Heterojunction Solar Cell (NiPcTs/CdS) Organic /Inorganic

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Abstract

In the present study, thin films of organic semiconductors Nickel Phthalocyanine Tetrasulfonic Acid Tetrasodium Salt (NiPcTs) and inorganic semiconductor (CdS) prepared from the mixing of liquids for these two materials with different size ratios by the spin coating method on prepatterned (Fluorine-doped Tin Oxide) FTO coated glass substrates and then the manufacture of solar cells. The properties of solar cells through the study of the optical properties (absorption spectra, absorption coefficient, energy gap) and electrical characteristics included (DC. Electrical conductivity, Hall Effect and solar cell efficiency measurements). The results obtained That the efficiency of a multiple solar cell ranging from (0.16-13.2) %

Keywords: Organic, Inorganic, NiPcTs/CdS, Solar cell

1. Introduction

Over the past years decades, organic photovoltaic devices have gained a broad interest in the last few years due to their potential for large-area low-cost From the first reports on molecular thin film devices more than 30 years ago, their power conversion efficiencies is (0.001%) in 1975 to (1%) in 1986 [1] and have increased considerably more recently to (5.5%) in(2006). This was seen in Organic compound Nickel (II) phthalocyanine-tetra sulfonic acid tetrasodium salt (NiPcTs) is a conjugated molecule. The molecular formula for NiPcTs is (C₃₂H₁₂N₈Na₄NiO₁₂S₄) and has (979.4 g/mol) molecular weight, the structure of NiPcTs in where that polar (SO₃Na) is attached to the angles of benzene rings and make this compound water-soluble [2]. The molecular structure of NiPcTs which used as active material in this work is shown in Fig 1. Organic photovoltaic devices including organic solar cells, gas sensors, field-effect transistors, Organic thin film deposition techniques like roll-to-roll
processing, ink-jet printing or spin casting are widely used, due to their cost-effectiveness,[3]. CdS is an II-VI compound semiconductor and has an energy band gap of 2.42eV. CdS thin films belonging to the Chalcogenide family are used as a window material for CdS/CdTe solar cells [4]. They are also useful as buffer materials for solar cells and continue to be a subject of intense research due to their potential applications in high-efficiency solar devices. Also, CdS thin film is one of the important materials for application in electro-optic devices such as photo-conducting cells, photo-sensors, transducers, laser materials, optical waveguides, and non-linear integrated optical devices[5]. There are many methods of fabricating CdS thin films, these included spray pyrolysis, chemical bath deposition [6], molecular beam epitaxy, close space sublimation, successive ionic layer adsorption and reaction, screen printing, physical vapor deposition, and spin coating method which was used in this study. Hybrid solar cells, which combine the advantages offered[7] by both organic and inorganic materials, are also highly versatile in terms of the device structure they can adopt depending on how the photoactive layer is constructed. Two basic solar cell device architectures can be obtained, i.e. bulk heterojunction (BHJ) and bilayer heterojunction as in the (fig. 2 a). Bilayer solar cells have the merit of a more direct charge transport path way at the expense of poorer exciton dissociation as compared to their BHJ counterpart as in the (fig. 2 b) [8]. Furthermore the bilayer solar cell with its simple architecture essentially consisting of a stack of two photoactive layers, provides an inexpensive and straight forward platform for device fabrication without the necessity for extensive morphological optimization[9]. In This work synthesis and electrical properties of thin films organic (NiPcTs), inorganic (CdS) and blend BHJ (NiPcTs-CdS) and manufacturing solar cell by spin coating method (FTO/PEDOT: PSS/blend/AL) and by bilayer (FTO/NiPcTs/CdS/Al) and Sandwich (FTO/NiPcTs/CdS/FTO).

