

Enhancement of Photoelectrochemical and Optical Characteristics Using a TiO₂ Nanoparticles Interlayer in MEH-PPV Heterojunction Devices

F. Habelhames^{*a}, M. Girtan^{**}, A. Manole^{***}, L. Lamiri^{*}, W. Zerguine^{*}, B. Nessark^{*}

^{*} Laboratoire d'électrochimie et matériaux Faculté de Technologie. Université Ferhat Abbas- Sétif 19000 – Algérie. habelhamesfarid@yahoo.fr

^{**} Laboratoire de Photonique d'Angers, Université d'Angers, 2, Bd. Lavoisier, 49045, Angers, France

^{***} Faculty of Physics, "Alexandru Ioan Cuza" University, 700506-Iași, Romania.

ABSTRACT

In this work, MEH-PPV+TiO₂ composite material was prepared by incorporation of titanium oxide nanoparticles (TiO₂) into poly[2-methoxy-5-(2'-ethylhexyloxy)-*p*-phenylenevinylene] (MEH-PPV) polymer matrix and deposited by spin coating on glass and indium thin oxide (ITO) substrates.

The absorbance of various MEH-PPV composites incorporating different concentrations of TiO₂ nanoparticles shows that addition of TiO₂ improves absorption of the composites. TiO₂ and the conjugated polymer have absorption in the UV and visible regions, respectively. As a result, the composite has slightly broader absorption. In addition, absorption of the composite shows that the polymer induces a certain structuring, as evidenced by the presence of fine structures.

The effect of inserting a TiO₂ nanoparticles interlayer in the MEH-PPV polymer heterojunction device on the photoelectrochemical and optical characteristics of the device has been studied. The modified device (MEH-PPV+TiO₂) shows improved photocurrent density characteristics, and increased with TiO₂ concentration.

The study showed that the presence of inorganic semiconductor nanoparticles (TiO₂) in polymer film improves the optical and the photovoltaic properties of MEH-PPV, and was designed to explore new approaches to improve light-collection efficiency in polymer photovoltaic.

Keywords: hybrid composite materials, MEH-PPV, morphology, photocurrent.

1 INTRODUCTION

Conjugated polymer photovoltaic devices have many positive properties that may provide the means to overcome the current hurdles toward low-cost photovoltaics. However, polymer-based organic photovoltaic are presently limited in their power efficiency due to a number of device and material parameters that have yet to be optimized. The first such limitation is that the band gap of the conjugated polymers needs to be decreased in order to absorb a larger portion of the solar spectrum and increase the photocurrent. The photovoltage could be increased by the proper optimization of the band offsets; where the lowest unoccupied molecular orbital of the donor and the valence band of the acceptor are close in

energy, but still allow for efficient electron transfer. If the band alignment between donor and acceptor materials was more appropriately engineered through the proper selection and design of active materials, this lost energy could be utilized resulting in improved device performance [1-6].

Another key factor in organic photovoltaic device design is the careful control of morphology, leading to efficient dissociation of all generated excitons, and subsequent transport of charge carriers out of the device. [7] Poly (2-methoxy-5-(2'- ethylhexyloxy)-1,4-phenylenevinylene) (MEH-PPV) is a photoactive polymer known to form excitons upon exposure to light [8]. Despite low electron mobility, MEH-PPV has been utilized in solar cells research due to high absorbance in the visible region [9]. Because MEH-PPV possess high hole mobility, it is often paired with an electron carrier to generate photovoltaic devices [10].

Recently, it has been shown that ultra-fast photoinduced charge transfer can also occur between a conjugated polymer and a metal oxide semiconductor such as SnO₂, TiO₂, ZnO, Nb₂O₅, etc. [11,12]. This has led to the fabrication of photovoltaic devices based on composites of oxide semiconductor nanoparticles embedded in a conjugated polymer matrix [13]. Polymeric materials could be deposited by the solution-based technique or electrochemical polymerization onto printable, flexible and large-scale film promising for various applications and commercialization of solar cells [14]. The TiO₂ nanocrystalline electrode is then filled with a conjugated polymer such as poly[2-methoxy, 5-(2'- ethyl-hexyloxy)-1,4-phenylenevinylene] (MEH-PPV) [15,16]

In this paper, we report the modification of MEHPPV proprieties by the addition of TiO₂ nanoparticles, which enhances the performance of this photovoltaic device.

