

Optimisation of inorganic-organic photoactive hybrid thin films

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Abstract. Photoactive hybrid films based on inorganic/organic nanocomposites have been widely employed for fabrication of low cost and environmental friendly photovoltaic devices [1-2]. However, silicon nanowires (SiNWs) and poly (3-hexylthiophene-2,5-diyl) also known as P3HT, are promising candidates that still require exploration due to high optical absorption and excellent charge carrier mobility associated with them, respectively [3-4]. An objective of the study was to establish optimised spin coating conditions for P3HT film deposition with high film uniformity and electrical conductivity in order to incorporate SiNWs for enhancement of optical and electrical properties of the film. Uniform hybrid films with satisfactory electric conductivities were obtained.

1. Introduction

In response to the global concern over issues of global warming and unsustainability of the current commercial source of energy based on fossil fuels, research towards the development of low cost renewable sources of energy has gained tremendous interest over the last two decades. Inorganic photovoltaics (PVs) based on crystalline silicon (c-Si) are ubiquitous and exhibit reasonable power conversion efficiency (PCE). However, high temperature and vacuum required for the processing of Si and fabrication of this type of PV leads to high production cost, which needs to be reduced. In this context, other PV technologies such as those based on organic semiconductors (OPVs) have emerged as promising candidates for fabrication of PV technologies at low cost [5, 6], on flexible substrates. In OPVs, the PCE is affected by the morphology of the active layer, the structure and the choice of electron donor (D) and acceptor (A) materials, the ratio of these materials and the interaction in the D-A interface within an active layer [7]. The major setback for OPVs involves the low PCE, which is due to limited charge carrier mobility, as a result of a rapid recombination rate within the active layer [8]. In dealing with shortcomings associated with OPVs, methods such as incorporating inorganic material into polymer matrices have been developed and employed [9-11].

Hybrid solar cells combine advantages of both organic and inorganic materials, where the conjugated polymer absorbs light and acts as the donor, whereas the inorganic material can act as acceptor and electron transporter in the structure. In our films the conjugated polymer and inorganic nanowires (NWs) are mixed together in specific weight ratios. The polymer poly (3-hexylthiophene-2,5-diyl) (P3HT) is

employed for its good hole transporting ability arising from the crystalline ordering of the polymer. As inorganic material, silicon nanowires (SiNWs) offer high surface area per volume ratio providing a large interface for exciton dissociation, therefore leading to high mobility of electrons [12]. This study is about optimizing the composition of P3HT: SiNWs photoactive hybrid layers in order to enhance its electric properties. Other factors contributing toward the improvement of the photoactive layer's conductivity are also taken into account.

2. Experimental details

2.1. Material Synthesis

The conjugated polymer P3HT (Sigma Aldrich) with a molecular weight average between 54000-75000 g mol^{-1} , was used as purchased without any further purification or modification. SiNWs were synthesized in the laboratory via metal assisted chemical etching (MACE) process as discussed in literature [4]. However, in this study, Si wafers were immersed into a second etching solution that consisted of a high concentration of hydrofluoric acid (HF) and hydrogen peroxide (H_2O_2), in a volume ratio of 10 ml of H_2O_2 , 10 ml of HF and 30 ml of H_2O for etching the bases of SiNWs prior to the removal of the silver nanoparticles (Ag NPs) in nitric acid (HNO_3) [4, 13]. In order to detach SiNWs from the bulk Si wafer, the base-etched SiNWs samples were immersed in 5% HF for 3 min to remove the oxide layer from the NWs, and subsequently immersed in a binary solvent of dichlorobenzene (DCB) and chloroform (CF) with (1:1) ratio, and sonicated in an ultrasonic bath for 10 minutes, during which the fragile bases of the SiNWs broke off into the binary solvent. The remaining SiNW-free bulk Si wafer were then removed from the solution containing the NWs.

