

# Functionalized Polypyrrole/CaTiO<sub>3</sub>:Eu<sup>3+</sup> nanocomposites for morphology and optical studies

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## Abstract

CaTiO<sub>3</sub>:Eu<sup>3+</sup> luminescent nanoparticles (NPs) and Ppy/CaTiO<sub>3</sub>:Eu<sup>3+</sup> nanocomposites (NCs) are synthesized via combustion and solution casting techniques respectively and their structural and optical properties are investigated. The powder X-ray diffraction patterns of the as-formed products show single orthorhombic phase. The crystallite size measurement is assessed utilizing Scherrer's technique and observed to be in the range of 40-45 nm. The impact of Eu<sup>3+</sup> ions on luminescence properties of the produced nanophosphors is examined and the results are given in detail. Therefore, the present phosphors are highly useful for display applications. The obtained results demonstrate that Ppy-assisted solution casting is an effective methodology for the synthesis of rare-earth doped CaTiO<sub>3</sub>:Eu<sup>3+</sup> nanocomposites (NCs). Biocompatible, Ppy/CaTiO<sub>3</sub>:Eu<sup>3+</sup> NCs possesses antibacterial activity against more multi-resistant bacterial and fungal phytopathogens. This additional information provides useful scientific information to prevent the various crop diseases.

## 1. Introduction

Over three decades, much effort have been made to study the Rareearth (RE) ions doped luminescent materials such as RE ions doped phosphors, glasses, ceramics, nanocomposites and polymers. These rareearth complexes are widely used in the fields of illuminations and displays, such as fluorescent lamps, field emission displays, plasmadisplay panels, cathode ray tubes, electro optical polarizers and white LEDs [1]. Day by day as special attention has been intensively focused on the RE ions doped complexes for their superior advantages in the science and technology such as sharp emission bands, long lifetime, largest Stokes shifts, high quantum efficiency and good processability. These materials are also considered as light converting molecular devices (LCMD) and this could become a great open new class of materials in the field of photonics [2]. These RE ions doped organic complexes are the good materials for novel optical displays, telecommunication systems, detectors, photoluminescence and electroluminescence devices. Moreover, they are also used in variety areas such as fluoro immuno assays, optical signal amplifications and energy-harvesting devices etc. [3-5]. Among all RE doped complex materials, RE ions doped polymers have several advantages over the inorganic devices in the device design and fabrication such as light weight, design flexibility of shape and size, ease of fabrication, excellent mechanical properties and good transparency [6]. PVA is one of the most interesting polymers because of their unique characteristics with respect structural, electrical and optical point of view. The microcrystalline nature of the PVA polymer matrix possesses both crystalline and amorphous regions. PVA is easily soluble in water and it is widely used in synthetic fiber, contact lens, paper, coatings, textile and other binding industry. It possesses good chemical resistance, good charge storage capacity and dielectric strengths. OH groups are become as source of hydrogen bonding and they play a major role in the formation of polymer composite, due to the presence of carbon chain with hydroxyl groups attached to methylene carbons [7]. Luminescence in the RE ions doped polymer materials emerges due to the parity forbidden intra configurational 4f-4f transition in lanthanide ions. The Eu<sup>3+</sup> ions doped matrix exhibits Stokes luminescence which described as the obtained emission is excited by higher energy than the emission radiation energy. The fluorescence emerges out by the electronic transitions between 5D<sub>0</sub> and 7F<sub>J</sub> (J=0, 1, 2, 3, 4) energy levels which explores the coordination environment and crystal field around Eu<sup>3+</sup> ions in its host matrix [8]. Europium (Eu<sup>3+</sup>) is characterized by very familiar prominent red fluorescence which is attributed to the electronic transition of 5D<sub>0</sub>-7F<sub>2</sub> under the UV excitation. Eu<sup>3+</sup> doped materials such as glasses, ceramics and polymer composites show intense red emission which is more suitable for solid state lighting and displays.

Generally, rare earth ions emission performances could depend upon the local chemical environment or co-doping ions in different host matrices [9]. Several methods have been employed to improve the luminescence efficiency of RE ions. The fluorescence intensity might be enhanced within increasing the ion concentration gradually, but it does not prosper at high concentration because of the aggregation. These aggregation portions act as quenching centers [6]. To overcome this quenching effect at higher concentration for better luminescence efficiency, the addition of second suitable sensitizer ion to the polymer complex is being employed. The primary RE ion fluorescence efficiency is significantly enhanced with the addition of secondary suitable ion by energy transfer process in the polymer system. In this co-doped system primary RE ion performs as an activator and secondary ion acts as sensitizer. The possible energy migration might be taking place from sensitizer to activator, whole or partly through non-radiative and/or radiative processes. This possibility of energy transfer phenomena have become a considerable effect for its practical utility in several photonic devices [10]. By increasing the sensitizer concentration in the co-doped polymer matrix, we can obtain the improved photoluminescence performance of activator ions. However, at higher concentration of sensitizer the emission will be quenched. In this situation it will not effect of quenching centers; it needs to be serve as an aggregation of ions. This aggregation portions performs as quenching centers [11].

