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Hybrid nanocomposites based on conducting polymer and silicon nanowires for photovoltaic application

Nadia Chehata^{a,*}, Adnen Ltaief^a, Bouraoui Ilahi^b, Bassem Salem^c, Abdelaziz Bouazizi^a, Hassen Maaref^b, Thierry Baron^c, Pascal Gentile^d

^a Equipe Dispositifs Electroniques Organiques et Photovoltaïque Moléculaire, Laboratoire de la Matière Condensée et des Nanosciences, Faculté des Sciences de Monastir, 5019 Monastir, Tunisia

^b Laboratoire de Micro-optoélectronique et Nanostructures, Faculté des Sciences de Monastir, 5019 Monastir, Tunisia

^c Laboratoire des Technologies de la Microélectronique (LTM), UMR 5129 CNRS - UJF, CEA Grenoble, 17 rue des Martyrs, 38054 Grenoble Cedex 9, France

^d Laboratoire Silicium Nanoélectronique Photonique et Structures, CEA Grenoble, 17 Rue des Martyrs, Grenoble, France

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ABSTRACT

Hybrid nanocomposites based on a nanoscale combination of organic and inorganic semiconductors are a promising way to enhance the performance of solar cells through a higher aspect ratio of the interface and the good processability of polymers. Nanocomposites are based on a heterojunction network between poly (2-methoxy-5-(2-ethylhexyl-oxy)-*p*-phenylenevinylene) (MEH-PPV) as an organic electron donor and silicon nanowires (SiNWs) as an inorganic electron acceptor. Nanowires (NWs) seem to be a promising material for this purpose, as they provide a large surface area for contact with the polymer and a designated conducting pathway whilst their volume is low. In this paper, silicon nanowires are introduced by mixing them into the polymer matrix. Hybrid nanocomposites films were deposited onto ITO substrate by spin coating method. Optical properties and photocurrent response were investigated. Charge transfer between the polymer and SiNWs has been demonstrated through photoluminescence measurements. The photocurrent density of ITO/MEH-PPV:SiNWs/Al structures have been obtained by *J*-*V* characteristics. The J_{sc} value is about $0.39 \mu\text{A}/\text{cm}^2$.

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1. Introduction

The discovery of semiconductor properties of conjugated organic materials [1], mostly conjugated polymers and small molecules, has led to a potential research in the field of optoelectronic devices and in particular of organic photovoltaic cells [2]. Compared to traditional technologies based on bulk silicon solar cells [3] and inorganic thin films devices [4], organic polymer materials offer a simple and low cost manufacturing techniques using solution processability process, such as spin-coating and ink jet printing techniques [5]. One of the key advantages of organic solar cells is overlooked in the introduction, namely, their lower embedded energy [6]. Moreover, the use of small weighted organic polymers is sufficient to produce photovoltaic devices in a large scale. Despite the advantages of investigating conjugated organic polymers as

* Correspondence to: Equipe Dispositifs Electroniques Organiques et Photovoltaïque Moléculaire, Laboratoire de la Matière Condensée et des Nanosciences, Faculté des Sciences de Monastir, 5019 Monastir, Tunisia. Tel.: +216 73 50 02 76; fax: +216 73 50 02 78.

E-mail address: nadiachehata2@gmail.com (N. Chehata).

active materials, the power conversion efficiencies (PCE) of organic solar cells are limited to a 10.7% [7]. Multiple factors are responsible for the limitation of the performance of organic solar cells and related to the degradation of organic active layer under continuous illumination, the limited light absorption of organic polymer, and the limited mobility of charge carriers [8]. To overcome these limitations and more explore the technology of organic polymer solar cells, research attention has recently focused on organic-inorganic hybrid nanocomposites. These structures are originated from the concept of organic polymer bulk heterojunction solar cells by combining inorganic nanostructures and organic polymers [9,10]. Multiple advantages are expected from the addition of inorganic nanostructures as acceptor materials, such as the enhanced absorption, the big surface area for contact with the polymer and the improved charge transport characteristics. The major inorganic materials used are cadmium compounds [11], metal oxide nanoparticles [12], low band gap nanoparticles [13] and silicon nanoparticles [14,15]. In principle, hybrid solar cells should show a better efficiency when compared with organic polymer bulk heterojunction solar cells due to the multiple advantages provided by the integration of inorganic semiconductor

nanomaterials. But, so far the performance of organic–inorganic hybrid solar cells still lower than organic bulk heterojunction solar cells in real experiment [16,17]. The limitation of hybrid devices is mostly related to the difference on structural, electronic and physical properties between organic semiconductors. So, it is important to select an appropriate inorganic nanomaterial to be coupled with organic polymer in order to control the nanoscale morphology of donor–acceptor phases. In this study, we present hybrid nanocomposite based on MEH-PPV as organic donor polymer and silicon nanowires (SiNWs) as inorganic acceptor materials. We aim to ensure the efficiency of the combination of these materials as donor–acceptor nanocomposites system, in order to optimize the different steps of the elaboration and the integration of MEH-PPV:SiNWs as photoactive layer to form interpenetrating and percolating bulk heterojunction solar cells.

