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Effect of cadmium sulfide nanoparticles on electrical properties of polymer photovoltaic cell

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Abstract: It has been known that by integrating semiconductor nanoparticles into a conjugated polymer films, the efficiency of the device increase significantly. This is due to their unique combined advantage of physical and optical properties. In this work, we propose a simple but yet promising bottom-up method for synthesis and embed the semiconductor nanoparticles inside the polymeric matrixes. The nanoparticles were grown by in-situ formation of the CdS nanoparticles inside a conjugated polymer films by exposing the films to the H_2S environment for several hours. The existence of CdS nanoparticles was confirmed by FESEM and EDX. The particle sizes were in the range of several nanometers, which suggests that their growth were restricted by the polymer chain. The existence of CdS nanoparticles effects the electrical properties of the polymer solar cell.

Keywords: CdS nanoparticles, EDX, electrical properties, FESEM, polymer photovoltaic cell

I. INTRODUCTION

Crystalline and multi-crystalline silicon photovoltaic are the most developed and produced accounting for about 80% of the photovoltaic market. The optical absorption of silicon is well matched with the solar spectrum and power conversion efficiencies of 25% and 20% have been obtained for crystalline and multi-crystalline silicon solar cells respectively [1]. However, the cost of production is very high due the facilities required for, among other activities, silicon purification, wafer production and cell processing. Organic-based solar cells, such as dye-sensitized solar cells (DSSC), organic photovoltaic (OPV) and organic-inorganic hybrid (OIH) photovoltaic were developed to pursue high power conversion efficiency at low manufacturing costs. In general, the power conversion efficiencies and lifetime stability of organic-based solar cells are much lower than the silicon solar cells, but their low fabrication costs, flexibility and light weight characteristics have made them attractive for special applications.

Organic materials have a conductor and semiconductor properties as well as the ability to produce photovoltaic devices using solution phase techniques such as ink jet printing and roll to roll techniques which allow for cheap and high throughput manufacturing [2]. Organic semiconductors also have very high absorption coefficients which allow the use of very thin films whilst still absorbing a sufficient portion of the solar spectrum. However, at present OPV have a poor conversion efficiency of about 6% only [3] which is grossly inefficient for normal applications. This is due to the organic polymer’s intrinsic properties such as low charge mobility [4], relatively narrow optical absorption spectrum [5], and large optical band gap [6]. To obtain acceptable efficiency levels, hybrid organic–inorganic solar photovoltaic (HOISPV) devices are under intense research.

Hybrid devices have the advantage of combining the desirable characteristics of inorganic materials such as stability, high carrier mobility and compatible fabrication processes with those of organic materials such as enhanced light absorption at a wide range of wavelengths [7] and adjustable molecular structures for energy band alignment [8]. Exciton generation is favorable in organic-inorganic cells due to the relatively large absorption cross section of the organic semiconductor. Using inorganic electron acceptor materials overcomes the photo-induced degradation of conjugated organic semiconductors. Also, excitons absorbed in the inorganic material assist in the photo-generation of charge carriers. In this study, we presented a new simple method of creating inorganic nanoparticles that is cadmium sulfide (CdS), in the polymeric photovoltaic layer.

II. EXPERIMENTS

Materials – Stearic acid (SA), conjugated polymer regioregular Poly(3-hexylthiophene-2,5-diyl) or P3HT (MW: 87,000), colloidal dispersion Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) or PEDOT:PSS and cadmium (II) chloride were purchased from Sigma Aldrich. Chloroform was used as the solvent to P3HT and stearic acid. All materials used were as-received unless stated otherwise. Indium tin oxide (ITO) coated glass substrates from Nanocs with a sheet resistance of 5 Ω/sq act as the cathode of the solar cell.