In recent years, conducting polymer/inorganic nanoparticle composites have attracted considerable attention because of their novel physical and chemical properties and potential applications. These composite systems can provide new synergistic properties that cannot be attained from individual materials [1,2], for example, enhanced thermal and mechanical stability can be obtained. Meanwhile, in the composite system, inorganic nanoparticles are encapsulated or entrapped into the conducting polymer which leads to remarkable improvement of physical properties [3].

Of conducting polymers, polypyrrole (PPy) is generally recognized to be one of promising conducting polymers for commercial application due to its high electrical conductivity, good environmental stability and ease of synthesis [4]. Until now, various composites of PPy with inorganic nanoparticles have been synthesized either by an electrochemical or by a chemical oxidative polymerization [5–8]. Among them, yttrium oxide (Y<sub>2</sub>O<sub>3</sub>) nanoparticles have been intensively studied because of their good thermal stability, as well as their wide applications in host matrices of phosphors [9], catalyst support or even catalysts [10], and dielectric insulators of electroluminescent devices [11]. Although there are lots of papers about PPy/inorganic nanoparticles composites, no study dealing with PPy/nano-Y<sub>2</sub>O<sub>3</sub> composites has been reported so far. Combination of rare earth oxide nanoparticles with semiconducting PPy may offer composites with unique properties.

In this study, we report on facile chemical synthesis of nano Y<sub>2</sub>O<sub>3</sub> encapsulated PPy composite. The structural properties and DC electrical conductivity of composite were investigated by different experimental techniques. Other properties and potential applications of the material will be given in future report. Phosphors are an important part of white-light LEDs, which require long life, high rendering index, high luminosity efficiency and environmental friendly characteristics [1–3]. Eu<sup>3+</sup> doped materials have high fluorescent efficiency and hypersensitive transition of <sup>5</sup>D<sub>0</sub>-<sup>7</sup>F<sub>2</sub> in their part of spectrum, and they have attracted considerable interest in the fields of high-performance luminescence devices, catalysts, time resolved fluorescence labels [4–6]. Eu<sup>3+</sup> concentrations of these doped materials have great influence on the luminescence intensity, and the optimum Eu<sup>3+</sup> concentrations have been reported from 1 mol% to 26 mol% [7–12].

In recent years, the white light-emitting diodes (white-LEDs) have attracted much attention owing to their excellent properties, such as high luminescence efficiency, superior color rendering index, low power consumption, long lifespan and environmentally friendly characteristics [1–3]. Therefore, they are regarded as one of the most promising solid state light sources to substitute the widely used incandescent and fluorescent lamps. Among these, the tricolor phosphor converted white-LEDs have been widely studied as an important illumination source for next-generation lighting and display systems, because of their superior color rendering index and tunable color temperature [4]. Currently, the tricolor phosphors for solid state lighting based upon the NUV GaN-LEDs are Y<sub>2</sub>O<sub>2</sub>S:Eu<sup>3+</sup> (for red), BaMgAl<sub>10</sub>O<sub>17</sub>:Eu<sup>2+</sup> (for blue) and

ZnS:Cu<sup>+</sup>, Al<sup>3+</sup> (for green)[5,6]. However, the red phosphors have much lower efficiency[7] compared with the green and blue phosphors. Therefore, it is essential to synthesize the highly efficient and environmentally friendly red phosphors for development of the white-LEDs.

Recently, the MTiO<sub>3</sub> (M=Ca or Sr) perovskites have attracted considerable attention because of their promising luminescent properties, environmental friendliness and the well-known chemical stability as an important class of mixed oxides[8–10]. Recent researches indicate that CaTiO<sub>3</sub>:Eu<sup>3+</sup> is one of the most promising red phosphors for using in the white-LEDs[11]. In order to further enhance the photoluminescence intensity of the phosphor CaTiO<sub>3</sub>:Eu<sup>3+</sup>, many attentions were concentrated on improving synthesis methods and co-doping with the ions, such as Al<sup>3+</sup>, Bi<sup>3+</sup>, Zn<sup>2+</sup>, Li<sup>+</sup>, Nb<sup>4+</sup> and B<sup>3+</sup> [12–19] ions. To the best of our knowledge, not many studies have been carried on in the solid solution Mg<sub>x</sub>Ca<sub>1-x</sub>TiO<sub>3</sub>:Eu<sup>3+</sup> phosphors. In this article, series of solid solution Mg<sub>x</sub>Ca<sub>1-x</sub>TiO<sub>3</sub>:Eu<sup>3+</sup> phosphors were synthesized via solid-state reaction method and the optical properties of the as-prepared phosphors were studied.

