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*Research Article*

# Photosensitization of Colloidal $SnO_2$ Semiconductor Nanoparticles with Xanthene Dyes

**N. Nagarajan, G. Paramaguru, G. Vanitha, and R. Renganathan**

*School of Chemistry, Bharathidasan University, Tiruchirappalli, Tamil Nadu 620 024, India*

Correspondence should be addressed to R. Renganathan; rrengas@gmail.com

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The photochemical behavior of xanthene dyes (fluorescein, erythrosine, and eosin) with colloidal $SnO_2$ nanoparticles was probed by UV-visible, steady state, and time resolved fluorescence measurements. The prepared $SnO_2$ nanoparticles were characterized by using UV-visible and powder XRD measurements. The xanthene dyes were adsorbed on the surface of colloidal $SnO_2$ nanoparticles through electrostatic interaction. Apparent association constant ($K_{app}$) was calculated from the relevant fluorescence data. The larger value of apparent association constant indicates a strong association between xanthene dyes and $SnO_2$ nanoparticles. The fluorescence quenching is mainly attributed to electron transfer from the excited state xanthenes to the conduction band of colloidal $SnO_2$. The electron transfer mechanism was explained based on the Rehm-Weller equation as well as the energy level diagram.

## 1. Introduction

The photosensitization of electron transfer across the semiconductor solution interface plays a vital role in light energy conversion in photoelectrochemical cells, wastewater treatment, nanoelectric devices, silver halide photography, and electrophotography. Effort in this area has concentrated on improving the visible light response of wide-band semiconductors such as $SnO_2$, ZnO, and $TiO_2$. Sensitization is achieved by adsorption of dye molecules at the semiconductor surface which, upon excitation, inject an electron into its conduction band [1, 2]. The first successful experiment of this type was described by Putseiko and Terenin [3] who found that the Dember effect of ZnO powder in visible light was sensitized by xanthene and cyanine dyes.

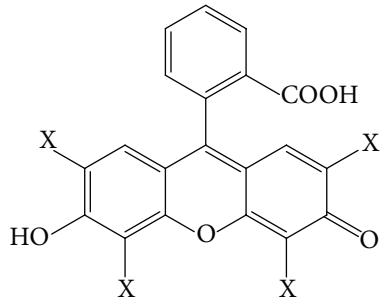
The investigation and development of the dye-semiconductor systems are essential for various fields of applications. Recently Ferrere et al. and Tian et al. used perylene-$SnO_2$ systems for dye sensitized solar cells [4–6]. The $SnO_2$ is a stable n-type semiconductor with a wide-band gap ($E_g$ = 3.6 eV) being used for various applications, including solid-state gas sensor, photovoltaic devices, dye-based solar cells, transparent conductive films for display and solar cells, catalysis, and anode materials of secondary lithium ion battery [7–9].

Xanthenes belong to the most widely used organic dyes, serving as luminophores [10], molecular probes, bioconjugates, stains, and biologically active substances [11, 12]. These dyes are utilized for photosensitization of redox processes [13, 14] in energy transfer and light sensitization studies [15]. They are also used in light-harvesting dendrimers [16], in biochemistry and medicine as reactants for determination of $Zn^{2+}$, NO [17], and $H_2O_2$ [18], in sensor devices for $H_2S$ [19], in studying carbon nanotubes [20], for creation of water-soluble fluorescent polymers [21] and new ionic liquids [22–25], and many other fields. Previously we have reported photosensitization of various dyes with semiconductor nanoparticles [26, 27]. The structures of xanthene dyes studied in the present work are shown in Scheme 1.

In the present work, we have studied the interaction between xanthene dyes, namely, fluorescein (FN), eosin (EN), and erythrosine (ERN) with colloidal $SnO_2$ nanoparticles by using steady state and life time measurements. The electron transfer mechanism is proved by Rehm-Weller equation.

