mixture of 13 mg CdO, 56 mg tetradecylphosphonic acid (TDPA), 0.35 g octadecylamine (ODA) and 0.65 g trioctylphosphine oxide (TOPO) were evacuated at 100°C for 30 minutes, then heated to 330°C under constant nitrogen flow to form an optically clear solution. After that, the temperature was decreased to 270°C and 1 mL Se-precursor was injected into the reaction solution. The temperature of the growth solution was kept at 270°C and the duration of heating time after the injection determined the size of synthesized CdSe core. Longer time would give rise to larger quantum dots having longer emission wavelength. After reaching the desired QD size, the flask was moved away from the hot plate and cooled down to 100°C. Afterwards, 20 mL acetone was added to the solution, leading to a precipitation of QDs. Centrifugation and de-
cantation were carried out with chloroform and acetone three times to remove residual precursors and the particles were sealed in tubes filled with nitrogen to avoid oxidation.

The core-shell structure of QDs was achieved by the following procedure: 1 g ODA and 4 mL ODE were loaded into a three-neck flask, heated to 100°C and evacuated for 30 min to eliminate the impurities. The CdSe QDs synthesized as mentioned before were dissolved in chloroform and injected into the reaction solution. After 30 min of heating at 100°C under vacuum, the chloroform and other undesired materials at low vapor pressure were removed. In the next step, the mixture was heated to and kept at 230°C under constant nitrogen flow for coating the CdSe core with multiple shells. Precursors were added into the reaction mixture gradually to allow the growth of shells layer by layer. The time interval for the growth of each layer is about 8 min and the amount and order of precursors are as following: Cd-: 0.2 mL, S-: 0.3 mL, Cd-: 0.4 mL, S-: 0.4 mL, CdZn-: 0.5 mL, S-: 0.5 mL, CdZn-: 0.6 mL, S-: 0.6 mL, Zn-: 0.7 mL, S-: 0.7 mL, Zn-:0.8 mL. After all the addition of shells, the temperature was adjusted to 260°C and kept for 30 min before stop the heat supply. The obtained core-shell QDs should be CdSe-core, CdS/CdS/Zn0.5Cd0.5S/ZnS/Zn from the inside out. Finally, the QDs was washed in the same way as to the cores. The resultant QDs are QDA-coated and oil soluble that can be dissolved in chloroform.

To make the QDs dispersed in water for bio-related applications, ligands exchange was performed by adding identical volume of a water solution containing 3-MPA in chloroform dissolved QDs. After vigorous stirring for 2 hours and resting for a while, it was visible that QDs moved from bottom (chloroform) to the upper (water) layer, indicating a successful exchange process. Then QDs coated with 3-MPA was extracted and washed with centrifugation and decantation. A 0.1 M NaOH solution was added to obtain a clear solution which was washed with acetone to remove residual 3-MPA. The resultant QDs are carboxyl-coated, negatively charged and dissolvable in water.

To characterize the synthesized colloidal quantum dots, UV-vis extinction spectra were acquired on a Hitachi U1900 spectrophotometer and photoluminescence spectra were measured using a FluoroMax-3 spectrofluorometer. This UV-vis and PL-spectra of the core-shell nanocrystals are shown in Figure 2.1(a). The QDs fluorescence peaks at 592 nm with a linewidth of 32 nm and the broad tail observed to the red of the main peak is due to the radiative emission from deep trap states on the surface of QDs. TEM image of CdSe cores and CdSe-CdS/ZnS core-multishell quantum dots are presented in Figure 2.1(b) and (c). The sizes of quantum dots before and after coating with shells are 3.6 nm and 5.6 nm, respectively.
Figure 2.1: (a) UV-Vis extinction (red line) and emission (black line) spectra of QDs in water; Transmission electron microscopy image of (b) CdSe quantum dot cores and (c) 3-MPA coated CdSe-CdS/ZnS core-multishell quantum dots. The scale bar is 10 nm. We made statistic of 50 particles and the size of the core is 3.61452 ± 0.10211 nm and for the multishell quantum dots is 5.60405 ± 0.22718 nm, indicating a shell thickness of 2 nm.

