Study of Some Structural and Optical Properties for P3HT: CBM Heterojunctions Blending of ZnS Nanoparticles

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Abstract. In this work, the preparation of P3HT: PCBM heterojunction blending ZnS nanoparticles (NPs) was demonstrated. Some structural and optical properties of the hybrid structure films were presented. ZnS NPs films were prepared by chemical route method and at different pH values. Then, the nanoparticles ZnS was incorporated in P3HT: PCBM solution in chlorobenzene with the weight ratios of 0, 5, 10 and 15 wt %. The X-ray diffraction patterns of the ZnS nanoparticles films and SEM images of the hybrid structure films are discussed. Also, the absorption spectra in the range of 200-1100 nm of the blends for variable weight ratios samples and the effect of ZnS pH values on these spectra are presented.

Keywords: nanostructure, organic materials, conjugated polymer, P3HT: PCBM, chemical rate method, x-ray diffraction, optical properties.

1. Introduction:
Organic materials are safe materials with unlimited availability which are used to develop the technology with active economy for extensive power generation. The organic semiconductors are cheap materials in comparable with the inorganic semiconductors. Also, the optical absorption coefficients of these materials are high which offer the prospect for the manufacture of thin film solar cells [1, 2]. Hybrid solar cells often use an incorporating of nanostructured materials as a network of electron-donor and electron-acceptor materials. These solar cells using the blending of materials are to convert sunlight into electricity [3]. P3HT polymers have been proposed to manufacture polymer : fullerene solar cells because they can absorb visible light and their glass transition temperature \( \approx 110^\circ\text{C} \) [4]. The morphology and the mobility of pure P3HT and blended P3HT: PCBM films are highly dependent on casting conditions [5, 6]. In the photoactive light absorbing thin film, a conjugated polymer is consider as organic part and a semiconducting nanocrystals (NCs) as an inorganic part [3].

In the present work, P3HT and C60 derivative PCBM material with the blending ZnS nanoparticles (NPs) on polymer-fullerene matrix are used. The inorganic semiconductor ZnS was used as the n-type material and the P3HT: PCBM as the photoactive layer. In this study, we concentrated on the effect of the concentration of ZnS on P3HT: PCBM photoactive layer and for three pH values. Hence, these materials combination has been used to study the light absorption characteristics.

2. Experiments:
P3HT: PCBM: ZnS NPs layers were prepared by spin coating as a precursor solution on pre-cleaned glass substrates. The glass substrates were first ultrasonicated in distilled water, ethanol, and subsequently dried in oven. The P3HT: PCBM layer was constructed by spin-coating method with 1:1 weight ratio solution in chlorobenzene at the glass substrate. Then, the ZnS nanoparticles were incorporated in P3HT: PCBM solution in chlorobenzene with the weight ratios of 0, 5, 10 and 15 wt %. Also, the ZnS NPs were prepared by the chemical route method. The ZnS NPs were prepared by mixing two chemical solutions. The first solution was prepared by dissolving 1.3g of (ZnCl$_2$) in 100 ml distilled water. Sodium hydroxide was used to reach the pH of the solution to the required amount of (pH=8.5, 9.5 and 10.5). The second solution was obtained by dissolving 0.7g from (Na$_2$S) in 100 ml distilled water [4]. Because of the common ion effect, the pH controlled the rate of reaction. With a spin-coating speed of 1000 rpm for 30s, P3HT: PCBM: ZnS NPs solution was deposited at the glass substrate. The annealing temperature was at 120 °C for 10 min. The ratios of P3HT: PCBM: ZnS NPs were (1:1:0, 1:1:0.05, 1:1:0.01 and 1:1:0.15), respectively. The film thickness of P3HT: PCBM: ZnS NPs was about 120 nm. The area of the sample was estimated to be (2.5x2.5) cm$^2$.

The structural properties of the films were investigated by using X-ray diffraction pattern (XRD). The surface morphology of the films was tested by using a field emission scanning electron microscope (FE-SEM, S-4200, and Hitachi) operated at 15 kV.

Also, the absorption spectra of the films were measured at room temperature using a SHIMADZU UV-1800 UV-VIS spectrophotometer. The spectrophotometer range is from (200-1200) nm.

3. Results and Discussion:

3.1 X-Ray Diffraction:

XRD of ZnS (NPs) films are illustrated in Figure 1. Three prominent broad peaks are presented for all samples. The values of 2θ for these peaks are located around of 28°, 47° and 56° corresponding to (111), (220) and (311) diffraction planes respectively. This result indicates to the cubic structure for the prepared nanocrystals. Also, 20 peaks located around 31°, 34°, 36°, 62° and 67 are related to (100), (002), (101), (013) and (112) planes respectively, which indicate to the hexagonal wurzite structure of polycrystalline ZnO. This result reveals the partial and complete oxidation of ZnS NPs in various mediums. In addition, the broadening of the peaks reveals to the formation of small size of ZnS nanocrystals [7, 8].

