

ENHANCEMENT OF MEH-PPV BY INTRODUCING ANATASE TiO₂ NANOPARTICLES FOR OLED DEVICE

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In this work, the characterization and application of thin films composites incorporated titanium dioxide (TiO₂) (0.002 and 0.008)g/ml anatase nanostructure with poly [2-methoxy-5-(2'-ethylhexoxy-p-phenylene vinylene)] (MEH-PPV) were deposited by spin-coating technique. X-ray diffraction results of MEH-PPV/TiO₂ were proved the anatase phase for TiO₂ predominantly observed in the composite. The morphology was demonstrated by Field Emission Scanning Electron Microscope (FESEM) images for MEH-PPV and MEH-PPV/TiO₂ films and prove agglomerated grains formation. The MEH-PPV/TiO₂ nanocomposite material have been worked as emissive layer (EML) in the organic light emitting diode (OLED), we obtained high current (7430 $\mu\text{A}/\text{mm}^2$) and high electroluminescence spectrum comparative of pristine polymer at the rate of TiO₂ (0.008) g/ml .

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1. Introduction

In the past few decades, conjugated aromatic polymers have attracted considerable interest because of their diverse applications, ranging from electronic devices to light emitting diodes and photovoltaic devices [1-2]. Although these polymers exhibit moderate photoluminescence (PL) quantum efficiencies and their application in light-emitting diode devices is hampered by the formation of chain aggregates in the solid state [5]. Many studies have attempted to enhance the quantum efficiency by controlling the conjugation length [6, 7], blending with small organic molecules [8], changing the polymer structures to form asymmetric poly(this p-phenylene vinylene) derivatives [3], or using an electron-transporting layer [4]. The major approaches to improve the luminescent efficiency of polymers are attaching bulky side groups to the main-chain structures to alter the polymer inter-chain distance [9]. In recent years, greater interest has been directed toward the study of hybrid organic/inorganic nanostructures, owing to the possibility of combining the electrical properties of semiconducting organic polymers with the optical peculiarities of inorganic nanostructures like rods, particles, and thin films [10,16]. The energy transport and electron transport properties of these conjugated polymer/inorganic nano-crystals nanocomposites have been explored in several studies [13,15]. TiO₂ nanocrystals blended with electroluminescent organics have shown lasing action with greatly reduced threshold pump powers [11, 14, 17]. Previous studies concerning TiO₂/MEH-PPV composites films indicated that their electroluminescence (EL) increases with the size of the TiO₂ nanoparticles, the crystal structure of TiO₂ also plays an important role [11, 12]. This is one of the reasons for increasing EL efficiency in the TiO₂ particles/MEH-PPV studies [11, 12].

In the present study, Anatase-TiO₂ mixing with MEH-PPV at volume rate (0.01:0.002 and 0.01:0.008)mg/ml for MEH-PPV/TiO₂ we propose a new approach which blends needlelike TiO₂ nanostructures into MEH-PPV polymer in order to form percolation network geometry. We investigate the effect of the addition of these TiO₂ nanoparticles on the electrical properties by I-V measurement and the spectrum of EL.

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2. Experimental

Preparation of Anatase TiO_2 by hydrothermal method (In a typical synthesis procedure, by using a sealed Teflon-lined autoclave reactor containing 12 ml aqueous solution of titanium trichloride (TiCl_3 , 0.921M), Poly(vinylpyrrolidone) (PVP, 2.205 mM), and sodium sulfate (Na_2SO_3 , 0.954M). The solutions were then put into 200°C oven for 3 hr. The as-synthesized TiO_2 films were rinsed with DI water and dried at room temperature. The polymer(poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) was dissolved by Chloroform solvent at the concentration of about 1 mg/ml and TiO_2 was dissolved by Chloroform solvent(0.002 and 0.008) mg/ml, MEH-PPV: TiO_2 mixed solution were prepared at the volume ration (0.01:0.002 and 0.01:0.008) mg/ml respectively, the mixed solutions were spin coated on glass and silicon P-type(111) substrates . The sample of Electroluminescence preparation by (ITO was cleaned by sequence steps in acetone, ethanol, methanol and de-ionized water in ultrasonic bath for 10 minute each then dried it by trace paper) used as Anode and PEDOT: PSS was coated by spin coating at (1 minute and 4000 rpm) and dried at 150°C for half hour as hole transport layer (HTL). MEH-PPV: TiO_2 with rate (0.01:0.002 and 0.01:0.008) mg/ml was deposited by spin coating for(1 minute and 1500 rpm) as active layer Emitting material layer (EML) , then drayed at 100°C for half hour to remove any residual of solvent. As electron transport layer (ETL) the Tris(8-hydroxyquinolinato)aluminium(Alq_3) by weighting 10 mg and dissolved in 10 ml of Methanol solvent (CH_3OH) to obtain 1 mg/ml concentration then deposited by spin coating for (1 minute and 1500 rpm), the result samples were drayed at 100°C for half hour and finally Deposited AL metal by thermal evaporation methods as Cathode). The schematic diagram of All layers Shows in Fig. 1.

