



Enhancement in photoluminescence properties of organic compound PS/PPO by cerium fluoride nanoparticles doping

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Abstract

Herein, a new polymeric nanocomposite of 2,5-diphenyloxazole (PPO) and polystyrene (PS) doped with cerium fluoride (CeF_3) nanoparticles (PS/PPO/ CeF_3) was prepared, characterized and its photoluminescence property was reported for the first time. The PS as a base matrix and PPO as a fluor were chose for a scintillator solution substrate and CeF_3 nanoparticles dispersed into it to construct a new nanocomposite scintillator. The PS liquid polymeric matrix with 0.5 wt% of PPO was loaded with different percentage of CeF_3 nanoparticles. Structural characterizations showed successful preparation of nanocomposites and a mean size of CeF_3 nanoparticles as (13 ± 3) nm in the base polymer matrix. The measured photoluminescence showed an enhancement about 3 times in comparison to PS/PPO composite when 10% of CeF_3 nanoparticles doped into the polymeric composite matrix under UV excitation. This effect is due to fluorescence resonance energy transfer in Ce^{3+} ions ($5d \rightarrow 4f$ transition energy) to the PPO within the PS/PPO/ CeF_3 nanocomposite. Observed results were presented and discussed.

Keywords Nanoparticles · CeF_3 · PS/PPO/ CeF_3 · Nanocomposite · Luminescence · Scintillator · Photoluminescence

1 Introduction

Conventional organic scintillators due to fast time response, easy fabrication and low cost are widely used in some sector of fundamental and applied field. Because of their low stopping power, they are unsuitable for high energy X and gamma radiation [1, 2]. In the last two decades new composites of polymer base organic scintillators doped by inorganic nanoparticles were suggested [3–9]. The transfer energy referred as forster mechanism could lead to the enhancement of composites luminescence.

Early organic–inorganic scintillator composites were made used a grinding method, but their transparency was low [3]. This problem can be solve by using small size of nanoparticles as a filler via increasing the index matching of the components [4]. For example, Kang et al. [5] matched index of nanoparticles and the polymer matrix

and reported some nanocomposites with high transparency. Cai et al. [6] reported on luminescence quenching of the polymer due to the charge transfer between the polymer and BiI_3 in a conjugated polymer composite with BiI_3 . Oleic acid as a matrix was loaded with high nanoparticle doping while keeping the transparency up to 70% [7]. Feller et al. [8] incorporated non-fluorescent Gd_2O_3 nanocrystals in polyvinyl toluene (PVT) matrix and reported an enhancement in its luminescence due to fluorescence resonance energy transfer (FRET) from PVT to Gd_2O_3 was reported.

CeF_3 nanoparticles due to the allowed $5d-4f$ transition in Ce^{3+} ion have significant fluorescence properties, high density, short decay time, fast response and high resistance to radiation. Due to $5d-4f$ transition in Ce^{3+} ions, the doped Ce^{3+} ions are good candidate materials for fast and efficient scintillators. However, most of the Ce^{3+} ions

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emission is within the UV range which could not directly detect by photodetectors. Therefore to transfer the emission energy from CeF_3 to higher wavelengths, a wavelength shifter is needed. Sahi et al. [9] used CeF_3 nanoparticles dispersed into PVT matrix with small amount of 2,5-diphenyloxazole (PPO) as a shifter wavelength. A luminescence enhancing is observed under UV excitation to 3 times due to FRET from CeF_3 to PPO.

Due to weak fluorescence efficiency and short optical attenuation length of polymers, they cannot be an effective scintillator. But their role as transfer energy of incident energy to fluor is important [10], and the most of plastic scintillators is PVT, PPO and polystyrene (PS) polymers matrix. In this research, due to low cost and availability of PS we chosen it as a scintillator solution substrate. The CeF_3 nanoparticles synthesized and dispersed into the PS matrix in conjunction with PPO to construct a new nanocomposite scintillator. The luminescence of PPO was enhanced under UV excitation.

