The Establishment of a Theoretical Model for the Estimation of Some Photo-Physical Processes in Laser Dyes

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Abstract

In this study, a new theoretical method for the estimation of absorption and fluorescence spectra is accomplished. These estimations were established following experimental measurements of absorption and fluorescence spectra for the solutions of fluorescein laser dye mixed with titanium dioxide (TiO₂) nanoparticles in distilled water. The used concentration of fluorescein dye was 1x10⁻⁵ M, whereas the masses of titanium dioxide nanoparticles were 0.0003g, 0.0005g, 0.001g and 0.002g. An absorption spectra improvement was observed upon raising the mass of TiO₂ nanoparticles, which specifies that doping the fluorescein dye with TiO₂ nanoparticles have an essential influence on the dye absorption spectra. On the other side, all fluorescence spectra for the dye quenched as TiO₂ nanoparticles mass was increased, because of the induced electron transfer. The new method of theoretical estimations was based on curve fitting using Logistic Power Peak (LPP) function to estimate theoretical models for the absorption and fluorescence spectra of these samples. The results revealed that these estimated models had exceptional matching shapes with the experimental shapes, so that the estimated models can substitute the experimental measurements.

Keywords: Logistic Power Peak, Fluorescein dye, TiO₂ Nanoparticles, induced electron transfer.

بناء موديلات نظرية لتخمین بعض العمليات الفيزيائية الضوئية للصبغات الليزیرية

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الخلاصة

تم تنفيذ طريقة نظرية جديدة لتخمین أطیاف الامتصاص والفلورصورة . تم أجراء هذه التجربات بعد اجراء تجارب عملية لأطیاف الامتصاص والفلورصورة لتمثیل روابط الفلورسين الليزرية مع مادة ثانیة أوکسید التيتانیوم النانوية في الماء المقطخ. استخدم تركیز (1x10⁻⁵ M) لصبغة الفلورسين. بينما كانت كميات مادة ثانیة أوکسید التيتانیوم النانوية هي (0.0003g، 0.0005g، 0.001g و 0.002g). تم ملاحظة تعیین أطیاف الامتصاص مع زيادة الكتل، مما يبين أن التجفیف بمجرد ثانیة أوکسید التيتانیوم النانوية له تأییر جوهری على أطیاف الامتصاص . من ناحیة أخرى، جميع أطیاف الفلورصورة تم كنبها ككما ازدادت كل أطیاف ثانیة أوکسید التيتانیوم النانوية نتيجة حدوث انتقال الالکترون المحرز. تم تعمید الطریقة النظریة الجديدة لتخمین أطیاف الفلورصورة على عملية مطابقة المنحنیات باستخدام دالة منحنی القوة الوجستی (LPP) لتخمین الموديلات النظریة

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Introduction

Various spectral analyses of the absorption and fluorescence emissions of xanthene dyes (especially fluorescein) were achieved, which included the doping of metal and non-metal nanoparticles in dye liquids. Such analyses were developed due to the essential uses of these dyes in medical and biological applications, including identification and therapy of cancer [1], in vitro and in vivo bio-imaging [2], imaging of tomography and angiography [3], and other medical applications of nanoparticles (e.g. silver nanoparticles) [4]. Organic laser dyes mixed with nanoparticles are also used for examining the optical properties of scattering media, as in laser action and random lasers [5], [6]. In 2012, Al-Kadhemy et al. explored the absorption spectra of styrene-butadiene in toluene, using the TableCurve 2D software [7], which opens the way for using a curve fitting software in the spectral measurements. Fluorescence quenching by electron transfer effects was inspected for nanoparticles with organic dyes by Asiri et al. [8], who explained the photodegradation of rhodamine 6G and phenol red by TiO$_2$ nanoparticles through electron transfer under solar irradiation. Also, Karunakaran et al. [9] found that the fluorescence of FPPBI dye was efficiently quenched by TiO$_2$ nanoparticles, due to electron transfer mechanisms.

