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Interaction of Schiff base ligand with tin dioxide nanoparticles: Optical studies

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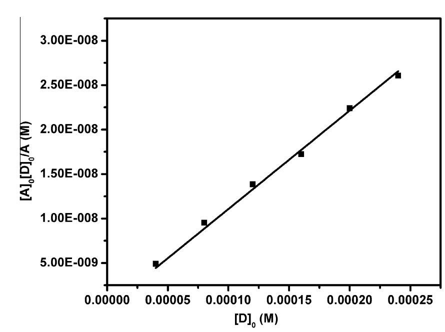
HIGHLIGHTS

- Optical studies of Schiff base (SB) ligand with semiconductor oxide NPs were studied.
- Weak interaction between BMTPMB and SnO_2 NPs was observed.
- Scott plot was employed to determine the molar absorptivity of the SB-NPs system.

GRAPHICAL ABSTRACT

Scott plot.



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ABSTRACT

Interaction between 1,4 Bis ((2-Methyl) thio) Phenylamino methyl benzene (BMTPMB) Schiff base with tin dioxide nanoparticles (SnO_2 NPs) of various concentrations in methanol have been studied using UV–Visible and Fluorescence spectroscopic techniques. The low value of Stern–Volmer quenching constant and non-linear plot of Benesi–Hildebrand equation suggests the less affinity of SnO_2 NPs towards the adsorption of BMTPMB Schiff base. The Scott equation has been employed to determine molar absorptivity of the Schiff base-NPs system.

Introduction

A Schiff base (or azomethine or imine) named after Hugo Schiff, is a functional group with the general formula of $R_1R_2C = N - R_3$, where *R* is an organic side chain. These bases can be synthesized by a nucleophilic addition of aromatic amine and a carbonyl compound followed a dehydration process to yield imine [1]. Schiff bases derived from aromatic amines and aromatic aldehydes have a wide variety of applications in many fields [2]. There has been an interest in the chemistry of metal complexes of Schiff bases containing N and S donor atoms because of their structural features and biological activities (antibacterial agents, antifungal agents, antitumour drugs) [3]. Neutral Schiff bases are used to prepare complexes with wide range of properties [4]. The preparation of mixed donor ligands has received great attention recently. Ligands that pair a hard donor group and a soft donor group are chiefly useful in catalysis [5]. Schiff bases may become promising dye

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sensitizer in molecular photovoltaic cells if combined with chelating activities and other properties [6]. 1,4 Bis ((2-Methyl) thio) Phenylamino methyl benzene (BMTPMB) is a neutral, sulfur-containing mixed-donor Schiff base ligand.

Nano-scale materials have fascinated much attention because of their excellent and attractive properties [7]. Semiconductor nanoparticles are the most promising ones due to their high photochemical stability and size tunable photoluminescence. Recently, n-type inorganic semiconductor materials have been studied because of their high electron mobility. Nanostructured metal oxides are interesting inorganic semiconductors because of the ease of fabrication, good control of film morphology, and interfacial properties [8]. Tin dioxide (SnO_2) is a n-type stable large band gap semiconductor (3.6 eV) which has been used in gas sensors and optoelectronic devices [7]. Although it does not respond to visible light excitation, it can be sensitized with organic dyes which in their excited state can inject electrons into the conduction band of a large band gap semiconductor [9,10]. Photosensitization is a convenient and useful method to extend the photo response of large band gap semiconductor [11]. In the recent years, surface modification of nanoparticles (NPs) with organic dye molecules has been intensively studied to obtain nanomaterials with enhanced optical, catalytic and sensing properties for molecular electronic application or light energy conversion system.

The electromagnetic interaction between the NPs and Schiff base dye molecules in the close vicinity modifies the electronic and optical properties of the surface bound molecule. As a consequence, the fluorescence intensity of dye molecule can be enhanced or decreased. That is, fluorescence quenching or enhancement depending on the location of the dye around the particle, its separation from the surface, and the molecular dipole orientation with respect to the particle surface. Taken into account of these features, here we report a study of interaction of BMTPMB Schiff base with SnO_2 nanoparticle.

