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A simple technique for the fabrication of zinc oxide-PEDOT:PSS nanocomposite thin film for OLED application

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ABSTRACT

We report in-situ synthesis of zinc oxide nanorods on pre-seeded substrates with poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) matrix resulting in thin films of ZnO nanorods (NR)-PEDOT:PSS nanocomposite. Prepared ZnO-PEDOT:PSS nanocomposite films were characterized by X-ray diffraction (XRD) and scanning electron microscopy. Wurtzite crystal structure of ZnO was confirmed by the XRD analysis and SEM images indicated the successful incorporation of ZnO in polymer matrix. These nanocomposite thin films were then used as hole injecting layers (HILs) in organic light emitting diodes. Devices were prepared using nanocomposite film and studied using current density-voltage (J–V) characteristics and electroluminescence (EL) measurements. Luminance was enhanced by 4.5 times with modified HIL of ZnO NR-PEDOT:PSS film as compared to the reference device with pristine PEDOT:PSS as HIL. Current efficiency was improved from 4.62 cd/A to 11.03 cd/A and power efficiency was enhanced by 2.4 times in the presence of ZnO nanorods.

1. Introduction

During the last few decades, enormous efforts have been made to enhance the performance of organic light emitting diodes (OLEDs) owing to their promising applications in display and lighting devices [1]. Their advantages including easy fabrication over large areas on glass as well as flexible substrates, light weight, wide viewing angle, improved brightness and self-luminous properties make them a strong candidate for next generation lighting in the world [2–4]. However, high cost and low stability are the major problems currently hindering the commercialization of these devices. Numerous efforts have been made to enhance efficiency, improve life time and to reduce the cost of OLEDs [5–7]. Hybrid technology is an important solution to these problems. Hybrid organic-inorganic material based composites have become popular among the researchers due to their combined properties of organic and inorganic components. Organic semiconductors can be classified as small molecules or polymers. Polymeric semiconductors have some remarkable properties like easy processability and ability to form thin films along with good conductivity which makes them suitable for device applications [8]. Whereas inorganic semiconductors also exhibit properties such as better charge mobility, low cost, improved thermal and chemical stability etc. Moreover, their electronic and optical properties become more interesting at nanoscale [9,10]. Hybrid nanocomposites based on polymers and inorganic nanostructures exhibit good film forming properties of polymers and electrical properties of inorganic nanostructures as well.

In the category of conducting polymers, PEDOT:PSS is known as a promising candidate for device applications like OLEDs, organic solar cells, organic thin film transistors and electrochromic devices etc. [11–13]. PEDOT:PSS thin films are fairly transparent and show the conductivity of approximately $\sim$10 Scm^{-1}. Thin films of PEDOT:PSS can easily be fabricated by spin coating technique which are stable in ambient conditions [14,15]. All these qualities of this polymer make it suitable to be used as charge transport/injecting layer in OLEDs. Electrical, optical and magnetic properties of conducting polymers in general can be modified by the incorporation of inorganic materials like zinc oxide (ZnO), titanium oxide (TiO_2), cadmium sulfide (CdS), cadmium selenide (CdSe) and metal nanostructures etc. [16–18]. Among these inorganic materials, ZnO is well-known for its remarkable properties like wide band gap (3.37 eV), large exciton binding energy (60 meV), good chemical stability, interesting electrical and optical properties etc. Therefore,

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development of ZnO/polymer nanocomposite for OLED application has a great potential. Recently, ZnO-PEDOT:PSS based nanocomposites have attracted substantial attention of material scientists in the area of optoelectronic, sensor and biomedical applications [19–21]. Their remarkable properties like high electrical and thermal conductivity, chemical and environmental stability and mechanical properties are due to the presence of an interfacial third phase between nanostructure and polymer matrix [22]. To use ZnO-PEDOT:PSS nanocomposite for OLEDs it is necessary that inorganic nanostructures must be amalgamated into the polymer matrix properly leading to a stable nanocomposite. Different approaches such as electro deposition, laser ablation, sol gel etc. have been used to develop ZnO-PEDOT:PSS nanocomposite, by various researchers [23–25]. However, agglomeration of these nanostructures is one of the major problems which lower the device performance. Sonication and addition of stabilizing agents or surfactants are some possible methods by means of which agglomeration can be avoided. These methods are not considered suitable as they result in polymer degradation and increased chances of addition of impurities during the process. To overcome these problems, in situ synthesis of nanostructures directly in the polymer matrix can be used to obtain stable nanocomposite without any addition of impurity.

It has been reported that the use of the seed layer is one of the important methods that can be used for the fabrication of ZnO thin films [26]. The fabricated seed layer is followed by the growth of ZnO nanorods from the aqueous solution. Further, the preparation of nanocomposite requires the addition of these nanorods to the polymer matrix which is a multiple step procedure and time consuming. In this paper, we report a novel approach that can be used for in situ synthesis of zinc oxide nano rods (ZnO NR) on the pre-seeded substrate dipped in PEDOT:PSS bath. PEDOT:PSS bath mixed with precursors was used as reaction site instead of water. This helps in the deposition of polymer thin film and ZnO nanostructure formation simultaneously resulting in nanocomposite thin film. Thin films of nanocomposite with uniformly distributed ZnO nanorods in PEDOT:PSS matrix can be obtained by this method efficiently. Films were found to be stable and strongly adherent to the substrate due to seeding layer. Growth of nanorods in PEDOT:PSS as a matrix has been demonstrated to be a convenient method to generate ZnO-PEDOT:PSS nanocomposite thin film without any degradation of polymer. Also the fabricated thin film of nanocomposite was tested as hole injecting layer for OLEDs. Experimental results of enhanced electrical and optical properties of OLEDs are reported.