The molar concentration of synthesized QDs was estimated by Lambert-Beer’s Law:

\[ A = \varepsilon CL \]  

where \( A \) is the absorbance of the solution at the first exciton wavelength \( \lambda \) (nm), \( \varepsilon \) is extinction coefficient of a single quantum dot. \( C \) is the molar concentration (mol/L or M) of QDs, \( L \) is the path length (cm) of the radiation beam used for recording the absorption spectrum (It’s usually 1 cm for a standard cuvette). The extinction coefficient was calculated according to Peng et al.[72]:

\[ \varepsilon = 5857(D)^{2.65} \]  

where \( D \) is the quantum dot’s diameter which can be obtained either from TEM image directly or with the fitting function from literature [72]:

\[
D = (1.6122 \times 10^{-9})\lambda^4 - (2.6575 \times 10^{-6})\lambda^3 + (1.6242 \times 10^{-3})\lambda^2 - (0.4277)\lambda + (41.57)
\]  

For our quantum dots having an absorption peak at 574 nm, the calculated diameter is 3.632241 nm which is close to what was observed from TEM.
image, suggesting that the approximation is reliable. Besides, compared to TEM, absorption measurements are readily accessible and inexpensive. One can easily predict the concentration of QDs solution using Eq. (2.1) with the help of an UV-vis spectrophotometer.

2.1.2 Gold nanorod

To date, there are various kinds of techniques reported in literature to synthesize gold nanorod, for instance, lithographic methods [33], template methods [28], electrochemical methods [29], and seed-mediated growth methods [30–32] which currently, are the most popular approaches due to their low cost, simplicity of the procedure, high quality and yield of nanorods, flexibility for particle shape and size control, and multiple choices for surface modification and etc.

In general, the seed-mediated growth method is a two-step wet-chemical process, starting with seeds production which is so well-controlled that a fairly mono-disperse population of particles with more or less the same shape and size, usually several nanometers, are fabricated. In the second step, proper amount of seeds are injected into a growth solution containing surfactants to stabilize the size and shape of the large grown particles, and catalysts favoring the growth of particular facets of the crystals. Temperature and pH value of the growth solution can also switch the growth towards different size and shape.

In this project, gold nanorods were synthesized by the seed-mediated growth method investigated by Murphy’s group [32] with a slight modification to increase the quantity. Typically, gold seeds solution were prepared by mixing 0.25 mL of 10 mM gold chloride trihydrate (HAuCl$_4$) with 7.5 mL of 0.1 M of cetyltrimethylammonium bromide (CTAB) in a small flask. Then, 0.6 mL of freshly prepared ice-cold sodium borohydride (NaBH$_4$) solution was injected quickly into the mixture solution. The solution turned into brownish yellow color and was kept under vigorous stirring for 2 min, and left for 2 hours before use. After that, the growth solution was prepared by adding 0.8 mL of 10 mM HAuCl$_4$ and 0.12 mL of 10 mM silver nitrate (AgNO$_3$) into 19 mL of 0.1 M CTAB solution, followed by addition of 0.128 mL of 0.1 M ascorbic acid with rapid inversion until the color of the solution change from orange to transparent. Finally, 0.02 mL seed solution was added to the growth solution, left undisturbed in 30°C water bath for 6 h to get a clear reddish-purple final solution. To achieve AuNRs with different aspect ratio, a simple way is to adjust the amount of AgNO$_3$ or seed, giving rise to solution with different color.
Materials and Methods

After the synthesis, AuNRs solution was centrifuged at 14500 rpm for 15 min to remove the excess reagents in the supernatant and resuspended in Milli-Q water. The process was repeated again at the same speed and time before use.

2.2 Fluorescence spectrum measurement

Fluorescence spectra of the QD solutions were measured by an optical spectrometer (FluoroMax-3, Horiba Jobin Yvon) which follows a classical configuration with a Xenon arc lamp, excitation and emission monochromators before and after the sample, a photomultiplier (PMT) for detection and a reference photodiode. Different excitation wavelength was achieved by tuning the optical gratings of the monochrometers which diffract incident light, dispersing it into constituent wavelength component. During the QD-AuNR interaction experiments, since the temporal responses of the QD fluorescence to the injection depend on the amount of the injected AuNRs, we repeatedly measured the fluorescence spectrum after the injection at a time interval of 5 min until the dynamic and static interactions between QDs and AuNRs get stable.