## 2. Experimental Methods

*2.1. Materials.* The xanthene dyes were obtained from Aldrich and used without further purification. Dihydrate tin




X = H; fluorescein (FN)
X = Br; eosin (EN)
X = I; erythrosine (ERN)

Scheme 1

(II) chloride ($SnCl_2{\cdot}2H_2O$) and ethylene glycol (EG) were purchased from Loba, and they were used as such. Double distilled water was used for preparing the solutions throughout. All measurements were performed at ambient temperature.

## 3. Instrumentation

*3.1. Steady-State Measurements.* The fluorescence quenching measurements were carried out with JASCO FP-6500 spectrofluorimeter. The slit widths 5 nm and scan rate (500 nm/min) for both excitation and emission were maintained constant for all the measurements. Quartz cells (4 × 1 × 1 cm) with high vacuum Teflon stopcocks were used for measurements. Absorption spectral measurements were recorded using JASCO V630 UV-visible spectrophotometer.

*3.2. Time Resolved Fluorescence Measurements.* Fluorescence lifetime measurements were carried out in a picosecond time correlated single photon counting (TCSPC) spectrometer. The excitation source was the tunable Ti-sapphire laser (Tsunami, Spectra Physics, USA). The fluorescence decay was analyzed by using the software provided by IBH (DAS-6).

*3.3. Powder X-Ray Diffraction Measurements.* X-ray diffraction was recorded with a PAN analytical X' Pert Pro MPD X-ray diffractometer using Cu K$\alpha$ radiation ($\lambda$ = 0.154 nm) with a Ni filter. The tube current was 30 mA with a tube voltage of 40 kV. The $2\theta$ angular regions between 20 and 80 were explored at a scan rate of $5^\circ$ $min^{-1}$.

## 4. Preparation of Colloidal $SnO_2$ Nanoparticles

Colloidal $SnO_2$ nanoparticles were prepared according to the literature method [28]. In a typical procedure, 0.2 g of $SnCl_2{\cdot}2H_2O$ (dissolved in 10 mL of EG) was added to 40 mL of EG that was hosted in a round-bottom flask. After the pH of the solution was kept at 3-4, the solution had been refluxed at 190°C for 2 hours with constant stirring under atmospheric pressure; the clear solution turned into a slight yellow colloid with the reaction time increasing. The resulting $SnO_2$ colloid was used for the further studies.

## 5. Results and Discussion

*5.1. Determination of Particle Size of Colloidal $SnO_2$ Nanoparticles.* The relationship between band gap shift ($\Delta E_g$) and

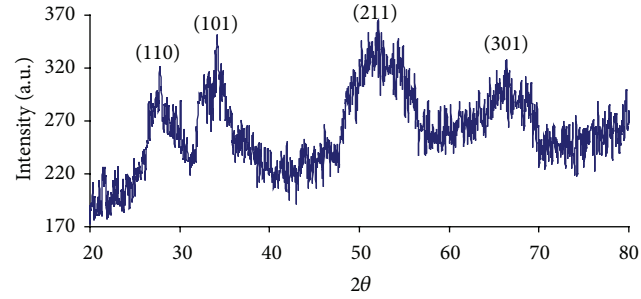



Figure 1: X-ray diffraction (XRD) spectrum of $SnO_2$ nanoparticles.

radius ($R$) of the particles is used to determine the particle size by using Brus equation:

$$\Delta E_g = \frac{\pi^2 \hbar^2}{2\mu R^2} - \frac{1.8e^2}{\varepsilon_R} + \text{Polarisation term}, \quad (1)$$

where $\hbar$ is the reduced Planck's constant, $R$ is the radius of the particle, $\mu$ is the effective reduced masses of the $e^-$ and $h^+$ in the semiconductor, $e$ is the electron charge, and $\varepsilon$ is the relative permittivity of the semiconductor.

Reduced effective mass of the exciton ($\mu$ = 0.275 $m_e$) [29] was used for the calculation. A columbic and polarization term in the equation was neglected. The calculated particle size of the prepared colloidal $SnO_2$ is 1.84 nm.

