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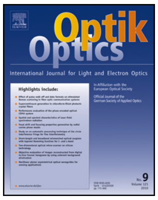

Preparation and characterization of ruthenium based organic composites for optoelectronic device application

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ABSTRACT

Ruthenium based solid state organic LED was fabricated by the dispersion of aluminum oxide nanocomposite using solution cast technique. Different analytical techniques such as XRD, FTIR, DSC, SEM, Photoluminescence, Electroluminescence and I–V characteristics were carried out on the prepared samples. XRD showed polycrystalline nature of the prepared films. DSC revealed that the microporous organic membrane was thermally stable up to 363 °C. SEM showed the degree of roughness of OLED. Photoluminescence studies were carried out on the prepared samples in the wavelength ranging from 300 to 900 nm. It is evident from the results that the intensity of the peak was increased with the dispersion of Al_2O_3 nanopaticles in the Ru complex. The I–V characteristics of Al_2O_3 doped OLED of $(bpy)_2$ Ru[bpy$(Al)_2O_3$]$(BF_4)_2$ have showed higher efficiency which is suitable for display device application. Thus it was found out that the ruthenium based composites could be promising candidates for organic light emitting device applications.

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1. Introduction

Nowadays organic light emitting diodes (OLEDs) are attaining a great interest in the display technology. New techniques have been devoted for better improvement of emission properties, electrical stability and efficiency of OLEDs [1]. Researchers have focused in the development of new type organic LEDs which show better performance than the ordinary LEDs. Organic materials have gained popularity due to their optical and electrical properties which are self emitting, consuming low power, having light weight and easily processable for display applications. Due to their excellent properties, OLEDs are widely used in many display applications [2,3] such as LED based electrochemical cells [4], microelectronic devices [5,6], flexible and display electronic devices [7,8], and active matrix organic lighting applications [9]. Solid state organic based complexes have higher chemical stability due to their strong bonding interactions between metal-ligands, higher emission quantum yields and longer excitation life times. Due to the addition of polymer in an organic material a flexible phenomenon has been attained to the OLEDs. The researchers have recently induced and stimulated interest on polymer based flexible OLEDs. The flexibility is gained due to the strong attraction between the complex in the material and also from higher chemical stability

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of the polymer chains [10,11]. The main advantage of polymer based OLEDs are self luminous, wide view angle ~160°, low power consumption, maximum efficiency of output, thinner and low cost material [12]. Moreover, the organic Ru (III) ion have spin-orbit coupling constant, where the excitations take place from the singlet to the triplets, thus the efficiency of the system is increased [13]. As a result, syntheses of Ru (III) complexes have been extensively studied from the past few years.

For comparison, an investigation has been done on OLEDs with TPD (N,N′-Bis(3-methylphenyl)-*NN*′-diphenylbenzidine) as a hole transport layer which is sandwiched between the ITO and $Ru(bpy)_3(BF_4)_2$ layer (+) ITO/TPD/$Ru(bpy)_3(BF_4)_2$/Ga:In(−). The results of TPD layer doped sample show a better performance and improves the efficiency of OLED. The Ru $(bpy)_3(BF_4)_2$ based OLEDs are less intense than the TPD doped $Ru(bpy)_3(BF_4)_2$. The emission spectra of the OLEDs employing (+) ITO/TPD/ $Ru(bpy)_3(BF_4)_2$/Ga:In(−) has maximum wavelength at 690 nm and half maximum width of 100 nm, with better color purity and a relatively narrower spectrum [14,15]. Having compared the prepared samples to the other literature of Ir(Br-DPQ)$_2$(acac) and Ir(Cl-BrDPQ)$_2$(acac) it was found out that the chlorine doped sample is highly stable over a wide range of temperature and shows good efficiency when compared to the Ir(Br-DPQ)$_2$(acac) which is more suitable for red-emissive material [16,17].

