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Improvement of optical and photoelectrochemical properties of conducting polymer by incorporation of ZnO nanoparticles

F. Habelhames*, W. Zerguine, B. Nessark
Laboratoire d'électrochimie et matériaux (LEM), Faculté de Technologie. Département de génie des procédés Université Ferhat Abbas Sétif-1, 19000 – Algérie.

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* Corresponding author. E-mail: habelhamesfarid@yahoo.fr

Abstract
In this work, MEH-PPV+Bis-PCBM+ZnO composite material was prepared by incorporation of Zinc oxide nonoparticles (ZnO) into poly[2-methoxy-5-(2'-ethylhexyloxy)-*p*-phenylenevinylene] (MEH-PPV) and Bis-(PCBM) polymers matrix and deposited by spin coating on glass and indium thin oxide (ITO) substrates.
The effect of inserting a ZnO nanoparticles interlayer in the MEH-PPV+Bis-PCBM polymer heterojunction device on the electrochemical and optical characteristics of the device has been studied. The absorbance of various MEH-PPV+Bis-PCBM composites incorporating of ZnO nanoparticles shows that addition of ZnO improves absorption of the composites. As a result, the composite has slightly broader absorption.
The study showed that the presence of inorganic semiconductor nonoparticles (ZnO) in polymer film improves the optical and the photovoltaic properties of MEH-PPV+Bis-PCBM, and was designed to explore new approaches to improve light-collection efficiency in polymer photovoltaic.

Keywords: MEH-PPV/Bis-PCBM, morphology, ZnO, Impedance spectroscopy.

1. Introduction
At the same time, the concept of the photovoltaic (PV) device structure has also evolved from single layer [1], double layer [2] to bulk heterojunction (BHJ) [3], which is now the most successful and widely adopted organic PV device structure. The active layer of bulk heterojunction is typically composed of a conjugated polymer (Poly[2-methoxy-5-(20- ethyl-hexyloxy)-1,4-phenylenevinylene](MEH-PPV) [4], P3HT [5] and P3CT [6]) and fullerene derivative such as C_{60} or PCBM (electron accepting molecule) [7–9].
Although various inorganic nanoparticles such as CdSe,[10] CdTe,[11,12] silicon [13, 14], InP [15], GaAs [16] or PbS [17,18] have been studied intensively in the field of hybrid BHJ solar and photoelectrochemical cells. In particular, hybrid BHJs based on the association of transition metal oxide compounds with organic semiconductors have shown promise for more than two decades, and among the metal oxides and especially titanium oxide (TiO_2) [19,20] and zinc oxide (ZnO) [21-23] are of particular interest due to their ease of fabrication, non-toxicity and relatively low production costs.
Hybrid polymer solar cells that use metal oxides as acceptors have been recently reviewed [24-26]. Therefore, in this work we report the morphology modification of MEH-PPV/bis-PCBM proprieties by the addition of ZnO nanoparticles, which enhances the performance of this photoconductive device.

2. Experimental
2.1. Materials
Poly [2-methoxy-5-(20-ethylhexyloxy)-*p*-phenylenevinylene] (MEH-PPV, 99 %), bis-[6,6]-phenyl-C_{61}-butyric acid methyl ester and Zinc oxide nanoparticles (~ 80 nm, 99 %) (Aldrich products) were dissolved and mixed in Chlorobenzene solvent (Aldrich), The supporting electrolyte used for electrochemical and photoelectrochemical characterization is the lithium perchlorate ($LiClO_4$, Fluka) dissolved in the acetonitrile solvent CH_3CN (Aldrich).

2.2. Films preparation
The Polymers (MEH-PPV+bis-PCBM) and Zinc oxide (ZnO) were dissolved in a suitable chlorobenzene solvent for 24 hours. The indium tin-oxide (ITO, from Merck with a sheet resistance ~ 10 Ohm/□) substrates are successively cleaned for 20 min in water and acetone in an ultrasonic bath and finally dried at 120°C. Once dissolved, polymers and ZnO are

deposited by pipetting a small amount into the cleaned ITO substrate then spin-coating on the ITO substrate at 900 rpm (round per minute) for 40 s. Following deposition, films are dried at 80°C during 15 min to evaporate the solvent.

2.3. Characterization

Morphology of the coated active layer (MEH-PPV/bis-PCBM+ ZnO) was examined by atomic force microscope (AFM), using an electron microscope ULTRA 55 (Zeiss, France).