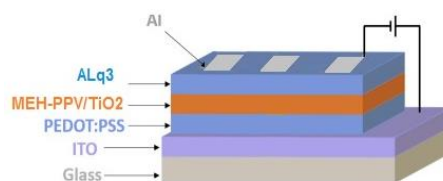


Fig. 1. Represented a scheme diagram of the fabrication OLED device.

The x-ray diffraction (XRD) pattern of the MEH-PPV film deposited on Si substrate is recorded by "SHIMADZU" XRD-6000 X-ray diffract meter ($\text{CuK}\alpha$ radiation $\lambda=0.154$ nm). Field emission scanning electron microscopy (FE-SEM), equipped with Energy-Dispersive produce by "MIRA3 model-TE-SCAN,(Dey Petronic Co.)". Photoluminescence were measured by "Agilent Tech. Cary Eclipse Fluorescence spectrophotometer".

3. Result and discussion

3.1. X-Ray Diffraction (XRD) Analysis

A featureless XRD profile for MEH-PPV and MEH-PPV mixing with (Anatase) TiO_2 at different rate (0.002and 0.008)g /ml , figure (2) shows no crystalline peaks are present in pure MEH-PPV and small concentration rate of Anatase TiO_2 but with increase rate the small peak appear with increase of TiO_2 concentration.

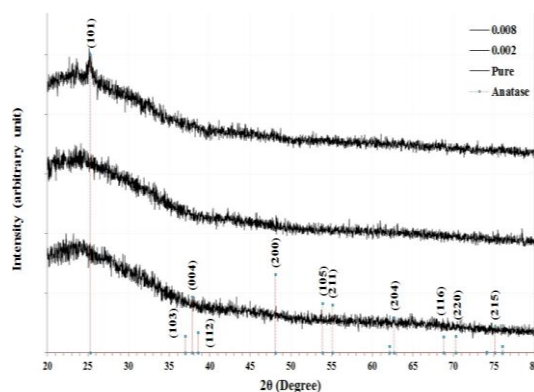


Fig. 2. The structure of MEH-PPV and MEH-PPV/(Anatase)TiO₂ thin films with *h* different rate (0.002,0.004,0.006 and 0.008).

Table 1. Shows the structural parameters for MEH-PPV/(Anatase) TiO₂ films which include the position of the diffraction angle (2θ), full width at half maximum (FWHM), the crystallite size (*D*).

| Ratio | 2θ (Deg.) | FWHM (Deg.) | d_{hkl} Exp.(Å) | G.S (nm) | d_{hkl} Std.(Å) | Phase | hkl | card No. |
|-------|------------------|-------------|-------------------|----------|-------------------|---------|-------|-------------|
| 0.008 | 25.2310 | 0.6620 | 3.5269 | 12.3 | 3.5169 | Anatase | (101) | 96-900-9087 |

3.2. Scanning Electron Microscope analysis (FESEM):

The morphology of the MEH-PPV/ and MEH-PPV/TiO₂ thin films were determined in a Field Emission Scanning Electron Microscopes (FESEM) images. The prepared MEH-PPV/(Anatase) TiO₂ at different rate (0.002 and 0.008) were deposited on Si substrate, figures (3,4,5) shows FESEM images of a composite sample MEH-PPV/(Anatase)TiO₂ nanocomposite. The surface of MEH-PPV appears much smoother than the one of composites with a larger percentage of TiO₂ particles or with larger size TiO₂ particles.

