

# Influence of solvent casting and weight ratios on the morphology and optical properties of inorganic-organic hybrid structures

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**Abstract.** Organic photovoltaic (OPV) solar cells have the advantage of simple processing, low cost, semi-transparency, high-mechanical flexibility, and light weight. Investigations into OPV solar cells using bulk heterojunction (BHJ) structures have driven extensive and successful efforts to enhance their power conversion efficiencies (PCE). It has been demonstrated that nanoscale morphology is essential for improved transport of charge carriers in the OPV cell containing poly (3-hexylthiophene) (P3HT) and (6,6)-phenyl C<sub>61</sub> butyric acid methyl ester (PCBM) structures, and for enhancing its efficiency. Inorganic semiconductors such as zinc oxide (ZnO) have been incorporated into the BHJ structures due to their high carrier mobilities; it is inexpensive and ZnO-nanorod arrays offer an excellent controllable transport path. In this contribution the effect of solvent to control the degree of mixing of the polymer, fullerene and ZnO nanoparticles components into a hybrid inorganic-organic structure, is investigated. Evolution of the domain size, structure and optical properties of hybrid ZnO:P3HT:PCBM thin films spin-coated from different weight is studied, using High Resolution Transmission Electron Microscopy (HRTEM), UV-visible spectroscopy, X-ray diffraction (XRD) and spectroscopic ellipsometry (SE).

## 1. Introduction

Solution based bulk heterojunction photovoltaic devices incorporate p-type conjugated polymers in combination with fullerenes, with the aim of boosting the efficiencies of organic photovoltaic devices [1]. In such hybrid devices the conjugated polymer may be combined with inorganic semiconductor nanoparticles such as zinc-oxide (ZnO) to take advantage of its high electron mobility [2]. In this contribution we use as active layer regioregular poly (3-hexylthiophene), commonly known as P3HT, in which (6,6)-phenyl C<sub>61</sub> butyric acid methyl ester (PCBM) has been blended with a set percentage weight ratio. We further incorporate nanoparticles of ZnO into the blend with the aim of studying the degree of mixing of the polymer, fullerene and ZnO components. Of importance is the domain size,

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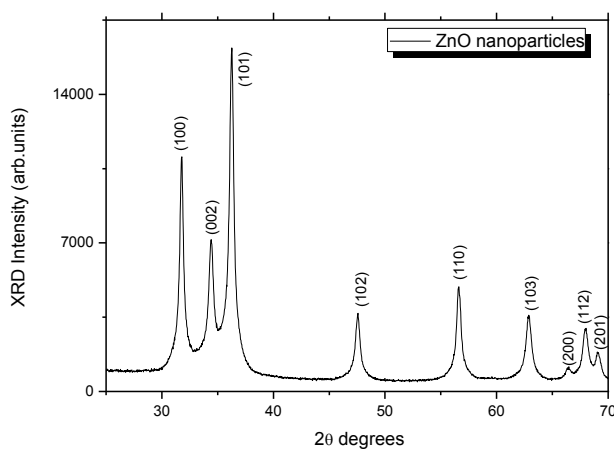
structure and optical properties of the thin films when ZnO:P3HT:PCBM is spin-coated from different weight ratios onto substrates.