Using this SiNWs ink, three solutions of different SiNWs concentrations by weight ratio were prepared, P3HT: 1.5 wt% SiNWs, P3HT: 3 wt% SiNWs, and P3HT: 6 wt% SiNWs. The fourth solution of P3HT dissolved in the binary solvent was used as a reference. These solutions were stirred overnight on a digital hot plate stirrer (Lasec) at rotational speed and temperature of 250 rpm and 23 °C respectively. Microscope slides with 1-1.2 mm thickness (Lasec), on which hybrid solutions were to be deposited, were ultrasonically cleaned in acetone, ethanol and isopropanol and then rinsed in deionized water. The solutions were then deposited at 1000 rpm for the duration of 80s using a G3P-series spin coater (Specialty Coating Systems) to form photoactive bulk heterojunction hybrid layers.

2.2 Characterization

SiNWs morphology and microstructure were characterized by High Resolution Scanning Electron Microscopy (HRSEM: Zeiss Auriga) and Optical Microscopy (Olympus U-CMAD3, Japan). Optical properties were investigated using UV-Vis absorbance and photoluminescence (PL), (Maya 2000PRO with Deuterium-Tungsten Halogen sources, and HORIBA Jobin Yvon Fluorolog-3 model FL322), respectively. A FEI Tecnai F20 field emission high resolution transmission electron microscope (HR-TEM) was used to examine the crystallinity of the hybrid material.

3. Results and Discussion

It can be seen that base-etched SiNWs before the detachment are vertically aligned on a Si wafer (fig 1 (a)). The diameters of the wires are between 0.17-0.27 μm , while the length is approximately 4.8 μm . Fig 1 (b) depicts that after detachment SiNWs are not of uniform length. This suggest that during sonication SiNWs break randomly due to two possibilities: (1) base-etching not occurring at the same level, and (2) as-synthesised SiNWs varied in length. A thoroughly discussion of SiNWs formation can be found in references 13, and 14&15.

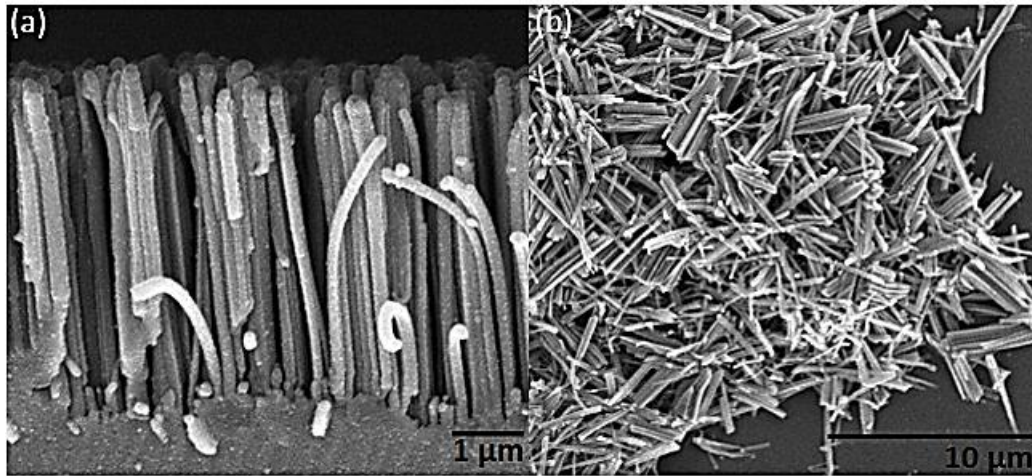


Figure 1: SEM micrographs of SiNWs, (a) cross sectional view of base-etched SiNWs and (b) SiNWs deposited onto a glass substrate by drop casting.

Prior to mixing the SiNWs with the polymer, spin-coating deposition parameters for pristine P3HT were optimised. Different solution concentrations (5, 7.5, 10 and 20 mg/ml of P3HT/DCB/CF), spinning speeds (500, 750, 1000 and 2000 rpm), and spinning durations (20, 40, 60 and 80 s) were investigated. The thickness and the uniformity of the films depended on the entire four distinct stages of the spin-coating process, i.e. dispense stage, substrate acceleration, spin-off and solvent evaporation. All spin coating parameters investigated in this study revealed to have a direct impact on the thickness and the uniformity of the film obtained. The film obtained from a solution concentration of 10 mg/ml spin coated at 750 rpm for the duration 80 s exhibited the highest conductivity and this was considered the optimal condition for pure P3HT.

