

## Study of Energy Transfer from Zinc Oxide Nanocrystals to Europium and Terbium Ions for the Development of Red, Green and White Light Emitting Thin-Films

Lanthanide rare-earth (RE) ions are important materials which have been extensively studied for their applications in lighting and display technologies. RE ions, especially Europium (III) ions and Terbium (III) have been used as phosphors to create red and green light emitting devices, respectively.  $\text{Eu}^{3+}$  ions give pure sharp red emission at 614 nm and  $\text{Tb}^{3+}$  ions give pure sharp green emission at 545 nm upon excitation. These are ideal for creating solid state lighting devices. However, these RE ions have their limitations, which is the case with any material used in engineering devices. Even though RE ions can be directly excited optically for photoluminescence emission, the direct excitations of the RE ions have some disadvantages. For instance, a specific excitation wavelength is required to excite a specific type of RE ion (e.g. 392 nm excitation wavelength is preferred to excite the  $\text{Eu}^{3+}$  ions while 348 nm is preferred to excite the  $\text{Tb}^{3+}$  ions). This makes excitation difficult in samples with more than one type of RE ions (e.g. to produce white light emitting sample with  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$  ions) as different wavelengths are required to excite different types of RE ions. Furthermore, the RE ions have low absorption cross-section.

One way to overcome these difficulties is to use semiconductor nanocrystals as sensitizers to excite the RE ions. Semiconductor nanocrystals like ZnO, Si, CdSe, etc. have higher absorption cross-section, which can be easily excited compared to the RE ions. These excited nanocrystals can then transfer the energy to RE ions, which in turn emit light through radiative de-excitation. Moreover, different RE ions can be excited using a single type of semiconductor nanocrystals, which can be excited using any wavelength above the optical band gap of the semiconductor. Thus, using semiconductor nanocrystals as sensitizers, various RE ions can be excited using a single excitation wavelength. In this regard, zinc oxide nanocrystals (ZnO-nc) are one of the widely studied sensitizers because they can excite a wide variety of RE ions like  $\text{Eu}^{3+}$ ,  $\text{Tb}^{3+}$ ,  $\text{Ce}^{3+}$ ,  $\text{Er}^{3+}$ , etc.. ZnO-nc is an important material which has attracted a lot of attention due to its inherent and intrinsic properties like size dependent luminescent properties, large absorption cross-sections and broad excitation spectra. The 3.37 eV wide band gap of ZnO with a large exciton binding energy of 60 meV results in the emission of light in the blue and ultraviolet (UV) region of the electromagnetic spectrum which excite the RE ions. In this work we specifically study the energy transfer from ZnO-nc to  $\text{Eu}^{3+}$  ions and ZnO-nc to  $\text{Tb}^{3+}$  ions.

Although, various studies show energy transfer from ZnO-nc to  $\text{Eu}^{3+}$  ions and ZnO-nc to  $\text{Tb}^{3+}$  ions, a complete understanding of the energy transfer is lacking and it needs to be investigated, which is the main focus of this work. For instance, a comprehensive understanding of the energy transfer mechanism and the contribution of energy transfer from the various ZnO-nc emissions has not been reported. Secondly, there have been almost no studies to understand the decay dynamics of the various ZnO-nc emission centers and their effect on the efficiency of energy transfer mechanism from ZnO-nc to RE ions. Moreover, the nature of energy transfer from ZnO-nc to  $\text{Eu}^{3+}$  ions based on the study of interaction distance between ZnO-nc and  $\text{Eu}^{3+}$  ions has also not been investigated. The interaction distance between ZnO-nc and  $\text{Eu}^{3+}$  ions is an important parameter that can greatly affect the energy transfer efficiency from the ZnO-nc to  $\text{Eu}^{3+}$  ions. Finally, understanding the nature of energy transfer between ZnO-nc to both  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$  ions combined in a single layer of thin film sample has also not been reported. This will help in the development of energy efficient white light emitting devices, by using a single excitation wavelength. Thus, in this work we investigate the above mentioned areas of research by studying the system of ZnO-nc and  $\text{Eu}^{3+}$  ions and  $\text{Tb}^{3+}$  ions. This will help in the development of energy efficient devices using semiconductor nanocrystals as sensitizers to excite RE ions which have wide ranging application in lasers, optical amplifiers, lighting and display technologies.

