Fabrication and Characterization of polyaniline /CdSe Device for Applications in Nano Structured Solar Cells

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Abstract. Organic/inorganic heterojunction solar cells have been fabricated based on CdSe/PVA nanocomposite as an acceptor and PANI-DBSA/PS nanofibers as a donor material. CdSe/PVA nanocomposite PANI-DBSA/PS nanofiber materials have been prepared by chemical and electrospinning methods, respectively. X-ray diffraction, Atomic Force microscopy and scanning electron microscopy measurements technique reveals that the two nanomaterials have deferent morphology with the crystalline cubic structure of CdSe/PVA nanocomposite and amorphous phase of PANI-DBSA/PS nanofibers. The absorption spectra of PANI-DBSA/PS and CdSe/PVA nanocomposite thin films were analyzed in the wavelength range from 400 nm to 800 nm. the current-voltage density measurements of the solar cell which were performed in the dark and under illumination are reveal that the ideality factor of all the devices is more than one and the maximum power conversion efficiency is 0.3%. The effects of temperature on the photovoltaic properties of solar cells have been investigated. The power conversion efficiency values increased with increasing temperature.

KEYWORDS: nanocomposite, electrospinning, polyaniline, CdSe, heterojunction solar cells.

1. Introduction

Cadmium selenide is one of the important compounds belonging to the binary compounds resulting from the synthesis of the II-VI groups. CdSe has n-type semi-conductive properties, has a direct and gap of about 1.74 eV so it is transparent at the infrared spectrum. As it is known, CdSe is present in three crystalline structures, one in the form of wurtzite (Hexagonal) and the other in the form of sphalerite Cubic type (Zinc-Blende)), and the third form is a mixture of the two crystalline phases. CdSe is involved in the structure of many optical-electronic devices[1], as well as in the installation of high-efficiency solar cells. [2] and in biomedical applications. [3]. Among the particle size affected properties are the fluorescent property which is important in optical devices applications such as semiconductor lasers [2], It is possible to obtain lasers covering a large part of the electromagnetic spectrum [4]There are many ways to prepare the CdSe compound, with nanoscale dimensions, including Dry gas-phase methods such as vacuum evaporation and chemical vapor deposition second:
Wet methods such as liquid phase deposition, chemical bath deposition technique (CBD) and electrochemical deposition. [5]. Polyaniline (PANI) is one of the conducting polymers which is attracting much attention in an electronic and optoelectronic application such as sensors, organic solar cells, transistors and Schottky diode due to its high electrical conductivity, low cost and easy polymerization[6]. Also, various PANI blends can be used to modify the characteristics of these devices. Polymeric blends are the combination of two or more types of polymers mixing physically or chemically. The purpose of blending polymers is to obtain new products with unique properties that combine the qualities of polymers used in the assembly of polymeric blends that increase their engineering applications and provide the desired desiccant at a lower cost[7]. Blending technology also provides significant opportunities for recycling and the use of polymeric waste.

Nanotechnology research has grown very rapidly over the last decade and has received considerable scientific interest in many fields of applications such as electronics, optics, aerospace, materials science and pharmaceuticals. The nanoscale size, materials acquire unique properties that are not available when they are in the sensible size, ie, nanomaterials acquire different electrical, optical and magnetic properties and properties. Due to the nanoscale nature of light absorption and photocurrent generation in solar energy conversion, the advent of methods for controlling materials on the nanometer scale opens new opportunities for the development of future generation solar cells. Therefore, we have used semiconductor nanoparticle as the inorganic phase in the construction of this solar cell.

In our research, we constructed a solar cell consisting of a nanometric CdSe-PVA compound as a n-type semiconductor and (PANI-DBSA / PS) polymer prepared by electrospinning method as a p-type semiconductor. Also, the structural, optical and electrical properties of a compound have been studied.

2. Experimental

2.1. MATERIALS

Cadmium acetate Cd (CH₃COO)₂ from Quoligeh, Sodium Selenite (Na₂SO₃) Merk company, Se from Loba Chime and PVA-polyvinyl Alcohol from Himedia. Polystyrene polymer of molecular weight (Mw=88,500) used in the current study has purchased from Aldrich. Aniline (99.0%) is purchased from fisher scientific. Ammonium Persulfate (NH₄)₂S₂O₈ (98.0%), Dodecyl Benzene Sulfonic Acid (DBSA) and HCl purchase from Fluke. All the chemicals used are of AR grade and are used as purchased without further purification.

2.2. Syntheses of materials

CdSe-PVA nanoparticles were synthesized by chemical methods. Sodium Selenosulphate (Na₂SeSO₃) Solution was prepared by dissolving 0.05mol of Se powder into 0.5M aqueous sodium sulfite solution (Na₂SO₃) and refluxing the mixture at 70℃ for 3 hours under constant stirring. Upon filtration, dissolved6gm from PVA in 100 ml water and resolve 0.75gm in 20ml of deionized water from cadmium acetate after that mix 20ml PVA solution with 16ml Cd solution and adding 2ml from (Na₂SeSO₃) After setting the pH at 10. The mixture was stirred for7h to obtain a red transparent solution. Cd (CH₃COO)₂ and (Na₂SeSO₃) were chosen as the sources of Cd²⁺ ion and Se²⁻ ion respectively. Polyvinyl alcohol used to a stabilizer, in addition, a host polymer matrix in the reaction medium. To prepared thin films, the solution was cast on a glass substrate and leave to dry.