2 Experimental

2.1 Materials

Polystyrene (PS), 2,5-diphenyloxazole (PPO), sodium fluoride (NaF) and cerium (III) nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) with high purity were purchased from Sigma-Aldrich.

2.2 Preparation of CeF_3 nanoparticles

Precipitation reaction method was used to synthesize the CeF_3 nanoparticles [9]. Briefly, 80 ml of NaF, 30 mmol, purged with argon gas and heated at 80 °C under vigorous stirring. After that 60 ml of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 10 mmol, added into the above solution dropwise and the temperature was kept at 80 °C for 4 h. The resulting CeF_3 precipitates were centrifuged and separated from the solution and then washed with deionized water, three times, and finally dried at 50 °C.

2.3 Preparation of PS/PPO/ CeF_3 nanocomposite

Firstly the PS/PPO with 0.5 wt% of PPO, 1.99 g of PS and 0.01 g of PPO were dissolved in 10 ml cyclohexane as solvent. Then solution was stirred for 24 h at room temperature. Then different amount of prepared CeF_3 nanoparticles, were added into the above mixture and vigorously stirred for 24 h at room temperature. Finally, the PS/PPO/ CeF_3 nanocomposite scintillator with 0.5 wt% of PPO and different amount (wt%) of CeF_3 nanoparticles were prepared.