Materials and methods

Chemicals

All chemicals used in this work were purchased from Merck with 99.9% purity and were used without further purification.

Preparation of Schiff base

1,4 Bis ((2-Methyl) thio) Phenylamino methyl benzene (BMTPMB) Schiff base was synthesized as follows: An alcoholic solution containing terphthalaldehde (1.34 g, 10 mM) and 2-(methylthio) aniline (2.78 g, 20 mM) taken in the 1:2 molar ratio was magnetically stirred for about 6 h and the contents were kept over-night. The pure yellow coloured fine crystals were filtered, washed with alcohol and dried. The dried powder was used for the analysis [5].

Preparation of SnO_2 nanoparticles

SnO_2 nanoparticles used in this study were synthesized using chemical precipitation method as follows: A 0.1 M solution of $SnCl_2 \cdot 5H_2O$ (4.5126 g) was prepared in the de-ionized water (200 ml) to get a mixed aqueous solution. Then ammonia was added into the mixed aqueous solution drop wise under vigorous stirring to get the pH value of the solution in the range of 8–9. Now, the precipitate had been formed at the bottom of the glass beaker. The precipitate was kept at room temperature for 2 h for ageing and then washed with deionized water. The washing was repeated for 5–6 times. The resulting precipitate was heated at 80 °C for 5 h. The dried precipitate was kept at 105 °C for 4 h, and it was loaded into the alumina crucible. Then it was annealed in a muffle furnace at 600 °C for 5 h in air to enhance the crystallinity of SnO_2. After the heat treatment, the product appeared to be white in color [12].

Experimental details

Procedure

The concentration of BMTPMB in methanol was maintained at 0.04 mM throughout the experiment. The concentration of SnO_2 nanoparticles in Schiff base solution was varied as 0.04 mM, 0.08 mM, 0.12 mM, 0.16 mM, 0.2 mM and 0.24 mM. For neat solution and also for each sample optical absorption and emission measurements were taken.

Measurements

The crystalline phase and size of SnO_2 nanoparticles annealed at 600 °C were determined by using XPERT-PRO X-ray powder diffractometer with Cu Kα radiation (λ = 0.1540 nm). High resolution Scanning electron microscopy (HRSEM) was performed using ZEISS field emission scanning electron microscope to observe the morphology of the SnO_2 nanoparticles. Absorbance and emission measurements were carried out with a Shimadzu UV-2450 UV–Visible spectrophotometer and Shimadzu RF-5301PC spectrofluorophotometer respectively. All measurements were performed at room temperature. The optical absorption and fluorescent measurements have been repeated for five times for each set of samples. It was noticed that the data are reproducible with an accuracy of ±0.1 nm. And hence, there is a good reliability of the data.

Results and discussion

Structural properties of SnO_2 nanoparticles

X-RD pattern of SnO_2 nanoparticles annealed at 600 °C is shown in Fig. 1. The diffraction peaks around 27°, 34°, 38° and 52° are assigned to (1 1 0), (1 0 1), (2 0 0), (2 1 1) (PDF No. 88-0287) planes of SnO_2 respectively. The planes in the X-RD pattern confirm the tetragonal structure of SnO_2.The broad diffraction peaks indicate that the crystalline size of the nanoparticles is small [13].

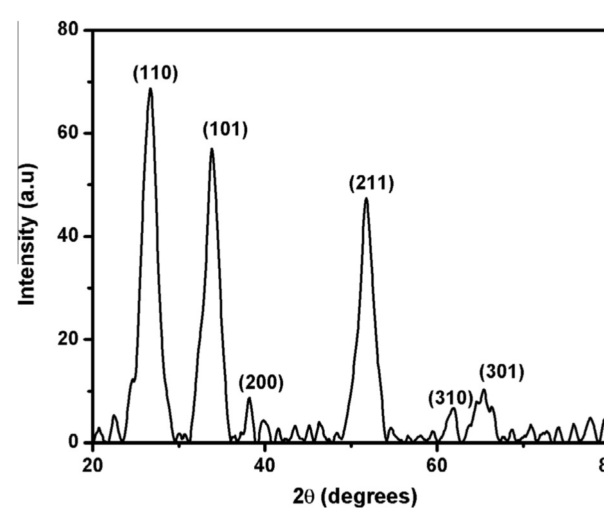

Fig. 1. X-RD pattern of SnO_2 nanoparticles.