*5.2. XRD Characterization of $SnO_2$ Nanoparticles.* To clarify the crystalline structure, an XRD pattern of the $SnO_2$ powder is collected and shown in Figure 1. The diffraction peaks at around 27, 34, 52, and 66° are assigned to $SnO_2$ (110), (101), (211), and (301) (PDF no. 411445), respectively. No diffraction peaks due to metallic Sn or other tin oxides were discerned. The diffraction peaks in the XRD pattern broadened because the particles in the sample are too small. The primary particle size calculated by Scherrer formula is about 1.65 nm.

*5.3. Absorption Studies.* In an aqueous suspension, the polar surface of metal oxide semiconductor nanoparticles assists adsorption of polar species in solution, and such interactions can lead to absorption spectra changes of these molecules [30, 31]. To find out whether there is any ground state interaction between the sensitizer, that is, xanthene dyes and colloidal $SnO_2$ nanoparticles, ground state absorption measurements

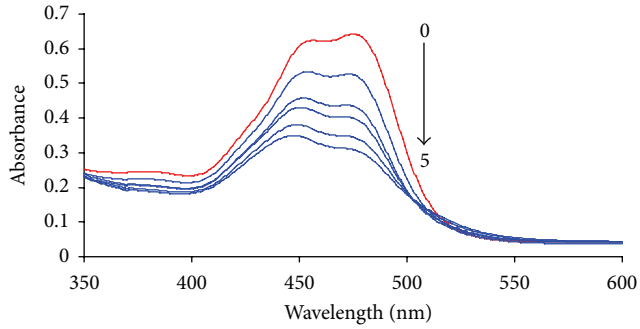



Figure 2: Absorption spectrum of FN ($1 \times 10^{-5}$ M; red color) in the presence of colloidal $SnO_2$ ($0–5 \times 10^{-4}$ M; blue color) in water. The arrow indicates the absorbance decreases on increasing concentration of colloidal $SnO_2$.

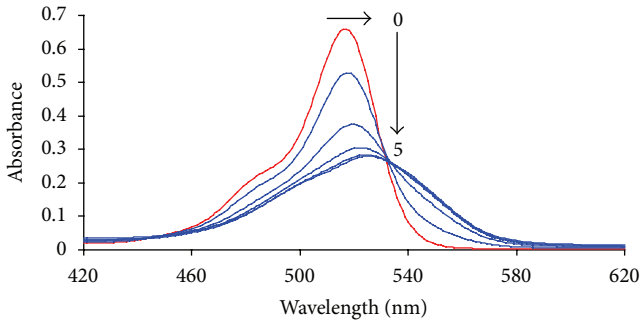



Figure 3: Absorption spectrum of EN ($1 \times 10^{-5}$ M; red color) in the presence of colloidal $SnO_2$ ($0–5 \times 10^{-4}$ M; blue color) in water. The arrow indicates the absorbance decreases with red shift on increasing concentration of colloidal $SnO_2$.

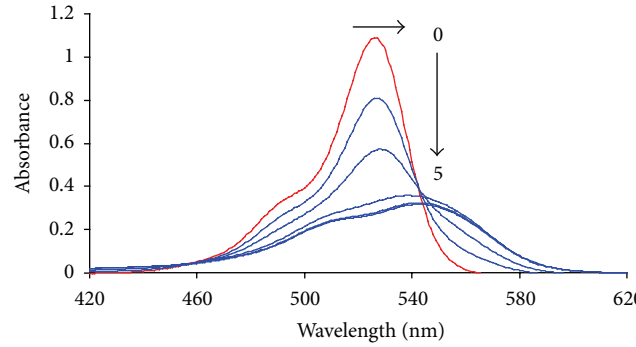



Figure 4: Absorption spectrum of ERN ($1 \times 10^{-5}$ M; red color) in the presence of colloidal $SnO_2$ ($0–5 \times 10^{-4}$ M; blue color) in water.The arrow indicates the absorbance decreases with red shift on increasing concentration of colloidal $SnO_2$.