2.3 Fluorescence lifetime measurement

QD fluorescence lifetime was measured by using a time-correlated single-photon counting machine (FluoroMax-3, Horiba Jobin Yvon). QDs were excited by 342nm and 495 nm pulsed diode laser and the detector was set at 592 nm (QD fluorescence peak wavelength) with a bandpass of 2 nm. The peak was preset at 2000 counts. The signal was recorded by DataStation v2.3 software (Horiba Jobin Yvon).

Before lifetime measurements, QDs fluorescence spectra were recorded repeatedly to ensure a stable fluorescence signal, indicating a complete interaction between QDs and AuNRs. And the data can also be used to study the effect of AuNRs on QDs fluorescence intensity and lifetime.
Chapter 3

Results and Discussions

3.1 Scattering and absorption property of AuNR-QD complex

The detector of fluorescence spectrometer collects all the light information at a 90° angle relative to the excitation (as shown in the inset of Figure 3.1(b)), which means that besides the fluorescence, scattering information of the sample is also recorded.

Figure 3.1(a) shows the fluorescence spectrum of 300nM quantum dot solution under 460nm excitation, measured by fluorescence spectrometer. Since the QDs used in experiments exhibit fluorescence centered around 592nm with a linewidth of 32nm, a sharp narrow peak corresponding to the Rayleigh scattering of quantum dots at 90° could be distinguished easily at the excitation wavelength. The intensity mainly depends on the concentration and size-dependent absorption property of quantum dot. In the case of gold nanorods, the fluorescence from AuNRs solution is too weak to be detected by the spectrometer, which means that the single peak in the spectrum shown in Figure 3.1(b) emerges from the Rayleigh scattering of AuNRs.

The change of the integral scattering intensity with the incident light wavelength ($\lambda$) and absorption spectra are plotted in Figure 3.2(a)(b). The Rayleigh scattering intensity of QDs was observed to be coincident with their absorption curve, with a distinct peak around 574nm, corresponding to the first exciton peak (Figure 3.2(a)). In the case of AuNR, due to the large optical field created by the surface plasmon resonance, both the absorption and scattering behaviors were enhanced over a special spectral range, as shown in Figure 3.2(b). The Rayleigh scattering intensity...
Results and Discussions

Figure 3.1: Emission spectra of (a) quantum dots solution and (b) gold nanorods solution, excited at 460nm. The Rayleigh scattering peak can be easily recognized at 460nm. The inset in (b) is a schematic representation of a typical fluorescence spectrometer.

increased much more rapidly when the wavelength of incident beam falls into the longitudinal plasmon band, compared to the transverse plasmon band, indicating that the splendid scattering enhancement property of AuNR mainly results from the longitudinal plasmon resonance which can be tuned from visible to near infrared by modifying the aspect ratio of nanorods. The experiment result agrees well with calculation of AuNR in water (Figure 3.2(c)). The simulation was calculated with discrete dipole approximation (DDA), assuming the shape of AuNR to be a cylinder with spherical end-caps embedded in water (n=1.33) having the same dimensions with the AuNR used in the experiment. The incident light was set to be circular polarized to simulate the arbitrary orientation of AuNRs in solution.

Gold nanoparticle is known as an efficient fluorescence quencher to semiconductor quantum dot [23–25], which will be discussed in the next section. It’s also interesting to investigate the Rayleigh scattering change after QDs solution is mixed with AuNRs solution. Figure 3.2(a) presents the scattering intensity change with the excitation wavelength. The scattering was slightly enhanced when the excitation wavelength run through the transverse plasmon band and a dramatic elevation was obtained as soon as the wavelength was close to the longitudinal plasmon band. When the wavelength was much less than the absorption band of the AuNR, a decrease similar to pure QD and AuNR solution in the scattering signal of the mixed solution was observed. The scattering intensity of the mixture with spectral range from 350nm to 480nm was extracted, together with pure QD solution and pure AuNR solution, and normalized to investigate the decrease gradients, as shown in Figure 3.2(b). Three sets of experimental data overlap well when the excitation wavelength is less than
3.1 Scattering and absorption property of AuNR-QD complex