2.4 Instrumentation

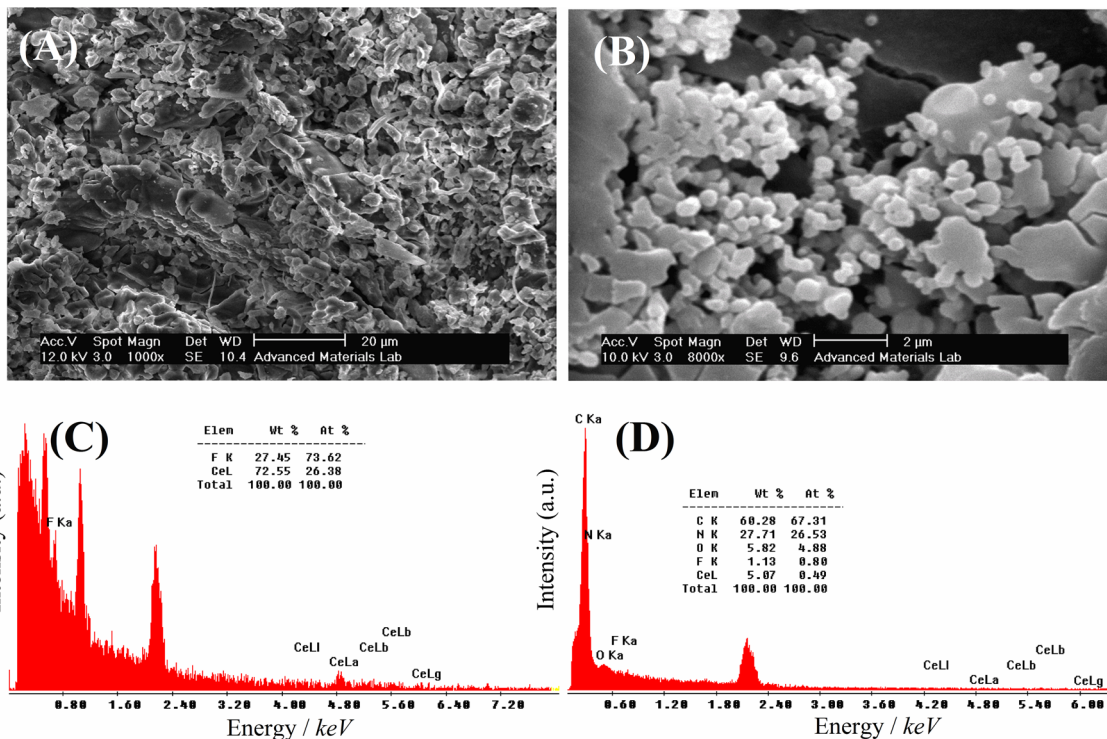
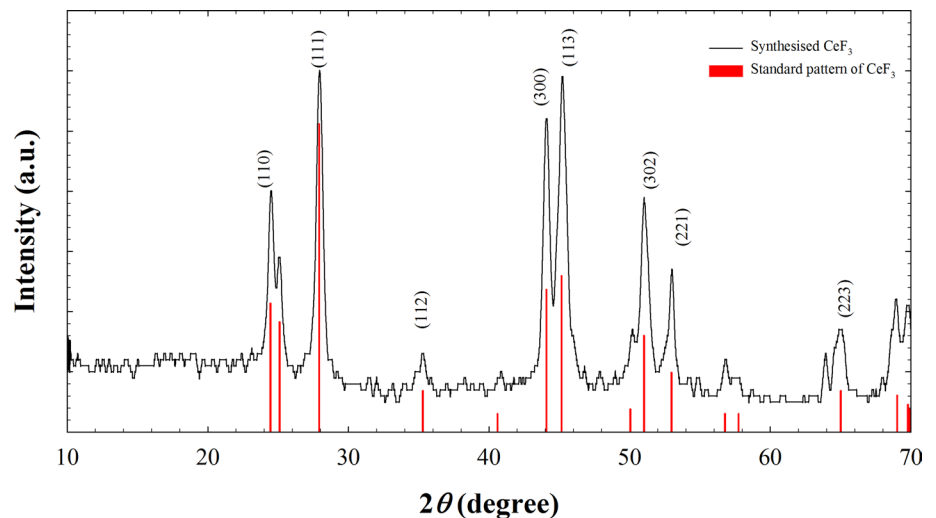
Crystalline structural, size and shape of the nanocomposites were studied by X-ray diffraction (XRD) using a Siemens D500 diffractometer with Cu K_α (operating at 40 kV and 30 mA), scanning electron microscope (SEM) and transmission electron microscopy (TEM) operating at 200 kV, respectively. Energy-dispersive X-ray analysis (EDAX) coupled with SEM was used for the semi-quantities investigation of the nanocomposites. The absorption spectra (UV-Vis) of samples dispersed in methanol were measured by using a spectrophotometer (SHIMADZU UV-3450). A SHIMADZU RF-5301 PC spectrofluorometer was used for recording the photoluminescence emission (PL) spectrums. All the measurements were carried out at room temperature.

3 Results and discussion

3.1 Characterization of prepared nanocomposites

XRD patterns of the prepared CeF_3 nanoparticles are shown in Fig. 1. In the range of 10°–70°, the observed peaks at 2θ positions of 24°, 28°, 35°, 44°, 45°, 51°, 53° and 65° are corresponding to space indexes as (110), (111), (112), (333), (113), (302), (221) and (223), respectively. This peak positions are agree with the data reported for CeF_3 crystal (JCPDS No. 08-0045) and confirmed hexagonal phase of CeF_3 crystals [9]. And also, it is demonstrated that no impurity peaks are detected and the high purity CeF_3 is synthesized. With assumption spherical shape for nanoparticles, a particle diameter of about 10 nm was calculated according to Scherrer's formula from the peak widths. This nanometer size of the prepared CeF_3 particles allow us to uniform dispersion of them in the polymer matrixes.

