

# Photoluminescent Eu<sup>3+</sup> Doped Polymer Nanofiber In Fabrics

**S. G. Itankar, M. P. Dandekar, Dr. S. B. Kondawar**

Department of Physics,  
Rashtrasant Tukadoji Maharaj Nagpur University,  
Nagpur, India.

skawadkar18@gmail.com

**Dr. B.M. Bahirwar**

Department of Physics,  
Gurunanak College of Science,  
Ballarpur, India

**Abstract**—This paper focus on the synthesis and photoluminescent properties of electrospun nanofibers of europium ion doped polymethylmethacrylate nanofibers. This fibers were characterized by scanning electron microscopy (SEM), energy dispersive spectroscopy (EDX) and photoluminescence (PL). The photoluminescence properties shows superior bright red emission spectra from the Eu<sup>3+</sup> and hence it is widely useful in optoelectronic devices and also specially in fabric designing in textile. All this happens because of relatively stronger hypersensitive behavior of the <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>2</sub> transition. This paper present the brief discussion on the potential application of smart fabric to address challenges in human life

**Keywords**—

photoluminescent, poly(methylmethacrylate), fabric, nanofiber s, electrospinning;

## I. INTRODUCTION

Polymer containing rare earth ions are useful in various photonic and optoelectronic devices [1]. It has been observed that the polymer doped RE ions possess improved photoluminescence properties and thermal stability, and are mechanically flexible with easy processability which are important parameters in manufacturing various optoelectronics devices and display systems[2-6]. The RE ions incorporated in the polymer matrixes represents a class of new materials that present the characteristics of both the complexes and the matrix materials, making them applicable in a broad range of new technologies[7]. The Eu<sup>3+</sup> doped polymer nanofibers have attracted a lot of attentions due to their high fluorescence emission efficiency .

Europium ions are usually incorporated into all types of material including organic, inorganic or organic/inorganic hybrid matrices[8] .RE ions in polymer , enhanced the luminescent efficiencies because of uniform distribution of the europium ions along macromolecular chains of the polymers. The presence of polymer increases the fluorescent intensity of the <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>2</sub> hypersensitive transition of Eu<sup>3+</sup> ions.

One-dimensional (1D) nano/micro-fibers have been of great attention due to their outstanding properties and potential applications in many fields[9-13]. The polymer optical fibers synthesized by the electrospinning technique acquired several advantages, such as exceedingly high surface-to-volume ratio, tunable porosity, malleability and the ability to control the fiber composition to accomplish the required performances from their properties and functionalities[14-17]. This light emitting fibers is a new trend in making light emitting fibers in textile industry, which are extensively used in large number of applications[18-21].

## II. SYNTHESIS OF NANOFIBERS

### A. Electrospun nanofibers of Eu<sup>3+</sup>/poly(methylmethacrylate)

PMMA solution was prepared by using 1 gm of PMMA powder in 10 ml N, N-dimethylformamide (DMF) and stirred for 5 hours at room temperature. Eu(Cl<sub>3</sub>) of different weights (0.1g and 0.5g) were separately dissolved in the PMMA solution to obtain Eu(Cl<sub>3</sub>)/PMMA solution with 1:10 and 1:2 concentrations. Each of Eu(Cl<sub>3</sub>)/PMMA solution was rigorously stirred for 12 hours at room temperature for homogenous mixing and then loaded into a 5 ml disposable glass syringe with a stainless steel needle having an orifice of 0.5mm. The needle was electrically connected to a positive high voltage 17 kV provided between the needle and the collector placed at a distance of 20 cm. The solution flow rate was kept at 0.4 ml/h and maintained using computer control programming. A dense web of PMMA/Eu<sup>3+</sup> nanofibers of two different concentrations were collected after around 10 hours on the grounded collector made of aluminum foil of thickness 0.05mm. The nanofibers were then dried in vacuum oven at 80°C for 12 hours. In the similar way PMMA/Eu<sup>3+</sup> nanofibers were prepared with the same processing condition of electrospinning to compare the photoluminescence properties.

B. Instrumentation and Characterization

Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray spectroscopy (EDX) were done by Carl Zeiss EVO-18 model SEM-EDX. Photoluminescence spectra were recorded on FP8200 spectrophotometer.

