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### Enhancement of the Efficiency of Polymer Solar Cells by Blending Nb/ZnO Nanoparticles into Poly(3-hexylthiophene):[6,6]-phenyl C61-butyric Acid Methyl Ester

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# Enhancement of the Efficiency of Polymer Solar Cells by Blending Nb/ZnO Nanoparticles into Poly(3-hexylthiophene):[6,6]-phenyl C61-butyric Acid Methyl Ester

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*Bulk-heterojunction (BHJ) solar cells utilizing P3HT:PCBM composite loaded with niobium-doped zinc oxide nanoparticles (Nb/ZnO NPs) produced by flame spray pyrolysis were fabricated. The devices loaded with and without Nb/ZnO NPs were compared. It was found that niobium doping led to a slight increase in open circuit voltage and an increase in short-circuit current. The effect of co-solvent (1,3,5-trichlorobenzene; TCB) in chlorobenzene in the polymer solution was also investigated on the morphology and performance of a P3HT:PCBM and P3HT:PCBM:Nb/ZnO bulk-heterojunction solar cells. The device efficiency was improved due to a good quality of the thin film nanostructure and annealing time.*

**Keywords** Conjugated polymer; flame spray pyrolysis; niobium-doped zinc oxide; polymer solar cell; 1,3,5-trichlorobenzene

## Introduction

Poly(3-hexylthiophene) (P3HT) is one of the most attractive soluble conjugated polymers for applications in organic photovoltaic cells (OPVs). For instance, charge separation of photogenerated excitons and enhanced electron mobility in conjugated polymers can be achieved by adding organic semiconducting materials as electron acceptors such as [6,6]-phenyl C61-butyric Acid Methyl Ester (PCBM) [1] or Nb/ZnO NPs [2]. Significant

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improvement has been achieved by controlling the nanomorphology of the phase separation in an interpenetrating bulk heterojunction [1,3]. The nanoscale morphology of the interpenetrating donor:acceptor materials could be optimized through appropriate preparation conditions such as annealing conditions and choice of solvents [1,4]. In this work, the effect of niobium doping on composite solar cells using the 3 mol%Nb/ZnO nanoparticles and the use of 1,3,5-trichlorobenzene (TCB) as co-solvent for enhancing nanostructured P3HT:PCBM:Nb/ZnO layer were investigated.

## Experimental

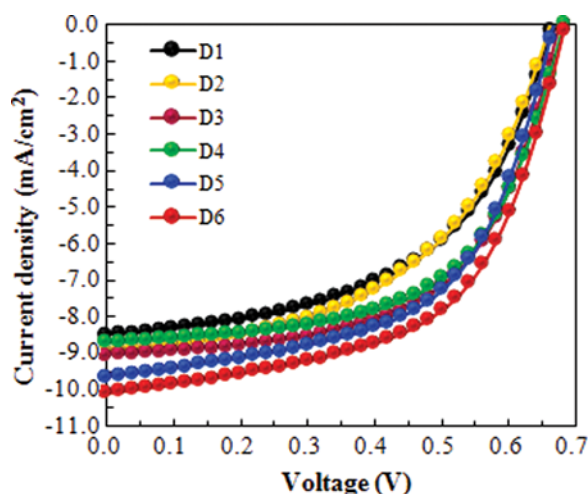
Nb/ZnO NPs were synthesized by FSP technique [2,5]. The fabrication of our BHJ solar cells was reported in our previous work [2]. For this study, three sets of devices were fabricated. The 3 mol%Nb/ZnO NPs were prepared in 1-butanol to give the concentration of 15 mg mL<sup>-1</sup>. Indium tin oxide (ITO) patterned glass substrates. An PEDOT:PSS film was spin coated onto the ITO glass substrate, which was then dried in vacuum oven at 100°C for 25 min. 15 mg of P3HT was dissolved in 1 ml of chlorobenzene and blended with PCBM in the ratio of 1:0.7 polymer to PCBM by weight. The composite materials were spin coated onto the PEDOT:PSS layer at 1500 rpm. Lithium fluoride (LiF) and aluminum (Al) electrodes were deposited via thermal evaporation at approximately 15 nm and 100 nm thick, respectively. The active area of these devices is 0.38 ± 0.04 cm<sup>2</sup>. For device set 1, D1 and D2 were annealed for 5 and 7 min respectively. For device set 2, D3 and D4 were prepared by adding 30 vol% of 3 mol%Nb/ZnO solution to P3HT:PCBM solution and annealed for 5 and 7 min respectively. Finally, device set 3, D5 and D6 were prepared by adding 30 vol% of 3 mol%Nb/ZnO solution and 1,3,5-trichlorobenzene (TCB) (3.5 mg) to P3HT:PCBM solution annealed for 5 and 7 min respectively.

