Excitation wavelength dependent fluorescence behaviour of nano colloids of ZnO

Litty Irimpan[1]**, Bindu Krishnan**[2]**, A Deepthy**[3]**, V P N Nampoori**[1] **and P Radhakrishnan**[1]

[1] International School of Photonics, Cochin University of Science and Technology, Cochin, Kerala, India
[2] Centre for Materials for Electronics Technology, Thrissur, India
[3] Amrita Institute of Medical Sciences, Cochin, India

E-mail: littyirimpan@yahoo.co.in

Abstract
In this paper, the fluorescence behaviour of nano colloids of ZnO has been studied as a function of the excitation wavelength. We have found that excitation at the tail of the absorption band gives rise to an emission that shifts with the change of the excitation wavelength. The excitation wavelength dependent shift of the fluorescence maximum is measured to be between 60 and 100 nm. This kind of excitation wavelength dependent fluorescence behaviour, which may appear to be in violation of Kasha's rule of excitation wavelength independence of the emission spectrum, has been observed for nano ZnO colloids prepared by two different chemical routes and different capping agents. It is shown that the existence of a distribution of energetically different molecules in the ground state coupled with a low rate of the excited state relaxation processes, namely, solvation and energy transfer, are responsible for the excitation wavelength dependent fluorescence behaviour of the systems.

1. Introduction

Semiconductor nanoparticles have been under continuous scientific interest because of their unique quantum nature, which changes the optical properties of materials [1]. ZnO is a wide and direct band gap (about 3.37 eV) II–VI semiconductor with many applications, such as a transparent conductive contact, thin-film gas sensor, varistor, solar cell, luminescent material, surface electro-acoustic wave device, heterojunction laser diode, ultraviolet (UV) laser and others [2]. Recently, interest in short wavelength display devices has increased. The possibility of tailor making of bulk material properties by varying the size, structure and composition of the constituting nanoscale particles make them candidates for various important applications in the field of new material research. Optical methods give rich experimental information about the energetic structure of these finite-size solids. Understanding of size-dependent optical properties of semiconductor clusters has been achieved in a number of

theoretical publications for a long time [3]. Development of methods of preparation and stabilization of monodispersed semiconductor nanoparticles in transparent colloids offers a good opportunity of experimental verification of theoretical predictions.

In this paper, the excitation wavelength dependent fluorescence behaviour of nano colloids of ZnO is reported. The steady state absorption and fluorescence behaviour of nano colloids of ZnO, in which spectra are sensitive to the polarity of the surrounding environment, has been studied with a view to obtaining information on the polarity of these liquids. Time-resolved fluorescence studies on dipolar solutes, which have revealed wavelength dependence of the fluorescence decay profiles and dynamic fluorescence Stokes shift in the ps–ns time scale [4–7], have thrown insight into the mechanism of solvation. The excitation at the tail of the absorption band gives rise to an emission that shifts with the change of the excitation wavelength [8–9]. This kind of excitation wavelength dependent fluorescence behaviour has

also been observed for some dipolar solutes in ionic liquids. In this paper, we have highlighted the excitation wavelength dependent emission behaviour of the nano colloids of ZnO. This behaviour is considered unusual as the literature suggests that ZnO does not exhibit excitation wavelength dependent behaviour [10, 11] and the observed behaviour is contrary to what is prescribed by the well-known Kasha's rule of excitation wavelength independence of the emission spectrum [12]. To understand the origin of this behaviour, we have undertaken the present investigation on nano ZnO colloids prepared in two different media of different viscosities. The behaviour of these systems that show excitation wavelength dependent fluorescence spectra is also examined by capping them with two different capping agents.

2. Experiment

In this work, ZnO is prepared by two different chemical routes and different capping agents like poly vinyl pyrrolidone(PVP) and poly ethylene imine(PEI) have been used. Synthesis by chemical route has the advantage of being more economical compared with the complex epitaxial methods. In addition, various capping agents can be used to prevent growth and modify the size and shape.

