The Influence of ZnO Content on Optoelectronic Properties of Films from MEH-PPV/ZnO Composite

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Abstract: In this work we present a result of optical and photoluminescence (PL) behavior of thin films from blend consisting of ZnO nanoparticles in a conjugated polymer, poly [2-methoxy-5-(2’-ethylhexyloxy)phenylene vinylene] (MEH-PPV), dependent on ZnO content in mixture. While in absorption spectra the blend does not behave absorption peak related to ZnO because of its small volumetric fraction to MEH-PPV, in PL spectra is clearly visible the influence of the ZnO present, which is manifested as changes in form of emission peak at 590 nm and the ratio between two emission peak. The small hypsochomic shifts of these peaks dependent on ZnO content were observed as well. The present of ZnO has been approved by EDX analysis.

Key-Words: MEH-PPV, ZnO nanoparticles, photoluminescence, absorption, dispersion, thin film

1 Introduction

Nanocomposites consisting of conjugated polymers and inorganic nanomaterials, where the electronically active materials are confined at the nanometer scale, are of great interests in recent years. These materials not only have many potential applications in electronics, energy conversion, sensors and etc. [1]

Incorporating inorganic nanoparticles into conjugated polymer matrices is an area of current interest in the fields of optoelectronics and photovoltaics. This approach can take benefits of the advantageous properties of both materials: superior optoelectronic properties of conjugated polymers and high electron mobility of inorganic semiconductors. In addition, polymers are technologically advantageous owing to the ease and flexibility of processing devices in solutions. [2]

Because of ZnO unique physical and chemical properties are offered additional advantages for optoelectronic devices due to the increased junction area, hole transport opportunities and improved carrier confinement in one dimension. [3]

Moreover, ZnO is bio-safe and biocompatible material and in combination with polymer matrix nontoxic as well. [4]

In light emitting devices, polymer based nanocomposites are most applied as hole injection layer and light emitting layer. In a heterojunction between a polymer and a wide band gap semiconductor such as the MEH-PPV/ZnO system, electron can diffuse from the polymer to the semiconductor. When the polymer is illuminated with photon of energy larger than band gap, electron-hole pairs are generated. The electrons are injected into the conduction band of the semiconductor and can move along the nanoparticles network. [5, 6]

Here we demonstrate the fundamental influences on the PL and optical properties of MEH-PPV if it’s in mixture with ZnO nanoparticles. Here are discussed effects of different ZnO content in blend also.

2 Experimental

The preparation of thin films involves three steps. First step is preparation of neat MEH-PPV solution. Concentration of this solution was 1%, used solvent a mixture of CHCl3 and toluene. The solution was stirred some hours for good dissolving of polymer. From such solution were coated thin films as references of behaviour neat MEH-PPV (by spin coating and drop casting method; drop cast films
were from 250 – 350 nm thick). Next step was the addition of ZnO nanoparticles. ZnO nanoparticles concentration sequences were mixed in appropriate concentration (10, 20, 30 and 40 wt. %) related to weight of polymer in blend. After addition of ZnO nanoparticles the solutions were sonicated. After sonication thin films were prepared by spin coating method on quartz glass substrate. The thickness of prepared films was about (50 ± 5) nm. The absorption spectra were measured by UV/VIS Spectrometer Cary 100 (Varian). PL measurements were taken by Fluorimeter FSL 920 (Edinburgh). EDX analysis, to approve ZnO nanoparticles in films, was achieved by SEM microscope VEGA II LMU (Tescan). The ZnO nanoparticles were delivered by Sigma Aldrich and the MEH-PPV as well.

### 3 Results and discussion

How the Fig. 1 shows, absorption spectra persevere in current form, it means that the form is not changed, but the value of absorbance is increasing in case of blend compared to neat MEH-PPV.