Figure 3.2: (a) Emission spectrum of quantum dot solution excited at 460nm. The Rayleigh scattering peak can be easily recognized at 460nm; Integrated scattering intensity (black square line) of (b) 30nM QD solution and (c) 150pM AuNR solution as a function of the incident light wavelength. The absorption spectra (red line) are measured with different concentration to match the capacity of the UV-Vis spectrometer. (d) Calculated scattering and absorption spectra of AuNRs in water with discrete dipole approximation (DDA) method.
transverse absorption band, indicating a linear scattering enhancement by AuNR. However, the enhancement was no longer linear when the wavelength fell into the absorption band of AuNR, as shown in Figure 3.2(c), where black squares stand for the sum of the scattering intensity of pure 30nM QD solution and 150pM AuNR solution and red dots represent the experiment data with the same concentration of nanoparticles in the solution. The mixture solution showed less scattering intensity than the accumulating sum when the wavelength was close to the longitudinal plasmon band. This can be explained by the spectra shown in Figure 3.2(d), in which the longitudinal plasmon resonance is red-shifted and broadened, and the absorption is also decreased when AuNR solution is mixed with QD solution, resulting the observed change in the scattering enhancement. This can be attributed to the formation of aggregated AuNRs, where negatively charged QDs act as bridges between positively charged AuNRs.

Red shift indicates the formation of end-to-end binding between AuNRs [26]. However, less shift and lower absorption is obtained with higher QD concentration (Figure 3.3(a)). A plausible mechanism is the difference in the coverage of QDs at the surface of AuNRs. In the case of low QD concentration, only small amount of the AuNR surface is covered with negatively charged QD and the rest part is still positively charged. As a result, when binding with second AuNR, the bodies of the two AuNRs tend to repulse each other due to the coulomb force created by the positive charges from CTAB bilayer at rods’ surface, as shown in the cartoon of Figure 3.3(b). Increasing QD concentration will increase the coverage of QDs on the AuNR surface. However, the same charges of QDs prevent the occurrence of dense coverage of QDs. In other words, bound QDs are separated with a certain distance from each other, creating an electrostatic competition between empty sites (positive charge from CTAB) and QDs occupied sites (negative charge from QDs). There will be less repulsive coulomb force between two binding rods because of the increasing number of QDs involved, resulting in a smaller included angle (Figure 3.3(c)), which explains the observation of less red-shift in the case of high QD concentration. Interestingly, with small AuNRs, both red-shift (end-to-end) and blue-shift (side-to-side) can occur randomly (Figure 3.3(d)(e)). A possible explanation for these two adverse types of assembly could be the lack of surface area due to the small size of AuNR. Thus, very few QDs can attach to the AuNRs surface and may create an electrically neutral area around AuNR. As a result, the binding between AuNRs is weak and random. Adding more QDs will increase the aggregation rate, resulting in the further red-shift or blue-shift with increasing QD concentration.

Precipitates were observed in some of the high concentrated QD-AuNR
3.1 Scattering and absorption property of AuNR-QD complex

Figure 3.3: (a) Integrated scattering intensity of 30nM QD and 150pM AuNR mixed solution as a function of the incident light wavelength. (b) Normalized scattering intensity of QD (black square), AuNR (red dot) and mixed solution (blue triangle) with a spectral range from 350nm to 480nm. (c) Sum of the scattering intensity of pure 30nM QD solution and 150pM AuNR solution (black square) and experiment scattering intensity of 30nM QD and 150pM AuNR mixed solution as a function of the incident light wavelength (red dot). (d) Absorption spectra of 150pM AuNR solution (black line) and 30nM QD and 150pM AuNR (red line).
Figure 3.4: (a)(d)(e) Absorption spectra of 150nM AuNR (black line) solution and same amount of AuNR mix with different concentration of QD. The arrow indicates the direction of increasing QD concentration, 30nM (red line), 100nM (blue line), 500nM (magenta line), 1500nM (green line), respectively in (a). (d) and (e) are measured with small AuNR. (b)(c) Graphical representation of AuNRs binding in the case of low and high QD concentration.
3.2 Effect of AuNR on the fluorescence intensity of quantum dot

Fluorescence spectra of pure QD and QD-AuNR mixture solution are plotted in Figure 3.5, where the ratio between QD and AuNR is increased from 1000 to 250, much higher than previous reports [23, 25]. Since the binding between nanoparticles is time-dependent, spectra were taken every five minutes until the fluorescence peak intensity got stable and the data shown in the figure correspond to the last measurements. 64% of QD photoluminescence intensity was quenched by adding 150pM AuNR, where the QD/AuNR ratio is about 1000. In previous study on AuNPs induced fluorescence quenching of quantum dots, this quenching effect was mostly attributed to energy transfer (ET), which is sensitive to the separation between nanoparticles. The efficiency, as aforementioned, decreases very rapidly as inverse fourth power of the separated distance in case of SET and inverse sixth power for FRET. Therefore, considering the large ratio between QD and AuNR in our experiments, most QDs should locate outside the range where SET can take place effectively.