Nanoparticles formation - Filtered PEDOT:PSS was spun on a cleaned ITO coated substrate at 4000 rpm, followed by annealing for 10 minutes at 120 ^{o}C. Then, the active layer for photovoltaic device is deposited on top of it using Angle Lifting Deposition and gas exposure method. The active layer comprised of polymer and nanoparticles that were grown directly in the polymer matrix. In preparing the active layer, KSV 2002 System 2 trough was employed. The trough was cleaned thoroughly using chloroform and ethanol and filled with 5 µMol of cadmium chloride in deionized water before dispensing 400 µl P3HT in chloroform (0.2 mg/ml) and 100 µl stearic acid in chloroform (0.14 mg/ml) onto the subphase to form a floating film. The film area was then compressed by the barrier at constant speed of 1 cm/min, consequently decreasing the area of the floating film.

As the area decreased, the pressure of the floating film increase accordingly and the change is monitored by an isotherm graph. Once the film reached solid phase, the films were deposited on the substrate (glass/ITO/PEDOT:PSS). The deposition was done by carefully touching one edge of the substrate onto the film surface at an angle of 45^{o} and slowly dropping it on the film and lifting it again by raising it the same way. The deposition was done at a constant surface pressure as that is controlled by computer. After every deposition, the film was dried using hot air for 15 seconds to ensure it is fully dry and to initiate polymerization. After the last deposition, the film was exposed to H_2S gas environment for 2 and 6 hours to embed CdS nanoparticles in between polymer layers and then annealed at 80 ^{o}C for 10 minutes. Finally, 100 nm thick aluminum (Al) was evaporated on the top of the active layer to complete the solar cell device.

Morphological Analysis and Device Measurement **-** Morphology of the active layer as well as Energy Dispersive X-ray (EDX) analysis was done by using Field Emission Scanning Electron Microscopy (FESEM) model SU 8020 UHRdel Hitachi. The current density–voltage (*J-V*) characteristics of solar cells were determined by a Keithley 2400 source meter unit assisted by a calibrated solar simulator with AM1.5 G illumination with light intensity of 100 mW/cm^2.

III. RESULTS AND DISCUSSION

Figure 1 shows the surface pressure versus mean molecular area isotherm of P3HT mixed with stearic acid (P3HT:SA) at room temperature. Isotherm graph is an important parameter to understand the characteristic surface behavior of a floating film on the subphase. From the graph, we can observe that no distinct liquid-solid phase transition occurs. The floating film is in the gas phase until the surface pressure starts rising at an area of 6878 Å^2/molecule. A gas phase is a phase where the interaction between molecules is very little. Once it enters a liquid phase, the molecules are closer and some interactions occur between them. When the surface pressure reached 19 mN/m, the molecules started to enter solid phase. In this phase, the molecules are relatively well oriented and closely packed. When the steepest linear section of the graph was extrapolated to zero pressure, the limiting area per molecule of P3HT:SA molecule occupied at a molecular area (A_o) of approximately 6300 Å^2.