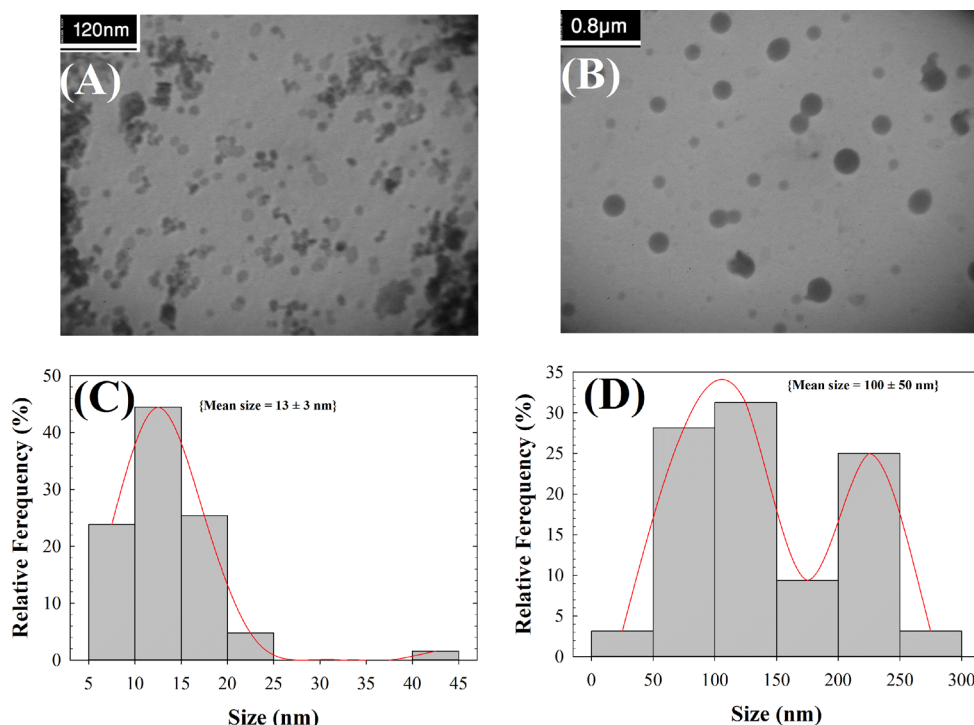
The morphology and size of as-prepared CeF_3 nanoparticles and PS/PPO/ CeF_3 nanocomposite were further examined by SEM and TEM (Figs. 2, 3). Figure 2 shows a typical SEM images of CeF_3 nanoparticles (Fig. 2a) and PS/PPO/ CeF_3 nanocomposite (Fig. 2b). As can be seen from the SEM image of Fig. 2a, morphology of bulk CeF_3 nanoparticles is irregular but their distribution is uniform. The strong peaks just for Ce and F atoms were observed in the corresponded EDXA spectrum (Fig. 2c) with atomic ratio as 1:2.8, which can match with CeF_3 and showed there is not any impurity in the synthesized CeF_3 nanoparticles. As can be seen from the SEM image of Fig. 2b, the CeF_3 nanoparticles are well dispersed within the polymer matrix and it also confirms the

Fig. 1 The XRD pattern of synthesized CeF_3 nanoparticles**Fig. 2** The typical SEM images (a, b) and corresponded EDX spectrum (c, d) of CeF_3 nanoparticles (a, c) and PS/PPO/ CeF_3 nanocomposite (b, d)

correct way of making polymer nanocomposite in this study. In the corresponded EDX spectrum of PS/PPO/ CeF_3 nanocomposite (Fig. 2d) the strong peaks of Ce and F atoms are still presented along with corresponded polymer elements, C, O and N atoms. Observed images and EDX results successfully confirmed preparation of CeF_3 nanoparticles with high purity and uniform dispersion of them into the polymer matrix.