Given the fact that most QDs were distributed larger than a wavelength away from AuNRs, the nonspecific absorption of the emitted light, known as the inner filter effect, should be taken into account before describing the steady states fluorescence quenching [64]. This effect can be estimated by

\[
\eta = \frac{A_0(1 - 10^{-A_i})}{A_i(1 - 10^{-A_0})}
\]

where \(\eta\) is the correction factor for the inner filter effect, \(A_0\) and \(A_i\) are the absorbance of QD and QD-AuNR mixture solution at the emission wavelength, respectively. The emission intensity after this nonspecific absorption should be \(\eta_i \times I_0\), where \(I_0\) and \(\eta_i\) are the QDs emission intensity in the absence of quencher and correction factors of different mixture solution. In the case shown in Figure 3.5, the calculated correction factors for the QDs solution mixed with different concentration of AuNRs are pre-
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Figure 3.5: Photoluminescence spectra collected from 150nM QD mixed with increasing concentration of AuNR. The excitation wavelength was 490nm. The inset shows normalized fluorescence spectra of 150 nM QD solution (black line) and 150 nM QD mixed with 600 pM AuNR solution (green line).
3.2 Effect of AuNR on the fluorescence intensity of quantum dot

<table>
<thead>
<tr>
<th>AuNR (pM)</th>
<th>$\eta_i$</th>
<th>$1 - I_i/(\eta_i \times I_0)$</th>
<th>$\eta_i \times I_0/I_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>0.8603</td>
<td>0.5752</td>
<td>2.35398</td>
</tr>
<tr>
<td>300</td>
<td>0.7200</td>
<td>0.8611</td>
<td>7.19892</td>
</tr>
<tr>
<td>450</td>
<td>0.6366</td>
<td>0.9150</td>
<td>11.76515</td>
</tr>
<tr>
<td>600</td>
<td>0.5949</td>
<td>0.9552</td>
<td>22.29524</td>
</tr>
</tbody>
</table>

Table 3.1: Correction factors $\eta$ for the QDs solution after mixed with different concentration of AuNRs, quenching efficiency $(1 - I_i/(\eta_i \times I_0))$ and intensity ratio $(\eta_i \times I_0/I_i)$ modified with inner filter effect.

Presented in table 3.1, along with the quenching efficiency considering the inner filter effect $(1 - I_i/(\eta_i \times I_0))$, where $I_i$ is the detected emission intensity of the mixture). With the increasing amount of the quencher injected in QDs solution, the correction factor decreased, or in other words, the QDs emission absorbed by AuNRs increased from 14% to 40%, revealing that inner filter effect certainly accounts for a considerable part of the total quenching. The quenching efficiency after modifying with inner filter effect was raised from 55.5% to 94.8%, which means that beside the absorption of QDs fluorescence from the quencher at far field, QDs in the vicinity of AuNR are also quenched dramatically.

In general, the quenching process after the nonspecific absorption can be quantified by Stern-Volmer equation [63]:

$$I_0/I = (1 + K_Q [AuNR])$$  \hspace{1cm} (3.2)

where $I$ is the QDs fluorescence intensities after the injection of the quencher (AuNRs), and $K_Q$ is the Stern-Volmer quenching constant. In our case, due to the fact that our QDs and AuNRs are oppositely charged, definitely there will be the formation of nonfluorescent ground-state complex between the QD and quencher. Thus, we attribute the PL quenching to both dynamic (collisional) and static process. Hence, we have

$$I_0/I = (1 + K_D [AuNR])(1 + K_S [AuNR])$$  \hspace{1cm} (3.3)

where $K_S$ is the association constant for binding of QD-AuNR pairs and $K_D$ is the dynamic quenching constant, which can be expressed by the product of the diffusion-controlled bimolecular rate constant ($k_0$) and the life time of the QD in the absence of quencher ($\tau_0$) [63]:

