



SYNTHESIS AND CHARACTERIZATION OF ELECTROSPUN Eu^{3+}

DOPED POLY (METHYLMETHACRYLATE) NANOFIBERS

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Abstract

One dimensional nanostructure materials have tremendous scope because of their important properties like high surface area to volume ratio, high porosity, high aspect ratio and reactivity. Rare earth ions are important because it possess high yield of luminescence and practical applications in modern lighting and display fields. In this paper, we report the synthesis of light emitting PMMA/ Eu^{3+} nanofibers by using electrospinning technique. The nanofibers are characterized by scanning electron microscopy (SEM), Fourier transform infrared (FT-IR) and photoluminescence (PL). The SEM image of PMMA/ Eu^{3+} nanofibers for weight composition $(\text{Eu}(\text{Cl})_3:\text{PMMA} = 1:9)$ as prepared by electrospinning reveals the diameter of the fibers less than 200 nm. FT-IR spectra of PMMA/ Eu^{3+} nanofibers indicated that upon addition of Eu^{3+} ions, there appeared a higher frequency shoulder in the spectra due to the strong interaction between PMMA molecule chain and Eu^{3+} ions. The intensity of emission could be controlled by the weight ratio of Eu^{3+} ions to PMMA molecule chain at the weight ratio 1:9. The fluorescence enhancement of Eu^{3+} ions in PMMA occurs because the PMMA keeps the donors and acceptors close, which results in the effective intermolecular energy transfer and consequently, the high enhancing efficiency. In our work the PMMA/ Eu^{3+} nanofibers showed excellent photoluminescence properties. It is expected that these materials would be applied in optoelectronic nanodevices.

Keywords: Electrospinning, Nanofibers, Rare earth ions, PMMA, Photoluminescence, Optical Properties

1. Introduction

The one dimensional nanostructures have been interesting because when the diameters of the material are shrunk to nanometers, several specific characteristics such as very large surface area to volume ratio, improved mechanical performance, and flexibility in surface functionalities appear



[1-3]. Recently, nanofibers have attracted much attention due to their large specific surface area, high aspect ratio and so on [4,5]. Among various nanomaterials processing technique, electrospinning has become one of the versatile, simple and convenient technique that uses electrostatic force to produce polymeric, ceramics and composite continuous ultrafine fibers with diameter ranging from microns to a few nanometers [6-8]. The properties of electrospun nanofibers significantly depend upon the material from which they are made. Currently nanofiber can be produced on an industrial scale from dozens of polymers including biocompatible or environmentally friendly biodegradable polymers. Polymer nanofibers are promising candidates for next generation photonic devices, e.g. fibrous dielectric nanostructures can be used as single mode light waveguides, sensors or building blocks of photonic band gap materials. Nanofibers with photoluminescence properties can provide a wide range of applications in photovoltaic devices, photodiodes, sensors, wave-guiding and all optical switching [9].

Since the last decade, rare-earth ion doped phosphor materials have gathered growing interests as a consequence of the unique electronic properties of the 4f electrons of the dopants. Rare-earth doped compounds are extensively applied to lighting, field emission displays (FED), cathode ray tubes (CRT) and plasma display panels. According to literature survey it was seen that Tb-doped yttrium/Gd borate (Y,Gd)BO₃:Tb³⁺ phosphor particles were used as green emitting phosphor for plasma display panels because of their high luminous efficiency. Looking to the tremendous work on Eu³⁺ ion doped polymer materials for light emitting properties, different polymeric materials are also be selected with Eu³⁺ ion so as to observe the enhance photoluminescence properties. The main reason behind choosing the europium ion is that they have unusual spectroscopic characteristics, including millisecond lifetime, very sharp emission bands and large stokes shifts. Europium ion has attracted much attention because of its excellent luminescent



properties. Europium composites are also used in alloys and in light projection systems. Its oxidized form is applied as a laser active medium and typically its red emission is used in TV sets. The rare earth ions such as Eu, Tb, and Sm exhibit high yields of luminance in the visible light region [10, 11]. Looking to the tremendous work on Eu^{3+} ion doped polymer materials for light emitting properties, different polymeric materials are also be selected with Eu^{3+} ion.

