Fluorescence Quenching Of Aqueous Solution Of Fluorescein Dye Dispersed With ZnS Nanoparticles

Mathew M. Mecheril, J. Philip

Abstract: Semiconductor nanoparticles exhibit excellent optical properties such as broad excitation spectra, size tunable emission peaks and long fluorescence life-times, which make them attractive for optical as well as optoelectronic applications. Semiconductor nanoparticles act as acceptors as well as donors in energy transfer processes in semiconductor nanoparticle-organic dye hybrid systems. They also function as effective quenchers for fluorescence emission in organic dyes. Metal and semiconductor nanoparticles exhibit optical properties comparable to that of organic dyes and their properties can be tuned by size, shape or concentration. In this work, energy transfer between the dye Fluorescein and nanoparticles of ZnS has been investigated following time domain and frequency domain spectral measurements. ZnS nanoparticles were synthesized by hydrothermal method and characterized by transmission electron microscopy. These have been uniformly dispersed in 0.5mM aqueous solution of Fluorescein and photoluminescence measurements were carried out. It is found that the optical energy gap decreases with nanoparticle concentration. Emission parameters such as quenching coefficient, energy transfer efficiency, and shift in peak wavelength have been evaluated. It is found that the fluorescence quenching time is indicative of resonant energy transfer between Fluorescein molecules (donor) and ZnS nanoparticles (acceptor). FRET (Foster Resonant Energy Transfer) efficiency and rate of FRET are evaluated from life-time data. Significant quenching is observed with the addition of ZnS nanoparticles, which is attributed to non-radiative and radiative energy transfers, of which the radiative process dominates.

Index Terms: Photoluminescence, Quenching, Resonant energy transfer, FRET, Life time.

1. INTRODUCTION

The Hybrid inorganic-organic systems are attracting attention because of their ease of processing and good optical and optoelectronic characteristics. These hybrid systems have wide range of applications such as use in dye lasers, solar collectors etc. [1]. Energy transfer in systems such as organic dyes is possible with different types of semiconductor nanocrystals, solution based complexes of nanocrystal based bio-conjugates, and hybrid structures of semiconductor and metal nanoparticles [2]. Semiconductor and metal nanoparticles as dopants influence the optical properties of laser dyes. The emission from Lissamine dye can be quenched by chemically attaching gold nanoparticles to the dye molecules and quenching is due to drastic decrease in the dye’s radiative emission rates [3]. Citrate stabilized silver nanoparticles can quench the fluorescence of Rh6G and emission can be tuned by varying the concentration of silver nanoparticles [4]. In semiconductor nanoparticle – dye systems, the dye acts as the donor as well as acceptor for energy transfer. CdS nanoparticles can act as donors for Rh6G, RbB and Texas Red dyes and the energy transfer efficiency is comparable with that of organic dyes [5]. CdSe nanocrystals enhance photoluminescence from various dyes and the emission can be tuned by altering the surface chemistry of CdSe nanocrystals [6]. Au nanoparticles-dye assemblies show photoluminescence quenching and shortening of decay times, which result from energy transfer from the dye to

2 BACKGROUND THEORY

Various optical constants such as band gap energy, quenching constant, quenching efficiency etc. for a nanoparticle-dye hybrid system can be evaluated from the absorption and photoluminescence spectra recorded from the samples. The quenching constant can be evaluated using the Stern – Volmer equation, given by [13],[15],[17]

$$\frac{I_D}{I_{DA}} = 1 + K_C[\text{Concentration}]$$

(1)

Where $I_D$ and $I_{DA}$ are the incident and fluorescence intensities respectively and $K_C$ is the quenching constant. The efficiency of quenching process or total transfer efficiency can be calculated using the equation [7]

$$E = 1 - \frac{I_{DA}}{I_D}$$

(2)

Different energy transfer constants can be evaluated using the following equations.

