ELECTROSPUN NANOFIBERS OF POLY(ACRYLONITRILE)POLYMER USING (RE = EU^{3+})IONS IN OPTOELECTRONICS AND PHOTONICS

S. G. Itankar[a], M. P. Dandekar[a], S. B. Kondawar[a], B. M. Bahirwar[b]
[a]Department of Physics, Rashtrasant Tukadoji Maharaj Nagpur University, Nagpur, India
[b]Department of Physics, Gurunanak College of Science, Ballarpur, India

Abstract

Photoactive rare-earth ions doped electrospun polymer nanofibers possess improved photoluminescence properties including thermal stability and mechanical flexibility. Photonic nanofibers with one dimensional unit are much more interested in research fields. In this paper, electrospinning technique is introduced for the fabrication of Eu3+ doped Poly(acrylonitril) (PAN) nanofibers. The surface morphology of fabricated fibers were characterized by scanning electron microscopy (SEM), the diffraction peaks were observed by using X- ray Diffraction, Fourier transform infrared spectroscopy (FTIR), energy dispersive spectroscopy (EDX) and photoluminescence (PL). Spectral analysis of PAN/Eu3+ nanofibers has been made based on the measurement of the emission spectra. The PL shows superior bright red emission spectra at 616nm due to relatively stronger hypersensitive behavior of the 5D0 → 7F2 transition. Eu3+ doped polymeric (PAN) nanofibers are very much familiar in the field ofelectronic and photonic applications including light emitting diodes, lasers as well as light fabric designing in smart textiles.

Keywords: Poly(acrylonitril) (PAN), nanofibers, electrospinning; , photoluminescence.

1.Introuction

Light emitting materials doped with rare earth elements are of great significance in science and technology. Modern solid state optical technology is mostly based on lanthanide doped materials, with applications ranging from solid state lighting, field emission diodes, in-vivo fluorescence imaging, white light emitting phosphor for UVLEDs, finger print detection, proton detector, lasers, drug delivery and optical & MRI imaging. The rare earth elements are well-matched for optic application due to their large Stokes shifts and extremely long emission life times compared to more conventional fluorophosphores. Along with rare earths, trivalent rare-earth ions show very strong photoluminescence upon irradiation with UV radiation. This RE ions has gathered growing interest in photonic devices. The unsaturated 4f electronic structure of rare earth elements makes them have special properties of luminescence, magnetism and electronics, which could be used to develop many new materials (V. Prajzler, O. Lyutakov, I. Hutte, J. Oswald, V. Jerabek & S. Tang, C. Shao, Yichun, R. Mu 2010). Europium is a well known member of lanthanide series. It is a chemical element having atomic number 63. Most applications of europium exploit the phosphorescence of europium compounds. Europium (III) compounds often show an intense luminescence due to the large energy gap between the $^5D_0$ excited state and the highest level of the ^7F_J main-fold ($^7F_6$ level). It is also convenient that the luminescence is in the visible spectral region (red) luminescence (K. Binnemans 2015). Nanofibers have emerged as exciting one-dimensional nanomaterials for a broad spectrum of research and commercial applications due to their unique physicochemical properties and characteristics. Nanofibers possess extremely high specific surface area and surface area-to-volume ratio.

The nanofibers with different compositions have been developed using electrospinning. It is one of the most established and widely adopted techniques (D. Harvey 2016, A.T. Rhys Williams 1981 & R. Ye, A.R. Barron 2011). Electrospinning is an effective and simple method for generating one dimensional nanomaterial with diameter ranging from nanometer to micrometer. The electrospun fibers possess properties like high surface to volume ratio, high aspect ratio, controlled pore size and superior mechanical performance. The superior mechanical properties associated with the electrospun fibers arise from the decrease in diameter that cannot be achieved through conventional spinning processes. The electrospinning technique has been developed for the synthesis of one dimensional nanomaterials using rich variety of materials such as polymers, organic, inorganic compounds. Polymers do not posses light emitting property, so they are incorporated with rare earth europium ions to produce light emitting fibers. The rare earth europium ions are well suited for optic application due to their large Stokes shifts and extremely long emission lifetimes (S.S. Tang, C.L. Shao, S.Z. Li 2007, J. Liang , F. Xie, X. Ren, Y. Chen, B. Chen , F. Guo 2013 C. Peng, G. Li, X. Kang, C. Li, J. Lin 2011 , S. Fan, X. Fei, X. Wang , J. Tian , L. Xu, P. Yang, Y. Wang 2014, S.G.Itankar 2017).