The electrochemical analysis including cyclic voltammetry and impedance spectroscopy of MEH-PPV/bis-PCBM and MEH-PPV/bis-PCBM+ ZnO composite films deposited on ITO (working electrode) by spin-coating were carried out in a one-compartment cell connected to a potentiostat/galvanostat (PGZ-301 Voltalab) coupled with a computer equipped with software (voltamaster 4) which makes it possible to select the electrochemical technique and to fix the parameters desired. The reference electrode is a saturated calomel electrode with KCl (SCE), and the auxiliary electrode is a platinum plate. The supporting electrolyte was 10^{-1} mol.l^{-1} lithium perchlorate ($LiClO_4$, Fluka) dissolved in acetonitrile solvent (CH_3CN, Aldrich). The identical cell is used in the current density measurements in the presence of light and was recorded with a 500 W halogen lamp as polychromatic light source, with illumination intensity of 100 mW/cm^2.

3. Results and discussion

3.1. Electrochemical characterization

The cyclic voltammorgams (CVs) of composite materials (MEH-PPV/PCBM), doped or no doped with ZnO nonoparticle deposited an ITO electrode, in $CH_3CN/LiClO_4$ (10^{-1} mol.l^{-1}) electrolyte solution (Figure 1) shows for all CVs tow peak of oxidation at 0.8 and 1.3 V/SCE correspondents to first an second oxidation of MEH-PPV respectively, another peak at 1.5 V/SCE correspondent to the oxidation of bis-PCBM. In the return scan it observed a large pick at 1.3 V/SCE correspondents to the reduction of composite material.

Currents density of oxidation and reduction peaks of (MEH-PPV/PCBM) increase with addition of ZnO. This suggests that the incorporation of ZnO increases the conductivity of the composite. The observed electrochemical stability of composite material is in good agreement with cyclic voltammograms of other organic/inorganic composites given in the literature [27,28].

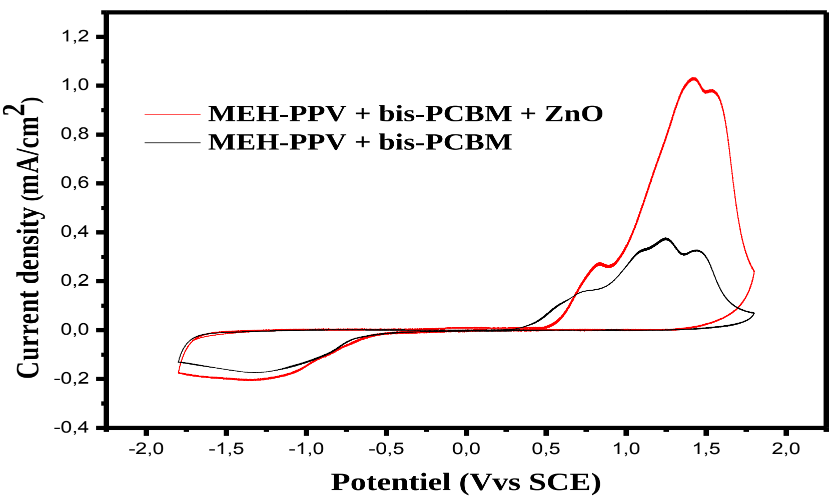

Figure1: Cyclic voltammograms of MEH-PPV/PCBM film and MEH-PPVPCBM+ ZnO composite, in $CH_3CN/LiClO_4$ solution with v = 50 mV/s.

The electrochemical impedance spectroscopy (EIS) responses (Nyquist diagrams) of MEH-PPV/PCBM and composite film (MEH-PPVPCBM+ ZnO) are shown in Figure 2. They were analysed in ($CH_3CN/LiClO_4$ 10^{-1}mol.l^{-1}). The nyquist diagrams were plotted in a frequency range between 100 mHz and 100 kHz, with an alternative current voltage of 10 mV. A scan be seen, EIS spectra have a single semicircle in the high frequency region and a straight line in the low-frequency region [29, 30], which are characteristic of a process of charge transfer and diffusion, respectively.

The semicircle results from the parallel combination of resistance and capacitance and the linear region is due to the diffusion process. From MEH-PPVPCBM+ ZnO composite film, it is observed that the semicircle which is less capacitative and resistant than the MEH-PPV/PCBM film, suggests the incorporation of ZnO semiconductor in polymer.

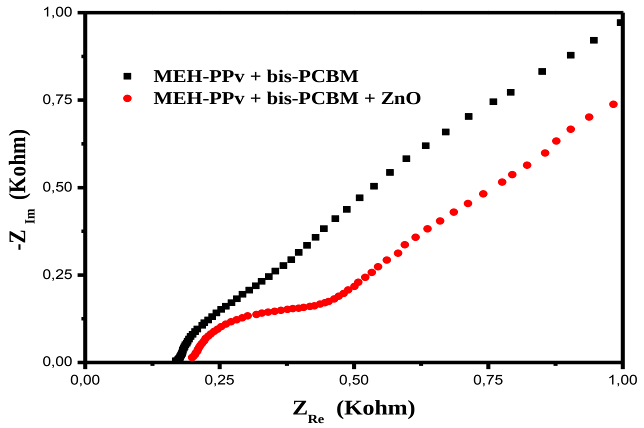

Figure 2: Impedance diagrams of MEH-PPV/bis-PCBMand MEH-PPV/bis-PCBM+ZnO composite film.