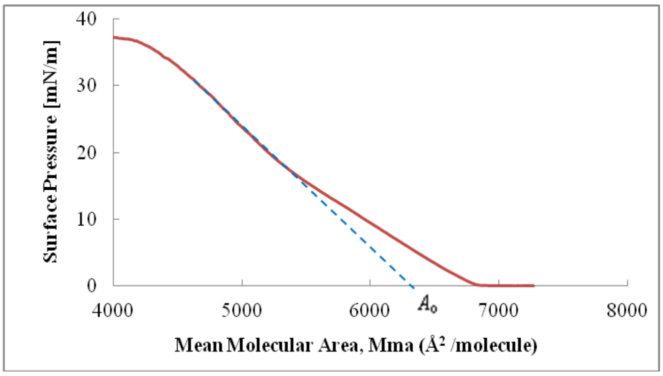
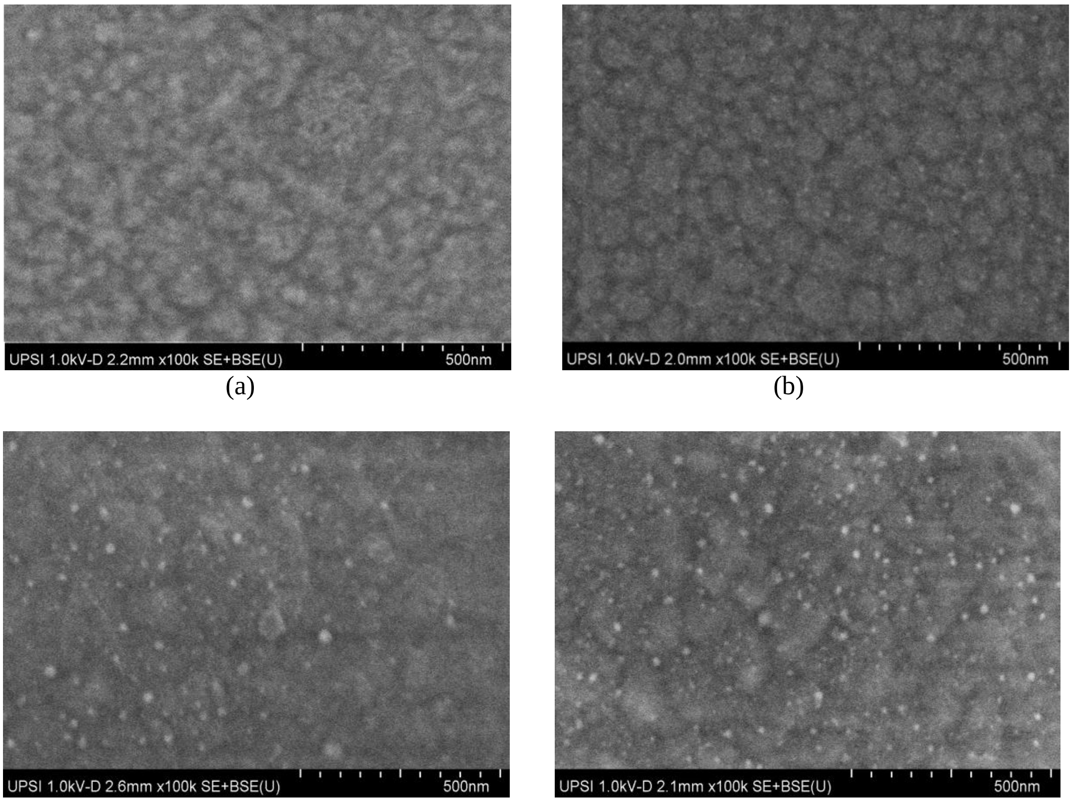


Fig.1 Isotherm graph of P3HT:SA

Field Emission Scanning Electron Microscopy (FESEM) was used to characterize the thin film before and after hydrogen sulfide (H_2S) gas exposure. Figure 2 (a) displays the surface of pristine P3HT thin film whilst Figure 2 (b) shows the thin film of P3HT:SA before H_2S gas exposure. Before the film was exposed to H_2S gas, we can clearly observe P3HT molecules that were surrounded by stearic acid. Initially, when the P3HT:SA monolayer were still on the $CdCl_2$ contained water subphase, stearic acid molecules capped cadmium ion becoming cadmium stearate, $CdSt_2$. When the thin film was exposed to H_2S gas, the S^{2-} ions are attracted to Cd^{2+} ions, initiating nucleation of CdS and further aggregation to form larger CdS nanoparticles. Figure 2 (c) and 2 (d) confirms the nanoparticle produced after the P3HT:SA thin films were exposed to H_2S gas for 4 and 6 hours.