The *J-V* (current-voltage) characteristics of the solar cells were test in air at room temperature. The light intensity was 100 mW cm<sup>-2</sup> on the sample surfaces measured by a photodetector. External Quantum Efficiency (EQE) measurements were performed using a Hitachi F-4500 fluorescence spectrophotometer with an AM 1.5 filter. Light intensity was adjusted in the wavelength range of 300–700 nm. All electrical measurements were performed in the air. The active area of the device irradiated by the light was defined by photo mask as 0.03 cm<sup>2</sup>. The surface morphological features of the films were examined using atomic force microscope (AFM) system.

## Results and Discussion

The *J-V* measurements are shown in Figure 1, Nb/ZnO particles synthesized with 3 mol% concentration of niobium were then used to investigate the effect of NPs on the photovoltaic characteristics of devices. From the data summarized in Table 1, there is a small increase in open circuit voltage ( $V_{oc}$ ) for Nb/ZnO doped devices. The Nb/ZnO solution-blended P3HT:PCBM films exhibited higher values of  $J_{sc}$  with the maximum value of 9.02 mA cm<sup>-2</sup> obtained with annealing time of 7 min. (8.94 mA cm<sup>-2</sup> for the unmodified device). The increased  $J_{sc}$  and  $V_{oc}$  lead to the enhanced power conversion efficiency ( $\eta$ ). This power conversion efficiency was a 16.4% improvement from the standard cell to the most efficient loading (from 2.90% to 3.47%).

The effect of TCB as co-solvent in the polymer solution on the performance of the devices was also investigated as shown in Figure 1. The best performance, with a



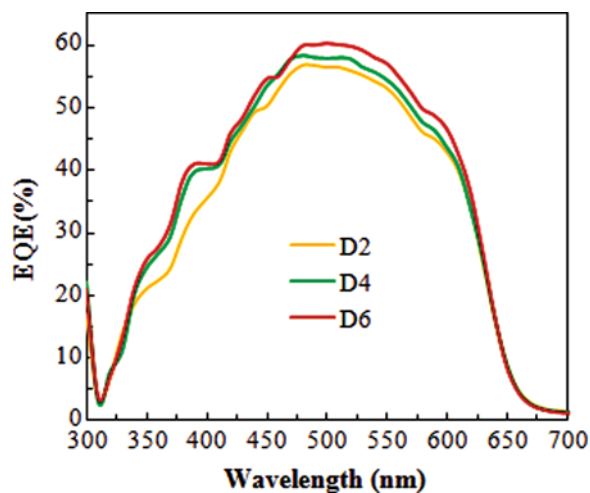
**Figure 1.**  $J$ - $V$  characteristics of P3HT:PCBM and P3HT:PCBM:3mol%Nb/ZnO bulk-hetero junction solar cells blends (both with and without added TCB) annealed for 5 and 7 min.

short-circuit current density  $J_{sc} = 10.1 \text{ mA/cm}^2$ , a fill factor  $FF = 0.567$ , an open-circuit voltage  $V_{oc} = 0.682 \text{ V}$  and a resulting efficiency of 3.79%, could be reached for a cell blended with 3mol%Nb/ZnO solution and annealed at  $150^\circ\text{C}$  for 7 min with a TCB concentration of 3.5 mg/ml. This yielded an 11% improvement over the devices obtained under the same conditions but without the inclusion of TCB. The FF of all devices was within what would be expected for standard devices made with this P3HT and annealed for 5 and 7 min.

The EQE measurements show an increase in photon collection, and thus photocurrent, across all wavelengths absorbed as seen in Figure 2. There is a prominent increase at 385 nm, corresponding to the probable band gap of 3.2 eV of ZnO. The morphology of P3HT:PCBM:3mol%Nb/ZnO layers from spin-coated CB solution and mixed solution (CB and TCB) after annealing at  $150^\circ\text{C}$  for 7 min., have been studied using AFM.