Optical microscope images of P3HT matrix incorporated with different SiNWs concentrations are depicted in fig 2. It has been reported that film uniformity depend strongly on the choice of organic solvent used [16]. In this study, the binary solvent of dichlorobenzene and chloroform was used due to the high solubility of P3HT in the former and quick evaporation of the latter, which together constructively influence the film produced. It is evident from fig 2 (a-d) that films investigated shows small particles associated with P3HT. This is an indication of the possibility of reorganisation of the polymer during thermal treatment of the film. From fig 2 (b-d) it is observed that SiNWs incorporated in the P3HT matrix are randomly distributed, and are of different sizes. As shown in fig 2 (d), a high concentration of SiNWs enlarges the D-A interface, which could be suitable for effective charge transfer for P3HT: SiNWs. However, this large number of wires could act as recombination sites; perhaps it is for this reason that other complementing techniques are employed to examine the concentration of SiNWs favourable for successful charge separation.

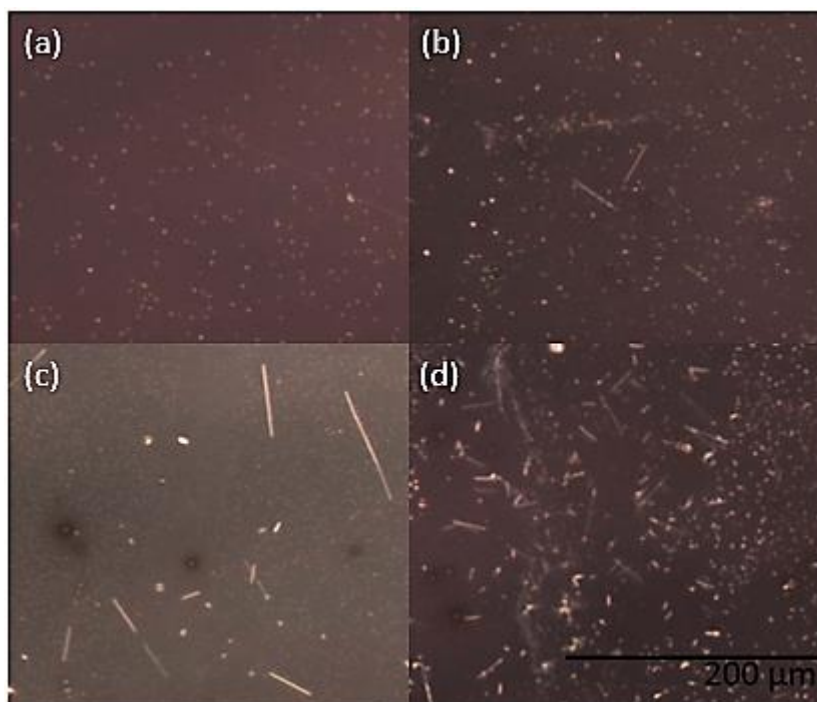


Figure 2: Optical micrographs of hybrid layers, (a) pure P3HT, (b) P3HT: 1.5 wt % SiNWs, (c) P3HT: 3 wt % SiNWs and (d) P3HT: 6 wt % SiNWs.

Fig 3 shows the optical properties of the hybrid layers. The P3HT spectrum in fig 3 depicts two maximum absorption peaks at wavelengths around 520 and 545 nm, which are attributed to the π - π^* transition [17]. In addition, a shoulder peak is observed around 600 nm. This shoulder peak is ascribed to the high crystallization and intrachain interaction ordering of the P3HT [1]. It is also noticed from the spectra that upon addition of SiNWs the shape of the P3HT spectrum is retained with a slight broadening of absorption peaks, which suggest better structuring of P3HT in the presence of SiNWs. In the wavelength range between 630-800 nm, it can be observed that addition of SiNWs reduces the absorption of the P3HT matrix. However, further addition of wires recovers the absorption intensity. PL spectra of P3HT and its blend with different concentration of SiNWs is shown in fig 3 (b). The PL peak appears at wavelength around 650 nm, which is characterized by the relaxation of excited π -electrons to its ground state. It is in our interest to observe that blending P3HT with SiNWs quenches the PL peak, this indicates the occurrence of successful charge dissociation at the D-A interface [18]. The maximum quenching is obtained for the blend ratio of P3HT: 3 wt % SiNWs. Further addition of SiNWs into the polymer matrix, i.e. P3HT: 6 wt % SiNWs results in an increased intensity of the PL peak. This increase in the emission intensity may be due to the formation of SiNWs aggregates, which decreases the D-A interface [19].