## 2. Experimental Procedure

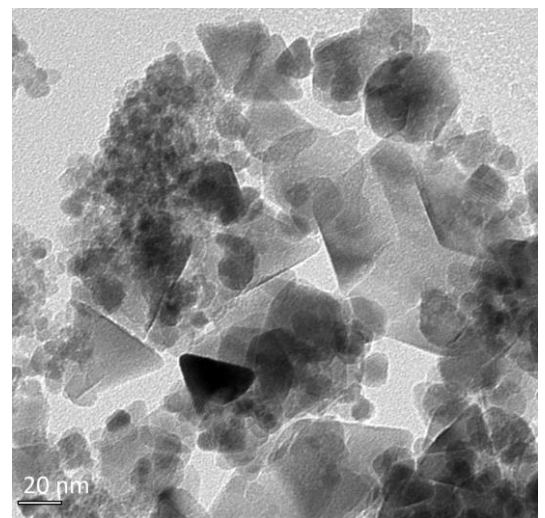
ZnO nanoparticles were prepared by hydrothermal method as discussed before [3]. The photoactive ingredients were prepared by mixing weight percentages of 5 mg P3HT with 5 mg PCBM, and dissolving in dichlorobenzene. The hybrid material was prepared similarly with 5 mg and 10 mg ZnO mixed into the photoactive blend. The solutions were then spin-coated onto Corning 7059 and c-Si wafer substrates at 2000 rpm for 30 s, and dried for 30 min on a hot plate at 50°C in order to evaporate the solvent. The crystal structure of the thin films was studied with a Panalytical X'pert PRO diffractometer with Cu  $K_{\alpha}$  radiation ( $\lambda = 0.154$  nm) in  $\theta - 2\theta$  mode, whereas the crystal structure of the ZnO powder was determined using a Bruker system. ZnO mixed in ethanol, and the hybrid ZnO:P3HT:PCBM in dichlorobenzene were inspected with a FEI Tecnai F20 FEGTEM after drying of the solvent. UV-visible absorption spectroscopy and spectroscopic ellipsometry (SE) were carried out with a Perkin-Elmer Lambda 750 UV-Vis and J. A. Woollam M2000 variable angle ellipsometry (VASE) system respectively. A Cauchy model [4] was used to extract the thickness of the films, and a B-Spline model [5] was used to calculate the optical functions of the thin films, assuming a homogeneous material.

## 3. Results and Discussion

The crystal structure of the as-synthesized ZnO was investigated with XRD and HRTEM, as shown in figures 1 and 2. The intense (100) and (101) diffraction peaks suggest a highly crystalline material, with  $\langle 100 \rangle$  and  $\langle 101 \rangle$  the main preferred growth orientations, in a typical hexagonal wurzite structure with average grain sizes of 19.2 nm and 17.1 nm respectively. The d-spacings were calculated using Bragg's Law from the (100) and (101) diffraction peaks and were found to be 0.281 nm and 0.248 nm respectively, with lattice constants  $a = 0.3245$  nm and  $c = 0.5301$  nm. These findings agree well with the data from the Joint Committee on Powder Diffraction Standards (JCPDS: 36-1451). The HRTEM image shows a random collection of small and larger pyramid-shaped structures intermixed together. No characteristic peaks from other impurities by XRD and Energy Dispersive X-ray Spectroscopy (EDS) were detected, indicating a high purity product.



**Figure 1.** XRD pattern of ZnO nano particles.



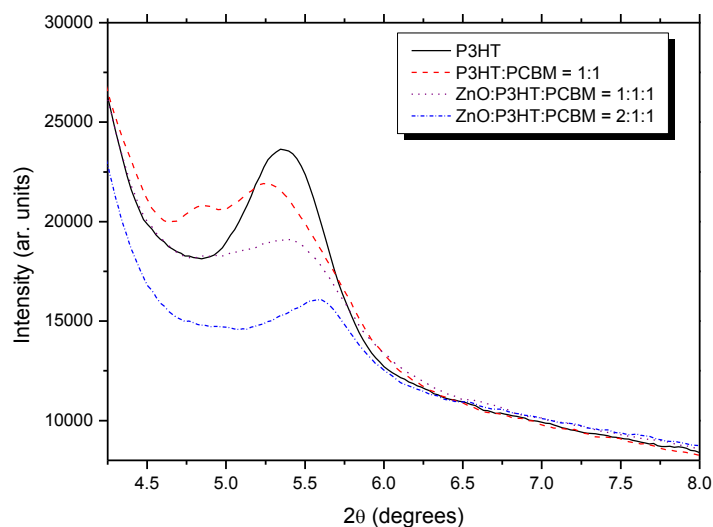
**Figure 2.** HRTEM micrograph of ZnO nanoparticles.

In order to take advantage of large film roughness to achieve high efficiency for devices it is advisable to spin-cast films of P3HT and PCBM blends prepared with dichlorobenzene as solvent [6]. A donor to acceptor ratio of 1:1 by weight was chosen, as photovoltaic devices utilizing P3HT:PCBM = 1:1 in dichlorobenzene blends gives the best device performance [7]. The XRD patterns of films prepared by spin-coating polymer blends and hybrid inorganic-organic are shown in figure 3. The pristine P3HT film exhibits a (100) peak around  $2\theta = 5.4^\circ$ , which corresponds to an ordered self-organized lamellar structure with an interlayer spacing formed by parallel stacks of P3HT main chains separated by regions filled with alkyl side chains[8]. It is evident that a peak shift to smaller angle occurs when PCBM is mixed into the polymer, with a hump occurring due to the broadening of the peak; this indicates an interference with the ordering of the P3HT due to the introduction of PCBM into the matrix.