Figure 1. Types of organic materials in order of increasing complexity
2. Experimental Work

2.1. Thin films preparation

Thin films of Nickel Phthalocyanine Tetrasulfonic Acid Tetrasodium Salt (NiPcTs) were synthesized on pre-patterned (Fluorine-doped Tin Oxide) FTO coated glass substrates of thickness (3.2 mm) and (10 × 10 cm) dimensions, that were cleaned ultrasonically 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 sol-gel spin coating methods, with thickness of (200±7) nm deposited by dissolving (0.65gm) organic powder of (NiPcTs), which was provided by in (10 ml) deionized water and used without any purification, then using magnetic stirrer to mix the solutions over 30 minutes and with using a special syringe to deposited the solution on FTO glass substrate, then leave samples for 60 minutes in spin coater type [Laurell-WS-650Mz-23NPP] with speed of (1500) rpm, then drying process of the sample in (70°C) temperature. Two (Al) electrodes of 200 nm thickness were deposited through a shadow mask by using the thermal evaporation method onto the glass substrate 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 maintained at a pressure of (5× 10−5) mbar throughout the evaporating process. CdS thin films prepared by two methods:

1. CdS thin films were deposited on glass substrates by a spin coating method. Two Solutions for CdS were prepared from dissolving (1.83gm) cadmium chloride (CdCl2), placed in a glass baker with a piece of magnet bar than using magnetic stirrer to mix the solutions over 60 minutes and then using a special syringe to deposited the materials on FTO glass substrate and leave it for 10 minutes for an hour. Turning it into a transparent liquid. Then, (0.76gm) of Thiourea was dissolved in (25ml) of 2- ethanol and added drop wisely to the mixture under stirring which was continued for 5 hours. The solution was dropped onto the glass substrate about 5 and 10 cycles at speeds of (1400) rpm for 30 sec. for each cycle. After deposition, the films were dried in air at 150°C for an hour.

2. CdS thin film preparation: Two Solutions for CdS were prepared first from dissolving (2gm) polyethylene glycol in (20 ml) of ethanol in glass baker for one hour on the magnetic mixer and inside it a small magnetic piece to mix the materials well. Then adding (1.83gm) cadmium chloride (CdCl2). The second method by adding (0.65gm) cadmium acetate powder as a source of cadmium element dissolving in (2gm) polyethylene glycol in (20 ml) of ethanol in glass baker for one hour until completely dissolved. In the process, we dissolve (0.25gm) thiourea powder as a source of sulfur in (5ml) ethanol for about an hour and then mix the two solutions for 6 hours in a row and filtered then get a transparent liquid, with using a syringe especially, we draw (0.5ml) of the fluid and deposit it on the prepared substrate glass and leave it for 5 min at room temperature and then place it in the spin coating device at a speed of.
(1500 rpm) for 30 seconds, then at a temperature of (200 °C) for one hour and thus get with thickness of (130 nm).

3. Preparation of thin film for (Heterojunction structure) is done by mixing the amounts of liquids of (NiPcTs) with the (CdS) to the preparation by preparing the cadmium chloride solution once and cadmium acetate once in different volume quantities and placed on the magnetic stirrer for two consecutive hours after that a certain amount is withdrawn by a special syringe and deposition on substrate glass and (FTO) proportion and leave it for 5 minutes at the temperature of the room and then put them in spin coating and the speed (1200) for (30 Second) to ensure the distribution of liquid on all substrate and then put them at (150 °C) a temperature.

2.2. Prepare of a solar cells:

1. We lay a thin film (CdS) on the substrate (FTO), and deposition of a thin film (NiPcTs) and then we match the two substrates as in Figure 3.

![Figure 3. Sandwich solar cell FTO/CdS/NiPcTs/FTO](image)

2. Layer by Layer: By depositing a thin film (CdS) on the Substrate (FTO) and thickness (130nm) and after cool deposition deposited a thin film (NiPcTs) and thickness (150nm) and after the formation of the poles as in the Figure 4

![Figure 4. Layer by layer solar cell FTO/CdS/NiPcTs/Al](image)
3. By depositing Thin film (PEDOT: PSS) organic connector on the substrate (FTO) and after preparation deposition Thin film (Heterojunction blend) and put it at the temperature (70 °C) and then the electrodes as in Figure 5.

