



# Metal oxide nanostructures-containing organic polymer hybrid solar cells: Optimization of processing parameters on cell performance



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## ABSTRACT

We report the chemical synthesis of various ZnO nanostructures and TiO<sub>2</sub> nanoparticles and their dispersion in a P3HT matrix. The photoluminescence studies revealed improved charge transport in the active layer of the optimized TiO<sub>2</sub> nanoparticles at a wt. ratio of 0.33, which demonstrated enhanced effective exciton dissociation at the interfaces between the P3HT, ZnO and TiO<sub>2</sub> domains. The influence of the synthesis reaction time for the various ZnO nanostructures and TiO<sub>2</sub> nanoparticles on the solar cell performances was investigated by varying the TiO<sub>2</sub> concentration. The device containing a 0.33 wt. ratio of TiO<sub>2</sub> nanoparticles in ITO/SnO<sub>2</sub>/P3HT:ZnO(24-h):TiO<sub>2</sub>/MoO<sub>3</sub>/Al ternary system showed a maximum efficiency of 2.84% under AM 1.5G illumination.

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## 1. Introduction

Organic photovoltaic (OPV) solar cells have attracted considerable interest due to their promising applications in next-generation global energy production [1]. OPV cells have been spotlighted as harnessing clean energy based on several simple process advantages, such as low cost, semi-transparency, high-mechanical flexibility, and light weight [2–5]. Among the several materials used to construct the active layer of OPV cells, poly-*N*-heptadecanyl-2,7-carbazole-*alt*-5,5'-4,7-di-2-thienyl-2,1,3-benzothiadiazole (PCDTBT) and [6,6]-phenyl C<sub>61</sub>-butyric acid methyl ester (PC<sub>71</sub>BM) blend systems have been shown to be the most promising materials due to their high-power conversion efficiency (PCE) of approximately 7.1% [6]. Similarly, about 7.4% was realized using benzodithiophene polymers (PTBs) with PC<sub>71</sub>BM [7]. Studies have revealed that the nanoscale morphology in the active layer of the blend is crucial to improving the transport of charge carriers in the OPV and its efficiency [8–10]. Recently, substantial advancements in the design and synthesis of novel semiconductors have led to certified efficiencies in a range of 9.2–10.8% [11–13].

Nonetheless, the PCE remains restricted in the polymer and fullerene blends because the charge carrier mobility is relatively low, with a short exciton diffusion length in the active layer [14]. Hence, hybrid solar cells, in which organic semiconductor blends

are mixed with inorganic nanostructures or nanoparticles, have been considered as one of the most promising concepts [15]. This is due to the fact that inorganic materials are environmentally friendly and inexpensive to be synthesized using wet chemical methods with various morphologies, thus allowing a complete compatibility with the solution-processable fabrication of polymer solar cells. Additionally, inorganic materials such as ZnO, TiO<sub>2</sub> have excellent charge transport properties that make their use in the active layer of bulk-heterojunction (BHJ) to enhance on charge carrier mobility. This enhancement reduces the recombination of electron-hole pairs and improves light harvesting as optical spacer to result into PCE with superior performance. The devices composed of organic and polymer materials are usually weak against resisting oxidation from air and light, thus suffers from poor long-term stability. As a result, the top electrode of a low working function metals such as aluminium can easily be oxidized [16,17]. Consequently, in the inverted structure the incorporation of inorganic materials such as SnO<sub>2</sub>, TiO<sub>2</sub> or ZnO can reduce a high energy of UV light and oxidation from oxygen or water thus resulting in an improved long-term stability [18–20]. Besides, the replacement of PCBM with a ZnO or TiO<sub>2</sub> can significantly reduce the cost of BHJ solar cells significantly particularly with regard to long-term stability performance [21].

Previous studies have indicated that the metal nanoparticles improve the optical absorption, either via the formation of scattered waves at the large diameter nanoparticles or due to the excitation of localized surface plasmon resonance modes at the

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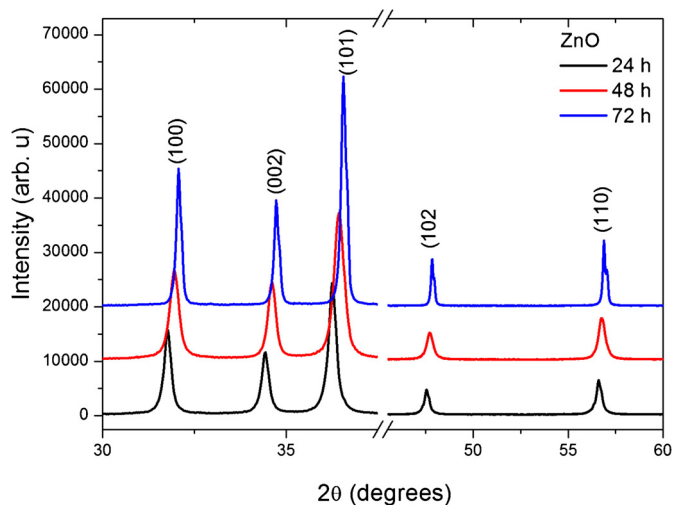


Fig. 1. XRD patterns of the ZnO nanostructures grown at various reaction times.

smaller diameter nanoparticles [22]. Moreover, Mock et al. [23] and Xu et al. [24] reported that the absorbance of a nanomaterial can be tuned by altering its size, shape, material, and the ligand. Therefore, we report herein the effect of the synthesis reaction time of various zinc oxides (ZnO) nanostructures on the photovoltaic properties. Additionally, the performance of the solar cells was studied by varying the concentration of titanium dioxide ( $\text{TiO}_2$ ) nanoparticles into the P3HT:ZnO matrix. The structural and optical properties of the hybrids were studied and correlated with solar cells performance.