Colloids of ZnO are synthesized by a modified polyol precipitation method [13, 14]. The monodisperse ZnO colloidal spheres are produced by a two-stage reaction process. The method of preparation involves the hydrolysis of zinc acetate dihydrate (ZnAc; Merck) in diethylene glycol medium (DEG; Merck). Among the different polyols, diethylene glycol is chosen because it is reported to give particles with uniform shape and size distribution. The size of the particles and hence the stability of this colloidal suspension depend on the concentration of zinc acetate as well as on the rate of heating. The molar concentration of precursor solution is varied from 0.01 mM to 0.01 M and a heating rate of 4 °C per minute is employed and the ZnO is formed at a temperature of 120 °C. The product from the primary reaction is placed in a centrifuge and the supernatant (DEG, dissolved reaction products, and unreacted ZnAc and water) is decanted off and saved. A secondary reaction is then performed to produce the monodisperse ZnO spheres. Prior to reaching the working temperature, typically at 115 °C, 5 ml of the primary reaction supernatant is added to the solution. After reaching 120 °C, it is stirred for 1 h, to get a monodisperse stable colloid.

In the second method that we adopted, 1 mM zinc acetate is dissolved in isopropyl alcohol (IPA-Merck, HPLC grade) by stirring at 50 °C in the presence of capping agent, PVP (Sisco). ZnO colloid is formed when it is hydrolyzed with sodium hydroxide under ultrasonification for 2 hours. In the third method, we used another cationic dispersant PEI (Sigma Aldrich) as capping agent [15]. PEI is a polyelectrolyte and it makes the surface positively charged. The positive charges repel from each other and prevent agglomeration. The long polymeric chains of PEI, on the other hand, effectively cap the surface as soon as nucleation occurs and prevents growth. Thus, a polyelectrolyte can make a stable nano semiconductor crystal colloid by a dual mechanism.

The ZnO colloids are characterized by optical absorption measurements recorded using spectrophotometer (JascoV-570 UV/VIS/IR). The cluster sizes are calculated from the
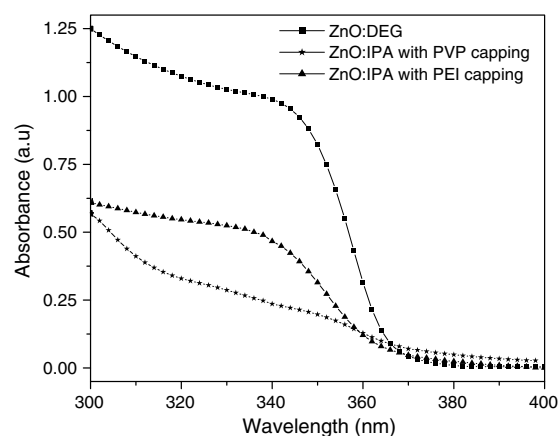

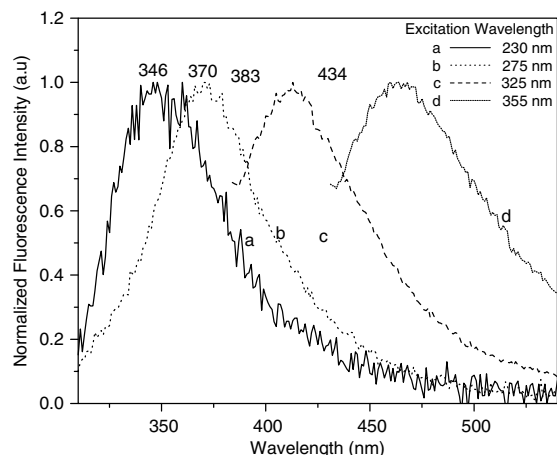**Figure 1.** Absorption spectra of nano colloids of ZnO.

absorption spectra using the analytical formula given by Viswanatha *et al* [16]. The fluorescence emission from ZnO colloids is recorded using a Cary Eclipse fluorescence spectrophotometer (Varian). The fluorescence spectra are corrected for the instrumental response.

3. Results and discussions

Figure 1 gives the room temperature absorption spectra of the ZnO colloids. The absorption edge is found to be blue shifted (370–350 nm) with decreasing particle size from that of bulk ZnO (375 nm) which could be attributed to the confinement effects [17]. The pronounced dependence of the absorption band gap on the size of ZnO nano crystals is used to determine the particle size. To get a precise measure of the shift, the first derivative curve of the absorption spectrum is taken and the point of inflection is taken as the absorption edge. From the shift of absorption edge, size of the dots is calculated with an error percentage of ±0.2 nm [16].

Figure 2 shows the excitation wavelength dependent fluorescent behaviour in nano colloids of ZnO prepared by polyol method. Although both the absorption and emission band positions are dependent on the polarity of the medium, the fluorescence spectrum is much more sensitive to the medium than the absorption spectrum. This is evident from the fact that, when the solvent is changed from isopropyl alcohol to polar diethylene glycol, the absorption maximum shifts by only 7–8 nm, whereas the emission maximum shifts by more than 20 nm. This behaviour is suggestive of an emitting state that is more polar than the ground state.