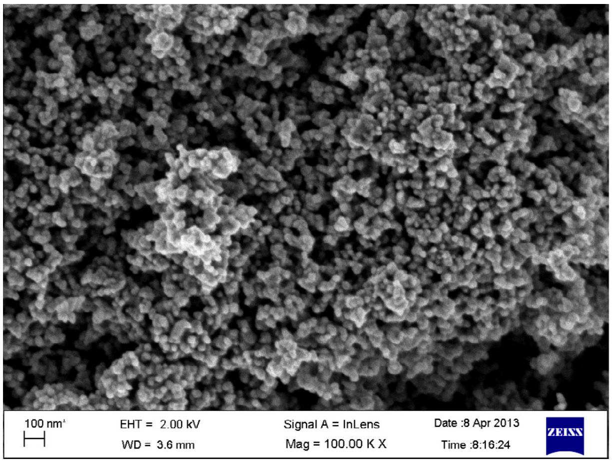

Fig. 2. SEM image of SnO_2 nanoparticles.

Fig. 2 shows the HRSEM image of the SnO_2 nanoparticles. The spherical grain morphology of SnO_2 nanoparticles is observed. The average particle size of the SnO_2 nanoparticles obtained from HRSEM is around 30 nm.

Optical absorption and emission studies

Molecular structure of BMTPMB is shown in Fig. 3. In this structure, the outer benzene rings are twisted away from coplanarity with the central benzene ring due to steric repulsion between the hydrogen atoms attached to the cyno group and CH group of the outer benzene ring [6]. The absorption spectrum of BMTPMB in methanol is presented in Fig. 4. A broad absorption band in the region 300–400 nm observed in the spectrum suggests the presence of π–π^* transitions involving the molecular orbitals located at the phenolic chromophores. And the bands in the UV region are due to n–π^* transitions relating the imine chromophore orbitals and phenyl ring electrons [14]. The broad band at 378 nm is taken for the present investigation. Fig. 5 shows the UV–Visible spectrum of SnO_2 nanoparticles in methanol. Fig. 6 exhibits the absorbance spectra of BMTPMP with various concentrations of SnO_2 nanoparticles. As the concentration of SnO_2 NPs varies, a change in optical density occurs without change in absorption maximum. This may due to the interaction of Schiff base compound and SnO_2 nanoparticles. Fig. 7 shows the emission spectrum of BMTPMB Schiff base in methanol. Emission spectra of Schiff base with SnO_2 NPs of various concentrations are displayed in Fig. 8. A decrease in fluorescence intensity is observed as the

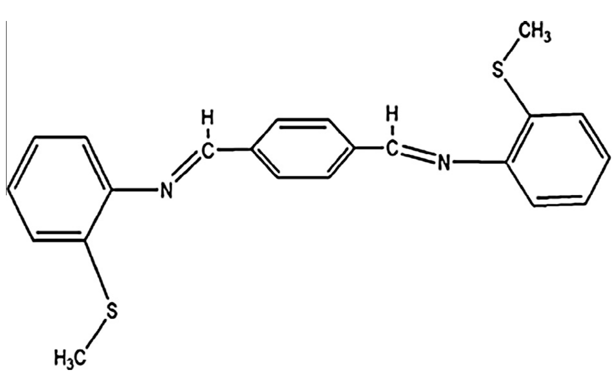

Fig. 3. Molecular structure of BMTPMB.