The basic structure of solid state organic device has two layers which are hole transporting and electron transporting. The recombination and light emission occur in the middle of the organic layer. This causes the emission of light between the layers and improves the efficiency of light [18–20]. The display phenomenon in organic light emitting diode occurs whenever the voltage is applied across the two ends of the electrodes break down electric filed is generated across the material. As the active layers are thin the electric field is intensely generated in the layers. Due to the break down voltage in an electric field the enhancement of charge carriers take place across the electrode/active layer interfaces. The holes and the electrons are injected from the anode and the cathode regions. The production of charge carries are drifted through polymer chains and unevenly recombined. By the excitation of molecules energy is released in the form of photons [21,22].

In the present study PVA is introduced for the preparation of NCP's films due to its excellent optical, mechanical and electrical properties. Other important properties of PVA are good chemical stability and potential resistance. Thus it may be used in electronic circuit boards and in display applications. PVA has high dielectric constant dissolubility and could form a large internal area of film formation with low cost [23]. PVA is easily soluble in distilled water and organic solvents. Due to its amorphous nature and low scattering loss, it can be more useful for optical applications resulting in good dispersion and surface formation. The main significance of nanofiller (Al_2O_3), which is used in the present work, has good properties like relatively high thermal conductivity ($30\,Wm^{-1}K^{-1}$) and very reactive with atmospheric oxygen. Due to the addition of nanofiller the mechanical integrity of the material increases. The aluminum oxide nanofiller protect the surface of the films from further oxidation [24].

In the present investigation reduced Al_2O_3 nanoparticles were incorporated in ruthenium complex which have resulted an intermediate medium in OLEDs. The novelty of the present work is to develop Ru (III) based solid state nanocomposite organic light emitting diodes with improved physical and electrical properties at laboratory scale. Development of cost effective sol-gel/electro-spinning technique, for membrane fabrication is highly relevant in view of the rapidly developing conventional alternative optoelectronic and advanced materials. The purpose of this work is to attain the nanocomposite based organic light emitting diodes with more efficiency and better stability. In this paper we have reported organic light-emitting diodes fabricated on ITO (indium tin oxide) 100 Ω/square coated glass substrates with solid state organic films of $Ru(bpy)_3](BF_4)_2$ and its derivative $(bpy)_2Ru(III)[bpy(Al)_2O_3]$ $(BF_4)_2$ as light emitters.

2. Experimental

2.1. Chemical Required

$RuCl_3{\cdot}3H_2O$, 2, 2′-dipyridyl, NaH_2PO_2, $NaBF_4$ and Al_2O_3 nanofiller were purchased from Sigma Aldrich Ltd., India. H_3PO_2 (50%) and NaOH pellets with 99% purity used in the present investigation for the preparation of OLEDs were obtained from pure Merck, India.

2.2. Synthesis of [Ru $(bpy)_3](BF_4)_2$

First 10 ml of 50% H_3PO_2 is added to 5 ml water and stirred slowly. Then add NaOH pellets ~ (3.9 g) to the prepared solution slowly until it becomes neutralized. After 0.083 g of $RuCl_3{\cdot}3H_2O$ is added to 8 ml of water. Add 0.188 g 2, 2′-dipyridyl to the solution and 0.44 ml of NaH_2PO_2. Cover the beaker with a watch glass and reflux for half an hour. Then add 0.333 g of $NaBF_4$which is to be dissolved in 1 ml of water. Finally it is mixed with the prepared complex solution. After that it is placed in a low temperature at −4 °C until some crystals are formed in the complex solution. Later the obtained crystals are centrifuged to get $Ru[(bpy)_3](BF_4)_2$ which is to be rinsed with ethanol.

2.3. Preparation of OLED

Initially 0.030 g of Ru $(bpy)_3](BF_4)_2$ is taken in 2 ml of water and stirred well. Add 0.05 g of Al_2O_3 to the solution and placed in a sonicator for few minutes such that the nanofiller is completely dispersed in the rubidium complex. Later the obtained solution of $(bpy)_2$ $Ru[bpy(Al)_2O_3]$ $(BF_4)_2$ is coated as a thin layer by avoiding some of the edges, which can act

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