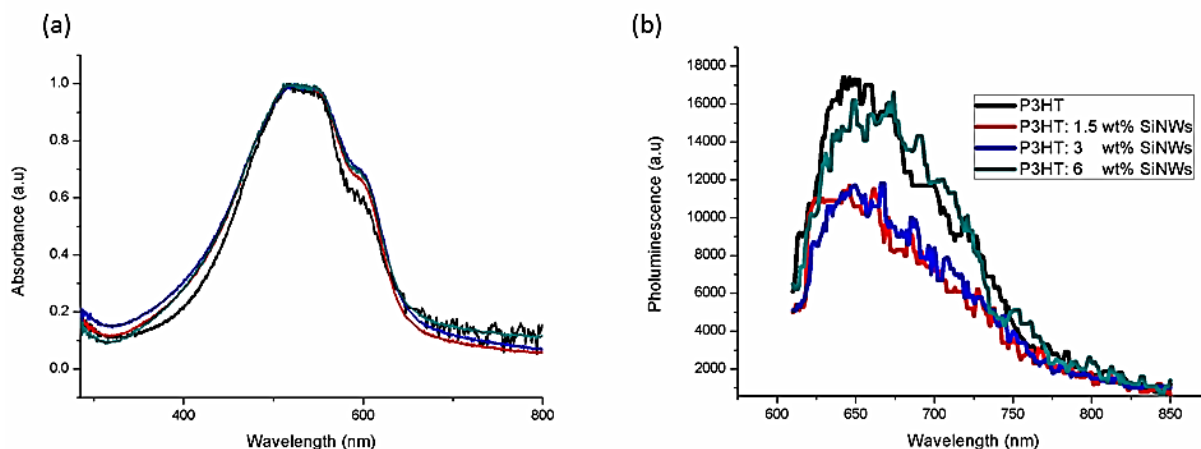


Figure 3: Optical properties of hybrid films, (a) Normalised UV-Vis absorption spectra and (b) photoluminescence spectra.

HRTEM was employed to examine the internal structure and crystallinity of the combination of P3HT and SiNWs. Fig 4 (a) shows that within the matrix, P3HT covers parts of the SiNWs. Fig 4 (b) and the inset indicate that the hybrid film is polycrystalline.

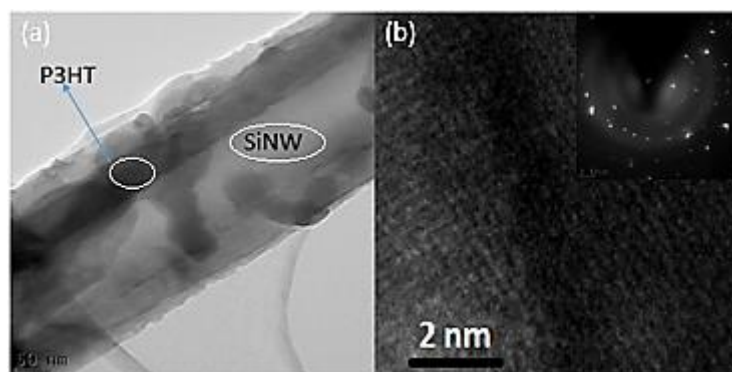


Figure 4: TEM images, (a) SiNWs covered by P3HT and (b) crystallographic information on P3HT: SiNWs, the inset is the SAED pattern for the combination of P3HT: 6 wt % SiNWs.