Photoluminescence is a process where a material absorbs photon energy (light) at one wavelength; stores it by exciting an electron to a higher energy state; photoluminescence (light emission) is observed when the excited electron returns to the lower energy state. The typical process of excitation and light emission takes fraction of seconds. By arrangement of molecules via doping with additives, one can extend the photoluminescent periods to more useful time scales of 10 minute to 20 hours. Photoluminescent products are finding applications in security and tamper- evident markers. In contrast to inorganic crystals, when polymeric materials are doped with rare earths, they also show good photoluminescence properties while retaining their mechanical properties, processability, and physico-chemical stability. Nanofibers have attracted the attention of researchers due to their remarkable nanostructural characteristics. This nanoscale diameter of fibers can give an enormous surface area per unit mass. Light emitting properties of polymeric nanofibers creates new kind of fabrics called as smart clothes due to its changing of color in light and dark. In this paper, we report the fabrication of europium doped PMMA polymer nanofibers using electrospining technique so as to study its photoluminescence properties.

2. Experimental

PMMA solution (9.0 wt %) was prepared by dissolving 0.9 g of PMMA(15,000) powders in 10 ml THF with stirring for 5h at about 60°C , and the solution was cooled to room temperature. 0.104 g of $\text{Eu}(\text{Cl})_3$

powder was slowly dissolved in the PMMA solution. The above composite solution was stirred for 12 h at room temperature. Then the PMMA/Eu³⁺ solutions with (9:1) weight composition was obtained [12,13] and filled in syringe for electrospun. Figure 1 shows the schematic diagram of electrospinning. It consists of a syringe pump, DC high voltage source and rotating a stationary collector. The spinning solution was kept in a vertical syringe with a stainless steel needle electrically connected to a positive high voltage. 15 kV was provided between the tip of the spinning nozzle and the collector at a distance of 20 cm and the solution flow rate was kept at 0.4 ml/h was maintained using computer control programmer. Thus, PMMA/Eu³⁺ nanofibers were prepared successfully.

3. Results and Discussion

Fig. 2 shows the SEM Image of the electrospun fibers of PMMA/Eu³⁺. It can be seen that fibers aligned in random orientation because of the bending instability associated with the spinning jet. When the Eu³⁺ ions were added to PMMA molecular chain, there is a strong interaction between them, which prevented the Eu³⁺ ions from coagulating [14]. Under the low operating voltage of 6kV broad diameter distribution of nanofibers was obtained and the diameter was about 200 nm.

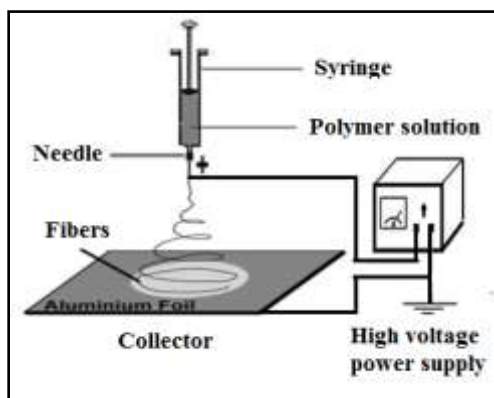


Figure 1: Schematic diagram of electrospinning

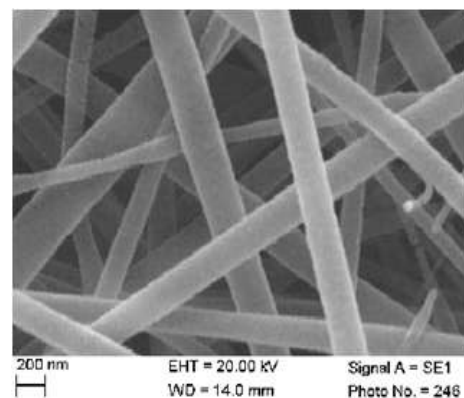


Figure 2: SEM images of PMMA/Eu³⁺ nanofibers

For a more detailed comparative study of the interaction between Eu^{3+} and PMMA, the FT-IR spectra of PMMA/ Eu^{3+} was obtained. The FT-IR spectra of PMMA indicate the details of functional groups present in the synthesized PMMA. FT-IR spectra of PMMA/ Eu^{3+} nanofibers indicated that upon addition of Eu^{3+} ions, there appeared a higher frequency shoulder in the spectra due to the strong interaction between PMMA molecule chain and Eu^{3+} ions. A sharp intense peak at 1731 cm^{-1} appeared due to the presence of ester carbonyl group stretching vibration. The broad peak ranging from $1260\text{-}1000\text{ cm}^{-1}$ can be explained owing to the C-O (ester bond) stretching vibration [15]. The broad band from $950\text{-}650\text{ cm}^{-1}$ is due to the bending of C-H. The broad peak ranging from $3100\text{-}2900\text{ cm}^{-1}$ is due to the presence of stretching vibration.

