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Thermal Annealing Impact on Optical Properties of Spin-coated P3HT: CdS Thin Film

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ABSTRACT

Polymers are flexible materials that can be easily processed and are formed into a thin film by several methods such as spin-coating, dip-coating, film-casting, and printing. The spin coating method has been extensively utilized in fabricating solution-prepared organic/inorganic electronic devices, this technique is positively efficient in generating thin film apart from being a flexible method to execute. In this study, poly(3-hexylthiophene) (P3HT) material is selected as polymer and cadmium sulphide (CdS) as nanoparticles to produce a hybrid nanocomposite thin film through the process spin-coating method. The P3HT and cadmium ion solution were used to fabricate a thin film onto a quartz glass substrate at a spin speed of 500 rpm for 10 seconds. This spin-coated thin film was heated at different temperatures such as 40°C, 80°C, 120°C, and 160°C for optical properties using a UV-Vis spectrophotometer. The UV-Vis absorption spectra of P3HT: CdS indicated absorption peaks in the UV region, which were ascribed to the band gap of the P3HT: CdS thin film. Our results showed that the optical properties of the P3HT: CdS be contingent on the annealing temperature. The film at room temperature yielded a band gap value of 1.98 eV, at 40°C it resulted in 1.99 eV. The band gap value was increased when annealed at 80°C with 2.02 eV. Annealing temperatures were then raised to 120°C and 160°C, leading to band gap values of 3.11 eV and 2.80 eV respectively.

Keywords: Thermal annealing, P3HT, CdS nanoparticles, optical properties, spin coating

1. INTRODUCTION

Polymer materials are inexpensive, easy to solution-processed, and possessed semiconducting properties. Polymer solar cells (PSCs) have garnered significant interest over recent years and have been considerable interest in the photovoltaic society, as shown by the growing variety of applications and scientific journals (Hu et al., 2020). Recent research has been involving the usage and applications of polymers in organic and inorganic electronic devices (Jin et al., 2019), solar cells (Shi et al., 2018), and polymer-based sensors (Alberti et al., 2021). Regioregular poly(3-hexylthiophene) (P3HT) is one of the highly significant important donor materials for polymer-based photovoltaic (PV) cells due to its outstanding solubility in numerous organic solvents and its easy processing for several fabrication processes such as spin coating, dip-coating, film-casting, and printing.

P3HT is an example of a p-type semiconductor that practically acts as an electron donor and it is recognized as the most vital donor material for polymer-based PV cells (Thompson &

Fréchet, 2008). P3HT is extensively used because of its outstanding properties such as ease of synthesis, low cost and superior thermal and environmental stability (Ghosekar & Patil, 2019). In the literature, reveals a number of scientific research data showed that the optical properties of P3HT thin film were indeed affected by thermal annealing. Increasing the annealing temperature of an active layer (P3HT: PCBM) can increase the absorption and the layer presents better optical properties when annealed at 140℃ (Abada et al., 2019). Other research shows that when the film was heated at 150℃, the film appear to exhibit the highest interchain and intrachain orders, thus preserving the initial morphological characteristics (Peng et al., 2011). Conceptually similar work but rather possess a dissimilarity in characterization method, has also been carried out by An and co-workers in 2013, they utilize the role of annealing temperature in affecting the properties of P3HT thin film. However, they were investigating the microstructure of the thin film that was directly affected by the process of thermal annealing (An et al., 2013). Between these two existing studies, it shows that thermal annealing not exclusively has an effect on the optical properties of the thin film but also its morphology.

This issue has been considered by recent work that there were significant morphological changes in the aligned blend films (P3HT nanowires aligned in a polystyrene matrix) after annealing at 200°C, due to the notable upsurge in thermally induced diffusion of the polymer chains (Jeong et al., 2020). There was multiple data research that suggests the association of absorption with structural properties of an annealed P3HT thin film and it is occasionally debatable and does not correlate with other studies. For example, it was proven that improved crystallinity due to thermal annealing at 150℃ leads to increased absorption (Cho et al., 2006). However, it has been experimentally demonstrated that absorption decreases and recrystallization occurs after thermal annealing (Gurau et al., 2007). This could be due to the utilization of different methods in prosecuting the experiment and the presence of influence from parameters such as the concentration of the liquid material, the cleanliness of the substrate and different nanoparticles from existing studies. Thus, the different experimental methods should be conducted and the optical properties are investigated so that we would have data concerning the optical characterization of P3HT thin film by varying the synthesis and sample preparation.