In this research, a new method for creating theoretical models in order to estimate the spectral performance of the fluorescein dye with TiO$_2$ nanoparticles was evaluated. These estimations were performed after experimental measurements of absorption and fluorescence spectra of fluorescein dye with TiO$_2$ nanoparticles of different masses. The curve fitting process was conducted using the TableCurve 2D software to estimate theoretical models for the spectra of absorption and fluorescence. These estimated models exploited the Logistic Power Peak (LPP) function, which was previously used for various objectives, such as estimating soil properties [10] and light emitted diode (LED) spectral calculations [11]. However, this is the first time to utilize the LPP function to estimate theoretical models of the spectral profiles of the fluorescein dye with TiO$_2$ nanoparticles.

Materials and Methods

In these tests, the samples consisted of a suspension of 0.0003g, 0.0005g, 0.001g and 0.002g of TiO$_2$ anatase nanoparticles (Nanoshel LLC, USA) with an average size of 15.7 nm and purity of 99% in fluorescein (C$_{20}$H$_{12}$O$_5$, $M_W=332.306$ g/mol, BDH) with 10 ml of distilled water. The solution of dye samples with a concentration of $1 \times 10^{-5}$ M was prepared using the following equation [12]:

$$m = C \times V \times M_w$$  (1)

where $m$ is the weight of the dye needed to obtain the desired concentration, $C$ is the required concentration of the dye, $V$ is the volume of solvent for the dye, and $M_w$ is the molecular weight of the dye. The dye chemical structure is shown in Figure-1.

Figure 1- Chemical structure of fluorescein dye [12].
All the used samples were prepared using a hot plate stirrer until the TiO$_2$ nanoparticles were homogeneously diffused within the fluorescein solution at room temperature (30°C). Fluorescence spectra were determined using a spectrofluorophotometer (SHIMADZU RF-5301pc).

Results and Discussion

The crystalline structure of TiO$_2$ nanoparticles was verified by X-ray diffraction (XRD) using SHIMADZU XRD – 6000, Cu K$_\alpha$, in the 2θ range of 10 to 80°.

The measured XRD pattern of TiO$_2$ nanoparticles is represented in Figure-2. The pattern reveals that the TiO$_2$ nanoparticles are crystalline and have a tetragonal crystal system with a lattice constant of $a = 3.7850$ Å and $c = 9.5140$ Å. The appearance of strong diffraction peaks at 25° (101), 48° (200), and 37° (004) indicated the presence of TiO$_2$ in the anatase phase. This finding is consistent with those from other published results [13-15].

![Figure 2: Measured XRD patterns of TiO$_2$ nanoparticles.](image)

Figure 3 shows the absorption and fluorescence spectra for fluorescein dye with a concentration of $1 \times 10^{-5}$ M, with and without TiO$_2$ nanoparticles of the tested masses.

![Figure 3: Absorption (a) and fluorescence (b) spectra of fluorescein (F) with different masses of TiO$_2$ nanoparticles.](image)
The peak maximum spectra of the fluorescein laser dye were $\lambda_e = 490$ nm for the absorption and $\lambda_f = 514$ nm for the fluorescence. The details of these results are presented in Table-1.

**Table 1 - Absorption and fluorescence spectra of fluorescein dye with different masses of TiO$_2$ nanoparticles**

| Dyes       | TiO$_2$ (g) | $\lambda_e$ (nm) | Absorption Intensity | $\lambda_f$ (nm) | Fluorescence Intensity |
|------------|-------------|-------------------|----------------------|-------------------|-----------------------|
| F (1x10$^{-5}$ M) | 0           | 490               | 0.468                | 514               | 180.8                 |
|            | 0.0005      | 490               | 0.689                | 516               | 72.37                 |
|            | 0.0008      | 490               | 0.71                 | 515               | 71.19                 |
|            | 0.001       | 490               | 0.731                | 514               | 47.48                 |
|            | 0.002       | 490               | 0.771                | 515               | 42.11                 |

From Figure-3 and Table-1, it is obvious that increasing the TiO$_2$ nanoparticle mass resulted in higher absorption spectra, while fluorescence intensities decreased instantly by the quenching process. The electron transfer effect between fluorescein dye and TiO$_2$ nanoparticle can explain this action. In addition, there was a very slight red shift in the fluorescence intensity with increasing TiO$_2$ nanoparticle mass, because of the process of re-absorption and re-emission produced by the scattering of the light from TiO$_2$ nanoparticle.