The low cost sol-gel technique was used in this work to develop thin film samples of ZnO-nc embedded in SiO<sub>2</sub> matrix co-doped with RE ions like Eu<sup>3+</sup> and Tb<sup>3+</sup>. The sol-gel technique was used as it has the advantage of excellent material stoichiometry, low-cost raw material and equipment, and the flexibility of controlling the material composition compared to other thin film preparation methods. The material characterisation was done by studying the photoluminescence emission, photoluminescence excitation and time-resolved photoluminescence emission from the thin film sample.

As mentioned above, this work studies the energy transfer contribution and mechanism of energy transfer from ZnO-nc to RE ions like Eu<sup>3+</sup> and Tb<sup>3+</sup> along with the factors affecting the energy transfer process, with the aim of developing energy efficient red, green and white light emitting thin-films. The study begins by investigating the efficient energy transfer occurring between ZnO-nc and Eu<sup>3+</sup> ions embedded in SiO<sub>2</sub>. A strong red emission was observed at 614 nm when the ZnO-nc were excited using a continuous optical excitation at 325 nm. This emission is due to the radiative <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>2</sub> de-excitation of the Eu<sup>3+</sup> ions and has been conclusively shown to be due to the energy transfer from the excited ZnO-nc to the Eu<sup>3+</sup> ions. The photoluminescence excitation (PLE) spectra are also examined to confirm the efficient energy transfer from ZnO-nc to the Eu<sup>3+</sup> ions. The PLE spectra show that the emission from the Eu<sup>3+</sup> ions is much higher when excited through energy transfer from ZnO-nc as opposed to the direct excitation of Eu<sup>3+</sup> ions. Furthermore, the various emission centers of excited ZnO-nc and their contribution to the energy transfer to Eu<sup>3+</sup> ions has also been studied. The excitonic emission and Zn defect emission centres of ZnO-nc is shown to have the highest contribution to the energy transfer from ZnO-nc to the Eu<sup>3+</sup> ions. While the oxygen defect emission centers of ZnO-nc have low energy transfer contributions but high energy loss due to the presence of Eu<sup>3+</sup> ions induced defect centers in the sample. The optimum fabrication process for maximum red emission at 614 nm from the samples is also reported, where a strong dependence on the annealing temperature and the Eu<sup>3+</sup> concentration in the sample is observed. The maximum red emission is observed with 12 mol% Eu<sup>3+</sup> sample annealed at 450°C [1].

The energy transfer from ZnO-nc to Tb<sup>3+</sup> ions is also studied in a similar manner. It is clearly demonstrated that the energy transfer from ZnO-nc results in sharp green emission from Tb<sup>3+</sup> ions due to radiative <sup>5</sup>D<sub>4</sub> → <sup>7</sup>F<sub>5</sub> transition of Tb<sup>3+</sup> ions. The concentration of Tb<sup>3+</sup> ion is optimised in this study to maximize the green emission from the Tb<sup>3+</sup> ions and 12 mol% was found to be the optimum concentration of the Tb<sup>3+</sup>, which is similar to Eu<sup>3+</sup> ions. Moreover, the energy transfer contribution of the various ZnO-nc emission centres to Tb<sup>3+</sup> ions is also analysed and it was found that the ZnO-nc The other ZnO-nc emission centers have low energy transfer contributions but high energy loss due to the presence of Tb<sup>3+</sup> ions induced defect centers in the sample [2].

The author also analysed the time resolved photoluminescence (TRPL) measurements from the samples to understand the contribution of energy transfer from the various ZnO-nc emission centers to Eu<sup>3+</sup> ions. The decay time obtained from the TRPL measurements were used to calculate the energy transfer efficiencies from the ZnO-nc emission centers and these results were compared with the energy transfer efficiencies calculated from steady state photoluminescence emission results. The results in this study confirm the results from the photoluminescence emission study of the sample, that the high transfer efficiencies from the excitonic and Zn defect emission centers is mostly due to the energy transfer from ZnO-nc to Eu<sup>3+</sup> ions which results in the radiative emission from the Eu<sup>3+</sup> ions at 614 nm. While the energy transfer from the oxygen defect emissions is most probably due to the energy transfer from ZnO-nc to the new defects created due to the incorporation of the Eu<sup>3+</sup> ions [3].