In this study, P3HT material is chosen due to its high absorption coefficient in the visible region of the solar spectrum and exhibits high mobility of the light-generated holes (Duan et al., 2019). The inorganic semiconductor nanoparticle used is cadmium sulphide (CdS). The CdS possess a direct bandgap of 2.4 eV, which is a good value for an acceptor in hybrid PV devices and it is also an effective charge transport material in optoelectronic devices (Yu et al., 2017). Moreover, semiconductor nanoparticles are better than larger particles in increasing the electronic properties, photoconduction, as well as photoluminescence (Lebeau & Innocenzi, 2011). This study concentrates on the insight into the different thermal annealing temperatures that affect the optical properties of the fabricated hybrid P3HT: CdS thin film. The optical properties of this film are investigated using different temperature values.

2. MATERIALS AND METHODS

Materials. Regioregular poly(3-hexylthiophene-2,5-diyl), hexamethyldisilazane (HMDS) (99.99%), cadmium chloride hydrate (99.995% trace metal basis), chloroform ($CHCl_3$), acetone, propanol, iron (II) sulphide (99.9% trace metal basis), hydrochloric acid, and stearic acid were all purchased from Sigma-Aldrich.

Film Preparation. Quartz glass substrates were thoroughly cleaned prior to usage. They were soaked and rubbed mildly in a decon bath and followed by sonication for 5 minutes in acetone. The quartz was then sonicated in deionized (DI) water for 2 minutes and was sonicated again in propanol for 5 minutes to cancel out the debris from acetone. The glass substrates were

cleaned with DI water and dried with nitrogen gas. The substrates were exposed to HMDS overnight before deposition. Quartz glass has polar OH bonds that make it hydrophilic. This feature is faulty for the non-polar of the photoresist. Thus, HMDS was used to make the substrates' surface hydrophobic and the exposure produce a coating that provide surface hydrophobicity by hindering water infiltration (Rudnick, 2018). P3HT solution (5 mg/mL) with $CHCl_3$ as the solvent, cadmium chloride solution (0.13 mg/mL) and the stearic acid solution (0.14 mg/mL) were used. P3HT solution was coated on the quartz and then followed with the deposition of cadmium chloride along with the stearic acid solution, and both of the depositions were then spin-coated at 500 rpm for 10 seconds onto quartz as shown in Figure 1.

The coating process was performed using a WS-400-6NPP-LITE spin processor from Laurell Technologies Corporation. The coater's system housing is made of a solid co-polymer blend that can resist solvents and strong acids and bases, making the post-coating cleaning process easier and hassle-free. After the deposition process, the samples were placed in a glass chamber with H_2S gas and exposed to the gas for an optimum amount of time (6 h) to embed CdS nanoparticles between polymer layers. The resulting films (Figure 2) were annealed at a certain temperature (T_{an} =40, 80, 120, 160°C) on a hotplate for 10 min and were cooled down before characterization.

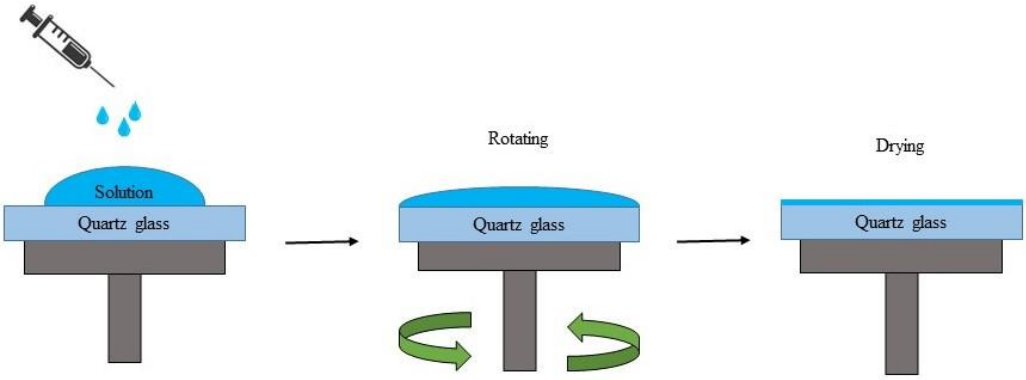

Figure 1. The schematic presentation of the spin-coating process

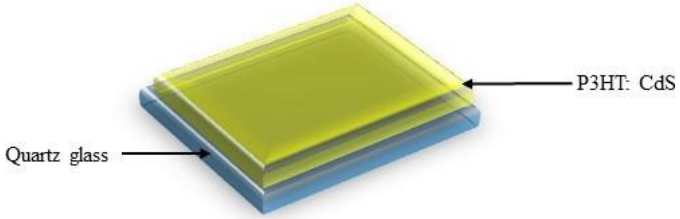

Figure 2. A schematic diagram of the P3HT: CdS thin film

Characterization. Optical characterization of all thin films was performed using JASCO V570 UV-Vis (Ultraviolet-visible) spectrophotometers in the 250-800 nm wavelength range and operated at a resolution of 0.5 nm. The characterization will represent the absorption spectra of the elements and the spectrometer functions as light passes through the grating diffraction.