2.Experimental

PAN solution was prepared by using 1 g of PAN powder in 10 ml N, N-dimethylformamide (DMF) and stirred for 5 h at room temperature. Eu(Cl_3) samples of different weight (0.1 g and 0.5 g) were dissolved separately in PAN solution to obtain Eu(Cl_3)/PAN solution at 1:10 and 1:2 concentrations. Each Eu(Cl_3)/PAN solution was stirred rigorously for 12 h at room temperature for homogenous mixing and then loaded into a 5 ml disposable glass syringe with a stainless steel needle 0.5 mm gauge. The needle was connected electrically to 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 controlled programming. Dense webs of PAN/Eu^{3+} nanofibres of two different concentrations were collected after 10 h on the grounded collector made of aluminum foil of thickness 0.05 mm. The nanofibres were then dried in a vacuum oven at 80°C for 12 h. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) were carried out using a Carl Zeiss EVO-18 SEM–EDX. Fourier transform infrared spectroscopy (FTIR) was performed using a Thermo Nicolet, Avatar 370 infrared spectrometer. Photoluminescence spectra were recorded on a FP8200 spectrophotometer.

3.Result and Discussion

3.5SEM Images of PAN/Eu^{3+}

Figure1 shows the SEM images of PAN/Eu^{3+} nanofibers. It was observed that the fibers with diameters ranging from 100 to 900 nm deposited on the collectors are randomly oriented in the form of non-woven fabrics. It was reported that the average fiber diameter is linearly related to the concentration of doping content. In order to investigate the effect of the doping of Eu^{3+} ions on the average fiber diameter, frequency distribution of different fibers is obtained from the corresponding SEM images. By calculation, the average diameters are 415 and 726 nm for (1:10 and 1:2) of nanofibers respectively. The results show that the average diameter of PAN/Eu^{3+} nanofiber increases with increasing Eu^{3+} ions into the polymer solution (S.G.Itankar, M.P. Dandekar & S.B. Kondawar, 2017).

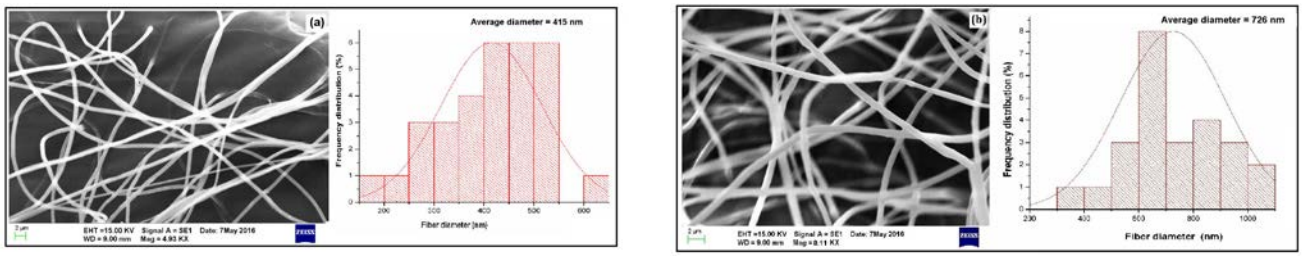

Figure 1. SEM images and histogram of electrospun nanofibers (a) PAN/Eu^{3+} (1:10) and (b) PAN/Eu^{3+} (1:2)

3.2 XRD of PAN/Eu^{3+} nanofibers

X-ray diffraction pattern of PAN/Eu^{3+} (1:2) nanofibers is shown in figure 2. From the literature available for PAN, it shows a single unique diffraction peak at 2θ = 17˚ indicating that sample is amorphous in nature (W. Pan, Y. Sun &Y. Chen 2012 & Y. Wang, L. Huang & W. Ma 2016). In XRD pattern of PAN/Eu^{3+} (1:2) electrospun nanofibers it is found that when europium ions are doped in PAN, small peaks at 2θ = 37.6˚, 46.2˚ and 58.3˚ are observed, which are attributed to the (101), (200) and (110) plane of the Eu3+ (JCPDS Card no. 38-0928 file) [20] are observed which shows the presence of europium ions including the peak of polymer 2θ = 17˚ in the synthesized PAN/Eu^{3+} (1:2) nanofibers. This confirms that Eu^{3+} ions are doped in PAN .