**Table 1.** Structural and morphological parameters of spin-coated films.

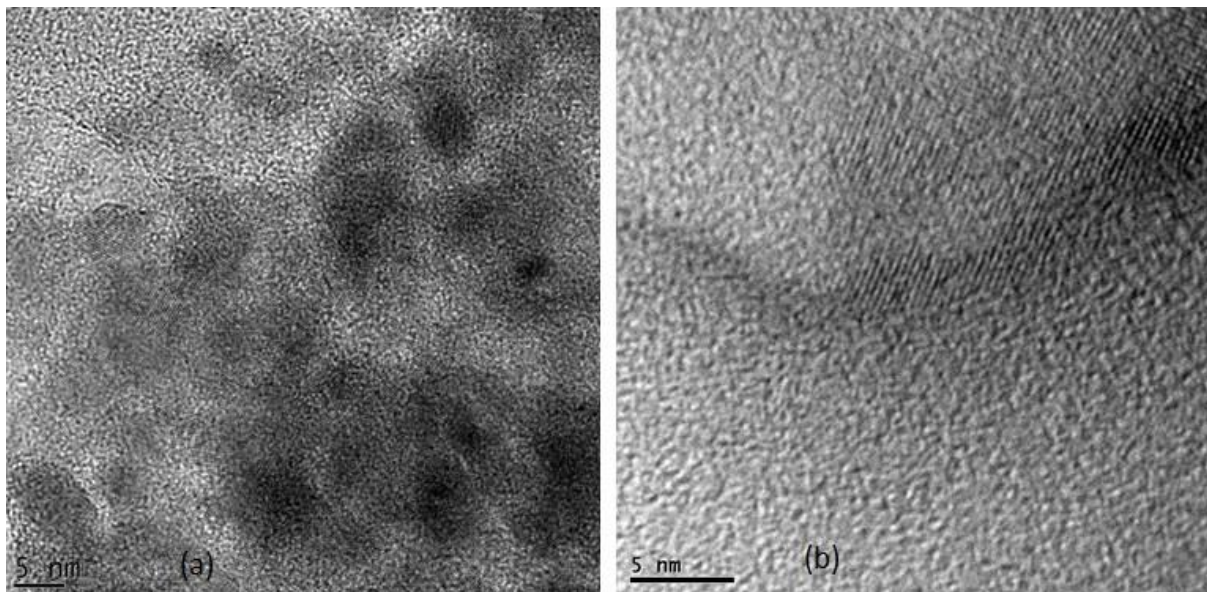
ZnO:P3HT:PCBM wt ratio	thickness (nm)	<100> 2 $\theta$ position ( $^\circ$ )	XRD fwhm ratio
0:1:0	84.5	5.39	1.00
0:1:1	44.4	5.35	-
1:1:1	47.6	5.43	1.43
2:1:1	48.3	5.57	1.09

The diffraction peak information for this peak is summarized in table 1, for the P3HT:PCBM blend and hybrid ZnO:P3HT:PCBM thin films. The ratio of the full-width at half-maximum (fwhm) of this peak for the nanocomposite thin films with respect to P3HT, gives an indication of the changes in the crystallite sizes that occur. The change in d-spacing upon adding the PCBM in the polymer matrix, hints that interdigitation or tilting of the side groups occurred, during the formation of ordered aggregates in the solution and this induced crystallinity during film deposition. Upon introduction of ZnO into the polymer blend matrix a further reduction in X-ray intensity is observed when the weight percentage of ZnO is increased, with a shift towards higher  $2\theta$  of the (100) peak.