The PANI-DBSA/PS nanofibers were synthesized as has been reported by our paper[8]. Polyaniline PANI doped with DBSA was synthesized by the oxidative polymerization of aniline in acidic media.
To prepare the Polyaniline/polystyrene blend, we dissolved PANI-DBSA and Polystyrene (PS) polymers powders with proper weights in chloroform. The PANI-DBSA/PS solution was used to prepare thin film samples by the electrospinning method.

Wide-angle X-ray diffraction (X’ Pert Pro MPD- Philips) an atomic force microscope (Angstrom Advanced Inc) was carried out to Characterized of thin films. Absorption spectra of the thin films on the glass substrate have been measured by a UV/VIS/NIR computer-controlled spectrophotometer Perkin Elmer LAMBDA 750 in the range 300–900 nm at room temperature.

2.3. Device fabrication and characterization

To prepare (PANI: DBSA- PS / CdSe) solar cell, the polymer nanofibers were deposited by the electrospinning method on the ITO glass substrate. The CdSe solution is then casting on the polymer film and then left to dry. Aluminum mesh has been deposited by the evaporation unit on CdSe thin film. The I–V measurements on the solar cell have been taken with Keithley 2400A electrometer.

3. Results and discussion

3.1. Characterization of CdSe/PVA nanocomposite

Figure 1 shows the XRD pattern of CdSe/PVA nanocomposite thin film. The reflection peak at 2θ = 25.4°, 42.3° and 49.9°, were corresponding to (111), (220) and (311) planes, respectively, of cubic CdSe [9]. Also, there are two intensity peaks at 2θ = 31.51° and 37.7° corresponding to the (103),(102) planes of hexagonal CdSe.[10] The peak at 2θ =19.4°match to the PVA partial crystalline phase[11]. The crystalline nature of PVA results from the strong intermolecular interaction between PVA through intermolecular hydrogen bonding[12] [11] The size of the Nano crystallites was evaluated using the Debye-Scherrer formula

\[ D = \frac{0.94\lambda}{\beta \cos \theta} \]  

where β is the full-widths-at-half maximum (FWHM) of the diffraction peak, λ (1.5418 Å) is the wavelength of X-ray radiation, and θ is the angle of diffraction. PVA is acting as a capping agent, smaller CdSe particles of an average size of 17 nm.[13][14]
Fig. 2 shows the UV–visible absorption spectra of CdSe/PVA nanocomposite thin film at room temperature. The spectrum shows a blue shift as compared to bulk sample[15] which is indicative of a quantum confinement effect [14][16] in CdSe nanoparticles which the electrons, holes, and excitons have limited space to move and their motion is possible for definite values of energies. The calculated energy gap from the Tauc plot[17], as shown as an inset in fig.2, was 2 eV. The blue shift of bandgap from standard bulk bandgap energy (Eg = 1.7 eV) confirms the nanostructure of the prepared thin films, which has been shown in the X-ray measurement.

Fig. 2. Absorption spectra of CdSe/PVA nanocomposite thin film at room temperature. Inset shows the (ahv)² vs. hv for CdSe/PVA nanocomposite thin film.

Fig. 3 shows AFM images of the films at room temperatures. the surface morphology was characterized by small surface roughness with symmetric crack-free, densely packed microstructure and the spherical nanoparticles are distributed regularly on the films. The surface roughness average (RMS) and roughness average values of the film are calculated by using the equipment’s software routine and is equal to 0.311nm and, respectively.

Fig. 3. AFM images of CdSe/PVA nanocomposite thin film

(I-V) characterizations at room temperature of samples, as shown in Fig. 4a, are displayed ohmic behavior in all voltage values. The amount of electrical conductivity that has been calculated from the
line slope is equal to $1.5 \times 10^{-5}$ S/cm. The activation energy is calculated according to the Arrhenius model\[20\]

$$\sigma = \sigma_0 e^{\frac{E_a}{k_B T}} \quad (2)$$

Where $\sigma$ is the electrical conductivity at temperature $T$, $\sigma_0$ is the pre-exponential factor, $k$ is the Boltzmann constant and $E_a$ is the activation energy it was equal (0.702 eV). As shown in Fig.4b, the plot of $\ln (\sigma / \sigma_0)$ versus $1000/T$ is a straight line, indicating that the conductivity increases with increasing temperature and this is confirming the semiconducting behavior\[21\].

![Fig. 4. (a) I-V characteristic and (b) variation of $\ln \sigma$ vs. 1000/T of CdSe/PVA nanocomposite thin film.](image)

**3.2. Characterization of PANI-DBSA/PS nanofibers**

SEM and X-ray diffraction measurements of the prepared PANI-DBSA/PS thin film show that it has alignment nanofibers with semi-crystalline structure \[8\]. The thin film topography is characterized by an Atomic force microscope (AFM) which shown in Fig.5. The AFM result confirms the nanofibrous alignments of thin film which has been shown by SEM measurement. The RMS roughness and roughness average value of the sample is 0.634 nm and 0.494 nm, respectively.