The rate constant for radiative energy transfer mechanism is given by [5]

$$\frac{I_D}{I_{DA}} = 1 + k \tau_{od} [A]$$

(3)

Where $I_D$ and $I_{DA}$ are the fluorescence intensities of the donor in the absence and presence of acceptor respectively, $\tau_{od}$ is the fluorescence life-time of the donor without acceptor, $k$ is

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Mathew M. Mecheril is currently pursuing doctoral degree program in Department of Instrumentation, Cochin University of Science and Technology, Kochi, India 682022. E-mail: mathewm@gecwyd.ac.in

J. Philip, is currently Professor, AmalJyothi Engineering College, Kanjirapally, Kottayam, India 686518
the total energy transfer rate constant, and \([A]\) is the acceptor concentration. The distance between donor and acceptor at which energy transfer from excited donor to acceptor and emission from excited donor are equally probable is called the critical radius, and is given by

\[ R_0 = \frac{2.4 \lambda}{[A]^\frac{1}{2}} \]  

(4)

Where \([A]\) is the half-quenching concentration which can be obtained as the concentration of acceptor at which fluorescence intensity of the donor is reduced to half, and is given by

\[ \frac{I_{od}}{I_{id}} = 2 \]  

(5)

FRET efficiency can be experimentally determined by comparing the donor life-time in the presence of the acceptor \(\tau_{da}\) and the intrinsic donor lifetime \(\tau_{id}\) as \[9\]

\[ E_{\text{FRET}} = \frac{1}{1 + \frac{R_0}{R}} \]  

(6)

The rate of FRET is given by

\[ k_{\text{FRET}} = \frac{1}{\tau_{id} (1 - E_{\text{FRET}})} \]  

(7)

3 EXPERIMENTAL METHOD

3.1 Synthesis and Characterization of ZnS Nanoparticles

ZnS nanoparticles were synthesized following the coprecipitation method using Zinc acetate and Sodium Sulphide as precursors. The morphology and particle sizes were estimated with high resolution TEM (Make Jeol, Model JEM-2100 Plus). The average particle sizes of synthesized ZnS nanoparticles were found to be 4nm.

![Fig 1. TEM Image of ZnS Nanoparticles](image)

3.2 Absorption Studies

ZnS nanoparticles were dispersed in an aqueous solution of Fluorescein at 0.05mM concentration, and absorption (Shimadzu UV-1800 Spectrophotometer) and photoluminescence measurements (Horiba FluoroMax-4 Spectrofluorometer) were carried out. Various optical parameters were evaluated using the data obtained from absorption and photoluminescence measurements. It was possible to interpret the observations on energy transfer between dye molecules and dispersed ZnS nanoparticles.

Absorption spectra of aqueous solution of Fluorescein dispersed with ZnS nanoparticles have been recorded using a spectrophotometer and are shown in Figure 3. The absorption spectra indicate that absorption is wavelength dependent and maximum absorption is observed in the wavelength range 450-550 nm. However, in this wavelength range variation in absorbance with ZnS concentration is small compared to wavelengths shorter than 450nm or longer than 525nm. The area under the absorption spectrum increases steadily with ZnS concentration and all the dispersed samples show much higher absorption than pure dye solution.

![Fig 2. Absorption spectra of aqueous solution of ZnS nanoparticles at different concentrations.](image)

![Fig 3. Absorption spectra of Fluorescein dye dispersed with ZnS nanoparticles at different concentrations. a. 0.5mM Dye, b. 0.5mM Dye+0.0025M ZnS, c. 0.5mM Dye+0.05M ZnS, d. 0.5mM Dye+0.01M ZnS, e. 0.5mM Dye+0.03M ZnS](image)

Absorption spectra at different concentrations of ZnS nanoparticles show an absorption edge at the longer wavelength region which corresponds to the band gap energy, and the absorption edge is evaluated using Tauc plots shown in Figure 4. The band gap energies and the corresponding wavelengths are tabulated in Table 1. The variation of the band gap energies with concentration of ZnS
nanoparticles is shown in Figure 5, and the variation of absorption edge of Fluorescein dye dispersed with ZnS nanoparticles at different concentrations of ZnS nanoparticles is shown in Fig.6. Concentrations of ZnS nanoparticles are shown in Fig.6.