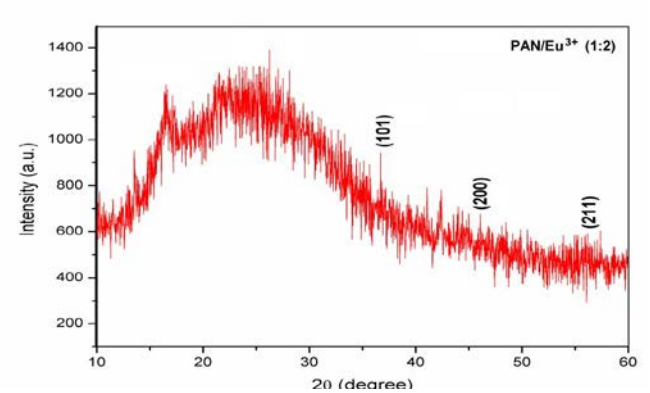

Figure 2. XRD of PAN/Eu^{3+}

3.3 FTIR of PAN/Eu^{3+} Nanofibers

For a more detailed comparative study of the interaction between Eu^{3+} and PAN, the FTIR spectra for the PAN nanofibers and PAN/Eu^{3+} (1: 2) nanofibers are studied (Fig.3). The peaks are related to existence of CH2, C N, C=O, C-O, and C-H bonds. In pure PAN nanofibers the peak in the range of about 2242 cm^{-1} is due to presence of nitrile group in polyacrylonitrile chain (S.S. Tang, C.L. Shao & S.Z. Li 2007). The absorption peak in the range of 1728 cm^{-1} is related to C=O or C−O bonds and are resulted from presence of comonomers. The bending vibration of methylene (-CH2-) functional group is seen at 1460 cm^{-1}. The peaks at 1228 cm^{-1} and 1373 cm^{-1} are assigned to the aliphatic –CH group vibrations of different modes in CH and CH2, respectively. In PAN/Eu^{3+} nanofibers the most striking feature is the appearance of a weak but obvious shoulder at about 2275cm^{-1} on the high frequency side of 2242 cm^{-1}, which was induced by the Eu^{3+} ions coordination with the C -N group of PAN molecule chains. The weak shoulder at 2275cm^{-1} must have represented the Eu^{3+} ions coordination with the nitrile group of PAN molecule chains (Brady, B. John, Newton, M. Robert, and Boardman & J. Shelby 1995 & Dutrow, Barb 1997). The position of peaks in PAN/Eu^{3+} nanofibers is observed to shift slightly lower values due to the interaction between PAN molecule and Eu^{3+}.

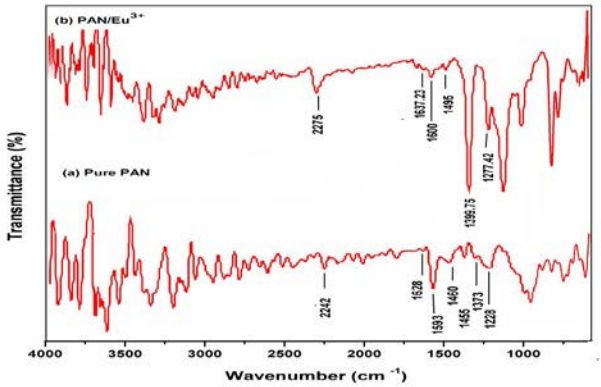

Figure 3. FTIR spectra for the PAN nanofibers and PAN/Eu^{3+} (1:2) nanofibers

3.4PL of PAN/Eu^{3+} nanofibers

Figure 4, shows the excitation of PAN/Eu^{3+} (1:2) nanofibers registered at room temperature by monitoring the luminescence intensity of the $^5D_0 \rightarrow {}^7F_2$ transition at 616 nm. It is observed that the nanofibers exhibit an intense broad excitation band at 411 nm. Figure shows the emission spectra of PAN/Eu^{3+} nanofibers with different weight compositions (1:10, 1:2) under 411 nm excitation at room temperature. From figure it is found that the emission intensity of PAN/Eu^{3+} nanofibers increased for high concentration of the europium ions. This may be due to increase in the number of luminescent centers produced by high impurity in polymer matrix. In emission spectra, peaks at around 592 and 616 nm are assigned to $^5D_0 \rightarrow {}^7F_J$ transition (J = 1, 2) respectively. The $^5D_0 \rightarrow {}^7F_2$ transition is a called as "hypersensitive transition" (electric dipole transitions). Transition $^5D_0 \rightarrow {}^7F_2$ shows a very high intense peak at 615 nm. Hypersensitive transitions obey the selection rules $|S| = 0$, $|L| \leq 2$ and $|J| \leq 2$ which are same as the selection rules for a quadrupole transition. The intensity of the hypersensitive transition $^5D_0 \rightarrow {}^7F_2$ is often used as a measure for the asymmetry of the Eu^{3+} site i.e. intensity is much more affected by the environment of Eu^{3+} ions also the nature of ligands. The $^5D_0 \rightarrow {}^7F_2$ transition is responsible for the typical red luminescence observed in europium (III). Another peak is because of $^5D_0 \rightarrow {}^7F_1$ 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 $^5D_0 \rightarrow {}^7F_1$ transition at 592 nm is because of independence of the coordination environment of the Eu^{3+}. There is an interaction between lanthanide ion and magnetic component of light through magnetic dipole. During transitions if the charge is displaced over a curved path then the transition will posses 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. (Hovis, Guy 1997, J.B.Brady 1997, , M.P. Dandekar, 2015, S.G.Itankar, M.P. Dandekar, S.B. Kondawar, B.M. Bahirwar 2017).

