Efficiency of Energy Transfer for TiO$_2$ Nanoparticles with Fluorescein Dye

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Abstract
For different amount of masses of TiO$_2$ nanoparticles in dye solution, absorption and fluorescence profiles of the suspension for TiO$_2$ nanoparticles with Fluorescein (F) in distilled water solution, has been explored. An absorption spectra enhancement was detected for changed amount of masses, which specifies that the doping with TiO$_2$ nanoparticles have a major effect on the dye absorption spectra. Contrarily, all fluorescence emission spectra for the dye were quenched as TiO$_2$ nanoparticles amount of masses increases because of Förster resonance energy transfer (FRET).

Keywords: Fluorescence Quenching, TiO$_2$ Nanoparticles, Fluorescein, Absorption Spectra, Energy Transfer Efficiency.

Introduction
There are many spectral studies of the absorption and fluorescence emissions, of the colloidal suspension of metal nanoparticles and non-metal nanoparticles in dye solutions, for its position in tuning luminescence intensity in medical and biological applications[1-6], and for examining optical properties of scattering media as in unsystematic laser dynamics. A normal random laser procedure contains a dye solution and nanopowder acts as the scatters wherein the emission properties depend on the dye amount of masses, the pumping power and scatter density. D.Q. Hoa, et al. inspected doping nanoparticles of gold with (DCM) dye on a laser-active medium[7]. J. John, et al. studied the optical characteristics of fluorescein dye mixed with gold nanoparticles[8] and M. Barzan and F. Hajiesmaeilbaigi[9] considered the gold nanoparticles effect on the optical properties of Rhodamine 6G, whereas Brito-Silva et al., identified the particle size influence and concentration on laser action[10].

Here, the Fluorescein spectral Characteristics with TiO$_2$ nanoparticles have been evaluated, according to different amount of masses of TiO$_2$ nanoparticles with dye molecules via absorption and fluorescence spectroscopy. The process of Förster resonance energy transfer (FRET) occurs when the fluorescence spectrum of a laser dye, known as the donor, overlays with the absorption spectrum of other molecule, known as the acceptor. No matter that the acceptor is fluorescent or not. The efficiency of Energy-transfer E can be calculated by[11]:

$$E = 1 - \frac{F}{F_0}$$

(1)
Where $F$ and $F_0$ are the fluorescence intensities of dye in presence and the absence of nanoparticles, respectively. The correlation of Stern–Volmer, gives us an exploration for the photophysical intermolecular deactivation kinetics of the (quenching) process. Overall, this process can be denoted by:[9]:

$$\frac{F}{F_0} = 1 + K[Q]$$  \hspace{1cm} (2)

Where $K$ is the quenching constant of Stern-Volmer equation, $[Q]$ is the amount of mass for the quencher. So, plotting $F_0/F$ and $[Q]$ would give a straight line, the slope of this line is equal to the quenching constant $K$.

**Materials and Methodology**

Suspension of TiO$_2$ nanoparticles (with an average diameter of 15 nm, Purity: 99%) in Fluorescein ($C_{20}H_{12}O_5$, AnalR, $M_W=332.306$ g/mol) with distilled water were prepared. The Fluorescein dye concentration was $(1 \times 10^{-5})$ M. A UV-visible spectrophotometer (T70/T80) used to observe absorption, while emission spectra were detected using spectro-fluorophotometer (SHIMATDZU RF-5301pc). Different amount of masses of nano TiO$_2$ were inspected for dye solution varying from 0.0005 g to 0.002 g. All samples prepared by using hot plate stirrer until the TiO$_2$ nanoparticles homogeneously diffused through the Fluorescein solution.

**Results and Discussion**

Figures 1 and 2, displays the spectra of absorption and fluorescence of Fluorescein with distilled water, without nanoparticles of TiO$_2$. The greatest absorption wavelength ($\lambda_{abs}$) was 490 nm, whereas the fluorescence wavelength ($\lambda_f$) was 514 nm.
Table 1: Spectral data.

<table>
<thead>
<tr>
<th>F0</th>
<th>TiO2 (g)</th>
<th>F</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>180.8</td>
<td>0</td>
<td>180.8</td>
<td>0</td>
</tr>
<tr>
<td>180.8</td>
<td>0.0005</td>
<td>72.37</td>
<td>0.942</td>
</tr>
<tr>
<td>180.8</td>
<td>0.0008</td>
<td>71.19</td>
<td>0.948</td>
</tr>
<tr>
<td>180.8</td>
<td>0.001</td>
<td>47.48</td>
<td>0.964</td>
</tr>
<tr>
<td>180.8</td>
<td>0.002</td>
<td>42.11</td>
<td>0.970</td>
</tr>
</tbody>
</table>

Table 1 expresses that with the raising the amount of masses of TiO2 has led to improve the spectral intensity for absorption, and lowering or quenching the spectral intensity of the fluorescence. Besides, Table 1 indicates very little spectral red shift, by increasing the amount of masses of TiO2 nanoparticles, the reason for that is, applying scatters to the dye solution gives longer random walk and also more absorption for emitted photons, so that the re-absorption and re-emission has led to red shift.

A dynamic quenching become governing and fluorescence intensities drops down simultaneously, with increasing TiO2 nanoparticle amount of masses. This action could be clarified on the basis of energy transfer between donor (Fluorescein) and acceptor (TiO2 nanoparticle). The efficiency of Energy-transfer E can be calculated by eq. (1).

The values of energy-transfer efficiencies of the samples listed in Table 2.

Table 2: Efficiencies of Energy-transfer for the samples.

<table>
<thead>
<tr>
<th>(F0/FO)</th>
<th>TiO2 (g)</th>
<th>Absorption intensity</th>
<th>λnm</th>
<th>Fluorescence intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.468</td>
<td>514</td>
<td>180.8</td>
<td></td>
</tr>
<tr>
<td>0.0005</td>
<td>0.689</td>
<td>516</td>
<td>72.37</td>
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<tr>
<td>0.0008</td>
<td>0.71</td>
<td>515</td>
<td>71.19</td>
<td></td>
</tr>
<tr>
<td>0.001</td>
<td>0.731</td>
<td>514</td>
<td>47.48</td>
<td></td>
</tr>
<tr>
<td>0.002</td>
<td>0.771</td>
<td>515</td>
<td>42.11</td>
<td></td>
</tr>
</tbody>
</table>

From information of Table 2, it clear that the energy-transfer (quenching) efficiencies increased with rising the TiO2 nanoparticles amount of masses. The famous Stern-Volmer equation, equation (2), can describe the lowering in the fluorescence intensity of Fluorescein dye with the addition of TiO2 nanoparticles.

The resulted straight line from the F0/F versus [Q] plot is presented in Figure 5. The value of the Stern-Volmer quenching constant, K, is 1820 M⁻¹. This high amount of the quenching constant infers an efficient quenching of Fluorescein fluorescence with TiO2 nanoparticles.

Figure 5: The plot of Stern-Volmer for the Fluorescein with nano TiO2 amount of masses.

Conclusions
This work implies that the amount of masses of TiO2 nanoparticles is an important factor for
enhancing the absorption and quenching the fluorescence of Fluorescein dye, by observing the spectra of absorption and fluorescence. With help of the Stern-Volmer equation, a relatively high value for the quenching constant is acquired, and it is hinted a proficient quenching in fluorescence of the Fluorescein dye with TiO₂ nanoparticles. Lowering the fluorescence intensity alongside the increasing amount of TiO₂ nanoparticles can be described by perception of energy transfer process between Fluorescein and silver nanoparticle.

References