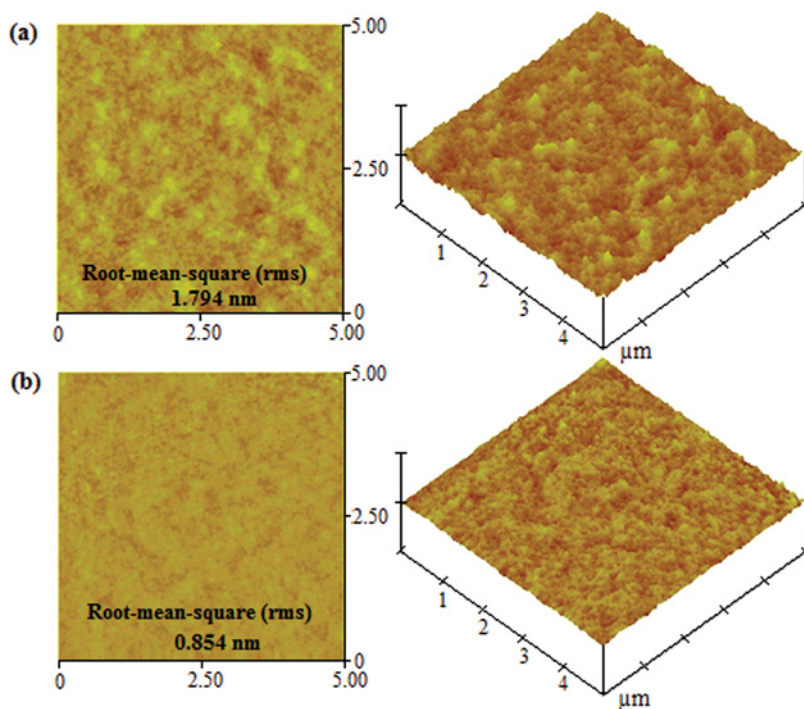
**Table 1.** Solar cells characteristics of P3HT: PCBM and P3HT:PCBM:3mol%Nb/ZnO bulk-hetero junction solar cells blends (both with and without added TCB) annealed for 5 and 7 min

Samples	$V_{oc}$ (V)	$I_{sc}$ ( $\text{mA/cm}^2$ )	FF	$\eta$ (%)
D1: P3HT:PCBM(CB-5 min)	0.663	8.49	0.529	2.89
D2: P3HT:PCBM(CB-7 min)	0.660	8.94	0.506	2.90
D3: P3HT:PCBM:3mol%Nb/ZnO (CB-5 min)	0.680	8.72	0.588	3.38
D4: P3HT:PCBM:3mol%Nb/ZnO (CB-7 min)	0.674	9.02	0.588	3.47
D5: P3HT:PCBM:3mol%Nb/ZnO (CB+TCB-5 min)	0.665	9.65	0.566	3.53
D6: P3HT:PCBM:3mol%Nb/ZnO (CB+TCB-7 min)	0.682	10.10	0.567	3.79



**Figure 2.** EQE spectra of P3HT:PCBM and P3HT:PCBM:3mol%Nb/ZnO bulk-hetero junction solar cells blends (both with and without added TCB) annealed for 7 min.

The atomic force microscopy (AFM) topography images indicate the smoother film surface of the P3HT:PCBM:3mol%Nb/ZnO when TCB was used as the co-solvent in the blend, as shown in Figure 3. Film as prepared from CB+TCB,



**Figure 3.** AFM images of P3HT:PCBM:3mol%Nb/ZnO spin-coated from (a) CB and (b) CB+TCB annealed for 7 min.

the surface is rather smooth with r.m.s. roughness of 0.854 nm, while the film prepared from CB shows r.m.s.  $\sim 1.794$  nm. The surface of film was smoother with the addition of TCB at 3.5 mg/ml, which in turn improved the organic/cathode contact. The power conversion efficiency of such fabricated solar cells was higher than that of cells formed without TCB solvent.

One possible explanation is that the Nb/ZnO particles act as scatterers within the active layer of the device. This scattering effect could lead to better absorption via optical confinement within the device. Charge transport could also be changed significantly with NP content, leading to suboptimal device characteristics (improved or degraded charge carrier mobility can affect the overall charge balance of the device). This could also be the reason that niobium doped particles have a positive effect on the device as opposed to the negative effect evidenced by the ZnO particles as the niobium could have an effect on how the NPs integrate into the BHJ film. The slight increase in  $V_{oc}$  can be attributed to the change in band alignment caused by the introduction of the Nb/ZnO NPs [2].

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