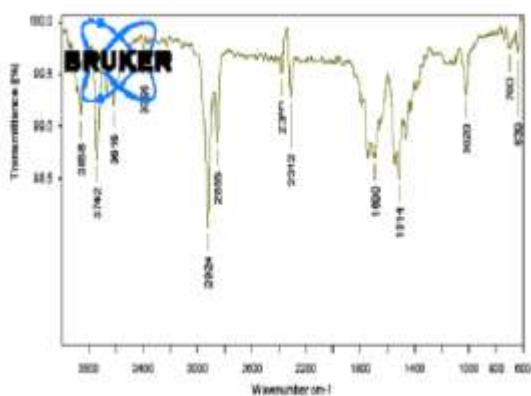


Figure 3: FT-IR spectra of PMMA/ Eu^{3+} nanofibers

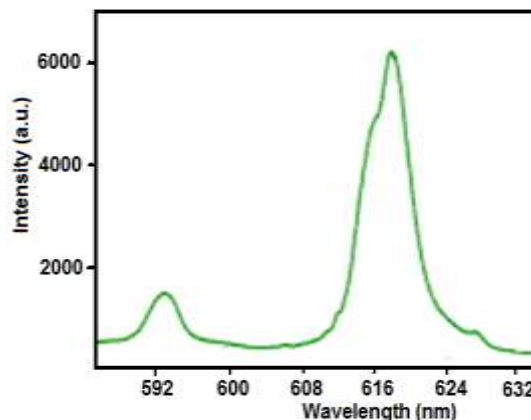


Figure 4: The photoluminescence (PL) spectra of PMMA/ Eu^{3+} nanofibers

Fig. 4 shows the photoluminescence (PL) spectra of PMMA/ Eu^{3+} nanofibers. The photoluminescence properties of the electrospun PMMA/ Eu^{3+} ions nanofibers were studied in comparison to those of the $\text{Eu}(\text{Cl})_3$ powders. It was showed that the ${}^5\text{D}_0 - {}^7\text{F}_J$ ($J=0,1,2,3,4$) emission appeared in the PL spectra of the electrospun PMMA/ Eu^{3+} ion nanofibers, whereas the ${}^5\text{D}_0 - {}^7\text{F}_J$ emission was completely absent in the PL spectra of $\text{Eu}(\text{Cl})_3$ powder [16] due to the different local environments



surrounding Eu^{3+} ions. It was interesting to note that the intensity ratios of the electric- dipole and magnetic- dipole transitions for the PMMA/ Eu^{3+} ions could be enhanced significantly by increasing electrospinning voltage. The pure PMMA nanofiber had no obvious emission band. Whereas in PMMA/ Eu^{3+} hybrid nanofibers .The emission intensity increased which was due to the increase in emission center, in the PMMA on a molecule due to the effect of electric field in the process of electrospinning [17]. This result suggested that Eu^{3+} ions as emission centers were homogeneously distributed.

4. Conclusion

PMMA/ Eu^{3+} nanofibers with a diameter of 200 nm had been prepared successfully using electrospinning technique. The fluorescence enhancement of Eu^{3+} ions in PMMA occurs because the PMMA keeps the donors and acceptors close, which results in the effective intermolecular energy transfer and consequently the high enhancing efficiency. PMMA/ Eu^{3+} nanofibers showed excellent photoluminescence properties. The possible PL mechanism was that the Eu^{3+} ions dispersed in the PMMA molecule chain and there could be some interaction between the C-O groups of PMMA and Eu^{3+} ions. The different types of electrospun nanofibers of Polymers/ Eu^{3+} . It is expected that these materials would be applied in optoelectronic nanodevices.

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