3.2. UV–vis spectra

Figure 3 show the UV-visible spectra of Bis-PCBM, MEH-PPV and polymer composites doped or no doped with ZnO semiconductor deposited on glass.

From the MEH-PPV spectra we observed an absorption band located at λ_{max} = 500 nm, is attributed to π– π * transition of the conjugated polymer [31, 32], Therefore, the bis-PCBM shows the absorbance increasing from 270 nm to 600 nm. [33]

We observe that the spectrum corresponding to the MEH-PPV film + Bis-PCBM shows absorbance at 500 nm resulting from the transition π - π * in the MEH-PPV and an increase in absorbance at 400 nm to 270 nm is due to the presence of bis-PCBM, which explains the expansion of the field of MEH-PPV absorbance by the addition of PCBM.

Also, there was a significant improvement in the absorbance of the composite material (MEH-PPV + PCBM-Bis) incorporation of semi-conductor (ZnO), these results are consistent with other results of which use other polymers and other semiconductor nonoparticles.

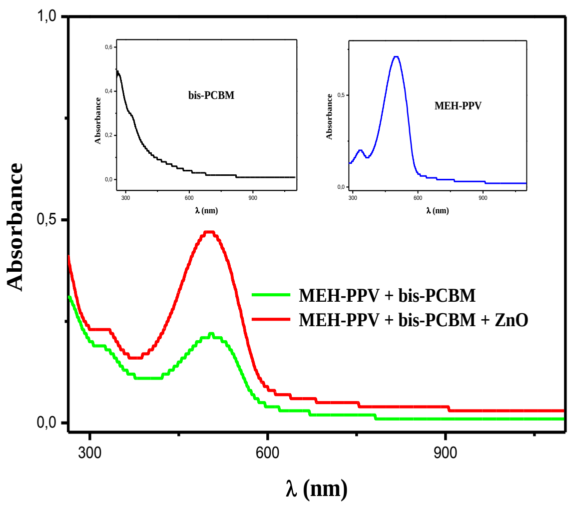

Figure 3: UV–vis absorption spectra of Bis-PCBM, MEH-PPV and polymer composites doped or no doped with ZnO semiconductor deposited on glass.

3.3. Atomic force microscopy (AFM)

The atomic force microscopy image give information about the height differences and also about the constituency of the composite thin film at the surface because the hard nanoparticles can easily be distinguished from the soft polymer.

The surface topography of (MEH-PPV + PCBM-Bis) composites film give more information on the distribution of phases by means of contact-mode atomic force microscopy. And it's shown in figure 4 the addition of zinc oxide (ZnO) nanoparticles increases the root mean square (RMS) roughness (Table 1) of the polymers [34].

