

Energy Transfer from CdSe/ZnS Nanocrystals to Tetraphenyl Porphyrin

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Abstract. CdSe/ZnS nanocrystals (NCs) and Tetraphenyl Porphyrin (TPP) are mixed uniformly to prepare CdSe/ZnS NCs/TPP complex. TPP can quench the fluorescent signal of CdSe/ZnS NCs. UV-Vis absorption spectra and fluorescence spectra are employed to analysis the energy transfer. The mechanism of energy transfer is the F rster resonance energy transfer from CdSe/ZnS to TPP.

1. Introduction

Photodynamic therapy is known as a potential modality dealing with tumor and other diseases by utilizing photosensitizers, which can be preferentially localized in the malignant tissues. Compared with conventional therapeutic technique, photodynamic therapy is a fast, direct, and nearly noninvasive technique [1, 2]. These features make it the focus of the laser-medical research scope. Porphyrins and their derivatives are typical photosensitizers for the photodynamic therapy with high singlet oxygen quantum yields and preferential accumulation in tumor and therefore have been studied with great interest [3–6]. However, the small two-photon action cross section limits their application in photodynamic therapy. This problem can be solved by using semiconductor nanocrystals (NCs) as an energy donor to indirectly activate the porphyrin sensitizers. NCs possess not only large two-photon action cross section but also high fluorescence quantum yields, superior photo and chemical stability, broad excitation spectra and narrow luminescence spectra, which make them perfect energy donors compared with traditional organic dyes for biomedical application [2]. QD-based energy transfer has been proved to be a valuable tool for the study of fluoroimmunoassay [7], biomacromolecular interaction [8], biosensor [9, 10], and PDT [11].

In this work, CdSe NCs are used as energy donors to activate tetraphenyl porphyrin (TPP). Shi et al. has shown that CdTe-Porphyrin nanocomposites can provide a singlet oxygen quantum yield of 0.43, which is sufficiently high for PDT application [12]. They have proved the existence of energy transfer in this sample system by using of traditional steady state fluorescence spectra. Our work justifies that this model system can also perform effective activation of photosensitizers. Moreover, we utilize the relative fluorescence intensity comparison method to investigate the role of the excitonic and trapping states of NCs, respectively, in the energy transfer process trying to find a way of improving the energy transfer efficiency and, consequently, increasing the singlet oxygen quantum yield for PDT application. Considering the complexity of the energy transfer mechanism in liquid condition, combination of absorption and fluorescence spectroscopy used in this study can also distinguish radiative and nonradiative energy transfer quantitatively.

2. Experimental procedures

2.1. Reagents and chemicals



Selenium, cadmium oxide, Zinc acetate, technical grade 1-octadecene (ODE), bis(trimethylsilyl) sulfide, hexadecylamine (HDA, 90%), trioctylphosphine oxide (TOPO, 90%), and trioctylphosphine (TOP, 90%) were purchased from Sigma-Aldrich. Technical grade stearic acid, TPP, toluene, acetone, hexane, and methanol were obtained from National Drug Group Chemical Company Ltd.