III. RESULT AND DISCUSSION

SEM images of electrospun nanofibers PMMA/Eu<sup>3+</sup> with the weight composition of EuCl<sub>3</sub>:PMMA=1:10 and 1:2 are shown in Fig. 1 (a, b). It can be observed from Fig. 1 that when more Eu<sup>3+</sup> ions were added by increasing weight composition of EuCl<sub>3</sub>:PMMA from 1:10 to 1:2, diameter size of the electrospun PMMA/Eu<sup>3+</sup> nanofibers increased. This is because the Eu<sup>3+</sup> ions and polymer chain molecules are get properly mixed in a magnetic stirrer for the longer time period of 12 hours[22]. Another reason behind increasing diameter is, the doping of Eu<sup>3+</sup> ions. This increases the electric conductivity of solution and hence surface charge of spinning jet also. Therefore solution become more fluent and increases the jet quantity of solution. In this way diameter of fibers increases[23].

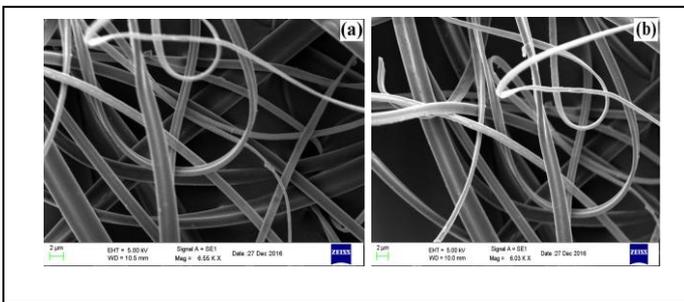


Fig. 1: SEM images of electrospun nanofibers with the weight composition of EuCl<sub>3</sub>:PMMA=1:10 (a) and 1:2(b)

Fig. 2 shows the energy dispersive x-ray spectra of PMMA/Eu<sup>3+</sup> nanofibers for weight composition of EuCl<sub>3</sub>:PMMA=1:2. Energy dispersive X-ray spectroscopy (EDX) has been also used along with SEM to investigate the elemental compositions in PMMA/Eu<sup>3+</sup> nanofibers. From the EDX spectra, the element Eu peak can be detected confirming its existence in PMMA/Eu<sup>3+</sup> nanofibers. PMMA/Eu<sup>3+</sup> contain maximum concentration of the elements like carbon along with oxygen.

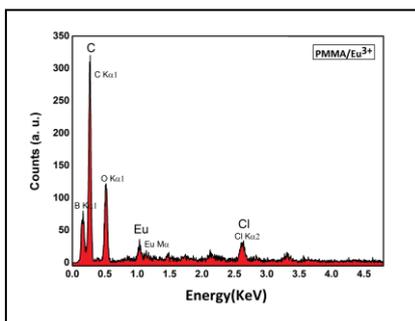


Fig. 2: EDX spectra of PS/Eu<sup>3+</sup> (1:2) nanofibers

Fig. 4 shows the PL spectra of PMMA/Eu<sup>3+</sup> nanofibers with different weight compositions (1:10, 1:2) under 411 nm excitation at room temperature. It is observed that no emission peak is observed in pure PMMA nanofiber while the emission intensity of PMMA/Eu<sup>3+</sup> nanofibers was found to be increased if we increase the concentration of the europium ions. It is because of increase in the number of luminescent centers in polymer matrix. In emission spectra, two peaks around 592 and 615 nm are assigned to <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>1</sub> transition (J = 1, 2) respectively. The <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>2</sub> transition is called as “hypersensitive transition” (electric dipole transitions). The intensity of the hypersensitive transition <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>2</sub> is often used as a measure for the asymmetry of the Eu<sup>3+</sup> site i.e. intensity is much more affected by the environment of Eu<sup>3+</sup> ions also the nature of ligands. The <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>2</sub> transition is responsible for the typical red luminescence observed in europium (III). The another peak is because of <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>1</sub> transition called as magnetic dipole transitions. Laporte selection rule is only applicable for this type of transition. The intensity of magnetic dipole transition is very weak as compared to electric dipole transitions. The weak emission intensity of <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>1</sub> transition at 592 nm is because of independent of the coordination environment of the Eu<sup>3+</sup> [24-26]. There is an interaction between lanthanide ion and magnetic component of light through magnetic dipole. During transition if charge is displaced over a curved path then the transition will possess magnetic dipole character. The curvature of the displacement will only be weakly apparent in a volume as small as the extent of a lanthanide ion and hence magnetic dipole transitions have a weak intensity.