Perovskite CaTiO<sub>3</sub> is widely used for electronic devices, micro-wave technology, varies or immobilization of nuclear waste and catalysis [13]. CaTiO<sub>3</sub> nanoparticles can be prepared by solid-state reaction, sol-gel, co-precipitation, combustion and hydrothermal microwave (HTMW). Flower-like, hollow and core-shell CaTiO<sub>3</sub> were obtained using soft or hard templates methods [14–19]. Nanosheet materials have high degree of crystallinity and anisotropy. These specialties show distinctive physicochemical properties in comparison with conventional nano-crystallites [20]. Rare earth doped CaTiO<sub>3</sub> phosphors have better chemical stability and environmental friendliness than metallic sulfides and oxides as luminescent materials [19–22]. In this work, we synthesized the Eu<sup>3+</sup> doped CaTiO<sub>3</sub> hexagonal nanosheets with the enhanced luminescent properties through a supercritical fluid method. This work presented for the first time the fabrication of Eu<sup>3+</sup> doped CaTiO<sub>3</sub> hexagonal nano-sheets and demonstrated their potential applications as a promising red phosphor for white-light LEDs.

## 2. Experimental

### 2.1. Materials

Calcium nitrate tetrahydrate (Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O), europium (III) nitrate hexahydrate (Eu(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O), tetrabutyl titanate (Ti(OC<sub>4</sub>H<sub>9</sub>)<sub>4</sub>), ethanol were purchased from Sinopharm Chemical Reagent Co. Ltd, China. All the chemicals were of analytical grade and used without further purification.

### 2.2. Instruments used

A Shimadzu made powder X-ray diffractometer (PXRD, 7000) with nickel filter was used to obtain diffraction data to study phase purity and crystallinity of the samples. Scanning Electron Microscopy (SEM, Hitachi 3000).

## 2. Results and discussion

### Morphological analysis

**Fig.1** shows SEM micrographs of pure Ppy. It can be seen from the figure that the pure Ppy is poorly adsorbed on the surface with no CaTiO<sub>3</sub>:Eu<sup>3+</sup> NPs. As we increase the CaTiO<sub>3</sub>:Eu<sup>3+</sup> (1-9 mol%) concentration the SEM micrographs show more and more number of particles deposited on the surface of Ppy layer (**Fig.1(b-f)**).