2. Material and methods

The materials used were procured from different sources. PEDOT:PSS (1.3 wt.% dispersion in water) was purchased from Sigma Aldrich. N,N′-Di(1-naphthyl)-N,N′-diphenyl-(1,1′-biphenyl)-4,4′-diamine (α-NPD) and Tris(8-hydroxyquinolinato)aluminium (Alq_3) were provided by Luminescence Technology Corp., Taiwan. Zinc acetate ($Zn(O_2CCH_3)_2$), Potassium hydroxide (KOH), zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$) and hexamethylenetetramine (HMT) ($C_6H_{12}N_4$) were purchased from Thermo Fisher. All chemicals were used as purchased without further purification.

ZnO NR- PEDOT:PSS nanocomposite was prepared by a two-step procedure as shown in Fig. 1. First step included the deposition of seeding layer from the solution of zinc acetate and potassium hydroxide in ethanol using Apex digital spin coater followed by annealing at temperature of 350 °C for 2 h. For the fabrication of nanocomposite thin films, precursors of zinc nitrate and hexamethylenetetramine were taken in a molar ratio of 3:2 and mixed with 20 ml PEDOT:PSS. This solution was stirred to ensure proper mixing of precursors in PEDOT:PSS. Seeded plates were dipped vertically and kept undisturbed at a temperature of 50 °C for 6 h. Finally, the obtained layer was heated at 80 °C for 2 h. The nanocomposite films thus obtained were characterized by XRD (Panalytical Xpert Pro) and Scanning Electron Microscopy (Carl Ziess).

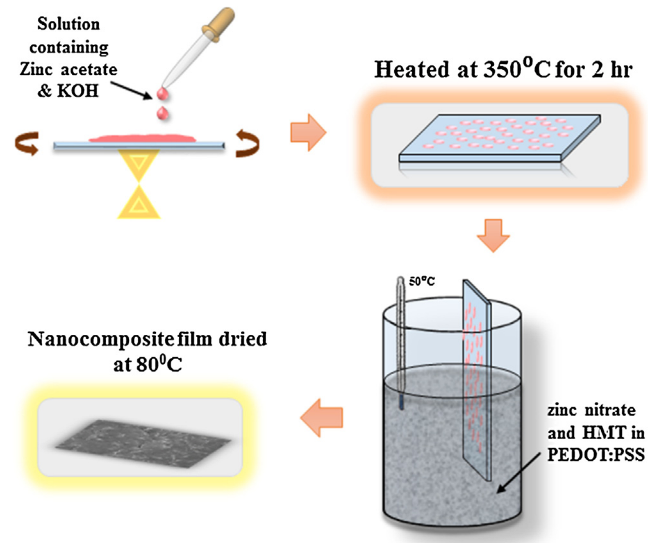

Fig. 1. Schematic diagram for nanocomposite film fabrication.

For OLED fabrication, same nanocomposite film was deposited over pre-cleaned and etched ITO coated glass substrate to act as HIL (Fig. 2(b)). On HIL, α-NPD and Alq_3 films were thermally evaporated under vacuum. LiF and aluminium were deposited to work as buffer layer and cathode, respectively. Reference device

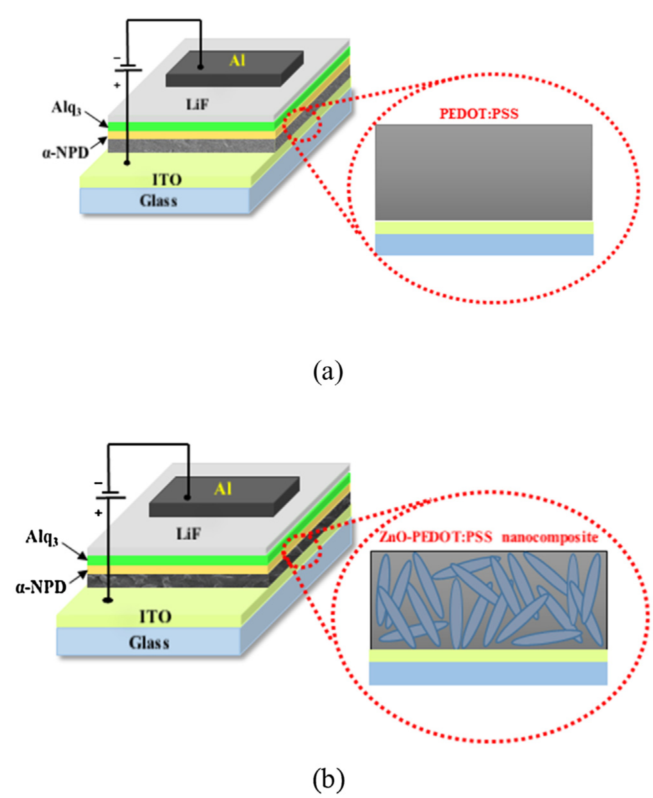

Fig. 2. Device structure of (a) reference and (b) hybrid device.