Conducting Polymer/CdSe Hybrid as Bulk Heterojunction Solar Cell

Kahtan A. Mohammed[a,*], Kareema M. Ziadan[b], Alaa S. AL-Kabbi[b], Rahman S. Zbibah[c] and Ali J. Alrubaie[d]

[a] *Department of medical Physics, Hilla University College, 51001, Babylon, Iraq*
[b] *Department of Physics, College of Science, Basrah University, 61007, Basrah, Iraq*
[c] *Medical Laboratory Technology Department, College of Medical Technology, The Islamic University, 54001, Najaf, Iraq*
[d] *Research and Studies Unit, Al-Mustaqbal University College, 51001, Hillah, Babil, Iraq*

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Doi: 10.12693/APhysPolA.141.198 *e-mail: qahtan_adnan@hilla-unc.edu.iq

We report a hybrid system based on conducting polymer-semiconductor from poly(o-toluidine) doped with camphor sulfonic acid and cadmium selenide CdSe capped with trisodium citrate by physical mixing method. The influence of CdSe nanoparticles weight percent on the electrical properties of hybrid thin films have been investigated. The conductivity of the hybrid films increases with increasing CdSe content, and then decreases with excess CdSe content. This work introduces a novel bulk heterojunction solar cell from the poly(o-toluidine)/camphor sulfonic acid hybrid nanocomposite material and provides useful evidence apropos the optimum use of CdSe nanoparticles in conductive polymer-based optoelectronics.

topics: bulk heterojunction, semiconductor, conducting polymer

1. Introduction

Advances in many fields of applied science and modern technology demand us to develop new materials to keep up with this growing technological evolution. We need to manufacture and develop inexpensive, flexible and easy-to-handle materials. These materials are hybrid materials. The term "hybrid" refers to the connotation of at least two components that are completely diverse to their chemical nature and, at the molecular level, either by simple blending or by bonding the constituents together through specific bonds [1]. Hybrid nanocomposite materials joint the benefits of the two phases, as the spreading of the second phase in the matrix of the first phase and the interfaces can affect the properties of the materials [2]. The most important of these hybrids are organic–inorganic hybrid nanomaterials. The organic–inorganic hybrid nanomaterials have received abundant attention to their unusual performance because of the amalgamation of the beneficial properties of the polymer and the size reliant properties of the nanostructure. Interactions among the polymers medium and the nanocrystalline additives produce magnificent structures, in which the constituents have good mechanical, electrical, thermal, magnetic, and optical properties [3].

Recently, more and more attention has been given to conductive polymer–inorganic nanocomposites with distinct combinations of two parts, because they have interesting physical properties and many possible applications in distinct fields [4]. Among these polymers, poly(o-toluidine) (POT) is important for its properties. Poly(o-toluidine) (POT) is a derivative of polyaniline that contains methyl group in its ortho position of the aniline monomer. POT was likely the most commonly studied among the ring-substituted PANI derivatives because it is one of the promising polymers used in various areas of applications such as light emitted diode, field-effect transistor, Schottky diode, solar cell and sensors [5–11].

One of the most important goals today is to produce affordable and sustainable renewable energy sources in order to achieve a world that is energy meaningful [12]. Solar energy and the solar cell are the most important sustainable renewable sources. Third-generation solar cells such as conducting polymers cells, quantum dot (QD) solar cells, dye-sensitized solar cells and perovskite cells have received significant interest in the last few periods owing to their benefits like mechanical flexibility and low cost in constructing large-area cells from the solution phase [13]. While the fullerene derivatives in these solar cells were replaced by semiconductor nanostructures, the greatest interest was in their extraordinary qualities, including variable band gap, low specific weight, wide spectrum range absorption and high photostability [14]. Cadmium selenide (CdSe) nanostructures in combination with different conducting polymer matrices is one of the most studied bulk heterojunction (BHJ) systems by several research groups [15–18].

The important question which we are attempting to address in this paper is whether the integration of CdSe nanoparticles into the polymer matrix causes any noticeable enhancement of its properties and we test the results materials as a bulk heterojunction solar cell application.

2. Experimental work

2.1. Materials preparation

CdSe nanoparticles (NPs) have been synthesized using trisodium citrate (TSC) as a capping agent using a green chemical route by eluding the toxic capping agents. The detailed experimental process and results were reported elsewhere [19]. Except that the final synthesized product was centrifuged at 3000 rpm for 10 min and washed two times (5 min) in ethanol and two times with acetone, then one time with distilled water.

POT–camphor sulfonic acid (CSA) has been synthesized by chemical polymerization according to our paper [20]. POT/CdSe hybrid material was prepared by the dispersions of TSC capped CdSe NPs in POT–CSA polymer. The POT–CSA mixed with different loading of CdSe–TSC NPs (H1 25%, H2 50%, H3 75%) and milled by a mortar. Mixing was dissolved in formic acid solution. The mixing was kept on a magnetic stirrer for 10 h until the solvent evaporated. Again, the powder was milled by a mortar and re-dispersed in 10 ml formic acid. Moreover, drop-cast onto a 2×2 cm^2 glass substrate that was pre-cleaned sequentially by ultrasonication in acetone, methanol, and deionized water. The drop-cast solution was rapidly dried in a vacuum oven at room temperature to form a uniform POT/CdSe hybrid film; the film thickness was 1000 nm as measured by FESEM as a cross-section. The POT–CSA film without CdSe was also prepared in the same technique. Details of the hybrid samples used in different studies are shown in Table I.

