

In-situ CdS Nanoparticles Synthesis in Polymeric Thin Film

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Abstract. Cadmium sulphide (CdS) nanoparticles were synthesized directly in a mixture of thin film poly(3-hexylthiophene) polymer and stearic acid. The mixture was spread on de-ionized water containing Cadmium (II) chloride in a hydrophobic bath and then compressed until the layer of polymer and stearic acid enters the solid phase. The gas-liquid-solid transformation of the mixture layer was determined by measuring its surface pressure. The film was subsequently transferred onto a substrate using the angle lifting deposition method. It was then exposed to hydrogen sulphide gas to create cadmium sulphide (CdS) nanoparticles in the film. FESEM results show that longer exposure times to the hydrogen sulphide gas created more CdS nanoparticles.

Keywords: CdS, P3HT, Thin Film, Angle Lifting Deposition

1. Introduction

The synthesis and characterizations of II-VI and III-V nanoparticles have been studied extensively in view of their potential uses in electronic devices, drug delivery systems [1] and non-linear optics [2]. The material most studied is cadmium sulphide (CdS) due to its good thermal stability in many polymers [3] and outstanding optical-electronic properties [4].

Various methods have been employed to fabricate nanoparticles including laser-assisted catalytic growth method, ultrasound or γ -irradiation and thermal decomposition of molecular precursors [5]. These procedures either produce nanoparticles with shells that are stable over long shelf-life but hamper the performance of the nanoparticles, or shell-free nanoparticles that are less stable and much more difficult to handle. Hence, for devices that need intimate contact between the nanoparticles and the matrices that surround it like ionic sensors, light emitting diodes and photovoltaics, direct growth of nanoparticles is a promising alternative. Liu et al employed copolymerization-sulfidation technique to create CdS nanoparticles in poly (styrene-co-vinyl acetate) [6] whilst Khan's group grew CdS nanowires on alumina using a one pot hydrothermal method [7]. Another simple method of producing nanoparticles is by using Langmuir Blodgett technique as reported by several groups of researchers [8, 9].

In this paper we report the production of CdS nanoparticles in poly (3-hexylthiophene-2,5-diyl) (P3HT) by modifying Langmuir-Schaeffer method and named it Angel Lifting Deposition (ALD) technique. The main objective of this work is to study the effect of gas exposure time variation on the properties of nanoparticles produced.

2. Methodology

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Stearic acid (SA), Poly (3-hexylthiophene -2, 5-diyl) or P3HT, cadmium (II) chloride, iron (II) sulfide were purchased from Sigma Aldrich. Chloroform (Mallinckrodt) was used as the solvent to P3HT and stearic acid. Indium tin oxide (ITO) coated glass (Nanocs) with a sheet resistance of 5 Ω /sq was used as the substrate. All materials used were as-received unless stated otherwise

We employed the ALD technique which is derived from the Langmuir layer principle to transfer the floating polymer monolayer onto a solid substrate. This technique overcomes the problem imposed by the high molecular weight of the long-chain polymer when using the common Langmuir-Blodgett and Langmuir-Schaeffer techniques. The ALD technique allows us to make large-area thin films and at the same time control the polymer ordering. KSV 2002 System 2 trough were filled with ultra-pure water (Milli-Q system, resistivity 18.2 M Ω at 25°C) containing 0.5 mM CdCl₂. The monolayer was formed by dispensing 400 μ l P3HT (0.2 mg/ml) and 100 μ l stearic acid (0.14 mg/ml) onto the water subphase. The chloroform was allowed to evaporate for 10 – 15 minutes prior to starting the compression. The floating film is compressed with one barrier at a constant rate of 1 cm/min. until it reached solid phase. Films were deposited by carefully depositing one edge of substrate onto floating film surface at an angle of 45° and slowly dropping it on the solid monolayer and lifting it again by raising it the same way. The deposition was done at a constant surface pressure that is being monitored by an electronic balance attached to Wilhemy plate. Thirteen layers of film were deposited in which 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 H₂S gas environment for 2 and 6 hours to embed CdS in between polymer layers.