When ZnO prepared in DEG medium is excited at the UV side (say, at 230–240 nm) of the absorption maximum, the fluorescence maximum (λ_{em}^{max}) of ZnO is observed at 346 nm. Interestingly, as seen from figure 2, as the excitation wavelength is progressively shifted towards the red side of the maximum, a small but steady shift of the fluorescence maximum is clearly visible. The dependence of λ_{em}^{max} of ZnO of different particle sizes prepared by polyol method on the excitation wavelength (λ_{ex}) is shown in figure 3. The extent of the shift, as measured from λ_{em}^{max}, is around 90 nm. Figure 4 shows the dependence of λ_{em}^{max} on the excitation wavelength of nano colloids of ZnO prepared in different media by using different capping agents. The excitation wavelength
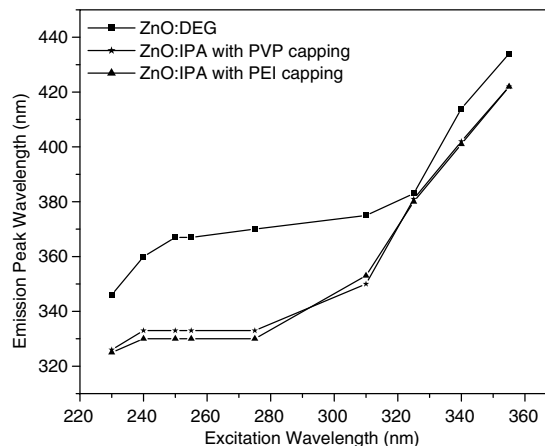
Figure 2. Normalized fluorescence spectra of ZnO nano colloid as a function of excitation wavelength. The fluorescence spectra have been corrected for the instrumental response.
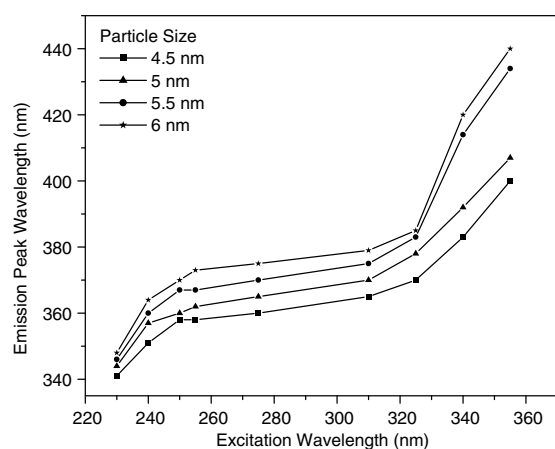
Figure 3. λ_{em}^{max} versus λ_{ex} plots of nano colloids of ZnO of different sizes prepared by polyol synthesis.

Figure 4. λ_{em}^{max} versus λ_{ex} plots of nano colloids of ZnO prepared in different media using different capping agents.

dependence of emission maxima is different for colloids prepared in different media. The shift remains the same when we change the capping agent in the same media. ZnO exhibits more pronounced excitation wavelength dependence in relatively more viscous diethylene glycol medium compared with isopropyl alcohol medium.

This is our first observation of an excitation wavelength dependent behaviour of nano colloids ZnO. When the homogeneous nature of the ZnO colloids and the literature data of fluorescence emission behaviour already studied are taken into consideration, the present observation appears to be quite unusual. However, we note that, when excited at the long wavelength edge of the first absorption band, a red shift of λ_{em}^{max} of the dipolar molecules is often observed in low-temperature glasses, polymer matrixes and organized assemblies such as micelles, vesicles, proteins and membranes [18, 19]. This phenomenon is termed the 'red-edge effect' (REE), [20,21] but is also sometimes called the edge excitation shift (EES) [19] the edge excitation red shift (EERS), [22, 23] or the red-edge excitation shift (REES) [24, 25]. We prefer to use the REE terminology, as this happens to be the first abbreviation for the observed phenomenon [20, 21]. This is primarily due to the fact that (i) the probe molecules absorbing at the red

edge of the absorption band have greater interaction with the solvent molecules than those absorbing in the blue side and (ii) the inhomogeneous broadening can only be probed at the red excitation edge where the excitation to the higher vibrational levels does not interfere with this selection.