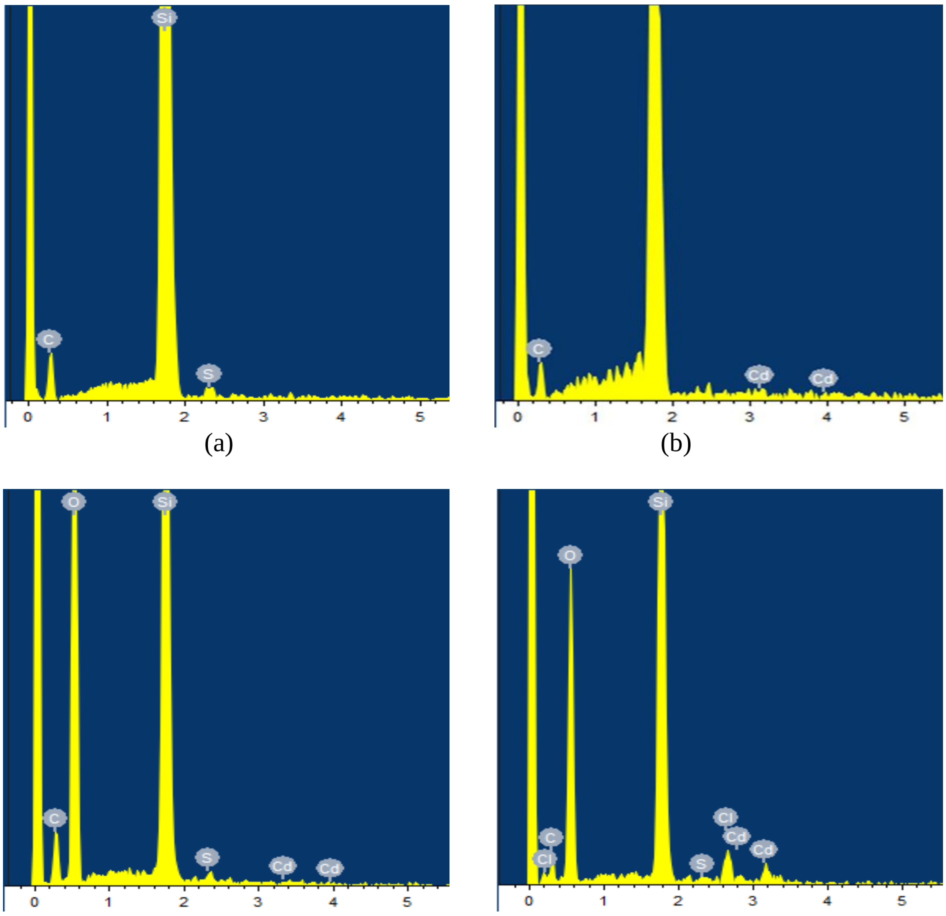
(a) (b)

(c) (d)

Fig.2 FESEM result for (a) Pristine P3HT (b) P3HT:SA before H_2S gas exposure (c) P3HT:SA exposed to H_2S gas for 2 hours (d) P3HT:SA exposed to H_2S gas for 6 hours

Apparently, the CdS nanoparticles size did not increase with an increment of the exposure time. For both time exposures, the CdS particles size range from 13 nm to 18 nm. This may be due to the long chain high molecular weight polymer restricting the growth of CdS nanoparticles. However, the quantities of CdS particles increased with time. On the contrary, Yang et al found that the CdS nanoparticles size increases with increase in reaction time when the thin film consists of stearic acid only [9]. This might be due to the small size of stearic acid molecules allow the molecules to shift from its original position easily when there is further aggregation of the CdS particles.

The Energy–Diffractive X-ray (EDX) analysis data of the Pristine P3HT, P3HT:SA composite before and after H_2S gas exposure is shown in Figure 3. EDX analysis has shown peaks for sulfide at 2.30 keV and an increment in weight percentage of Sulfur (S) with longer H_2S gas exposure time, indicating more S^{2-} ions have been absorbed and combined with Cd^{2+} (Figure 3 (c) and 3 (d)).