3. RESULTS AND DISCUSSION

The P3HT: CdS thin film was annealed at 40°C, 80°C, 120°C, and 160°C, and the absorption spectra of the thin film at room temperature were also recorded. Figure 3 shows the absorption spectra of P3HT: CdS thin film at different annealing temperatures. The absorption peak at 525 nm of P3HT: CdS at room temperature is caused by the π-π conjugated chain transition. The peak is assumed to have been caused by the vibronic structures when P3HT

polymer molecules aggregate (Na et al., 2017). The value of the absorption peak of the thin film annealed at 40°C is higher than 80°C. On the other hand, the difference in absorption peak between film at room temperature and film with thermal annealing at 40°C is subtle because the significant molecular ordering of P3HT can be observed even without thermal annealing since P3HT can be dissolved at moderate temperature (Park & Kim, 2019). However, the absorption peak for the film thermally annealed at 120℃ and 160℃ is not visible but rather exhibits a peculiar absorption spectrum that is extremely different from those annealed at lower temperatures. The reason that has caused the unexpected absorption trend could not be explained but it has been stated that thermal annealing depends on the solubility of P3HT and intermolecular interactions of the solution and substrate are related to the boiling point of the solvent, thus solvent with higher boiling point should be used (Na et al., 2017). According to the results, the maximum absorption of the film at 525 nm and P3HT typically reaches a maximum absorption at 450 nm and the emission peak appears at 570 nm (Smolarek et al., 2013).

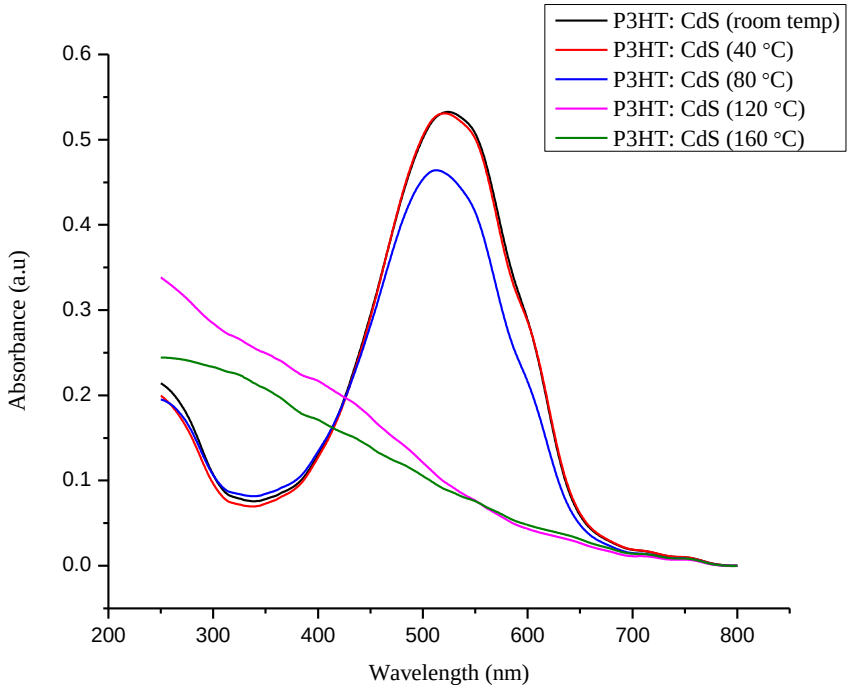

Figure 3. The absorption spectra of P3HT: CdS thin film with different thermal annealing temperatures

The solid-state absorptions of P3HT are reaching from 520 nm to 530 nm, and in Figure 3 the presence of absorption peaks in the UV region is an indication of the quantum confinement effect caused by CdS nanoparticles (Maity et al., 2006). The transition absorption peak at a shorter wavelength indicates that the blue shifts are caused by the growth of CdS nanoparticles in the P3HT matrix, which lead to the consequent destruction of the P3HT chain order during solvent evaporation (Liao et al., 2011). Absorption spectra of film at room temperature, annealed at 40℃ and 80℃ show a slight appearance of a shoulder at 590 nm due to the inter-chain interactions (Motaung et al., 2009), whereas there was no shoulder formed when annealing at much higher temperatures which are 120°C and 160°C and the absorption spectra profile of P3HT also not obtainable.