**Figure 3.** XRD pattern of nano-composites.

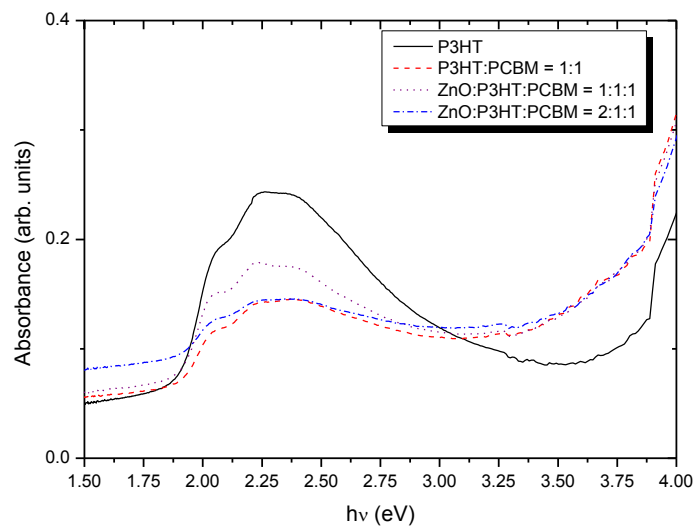
The HRTEM image in figure 4 (a) displays the random dispersal of ordered, crystalline regions embedded in amorphous tissue for an equal weight percentage hybrid mixture. In figure 4 (b) a further reduction in the degree of crystallinity, and an increase in the crystallite size is noted when the weight percentage of ZnO is doubled. This is probably due to an excess of inhomogeneously dispersed ZnO in the polymer matrix at higher concentrations, which give rise to the effects of disorder or segregation in the structure. These effects can thus account for the shifts in peak position and the changes in the fwhm of the diffraction peak in the XRD patterns.



**Figure 4.** TEM micrographs of ZnO:P3HT:PCBM thin films for (a) 1:1:1 wt. ratio, (b) 2:1:1 wt. ratio.

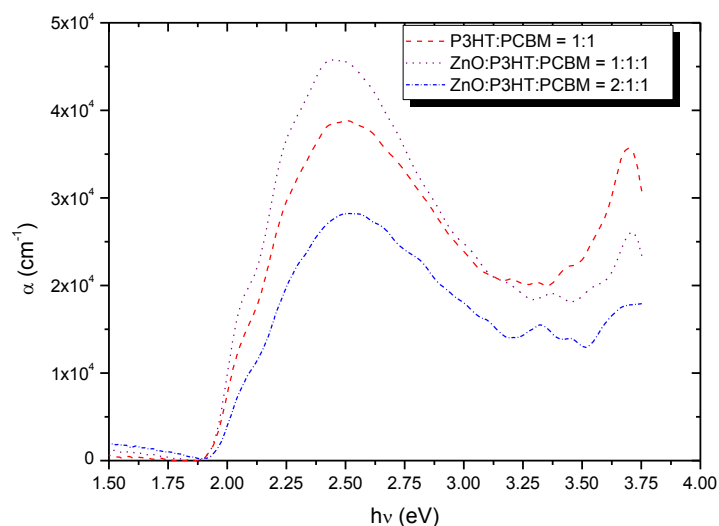
The morphology of the spin-coated polymer film is thus an important factor in understanding the property of the metal-polymer interface. In the final device the interface between the polymer and the cathode is important as it contributes greatly to the electrical characteristics of the devices [9]. It is expected that the hybrid active layer could enhance the electron transportation to the cathode due to the high electron mobility offered by ZnO nanoparticles present in the active layer, and depending on the shape and size of the ZnO nanostructures the transport rate of charge carriers can be improved and the recombination rates of excitons reduced [10]. The formation of large aggregates (rougher surface) lowers the degree of phase separation between P3HT and ZnO interfaces such that more charge generation can occur; in addition more percolation pathways for charge carriers become available [10].

The contribution from the heterojunction electric field formed between ZnO and organic materials enhance the separation of the electron-hole pairs and hence result in the increase of the photovoltaic property of the hybrid layer [9]. It is also expected that the ZnO: P3HT: PCBM film surface will result in greater light absorption due to the diffuse reflection from the surface of the active layer. UV-vis absorbance is therefore employed to inspect absorption properties of the thin films under study. Figure 5 displays the optical UV-vis absorbance whereas the absorption coefficient obtained from an independent method, spectroscopic ellipsometry, is shown in figure 6.



**Figure 5.** UV-vis absorbance spectra of spin-coated P3HT- based films obtained by UV-vis spectroscopy.

The absorption coefficient was calculated from the extinction coefficient. Regression is performed on the initial parameters inputted by the user; as such the accuracy of the initial values may significantly influence the accuracy of the final results. The spots on the thin films, i.e. the areas measured by UV-Vis and SE may also not necessarily be the same, which can also contribute to a discrepancy between the results obtained by the two methods [7]. It is encouraging however to note that the same features in absorbance and absorption coefficient dispersions can nevertheless be inferred from both figures.