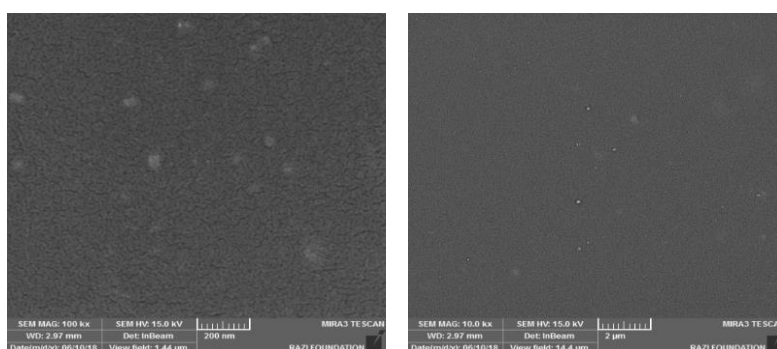


Fig. 3. SEM image of MEH-PPV thin films.

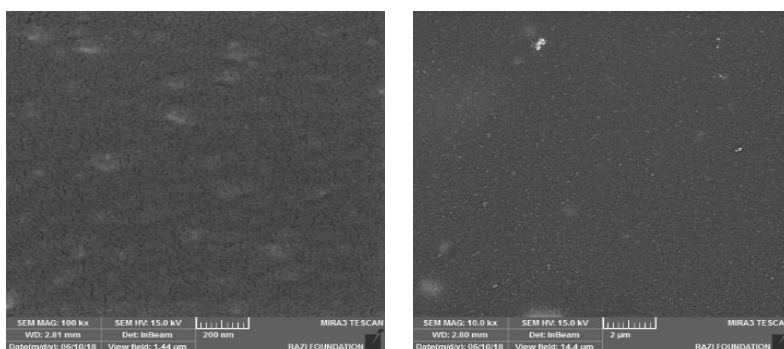


Fig. 4. SEM image of MEH-PPV/(0.002) Anatase TiO_2 nanocomposite thin films.

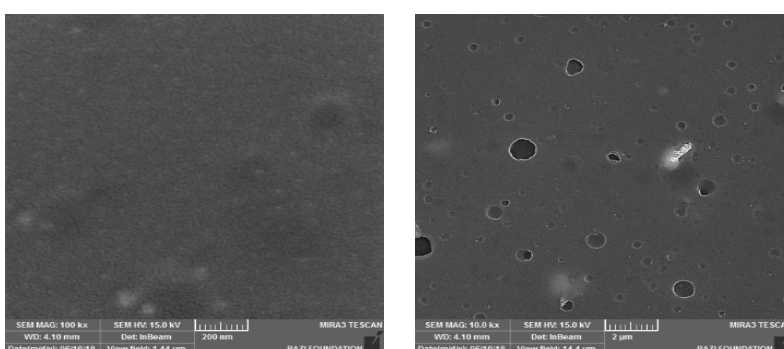


Fig. 5. SEM image of MEH-PPV/(0.008) Anatase TiO_2 thin films.

3.3. Photoluminescence measurements (PL)

Photoluminescence spectrum or emission spectrum has great importance since it gives information about the optical energy band gap, excitons and traps energy level. The photoluminescence spectra of MEH-PPV and MEH-PPV doping with (Anatase) TiO_2 with different rate (0.002 and 0.008)g/ml excited at the wavelength 470 nm and in the range between 530-800 nm . Figure (6) shows the excitation wavelength of the pure MEH-PPV and MEH-PPV mixing with Anatase TiO_2 hybrid films as 470 nm, it is seen that all the samples have broad photoemission at two peaks: one higher at 580 nm and the other lower at 632 nm. This negligible difference in wavelength values and intensity of the emission peaks can be explained due to electroluminescence. The emission peaks are shifted to longer wavelengths with respect to the main absorbance band. This red-shift is explained by emission of most extensively conjugated segments of the polymer. It is seen that photoemission of all the hybrid samples exhibit higher luminescence intensity than that of the pure MEH-PPV. The photoluminescence spectra of hybrid MEH-PPV/ TiO_2 were enhanced with an increase of TiO_2 components (0.002 and 0.008 g/ml, respectively), the enhancement of PL intensity of the composite may be attributed to the presence of interfaces between nanoparticles oxide particles and polymer. At the interfaces of hybrid MEH-PPV/ TiO_2 , charge-space regions are expected to be formed, due to the charge distribution difference between the oxide and the polymer. Under the excitation of a large energy photonic beam, both of conjugated polymer MEH-PPV and TiO_2 nanoparticles were excited. Electrons from the Highest Occupied Molecular Orbital (HOMO) levels of the polymer move toward the Lowest Unoccupied Molecular Orbital (LUMO) and leave holes in the first one. Correspondingly, electrons from the valence band of TiO_2 can jump to the conduction band, creating holes in the first band and resulting in the decrease of the Schottky barrier height in the second band. As a result, the new electron-hole pairs in the emitting layer are generated, leading to an increase of the photoluminescence intensity.

