1. Introduction

Over the past few decades, considerable attention has been paid towards the organic materials being used in fabrication of organic solar cells (OSCs). This was obviously seen in metal phthalocyanines (MPc) which are molecular organic semiconductors. Organic photovoltaic devices including organic solar cells, gas sensors, field effect transistors, optical data storage have wide range of industrial applications; due to their unique optical and electronic properties as well as their chemical and thermal stability. In addition the low cost
and simple device preparation via solution processing makes them more interested in some technology applications [1-2]. The power conversion efficiencies of solar cells were clearly improved from 0.001% to 5.5% within the years of (1975 -2006). Development and new inventions in polymer science in parallel with participate significantly to the amount of investigations about OSC [3-4]. Possibly the development in efficiency will make them a competitive alternative to inorganic solar cells in the near future [5-8]. Organic thin films deposition techniques like roll-to-roll processing, ink-jet printing or spin casting are widely used, due to their cost effectiveness, and less material consumption can be obtained from the wet processing method to deposition of thin films [9-12]. CdS is one of compound belong to II-VI semiconductor with an energy gap ranging from (2.82- 2.5)eV. The chalcogenide families are used as window and buffer layer for CdS/CdTe solar cells, and continue to be a good choice to enormous researches due to their high-efficiency in solar devices [13-14]. Examples on the photoelectronic devices, like transducers laser materials, photo-sensors, optical wave guides and non-linear integrated optical devices. [15-16]

In this work synthesis and physical characteristics of organic NiPcTs inorganic CdS, and Blends of NiPcTs -CdS semiconductors thin films, have been studied.

2. Device structure and experimental method

The studied thin films of Nickel Phthalocyanine Tetrasulfonic Acid Tetrasodium Salt NiPcTs films were synthesized on pre-patterned (Fluorine-doped Tin Oxide) FTO coated glass substrates of thickness (3.2mm) and (10 × 10 cm) dimensions. The substrates were cleaned in acetone, ethanol, and deionized water for 10 min respectively. After drying in 70°C, the substrates were cut into four equal pieces with dimensions (2.5x2. 5) cm.

Thin films of NiPcTs prepared by gel-spin coating methods, with thickness of (130±7) nm, this is achieved by dissolving (0.65gm) organic powder of (NiPcTs), which was provided by (Sigma- Aldrich) in (10ml) deionized water. The solution has been deposited on FTO glass substrate, and, leave samples for 60 minutes in spin coater type [Laurell-WS650Mz-23NPP] with speed of (1500) rpm, then drying process in (70°C) temperatur.

Two (Al) electrodes of 200 nm thickness were deposited through a shadow mask onto glass substrate using thermal evaporstion method with 40 ± 5 μm gaps between them. The evaporation rate of (0.3 nm/s) was choosing to deposit electrode films, and the Vacuum chamber was maintained at a pressure of (5× 10^-5) mbar throughout the evaporation process.

CdS films were deposited on glass substrates by spin-coating method. CdS solutions were prepared by dissolving (1.83gm) cadmium chloride (CdCl2), with (25ml) of ethanol, purchased from (Edwards), 50ml of ethanol, placed in a glass baker with a piece of magnet bar was used to mix the solutions over 60 minutes. A special syringe was used for depositing the materials on FTO glass substrate that has been left for 10 minutes.. Then, (0.76gm) of Thiourea was dissolved in 25ml of ethanol, then dropped wisely to the mixture under stirring for 5 hours. The sol solution was dropped onto the glass substrate about 10 cycles at speeds of 1400 rpm for 30 Sec. After deposition, the films were dried in air at 150 °C for one hour.Blends of NiPcTs -CdS were fabricated with 1:2 content concentrations ratio of CdS solutions. The preparation procedure as follows: The organic NiPcTs and CdS materials were dissolved separately with concentrations of 1:2 g/L for NiPcTs -CdS respectively then starrer over one hour on the hot plate with elevated temperature of 70°. A solution of CdS was filtered using polytetrafluoroethylene (PTFE) filter with pore size of 0.2 μm. 0.5 ml of the final solutions for NiPcTs and CdS were dropped onto the FTO glass substrate with the thickness of 130 nm. The film was left about 10 cycles at speeds of 1500 rpm for 30 Sec.
After deposition, the films were dried in air at 70 °C for one hour. Film thicknesses were examined using Dektak profilometer instrument. Structural characterization for both of thin films and blends were identified using XRD, atomic force microscopy, EDS and SEM measurements.