![Figure 5. blend Heterojunction cell FTO/ PEDOT:PSS /Al](image)

4. Results and discussion

3.1. Optical properties

The optical properties (Absorption, absorption coefficient, Transmittance spectrum, and energy gap) of the prepared (NiPcTs) and (CdS) prepared in cadmium chloride, cadmium acetate and Heterojunction Blend (NiPcTs/ CdS) were studied. The permeability has an accompanying behavior to the concept of absorptive, it is usually the opposite of the absorption behavior, and depends on the properties of the material and thickness of thin films by Spin Coating. The thickness of the thin film was (200-150 nm) on the (FTO) substrate. Figure 6(a) represents the permeability spectrum of cadmium sulfide packaged from cadmium chloride and cadmium acetate, the highest permeability of cadmium chloride solution was equal (77%). Figure 6b, which represents the Transmittance of the thin film (NiPcTs), the precipitation on the floor of the glass and the thickness (200 nm). It is noted from the figure that the transmittance spectrum has two growing regions, the first two areas of permeability at wavelength (525 nm) Where it starts with a gradual increase at wavelength (300 nm) to wavelength (525 nm) where the transmittance is 50% and then starts gradually increasing until the transmitting (65%) of the wavelengths (640-1100nm) and the gradual reduction to the lowest spectrum at wavelengths (530-640nm). However, the permeability spectrum of the first junction is higher than that of the second junction (10%) figure 6(c).
Absorption depends on the energy of the photons that fall on the semiconductor material, the surface roughness, the type of material and the nature of its crystalline structure. The spectrum of thin films (NiPcTs, CdS, HJB (CdS / NiPcTs)) was calculated for wavelengths (300-1100 nm) within the visible region (UV-Vis). Figure 7 shows the Film absorbance spectra (NiPcTs) prepared by spin coating method and thickness (200nm) as a function of wavelength. As shown by the absorptive form it increases sharply and rapidly until its peak (550 nm). The appearance of two spectrum peaks at wavelengths (325, 625 nm) which range back to the range (Q, B) respectively and the same behavior as for the cadmium sulfide samples as seen in Figure (6b), where the absorbance spectra, are decreasing significantly by increasing wavelengths, particularly from cadmium chloride solution and cadmium cells for wavelengths (800-1100nm), This is due to the density of the local levels formed by the atoms of the material in the similar material between the parity and conductivity packages.

The absorption coefficient (α) for all films prepared from the thin film adsorption spectrum (NiPcTs, CdS, Heterojunction Blend) was calculated according to the equation:

\[ \alpha = \frac{1}{d} \ln \left( \frac{1}{T} \right) \quad \text{[8]} \]

Where is the film thickness. All thin films have a coefficient of absorption ranging from 4- (6x10^5) and thickness (200,130,200nm), respectively. This means that it has a direct energy
gap and the value of ($\alpha$) for CdS prepared by cadmium acetate solution ($4.5 \times 10^5 \text{ cm}^{-1}$) and Blend sample (CdS) ($35 \times 10^4 \text{ cm}^{-1}$). The blend prepared by the cadmium acetate solution has an absorption coefficient ($55 \times 10^5 \text{ cm}^{-1}$) and the sample (NiPcTs) has an absorption coefficient ($57 \times 10^5 \text{ cm}^{-1}$). All calculated were within the Visible region. The relationship between the absorption coefficient ($\alpha$) and the wavelength of the falling photon ($\lambda$) of the prepared membranes was plotted as shown in Figure 8.

The energy gap for NiPcTs, CdS, Blend was calculated by plotting the relation between ($\alpha hv$)$^2$ as a function of the photon and the ($hv$) observed in Figure 9. The photon energies (the range of the visible ray area) are linear, indicating that the energy gap is a direct energy gap and that the nature of transitions is transient Direct. In order to determine the optical energy gap ($E_g$) from the optical absorption spectra, measured around the absorption edge, we have used Tauc equation [9]

$$\frac{(\alpha hv)^n}{hv} = B (hv-E_g) \ldots ..(2)$$

where $B$ is a parameter depending on the transition probability and $n$ is a number characterizing the transition process.
Figure 7. Absorption (a) NiPcTs (b) CdS (C) HJB (CdS-NiPcTs)
Figure 8. Absorption coefficient for all prepared films

The energy gap for NiPcTs, CdS, Blend was calculated by plotting the relation between \((\alpha h\nu)^2\) as a function of the photon and the \((h\nu)\) observed in Figure 9. The photon energies (the range of the visible ray area) are linear, indicating that the energy gap is direct and that the nature of transitions is transient Direct. To determine the optical energy gap \((E_g)\) from the optical absorption spectra, measured around the absorption edge, we have used Tauc equation [9] in Figure 9:

\[
(\alpha h\nu)^{1/n} = B(h\nu - E_g)
\]

where \(B\) is a parameter depending on the transition probability and \(n\) is a number characterizing the transition process.
Figure 9. Energy gap (a) NiPcTs (b) CdS From CdCl2.sol (c) CdS From CdcooH3.sol (d) HJB 1 (e) HJB 2