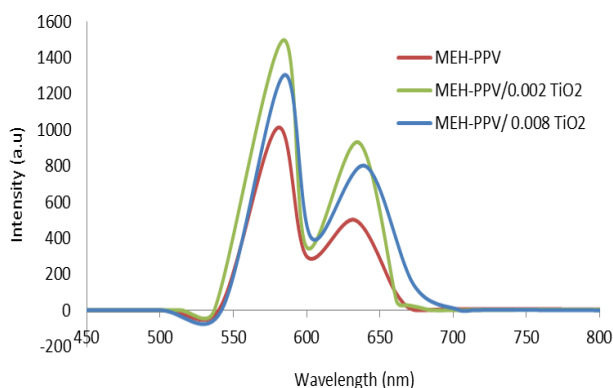


Fig. 6. Photoluminescence spectra for MEH-PPV:AnataseTiO₂ nanocomposite solutions at the 0.01mg/ml mixing with different volume ratio(0.002 and 0.008)mg/ml.

3.4. Organic Light Emitting Diode

I-V characteristics of MEH-PPV and MEH-PPV/(Anatase)TiO₂ nanocomposite preparing by multi layers using ITO(anode)/PEDOT:PSS(HTL)/MEH-PPV:TiO₂ (EL)/Alq₃ (ETL)/AL (cathode) were deposit using spin coater, We assume the formation of HTL as PEDOT:PSS and ETL as Alq₃ during anode and cathode electrode , lowering the barrier or creating a tunneling path for majority and minority carrier[18]. The current–applied voltage curves of nanocomposites with different weight ratios of Titania nanoparticle are shown in figure (7). As the weight ratio of nanoparticles increases, the device current increases. The p-type conductive property of Titania nanoparticles can improve the hole-transporting ability of the MEH-PPV layer. Significantly lower injection barriers are achieved in the nanocomposites because of the reduction barrier for the injection of holes from the ITO anode to the Titania nanoparticles. Also, as a result of doping with Titania nanoparticles the onset voltages decreased from (1 to 0.5) V up to (0.002) g/ml. For higher doping ratios of Titania nanoparticles, no changes in the onset voltages are observed.

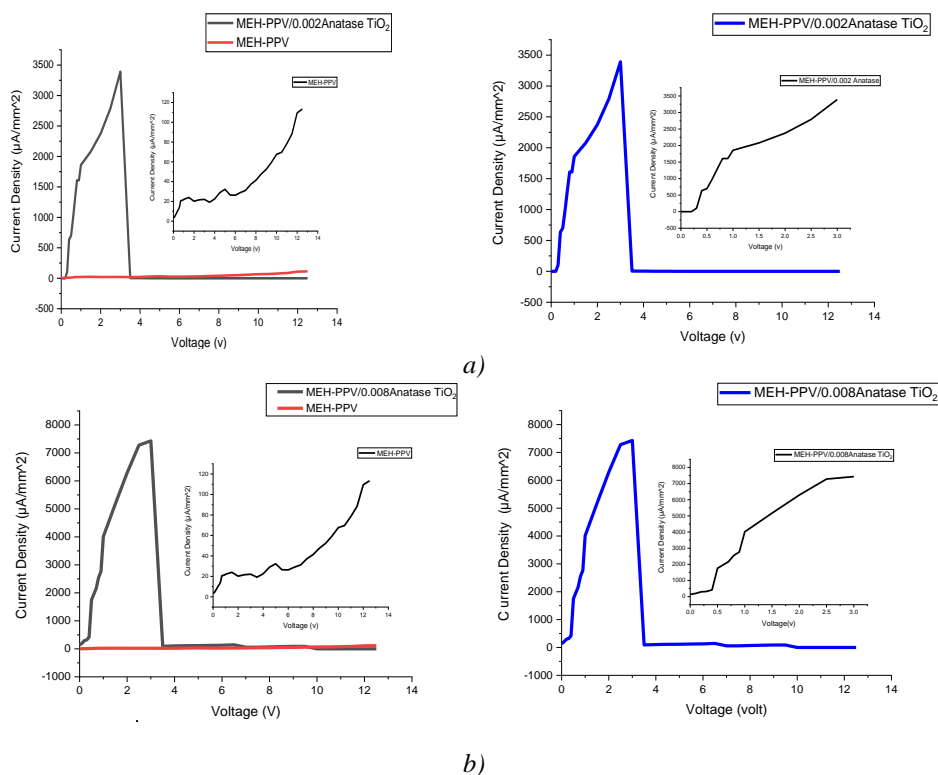


Fig. 7. (a) J-V characterize of pure organic polymer MEH-PPV and mixing with (0.002) TiO₂,(b) J-V characterize of MEH-PPV and mixing with (0.008) TiO₂.

