TiO_2 DOPED PDPP3T NANOCOMPOSITE THIN FILM FOR PHOTOVOLTAIC APPLICATION

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In present work, an inorganic dopant TiO_2 nanoparticles are introduced into the PDPP3T polymer host material and deposited as thin films via spin coating. Different solvent are investigated to get efficient dispersion of TiO_2 nanoparticles as well as effective dissolution of PDPP3T material. The role of TiO_2 particles towards optical absorption of PDPP3T material is studied by preparing different PDPP3T/TiO_2 blend ratios and annealed at different temperatures. Toluene is found an efficient solvent for the dispersion of TiO_2 nanoparticles as well as dissolution of PDPP3T material. Significant increase in optical absorption in UV region 300-400nm is observed for the PDPP3T/TiO_2 blend ratio 1:0.2 and the annealing temperature 310^{o}C. The deposited thin film with four layers have demonstrated significant blue shift in peak wavelength and increase in the absorption in UV region (300-400nm). XRD analysis reveals amorphous nature of all deposited thin film. No significant variations in chemical structure are observed with increase in thickness of deposited layer. The addition of TiO_2 particle in PDPP3T material significantly enhanced the optical absorption in UV region.

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Keywords: Thin Film; Nanocomposite; Solution Processing; Spin Coating

1. Introduction

Over the past decade, organic materials have achieved significant developments in the field of organic based electronic devices [1–3] due to their excellent chemical and physical properties, such as ease to molecular design ability, optical selectivity and electronics tunability [4–9]. Various types of organic materials are used to fabricate different devices such as solar cells [10], light emitting diodes [11], transistors [12], electronic memories [13], spin valves [14], and sensors [15], etc. Recently, organic solar cells (OSC) have received great attentions, attributes to light weight, flexibility, low cost and large-area implementation. Organic materials have the advantages of function tunability, flexibility as well as easy film-forming properties. The typical high absorption coefficient of organic materials allows the solution processing onto large scale by utilizing common solution base deposition techniques [16]. However, the power conversion efficiency (PCE) of organic solar cells are still low [17]. Various researches have reported the fabrication of OSC, which demonstrate excellent PV properties but with power conversion efficiency

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(PCE) far lower than conventional silicon based photovoltaic (PV) solar cell. Low carrier mobility, short excitation and amorphous nature of materials are responsible for low PCE. Moreover, the process reliability for OSC is also low and shown different performance even deposited under identical experimental conditions. The emission properties, absorption behaviour and charge transport response are three main features that are largely contribute towards the performance of organic electronic devices. These properties are highly dependent on the growth condition of the films, annealing temperature, chemical solvents and dopant materials[18]. The low power conversion efficiency (PCE), materials cost, environmental impact and durable structure are the major challenges in organic photovoltaic technology [19–22].

Poly[2,2′-[(2,5-bis(2-hexyldecyl)-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrole-1,4-diyl)dithiophene]-5,5′-diyl-alt-thiophen-2,5-diyl} (PDPP3T) with band gap (Eg) of 1.30 eV, and carrier mobility of 10^2 $cm^2V^{-1}S^{-1}$ is one of the promising organic materials as the donor component in the active layer of organic and perovskite solar cells [23, 24] owing to its broad absorption in the visible range [25]. To introduce large excitation binding energy, the heterojunction in organic photovoltaic OPV cells is introduced which incorporates constraints on the design of the photoactive layer. The blend composition, i.e. the donor and acceptor materials in form of thin film, is crucial to determine the different aspects of the bulk heterojunction (BHJ) absorber layer [26]. It is expected that doping PDPP3T with a specified inorganic material can open up a wide flexibility of its application, through tuning its optical, structural and morphological properties. Titanium dioxide (TiO_2) is an n-type semiconductor with a wide energy band gap, and well-known for its potential applications in the field of photocatalysis and photoelectrochemistry due to its unique optical transmittance, high refractive index and chemical stability [27]. Therefore, these properties, in different extends, can be interestingly combined with those of the PDPP3T via a doping process. In this research work, PTPP3T:TiO_2 hybrid nanocomposite films are grown via solution processed coating to investigate the optical, structural and morphological properties of the host polymer for different ration of TiO_2 material using different solvents. The prepared solutions and deposited as thin films are characterized using UV-Vis-NIR spectroscopy to study the optical behaviour, XRD to study the structural properties, and AFM to study the morphological properties of thin films.