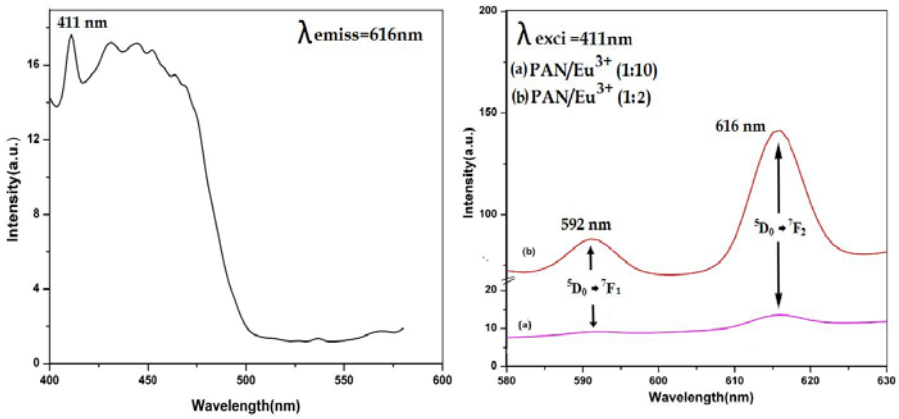

Figure 4. Excitation and emission spectra of PAN/Eu3+ (1:10,1:2)

3.5 CIE Chromaticity Coordinates

To evaluate the material performance on color luminescent emission, CIE chromaticity coordinates are evaluated for the PAN/Eu^{3+} at excitation wavelengths of 411 nm. It can be clearly seen from the diagram and the calculated values that polymer/Eu^{3+} samples give an intense red emission due to the presence of relatively intense 614 nm lines ($^5D_0 \rightarrow {}^7F_2$) under 411 nm excitation. The CIE coordinates (x, y) is represented as the point ' . ' in the CIE diagram.The CIE diagram shows emission color coordinates. The CIE coordinates for the prepared nanofibers are with the help of CIE diagram as shown in figure 5. From figures it is observed that with an increase in the concentration of doping of the Eu^{3+} ions with polymer, there is a small shifting of CIE color

coordinates towards the more intense red light and hence showing increase in the emission intensity. It confirms that along with the increase in concentration of europium, the intensity of red light emission also increases.

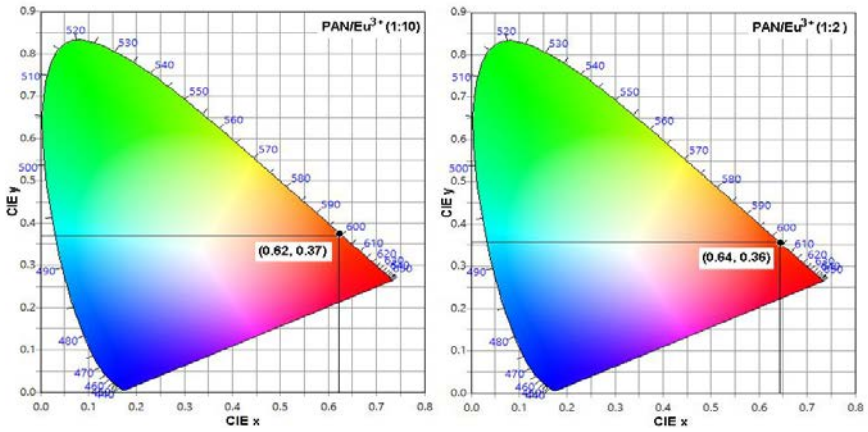

Figure 5. CIE Chromaticity Coordinates of PAN/Eu^{3+} (1:10,1:2)

Conclusion

The nanofibers of PAN/Eu^{3+} are fabricated successfully by electrospinning technique having average diameter of 415 and 726 nm. SEM images clears that the Eu^{3+} ions are well homogeneously mixed in the polymer molecule chain because as the concentration of Eu^{3+} increases the diameter of the fibers are also increases. This electrospun nanofibers has great effect on the PL properties of Eu^{3+} ions due to the strong coordination interaction between Eu^{3+} and PAN polymer. The fluorescent intensity of Eu^{3+} ions increased with the effect of high surface area of PAN/Eu^{3+} nanofibers. This is due to the effect on the fluorescent intensity of the $^5D_0 \rightarrow {}^7F_2$ hypersensitive transition of Eu^{3+} ions. Due to the good morphology and outstanding fluorescent property, nanofibers show potential applications in light emitting fabric designing and also electronic and photonic devices.

Aknowledgement

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