3. Results and discussion

3-1 X-Ray Diffraction Technique (XRD):

The crystalline of NiPcTs, CdS thin films and heterojunction blends of NiPcTs-CdS were investigated using x-ray diffraction type (Shimadzu XRD- 6000), with source of radiation Cu-Kα of wavelength, 1.5418 Å, measurements recorded in the range of 2θ between (0 - 80°). As shown in figure (1-a), NiPcTs thin film has polycrystalline structure, with monoclinic phase. The XRD patterns of NiPcTs film has shown two predominant sharp peaks belonging to the reflection surfaces (100) and (102) at diffraction angles (6.90°) and (8.96°) respectively, this result matched with the standard JCCDD card No.( 11-0744), with simple difference. CdS thin film has polycrystalline hexagonal structure, with unsharp peaks belonging to the reflection surfaces (100), (002), (101), (110), (103), (112) at diffraction angles 24.75°, 26.465°, 28.1781°, 43.5010°, 47.7362°, 51.7811° respectively; as compared with the standard JCCDD card No. (96-101-1055), and the best growth at orientation (101) as shown in figure. (1- b). The NiPcTs/CdS blend heterojunction(BHJ) had two polycrystalline structure, the first one was cubic structure which was predominant and belong to the organic semiconductor (NiPcTs), and the other one was the hexagonal structure which was belong to inorganic (CdS) semiconductor, as shown in figure ( 1-c), also one can notice that predominant crystalline planes (101) and (102).

The value of the crystallite size was estimated using the relation[4].

\[ L = \frac{K\lambda}{\beta \cos \theta} \]  

Where, L is the mean crystallite size, K is the Scherer constant with value 0.94, \( \lambda = 1.542 \text{ Å} \) of the X-ray source wavelength and \( \beta \) is the full width at half maximum (FWHM), value. The FWHM, interplane distance (d) and crystallites size (G.S) of NiPcTs, CdS thin films and The NiPcTs/CdS blend heterojunction(BHJ) are listed in Table 1.

One can observe from table (1) that the average crystallite size is small. This may be due to the effect of temperature throughout the deposition and preparation method. The crystallite size of organic semiconductor (NiPcTs) was decreased while the grain size of CdS increased in the blend structure as compared with thin films structure, this might be attributed to the interaction between organic and inorganic semiconductors. The experimental values for interplanar spacing are in good matching with the joint committee on powder diffraction standards(JCPDS) with number (96-101-1055)
Figure (1): XRD pattern of (a): NiPcTs thin film. (b): CdS Thin Film
(c): Blend heterojunction NiPcTs -CdS.
Table (1): XRD results for NiPcTs, CdS thin films and blend heterojunction (BHJ)NiPcTs–CdS.

| Sample                      | 2θ (Deg) | FWHM | dhkl (Exp) (A) | C.S (nm) | dhkl (standard.) | hkl   | phase          |
|-----------------------------|----------|------|----------------|----------|------------------|-------|----------------|
| NiPcTs                      | 6.9000   | 0.2400 | 12.8005        | 33.2     | 12.6519          | 100   | Monoclinic.CuPc |
| NiPcTs                      | 8.9600   | 0.1866 | 9.8616         | 42.7     | 9.8591           | 02    | Monoclinic.CuPc |
| CdS                         | 24.7519  | 0.6186 | 3.5941         | 13.1     | 3.5940           | 100   | Hex.CdS        |
| CdS                         | 26.4650  | 0.6187 | 3.3652         | 13.2     | 3.3685           | 002   | Hex.CdS        |
| CdS                         | 28.1781  | 0.6186 | 3.1644         | 13.2     | 3.1710           | 101   | Hex.CdS        |
| CdS                         | 43.5010  | 0.7138 | 2.0787         | 12.0     | 2.4577           | 110   | Hex.CdS        |
| CdS                         | 47.7362  | 0.9041 | 1.9037         | 9.6      | 2.0750           | 103   | Hex.CdS        |
| Blend heterojunction(BHJ)   | 51.7811  | 1.0469 | 1.7641         | 8.4      | 1.9045           | 112   | Hex.CdS        |
| NiPcTs-CdS                  | 7.0019   | 0.6983 | 12.6519        | 11.4     | 12.6145          | 100   | Monoclinic.CuPc |
| NiPcTs-CdS                  | 8.9106   | 0.4190 | 9.8591         | 19.0     | 9.9161           | 002   | Monoclinic.CuPc |
| NiPcTs-CdS                  | 10.3538  | 0.3724 | 8.4792         | 21.4     | 8.5370           | 002   | Monoclinic.CuPc |
| NiPcTs-CdS                  | 12.6350  | 0.3259 | 7.2111         | 24.5     | 7.0003           | 102   | Monoclinic.CuPc |
| NiPcTs-CdS                  | 15.7076  | 0.3258 | 5.7751         | 24.6     | 5.6372           | 102   | Monoclinic.CuPc |
| NiPcTs-CdS                  | 24.1806  | 0.4190 | 3.5940         | 19.4     | 3.6777           | 100   | Hex.CdS        |
| NiPcTs-CdS                  | 26.2291  | 0.3724 | 3.3685         | 21.9     | 3.3949           | 002   | Hex.CdS        |
| NiPcTs-CdS                  | 28.6499  | 0.4656 | 3.1710         | 17.6     | 3.1133           | 101   | Hex.CdS        |
| NiPcTs-CdS                  | 43.7803  | 0.4656 | 2.0750         | 18.4     | 2.0661           | 110   | Hex.CdS        |