2 EXPERIMENTAL

2.1 Materials

The poly [2-methoxy-5-(2'- ethylhexyloxy)-*p*-phenylenevinylene] (MEH-PPV) (Aldrich) and titanium oxide nanoparticles (40-60 nm) were dissolved and mixed in Chlorobenzene solvent (Aldrich) then spin-coated at 900 rpm (round per minute) for 40 s.

The supporting electrolyte used in photoelectrochemical characterisation is the lithium perchlorate

(LiClO₄, Fluka) dissolved in acetonitrile solvent (CH₃CN, Aldrich).

The indium tin oxide (ITO) coated glass substrate from Merck (sheet resistance ~ 10 Ohm/□) were pre-cleaned by acetone, ethanol and de-ionized water for 15 min consecutively and dried by dry nitrogen.

2.2 Characterisations

The absorption spectra of the active layer MEH-PPV and MEH-PPV+TiO₂ composites deposited on glass were measured with PERKIN ELMER UV/Vis/NIR spectrometer Lambda 19. The film thickness was determined via an Ambios Technology XP-2 surface profiler. AFM images were obtained using an electron microscope ULTRA 55 (Zeiss, France)

The electrochemical analysis including cyclic voltammetry of the single-layer MEH-PPV or MEH-PPV+TiO₂ composite films deposited an ITO (working electrode) by spin-coating were carried out in a one-compartment cell containing a CH₃CN/LiClO₄ 10⁻¹ mol l⁻¹ solution. The cyclic voltammogram (CV) were recording at scan rate $v=50$ mV/s in the potential range of 0 to +1.5 V/SCE. The photocurrent measurements were recorded with a 500 W halogen lamp as polychromatic light source, and the illumination intensity is 100 mW/cm². All measurements were taken at the atmosphere and room temperature.

3 RESULTS AND DISCUSSION

3.1 Atomic force microscopy

As described above, exciton separation only takes place at the interface between the donor (D) and acceptor (A). Thus, the D/A interface plays a significant role in determining the power conversion efficiency of the PV devices. [7]

Investigating the surface topography of MEH-PPV+TiO₂ composites film (~ 120 nm of thickness) can reveal more information on the distribution of phases by means of contact-mode atomic force microscopy, as shown in Fig. 1. Generally, AFM image can give information about the height differences and also about the constituency of the composite thin film at the surface because the hard nanoparticle can easily be distinguished from the soft polymer. And it's shown the addition of titanium oxide (TiO₂) nanoparticles increases the roughness of polymer film (MEH-PPV) [17].

A feature of a better dispersion of TiO₂ nanoparticles structure is found and inevitably leads to providing more donor (MEH-PPV)/acceptor (TiO₂) interfaces and forming their own networks in the active layer.

The results indicate that the interpenetrating network and the small feature size the MEH-PPV-TiO₂ film will facilitate more efficient exciton dissociation, provide more conducting channels for charge transfer and then lead to enhance device performance.

3.2 UV-Vis spectra

Fig. 2 shows the UV-vis absorption of pure MEH-PPV and MEH-PPV + TiO₂ composite films. For all the films, the peak at ~ 500 nm is attributed to $\pi-\pi^*$ transition of the conjugated polymer [18, 19], and the absorbance of various MEH-PPV composites incorporating different concentrations of titanium dioxide shows that addition of TiO₂ nanoparticles improves absorption of the composites before annealing.

TiO₂ and the conjugated polymer have absorption in the infrared and visible regions, respectively. As a result, the composite has slightly broader absorption.

In addition, absorption of the composite shows that the polymer induces a certain structuring, as evidenced by the presence of fine structures.