**Fig. 4:** The Tauc plots used to estimate the energy band gaps of Fluorescein dye dispersed with ZnS nanoparticles at various concentrations indicated in Table 1

<table>
<thead>
<tr>
<th>Sample Details</th>
<th>Band Gap energy (eV)</th>
<th>Wavelength (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a  0.5mM Dye</td>
<td>2.37</td>
<td>524.1</td>
</tr>
<tr>
<td>b 0.5mM Dye with 0.0025M ZnS</td>
<td>2.36</td>
<td>526.4</td>
</tr>
<tr>
<td>c 0.5mM Dye with 0.005M ZnS</td>
<td>2.35</td>
<td>528.6</td>
</tr>
<tr>
<td>d 0.5mM Dye with 0.01M ZnS</td>
<td>2.34</td>
<td>530.9</td>
</tr>
<tr>
<td>e 0.5mM Dye with 0.03M ZnS</td>
<td>2.31</td>
<td>537</td>
</tr>
</tbody>
</table>

**Table 1**

Band gap energy and corresponding wavelength for Fluorescein dye doped with different concentrations of ZnS nanoparticles

The decrease of band gap energy with particle concentration may be due to the band structure modification after the dye molecules got adsorbed on to the nanoparticle surfaces. Similar band gap shrinkage has been observed and reported in heavily doped semiconductors and explained using Burstein – Moss model [15,16].

3.3 Photoluminescence measurements

Photoluminescence measurements have been carried out on Fluorescein dye dispersed with different concentrations of ZnS nanoparticles, with UV excitation (wavelength: 450 nm) (Horiba FluoroMax-4 Spectrofluorometer). The results enable us to understand the influence of ZnS nanoparticles on the photoluminescence emission of this dye. Fig. 7 shows the fluorescence emission spectra of the dye in the absence and presence of ZnS nanoparticles at different concentrations. The concentration corresponding to each curve is as indicated in Table 1. It can be noticed from the figure that significant fluorescence quenching occurs when the dye is doped with these nanoparticles and the quenching increases with the level of doping.

**Fig. 5:** Variation of band gap energy of Fluorescein dye dispersed with ZnS nanoparticles at different concentrations

**Fig. 6:** Variation of absorption edge of Fluorescein dye dispersed with ZnS nanoparticles at different concentrations.

**Fig. 7:** Photoluminescence Spectra of Fluorescein dye dispersed with ZnS nanoparticles at different concentrations

It is found that the quenching constant increases with ZnS nanoparticle concentration and the rate of quenching decreases at higher concentrations. This may be because at higher concentrations all the dye molecules are adsorbed to the ZnS nanoparticle surface and energy transfer gets saturated. Figure 8 shows the variation of relative intensity with particle concentration in the dye. It can be seen that the
relative intensity initially increases linearly and gradually saturates at higher concentrations of nanoparticles. The variation of the shift in wavelength corresponding to the peak intensity with nanoparticle concentration is shown in Figure 9. It can be seen that the peak wavelength shows a red shift with increase of concentration of ZnS nanoparticles.

**Table 2**

Various optical parameters of Fluorescein dye doped with different concentrations of ZnS nanoparticles

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>Sample Details</th>
<th>intensity peak (nm)</th>
<th>PL Intensity (A.U)</th>
<th>Quenching Efficiency (M-1)</th>
<th>Quenching Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>0.5mM Dye</td>
<td>538.1</td>
<td>487.98</td>
<td>92.13</td>
<td>18.7</td>
</tr>
<tr>
<td>b</td>
<td>0.5mM Dye with 0.0025M ZnS</td>
<td>539.5</td>
<td>396.63</td>
<td>87.33</td>
<td>30.4</td>
</tr>
<tr>
<td>c</td>
<td>0.5mM Dye with 0.005M ZnS</td>
<td>5432</td>
<td>339.66</td>
<td>75.12</td>
<td>42.9</td>
</tr>
<tr>
<td>d</td>
<td>0.5mM Dye with 0.01M ZnS</td>
<td>550.6</td>
<td>278.65</td>
<td>87.33</td>
<td>30.4</td>
</tr>
<tr>
<td>e</td>
<td>0.5mM Dye with 0.03M ZnS</td>
<td>556.9</td>
<td>227.75</td>
<td>38.09</td>
<td>53.3</td>
</tr>
</tbody>
</table>