![Absorption spectra](image1)

**Fig. 1** Absorption spectra of neat MEH-PPV, curve (a), and blend MEH-PPV/ZnO (content ZnO: b – 10%, c – 20%, d – 30%, e – 40%).

However, the absorbance magnitude at peak 510 nm is not linear to content of ZnO in blend MEH-PPV/ZnO. Because the ZnO nanoparticles do not became evident in absorption spectra, the EDX analysis has been done to present the ZnO in blend. This fact is documented in Fig. 2. The film prepared by drop casting method was not measured by UV/VIS spectrometry due the high scattering and similar effect caused by overmunch thickness.

![EDX analysis](image2)

**Fig. 2** EDX analysis of spin coated sample. Y-axis represents percentage content of components in layer.

The ZnO peaks clearly show the present of ZnO nanoparticles on the substrate.

![Excitation spectra](image3)

**Fig. 3** Excitation spectra of neat MEH-PPV (a-spincoated film, f-dropcast film) and MEH-PPV/ZnO blend (content ZnO: b – 10%, c – 20%, d – 30%, e – 40%), λ_{em} = 590 nm.

The excitation spectra, Fig. 3 and Fig. 4, exhibit just small change, which is given in case of thick film, where the thickness is about 300 nm. The curve of this film is broader than curves of the other. This fact could be explained in terms of interchain absorption transition and could be related to aggregation of polymer chain. This can be supported by the idea that in larger volume of film can be polymer chain easily aggregated and entangled. [7]
Fig. 4 Excitation spectra of neat MEH-PPV (a-spincoated film, f-dropcast film) and MEH-PPV/ZnO blend (content ZnO: b – 10%, c – 20%, d – 30%, e – 40%), $\lambda_{em} = 640$ nm.

From Fig. 5 the influence of nanoparticles on optoelectronic properties of MEH-PPV is evident. The film under irradiation of light exhibits changes in form of spectra. On the curves (a) in Fig. 5 it is denotes how neat MEH-PPV behaves, partially different is behavior of neat MEH-PPV in case of thick film, where are differences in ratio between emission peaks, but the first peak (at 590 nm, transition 0-0) is not quite suppressed.

On the other hand spectra related to blended material are essentially different than spectra for neat MEH-PPV. Transition 0-0 is suppressed and the integration of both emission peaks in one broad band arises. Differences can be explained as an effect of zinc oxide nanoparticles on the intermolecular interaction and exciton recombination, which leads to the unification of energy levels, resulting in integration of the two emission peaks in one and thus the emission on 0-0 transition is quenched. In accordance with Nelson et. all. [8]

In emission spectra was observed clearly blue shift (more than 10 nm from spectra with ZnO content 10 % to 40 %) at transition 0-1. This could be explained as integration of conductive and valence band in composite due the addition of zinc oxide nanoparticles.

Nonlinear discourse content of zinc oxide in blend can be caused by non-integral placement of nanoparticles in the film, where the formation of layer by spin coating is caused by uneven particles disintegration.

To summarize, using our new blending method of MEH-PPV highly filled by ZnO nanoparticles led to a material with different and, moreover, adjustable optoelectrical properties in comparison with neat MEH-PPV as well as with low and moderately loaded composites described in previous literature given in References.

4 Conclusion

To conclude, optoelectrical properties of MEH-PPV are essentially influenced by addition of certain amount of ZnO. The 0-0 transition is after addition of ZnO to blend suppressed and the ratio between 0-0 and 0-1 transition (emission peak at 690 nm) is changed. The ratio between 0-0 and 0-1 transitions is dependent on content of ZnO. Zinc oxide nanoparticles seem to be an appropriate additive to modify luminescent materials used in electronics and photovoltaics with prospective impact on practical application in industrial scale.

To confirm our theories the estimation of exciton diffusion length in MEH-PPV polymer and MEH-PPV/ZnO composite is needed. To estimate exciton diffusion length the surface photovoltage measurements have to be carried out.

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