2. Experimental

2.1. Raw materials

PDPP3T powder purchased from Ossila Company (UK), TiO_2 nanoparticles (having average size of 20 nm) obtained from Sigma-Aldrich (Malaysia) and DMSO, Dichlorobenzene, Toluene and mixture of Ethanol and Acetic Acid (as solvent) were used as starting material without further purification.

2.2. Solution preparation

Different solvents as DMSO (C_2H_6OS), Dichlorobenzene ($C_6H_4Cl_2$), Toluene (C_7H_8) and mixture of Ethanol and Acetic Acid (C_2H_5OH+ C_2H_3OOH) were used to obtain effective dissolution of TiO_2 particles. In each case, 75 mg of TiO_2 was added in 5ml of solvent and characterized by UV-Vis spectroscopy. To get efficient dissolution, solutions were heated up to 70 ^oC for 24 hours along with continuous magnetic stirring.

150 mg of PDPP3T powder was dissolved in 10 ml of toluene, and 30 mg of TiO2 nanoparticles were mixed in 2 ml of toluene in two different vials. Two solutions were mixed in different ratios by volume and stirred on a hotplate at 70 ℃ for 24 h, as a result stable white TiO_2 colloid solutions was obtained.

2.3. Thin film deposition

PDPP3T:TiO_2 solutions were deposited on soda lime glass substrates (25×25 mm square) as thin film using spin coater (POLOS^{TM}). The spinning speed was initially set on 1500 rpm and increased to 3000 rpm to get a uniform deposition. The thin films were dried on a hotplate at 70 ℃

for 20 min. The process was repeated to achieve different thicknesses. In the final step, thin films were subjected to annealing process in a furnace at different temperatures (25, 150, 200, 250, 310 and 380 ℃). The light absorption properties of deposited thin films were tested by UV-Vis spectrophotometer (UV-3600 Plus UV-Vis-NIR spectrophotometer). The surface roughness was scanned by atomic force microscopy (AFM, SII SPI3800N scanning probe microscopy), using tapping frequency of 0.22 Hz in N_2 environment. The coated thin film's thickness were measured by a surface profilometer (Alpha step IQ Surface profilometer).

3. Results and discussion

Fig 1 shows the UV-Vis absorption spectra of TiO_2 solutions prepared in different solvents as Toluene, Dichlorobenzene, DMSO, cholorobenzene, and blend of acetic acid & ethanol. All the solutions contain equal amount of TiO_2 particles in equal amount of solvents.

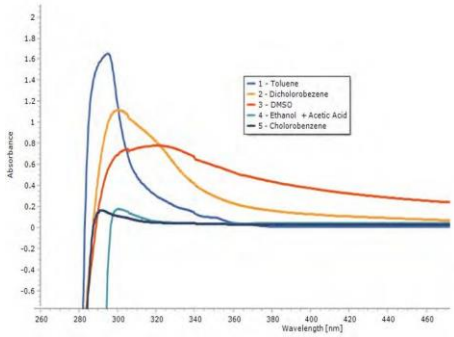

Fig. 1. UV-Vis absorbance spectra of TiO_2 particles dissolved in different solvents.

The characteristic absorption peak of TiO_2 is observed at 296.3 nm [28]. It is inferred that toluene is an efficient solvent for dispersion of TiO_2 particles, and at the same time, also favorable for dissolving the polymer host PDPP3T. Whereas, other solvents show low absorption in UV-Vis region as compared to the Toluene. Toluene has selected as effective solvent for the preparation of PDPP3T/TiO_2 solution and deposition of thin film.

Fig 2 shows the UV-Vis absorption spectra of PDPP3T/TiO_2 solutions in Toluene solvent with different volume ratios. Two main absorption peaks at 796 nm and 421 nm are observed. The presence of TiO_2 does not show any obvious change in the spectral shape. It is observed that the absorption of light by the composite films is decreased with increase in the ratio of TiO_2 particles (1:0.0, 1:0.2, 1:0.4, 1:0.6, 1:0.8) within PDPP3T polymer as the addition of TiO_2 reduces the overall PDPP3T concentration.