2.2. Synthesis procedure of CdSe/ZnS NCs and CdSe/ZnS NCs/TPP complex

CdSe/ZnS NCs were prepared according to the previous method [13, 14]. A stock cadmium stearate solution was prepared by heating a mixture of 0.228g of stearic acid, 0.0256 g of cadmium oxide and ODE in a 50 ml three-neck flask to 200 °C under stirring and continuously flowing of nitrogen until a clear solution was obtained. After this solution was cooled to room temperature, HDA and TOPO were added into the flask with the molar ratio of 4:1. Under nitrogen flow, the mixture was reheated to 280°C. At this temperature, a selenium solution (prepared by dissolving 0.158 g Se powder into the TOP and ODE mixture under ultrasonic conditions) was quickly injected. The temperature was reduced to 240 °C within several minutes for core growth. After the reaction was completed, the reaction flask was removed from the heating mantle and allowed to cool to 40 °C. The reaction mixture was extracted by the hexane/methanol system to purify the NCs (remained in the hexane/ODE layer) from side products and un-reacted precursors (remained in the methanol layer). Then, the hexane system was extracted. The acetone was added to precipitate the NCs. The NCs precipitate was collected by centrifugation and re-dissolved in hexane or chloroform. The amounts of Zn and S precursors (Zinc acetate and bis(trimethylsilyl) sulphide) needed to grow a ZnS shell of desired thickness for CdSe NCs were determined. The reaction flask containing CdSe NCs dispersed in TOPO and TOP was heated to 200 °C under an atmosphere of N₂. When the desired temperature was reached, the Zn and S precursors were added dropwise to the vigorously stirring reaction mixture over a period of 5–10 minutes. By systematically changing the nuclei temperature and growth time, it was possible to finely tune the size of the CdSe/ZnS NCs. The CdSe/ZnS NCs and TPP were mixed and stirred thirty minutes in hexane on magnetic stirring apparatus. Then, the CdSe/ZnS NCs-TPP complex is synthesized.

2.3. Apparatus

UV-Vis absorption spectra were recorded with an UV-Vis 3101 spectrometer having a resolution of 1.0 nm. Photoluminescence experiment was conducted on a Hitachi F-4500 fluorescence spectrometer with collection resolution of 2.5 nm. The excitation wavelength of 375nm was selected.

3. Results and discussions

3.1. CdSe/ZnS NCs-TPP complex's synthesis

At present, the oil phase synthesis for NCs is a relatively mature technical method. But the precursor like TOPO is expensive. As a result, we used ODE instead of TOPO as solvent for the synthesis of CdSe/ZnS NCs. A small amount of TOPO was used as surface ligand to stabilize NCs, so the cost of synthesis was greatly reduced. The reaction speed of pure TOPO (99.9%) is fast than technical grade TOPO (90%), thus it is difficult to control the growth of NCs. So the technical grade TOPO (90%) was added. We can control the growth of CdSe NCs through the adjustment of different proportion between HDA and TOPO. The mole ratio of HDA verse TOPO is 4:1 in this experiment [13, 15].

The different amount of TPP were respectively mixed with CdSe/ZnS NCs, and stirred well through the magnetic stirring apparatus for thirty minutes. Then the CdSe/ZnS NCs/TPP complex was prepared. The key problem of the directly mixed methods is how to disperse NCs homogeneously. Usually, the mixes of different materials cause serious phase separation and lead to gather, destroy the original performance. But, in this experiment we find that the dispersion between NCs and TPP is homogeneous.

3.2. Absorption and fluorescence properties

The absorption spectrum of CdSe/ZnS NCs is shown in Fig. 1. The first exciton absorption peak is 510 nm of CdSe/ZnS NCs. There is an obvious first exciton absorption peak, which indicates that the size distribution of CdSe/ZnS NCs is more uniform. The surface state absorption in the area of 575nm-650nm is weak because the surface of the CdSe NCs can be coated with the ZnS shell to reduce the surface defects. The fluorescence spectrum of CdSe/ZnS NCs is shown in Fig. 2. The fluorescence peak of CdSe/ZnS NCs is 530nm.

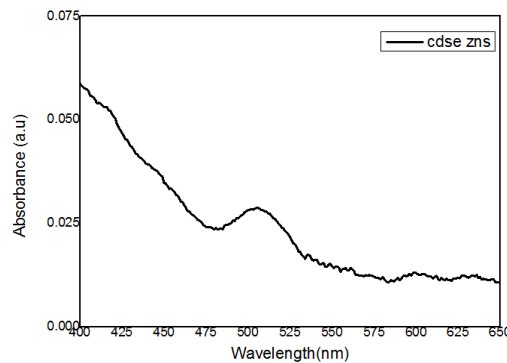


Fig. 1. CdSe/ZnS NCs absorption spectrum.