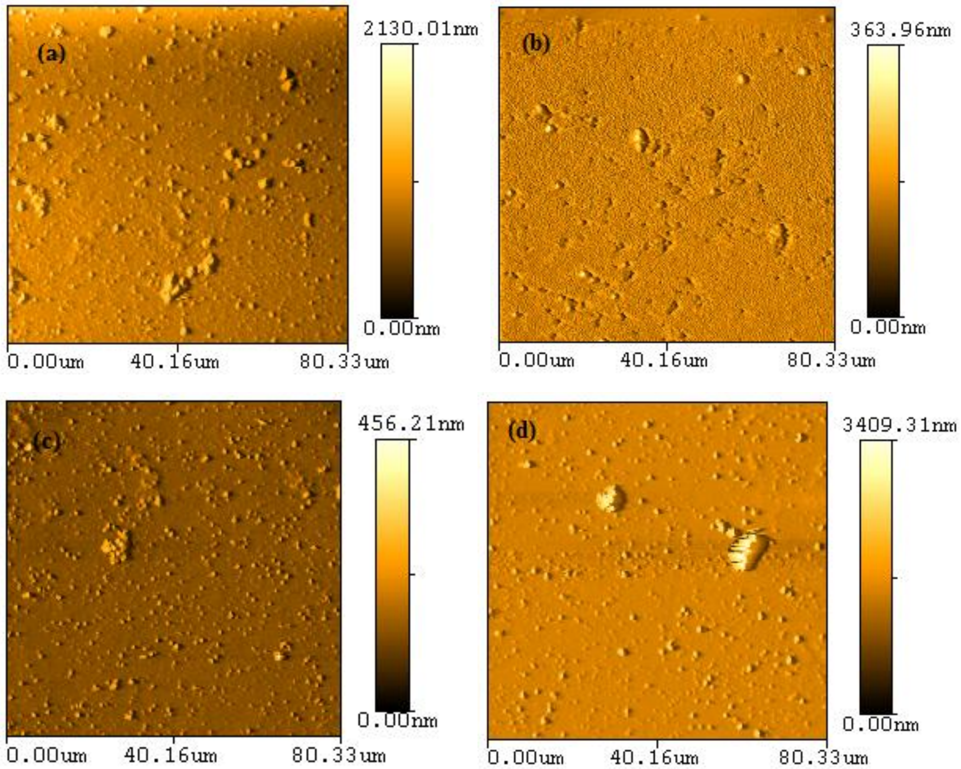

Figure 4: AFM images of (a) MEH-PPV, (b) bis-PCBM (c) MEH-PPV+ bis-PCBM, (d) MEH-PPV+bis-PCBM+ZnO (1:1:1)

Table 1: Root mean square (RMS) roughness determined from AFM characterization of film presented in figure 4.

	MEH-PPV	bis-PCBM	MEH-PPV+bis-PCBM	MEH-PPV+bis-PCBM+ZnO (1:1:0.25)	MEH-PPV+bis-PCBM+ZnO (1:1:1)
(RMS)	281.88	15.80	14.18	120.60	191.88

3.4. Photo-electrochemistry

MEH-PPV, MEH-PPV/bis-PCBM and MEH-PPV/bis-PCBM+ZnO composite films deposited an ITO substrate used as working electrode in photoelectrochemical cell containing acetonitrile/$LiClO_4$ (0.1 mol $l^{-1)}$ electrolyte.

The polymers and composite film were polarised at 0 mVvs.SCE, and after the stabilisation of the current, the working electrode was irradiated with polychromatic light illumination intensity of 100 mW cm^{-2} (Figure 5), it's shows that the polymer film presents a cathodic peak of photocurrent immediately after irradiation.

However, the addition of ZnO in the film polymers increases the intensity of the photocurrent generated by a factor of 2.5 (5.5 to 15.5 µA/cm^2). This suggests that the inorganic semiconductor increasing the number of charge carriers occurs in the composite material. Our results are in agreement with p-type polymer conducting behaviour [35, 36].

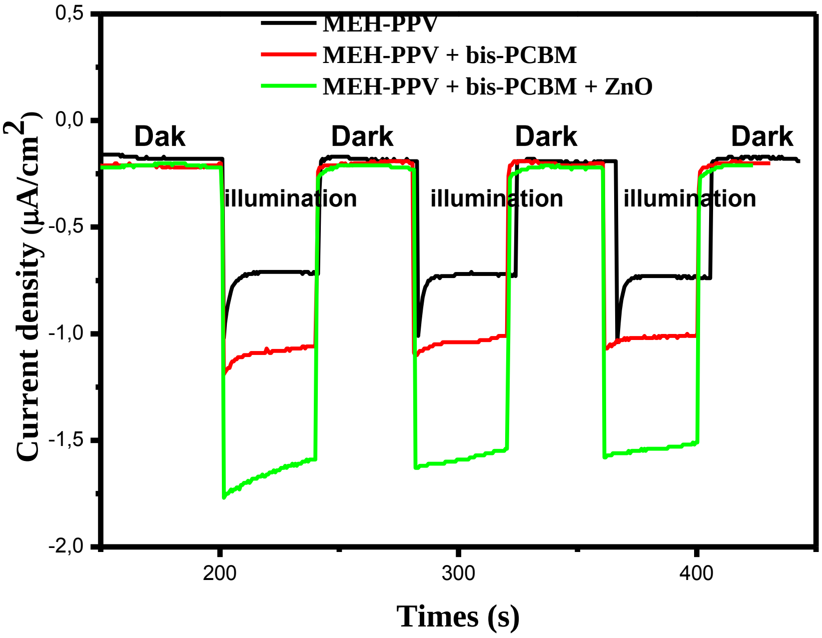

Figure 5: Current density–time dependencies obtained with MEH-PPV/ITO, MEH-PPV+ bis-PCBM/ITO and MEH-PPV+TiO_2/ITO electrode in $CH_3CN/LiClO_4$ at a potential of 0 mV observed upon switching the light on and off, at light intensity of 100 mW cm^{-2}

Conclusion

Organic/inorganic composite films have been obtained by dissolving of MEH-PPV/bis-PCBM with ZnO nonoparticles and were deposited by spin coating on indium thin oxide (ITO) substrates. It's shown that the additions of ZnO nanoparticles improve the absorption of the polymers film and it was observed that the photocurrent of the composites (MEH-PPV/bis-PCBM +ZnO) was higher than that of the MEH-PPV/bis-PCBM without zinc oxide nonoparticles. The study showed that the presence of ZnO nonoparticles in the polymeric film improves the optical and the photoelectrochemical properties of MEH-PPV/ bis-PCBM polymers.

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