**Figure 6.** Absorption coefficient of blend and hybrid ZnO:P3HT:PCBM thin films obtained by spectroscopic ellipsometry.

For the pristine P3HT film the absorbance spectrum shows a peak at 2.38 eV, and two humps at 2.04 eV and 2.24 eV respectively. These correspond well with other studies, which ascribe the features to

bands attributed to the 0-0, 0-1, and  $\pi$ - $\pi^*$  transitions [11]. The absorption wavelength range between 450 nm to 600 nm (2.06 eV - 2.76 eV) is considered to be the peak absorption wavelength band for P3HT. The peak absorption wavelength (energy) experienced a slight blue shift for the P3HT:PCBM blend compared to P3HT; and a concomitant loss of the weak vibronic structures [12]. The shift is attributed to a loss of P3HT polymer-chain stacking and conformational disorder, caused by the mixing of PCBM with the P3HT [12]. For the hybrid mixtures the blue shift is almost reversed completely. However, the maximum absorption intensity changed significantly for the thin films. The blend experienced a significant drop in maximum absorption intensity from pristine P3HT. Further, in both hybrid films the relative contribution from the ZnO absorbance peak at 3.54 eV should increase compared to the  $\pi$ - $\pi^*$  band of P3HT in the energy range of 2.06 eV to 2.76 eV. Upon introduction of ZnO in equal weight percentage the maximum absorption intensity recovers again, but to less than that of pure P3HT. The quenching of the film absorption when excess ZnO concentration is introduced evidences this. Additional information is further supplied by the absorption coefficient dispersion, which shows an improvement for the 1:1:1 hybrid film over the P3HT:PCBM blend, while the excess ZnO concentration in the 2:1:1 hybrid film causes degradation in the optical properties due to increase in grain size, i.e. increased segregation, as discussed above.

#### 4. Conclusion

It was established that the introduction of pyramid-shaped ZnO nanoparticles into a P3HT:PCBM blend leads to improved absorption of spin-cast films made from the solution, over films made by the P3HT:PCBM blend. The ZnO:P3HT:PCBM = 1:1:1 weight ratio film also exhibits superior absorption properties compared to double the ZnO weight ratio film. It was further noted that spectroscopic ellipsometry is a useful tool to obtain complimentary absorption coefficient information of the spin-cast films, which are notoriously inhomogeneous in thickness across the surface.

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#### References

- [1] Yu G, Gao J, Hummelen J C, Wudl F and Heeger A J 1995 *Science* **270** 1789
- [2] Olson D C, Piris J, Collins R T, Shaheen S E and Ginley D S 2006 *Thin Solid Films* **496** 26
- [3] Motaung D E, Malgas G F, Arendse C J and Mavundla S E 2012 *Mater. Chem. Phys.* **135** 401
- [4] J. A. Woollam Inc. *Complete Ease™ Data Analysis Manual*, June 15 2008
- [5] Johs B and Hale J S 2008 *Phys. Status Solidi A* **205** 715
- [6] Li G, Shrotriya V, Yao Y and Yang Y 2005 *J. Appl. Phys.* **98** 043704
- [7] Ding Y, Lu P and Chen Q 2008 *Proc. SPIE* **7099** 709919-1
- [8] Zhokavets U, Erb T, Hoppe H, Gobsch G and Sariciftci N S 2006 *Thin Solid Films* **496** 679
- [9] Oh S H, Heo S J, Yang J S and Kim H J 2013 *Appl. Mater. Interfaces* **5** 11530
- [10] Malgas G F, Motaung D E, Mhlongo G H, Nkosi S S, Mwakikunga B W, Govendor M, Arendse C J and Muller T F G 2014 *Thin Solid Films* **555** 100
- [11] Brown P J, Thomas D S, Kohler A, Wilson J S, Kim J S Ramsdale C M, Siringhaus H, Friend R H 2003 *Phys.Rev. B* **67** 064203
- [12] Beek W J E, Wienk M M and Janssen R A J 2006 *Adv. Funct. Mater.* **16** 1112