The structural size of the prepared nanomaterials were calculated by TEM. Figure 3 shows the typical images of CeF_3 nanoparticles (Fig. 3a), PS/PPO/ CeF_3 nanocomposite (Fig. 3b) and related distributions size of them (Fig. 3c, d). As displayed in Fig. 3a, the CeF_3 nanoparticles exhibited spherical morphology and its agglomeration is small. Their distribution is shown in Fig. 3c that indicates the main average size of prepared CeF_3 nanoparticles (13 ± 3 nm)

Fig. 3 The TEM images (a, b) and its distribution size (c, d) of the CeF₃ nanoparticles (a, c) and the PS/PPO/CeF₃ nanocomposite (b, d)



is in good agreement with the result of the XRD pattern. The typical TEM image of PS/PPO/CeF₃ nanocomposite is shown in Fig. 3b. As can be seen CeF₃ nanoparticles uniformly dispersed in the polymer matrix with totally spherical shape. But, the size of the spherical CeF₃ nanoparticles increased during dispersion in the polymer matrix and an agglomeration was occurred during synthesise of the PS/PPO/CeF₃ nanocomposite. However, the observed uniform nanocomposite contains the CeF₃ with the mean size as 100 ± 50 nm (Fig. 3d).

3.2 Photoluminescence study of the nanocomposites

The photoluminescence of the composition of components for construction of the PS/PPO/CeF₃ nanocomposite is studied and compared together to show the observed enhancements. The photoluminescence (PL) emissions of PS and PPO, along with absorption spectrum of PPO measured at room temperature is shown in Fig. 4. As can be seen from Fig. 4, the existing overlap between the PPO absorption and PS emission spectrums is adequate to transfer energy between them. Consequently, more emission will be observed by PPO at longer wavelength.

The absorption and PL emission spectrum of PS/PPO, along with PL emission spectrum of CeF₃ nanoparticles are presented in Fig. 5. As can be seen from Fig. 5, there is an overlaps between the emission of CeF₃ and absorption of PS/PPO that in turn accomplish the condition for FRET.

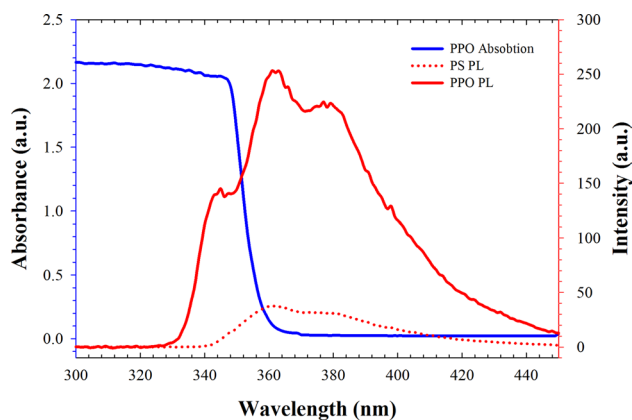


Fig. 4 The absorption spectrum of PPO (blue line) and PL spectrums (red lines) of PPO (solid line) and PS (dotted line) in cyclohexane at 2 g/l of them

Thereupon energy can be transferred from CeF₃ nanoparticles to PS/PPO. In addition, the lifetime of CeF₃ (30 ns) [11, 12] is sufficiently longer than that of PPO (1.6 ns) [13] satisfy FRET condition to occur.

Different percentage of CeF₃ nanoparticles were added into the PS matrix that contains constant percentage of PPO, 0.5 wt%, to proof enhancement effect of CeF₃ nanoparticles on the emission of PS/PPO. Figure 6 shows the PL spectrum of excited PS/PPO/CeF₃ nanocomposites at 290 nm. As can be seen the photoluminescence of PS/PPO composites notably enhanced by the CeF₃ nanoparticles.

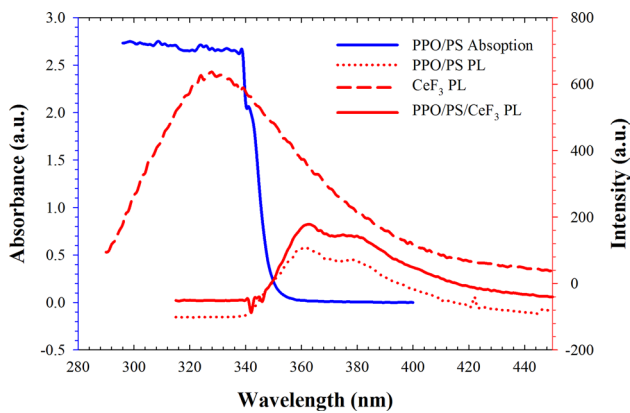


Fig. 5 The absorption spectrum of PS/PPO (blue line) and PL spectrums (red lines) of PS/PPO (dotted line), CeF_3 nanoparticles (dashed line), and PS/PPO/ CeF_3 (5 wt% CeF_3) nanocomposite (solid line) in cyclohexane at 2 g/l of them

