Influence of Europium & Europium complex Eu (TTA)3phen on luminescence properties of electro spun polymer nanofibers.

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Abstract
The europium ion (Eu³⁺) is well acknowledged and more popular for its strong luminescence when it is compared with other RE ions. Here we report the comparative study of electrospun polymer nanofibers by using europium and europium complex Eu(TTA)3phen by electrospinning technique. Electrospun fibers of Europium chloride and Europium complex Eu(TTA)3phen were prepared by using polymer PVDF to study the photoluminescence properties. Photoluminescence spectra of these electrospun nanofibers show very high intense red emission because of the strong hypersensitive behavior of the 5D0 →7F2 transition. These electrospun nanofibers are very much useful in the latest technology of Smart Textiles, for developing protective fabrics with thermal comfort. These fabrics also used to defend from wide variety of environmental hazards. This paper highlights the promising applications of electrospinning for developing protective fabrics and also shows the potential application in various polymer optoelectronic devices.

Keywords Electrospinning, nanofibers, E-Textile, Photoluminescence.

1. Introduction
Light emitting materials with rare earth elements are of great significance in the field of research, science and technology. Some modern optical technologies are mostly based on lanthanide doped materials, with wide range of applications in field emission diodes, white light emitting phosphor for UVLEDs, detection of finger print, detector, lasers, drug delivery and optical & MRI imaging. The rare earth elements are well-suited for optic application due to their large Stokes shifts and extremely long emission life times. Lanthanide organic complexes absorb the excitation light and it transfer its energy to the higher level of the europium ions. These complexes are applicable in large number of areas such as fluorescence probes, energy-harvesting diketone complexes. But due to low ability of processing; less thermal stability and mechanical strength have limitation in its applications in past years. To overcome this type of limitations, β-diketone complexes were used by addition of organic, inorganic, or organic/inorganic composite materials in it [1, 2].

Use of nanotechnology has encouraged material scientists to walk around the use of nonorange materials and fibers for the development of functional and technical textiles. This Developed functional fiber materials used in all over the fields such as healthcare, industries, agriculture, military etc. Looking over all fields, fibers have attracted huge amount of interest for the development of protective clothing because of their excellent features like inexpensive, lightweight and excellent protection [3-5]. Due to the unique physicochemical properties and characteristics of 1-Dimensional nanofibers have a broad spectrum of research and commercial applications. Nanofibers have a excellent structural property called high surface
area and surface area-to-volume ratio. This property made the nanofibers unique from all other materials, high surface area means high rate of reactivity with other materials. The nanofibers with different compositions have been developed by using electrospinning machine. It is one of the most established and widely adopted techniques for fabrication of nanofibers [6-8]. Electrospinning is an effectively simpler method for fabricating the one-dimensional nanofibers with diameter belonging from nanometer to micrometer. On the other hand, the electro spun nanofibers possess properties like high aspect ratio i.e., diameter to length ratio, controlled pore size and superior mechanical performance. The superior mechanical properties can be achieved by decreasing the fiber diameter, which cannot be possible by conventional spinning processes. Rich variety of materials such as polymers, organic, inorganic compounds can be prepared by electrospinning technique, which has been used for the synthesis of one-dimensional nanomaterials [9-12]. A polymer does not emit light. To get optical property with polymers they have to use with rare earth ions. Such optical properties are obtained with polymers because rare earth europium ions are well suited for optic application due to their large Stokes shifts and extremely long emission lifetimes [13-15]. Light-emitting fibers, in the wearable light-emitting devices, are the chief fundamental of the research areas. This paper reports the effects of different types europium complexes with polymers cavities. Enhanced photoluminescent nanofibers of these materials are obtained by electrospinning.

2. Experimental

2.1. Materials
EuCl$_3$ (99.99%), 2-thenoyltrifluoroacetone (TTA) (C$_8$H$_5$F$_3$O$_2$S) (99%) (Mw=222.2), 1, 10-phenanthroline (phen) (Mw=198.22), PVDF (Mw=15,000).