**Fig. 8:** Variation of relative intensities with concentration of ZnS nanoparticles dispersed in Fluorescein dye

**Fig. 9:** Variation of the peak wavelength with concentration of ZnS Nanoparticles in Fluorescein dye

It can be noted that a red shift in the peak wavelength of emission spectrum occurs as the concentration of ZnS increases. When concentration ZnS nanoparticles increase their band structure gets modified and magnitude of the band gap decreases. When a dye molecule gets adsorbed on to the surface of a nanoparticle the energy levels of the dye molecules get modified, which causes a red shift in the fluorescence emission spectrum. The critical transfer radius R0 at which radiative and non-radiative transfer are equally probable is calculated from emission spectrum. In the system under study the value of critical radius is 2.5 nm. But the nanoparticle has an average size of 5 nm. So the adsorbed dye molecule is closer to nanoparticle surface which favours non-radiative energy transfer.

**3.4 Life-time measurements**

Change in life time is an indication of the non-radiative energy transfer process. Life-time of different samples have been measured using time correlated single photon counting (TCSPC) technique (HORIBA Scientific, Deltaprobe Fluorescence life-time system). It is observed that life-time of the dye get considerably reduced on addition of ZnS nanoparticles, as is evident from Figure 10. Also the life-time and thus energy transfer remains constant even though the acceptor concentration increases. Results of life-time measurements are consolidated in Table 3.

**Table 3**

Life time, FRET Efficiency of Fluorescein dye doped with different concentrations of ZnS nanoparticles

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>Sample Details</th>
<th>Life Time (ns)</th>
<th>FRET Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>0.5mM Dye</td>
<td>3.22</td>
<td>0.962</td>
</tr>
<tr>
<td>b</td>
<td>0.5mM Dye with 0.0025M ZnS</td>
<td>0.12</td>
<td>0.962</td>
</tr>
<tr>
<td>c</td>
<td>0.5mM Dye with 0.005M ZnS</td>
<td>0.124</td>
<td>0.961</td>
</tr>
<tr>
<td>d</td>
<td>0.5mM Dye with 0.01M ZnS</td>
<td>0.102</td>
<td>0.968</td>
</tr>
<tr>
<td>e</td>
<td>0.5mM Dye with 0.03M ZnS</td>
<td>0.113</td>
<td>0.964</td>
</tr>
</tbody>
</table>

It can be observed that FRET efficiency and rate of energy transfer remains constant at the chosen concentration of ZnS. This indicates that most of the dye molecules are adsorbed on to the nanoparticle surface. The decay time of the system has been reduced by an order of two which means that excited states are de-populated immediately after excitation when ZnS nanoparticles are dispersed in the dye. This indicates FRET process takes place in the sample. The FRET efficiency is calculated and tabulated in Table 3. Data presented in Table 3 shows that FRET efficiency remains constant in the studied concentration range which means all the dye molecules are adsorbed on to the surface of nanoparticles.
4. CONCLUSIONS
It is found that at low doping concentrations photoluminescence quenching varies uniformly with the quencher concentration and at higher concentrations quenching saturates. The de-excitation of the dye molecules takes place by radiative and non-radiative pathways. Life-time measurements indicate that at low doping concentration itself, decay time decreases by an order of two and efficiency of non-radiative decay is over 95% for all samples. This rapid decrease of life time indicates Förster type energy transfer through non radiative path. The Dye molecules may be adsorbed at the nanoparticle surfaces and the band structure of the dye molecule gets modified in the vicinity of ZnS nanoparticles. Absorption measurements show that absorption bandwidth can be enhanced by the addition of nanoparticles. So excitation power can be reduced for nanoparticle-dye hybrid systems compared to pure dye system. In short it is possible to tune the optical properties of dyes and improve their performance with nanoparticle addition.

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REFERENCES