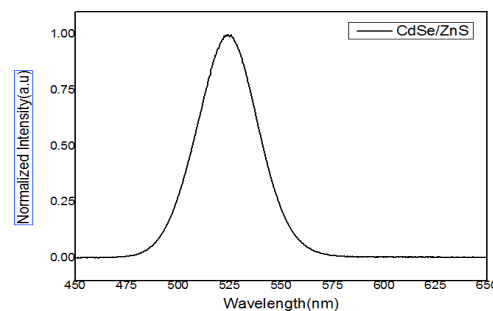


Fig. 2. CdSe/ZnS NCs normalized fluorescence spectrum.

Fig. 3 is the absorption spectrum of TPP (300 nm-750 nm). It can be seen from the diagram that the absorption of TPP covers a wide range of wavelengths in the UV-visible region. There is a strong absorption peak near 400nm which is called the Soret band. In addition, there is a weak absorption peak near 519nm, 549nm, 590nm and 650nm which is called the Q band. According to the electron absorption spectrum model of porphyrin compounds, it is believed that the Soret absorption band is produced by the transition of $a_{1\mu}(\pi) \rightarrow e_g(\pi^*)$, and the Q band is produced by the transition of $a_{2\mu}(\pi) \rightarrow e_g(\pi^*)$. It is difficult to detect the fluorescence of porphyrin from Soret band because the strong absorption of Soret band leads to reabsorption and light scattering.

The fluorescence spectrum of TPP is shown in Fig. 4. Two fluorescence peaks can be seen. The fluorescence emission in 650nm is accompanied by the transition of the lowest vibrational level of the single state to the lowest ground state. The fluorescence emission of 718nm is associated with the transition of the lowest vibrational level of the single state to the higher vibrational level of ground state. The fluorescence intensity of 650 nm is the largest, so the fluorescence band of Q band at 654nm is taken as the research object in the energy transfer between CdSe/ZnS NCs and TPP.

It can be seen by comparing the Fig. 2 and Fig. 3 that the fluorescence emission spectra of CdSe/ZnS NCs intersected with the absorption peaks of the TPP Q band. It satisfies the basic conditions of the Förster resonance energy transfer.

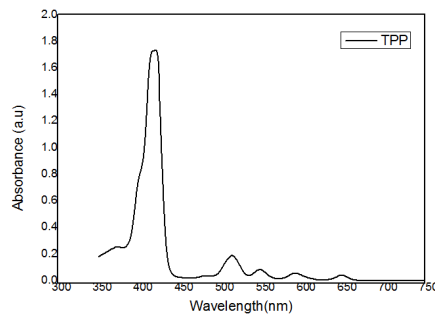


Fig. 3. TPP absorption spectrum.

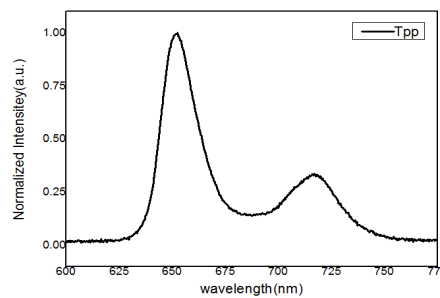


Fig. 4. TPP normalized fluorescence spectrum.

In order to investigate the energy transfer characteristics of different receptor/donor concentration ratio, the different amount of TPP was respectively mixed with the same amount of CdSe/ZnS NCs. The fluorescence spectra of the CdSe/ZnS NCs/TPP complex with different TPP concentrations are shown in Fig.5. The curve B is the fluorescence spectrum of CdSe/ZnS NCs and it can be seen that there is a fluorescence peak at 530nm.