(a) (b)

(c) (d)

Fig.3 EDX result for (a) Pristine P3HT (b) Before H_2S gas exposure
(c) After 2 hours exposure (d) After 6 hours exposure

The solar cell performance under a simulated AM 1.5G illumination with light density of 100 mW/cm^2 is shown in Table 1. The number of the deposited active layers was kept at a constant value of 13 layers before it was exposed to H_2S gas for 2 or 6 hours. From the *J-V* measurement, the short circuit current density for device exposed for 2 hours, J_{sc} = 1.14 µA/cm^2, whereas for 6 hours, the J_{sc} was 1.22 µA/cm^2.

The open circuit voltage, V_{oc} after 2 hours exposure was estimated to be around 0.2 V and V_{oc} for 6 hours was 0.56 V. Fill factor, FF or the ratio of maximum output power to input power for 2 hours was 0.23 and 0.64 for 6 hours. It is desired to have high FF because it is related to better charge transport and therefore to increase charge carrier mobility as to prevent significant loss by recombination [10, 11]. The larger the FF, the greater is the device efficiency. The efficiency, η for devices exposed for 2 hours and 6 hours was 5.3×10^{-5} and 1.2×10^{-4} respectively.

Table 1: Characteristics of the solar cells under the illumination of AM 1.5 simulated solar light

Exposure time	J_{sc} (µA/cm^2)	V_{oc} (V)	**FF**	η (%)
0 hour	0.84	0.60	0.19	9.79×10^{-5}
2 hours	1.14	0.2	0.23	5.3×10^{-5}
6 hours	1.22	0.56	0.19	1.2×10^{-4}

Among the reasons of PV low short circuit density is small size CdS nanoparticles created, around 13 – 18 nm. The size of the nanoparticles affects performance of the solar cell, where the increment of nanoparticle size will increase the short circuit current [12]. The study of Yang's group showed that the longer exposure time is needed to create bigger nanoparticles in the thin film [13] however, the long chain of P3HT restricted the growth of the nanoparticles.

Crystallinity of the P3HT**:** SA also affects the device's J_{sc} where crystallinity can be achieved by annealing the film after deposition. The film was not annealed because it would need to be exposed to H_2S gas in order to create the nanoparticles. Annealing will result in P3HT polymerization, thus Cd^{2+} ions unable to interact with S^{2-} ions to create CdS in then polymer matrix. However, without annealing as a post treatment, the active layer will have a lower degree of crystallinity, and significantly reduces the performance of solar cells [14, 15, 16]. Studies also showed polymer crystallinity improved the contact between the polymer and the electrode and better phase separation, thereby increasing the charge carrier mobility and improve charge transfer rate of the films [17].

IV. CONCLUSION

Isotherm of P3HT:SA monolayer has been studied to determine the gas-liquid-solid phase transformation in order to deposit the active layer using the ALD technique. When the P3HT:SA film was exposed to H_2S gas, CdS nanoparticles were formed inside the films. FESEM and EDX characterization show that the longer the film exposed to H_2S gas, the more nanoparticles quantity formed in the polymeric active layer. Film crystallinity, quantity and size of the nanoparticles directly affecting the electrical properties of the photovoltaic device. However, their growth was restricted by the polymer chain. The CdS nanoparticles affect the electrical properties of the polymer solar cell.

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REFERENCES

[1]. M.A. Green, K. Emery, Y. Hishikawa, W. Warta, E.D. Dunlop, Solar Cell Efficiency Tables (Version 43), *Progress in Photovoltaics: Research and Applications*, *22*, 2014, 1-9.

[2]. R. Gaudiana, C.J. Brabec, Organic Materials – Fantastic Plastic. *Nature Photonics*, *2*, 2008, 287–289.

[3]. Y.Y. Liang, D.Q. Feng, Y. Wu, S.T. Tsai, G. Li, C. Ray, L.P. Yu, Highly Efficient Solar Cell Polymers Developed Via Fine–Tuning of Structural and Electronic Properties. *Journal of American Chemical Society*, *131*, 2009, 7792–7799.