Heat treatment at 120°C and above is possibly excessive in this work and destroys the chain structure of the polymer, but other studies by Peng and associates show that increasing annealing temperature up to 150°C improves the interchain as well as intrachain orders that lead to higher absorption intensity of films (Peng et al., 2011). The outcome of the study also lead to the conclusion

that when the annealing temperature increased to 200°C (the melting point of the polymer is 218°C), the absorption intensity and interchain order declined. Optical measurements show a 15 nm blue shift in absorption in P3HT: CdS as compared to pristine P3HT, indicating that charge transfer between P3HT and CdS occurs (Khan & Almohammedi, 2017). On the other hand, the incorporation of CdS into P3HT favours the crystallinity of P3HT chains in the P3HT: CdS nanocomposites, since the peaks ascribed to the crystalline phase are more intense (García-Carvajal et al., 2019). The value of the energy bandgap is calculated using the Tauc relation method, and the initiate wavelength ($\lambda_{initiate}$) is calculated according to the Eq. 1;

$$E = \frac{hc}{\lambda_{initiate}} \quad (1)$$

h is a Planck constant and *c* is the speed of light. Then, the absorption coefficient of the thin film is calculated using Beer-Lambert's law expressed as Eq. 2;

$$\alpha = 2.302\frac{A}{l} \quad (2)$$

where *A* is the absorbance and *l* is the thickness of the film. Then the plot of *αhv* against *hv* is constructed by using the expression of the Tauc relation (Horti et al., 2019) as stated in Eq. 3;

$$(\alpha hv)^n = A(hv - E_g) \quad (3)$$

E_g represents the bandgap energy of the material, *n* is a constant value that signifies the nature of the electronic transition. When $n = 2$, it is a direct allowed transition, indirect allowed transition ($n = 1/2$), direct forbidden transition ($n = 2/3$), and indirect forbidden transition ($n = 1/3$). The allowed transitions usually dominate the absorption process which produces direct or indirect transitions. Plotting the $(\alpha hv)^{\gamma}$ versus *hv* is a major step in order to determine whether $n = 2$ or $n = 1/2$ is giving a better fit which allows us to identify the correct transition type. After *αhv* against *hv* is plotted, extrapolating a linear portion on the energy axis should be done and in this study, the bandgap is estimated from the intercept of the linear portion of the αhv^2 versus *hv* on the *hv* axis. The energy bandgap value for each thin film annealed at several temperatures is given in Table 1.

Table 1. The energy bandgap values of the thin film with various annealing temperatures

Thermal Annealing Temperature (℃)	Energy Bandgap (eV)
Room temperature	1.98
40	1.99
80	2.02
120	3.11
160	2.80

The P3HT: CdS thin film at room temperature and the one that annealed at 40°C yield good energy bandgap values of 1.98 eV and 1.99 eV respectively. This correlates with the fact that P3HT is a low bandgap polymer of 1.90 eV (Dou et al., 2015). The bandgap value slightly changes when the temperature were increased and other research also shows that the bandgap value lessens as the annealing temperature rises. It has been shown that the absorption of photon energy increases as the annealing temperature increases (Sanjeev & Kekuda, 2015). When the temperature was increased from 40°C to 80°C, the bandgap value was increased as well. This also occurs in other investigations, which found that when the annealing temperature of P3HT: PCBM-based organic solar cells were increased to an optimal temperature of 120°C, the absorption increased and the absorption band expanded (Guney et al., 2019).

4. CONCLUSION

P3HT: CdS thin films were fabricated onto a quartz glass substrate and the effect of thermal annealing on the optical properties of the film was investigated. The films produced

absorption spectrum results as expected and based on the obtained data, the absorption peak value of film annealed at 40°C is greater than 80°C and obtained band gap values of 1.98 eV and 1.99 eV correspondingly. This can be concluded that the indication of the presence of CdS nanoparticles in the P3HT matrix can be seen by the appearance of absorption peaks in the UV region. However, the absorption spectra of the P3HT: CdS thin film at 120°C and 160°C do not show any similarities or absorbance peaks because the chain of the polymer was destroyed during the annealing process.

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