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Investigations of optical properties of MEH-PPV/ZnO nanocomposites by photoluminescence spectroscopy

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ABSTRACT

The optical properties of hybrid composite films based on poly [2-methoxy-5-(2-ethyl-hexyloxy)-1,4-phenylene-vinylene] (MEH-PPV) and zinc oxide (ZnO) nanoparticles of various sizes (5–20 nm) and with different concentrations have been investigated. The steady-state and time-resolved photoluminescence (PL) spectroscopy have been performed on nanocomposite films at room temperature. The PL results showed a significant enhancement in intensity in nanocomposites when using low nanoparticle concentrations (<5% ZnO). The particle size also impacts on the emission intensity by a larger emission efficiency in thin films containing small particles. In addition, a decrease in the photoluminescence lifetime of MEH-PPV composites has been also observed. Analysis of the time resolved PL decay of nanocomposite films suggests an energy transfer process from the nanoparticles to the polymer chains, in agreement with the steady state measurements.

1. Introduction

Conjugated polymers containing inorganic nanoparticles have been the subject of considerable research because of their potential for optical, electrical, and photovoltaic applications [1–4]. Recent investigations of promising materials for organic light emitting diodes (OLEDs) have demonstrated that introducing n-type inorganic nanoparticles into conjugated polymers is efficient to produce stable and high performance devices [5]. Although the used nanoparticles are usually metal oxides (such as titanium or silicon oxides), their distribution inside the polymer matrix is such that the charge transport could be improved and the performance of the devices is improved. In particular, composites of n-type zinc oxide (ZnO) nanoparticles and p-type conjugated polymers are very interesting for UV LEDs and OLED applications. ZnO has strong absorption in the UV light range and therefore can be used to protect the devices from oxidation to increase the lifetime of organic devices [6,7]. Among the conjugated polymers which are used as active materials in OLEDs, poly [2-methoxy-5-(2-ethyl-hexyloxy)-1,4-phenylene-vinylene] (MEH-PPV) is used in numerous emitting devices thanks to its high stability and good electrical conductivity. Composites made of MEH-PPV and nanoparticles have been investigated to provide stable active materials in OLEDs in order to enhance their lifetime [8]. Using low particle concentrations, light emission by the composite film remains identical to that of the pristine polymer. It has been recently demonstrated that such composites have lower defect concentrations than those of polymer [9], which results in a better charge carrier transport and a better efficiency of devices. As ZnO (n-type) has higher electron mobility than hole mobility and conjugated polymer shows higher hole mobility than electron mobility, which makes electronic properties of both materials advantageous when mixing them together in order to improve the light emission efficiency [10].

In this paper we have investigated the optical properties of hybrid materials made of MEH-PPV loaded with ZnO nanocrystals of various sizes and concentrations. We delineate the optimal loading percentages of ZnO nanoparticles in the composite film by using both steady state and time-resolved photoluminescence (PL) techniques.

2. Experimental

2.1. Preparation of ZnO nanoparticles

Various sizes of ZnO nanoparticles (5–20 nm) were synthesized using different chemical routes.

Method I – ZnO nanoparticles with average size of about 20 nm were prepared from zinc nitrate hydrate $Zn(NO_3)_2{\cdot}6H_2O$ (99%) and sodium hydroxide (NaOH) according to the procedure previously reported by Uekawa et al. [11]. An amount of 22.536 mg of zinc nitrate hydrate and 3.09 mg of NaOH were added to 100 mL of

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distilled water (DW) separately. Zinc nitrate hydrate and sodium hydroxide were stirred until the powder dissolves completely in DW. The mixture was centrifuged for 20 min. The supernatant liquid was removed in order to keep the precipitated powder. A small amount of DW is added to it (equivalent to 5% of the total volume amount) in a vessel which was shaken until a white and viscous product is formed. The mixture ($Zn(OH)_2 + H_2O$) was stirred and heated at a temperature of 75 °C for 2 h, then centrifuged to separate the supernatant from the precursor (ZnO_2). The precipitated products (ZnO_2) were washed twice with ethanol, then dried, and heated at 220 °C for 2 h to obtain the ZnO nanoparticles.

Method II – Colloidal solutions of ZnO nanoparticles (5 nm in diameter) were obtained according to the method described elsewhere [12,13]. Briefly, an amount of 5.5 g of zinc acetate dehydrate (98+%, Sigma Aldrich) in 250 mL of ethanol was heated until the solution became clear. This solution was refluxed for 1 h, and 150 mL of the solvent was removed by distillation and replaced by the same amount of fresh ethanol. After, 1.39 g of lithium hydroxide monohydrate (Aldrich) was added to the solution in an ultrasonic bath at 0 °C. The mixture was dispersed for 2 h to obtain a transparent solution consisting of ZnO nanoparticles in suspension with apparent diameters of about 5 nm, respectively. The solution was filtered through a 0.1 μm membrane filter to remove undissolved LiOH.

To synthesize ZnO nanoparticles of 10 nm diameter, the method of Hoyer was used [14,15]. The solution containing the 5 nm particles was heated and mixed with 5% of deionized water at 60 °C for 10 min. During this procedure, a white powder was formed and precipitated, and then the solution was centrifuged to recover the precipitate. Afterward, the product was washed with an ethanol–water mixture (19:1) and again centrifuged. The last step was repeated four times to remove physisorbed ionic compounds.