The thickness and conductivity of the hybrid films measured at room temperature using a Dektak Profilometer and four point probe Hall Effect measurement system are presented in table 1. As expected, the thickness of the hybrid films increase with an increasing content of SiNWs, this could be attributed to the enhanced surface tension of the solutions with an increasing content of SiNWs. Table 1 also reveals that, adding SiNWs into the P3HT matrix increases the electrical conductivity, which is in good agreement with PL results. The decrease in the conductivity of P3HT: 6 wt % SiNWs seems to confirm the suggestion made earlier that an excessive amount of SiNWs encourages formation of recombination sites which degrade the quality of the hybrid film.

Table 1: Thickness and conductivity of spin coated films.

P3HT: SiNWs wt % ratio	Thickness (nm)	Conductivity ($\times 10^{-5} \Omega^{-1} \cdot \text{cm}^{-1}$)
P3HT	87	3.39
P3HT: 1.5 wt % SiNWs	89	3.41
P3HT: 3.0 wt % SiNWs	95	3.61
P3HT: 6.0 wt % SiNWs	125	2.52

4. Conclusion

In conclusion, bulk heterojunction photoactive hybrid films composed of P3HT and SiNWs have been prepared by spin coating to establish optimal composition of these materials of interest. Within the photoactive hybrid layer, SiNWs are randomly distributed and the polymer covers SiNWs, thus forming various D-A interfaces essential for charge separation. The maximum conductivity of $3.61 \times 10^{-5} \Omega^{-1} \cdot \text{cm}^{-1}$ was obtained for the blend ratio of P3HT: 3 wt % SiNWs. There is good correspondence between the optical and the electrical properties of the as-prepared hybrid films and these results agree well with literature.

5. Acknowledgements

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References

- [1] Braik M, Dridi C, Rybak A, Davenas J and Cornu D 2014 *Phys. Status Solidi A* **211** 670
- [2] Davenas J, Dkhil S B, Cornu D and Rybak A 2012 *Energy Procedia* **31** 136
- [3] Wright M and Uddin A 2012 *Sol. Energy Mater. Sol. Cells* **107** 87
- [4] Liu K, Qu S, Zhang X, Tan F and Wang Z 2013 *Nanoscale Res. Lett.* **8** 88
- [5] Krebs F C 2009 *Sol. Energy Mater. Sol. Cells* **93** 394
- [6] Yue D, Khataou P, You F and Darling S B 2012 *Energy Environ. Sci.* **5** 9163
- [7] Muller T, Ramashia T A, Motaung D E, Cummings F, Malgas G, Oliphant C and Arendse C 2016 *Phys. Status Solidi A* **213** 1915
- [8] Hoppe H and Sariciftci S N 2004 *J. Mater. Res.* **19** 1924
- [9] Azizi S, Braik M, Dridi C, Ouada H B, Ryback A and Davenas J 2012 *Appl. Phys. A* **108** 99
- [10] Chahata N, Ltaief A, Beyou E, Ilahi B, Salem B, Baron T, Gentile P, Maaref H and Bouazizi A 2015 *J. Lumin.* **168** 315
- [11] He L, Jiang C, Wang H, Lai D, Tan Y H, Tan CS and Rusli 2012 *Appl. Phys. Lett.* **100** 103104
- [12] Charrier J, Najjar A and Pirasteh P 2013 *Appl. Surf. Sci.* **283** 828
- [13] Liu Y, Ji G, Wang J, Liang X, Zuo Z and Shi Y 2012 *Nanoscale Res. Lett.* **7** 663
- [14] Chartier C, Bastide S and Levy-Clement C 2008 *Electrochim. Acta* **53** 5509
- [15] Smith Z R, Smith R L and Collins S D 2013 *Electrochim. Acta* **92** 139
- [16] Luo S C, Cranium V and Douglas E P 2005 *Langmuir* **21** 2881
- [17] Chen T A, Wu X and Rieke R D 1995 *J. Am. Chem. Soc.* **117** 233
- [18] Saidi H, Walid A, Bouaziz A, Herrero B R and Saidi F 2017 *Mater. Res. Express* **4** 035007
- [19] Dkhil S B, Elbdelli R, Dachraoui W, Faltakh H, Bourguiga R and Davenas J 2014 *Synth. Met.* **192** 74