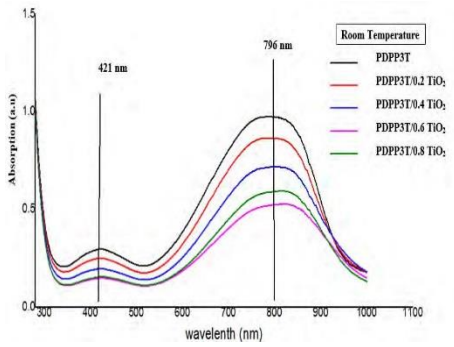

Fig. 2. UV-Vis absorption spectra of PDPP3T/TiO_2 blend with different volume ratio.

The UV-Vis spectroscopic analysis is performed for the deposited PDPP3T/TiO_2 thin film for different PDPP3T/TiO_2 blend volume ratios (1:0.2, 1:0.4, 1:0.6 and 1:0.8), and different annealing temperatures (75 ^{O}C, 150 ^{O}C, 250 ^{O}C, 310 ^{O}C and 380 ^{O}C). Fig 4.3 presents the UV-Vis spectra for one layer thin films of blend (PDPP3T/TiO_2) with different volume ratios annealed at different temperatures form 75^{o}C to 380^{o}C. A decreased in the absorption is observed with increase in the TiO_2 volume ratio in PDPP3T/TiO_2 thin film annealed at different temperatures.

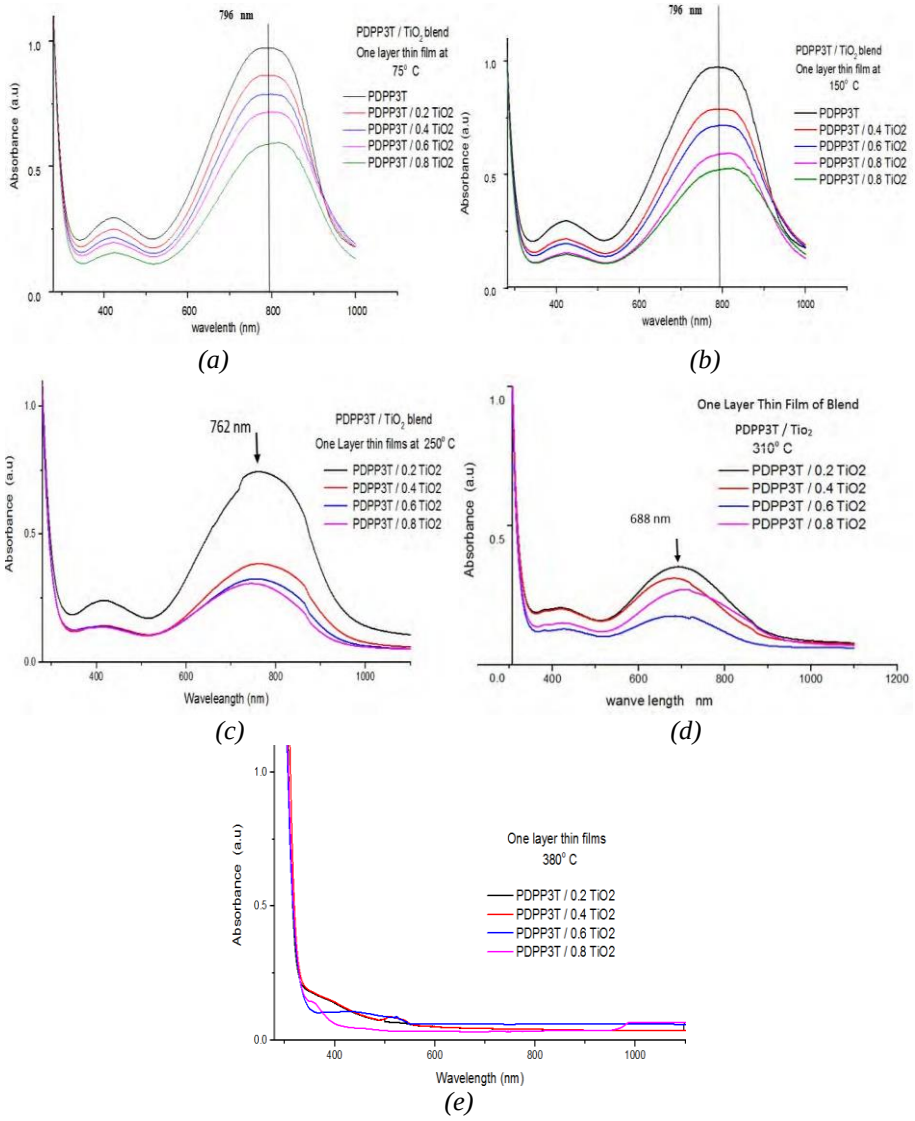

Fig. 3. UV-Vis spectra of PDPP3T/TiO_2 one layer thin films for different volume ratio annealed at (a) 75^{O}C, (b) 150^{O}C, (c) 250^{O}C, (d) 310^{O}C and (e) 380^{O}C temperatures.