$$K_D = k_0 \tau_0$$  \hspace{1cm} (3.4)
Using the Smoluchowski equation, the constant can be calculated as:

$$k_0 = \frac{4\pi N_A}{1000} (R_f + R_q)(D_f + D_q)$$  \hspace{1cm} (3.5)

where $N_A$ is Avogadro’s number, $R_f$ and $R_q$ are the molecular radii of the fluorescent molecule (QD) and quencher (AuNR), $D_f$ and $D_q$ are their diffusion coefficients respectively. The radius of QD can be estimated directly from TEM image and for AuNR, we used “effective radius”, the radius of a sphere of equal volume of a nanorod. To simplify our model, we only considered translational diffusion coefficients which can be obtained from Stokes-Einstein equation:

$$D = \frac{k_B T}{6\pi \mu R}$$  \hspace{1cm} (3.6)

where $k_B$ is Boltzmann’s constant, $T$ is the absolute temperature, $\mu$ is the viscosity of the solution (for water at 20°C, $\mu = 1.002 \times 10^{-3} \text{Ns/m}^2$), and $R$ is the radius of the molecule. Combining QDs lifetime ($\tau_0 = 20.86 \pm 0.17\text{ns}$) measurements (see next section) and our calculation, $K_D$ is predicted to be $0.238\text{M}^{-1}$, which compared to the large intensity ratio $\eta_i \times I_0/I_i$ (table 3.1), is so small that can be neglected, indicating that most of the quenching results from static processes via the formation of QD-AuNR pairs or some non-contact pathways. As a result, however, after plotting intensity ratio as a function of the concentration of the quencher (Figure 3.6(a)), known as Stern-Volmer plot, we found that the curve was not linear as expected from equation 3.3 (the dynamic term was neglected). Thus, we performed another control experiment with less concentration and interval as shown in Figure 3.6(b). It’s important to note that when the concentration of the quencher was low (less than 100 pM), the intensity ratio $I_0/I_i$ increased linearly while with the increasing injection of AuNR, the curve lost linearity and boosted dramatically, revealing the presence of additional quenching factors besides static quenching, which can not be explained by our Stern-Volmer model. This will be further discussed in the next section.

As mention in Section 1.3, electron transfer [23] and energy transfer [53] are reported to be the two main mechanisms to explain QD-AuNR quenching systems. In our case, electron transfer is not likely because of the thick coating shells and layers of nanoparticles (for QDs, the thickness of multishells and ligands is estimated to be around 2 nm [62], and the thickness of CTAB bilayer covered around AuNR is about 3nm [65]). These thick layers induce a high barrier for electron transfer [66], confining electron-hole
3.2 Effect of AuNR on the fluorescence intensity of quantum dot

![Figure 3.6: Intensity ratio $\eta_i \times I_0 / I_i$ as a function of AuNR concentration (a) in the case shown in Figure 3.5 and (b) another experiment with less AuNR concentration interval.](image)

Pairs and their recombination inside CdSe core. And the electron tunneling probability decays exponentially with distance, preventing the occurrence of electron transfer. While for energy transfer, regardless of FRET or SET mechanism, is still efficient at a distance around 10 nm, suggesting that energy transfer could be a reasonable way to explain the quenching process. There are plenty of studies investigating the distance-dependent energy transfer efficiency by conjugating AuNP and QD with molecules of various size (e.g. DNA [25, 52, 53], $PEG_m$ [51], $YEHK_m$ [24]). However, in these literature, either SET or FRET mechanism was reported and usually the other mechanism was excluded by the authors. This divergence in similar experiments alludes the presence of other factors that may affect the fluorescence quenching process of QDs by AuNPs. We investigated the excitation wavelength dependence on the fluorescence quenching of QDs induced by AuNRs and propose that the strong external electric field created by adjacent plasmons could be a possible explanation.