The excitation wavelength dependence can arise when there exists a distribution of the molecules in the ground state that differ in their solvation sites and, hence, their energies. This inhomogeneity can originate from the difference in the interaction energies between the medium and the nano particles. However, the presence of an ensemble of energetically different molecules in the ground state *alone* does not guarantee an excitation wavelength dependent fluorescence behaviour because rapid relaxation of the excited state, such as the solvation of the fluorescent state or energy transfer between the energetically different excited states of the molecules, is expected to result in emission from the lowest energy state irrespective of the excitation. It is only when a system allows selective excitation of the energetically different species and the relaxation of the fluorescent state is slow (hence, incomplete) that REE can be expected.

Since inhomogeneous broadening, which dictates photo-selection of the energetically different species, is directly proportional to the change of dipole moment ($\Delta\mu$) on electronic excitation, the probe molecules with large $\Delta\mu$ values are the most suitable candidates to exhibit REE. The change in the dipole moment of ZnO upon electronic excitation is reported to be high [26]. The second factor, which is even more important than the first, is that ZnO has a rather short fluorescence lifetime (τ_f). The bandgap fluorescence of ZnO has an extremely short lifetime and it is reported to be 100 ps [27]. On the other hand, recent studies on solvation dynamics suggest that solvation is a rather slow process [28]. The solvent relaxation time (τ_{sol}) of the medium is of the order of nanoseconds. Because τ_{sol} around the photoexcited molecule is an order of magnitude higher than the τ_f value, it is not difficult to understand why unrelaxed fluorescence, which gives rise to the excitation wavelength dependent emission behaviour, could be observed in the case of nano colloids of ZnO. When the τ_f values are higher than the τ_{sol} value of the solvent, the fluorescence occurs from a fully solvated state in these molecules. Potentially, lifetime shortening with decrease in particle size has been recently

found in KrN clusters [15]. This model also explains that the more short wave emission with a shorter lifetime originates from smaller clusters. Due to the low concentration of ZnO colloids of small particle size, the energy transfer between the upper vibrational level and the lower vibrational level of the excited state of these particles is inefficient owing to the short fluorescence lifetime and thus the emission characteristics change with excitation wavelength.

Probe molecules with short fluorescence lifetimes are more likely to exhibit REE than those with long lifetimes. The larger the polarity and nuclear polarizability of the medium, the stronger is the interaction of the probe molecule with the solvent and higher is the chance to observe REE. The more viscous is the medium, the slower is the excited state relaxation process (intramolecular) and higher is the possibility to observe REE. The molecule fluoresces efficiently and the quantum yield increases strongly with increase in viscosity. This dependence of the fluorescence yield on viscosity and polarity was studied previously [29]. The viscosity and possibly hardness of the medium play a dominant role in the fluorescence efficiency of the molecule. These data can be understood by considering the effect that viscosity has on the rotation of the active molecule. When these levels, modes, are hindered because of the increase in the viscosity, the rates of rotation and vibration decrease with the eventual cessation of several modes of rotation and vibration in viscous medium and solid matrices. This decrease in the active modes leads to a weaker coupling of the excited electronic states with upper levels of the ground state, which results in a decrease in the energy dissipation rate of the excited state by means of internal radiationless channels to the ground states. Consequently the rate of population decay via radiative transitions increases and there is higher possibility to observe REE. Thus the high viscosity of the medium and short fluorescence lifetime, which makes the relaxation of the photoexcited species inefficient, contributes to REE-like behaviour in nano colloids of ZnO with smaller particle size.

The excitation wavelength dependent emission behaviour in nano collids of ZnO is not due to any specific interaction between the medium and ZnO, but is due to incomplete solvation of the fluorescent state in the viscous medium. This is evident from the fact that ZnO exhibits shift of the λ_{em}^{max} in two mediums prepared by different methods. Therefore, it can be concluded that it is the incomplete solvation (relaxation) in these viscous media that is primarily responsible for the excitation wavelength dependent spectral shift of nano colloids of ZnO.