There is no significant variations in peak position for the annealing temperatures 75^{o}C and 150^{o}C. However, the heating caused a shift of peak towards the shorter wavelength for temperature 250^{o}C and 310^{o}C. For annealing temperature 380^{o}C, the physical and chemical structure of the host polymer PDPPD3T material is compromised. As result, no absorption in UV-Vis region is observed. Based on the UV-Vis spectroscopic analysis (Fig 3), the PDPP3T/TiO_2 blend ratio 1:0.2 has selected to deposit the multilayer due to significant increase in abortion particularly in 300 to 500 nm spectral region. The UV-Vis spectra of PDPP3T:TiO_2 (with blend ratio 1:0.2) thin films on the glass substrate annealed at different temperatures are plotted in Fig 4.

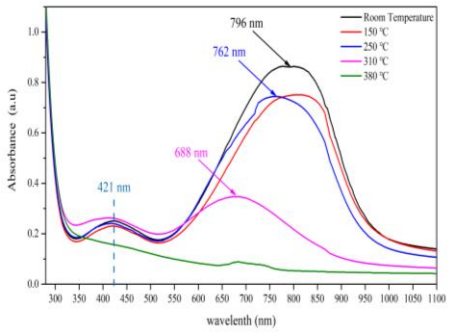

Fig. 4. UV-Vis spectra of solution and thin film of PDPP3T:TiO_2 (with blend ratio 1:0.2) annealed at different temperatures.

Two absorption peaks located at position 421 nm and 796 nm are observed for all spectra. A blue-shift phenomenon from 796 nm to 762 nm and then to 688 nm is observed as the annealing temperature is increased to 250 ℃ and higher, respectively. The overall absorption intensity is decreased as the annealing temperature increased which may be due to increase in evaporation of residue inside the deposited film, which in turn reduced the films thickness as well as absorption. The absorbance of thin films annealed at 150 ^{o}C and 250^{o}C are very similar, the only difference is the peak position, implying that toluene has been totally removed and caused slight structural redistributions. This structural change can be defined by the modified molecular packing/stacking [29] and nanosize domination by TiO_2 particles (increased strength of TiO_2). As the annealing temperature is increased to 310℃, the peak position is further shifted to 688 nm and a wide absorption range in the UV region is produced, which can be attributed to TiO_2. This can be understood as thermal stability of TiO_2 is higher than that of PDPP3Tand hence the light absorbance is dropped when the film is annealed at 310℃, leading to the evaporation of PDPP3T host material.

In order to study the relation between thin film thickness and light absorption, five different thin films are deposited by repeating coating cycles from 1 to 5 and annealed at 310^{o}C. The measured thickness of each film is given in Table 1 and the UV-vis spectra are plotted in **Error! Reference source not found.**. The thickness of films is increased from 0.28 to 0.81 m with increase in number of layers from 1 to 5. The absorption peaks positions are shifted slightly towards the short wavelength (blue shift) with increase in number of coated layers, from 421 nm to 408 nm for the first peaks and from 688 nm to 629 nm for the second peak. Significant increase in the absorption is observed with increase in the number of deposited layers, particularly in UV region (400 nm) which may attribute to presence of TiO_2 particles in host structure. Thin film with 4-layer has shown highest absorption intensity and largest blue shift among all the five samples. By increasing the number of deposited layers, the density of TiO_2 nanoparticles is increased at the expense of the PDPP3T material. This is well confirmed from the absorption peaks in Fig 5, where the first peak intensity (which is attributed to TiO_2) is increased, while the second peak intensity (due to PDPP3T) is lowered with the increase of deposition layers.

Table 1. Thin film thickness of different coating layers.