Fig. 8 shows the EL spectra, which studies the effect of mixing TiO_2 into organic polymer "MEH-PPV" as active layer in geometric structure of bottom organic light emitting diode (OLED). The normalized electroluminescence (EL) spectra of nanocomposites with different weight ratios of Titania nanoparticles are shown in figure (8). The emitting light is orange color for MEH-PPV and when mixing with (0.002 and 0.008) of TiO_2 besides both orange at 580 nm and red light 630 nm color, which contributed to the irradiative recombination of MEH-PPV excitons, a blue emission at 430 nm was observed. On increasing the doping fraction of Titania nanoparticles from (0.002) to (0.008) in nanocomposites, the relative intensity of this blue emission increased (as shown in the figure (8)). The blue emission must come from band-to-band transitions of titania nanoparticles. In addition, the MEH-PPV exciton emission is blue-shifted with increasing titania nanoparticles mixing ratios. This is due to polarization effects caused by different dielectric constants between the host and guest materials [19].

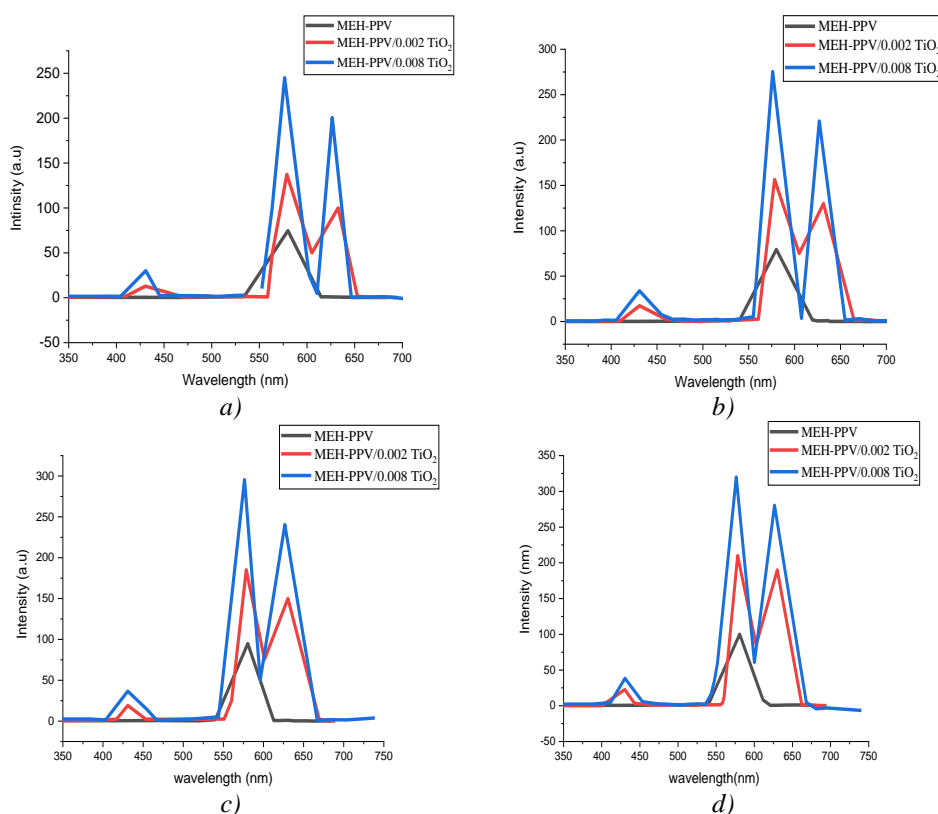


Fig. 8. Normalized EL spectra of LEDs mixing with (0.002 and 0.008) of Anatase TiO_2 at a) 1 volt, b) 3.5 volt, c) 6 volt, d) 8 volt.