Table 1. Energy gaps for preoared thin films and BHJ.

| Samples of thin films | Energy gap (eV) |
|-----------------------|-----------------|
| NiPcTs                | 3.1             |
| CdS (1)               | 3.4             |
| CdS(2)                | 3.2             |
| Heterojunction (Blend)1 | 3.2            |
| Heterojunction (Blend)2 | 3.2            |

3.2 Electrical Properties:

The conductivity of all thin film prepared by spin coating (NiPcTs, CdS, HJB (CdS / NiPcTs)) was calculated by measuring electrical resistance (R) as a function of temperature change within the thermal range (30-150°C) and from the creation of resistivity values (ρ). Then find...
the electrical conductivity of those inverted values, Drawing the natural logarithm of the latter as a function of the inverse absolute temperature (1000 / T) figure 10. The resulting graph after being hit by Boltzmann's constant, The values of activation energies are obtained from the electrical conductivity of thin films (NiPcTs), CdS, and hybrid (CdS / NiPcTs) (HJB). The presence of two bending regions in the curved decree for each sample which indicates two energizing mechanisms, one at low temperatures (30-90 C)) and the other at high temperatures (90-150 C) and for all samples prepared as shown in table 2.

![Figure 10](image)

**Figure 10**. Continuous conductivity to thin film

| Samples               | E$_{a1}$(eV) | Tem.Range (K) | E$_{a2}$(eV) | Temp. Ranage(K) |
|-----------------------|--------------|---------------|--------------|-----------------|
| CdS 1                 | 0.051        | 293-343       | 0.180        | 243-423         |
| CdS 2                 | 0.075        | 293-343       | 0.166        | 243-423         |
| Blend Heterojunction  | 0.091        | 293-343       | 0.162        | 243-423         |
| Blend Heterojunction  | 0.155        | 293-343       | 0.191        | 243-423         |
| NiPcTs                | 0.100        | 293-343       | 0.158        | 243-423         |

Hall effect measurements were made to determine the concentration of the major load carriers, the electrical conductivity and the electrical conductivity values of the thin films prepared (NiPcTs, CdS, HJB) on a glass substrate. Table 3 shows that the concentration of charge carriers of the organic thin film (NiPcTs) is lower than that of the inorganic semiconductor thin film. As for the concentration of the HJB charge carriers and the cadmium sulfide sample of both solvents (cadmium chloride and cadmium coke), we note a difference in the concentration of the carriers of both types due to the different solutions of the
crystalline structure in both cases. As for the dynamics, we observe that the organic values of the organic substances are represented in a sample of NiPcTs of the same rank (102) but slightly higher than the inorganic sample, HJB and recorded from the cadmium sulfide membrane produced from cadmium chloride solution are higher than those of the recorded hybrid junction of the cadmium sulfide sample produced from the cadmium acetate solution. Due to the difference in the crystalline structure of the two decomposers. The low values of the motility are obtained from the process of clarification by the granules.

Table 3. Measurements of Hall Effect

| Samples                   | n*10^{13} cm^3 | \(\mu_H*10^2\) (m^2/V.s) | \(\rho*10^2\) (\(\Omega.cm\)) | \(\sigma*10^{-3}\) (\(\Omega.cm^{-1}\)) | \(R_H*10^6\) (cm^2/c) |
|---------------------------|-----------------|---------------------------|-------------------------------|----------------------------------------|--------------------------|
| NiPcTs                    | 0.19            | 4.545                     | 0.722                         | 0.1383                                 | 3.285                    |
| CdS from CdCl_2 Sol.      | -1.448          | 2.696                     | 0.1599                        | 0.6253                                 | -0.4311                  |
| CdS from CdCOOH_3 Sol.    | -8.827          | 2.029                     | 0.3485                        | 0.2869                                 | -0.7707                  |
| BHJ CdS/ NiPcTs CdCl_2 Sol.| -2.425         | 9.640                     | 2.671                         | 3.744                                  | -0.2575                  |
| BHJ CdS/ NiPcTs CdCOOH_3 Sol.| -2.393      | 2.699                     | 9.670                         | 1.034                                  | -20.08                   |