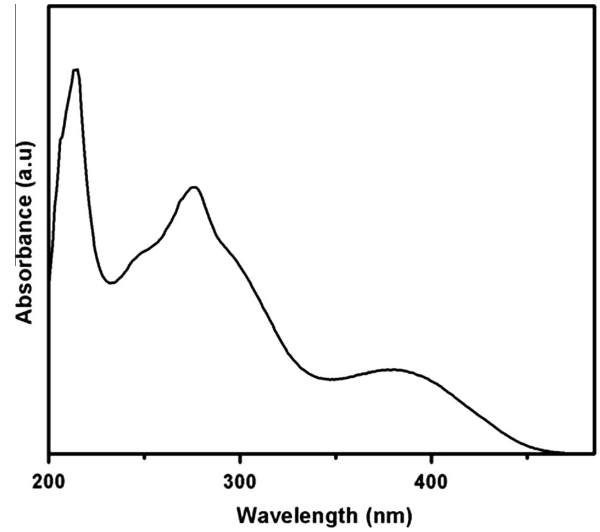

Fig. 4. Absorption spectrum of BMTPMB in methanol.

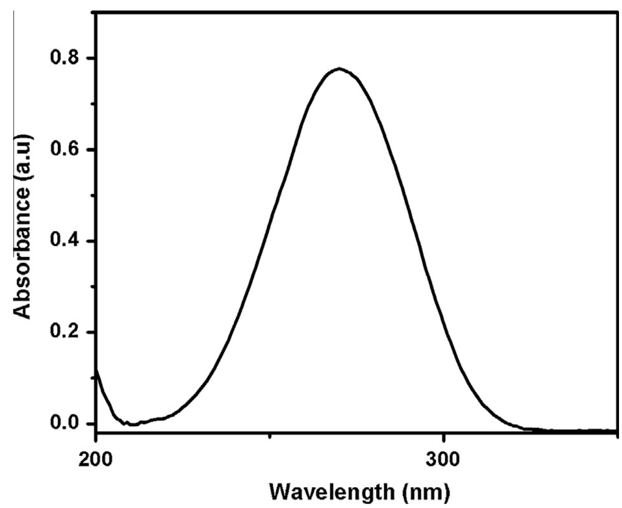

Fig. 5. UV–Visible spectrum of SnO_2 NPs in methanol.

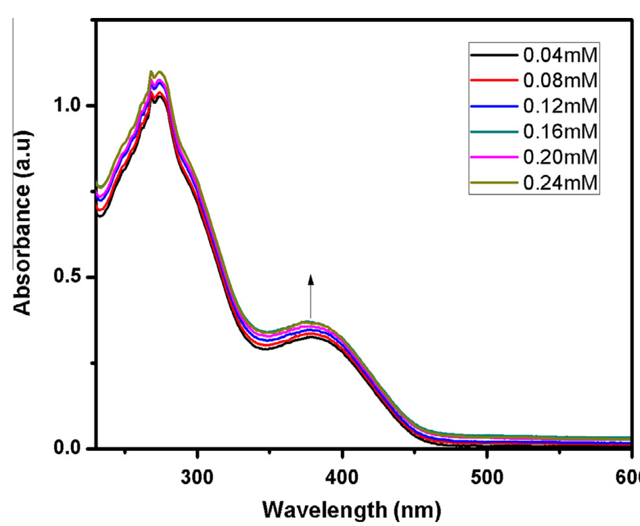

Fig. 6. Absorption spectrum of BMTPMB in various concentrations of tindioxide nanoparticles.