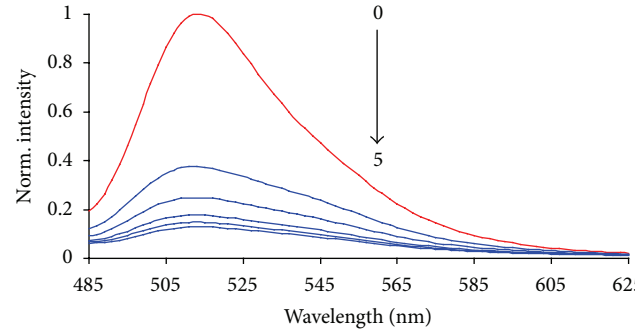



Figure 5: Fluorescence quenching of FN ($5 \times 10^{-6}$ M; red color) with colloidal $SnO_2$ ($0–5 \times 10^{-4}$ M; blue color) in water.

of Xanthene in the presence and absence of colloidal $SnO_2$ nanoparticles have been carried out. Figure 2 shows the absorption spectra of FN ($1 \times 10^{-5}$ M) in water with different concentrations of $SnO_2$ nanoparticles ($0–5 \times 10^{-4}$ M). Upon increasing the concentration of $SnO_2$ nanoparticles, the absorption decreases gradually [32]. But EN and ERN show red shift with decrease in absorbance (Figures 3 and 4). The presence of an isosbestic point at 531 nm for EN and 543 nm for ERN in these absorptions shows the existence of dye in the adsorbed and unadsorbed state. Such a red shift of 14 nm and 17 nm in the absorption peak indicates a strong interaction of the dye with $SnO_2$ surface. Similar spectral changes have been observed for several organic dyes on metal oxide surfaces [33].

*5.4. Fluorescence Quenching Studies.* The excited state interaction between xanthene dyes and $SnO_2$ colloid is observed by spectrofluorimetric measurements. Figure 5 shows the emission spectrum of FN in absence and presence of $SnO_2$ colloid. The fluorescence emission of FN ($5 \times 10^{-6}$ M) was quenched upon successive addition of $SnO_2$ colloid ($0–5 \times 10^{-5}$ M). Other two dyes also show similar type of spectral behavior (spectra are not shown here). The quenching of FN fluorescence by $SnO_2$ colloid can be described by Stern-Volmer:

$$\frac{I_0}{I} = 1 + K_{SV}[Q], \quad (2)$$

where $I_0$ and $I$ are the fluorescence intensities of xanthene dyes in the absence and presence of $SnO_2$ colloid, respectively. $K_{SV}$ is Stern-Volmer constant and [Q] is the concentration of respective quencher. The ratios $I_0/I$ were calculated and plotted against quencher concentration according to (2).

The Stern-Volmer plot (Figure 6) for EN and ERN is obtained as upward curvature. These types of upward curvature suggest that it may follow static type of mechanism [34]. But, in the case of FN, it gives linear plot. The linear plot mostly results in dynamic quenching. But its $k_q$ value exceeds ($1 \times 10^{13}$ $M^{-1}$ $s^{-1}$) the limited values of dynamic quenching ($2 \times 10^{10}$ $M^{-1}$ $s^{-1}$), so it also may follow the static quenching.

*5.5. Fluorescence Lifetime Measurements.* In general, time resolved measurement is the most definitive method for differentiating static and dynamic quenching process. Figure 7 presents a representative plot of the logarithm of the relative fluorescence intensity versus time of EN in absence and presence of $SnO_2$ colloid, from which the lifetimes ($\tau_f$) of the excited singlet states were obtained by iterative reconvolution of the measured instrument response function.