3.3 Current-Voltage measurements of solar cells

Figures 11, 12 shows Current-Voltage measurements of solar cells were prepared from the cadmium chloride solution and cadmium acetate solution follows:

1 – FTO/PEDOT: PSS/HJB/Al 2-FTO/CdS/NiPcTs/Al 3-FTO/CdS/NiPcTs/FTO

Shows that The best efficiency of the models is FTO/PEDOT: PSS/Blendl/Al equal to (13.24%) as shown in Figure 11. Table (4) represents the efficiency values of the prepared solar cells. It is clear from the table that the highest efficiency value was for the hybrid junction (FTO / PEDOT: PSS / blendl / Al of 13.2%). The high value of this value is due to the presence of the polymeric material (PEDOT: PSS) and the high conductivity of the blend of CdS / NiPcTs and the formation of a group of excitons as a result, which becomes an electron-gap as an active substance. The lowest efficiency was for hybrid (FTO / CdS / NiPcTs / FTO (0.16%) and prepared by the cadmium sulfide sample produced by the cadmium acetate solution. This is due to the method of manufacturing the hybrid divider.
where the two-layer method (Sandwich) was used in the preparation method. The characteristics of current-voltage under dark and light conditions were measured by the solar cell efficiency measurement system (C100AAA). Cell efficiency is obtained by:

\[
F.F = \frac{J_m V_m}{V_{oc}/I_{sc}} \ldots .(4)
\]

\[
\eta = \frac{P_m}{P_{in}} = \frac{V_{oc}I_{sc}F.F}{P_{in}A} \ldots \ldots (5)
\]

$I_{sc}$: Short-circuit current: Current value when $V = 0$, $V_{oc}$: Open-circuit voltage :Voltage value when $I = 0$, $P$: Power output of the cell $P = IV$, $F.F$: Fill factor. Table (4) represents the efficiency values of the prepared solar cells.

Table (4) represents the efficiency values of the prepared solar cells

| Samples                                      | F.F   | $I_m$ | $V_m$ | $P_m$ | $I_{sc}$ | $V_{oc}$ | $\eta$ |
|----------------------------------------------|-------|-------|-------|-------|----------|----------|--------|
| FTO/BEDOT:PSS Blend1 (CdCl2 Sol.)            | 0.401 | 292.85| 452.1 | 132.39| 557.97   | 591      | 13.2   |
| FTO/CdS/NiPcTs CdS (CdCl2 Sol.)              | 0.349 | 216.02| 442.1 | 95.51 | 463.3    | 591      | 9.5    |
| FTO/CdS/NiPcTs/ FTO CdS (CdCl2 Sol.)         | 0.24  | 51.464| 297.5 | 15.31 | 139.20   | 515.0    | 1.53   |
| FTO/BEDOT: PSS Blend2 from (CdCOOH$_3$ Sol.)| 0.4   | 252.28| 424.9 | 107.18| 448.8    | 594.7    | 10.7   |
| FTO/CdS/NiPcTs/Al CdS from (CdCOOH$_3$ Sol.)| 0.3   | 245.92| 352.7 | 86.74 | 421.38   | 591.1    | 8.67   |
| FTO/CdS/NiPcTs/ FTO CdS from (CdCOOH$_3$ Sol.)| 0.45  | 11.05 | 205.8 | 2.28  | 13.44    | 377      | 0.16   |
Figure 11. The efficiency of the prepared solar cells in which the CDS is a product of cadmium chloride solution (a) FTO / PEDOT: PSS / Blend / AL (b) FTO / CdS / NiPcTs / Al (c) FTO / CdS / NiPcTs / FTO
Figure 12. The efficiency of the prepared solar cells in which the CdS is a product of cadmium acetate solution (a) FTO / PEDOT: PSS / Blend / Al (b) FTO / CdS / NiPcTs / Al (c) FTO / CdS / NiPcTs / FTO
4. Conclusions

Organic NiPcTs and inorganic CdS semiconductors have been mixed because of their good price, low conductivity, and easy deposition by a very simple Spin Coating technology to manufacture highly efficient solar cells and The best efficiency was for hetrojunction (FTO/PEDOT:PSS/HJB).

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