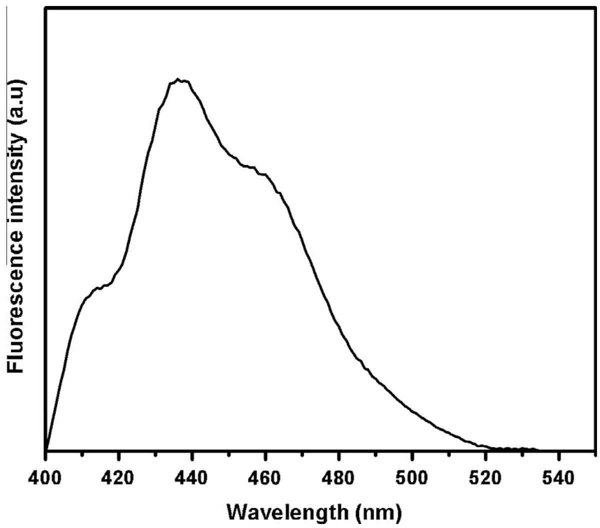

Fig. 7. Fluorescence spectra of BMTPMB in methanol.

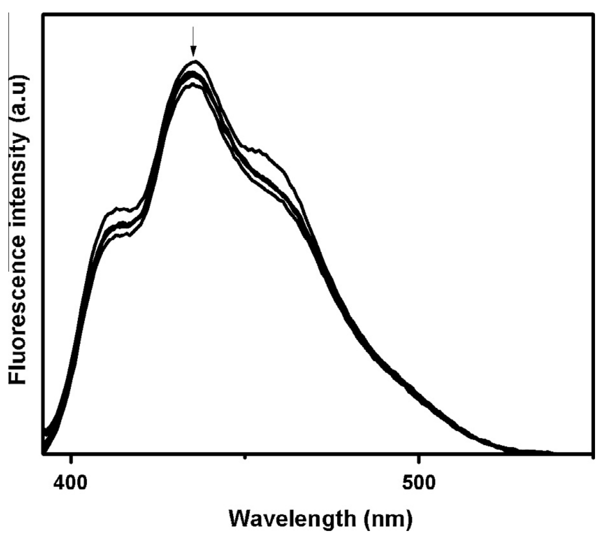

Fig. 8. Fluorescence spectra of BMTPMB in various concentrations of tindioxide nanoparticles.

concentration of SnO_2 NPs increases. This decrease suggests the existence of the interaction of probe molecule and SnO_2 NPs.

Fluorescence quenching is the decrease of the quantum yield of fluorescence from a fluorophore induced by a variety of molecular interactions with a quencher molecule. Fluorescence quenching can be static, resulting from the formation of a ground state complex between the fluorophore and a quencher or dynamic, resulting form collisional encounters between the fluorophore and quencher. In both cases, molecular contact is required between the fluorophore and the quencher. Collisional quenching of fluorescence has been thoroughly studied during the last decades because it is of considerable interest for physical chemistry as well as for biochemistry and biophysics where quenching is frequently used to elucidate structure and functional features of the systems [15]. Under the experimental condition, it is important to note that excitation wavelength of the Schiff base does not coincide with the absorption peak of SnO_2 NPs. Therefore, it can be concluded that the absence of Forster energy transfer between Schiff base and SnO_2 NPs. The quenching of Schiff base indicates that the nanosize particles are responsible for this effect. And no discernible change in shapes of the fluorescence spectra was observed upon quenching. To illustrate the quenching effect of SnO_2 NPs on the fluorescence intensity of Schiff base, Stern–Volmer equation, $F_0/F = 1 + K_{sv}[Q]$ where F_0 and F are the fluorescence intensities of Schiff base in absence and presence of quencher [Q] respectively, is applied. The plot of F_0/F vs $[SnO_2]$ has been shown in Fig. 9a. The relative intensity of the Schiff base is found to increase with increasing SnO_2 NPs concentration. The plot is linear with $K_{sv} = 52$ M^{-1}. The linearity of the S–V plot indicates that only one type of quenching occurs in the system. In the presence of quencher, the absorption spectra of Schiff base remain unaltered. This indicates that static quenching does not occur [16]. The Stern–Volmer quenching constant is low indicating the adsorption of only a few probe molecules on the quencher surface. The quenching of the fluorescence of probe by SnO_2 NPs in methanol also suggests that the electrostatic effect between the sulfur containing mixed-donor dye and the n-type quencher may be responsible for the low quenching effect. As BMTPMB molecule exhibits TICT (Twisted intramolecular charge transfer) in the excited state [4], the outer benzene rings in the probe molecule are twisted such that they come into coplanarity with the central benzene ring. Now all the benzene rings come to the same plane and this geometrical arrangement may restrict the collisions between the fluorophore and the SnO_2 NPs. This could also be a possible reason for the observed low quenching effect.