2.2 Preparation of EuCl$_3$

The synthesis process of EuCl$_3$ is explained through flow chart as shown in figure 1. EuCl$_3$ was obtained by dissolving the europium oxide (Eu$_2$O$_3$) in a dilute hydrochloric acid (HCl) solution. Stirring the solution at 100$^\circ$C. When solution was mixed well then dried the solution under vacuum. After heating, excess HCl was evaporated and EuCl$_3$ powder was obtained. [16].

2.3 Preparation of Eu (TTA)$_3$ phen Powder

Eu (TTA)$_3$ phen Powder was prepared by taking 2-thenoyltrifluoroacetone (TTA) (1.5 mol) and phen (0.5 mol). They were dissolved in 20 ml of ethanol and then neutralized with NaOH solution by maintaining pH-7. EuCl$_3$ solution was prepared by using 10 ml of double distilled water and added it into the prepared solution of TTA and phen. Final prepared solution was stirred and heated at 60$^\circ$C for 1 hour. The pale color precipitate was formed which then dried for 2 hours at 80$^\circ$C in oven [17].

![Figure 1. Flow chart for preparation of EuCl$_3$.](image-url)
2.4 Preparation of solution Eu (TTA)₃Phen /PVDF and Eu³⁺/PVDF
To prepare electrospinning solution, 1g PVDF was dissolved in 10 ml THF solvent and magnetically stirred for 12 hours for well mixing of solution. Eu (TTA)₃phen was added in uniform PVDF solution and again magnetically stirred for 12 hours for homogeneous mixing.

Eu³⁺/PVDF electrospinning solution was prepared by taking 1g of PVDF polymer powder in 10 ml N, N-dimethylformamide (DMF) and stirred for 5 h at room temperature. Then EuCl₃ were added in the prepared solution of PVDF and stirred rigorously for 12 h for well mixing.

2.5 Preparation of Electrospun Nanofibers
After preparation of solutions, it was loaded into disposable syringes having stainless steel needle 0.5 mm gauge. High voltage (17 KV) was provided between the needle and the collector keeping distance 20 cm between them. The solution flow rate was kept at 0.4 ml/h. After 10 hours dense web of nanofibers of Eu (TTA)₃Phen /PVDF and PVDF/Eu³⁺ were collected on the grounded collector. Preparation of nanofibers is shown in figure 2.

3. Results and Discussion
3.1. SEM images of Eu (TTA)₃phen/PVDF and Eu³⁺/PVDF nanofibers
The SEM images of the electrospun nanofibers was studied by scanning electron microscope (SEM) using model JSM-7600F. The diameter of the electrospun fibers was totally dependent on various factors or physical, chemical parameters of the solutions, like conductivity of solution, concentration, viscosity, molecular weight of polymers, applied voltage, distance between syringe and collector and the flow rate [18]. Fig. 3(a) and 3(b) shows the SEM images of Eu (TTA)₃phen/PVDF and PVDF/ Eu³⁺ fibers respectively. The diameters range of the prepared Eu (TTA)₃phen/PVDF nanofibers were found to be in between 500 to 900 nm. And the diameter of PVDF/Eu³⁺ was found to be 200 nm and 700 nm. SEM images of prepared sample shows a dense web of fibers and their diameters were calculated by using histograms. There is a slight change in diameter of the electrospun fibers for different samples, which was due to the effect of doping of europium and europium complex. This doping effect i.e., addition of Eu (TTA)₃phen affects the conductivity of the electrospinning solution. Figure 4 shows the histogram for the electrospun nanofibers which is used to get the diameter of the nanofibers. From histogram it is seen that the diameters are lying in the range of 200-300 nm.
3.2 Photoluminescence Spectra of Eu (TTA)₃phen/PVDF and PVDF/ Eu³⁺ nanofibers