Field Emission Scanning Electron Microscope (FESEM) model Hitachi SU 8020 UHR were used to investigate the size and distribution of CdS, and current density–voltage (*J-V*) characteristics of the thin film were determined by a Keithley 2400 source meter unit assisted by a calibrated solar simulator with AM 1.5 illumination with light intensity of 100 mW/cm².

3. Results and Discussion

Figure 1 shows the surface pressure versus mean molecular area isotherm of pristine P3HT on water subphase. The monolayer behavior of the pristine P3HT shows no distinct gas-liquid-solid phase development due to the long polymer chains that cause a two-dimensional lattice to form [10]. However, when P3HT is mixed with stearic acid, the isotherm of P3HT:SA on water subphase follows the stearic acid monolayer trend – higher surface pressure and distinguishable phase changes even though the volume of stearic acid added and stearic acid molecule size's is very small as compared to P3HT. Solid-liquid phase transition occurs at a surface pressure of 26 mN/m. This result is comparable with Singhal et al. [11] in which the liquid-solid phase transition occurs when the surface pressure reaches 28 mN/m at 30 °C. The improvement of P3HT isotherm is consistent with Aoki et al. [12] where the P3HT isotherm improved tremendously when mixed with poly (N-dodecylacrylamide) or pDDA. This phenomenon is due to the long tail fatty acid (e.g. stearic acid) and inert polymer matrix (e.g. pDDA) acting as a stabilizer to P3HT on the air-water interface.

However, when cadmium (II) chloride (CdCl₂) were added into the water subphase, no distinct liquid-solid phase transition occurred and the graph is smoother. When the steepest linear section of the graph was extrapolated, P3HT:SA molecule occupied at a molecular area (*A*₀) of approximately 6300 Å². The observed profile is due to capping of cadmium ion by stearic acid in between the polymer matrix, consequently, breaking the P3HT long chain.

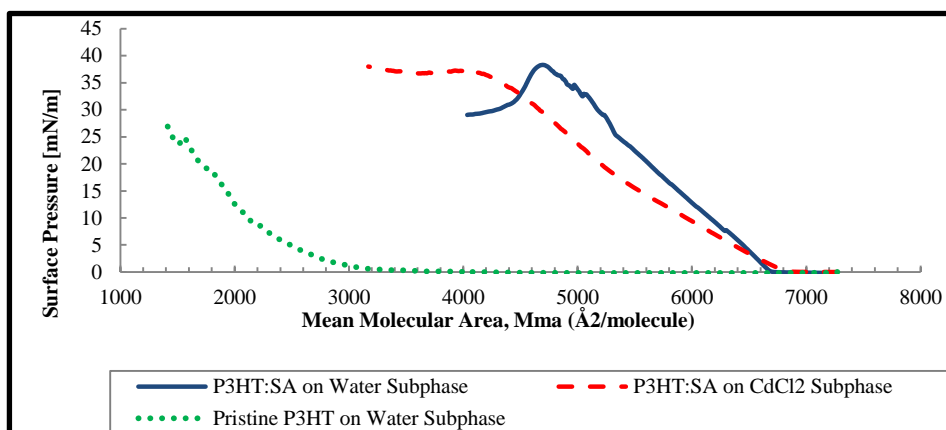


Fig.1: Isotherm of pristine P3HT, P3HT:SA monolayer on water and water contained cadmium (II) chloride subphase

Field Emission Scanning Electron Microscopy (FESEM) was used to characterize the thin film before and after hydrogen sulfide (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 (Figure 2 (a)). 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 (b) and 2 (c) shows the nanoparticle produced after the P3HT:SA thin films were exposed to H_2S gas for 2 and 4 hours. Apparently, the range of size of the CdS nanoparticles did not increase with increment of the exposure time. For both time exposures, the CdS particles size range from 13nm 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]. The small size of stearic acid molecules, $\sim 22 \text{ \AA}^2$, allow the molecules to shift from its original position easily when there is further aggregation of the CdS particles.