2. Experimental details

2.1. Materials

MEH-PPV is among the most studied conjugated polymers for its luminescence properties and has been considered as hole transporting semiconductor for making organic and hybrid solar cells. Several studies are reported showing the photoluminescence of MEH-PPV in solutions and in films prepared by distinct techniques [18–20]. MEH-PPV used in this study was purchased from Sigma-Aldrich and the molecular weight of the MEH-PPV was 86,000 g/mol. Silicon nanowires (SiNWs), acting as acceptor semiconductor to form the organic–inorganic hybrid nanostructure, were grown using Vapor–Liquid–Solid (VLS) mechanism. The different steps describing the synthesis of SiNWs will be mentioned later. The common solvent used to disperse MEH-PPV and SiNWs is 1,2 dichlorobenzene (ODCB).

2.2. SiNWs synthesis

The Silicon nanowires were grown using Vapor–Liquid–Solid (VLS) mechanism on nanocrystalline Si (1 1 1) substrate. The growth step was performed in a horizontal low pressure chemical vapor deposition (LPCVD) reactor at 600 °C at a total pressure of 3 Torr using SiH₄ as the Si source and gold colloids as catalyst [21]. We note that the diameter and the length of the nanowires are around 100 nm and 16 μm, respectively.

2.3. Device elaboration

The elaboration of MEH-PPV:SiNWs hybrid structures involves several steps. First, the suprasil glass and ITO-coated glass substrates were cleaned by ultrasonication for 15 min in acetone and followed by extensive rinsing with deionized water and then isopropanol. The ITO-coated glass substrates were dried under vacuum in an oven for 20 min at 100 °C.

Before the dispersion of the nanowires in ODCB, HF (2%) bath was used to remove native oxide from the SiNW surface. Then the nanowires were detached from the substrate wafer by sonication in ODCB for 20 min.

Once MEH-PPV was dissolved in ODCB at a concentration of 15 mg/ml, the obtained homogenous solution was mixed with SiNWs dispersed in ODCB with different ratios of volume. The mixed solutions were stirred for 2 h at room temperature. Under ambient air, MEH-PPV:SiNWs nanocomposite films were prepared by spin coating (1500 rpm for 30 s) a solution of these two components in 1,2 dichlorobenzene (ODCB), into suprasil glass and ITO substrates for optical and electrical measurements, respectively. The obtained photoactive layers are annealed at $T=120$ °C for 20 min under vacuum condition, in order to remove the residual solvent. Finally

and for contact, an aluminum layer of 200 nm of thickness was deposited by thermal evaporation under primary vacuum.

3. Results and discussion

3.1. Morphological properties

Scanning electron microscopy (SEM) images of MEH-PPV:SiNWs (1:1) and MEH-PPV:SiNWs (1:2) were shown in Fig. 1a and b, respectively. We observe that the SiNWs in the MEH-PPV matrix present a homogenous distribution within polymer matrix and their density more important at MEH-PPV:SiNWs (1:2) blend than MEH-PPV:SiNWs (1:1) blend. From Fig. 1c and d, we can observe that the dimensions of SiNWs are changed due to the effect of sonication. A relatively homogenous dispersion of SiNWs in MEH-PPV is observed for different amounts of SiNWs. The homogenous dispersion of SiNWs within the polymer matrix will have a good impact into the photoluminescence response, as the probability of excitons dissociation will be more important on detriment of recombination phenomena. Some studies have investigated the morphology of polymer/SiNWs and its effect on photoluminescence response of these structures [22]. They demonstrated that there is a critical concentration of SiNWs where large aggregates are observed for the highest SiNWs concentration and the PL intensity was increased again. The low density of SiNWs is related to the small ratio of the wires removed from the substrate wafer after the sonication process. SEM observations of an isolated SiNW have been demonstrated that the dimensions of SiNWs are changed, and this is attributed to the effect of sonication. It was demonstrated that for small silicon nanowires, the band gap become direct and then the optical response will be greater than silicon wafer [23]. Moreover, for the solution processable solar cell, the quality of film is very important. So, AFM images of studied devices based on MEH-PPV:SiNWs (1:1) and MEH-PPV:SiNWs (1:2) are provided as shown in Fig. 2.

3.2. UV–visible absorption

In the ground state, if there are an interaction between donor conjugated polymer and acceptor material, it will be observed by a band shift or/and a broadening of the polymer's characteristic absorption bands. These features are owing to the change of the effective conjugation length of the conjugated polymer by the introduction of acceptor material [24]. From Fig. 3, which display the absorption spectra of pure MEH-PPV and MEH-PPV:SiNWs (1:2) nanocomposite, we can observe a band broadening and a red-shift of absorption of MEH-PPV. Moreover, compared with the absorption spectrum of MEH-PPV polymer, the addition of SiNWs has an advantages of improving the light harvesting in the near-infrared and visible region. In most donor–acceptor systems, the donor polymer material is the responsible of the absorption of light and then the excitons will be only there created. In our case, and by the combination of donor polymer and acceptor silicon nanowires, the absorption of light is shared between acceptor (SiNWs) and donor (MEH-PPV) semiconductors. The excitons will be created both in donor and acceptor materials and thus the photocurrent will be generated by SiNWs and MEH-PPV both. In addition and compared to silicon wafer, silicon nanowires have better optical absorption properties. Due to their major surfaces, multiple reflexions of light will contribute to more diffusion of photons [23].

3.3. Photoluminescence measurements

The investigation of photoluminescence response of nanocomposites represents an efficient way to control the dispersion of SiNWs within the polymer matrix and consequent charge transfer

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