Quenching efficiencies as a function of the excitation wavelength in different solution are illustrated in Figure 3.7, along with the absorption spectrum of AuNR. It is conclusive that these quenching efficiencies follow the trend of the absorption of AuNR with a distinct slope at transverse plasmon band, which insinuates that the excitation of plasmon amplifies the quenching efficiency. At resonance, the coherent oscillation of
Figure 3.7: Quenching efficiency of different QD-AuNR solution versus excitation light wavelength (red square line) and AuNR absorption spectrum (black line)
3.2 Effect of AuNR on the fluorescence intensity of quantum dot

Figure 3.8: Schematic representation of band gap tilting in a QD after applying an external field E (right). Electrons at conduction band (CB) shift to lower energy states and holes in valence band (VB) shift to high energy states, resulting a reduction in band gap and redshift in PL wavelength.

free electron at the surface of the AuNR induced by the electric field of incident light can be identified as an oscillating electric dipole, giving rise to a dipole-like electric field around the nanorod [67]. The QDs near an excited AuNR undergo the so called quantum-confined Stark effect [68]. The external electric field pulls the electrons and holes towards opposite sides of the quantum dot, shifting the electron occupying conduction-band ground state to lower energy, while the hole at valence-band ground state to higher energy [69], giving rise to a decrease in the electron-hole wave function overlap. As a result, the radiative recombination rate, which is proportional the overlap between the two ground states, drops when the excitation wavelength falls into the plasmon band of AuNR, engendering a reduction in fluorescence intensity, which explains the observed slope at the transverse plasmon band. Furthermore, a slight redshift (3nm) in the QDs emission wavelength was detected (as shown in the inset of Figure 3.5), which corresponds to the decline in the band gap between conduction band and valence band of QD (Figure 3.8). These observations are coincident with recent theoretical study by Niculescu [70] who studied the Stark effect on CdSe-ZnS core shell quantum dot and experimental study on a single CdSe/ZnSe quantum dot [71].

Note that the change in the quenching efficiency is larger and more noticeable in case of high QD/AuNR ratio. More specifically, this disparity is reduced from 0.04252 to 0.01168 while the concentration of AuNRs injected in QDs solution varies from 150 pM \( (QD : AuNR = 1000 : 1) \) to 600 pM \( (QD : AuNR = 250 : 1) \). We attribute this loss to the escalation of QDs within the effective range of energy transfer, where ET is dominant.
in the quenching process. Hence, although stark effect kept modifying PL intensity, less variation in the quenching efficiency was observed with excitation wavelength within and outside the plasmon band of AuNRs when more AuNRs were injected in the QDs solution.

3.3 Effect of AuNR on the fluorescence lifetime

The effect of AuNR on the fluorescence lifetime was also studied, as shown in Figure 3.9(a)(b) and their fluorescence lifetime characterizations are presented in Figure 3.9(c)(d). Fitting of the fluorescence decay curves by a single exponential decay did not converge. Thus, we tried to fit with

$$ y = y_0 + A_1 \exp \left( -\frac{t-t_0}{\tau_1} \right) + A_2 \exp \left( -\frac{t-t_0}{\tau_2} \right) $$

which dovetails well with all the fluorescence decay curves. The lifetime fitting results are presented in Figure 3.9(c)(d) including statistical standard errors. Two processes can be discriminated, including a slow one with an initial lifetime $\tau_1 = 17.96411 \pm 0.12301$ ns (342 nm) and $\tau_1 = 17.50764 \pm 0.11874$ ns (495 nm), and the other fast one with $\tau_2 = 3.57685 \pm 0.0458$ ns (342 nm) and $\tau_2 = 3.34823 \pm 0.05058$ ns (495 nm). There is no significant difference between the results obtained with two pulsed diode laser (342 nm and 495 nm which is within the transverse absorption band of AuNR), even after the injection of quencher, which implies that the excitation of plasmon does not alter the fluorescence lifetime of QDs. The slight disparity that the fluorescence lifetime measured with 342 nm excitation was a little bit larger than that with 495 nm excitation results from the fact that after the absorption of a photon with higher energy, it will take more time for the system to relax to the ground state.