It is observed that when more europium ion is doped with polymers the intensity of emitting light increased because of the well homogeneous distribution of the Eu<sup>3+</sup> ions with the polymers as well as high surface area of the nanofibers due to which more emission centres could be excited. So, the emission intensity of the hybrid nanofibers had a significant increase. Thus, Eu<sup>3+</sup> doped polymeric nanofibers are suitable for photoluminescent fabric designing.

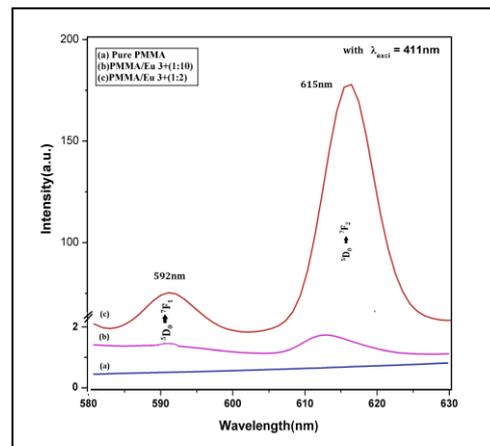


Fig. 4: Emission spectra of pure PMMA (a) and PMMA/Eu<sup>3+</sup> nanofibers for composition (b) 1:10 and (c) 1: 2

### Conclusion

The nanofibers of PMMA/Eu<sup>3+</sup> are fabricated successfully by electrospinning technique having average diameter of 200 nm. SEM images clearly show that the Eu<sup>3+</sup> ions are homogeneously mixed in the PMMA molecule chain. This fabricated nanofibers has great effect on the PL properties of Eu<sup>3+</sup> ions due to the strong coordination interaction between Eu<sup>3+</sup> and polymers.

### Acknowledgment

This work is supported by the Department of Science and Technology (DST, New Delhi, India) Support under DST-FIST Program, Grant No. SR/FST/PSI-178/2012(C).