## 2. Experiment details

### 2.1. Materials and chemicals

Regioregular-P3HT (molecular weight  $\sim 64,000 \text{ g mol}^{-1}$ , 99.9 purity), indium tin oxide (ITO) coated on a 1 mm glass substrate

Table 1

Summary of the unit cell parameters of the (002) orientation for ZnO nanostructures prepared at various reaction times.

Films	$2\theta_{(002)}$ ( $^\circ$ )	$L_{(101)}$ (nm)	$L_{(002)}$ (nm)	$a_{100}$ ( $\text{\AA}$ )	$c_{002}$ ( $\text{\AA}$ )	$V$ ( $\text{\AA}^3$ )
ZnO-24 h	34.460	27.047	11.170	3.2482	5.2044	47.5526
ZnO-48 h	34.501	33.681	22.881	3.2307	5.1770	46.7939
ZnO-72 h	34.518	52.382	23.282	3.2179	5.1601	46.2723

(resistivity of  $8\text{--}12 \Omega \text{sq}^{-1}$  and transmittance  $>83\%$ ), 1,2 dichlorobenzene (anhydrous,  $\geq 99\%$ ), zinc nitrate hexahydrate [ $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ], Tin (Sn) powder, poly(vinyl pyrrolidone) (PVP, 99.9% purity), titanium isopropoxide (99.9% purity), ammonium hydroxide ( $\text{NH}_4\text{OH}$ ) (33%  $\text{NH}_3$  in water, 99.99%), and 70% nitric acid ( $\text{HNO}_3$ ) were purchased from Sigma–Aldrich, South Africa and used as received without any purification.

### 2.2. Synthesis procedure of ZnO nanostructures

ZnO nanostructures were synthesized by adding 3.0 g of [ $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ] to 80 ml of ethylene glycol in a 250 ml round-bottom flask. In addition, 0.8 g of PVP was added as a structure-directing template agent, and the reaction mixture pH was adjusted to 11 using  $\text{NH}_4\text{OH}$ . The reaction mixture was continuously stirred under reflux for various reaction times of 24, 48 and 72 h. The solids slurries obtained were collected by filtration, washed thoroughly with ethanol and dried at  $120^\circ\text{C}$  for 12 h. The prepared nanostructured powders were subsequently calcined by being heated at a rate of  $5^\circ\text{C}/\text{min}$  from room temperature to  $550^\circ\text{C}$  in air for 1 h. The obtained ZnO nanostructures were then denoted as ZnO-24, ZnO-48 and ZnO-72 depending on the synthesis reaction time of 24, 48 and 72 h, respectively.

### 2.3. Synthesis of $\text{SnO}_2$ nanoparticles

Tin oxide ( $\text{SnO}_2$ ) nanoparticles were synthesized using a hydrothermal method. A one gram of Sn powder was mixed with

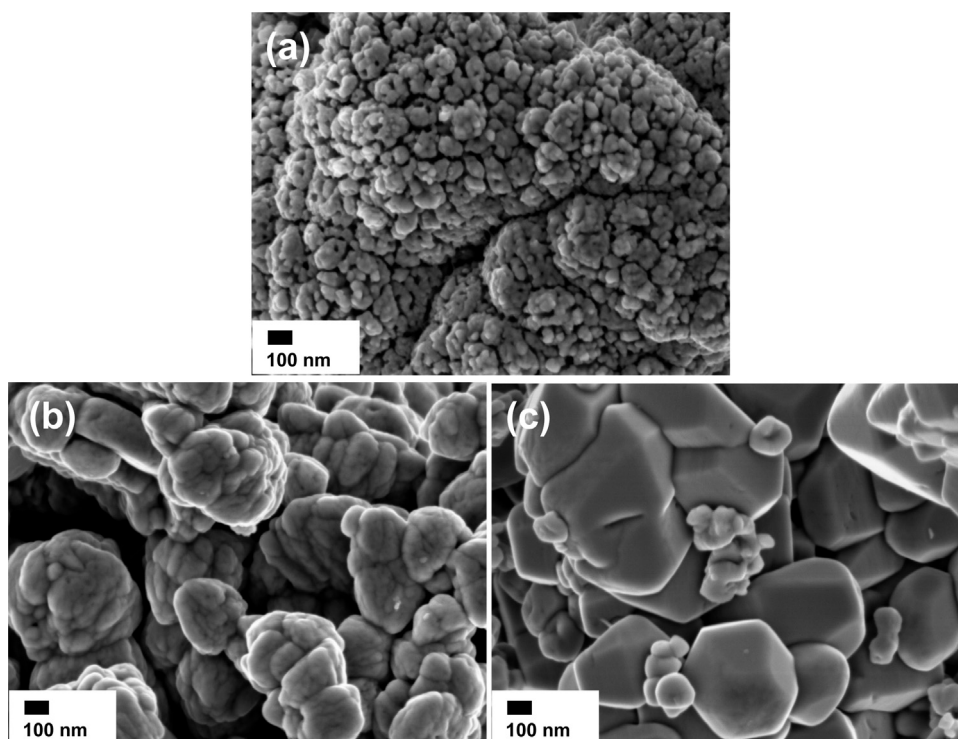


Fig. 2. HR-SEM images of ZnO grown at various reaction times: (a) 24 h, (b) 48 h and (c) 72 h.

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