No. of Layer	Films Thickness (µm)
1	0.283
2	0.337
3	0.529
4	0.768
5	0.818

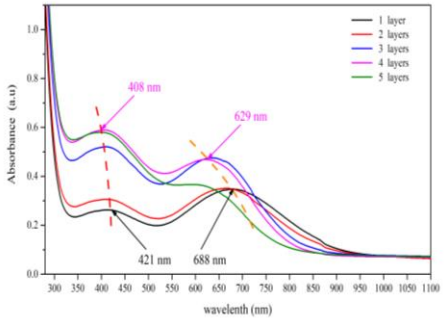

Fig. 5. UV-vis spectra of different layer thin films annealed at 310℃

The XRD pattern of each sample with different thicknesses is plotted in Fig 6Fig. 6. The absence of sharp peak in all five samples indicates amorphous structure, even for the TiO_2 nanoparticles, as TiO_2 crystalize temperature is above 450℃ [30]. The broad peak around 23.6 ° is associated to the glass substrate.

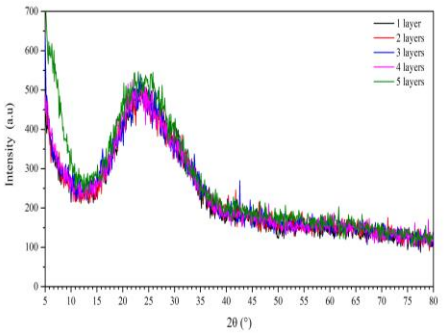

Fig. 6. XRD patterns of PDPP3T:TiO_2 thin films with different thicknesses and annealed at 310℃

The surface roughness of each film is characterized by AFM, the images are shown in Fig 7. The surface roughness is increased with increase in number of layers with RMS of each thin film 1.658, 1.541, 1.857, 2.014, 2.047 nm, for 1 to 5 layers respectively. A smaller boundary region is observed for the high layered films, which can be due agglomerated TiO_2.

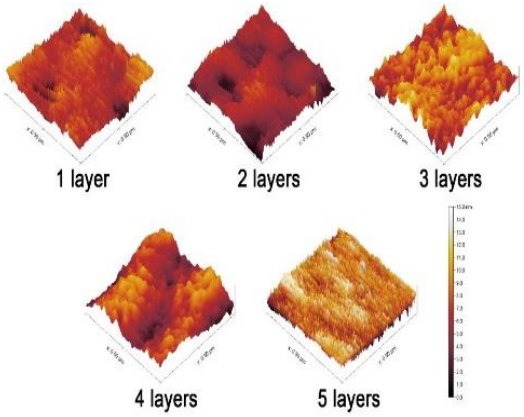

Fig. 7. AFM images of PDPP3T:TiO2 thin films with different number of layers and annealed at 310℃.

Fig. 8 shows FTIR spectra of PDPP3T/TiO_2 blend (1:0.2) thin films for different number of layers, annealed at 310^{O}C. All FTIR spectra of deposited thin films have shown the similar pattern. The peaks observed at 2923.87 cm^{-1}, 2853.80 cm^{-1}, 1665.15 cm^{-1}, 1560.55 cm^{-1}, 1432.02 cm^{-1}, corresponds to O-H, - CH_2, Ti-OH, C-H and C-O, vibrational bonds [31]. FTIR spectra show strong absorption in spectral range 500 to 1000 cm^{-1}, which is ascribed to the stretching or deviational vibration of Ti-O- Ti bonds of TiO_2.

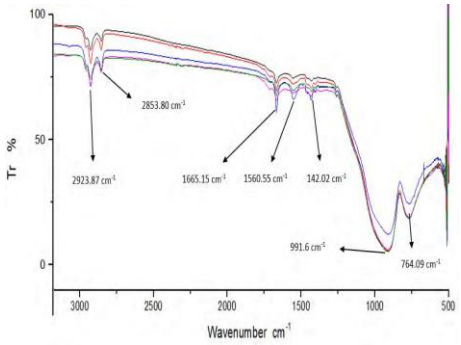

Fig. 8. FTIR spectra of deposited PDPP3T/TiO_2 thin films for different number of layers.

4. Conclusions

The hybrid thin film of PDPP3T doped with TiO_2 nanoparticles were successfully deposited on glass substrate. Toluene was found an efficient solvent for the dispersion of TiO_2 nanoparticles and PDPP3T material and high optical absorption was observed for PDPP3T/TiO_2 blend ratio 1:0.2.

The annealing temperature and film layer play a crucial role in the behaviour of light absorption and surface roughness. Whereas, the structure has remain amorphous regardless the annealing temperature.

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