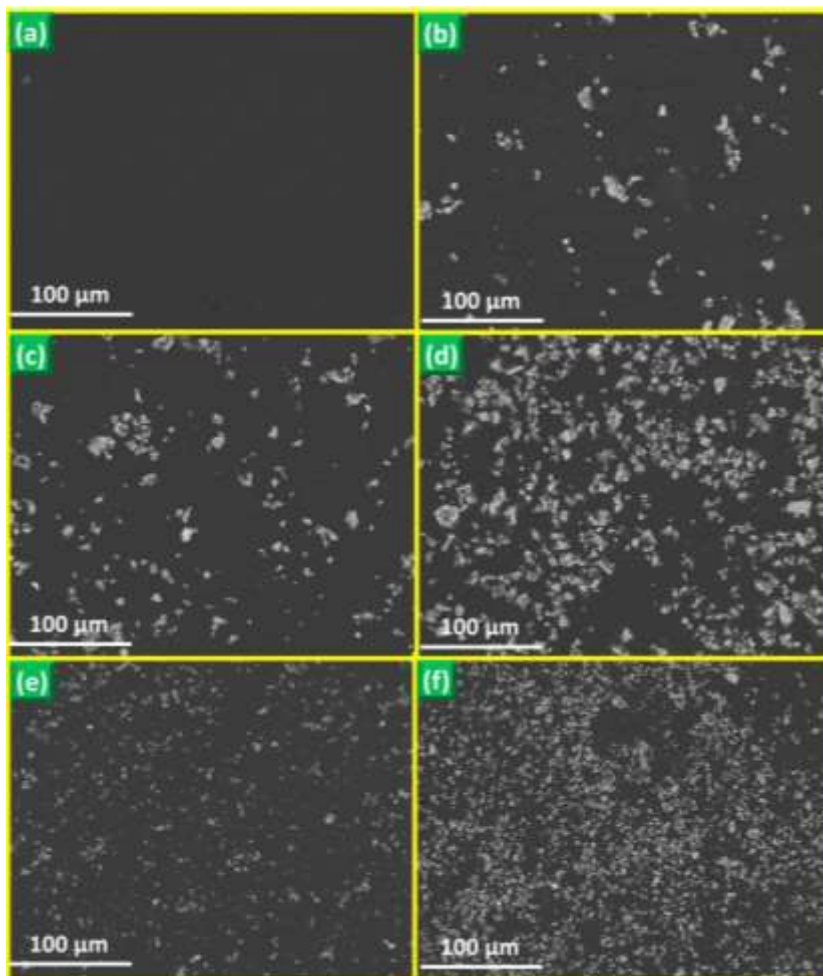


Fig.3 SEM micrographs of (a) pure Ppy and (b – f) Ppy/ CaTiO<sub>3</sub>:Eu<sup>3+</sup> (1-9 mol %) NCs.

### 3.4 Diffuse reflectance spectral studies

Diffuse reflectance (DR) spectra of CaZrO<sub>3</sub>:Eu<sup>3+</sup> (1-11 mol%) NPs are shown in Fig.10 (a). By utilizing Kubelka–Munk (K-M) relations[18] (Eqn-3, 4) the energy band gaps ( $E_g$ ) are estimated and shown in Fig.10 (b).

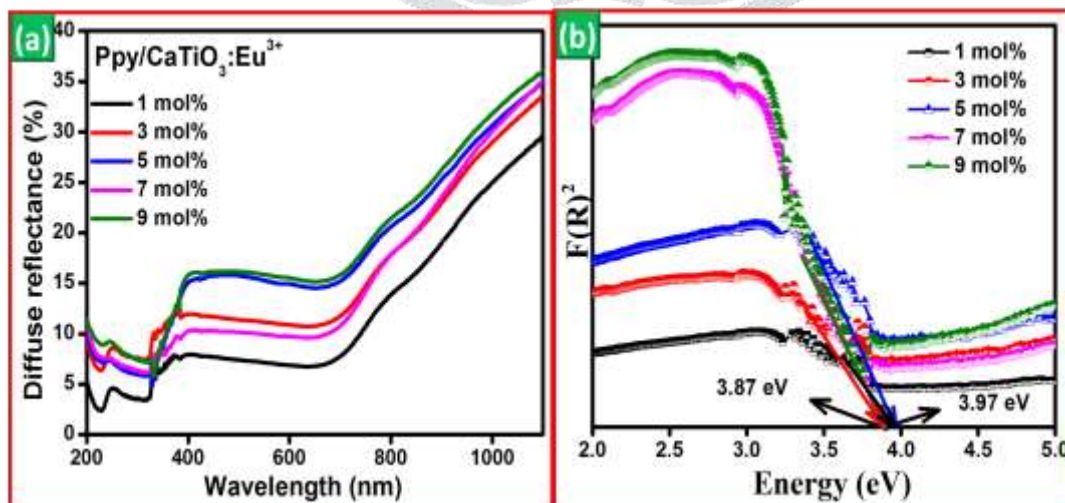


Fig.2 (a) diffuse reflectance spectra and (b) energy band gap plots of Ppy/ CaTiO<sub>3</sub>:Eu<sup>3+</sup>NCs.

$$F(R_{\infty}) = \frac{(1 - R_{\infty})^2}{2R_{\infty}} \text{----- (3)}$$

$$h\nu = \frac{1240}{\lambda} \text{----- (4)}$$

where  $R_{\infty}$ ; reflection coefficient of the sample,  $\lambda$ ; absorption wavelength. The  $E_g$  values of the corresponding  $\text{Eu}^{3+}$  concentrations (1-11 mol%). It can be evident from the table the  $E_g$  values are found to be increased with  $\text{Eu}^{3+}$  concentration.

## 5. Conclusions

We have successfully prepared the Ppy/CaTiO<sub>3</sub>:Eu<sup>3+</sup> (7 mol%) NCs by using solution casting method. The XRD profile discloses that the prepared Ppy polymer composite powders display semi-crystalline nature. The optical properties are deliberately studied by luminescence spectral measurements. Ppy/CaTiO<sub>3</sub>:Eu<sup>3+</sup> (7 mol%) displays a red emission with UV excitation wavelength. The optimized concentration of the Eu<sup>3+</sup> ions has been found to be 7 mol % in singly doped Eu<sup>3+</sup>: Ppy polymer matrix

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