Fig. 9 shows the electroluminescence spectra of nanocomposites mixed with Titania nanoparticles at same ratios under different applied voltages. With increasing applied voltages, the relative intensity of the blue emission from Titania nanoparticles increased. The phenyl groups of MEH-PPV are located in the main chain and they connected to each other with double bonds, so the MEH-PPV molecules become rigid. It is difficult to form the cofacial configuration between the planar geometries of the phenyl group of MEH-PPV and the surface of Titania nanoparticle, which results in inefficient energy and charge transfer. Due to the higher electron mobility and the larger electron affinity potential of Titania nanoparticles (compared with organic materials), electrons injected from the cathode are mainly transported by the Titania nanoparticles in the nanocomposites. It is difficult for the electrons transported in the Titania nanoparticles to transfer to MEH-PPV to form excitons. So electrons transported by the Titania nanoparticles can recombine with holes directly by band to-band transitions to emit blue light.

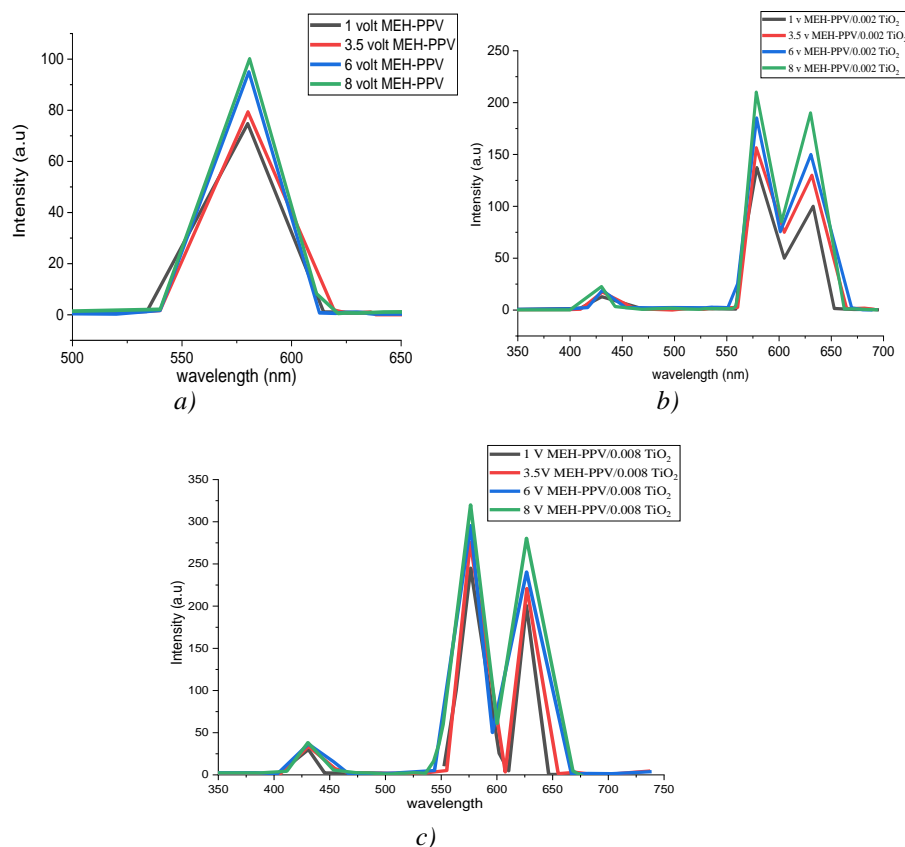


Fig. 9. Normalized EL spectra of LEDs doped with Titania nanoparticles under different applied voltages .(a)MEH-PPV. (b) mixing with (0.002)Anatase TiO₂. (c) mixing with (0.008)Anatase TiO₂.

4. Conclusions

In this work, un-doped and doped MEH-PPV with TiO₂ (anatase) on different substrates has been successfully prepared by spin coating method. The XRD films proved the composite has anatase structure belonging to TiO₂ embedded into polymer matrix. The best electroluminescence and J-V characterization of the OLED (ITO/PEDOT:PSS/MEH-PPV:TiO₂/Alq₃/Al) is for 0.008 rate of TiO₂ , which the current density comparative with the pristine polymer increased from (109.5 to 7430) $\mu\text{A}/\text{mm}^2$ and we have obtained blue color resulting from direct band-to-band transitions of Titania nanoparticles (doped into MEH-PPV).

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