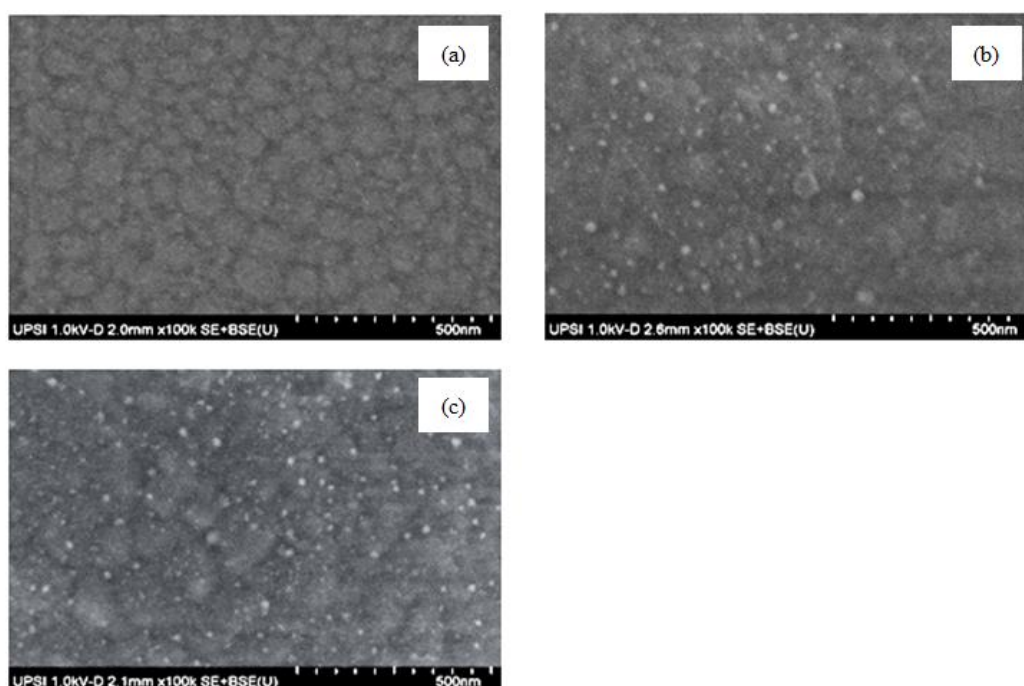


Fig. 2: FESEM images for: (a) Unexposed active layer (b) Active layer exposed to H_2S gas for 2 hours (c) Active layer exposed to H_2S gas for 6 hours.

The thin films were then illuminated under solar simulator with light density of 100 mW/cm² to investigate their electrical performance. From the J - V measurement, the short circuit current density J_{sc} before the thin films were exposed to H₂S gas is 0.84 μ A/cm². However, when they were exposed for 2 hours, the J_{sc} increased to 1.14 μ A/cm², and after 6 hours exposure, the $J_{sc} = 1.22$ μ A/cm². Short circuit current density determination is crucial in designing electrical and electronic systems because performance of a circuit relies strongly upon the designed current level. The open circuit voltage, V_{oc} for non-exposed film is 0.6 V, V_{oc} after 2 hours of exposure and V_{oc} for 6 hours was 0.56 V. Summary of the J - V measurements is indicated in Table 1.

Table 1: Current density – Voltage (J - V) characteristics of the thin film under light power density of 100 mW/cm².

Exposure Time	J_{sc} (μ A/cm ²)	V_{oc} (V)
0 hour	0.84	0.6
2 hours	1.14	0.2
6 hours	1.22	0.56

4. Conclusion

Angle lifting deposition and gas exposure method have been employed in order to produce large area hybrid polymeric-nanoparticles thin film. The methods used were cost effective both in terms of materials and time consumption. The surface pressure-area isotherm of pristine P3HT and P3HT:SA monolayer on different subphases have been studied to elucidate the effect of mixing small molecule materials with long chain polymers and to determine the liquid-solid phase transformations. P3HT:SA monolayer isotherm showed increment in solid phase surface pressure and mean molecular area. The composite of P3HT:CdS thin film can be applied in the fabrication of electronic applications that need intimate contact between p- and n-type materials such as photovoltaics, light emitting diodes and field effect transistors. On the basis of these results, future work will be directed to the improvement of nanoparticle size and quantity.

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6. References

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