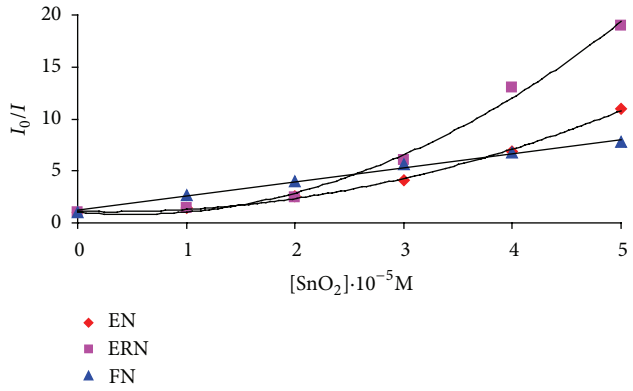



FIGURE 6: Stern-Volmer plot $I_0/I$ versus $[SnO_2]$ of FN, EN, and ERN dyes.

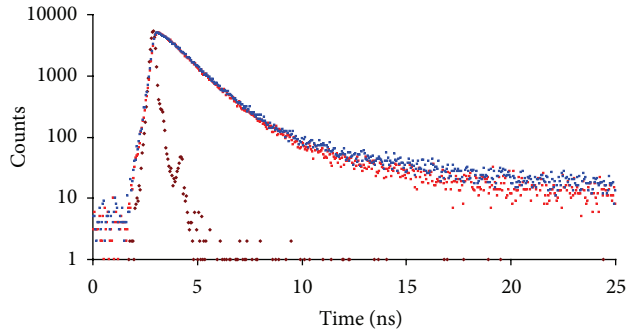



FIGURE 7: Fluorescence decay curve of (i) instrument response curve (Brown color decay), (ii) EN ($4 \times 10^{-6}$ M; red color), and (iii) EN in the presence of colloidal $SnO_2$ ($5 \times 10^{-4}$ M; blue color).

Fluorescence lifetime observed for EN is unchanged with addition of colloidal $SnO_2$. The other two dyes also follow the same trend (spectra are not shown here). This observation shows that quenching follows static mechanism. Static quenching does not decrease the lifetime because only the fluorescent molecules are observed, and the uncomplexed fluorophores have the unquenched lifetime [35]. Static quenching arises due to the formation of complex between fluorophore and the quencher. Hence the association constant ($K_{app}$) was calculated by the method given below.

The equilibrium between the adsorbed and unadsorbed dye molecules is expressed by using (3); in this equation $K_{app}$ is the apparent association constant which can be calculated from the fluorescence data by using the reported method [31]:

$$\mathrm{Dye} + \mathrm{SnO_2} \overset{K_{app}}{\rightleftharpoons} \mathrm{Dye}\cdots\mathrm{SnO_2}$$

$$K_{app} = \frac{[\mathrm{Dye}\cdots\mathrm{SnO_2}]}{[\mathrm{Dye}]\cdot[\mathrm{SnO_2}]} \tag{3}$$

$$\frac{1}{F_0 - F} = \frac{1}{F_0 - F'} + \frac{1}{K_{app}(F_0 - F')[\mathrm{SnO_2}]},$$

where $K_{app}$ is the apparent association constant, $F_0$ is the initial fluorescence intensity of dye molecules, $F'$ is the fluorescence intensity of $SnO_2$ adsorbed dyes, and $F$ is the observed fluorescence intensity at its maximum. Figure 8 shows the linear straight line dependence of $1/(F_0 - F)$ on the reciprocal concentration of colloidal $SnO_2$. The values are listed in Table 1.

$$\mathrm{Dye} + \mathrm{SnO_2} \rightleftharpoons [\mathrm{Dye}\cdots\mathrm{SnO_2}]$$
$$[\mathrm{Dye}\cdots\mathrm{SnO_2}] \overset{h\nu}{\rightleftharpoons} [\mathrm{Dye}^*\cdots\mathrm{SnO_2}]$$
$$[\mathrm{Dye}^*\cdots\mathrm{SnO_2}] \rightleftharpoons [\mathrm{Dye}^{\bullet+}\cdots{}^{\bullet-}e_{cb}\,\mathrm{SnO_2}]$$
$$[\mathrm{Dye}^{\bullet+}\cdots{}^{\bullet-}e_{cb}\,\mathrm{SnO_2}] \longrightarrow \mathrm{Dye}^{\bullet+} + {}^{\bullet-}e_{cb}\,\mathrm{SnO_2}$$

SCHEME 2: Schematic diagram describing the conduction and valence band potentials of $SnO_2$ and the electron-donating energy levels of dyes.