### References

- [1] Liang Hao, Fang Xie . (2013). Luminescence of a conjugated polymer containing europium (III) chelate. *Journal of Luminescence*, 144:230–233
- [2] A.C.J Hongfang , B. D. Jianjun, A. Sun Youyi, B. Bao Jun, B. Gao Chen, A. Zhang Qijin Fluorescence enhancement of europium complex co-doped with terbium complex in a poly(methylmethacrylate) matrix, *Journal of Non-Crystalline Solids*, 2006, 352, 197–202.
- [3] J. Zhu, C. Yan, Q. Li, H. Ouyang, K. Wang, F. Yuan, X. She, Superior photoluminescence properties of poly (N-vinylcarbazole) and lanthanide complexes ternary co-doping system, *Nano Reports*, 2016, 2, 7-12.
- [4] K. Binnemans, Interpretation of europium (III) spectra, *Coordination Chemistry Reviews*, 2015, 295, 1–45.
- [5] M. Enculescu, N. Preda, E. Matei, I. Enculescu, Wet-chemical synthesis of luminescent europium (iii) doped nanofibers, *Composite Structures ICCS*, 2011, 16, 1-2.
- [6] H. Jiu, J. Ding, Y. Sun, J. Bao, C. Gao, Q. Zhang, Fluorescence enhancement of europium complex co-doped with terbium complex in a poly(methyl methacrylate) matrix, *Journal of Non Crystalline solid*, 2006, 352, 197-202.
- [7] Edison B ., Gibelli, Jiang Kaib, E.S. Ercules , Teotoniod, Oscar L. , Malta, C.F.C. Felintoa, F. Hermi, Brito. (2013). Photoluminescent PMMA polymer films doped with Eu<sup>3+</sup>-diketonate crown ether complex. *Journal of Photochemistry and Photobiology A: Chemistry*, 251: 154–159
- [8] Torres G., Jimenez P., Elena T., Kennedy M., Ahmed H., Doranc J. Modulating the photoluminescence of europium-based emitting polymers: Influence of the matrix on the photophysical properties. *Journal of Photochemistry and Photobiology A: Chemistry*, 275:103–113
- [9] Z. Rožek, W. Kaczorowski, D. Lukáš, P. Louda, S. Mitura, Potential applications of nanofiber textile covered by carbon coatings, *Journal of Achievement in Material and Manufacturing Engineering*, 2008, 27, 35-38.
- [10] Y. Wang, L. Huang, J. Tang, Y. Wang, X. Li, W. Ma, Luminescent polyacrylonitrile (PAN) electrospinning nanofibers encapsulating silica nanoparticles carried ternary europium complex, *Int. J. Electrochem. Sci.*, 2016, 11, 2058–2065.
- [11] S. Tang, C. Shao, Y. Liu, R. Mu, Electrospun nanofibers of poly(acrylonitrile)/Eu<sup>3+</sup> and their photoluminescence properties, *Journal of Physics and Chemistry of Solids*, 2010, 71, 273-278.
- [12] H.Q. Hou, J.J. Ge, J. Zeng, Q. Li, D.H. Reneker, A. Greiner, S.Z.D. Cheng, Electrospun polyacrylonitrile nanofibers containing a high concentration of well-aligned multiwall carbon nanotubes, *Chem. Mater.*, 2005, 17, 967–973.
- [13] L.Q. Liu, D. Tasis, M. Prato, H.D. Wagner, Tensile mechanics of electrospun multiwalled nanotube/poly(methyl methacrylate) nanofibers, *Adv. Mater.*, 2007, 19, 1228–1233.
- [14] A.C.J Hongfang , B. D. Jianjun, A. Sun Youyi, B. Bao Jun, B. Gao Chen, A. Zhang Qijin Fluorescence enhancement of europium complex co-doped with terbium complex in a poly(methylmethacrylate) matrix, *Journal of Non-Crystalline Solids*, 2006, 352, 197–202.
- [15] Judd B. R. (1962). Optical absorption intensities of rare-earth ion. *J. Phys. Rev.* 127: 750-761.
- [16] P. Wang, Li ZY, L. Zhang, LM. Tong, Electron-beam-activated light-emitting polymer nanofibers, *Opt. Lett.*, 2013, 38, 1040–1042.
- [17] M. Stoppa and A. Chiolerio, Wearable Electronics and Smart Textiles: A Critical Review, *PMC Sensors (Basel)*, 2014, 14, 11957–11992.
- [18] L. H. Slooff, A. V. Blaaderen, A. Polman, Rare-earth doped polymers for planar optical amplifiers, *Journal of Applied Physics*, 2002, 91, 3955-3980.
- [19] H.G. Liu, F. Xiao, W.S. Zhang, Y. Chung, Influences of matrices and concentrations on luminescent characteristics of Eu(TTA)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>/polymer composites, *J. Lum.*, 2005, 114, 187–196.
- [20] H. Liu, Y. Lee, W.P. Qin, K. Jang, X.S. Feng, Studies on composites formed by europium complexes with different ligands and polyvinylpyrrolidone, *Mater. Lett.*, 2004, 58, 1677–1682.
- [21] T. Hayakawa, K. Furuhashi, M. Nogami, Enhancement of <sup>5</sup>D<sub>0</sub>–<sup>7</sup>F<sub>3</sub> emissions of Eu<sup>3+</sup> ions in the vicinity of polymer-protected Au nanoparticles in sol-gel derived B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> glass, *J. Phys. Chem. B*, 2004, 108, 11301–11307.
- [22] S.G. Wang, Y.X. Li, Y.Z. Wang, Q.B. Yang, Y. Wei, Introducing CTAB into CdTe/ PVP nanofibers enhances the photoluminescence intensity of CdTe nanoparticles, *Mater. Lett.*, 2007, 61, 4674–4678.
- [23] X.H. Qin, E.L. Yang, N. Li, S.Y. Wang, Effect of different salts on electrospinning of polyacrylonitrile (PAN) polymer solution, *J. Appl. Polym. Sci.*, 2007, 103, 3865–3870.
- [24] Xuping Li, Guobing Shen, Xuting Jin, Miaoqing Liu, Lijuan Shi, Jianjun Lu, Novel polyimide containing 1,10-phenanthroline and its europium(III) complex: synthesis, characterization, and luminescence properties, *J. Mater. Sci.*, 2016, 51, 2072–2078.

- [25] J.Zhao, W.Zang, E.Xie,Z. Ma,A.Zhao, Z.Liu, Structure and photoluminescence of  $\text{Ga}_2\text{O}_3:\text{Eu}^{3+}$  nanofibers prepared by electrospinning, *Applied Surface Science*, 2011, 275, 4968-4972.
- [26] M. Mondragón, G. Trujillo, I. Moggio, E. Arias, Luminescent polylactic acid and polysulfone electrospun fibers containing europium (III) complexes, *European Polymer Journal*, 2016, 80, 126–133.