To observe one-to-one binding between a Schiff bases (Guest) and the NPs (Host), the Benesi–Hildebrand method can be employed [10]. The dependence of the fluorescence intensity upon quencher concentration is also presented as a plot between [D]/A and $1/[SnO_2]$ (Fig. 9b). Benesi–Hildebrand plot deviates from its linear nature and exhibits scatter plot characteristics. This suggests a weak association between the probe and SnO_2 NPs. Hence, the association constant could not be deduced. The Scott's equation [17] which is given below as

$$[A]_0[D]_0/A = (1/\varepsilon)[D]_0 + 1/K,$$

where $[A]_0$ is the concentration of Schiff base and $[D]_0$ concentration of SnO_2 NPs and A is the absorbance of the Schiff base – NPs system, ε is the molar absorptivity and K is the association constant. This is made use of presenting a plot (Fig. 9c) of $[A]_0[D]_0/A$ vs $[D]_0$, which is

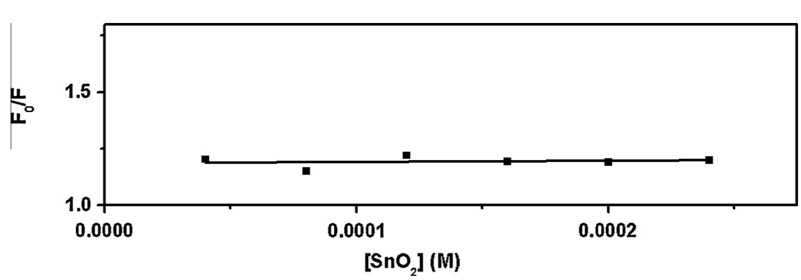

Fig. 9a. Relative fluorescence intensity of BMTPMB in various concentrations of tindioxide nanoparticles.

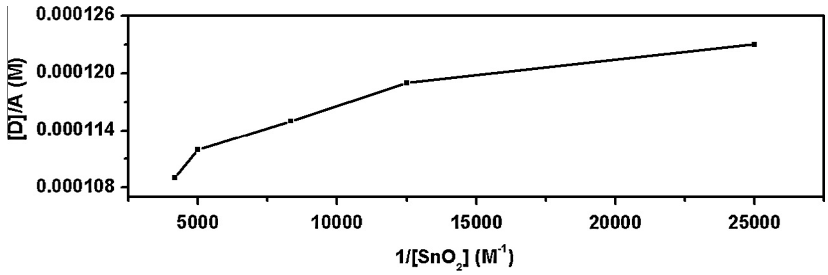

Fig. 9b. $[D]/[A]$ vs $1/[SnO_2]$.

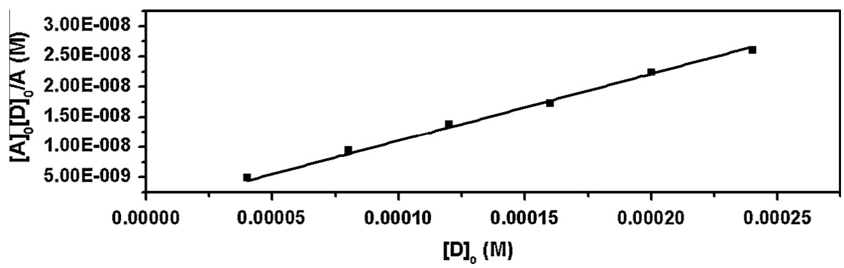

Fig. 9c. Scott plot for the BMTPMB–SnO_2 NPs system.

linear with the intercept at origin as expected. Hence only molar absorptivity ε can be evaluated. From the slope, ε is deduced as $9.03 \times 10^3\ M^{-1}\ m^{-1}$. The lower molar absorptivity compared to the neat Schiff base solution ($1.5 \times 10^6\ M^{-1}\ m^{-1}$) could be due to the reduced intensity of π–π^* transitions of Schiff base–NPs system.