TABLE 1: Excitation ($\lambda_{ex}$) and emission ($\lambda_{em}$) wavelengths of the xanthene dyes and apparent association constant ($K_{app}$) from fluorescence data for dyes with colloidal $SnO_2$.

| S. number | Dyes | $\lambda_{ex}$ (nm) | $\lambda_{em}$ (nm) | $K_{app} \times 10^3$ $M^{-1}$ |
|---|---|---|---|---|
| 1 | Fluorescein | 478 | 513 | 16.6 |
| 2 | Eosin | 517 | 538 | 0.8766 |
| 3 | Erythrosine B | 526 | 550 | 0.7241 |

*The uncertainties of the estimated constants are ±6%.

The $K_{app}$ values decrease in the following order:

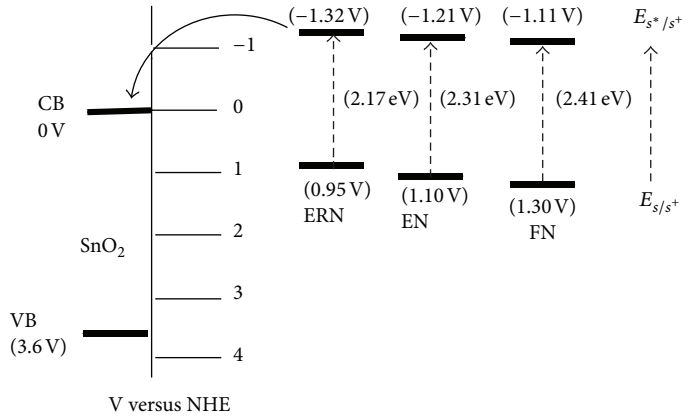
FN > EN > ERN.

This trend is observed due to the absence of bulkier electronegative group in FN. So the electrostatic interaction between the dye molecule and $SnO_2$ will be more. So it has higher $K_{app}$ values. But in the case of EN and ERN, it has four bulkier electronegative bromine and iodine atoms. So it has lower $K_{app}$ values.

*5.6. Mechanism of Quenching.* The fluorescence quenching of dyes by $SnO_2$ colloid may occur through two possible mechanisms such as energy or electron transfer. There is no overlap between the emission spectra of dyes with the absorption spectrum of $SnO_2$ colloid (Figure 9), and also the band-gap energy of $SnO_2$ ($E_g$ = 3.6 eV) [36] is greater than the excited state energy of dyes ($E_s$) shown in Table 2. Thus, energy transfer from excited dyes to $SnO_2$ colloid is not possible. It can therefore be concluded that the fluorescence quenching shown in Figure 5 should not be caused by energy transfer.

The possible way of quenching is through electron transfer from excited state dye molecules to the conduction band of $SnO_2$ colloid as shown in Scheme 2.

The feasibility of electron transfer from dyes to $SnO_2$ can be explained on the basis of energy level diagram based on the excited state oxidation potential of dyes obtained from the oxidation potential of dyes and their singlet state energy according to the equation, $E_{s/s^+} = E_{s/s^+} - E_s$, in Table 2, and the conduction band potential of $SnO_2$ lies around 0.0 eV as shown in Scheme 3. From the scheme we observed that the electron transfer process is feasible.




Scheme 3: Proposed electron transfer mechanism.