2.2. Elaboration of nanocomposite materials

The MEH-PPV was purchased from (Aldrich) and used without purification. In the preparation of hybrid materials, the ZnO nanoparticles with various sizes (5, 10 and 20 nm) were dispersed in toluene, and the MEH-PPV solution was prepared by dissolving MEH-PPV in toluene with a concentration of 10 mg/mL. Solutions of hybrid materials with 0, 2, 5, 10, and 20 wt% ZnO were obtained by mixing the required amount of ZnO nanoparticles with MEH-PPV solution and subjected to ultrasonic treatment for 4 h to improve the dispersion of ZnO nanoparticles. Thin-films of hybrid material were prepared by spin coating the solution on glass substrates. The samples were dried and kept in vacuum. UV–visible absorption spectra of composite films were obtained using a Varian Cary Scan UV–Vis spectrophotometer. Steady state PL spectra were collected from the front face geometry of the samples with a Jobin-Yvon Fluorolog spectrometer using a xenon lamp (500 W) as an excitation source. Ultrafast PL experiments were carried out with a regenerative amplified femtosecond laser system (Spectra Physics Hurricane X) delivering 100 fs pulses at 1 kHz, 800 nm, and 1 W mean power. Composite samples were excited at 267 nm by triple harmonic generation. Transient signals were spectrally dispersed into an imaging spectrograph. The time-resolved emission spectra were detected with a streak camera of temporal resolution < 20 ps.

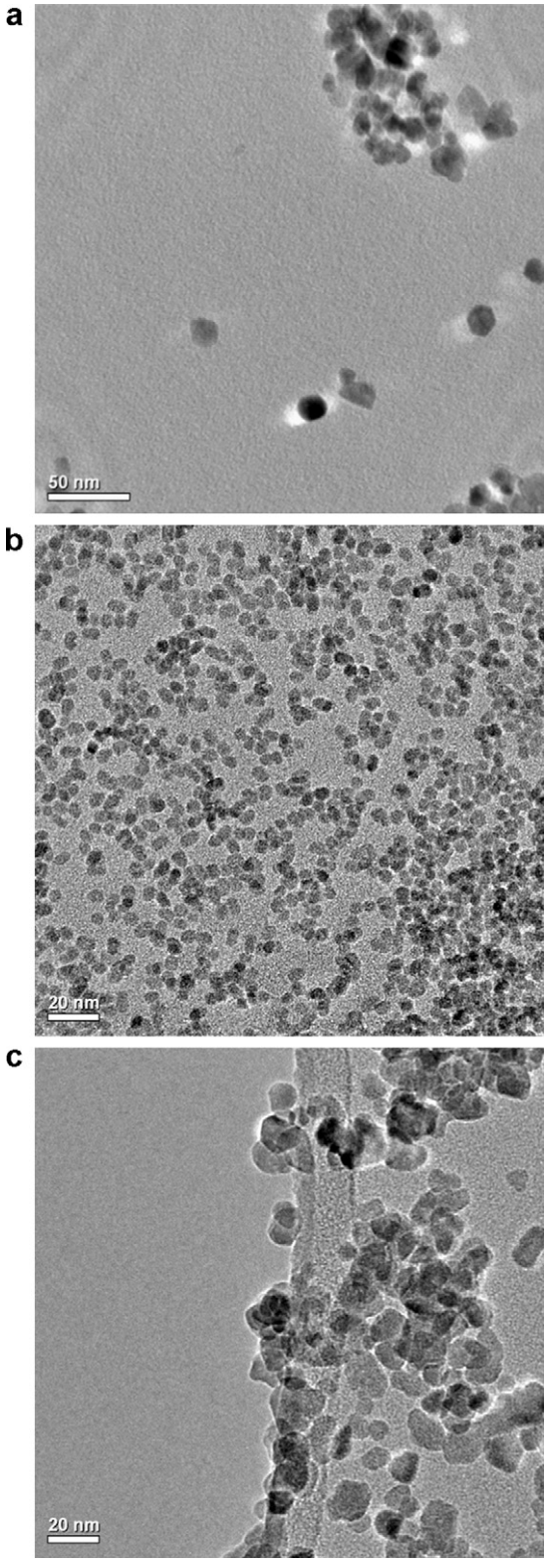

Fig. 1. (a) TEM image for MEH-PPV–ZnO nanocomposites corresponding to 20 nm nanoparticles and 10% concentration, and TEM images of ZnO nanoparticles of sizes: (b) 5 nm, (c) 10 nm.

3. Results and discussion

A transmission electron microscopy (TEM) picture for MEH-PPV–ZnO composites with average particle size of 20 nm and 10 wt% concentration is displayed in Fig. 1(a). In this image, the ZnO particles have a characteristic hexagonal shape. Also, it can be noticed that these particles in some area are dispersed and others aggregate among of polymer. Representative TEM images of ZnO nanoparticles with apparent sizes 5 and 10 nm prepared by method II are presented in Fig. 1(b) and (c).The transient PL spectrum of ZnO nanoparticles of size 10 nm at room temperature is shown in Fig. 2. It is composed of a UV emission band and a broad emission band.