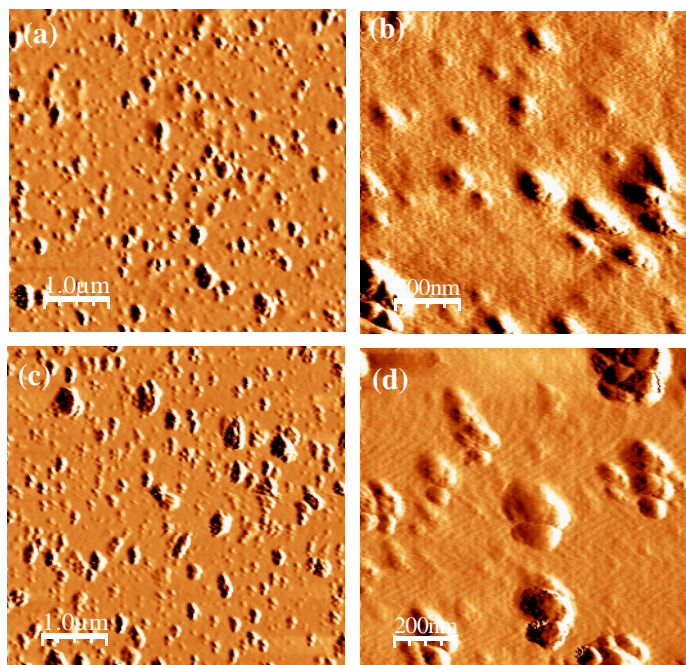


Fig.1. AFM images of (a), (b) MEH-PPV and (c), (d) MEH-PPV+TiO₂ composite film
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This is in agreement with previous results reported by other researchers with other composites based on MEH-PPV [20].

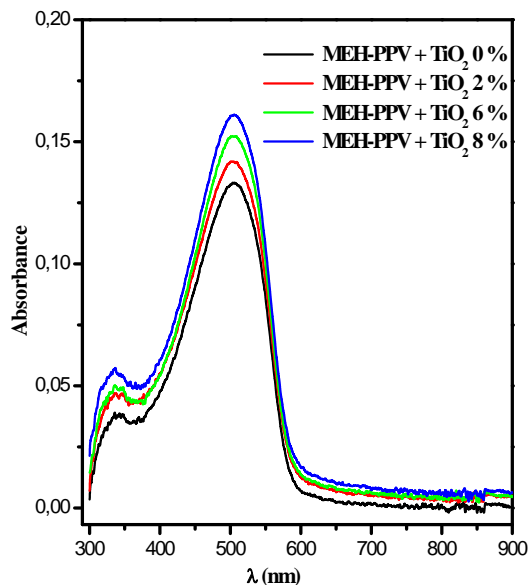


Fig.2. UV-vis absorption spectra of MEH-PPV+TiO₂ obtained for different content of TiO₂

3.3 Photo-electrochemistry

MEH-PPV and MEH-PPV+TiO₂ composite films deposited on an ITO substrate used as working electrode in a photoelectrochemical cell containing acetonitrile/LiClO₄ (0.1 mol l⁻¹) electrolyte.

Fig. 3 shows the photocurrent density as a function of applied potential (-800 to +800 mV vs. SCE) of MEH-PPV+TiO₂/ITO electrode obtained for different content of TiO₂ at a light intensity of 100 mWcm⁻². It is observed that the photocurrent of the modified polymer with inorganic semiconductor nanoparticles at all ranges of potential was negative and higher than that of the non-modified polymer [21].

This response indicates that recombination processes are occurring in the film, probably due to the presence of charge carriers in the polymer bulk, mainly due to structural disorder. The presence of the space-charge region suggests that these polymers may produce photocurrents when illuminated. Furthermore, it has been shown that polymers modified with TiO₂ semiconductor particles could feature higher photocurrents as compared to the pure polymer, MEH-PPV. This shows typical photocurrent transients observed in identical conditions for the MEH-PPV polymer and MEH-PPV+TiO₂ composites at different concentrations of titanium dioxide.

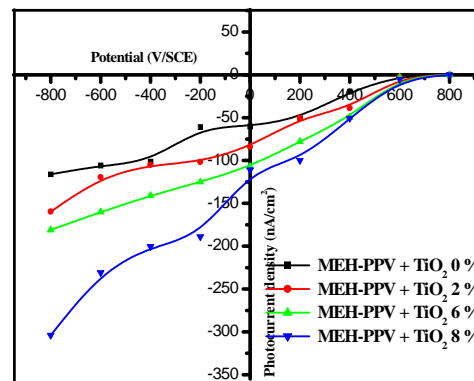


Fig.3. Photocurrent density as a function of applied potential of MEH-PPV+TiO₂/ITO electrode obtained for different content of TiO₂ in CH₃CN/LiClO₄ solution at a light intensity of 100 mWcm⁻².

4 CONCLUSIONS

Composite films of conducting polymer and semiconductor nanoparticles have been obtained by dissolving MEH-PPV with various TiO₂ contents and were deposited by spin coating on glass and indium tin oxide (ITO) substrates.

However, the absorbance of various composites shows that the addition of TiO₂ nanoparticles improves the absorption of the polymer and increases with TiO₂ concentration. The modified device (MEH-PPV+TiO₂) shows improved photocurrent density characteristics, and increases with TiO₂ contents.

The study showed that the presence of TiO₂ particles in the polymeric film improves the optical and the photoelectrochemical properties of MEH-PPV.

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