Table 2: Photophysical properties of xanthene dyes.

| S. no. | Dyes | $E_{(s)}$ (eV)[a] | $E_{s/s+}$ (V)[b] | $E_{s^*/s+}$ (V)[c] | $\Delta G_{et}$ (eV)[d] |
|---|---|---|---|---|---|
| 1 | Fluorescein | 2.41 | 1.30 | −1.11 | −1.11 |
| 2 | Eosin | 2.31 | 1.10 | −1.21 | −1.21 |
| 3 | Erythrosine B | 2.17 | 0.95 | −1.32 | −1.22 |

[a]Excited state energy of the dyes.
[b]The oxidation potentials of the ground state dyes in water versus NHE.
[c]Calculated from the equation, $E_{s^*/s+} = E_{s/s+} - E_s$, where $E_{s^*/s+}$ is the oxidation potential of the excited state dyes.
[d]Calculated from the Rehm-Weller equation.

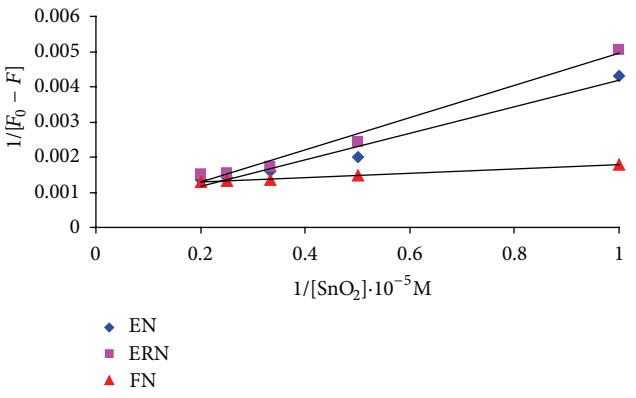



Figure 8: Linear straight line dependence of $1/F_0 - F$ on the reciprocal concentration of colloidal $SnO_2$.

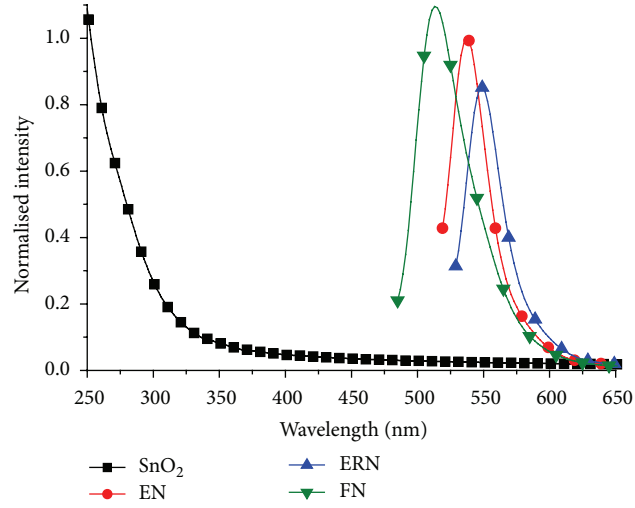



Figure 9: Combined absorption spectrum of colloidal $SnO_2$ (black) and emission spectra of dyes (green: FN, red: EN, and blue: ERN).

*5.7. Calculation of Free Energy Changes ($\Delta G_{et}$) for the Electron Transfer Reactions.* To have a better understanding of electron transfer, we have estimated free-energy change ($\Delta G_{et}$) for each dye-$SnO_2$ systems following Rehm-Weller equation [37]:

$$\Delta G_{et} = E_{1/2}{}^{(ox)} - E_{1/2}{}^{(red)} - E_{(s)} + C, \quad (4)$$

where $E_{1/2}{}^{(ox)}$ is the oxidation potential of the donor, $E_{1/2}{}^{(red)}$ is the reduction potential of the acceptor, $E_{(s)}$ is the excitation energy of the fluorescent state, and $C$ is the columbic term. Since one of the species is neutral and the solvent used is polar in nature, the columbic term in the above expression is neglected [38]. The $\Delta G_{et}$ values thus calculated for the electron transfer processes in the systems studied in water are all negative (Table 2). Hence, the ET processes were thermodynamically feasible [39].