3.2 Atomic Force Microscope (AFM)

The AFM surface images of spin coated nanostructures NiPcTs, CdS thin films and Blend Heterojunction NiPcTs–CdS respectively are analysed and shown in Figure 2. It well defined that Topography with sample morphology obtained by AFM give good information about surface features like the root mean square surface roughness, ten point heigh, and average diameter of grain size. These images confirm that the films are homogeneous without any defects like cracks and continuous with very well assembled grains to uniformly covering all surface of the substrate with a good adherence. The surface of all samples are quite smooth and they are comprised of spherical numerous nanoparticles with diameter less than 70 nm, and one can observe that the height of each surface was in the range of (6–12) nm, which is advantage of the spin coating technique for preparation smooth surfaces. The results of AFM measurement were listed in Table (2). The root mean square of the NiPcTs, CdS films was 1.74 nm and 2.22 nm respectively and 3.6 nm for blend heterojunction (BHJ) NiPcTs–CdS. These results confirm the XRD results about the nanostructure of our samples.
Figure (2): AFM images for (a): NiPcTs thin films. (b): CdS thin films. (c): Blend heterojunction of NiPcTs - CdS.
EDS Spectrum Measurement:
A qualitative elemental analysis was carried out to investigate the chemical composition of the novel molecular materials of the nanostructure NiPcTs, CdS films and for heterojunction blend NiPcTs – CdS. For this purpose an EDS analyzer which installed with scanning electron microscope was made for 150 second and measured peaks were compared with the database to distinguish the chemical elements. Figure (3 a-c) shows EDS spectra for NiPcTs, CdS and for heterojunction blend NiPcTs – CdS respectively. As seen from this figure spectra,( a ),(b)and (c) , the existence of essential elements of thin films and HJB of NiPcTs –CdS.

3-4 Scanning Electron Microscopy (SEM)
Figure (4-a-c) represent the Scanning electron micrographs images of as-deposited NiPcTs, CdS, and for heterojunction blend NiPcTs –CdS respectively. It is seen that no particular crystal orientations in the all samples. Scanning electron micrographs of NiPcTs, CdS thin films are It can be noticed a polycrystalline structure, consist of many smaller crystallite of the size about few tens of nanometers.SEM images also indicated some uncovered parts of the substrate are evidently granular structure with low homogeneity and the distribution of the grains is not uniform. The morphology of BHJ NiPcTs –CdS is present in figure 4 (c) indicated a network of nanotube.

Table(2): AFM parameters of NiPcTs,CdS thin films and blend heterojunction(BHJ) NiPcTs -CdS.

| Samples                          | Root Mean Square (RMS) (nm) | Roughness (nm) | Ten point Height (nm) | Average diameter (nm) |
|----------------------------------|-----------------------------|----------------|-----------------------|------------------------|
| NiPcTs                           | 1.74                        | 1.51           | 6.03                  | 69.79                  |
| CdS                              | 2.22                        | 1.93           | 7.7                   | 51.99                  |
| Blend heterojunction(BHJ) NiPcTs -CdS | 3.6                      | 3.1            | 12.6                  | 68.4                   |
Figure (3): EDS Spectra of (a): NiPcTs Thin Films. (b): CdS Thin Films (c): Blend heterojunction NiPcTs - CdS.
4. Conclusions:

Thin film of NiPcTs, CdS were deposited successfully on the FTO substrates and heterojunction blend NiPcTs- CdS was fabricated using spin coating technique with 130 nm thickness. All structural measurements show that the films and blend heterojunction have polycrystalline structure and EDS analysis examine the chemical elements concentration of the initial materials. The surface morphology measurement displays that the NiPcTs, CdS and blend heterojunction NiPcTs- CdS exhibits excellent performance and the grains uniformly covering all surface of the substrate with a good adherence. SEM images show many smaller crystallite of the size about few tens of nanometers.
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