Conclusion

Optical absorption and fluorescence emission studies on Schiff base with SnO_2 NPs of various concentrations have been carried to study the interaction of BMTPMB Schiff base with SnO_2 nanoparticles. The signatures, change in optical density and a decrease in fluorescence intensity of BMTPMP with various concentrations of SnO_2 nanoparticles, attribute to the interaction of probe molecule with SnO_2 NPs. The low quenching constant value and the scatter plot characteristics of Benesi–Hildebrand plot suggest the interaction between Schiff base and SnO_2 NPs is weak. The Scott's plot is linear with the molar absorptivity value as $9.03 \times 10^3\ M^{-1}\ m^{-1}$.

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References

[1] Mohammad Reza Ganjali, Mehdi Tavakoli, Farnoush Faridbod, Siavash Riahi, Parviz Norouzi, Masoud Salavati-Niassari, Int. J. Electrochem. Sci. 3 (2008) 1559–1573.
[2] Mohamed N. Ibrahim, Salah E.A. Sharif, E-J. Chem. 4 (2007) 531–535.
[3] C.G. Hamaker, O.S. Maryshina, D.K. Daley, A.L. Wadler, J. Chem. Crystallogr. 40 (2010) 34–39.
[4] G. Suganthi, S. Sivakolunthu, V. Ramakrishnan, J. Fluoresc. (2010) 666–675.
[5] Christopher.G. Hamaker, Benjamin.P. Oberts, J. Chem. Crystallogr. 36 (2006) 735–742.
[6] Haulk Dincalp, Sinem Yavuz, Ozgul Hakli, Ceylan Zafer, Cihan Ozsoy, Inci Durucasu, Siddik Icli, J. Photochem. Photobiol. A 210 (2010) 8–16.
[7] Srabanti Ghosh, Abhijit Saha, Nano. Res. Lett. 4 (2009) 937–941.
[8] Naomi kudo, Yuta Shimazaki, Hideo Ohkita, Masataka Ohoka, Shinzaburo Ito, Sol. Energy Mater. Sol. Cells 91 (2007) 1243–1247.
[9] Said Barazzouk, Hong Lee, Surat Hotchandani, Prashant V. Kamat, J. Phys. Chem. B 104 (2000) 3616–3623.
[10] G. Suganthi, C. Meenakshi, V. Ramakrishnan, J. Fluoresc. 20 (2010) 1017–1022.
[11] Di. Liu, Richard W. Fessenden, Gordon L. Hug, Prashant V. Kamat, J. Phys. Chem. B 101 (1997) 2583–2590.
[12] P. Sangeetha, V. Sasirekha, V. Ramakrishnan, J. Raman spectrosc. 42 (2011) 1634–1639.
[13] K. Anandan, V. Rajendran, J. Non-oxide Glasses 2 (2010) 83–89.
[14] Jose Maria Abad, Monica Revenga-Parra, Tania Garcia, Miriam Gamero, Encarnacion Lorenzo, Felix Pariente, Phys. Chem. Chem. Phys. 13 (2011) 5668–5678.
[15] Ping Mei, Li-Xia Zhang, Yi Liu, Li-Hua Cai, Pei-Zhi Hu, Chin. J. Chem. 26 (2008) 85–91.
[16] Smritimoy Pramanik, Subhash chandra Bhattacharya, Toyoko Imae, J. Lumin. 126 (2007) 155–159.
[17] Pushkin M. Qureshi, Rishi K. Varshney, Sant Bahadur Singh, Spectrochim. Acta A. 50 (1994) 1789–1790.