In the case of ZnO, the electrostatic interaction is expected to dominate the other interactions and probably plays the most important role in creating a distribution of energetically different molecules in the ground state that allows their photoselection. Two factors could be responsible for the slow relaxation of the excited state: retardation of solvation due to the electrostatic forces induced by charged ZnO and/or an inefficient energy transfer between the energetically different species. In the absence of any literature data on solvation dynamics, it is not possible to pinpoint at this stage whether one or both the factors contribute to REE in ZnO. Further studies, both theoretical and experimental, need to be carried out to obtain insight into this aspect and is in progress. Regarding

excited state relaxation, an inefficient energy transfer between the energetically different molecules, as has been demonstrated earlier [20, 21] presumably contributes to the excitation wavelength dependent fluorescence behaviour in this case.

4. Conclusions

Herein, we have highlighted some of our recent observations on the excitation wavelength dependence of the fluorescence behaviour in nano colloids of ZnO. The fluorescence maximum shifts towards red as the excitation wavelength is increased. This observation has been attributed to the presence of energetically different associated forms of the constituent molecules and slow rate of the excited state relaxation process in these media. In essence, the inefficient energy transfer between the upper and the lower vibrational levels of the excited state of these particles owing to short fluorescence lifetime is primarily responsible for the excitation wavelength dependent spectral shift of ZnO colloids.

Acknowledgments

References

[1] Wang Y and Herron N 1991 *J. Phys. Chem.* **95** 525
[2] Studenikin S A, Cocivera M, Kellner W and Pascher H 2000 *J. Lumin.* **91** 223
[3] Brus L 1986 *J. Phys. Chem.* **90** 2555
[4] Karmakar R and Samanta A 2003 *J. Phys. Chem.* A **107** 7340
[5] Saha S, Mandal P K and Samanta A 2004 *Phys. Chem. Chem. Phys.* **6** 3106
[6] Chakrabarty D, Seth D, Chakraborty A and Sarkar N 2005 *J. Phys. Chem.* B **109** 5753
[7] Mandal and Samanta A 2005 *J. Phys. Chem.* B **109** 15172
[8] Paul A, Mandal P K and Samanta A 2005 *Chem. Phys. Lett.* **402** 375
[9] Paul A , Mandal P K and Samanta A 2005 *J. Phys. Chem.* B **109** 9148
[10] Nyffenegger R M, Craft B, Shaaban M, Gorer S, Erley G and Penner R M 1998 *Chem. Mater.* **10** 1120
[11] Kim S-W, Fujita S and Fujita S 2002 *Appl. Phys. Lett.* **81** 5036
[12] Birks J B 1970 *Photophysics of Aromatic Molecules* (New York: Wiley)
[13] Jezequel D, Guenot J, Jouini N and Fievet F 1995 *J. Mater. Res.* **10** 77
[14] Seelig E W, Tang B, Yamilov A, Cao H and Chang R P H 2002 *Mater. Chem. Phys.* **9712** 1
[15] Monticone S, Tufeu R and Kanaev A V 1998 *J. Phys. Chem.* B **102** 2854
[16] Viswanatha R, Sapra S, Satpati B, Satyam P V, Dev B N and Sharma D D 2004 *J. Mater. Chem.* **14** 661
[17] Luna-Moreno D, De la Rosa-Cruz E, Cuevas F J, Regalado L E, Salas P, Rodríguez R and Castano V M 2002 *Opt. Mater.* **19** 275
[18] Demchenko A P 2002 *Luminescence* **17** 19
[19] Lakowicz J R and Keating-Nakamoto S 1984 *Biochemistry* **23** 3013
[20] Valeur B and Weber G 1977 *Chem. Phys. Lett.* **45** 140
[21] Weber G and Shinitzky M 1970 *Proc. Natl. Acad. Sci. USA* **65** 823
[22] Itoh K and Azumi T 1973 *Chem. Phys. Lett.* **22** 395
[23] Itoh K-I and Azumi T 1975 *J. Chem. Phys.* **62** 3431

[24] Lakowicz J R 1999 *Principles of Fluorescence Spectrosopy* 2nd edn (New York: Plenum)

[25] Chattopadhyay A and Mukherjee S 1999 *J. Phys. Chem.* B **103** 8180

[26] Bhatti H S, Gupta A, Verma N K and Kumar S 2006 *J. Mater. Sci.: Mater. Electron.* **17** 4

[27] Bahnemann D W, Kormann C and Hoffmann M R 1987 *J. Phys. Chem.* **91** 3789

[28] Smith I K, Andrews S R, Williams G and Holmes P A 1996 *J. Mater. Chem.* **6** 539

[29] Dvornikov A, Liang Y and Rentzepis P 2005 *J. Mater. Chem.* **15** 1072