Table Curve 2D software was used for the theoretical estimation of the experimental absorption and fluorescence spectra of a single concentration of fluorescein dye with changing the mass of TiO$_2$ nanoparticles. A curve fitting process was achieved for all curves observed in Figure- 3, as shown in Figures- 4 and 6, to discover an appropriate individual curve fitting equation that can be used for all of these spectra.

The used curve fitting equation, in this research, is another type of the Gaussian function which is called the Logistic Power Peak (LPP). A mathematical description of this function is given by Eq. (2):

$$Y = \frac{a + b}{e^{1 + \exp\left((x + d \ln (e - c)/d)^{(e - 1)/e}\right)} \exp\left((x + d \ln (e - c)/d)(e + 1)^{(e + 1)/e}\right) \left((e + 1)/e\right)}$$

for $e \geq 1$, $d \neq 0$.

where $a$ and $b$ are the minimum and maximum amplitudes, respectively, $d$ is the width of the spectrum over time, $c$ is position of maximum, and $e$ is the symmetry around the peak ($e = 1$) or not ($e > 1$).

The equation of the theoretical estimation was applied for values of TiO$_2$ nanoparticles mass, which were not used experimentally, mixed with fluorescein dye solution in distilled water within a concentration of 1x10$^{-5}$ M. The theoretical study involves the absorption and fluorescence spectra for the samples.

Figures-(4 and 5) demonstrate the fitting curves and their parameters, respectively, for the experimental absorption spectra, while Figure- 6 and 7 show the fitting curves and their parameters, respectively, for the experimental fluorescence spectra for fluorescein dye solution mixed with TiO$_2$ nanoparticles.
Figure 4- Curve fitting of absorption spectra for fluorescein with TiO$_2$ nanoparticles.
Figure 5- The parameters of fluorescein with TiO$_2$ nanoparticles for absorption spectra.
Figure 6- Curve fitting of fluorescence spectra for fluorescein with TiO$_2$ nanoparticles.
Figure 7- The parameters of fluorescein with TiO$_2$ nanoparticles for fluorescence spectra.

The curve fitting parameters from Figures-(5 and 7) are presented in Tables- 2 and 3, which contain the absorption and fluorescence parameters, respectively, of both the experimental and theoretical values of the mass of TiO$_2$ nanoparticles which were mixed with fluorescein dye. The symbol $r^2$ refers to the correlation coefficient, which was used to measure the strength of a relationship between the two variables (experimental and theoretical data).
Table 2- Parameters of fluorescein with TiO$_2$ nanoparticles for absorption spectra

| TiO$_2$ (g) | a    | b    | c    | d    | e    | $r^2$ |
|------------|------|------|------|------|------|-------|
| 0                      | 0.0019645 | 0.4547493 | 490.6841 | -5.2948479 | 4.2251472 | 0.9976 |
| 0.0003 Theo    | 0.0137 | 0.6456 | 490.7452 | -5.3083 | 4.2158 |
| 0.0005         | 0.0398001 | 0.6340074 | 490.88002 | -5.3361234 | 4.2066455 | 0.9976 |
| 0.0008         | 0.1745554 | 0.5087189 | 490.94091 | -4.8963422 | 7.0074288 | 0.9925 |
| 0.0009 Theo    | 0.2463 | 0.4533 | 490.0668 | -4.883 | 10.4072 |
| 0.001         | 0.3028289 | 0.3968275 | 489.77423 | -4.8977414 | 12.599133 | 0.9871 |
| 0.002         | 0.3415867 | 0.3883975 | 490.27659 | -4.6517563 | 15.099479 | 0.9775 |
| 0.0025 Theo    | 0.3416 | 1.2442 | 490.0593 | -4.6701 | 15.1019 |