[4]. H. Sirringhaus, Device Physics of Solution–Processed Organic Field Effect Transistors. *Advanced Materials*, *17*, 2005, 2411–2425.

[5]. P.G. Nicholson, F.A. Castro, Organic Photovoltaics: Principles and Techniques for Nanometer Scale Characterization. *Nanotechnology*, *21*, 2010, 492001-492026.

[6]. J. Godlewski, M. Obarowska, Application of Organic Materials in Electronics. *The European Physical Journal Special Topics*, *144*, 2007, 51−66.

[7]. S. Günes. N.S. Sariciftci, Hybrid Solar Cells. *Inorganica Chimica Acta, 361*, 2008, 581–588.

[8]. H.J. Lee, J.H. Yum, H.C. Leventis, S.M. Zakeeruddin, S.A. Haque, P. Chenz, M.K. Nazeeruddin, CdSe Quantum Dot-Sensitized Solar Cells Exceeding Efficiency 1% at Full-Sun Intensity. *Journal of Physical Chemistry C*, *112*, 2008, 11600–11608.

[9]. M.T. Khan, A. Kaur, S.K. Dhawan, S. Chand, Hole Transport Mechanism in Organic/Inorganic Hybrid System Based on In-Situ Grown Cadmium Telluride Nanocrystals in Poly(3-Hexylthiophene), *J. Appl. Phys*. *109*, 2011, 114509.

[10]. S. Cho, K. Lee, J. Yuen, G. Wang, D. Moses, A. J. Heeger, M. Surin, R. Lazzaroni, Thermal Annealing-Induced Enhancement of the Field-Effect Mobility of Regioregular Poly(3-Hexylthiophene) Films, *J. Appl. Phys 100*, 2006, 114503–114508.

[11]. P. Schilinsky, C. Waldauf, J. Hauch, C. J. Brabec, Simulation of Light Intensity Dependent Current Characteristics of Polymer Solar Cells, *J. Appl. Phys*. *95*, 2004, 2816–2819.

[12]. J. Yang, A. Tang, R. Zhou, J. Xue, Effects of Nanocrystal Size and Device Aging on Performance of Hybrid Poly(3-Hexylthiophene):Cdse Nanocrystal Solar Cells, *Sol. Energy Mater. Sol. Cells*, *95*, 2011, 476–482.

[13]. X.M. Yang, G.M. Wang, Z.H. Lu, Characterization of Cds Nanoparticles Formed and Aggregated in Stearic Acid Langmuir-Blodgetts Films by Atomic Force Microscopy, *Supramol. Sci*. *5*, 1998, 549–552.

[14]. I. Riedel, V. Dyakonov, Influence of Electronic Transport Properties of Polymer-Fullerene Blends on the Performance of Bulk Heterojunction Photovoltaic Devices, *Phys. Status Solidi A*, *201*, 2004, 1332–1341.

[15]. D. Bi, F. Wu, W. Yue, Q. Qu, Q. Cui, Z. Qiu, C. Liu, W. Shen, M. Wang, Improved Performance of MEH-PPV/ZnO Solar Cells by Addition of Lithium Salt, *Solar Energy*, *85*, 2011, 2819–2825.

[16]. C. S. Ho, E. L. Huang, W. C. Hsu, C. S. Lee, Y. N. Lai, W. H. Lai, Effects of Annealing on Polymer Solar Cells with High Polythiophene–Fullerene Concentrations, *Jpn. J. Appl. Phys*., *50*, 2011, 04DK21.

[17]. G. Li, V. Shrotriya, Y. Yao, Y. Yang, Investigation of Annealing Effects and Film Thickness Dependence of Polymer Solar Cells Based on Poly(3-Hexylthiophene), *J. Appl. Phys*. *98*, 2005, 043704.