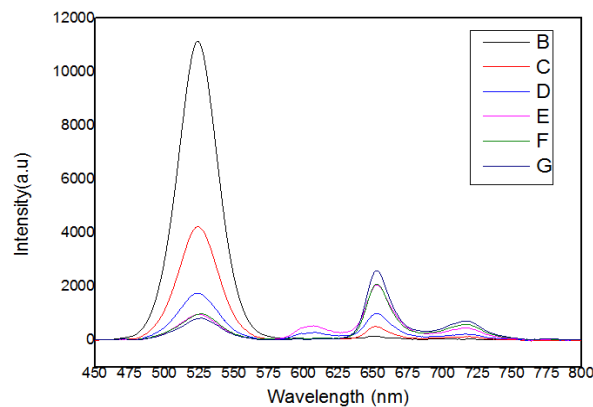


Fig. 5. Fluorescence spectra of CdSe/ZnS NCs-TPP composite system. B, CdSe/ZnS NCs. C, D, E, F and G for CdSe/ZnS NCs/TPP complex with different TPP concentration. C, 1×10^{-6} mol/L; D, 1×10^{-5} mol/L; E, 1×10^{-4} mol/L; F, 2×10^{-4} mol/L; G, 3×10^{-4} mol/L.

The curves of C, D, E, F and G are the fluorescence spectra for CdSe/ZnS NCs/TPP complex with different TPP concentration. (C, 1×10^{-6} mol/L; D, 1×10^{-5} mol/L; E, 1×10^{-4} mol/L; F, 2×10^{-4} mol/L; G, 3×10^{-4} mol/L). It can be observed that there are fluorescence peaks at 530nm, 650nm and 718nm. The fluorescence intensity of CdSe/ZnS NCs at 530nm decreases gradually with the increase of the concentration of TPP in the CdSe/ZnS NCs/TPP complex. Through the analysis of the changes in the relative fluorescence intensity between the receptor (650nm) and the donor (530nm) it is found that the excited state energy of CdSe/ZnS NCs is transferred to TPP.

3.3. The mechanism of fluorescence quench

The fluorescence intensity of CdSe/ZnS NCs reduces sharply after adding TPP. The possible physical mechanisms of fluorescence quench are listed: (1) forming new radiation center or non-radiation center. The probability can be excluded because CdSe/ZnS NCs fluorescence emission peak position is not changed almost, and new fluorescence peak does not appear after adding TPP. (2) Excitation competition leads to the decrease of excitation density. This mechanism can also be excluded because the excitation wavelength is 375 nm. The absorption cross section for CdSe/ZnS NCs is larger than TPP. (3) Energy transfer. The donor (CdSe/ZnS NCs) in the excitation state transfer energy to the receptor (TPP) and it go back to ground state. The energy transfer mechanism of fluorescence quench is possible. (4) Charge transfer. That is excited state charge transfers between CdSe/ZnS NCs and TPP leading to the interruption of radiative recombination. This mechanism also can be ruled out because TPP is a poor conductor of electricity [16].

According to the different energy transfer environment of the donor and receptor, the kinds of energy transfer mechanism have: Förster resonance mechanism and exchange electronic mechanism. The rate index of energy transfer for electronic exchange mechanism decreases with the increase of the distance between donor and receptor (R). When R is larger than 0.1nm, the rate of energy transfer caused by electronic exchange mechanism can be omitted compared to other inactivation process. The distance between CdSe/ZnS NCs and Tpp is far over 0.1 nm in solution. So the main energy transfer mechanism is the Förster resonance mechanism on the composite system of CdSe/ZnS NCs and TPP.

4. Conclusions

The complex of CdSe/ZnS NCs and TPP are synthesized and analyzed the energy transfer from CdSe/ZnS NCs to TPP. TPP can quench the fluorescent signal of CdSe/ZnS NCs. The fluorescent intensity of CdSe/ZnS NCs/TPP complex is related to the concentration of TPP. The fluorescence quench mechanism is the Förster resonance energy transfer from CdSe/ZnS NCs to TPP.

Acknowledgements

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