Table 3-Parameters of fluorescein with TiO$_2$ nanoparticles for fluorescence spectra

| TiO$_2$ (g) | a    | b    | c    | d    | e    | $r^2$ |
|------------|------|------|------|------|------|-------|
| 0                      | -1.6608078 | 181.82968 | 513.60057 | 5.5025927 | 4.3808979 | 0.9988 |
| 0.0003 Theo    | -0.5105 | 89.8488 | 515.3271 | 5.258 | 4.4276 |
| 0.0005         | -0.4727865 | 72.462063 | 515.33615 | 5.2592695 | 4.465926 | 0.9988 |
| 0.0008         | -0.5183223 | 71.604956 | 515.02443 | 5.304727 | 4.4361017 | 0.9989 |
| 0.0009 Theo    | -0.5223 | 58.2915 | 514.7349 | 5.4831 | 4.489 |
| 0.001         | -0.5279488 | 47.310278 | 514.47883 | 5.6440892 | 4.7430857 | 0.9980 |
| 0.002         | -0.4478189 | 41.827018 | 514.47902 | 5.7264238 | 4.6437646 | 0.9980 |
| 0.0025 Theo    | -0.2076 | 39.2809 | 516.8384 | 5.7371 | 4.5198 |

For the additional exploration of the theoretical models of the estimated absorption and fluorescence spectra, a profile containing the theoretical values of the mass of TiO$_2$ nanoparticles that were mixed with fluorescein dye, is provided in Figure-8. The performance of the theoretical absorption and fluorescence spectra was similar to that of the experimental spectra (Figure-3), i.e., the theoretical models based on the used curve fitting equation (Eq. 2) showed a very good matching with the experimental results.

![Figure 8- Theoretical absorption (a) and fluorescence (b) spectra for fluorescein with TiO$_2$ nanoparticles.](image-url)
For comparison, all the experimental and theoretical results of TiO$_2$ nanoparticles mixed with fluorescein dye are presented in Table-4.

Table 4- The spectral behavior of the fluorescein dye mixed with different experimental and theoretical masses of TiO$_2$ nanoparticles.

| F (1x10$^{-5}$ M) | TiO$_2$ (g) | $\lambda_a$ (nm) | Absorption Intensity | $\lambda_f$ (nm) | Fluorescence intensity |
|-------------------|-------------|------------------|----------------------|------------------|-----------------------|
|                   | 0           | 490              | 0.468                | 514              | 180.8                 |
| 0.0003 Theo       | 490         | 0.658            | 515                  | 89.3             |
| 0.0005            | 490         | 0.689            | 516                  | 72.37            |
| 0.0008            | 490         | 0.71             | 515                  | 71.19            |
| 0.0008 Theo       | 490         | 0.674            | 515                  | 52.611           |
| 0.0009 Theo       | 490         | 0.699            | 515                  | 57.75            |
| 0.001             | 490         | 0.731            | 514                  | 47.48            |
| 0.002             | 490         | 0.771            | 515                  | 42.11            |
| 0.0025 Theo       | 490         | 1.585            | 516                  | 38.99            |

Conclusions
A new theoretical model for the estimation of the absorption and fluorescence spectra of fluorescein dye, mixed with different TiO$_2$ nanoparticles masses, was accomplished. The Logistic Power Peak (LPP) equation was found to be the best fitting equation for both absorption and fluorescence spectra of these samples. The performance similarity of the theoretical and practical spectra profiles can make the estimated models an exceptional alternative for the experimental measurements. This alternative would save the time, cost, and overcome the availability of the measuring devices. It also provides a suitable speculation of the overall spectral behavior resulting from mixing TiO$_2$ nanoparticles with fluorescein laser dye.

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