## 6. Conclusion

The effect of colloidal $SnO_2$ nanoparticles on the absorption and fluorescence spectra of dyes such as eosin, erythrosine, and fluorescein has been studied. The result in perturbation

of the absorption spectrum shows the surface complex formation through adsorption of dyes on the surface of colloidal $SnO_2$. Static nature of quenching has been confirmed by unaltered fluorescence lifetime from time resolved measurements. Based on the energetic calculations the mechanism of electron transfer from excited state dyes to the conduction band of colloidal $SnO_2$ was suggested.

## Conflict of Interests

The authors declare that they have no conflict of interests.

## Acknowledgments

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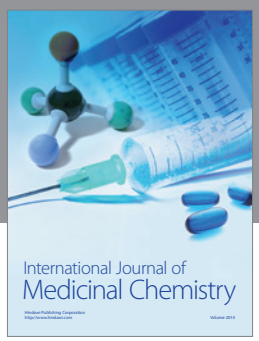

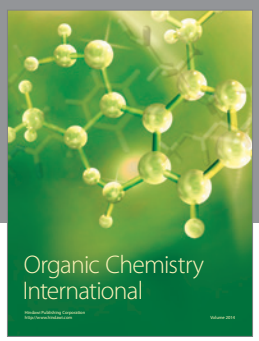

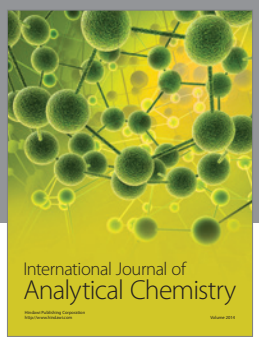

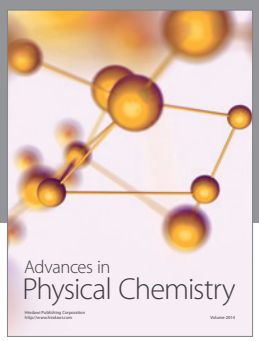

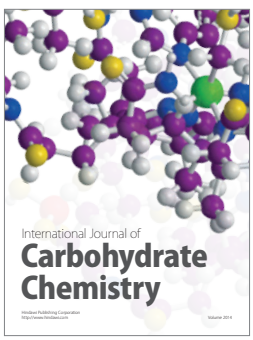

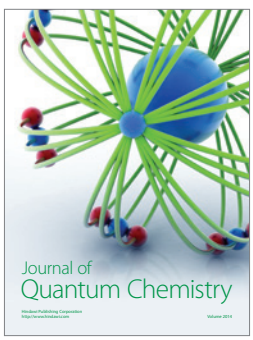

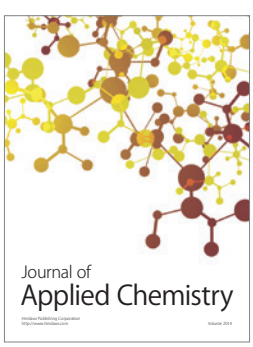

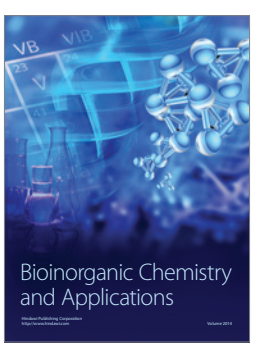

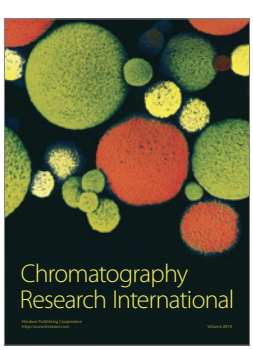

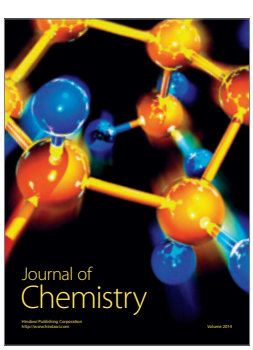

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