![Fig.5: AFM images to PANI-DBSA/PS.](image)
UV–visible absorption spectra of PAni-DBSA/PS NFs polyblend polymer are shown in fig.6. The shoulder in the range of 300–600 nm is due to the association interaction between the neighboring phenyl groups in PS. The flexibility of the PS chains allows free rotation of two phenyl groups about the carbon-carbon bond. The UV exposed sample exhibits an increase of absorbance over the 380-420nm range, which indicates the absorbing photoproduct conjugated double bond is present in PS. Due to the UV absorption of PANI, the absorption of PS/PANI composite film is increased. This may be due to the fact that minute dispersion of PANI in the PS film may produce some photogenerated electrons and holes under UV light illumination[22]. The calculated energy gap from the Tauc plot [17], as shown as an inset in Fig.7, is found equal to 2.93eV.

Fig.6. Absorption spectra of PAni: DBSA/PS NFs at room temperature. Inset shows the $(\alpha h\nu)^2$ vs. h\nu for PAni: DBSA/PS NFs.

### 3.3. I-V characteristics of solar cell

Using the (PANI-DBSA/PS) nanofibers as P-Type and CdSe/PVA as n-type to applied in the solar cell. Measurement (I-V) characteristics in dark at room temperature shown in Fig.7. At Forwarding bias, the current passes unless outdo the junction voltage 0.1V. The current increases by the increasing voltage which is the result of majority carriers charge, electrons in CdSe. In the reverse bias, the current is small and produced by the minority carriers charge. The dark current density is given by

$$J = J_S \left( e^{qV/n^*kT} - 1 \right)$$  \hspace{1cm} (3)

where $J_S$ is the (reverse bias) saturation current density, $V$ the applied voltage, $q$ the elementary charge, $k$ Boltzmann’s constant, $T$ temperature, and $n$ the ideality factor.

The ideality factor and the reverse saturation current density have been determined from the J-V characteristic. A plot of ln(J) Vs. $V$ is needed in order to estimate $n$ and $J_o$. The natural logarithm of the diode equation is:

$$\ln(J) \equiv \ln(J_S) + \left[ \frac{qV}{n^*kT} \right]$$  \hspace{1cm} (4)

This represents the equation of a straight line, with $q/nkT$ as its slope and $(V, \ln(J))$ as the variables. Inset of Fig. 7 shows the relation between Ln(J) and V to P-N junction. Once the slope of the curve is known, the ideality factor can be easily computed, as the values of $q$, $k$ and $T$ are known already. The y-intercept of the line would give the value of ln($J_S$), from which the reverse saturation current density can be calculated. In the case of practical diodes, the value of $n$ deviates from 1 due to various reasons.
such as generation-recombination processes in the depletion region, high-injection conditions and tunneling of carriers between states in the bandgap. The reverse saturation current density ($I_s$) and ideality factor ($n$) are found to be $3.1 \times 10^{-6}$ mA/cm$^2$ and 2.8 at 300K, respectively.

Fig.7. The (I-V) characteristics and ln($I$) vs $V$ of P-N junction in dark at room temperature.

Fig.8. Current-voltage (I-V) characteristic of the (ITO/ (PANI: DBSA/PS/CdSe-PVA) /Al) at room temperature in light. The open-circuit voltage (VOC), short circuit current density (Jsc), fill factor (FF), and efficiency ($\eta$) of the solar cell are calculated and shown in Table 1.

Table1. Photovoltaic parameters for the solar cell under illumination intensity.

| (ITO/ (PANI: DBSA/PS) NPs/CdSe/Al) | $V_{oc}$ (V) | $J_{sc}$ (mA/cm$^2$) | $V_{max}$ (V) | $J_{max}$ (mA/cm$^2$) | F.F | $\eta$ | $R_{sh}$ (Ohm) | $R_{s}$ (Ohm) |
|-----------------------------------|--------------|------------------|--------------|-----------------|-----|------|-------------|-------------|
|                                   | 0.425        | 0.72             | 0.229        | 0.44            | 33  | 0.0034 | 33818       | 13254       |
4. Conclusions

CdSe nanoparticles capped in the PVA polymer have been prepared at room temperature. The diffraction pattern of the thin film showed that it has two crystalline structures, cube and hexagonal. The prepared CdSe thin films show high energy gap value in comparison to bulk which can be due to the quantum confinement effect. Solar cells have been successfully manufactured from the prepared PANI: DBSA/PS nanofibers and CdSe/PVA nanocomposite material. The different parameters like open-circuit voltage (Voc), short circuit current density (Jsc), fill factor (FF) and efficiency (η) has been calculated from I-V characteristics of organic/inorganic solar cell at room temperatures.

Acknowledgments

This work is financially supported by the University of Basrah. Mrs. Dalal M. Alhilfi is thankful to Basrah University, Iraq for providing the fellowship.

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