The author also studied the effect of average shortest interaction distance between the ZnO-nc and Eu<sup>3+</sup> ions and between two Eu<sup>3+</sup> ions in the energy transfer process between ZnO-nc and Eu<sup>3+</sup> ions embedded in SiO<sub>2</sub> matrix. A detailed model to calculate the two interaction distances based on the ratio

of Zn, Si and  $\text{Eu}^{3+}$  ions in the samples and using the density and molecular mass of ZnO and  $\text{SiO}_2$  was derived. Based on these calculations together with the photoluminescence emission from the samples, it is clearly shown that the energy transfer from ZnO-nc to  $\text{Eu}^{3+}$  ions is higher in samples with shorter distance between ZnO-nc and  $\text{Eu}^{3+}$  ions. The maximum red emission at 614 nm due to the efficient energy transfer from ZnO-nc to  $\text{Eu}^{3+}$  was found in the sample with 5.11 nm distance between the ZnO-nc and  $\text{Eu}^{3+}$  ions. However, the red emission from the  $\text{Eu}^{3+}$  ions does not increase as the distance between ZnO-nc and  $\text{Eu}^{3+}$  ions is reduced below 5.11 nm by the increasing  $\text{Eu}^{3+}$  concentration. This is due to  $\text{Eu}^{3+}$  ion concentration quenching effect, where the distances between the  $\text{Eu}^{3+}$  ions become shorter than 0.57 nm resulting in migration of energy between the  $\text{Eu}^{3+}$  ions which is non-radiatively dissipated. It is also shown that the energy transfer from ZnO-nc to  $\text{Eu}^{3+}$  ions occurs mostly due to radiative energy transfer process when the interaction distance between the ZnO-nc and  $\text{Eu}^{3+}$  ions is 6.53 nm or greater [4].

Finally, thin film samples of ZnO-nc co-doped with both  $\text{Eu}^{3+}$  ions and  $\text{Tb}^{3+}$  ions were also fabricated with the objective of creating a white light emitting sample. This was achieved by analysing the photoluminescence emission intensity from twenty four different thin film samples of ZnO-nc in  $\text{SiO}_2$  with varying concentrations of  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$  ions which were then used to obtain a parametric equation for the emission intensity of the thin film samples as function of  $\text{Eu}^{3+}$  ions and  $\text{Tb}^{3+}$  ions concentration. The parametric emission intensity equation was subsequently used to predict the concentration of  $\text{Eu}^{3+}$  ions and  $\text{Tb}^{3+}$  ions which gives white light emission according to the CIE xyz chromaticity values. Finally, the white light emitting sample was also fabricated using the sol-gel process to experimentally confirm the emission of white light. Thus, in this sample white light emission was achieved using a using a single excitation wavelength which excites the ZnO-nc and the ZnO-nc in turn excites the  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$  ions through the energy transfer [5].

The results from these works are important and can help in the development of future proficient red, green and white luminescent solid state devices based on a low-cost sol-gel technique. Extending these key analyses to systems with other rare earth elements will also help in making efficient light sources for various applications in photonics.

## Publication List

- [1] V. Mangalam, K. Pita, and C. Couteau, "Study of energy transfer mechanism from ZnO nanocrystals to  $\text{Eu}^{3+}$  ions," *Nanoscale Research Letters*, journal article vol. 11, no. 1, pp. 1-9, 2016.
- [2] V. Mangalam and K. Pita, "Energy transfer from ZnO nanocrystals to Terbium ( $3+$ ) ions: A spectral overlap study," presented at the 2016 IEEE Photonics Conference (IPC), Hawaii USA, 2-6 Oct. 2016, 2016.
- [3] V. Mangalam and K. Pita, "Energy Transfer Efficiency from ZnO-Nanocrystals to  $\text{Eu}^{3+}$  Ions Embedded in  $\text{SiO}_2$  Film for Emission at 614 nm," *Materials*, vol. 10, no. 8, p. 930, 2017.
- [4] V. Mangalam and K. Pita, "Effect of the interaction distance on 614 nm red emission from  $\text{Eu}^{3+}$  ions due to the energy transfer from ZnO-nc to  $\text{Eu}^{3+}$  ions," *Optical Materials Express*, vol. 8, no. 10, pp. 3115-3132, 2018/10/01 2018.
- [5] V. Mangalam and K. Pita, "White light Emission from Thin-Film Samples of ZnO Nanocrystals co-doped with  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$  ions in  $\text{SiO}_2$  matrix," 2018. [Ready for Submission to a reputable Journal]