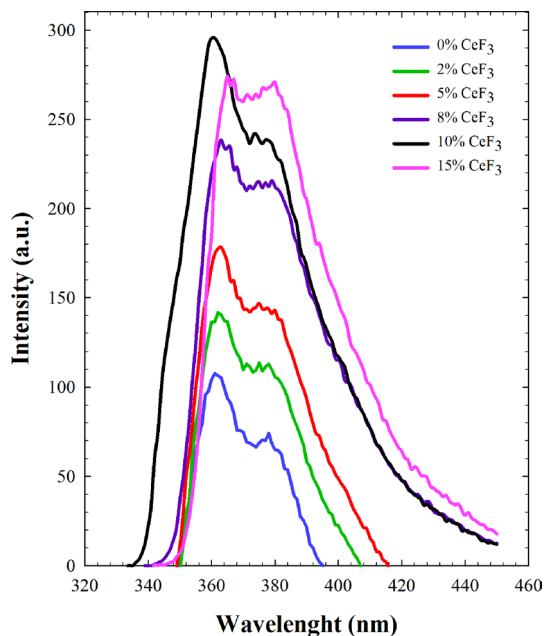


Fig. 6 The PL spectrums of PS/PPO/ CeF_3 nanocomposites with different loading percentage of CeF_3 nanoparticles

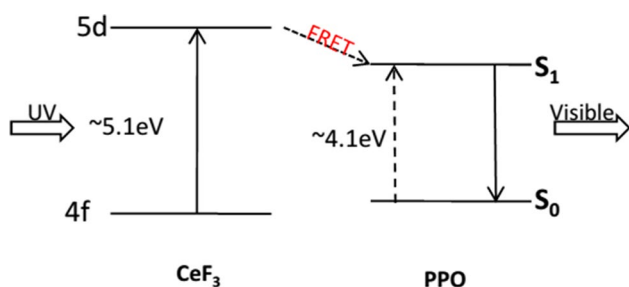


Fig. 7 Diagram of fluorescence resonance energy transfer (FRET) from CeF_3 to PPO

As expected, due to the energy transfer from CeF_3 nanoparticles to the PPO in the PS matrix as shown in Fig. 7, an enhancement in the emission intensity of nanocomposite are presented. Furthermore, absence of CeF_3 nanoparticles emission in the spectrums, confirm the FRET phenomenon occurred between CeF_3 nanoparticles and PS/PPO composite. Also, as can be seen from Fig. 6, an enhancement about 3 times was observed in the emission of nanocomposites up to 10 wt% of CeF_3 doping, and then reduced to less than 1.5 times for 15 wt% of CeF_3 . It is clear that increasing in percentage of CeF_3 in the nanocomposite, cause to a red shift in the emission of nanocomposites.

4 Conclusion

PS/PPO/ CeF_3 nanocomposite was prepared with 0.5 wt% PPO and various percentage of CeF_3 nanoparticles. Its structure and luminescence properties of constituents were studied systematically. Our results showed an enhanced luminescence in PS/PPO when embedded with CeF_3 nanoparticles. Enhancement in the luminescence of PS/PPO scintillator reaches about 3 times when doped with 10 wt% of CeF_3 nanoparticles. This enhancement can be assigned to the energy transfer, the increase of the stopping power by doping CeF_3 nanoparticles. However, our findings represent a new method to improve PS/PPO organic scintillators for radiation detection.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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