The prepared samples of pH (8.5, 9.5 &10.5) have average crystallite size of (11.5, 14.3 &12) nm respectively. The increasing of the intensity of ZnS NPs (111) peak indicates to the increasing of the crystallinity which is due to the increasing of the pH value of the samples. This result is comparable with result of other researchers [8].
3.2 Scanning Electron Microscope Analysis (SEM):

Figure 2 shows the SEM images of ZnS NPs film, P3HT: PCBM film and P3HT: PCBM blending ZnS NPs hybrid film. The SEM study of the ZnS NPs film is shown in Figure 2a. The distributions of ZnS NPs are of irregular shape in the entire region with an average diameter of ZnS NPs about 85 nm. Figure (2b) shows the SEM image of P3HT: PCBM film. It can be noticed from this figure the uniform distribution of the film. To study the distribution of ZnS NPs in this layer, the microstructures of the P3HT: PCBM blending ZnS NPs hybrid film by SEM was used, as shown in Figure 2c. It was found that the distribution of the ZnS NPs is irregular distribution and the average diameter was about 57 nm. It is estimated that the decreasing of surface energy is attributed from the assemble effect results from nanoparticles [9].

![XRD patterns of the ZnS nanoparticles prepared by chemical route method](image-url)
3.3 Optical Properties Study:

The absorption spectra of the blends and for variable weight ratios samples of ZnS NPs are illustrated in Figure 3. The broad absorption peaks from 400 nm to 650 nm is resulted from the $\pi-\pi^*$ transitions. Absorption spectra of the blends shown in this figure are simply reveals to the combination of nanoparticles and polymer without any further absorption peaks [10, 11] because there is no any ground state interaction between them [12]. The little stretching of absorption edge of the P3HT: PCBM: ZnS NPs to the lower wavelength region is resulted from the quantum confinement effect from the inorganic nanoparticles. Also, the blue shift is due to the rising in band gap between $\pi$ and $\pi^*$ energy levels. The insertion of the nanoparticles decreases the inter- chain interaction and conjugation length of P3HT.

Also, the addition of ZnS NPs into the P3HT: PCBM matrix increased the crystallization of the P3HT and captures more incoming light, therefore the magnitude of the absorption is increased [13]. It can be noticed, that the increasing of the ZnS NPs ratio leads to decreasing the absorbance, and this is because of the aggregation of ZnS NPs martial which can increase the recombination of exitons. Due to the high amount of the light absorption intensity, the generation rate of excitons is improving [9].

Figure 2. The SEM images of (a) ZnS nanoparticles, (b) P3HT: PCBM film and (c) P3HT: PCBM: ZnS NPs hybrid film.
Figure 3. Optical absorption spectra of P3HT, P3HT: PCBM and P3HT: PCBM: ZnS NPs hybrid films for different pH values and concentrations of ZnS nanoparticles.

Also, the previous figure shows that the spectrum has two bands, one in UV region which is called B-band (or soret) band in the range about (240-350) nm due to the direct transition between the bonding \( \pi \) in HOMO and the anti-bonding \( \pi^* \) in LUMO for all samples, and the other band is in the visible region which is called Q-band, and it consists of two close peaks in the range of 530-750 nm.

Figure 4 illustrates the relation between \((\alpha h\nu)^2\) and the photon energy \((h\nu)\). The optical energy gap values \((E_{opt})\) for P3HT: PCBM and P3HT: PCBM: ZnS films with different pH values have been calculated using Tauc equation [11]. This figure reveals that the values of direct optical energy gap, increases by adding ZnS nanoparticles and for the lower concentration of 5% and for different pH is attributed to the increase of absorbance intensity in the visible region. Whereas, it decreases for other ZnS loading (10% & 15%) and for different pH values due to the decreasing of the absorbance in the visible region. Table 1 illustrates optical constants for P3HT: PCBM:ZnS films for different pH and concentrations of ZnS nanoparticles.
Figure 4. \((\alpha h \nu)^2\) versus photon energy \((h \nu)\) for P3HT:PCBM:ZnS films with various pH values of ZnS nanoparticles.

Table 1. Optical constants for P3HT: PCBM: ZnS films for different pH and concentration values of ZnS nanoparticles.

| pH  | ZnS Conc. | Eg (eV) | Eg (eV) | Eg (eV) |
|-----|-----------|---------|---------|---------|
|     |           | Q1-band | Q2-band | B-band  |
| 8.5 | 5%        | 1.92    | 1.98    | 3.26    |
|     | 10%       | 1.87    | 1.92    | 3.1     |
|     | 15%       | 1.92    | 2       | 3.2     |
|     | 5%        | 1.89    | 1.94    | 3.16    |
| 9.5 | 10%       | 1.8     | 1.88    | 3.02    |
|     | 15%       | 1.9     | 1.99    | 3.04    |
|     | 5%        | 1.91    | 2       | 3.24    |
| 10.5| 10%       | 1.85    | 1.82    | 3.23    |
|     | 15%       | 1.91    | 2       | 3.26    |

4. Conclusions:
In this work, it is shown that the surface morphology and optical properties of the P3HT: PCBM blend film is influenced by the adding of ZnS NPs on polymer-fullerene matrix. This result is attributed to the interpenetrating network of ZnS nanoparticles which grow in P3HT: PCBM layer. Also, there is an improvement of the light absorption intensity for P3HT: PCBM matrix due to the addition of ZnS NPs material. Hence, it can be used as an active layer to achieve an efficient solar cell.

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