Spectrofluorometer model FP8200 recorded the photoluminescence spectra of Eu (TTA)₃phen/polymer nanofibers and PVDF/ Eu³⁺ nanofibers. The photoluminescence (PL) spectra are used to compare the emission properties of Eu (TTA)₃phen/PVDF nanofibers with PVDF/ Eu³⁺ nanofibers. Emission spectrum of Eu (TTA)₃phen/ PVDF nanofibers is shown in Fig. 5(a), whereas Fig. 5(b) represents the emission spectra of PVDF/ Eu³⁺ nanofibers. These emission spectra give the characteristic sharp peaks in the range between 570-725 nm. Generally, europium ion compounds lie their transitions in between ⁵D₀→⁷F_J, where (J = 0-6). In this transition ⁵D₀ shows excited state and ⁷F_J shows ground state. Only few transitions are observable because many transitions are beyond the wavelength range of the detector of spectrofluorometer. The two main transitions are responsible for the red emission of light. Transition ⁵D₀→⁷F₁ and transition ⁵D₀→⁷F₂ are called magnetic dipole and hypersensitive transitions respectively. High intense emission is recorded at
wavelength $\lambda=612\text{nm}$ and $615\text{nm}$. This luminescence spectrum is used to get the information of the surrounding environment of the europium ions and group symmetry. Also, it gives the information of energy levels and intensities off-f transitions, decay time of higher levels and also for the determination of site environment symmetry. Maximum information is obtained through these optical photoluminescence spectra. In $^5\text{D}_0 \rightarrow ^7\text{F}_J$ transition, some transitions like $^7\text{F}_{4,5}$ are not visible in spectra because they are lying outside the wavelength range of the detector of the spectrafluorometer. From spectra it is observed that the distance between the transition lines is increasing with increasing $J$ values, which is due to the behavior of energy levels which are proportional to the angular momentum values $J$. Maximum transitions are due to induced electric dipole transitions which are well described by JO theory. The magnetic dipole transitions are very less as compared to electric dipole hence good emission spectra at ED transition i.e. at $^5\text{D}_0 \rightarrow ^7\text{F}_2$. [19-21].

3.3 EDX Spectra

Energy dispersive X-ray spectroscopy (EDX) is also used along with SEM to examine the elemental compositions in prepared nanofiber sample. Figure 6 shows EDX spectrum of the sample. When this EDX spectra is compared with only EuCl$_3$ powder then it shows the composition of only europium and chloride. But when it is compared with the samples of electro spun nanofibers then it shows each and every components or polymers which are involved in it. The idea clears from figure 6. In figure 6(a) shows EDX of europium chloride (EuCl$_3$), peaks of oxygen, Europium and chlorine are clearly visible which shows the concentration of chlorine is much greater than oxygen and europium and also the indicate the successful preparation of the europium chloride (EuCl$_3$) during the synthesis process. Figure 6 (b) and (c) shows the peaks for Eu as well as the elements of polymer PVDF i.e., fluorine and carbon in the synthesized nanofibers.
3.4 CIE chromaticity coordinates

The calculated CIE shows good color saturation. It is observed that as europium complex doped polymers matrix, the emission intensity increased and the CIE color coordinates moves towards pure or saturated red emission. In figure 7, CIE color coordinates shows complex incorporated polymer matrix showed saturated red emission. The most favorable situation is achieved in the case of the Eu (TTA)₃Phen/PVDF composite where the dominant 612 nm peak provides photoluminescence emission with a higher level of chromatic purity, thus allowing “deeper” red emission as shown in CIE graph with coordinates (0.64, 0.33). This is due to the doping of polymer PVDF in the europium complex.
4. Conclusion
Electrospinning technique has gained too much popularity due to its excellent properties. The Eu (TTA)3phen/PVDF and PVDF/ Eu3+ nanofibers are in the series of nanometer were prepared successfully by electrospinning. This fabrication technology provides the ability to control fiber diameter, alignment, geometry, and voltage control, flow rate etc. Polymer PVDF shows good optical property, because Eu3+ ions detached in the PVDF chain of molecule and hence more interaction will be there in between PVDF and Europium complexes. This was achieved by the uniform distribution of the Eu3+ in the PVDF nanofibers. Electro spun nanofibers have the use in fabricating the fabric for the soldiers which act as a bullet free jacket to protect them from enemies’ attack because this fabric possesses strength and flexibility.

5. References
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