Dramatic decrease in QD excited-state lifetime upon injection of AuNRs was observed, suggesting the presence of an additional non-radiative pathway, energy transfer in this case. However, this drop tends to saturate after the addition of certain amount of AuNRs. As delineated in Figure 3.9(a)(b), the curves after mixing 150 nM QDs solution with 300 pM AuNRs exhibit similar decay behavior (blue, magenta, green lines), while the fluorescence intensity kept decreasing (Figure 3.5). On the basis of this observation, we can firmly conclude that after the injection of 300 pM AuNRs, most of the QDs were located within the effective range of energy transfer with AuNR, in other words, further injection of the quencher will not have too much influence on the non-radiative decay rate of QDs. This is
3.3 Effect of AuNR on the fluorescence lifetime

Figure 3.9: (a)(b) Fluorescence decays of QDs with different AuNRs concentration under (a) 342nm and (b) 492nm excitation. (c)(d) Fluorescence lifetime parameters $\tau_1$ and $\tau_2$ as a function of AuNRs concentration, obtained by fitting fluorescence decay data with Eq. (3.7)
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Figure 3.10: \( \tau \) and slope of \( \sqrt{1/f(t)} \) under (a) 342 nm and (b) 495 nm excitation.

coincident with previous analysis on the loss of disparity in the quenching efficiency within and outside the plasmon band of AuNRs when large amount of AuNRs were injected in the QDs solution. As a result, we attribute the further quenching behavior of concentrated QD-AuNR complex solution to the strong scattering property of AuNR, as discussed in Section 3.1. Besides, the growing particle number increases the probability of multiple scattering which also contributes to the loss of detected fluorescence intensity. These effects can even be recognized by eyes: the color of the solution turned into dark purple after the injection of 300 pM AuNR.

To have a better understanding of the quenching process, we introduce another way to analyze the QD fluorescence decay in terms of the energy relaxation and radiative combination of the photoexcited exciton in the QD. Briefly, fluorescence decay spectrum is shown to be characterized by an exponential decay directly after the photoexcitation (characterized by \( \tau \)), which represents the energy relaxation of the photo-generated exciton from its initial high-energy state to the ground exciton state. Fluorescence decay spectrum of long time is in the form of \( \beta / t^2 \), where \( \beta \) is the radiative recombination time of the ground-state exciton and \( t \) is the decay time. In other words, after plotting \( \sqrt{1/f(t)} \), a linear relation in \( t \) should be obtained at long time fluorescence range, where \( f(t) \) is the measured time-resolved fluorescence spectrum as a function of decay time. Figure 3.10 presents the results after fitting the fluorescence lifetime spectra with our method: \( \tau \) was obtained by fitting the short-term decay curves with single
exponential decay within photon counts $\in (1800,800)$, corresponds to 90% - 40% of total counts. While the slope was obtained from $\sqrt{1/f(t)}$ in a time window of 60-100 ns. It’s evident that under two different excitation, both $\tau$ decreased when the AuNR concentration was increased. Whereas there is a discrepancy in the slope trend: the slope under 495 nm excitation tended to decrease with the increase of AuNR concentration, while the other seems to be stable. Note that the slope of QD sample with 600 pM AuNR was abnormal because of measurement errors marked by vertical arrows in the inset of Figure 3.10(a).

The physical mechanism behind Figure 3.10 is explicit and unequivocal. The QD at the vicinity of an AuNR undergoes energy transfer process as a donor. The introduction of this additional non-radiative energy relaxation pathway results in a shorter $\tau$ and it does not affect the radiative recombination of the exciton. However, when plasmon is excited, the generated dipole-like electric field increases the spatial separation between the electron and the hole, giving rise to a reduction in the radiative combination of the exciton and the overlap between the wave functions of the states occupied by the electron and the hole, resulting in an increased $\beta$ (note that $\beta$ is inversely proportional to the square of the slope in Figure 3.10).

3.4 Conclusion

To conclude, in this master research project, AuNR induced fluorescence quenching of CdSe-CdS/ZnS multishell Quantum Dot was investigated. Our experiments were carried out in the condition of high QD/AuNR ratio ranging from 250 to 1000, resulting in the formation of large QD-AuNR conjugation. To explain the quenching process, we took into account the inner filter effect at far field and static quenching at near field. An excitation dependent quenching efficiency was observed and attributed to Stark effect induced by the electric field created by excited AuNRs, which could be a possible explanation for the divergence of FRET and SET mechanism in previous reports. From fluorescence lifetime measurements, we confirmed that energy transfer between QD and AuNR induces an additional QD PL nonradiative pathway and the further quenching in concentrated sample is due to the scattering of QD emission. These results could help to understand the mechanism of plasmon-induced fluorescence quenching of semiconductor QDs and pave the way for applying them in sensor and imaging applications.
References


References