2.2. Solar cell fabrication

FTO-coated glass substrates were washed serially with soap water, deionized water, and ethanol under an ultrasonic bath for 10 min. The substrates were then dried in an oven, after which a dense TiO_2 film was deposited on top by doctor blade method then annealed at 460°C for 70 min. POT/CdSe hybrid solutions were dropped cast on the ITO/TiO_2 substrates. The PEDOT/PSS layer was spin-coated at 3000 rpm on the substrate and then heated at 85°C for 20 min. The upper electrode was formed by thermally evaporating aluminium under a high vacuum. The current–voltage (I–V) characteristics of the solar cells have been recorded using a Keithley electrometer (2400) at room temperature with a light source simulated to a solar light-producing intensity equal to 100 m W/cm^2.

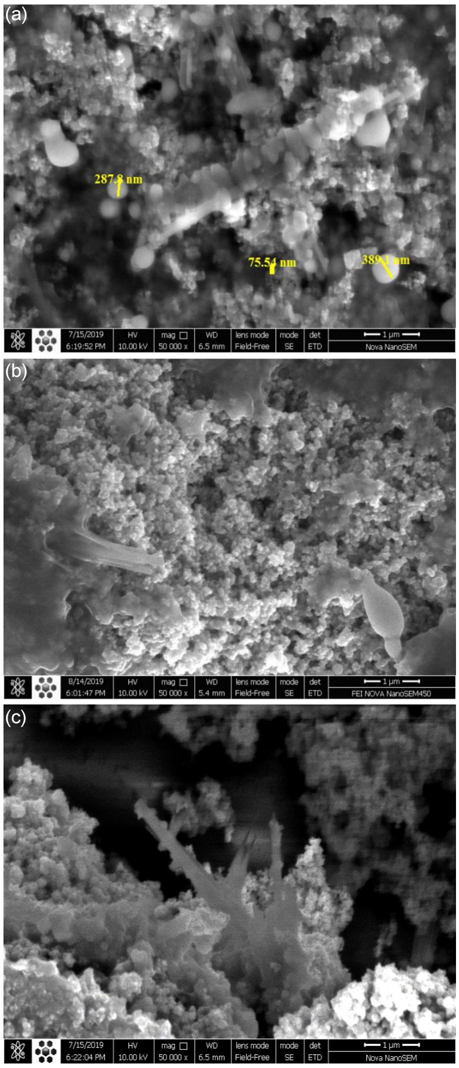

Fig. 1. FESEM images of hybrid films (a) H1 (25% CdSe), (b) H2 (50% CdSe) and (c) H3 (75% CdSe).

TABLE I

Hybrid thin film details.

Compositions	Sample name	Weight ratio
POT/CdSe	H1	75:25
POT/CdSe	H2	50:50
POT/CdSe	H3	75:25

3. Result and discussion

The morphology of the prepared hybrid films was illustrated by FESEM. The FESEM photograph of POT/CdSe hybrid films is shown in Fig. 1. As can be seen, the nanoparticles diffuse homogeneously

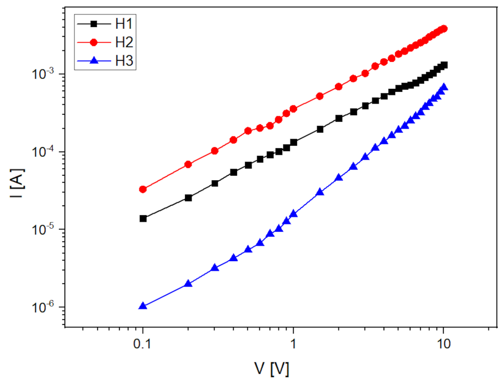

Fig. 2. Current–voltage characteristic of hybrid films.

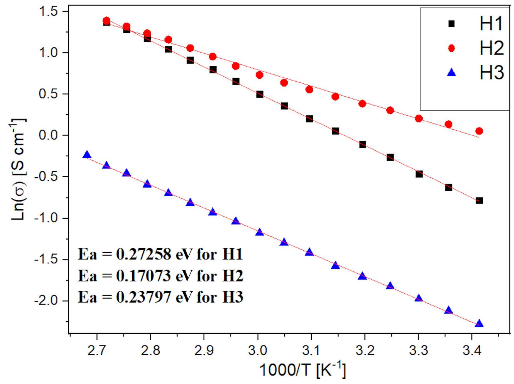

Fig. 4. The Arrhenius plot of DC conductivity vs temperature for hybrid thin films.

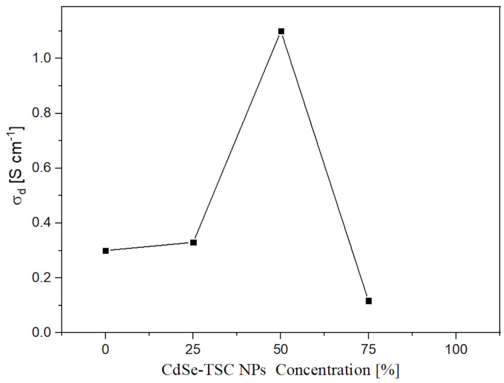

Fig. 3. The conductivity of hybrid films with different weight percentage of CdSe.

in hybrid films of low concentrations H1 and H2 with the preference homogeneity of the membrane of H2. The interface between the POT and CdSe nanoparticles is sufficiently attractive to prevent of microphase separation between them.

Figure 2 displays the alternation of I–V characteristics of POT with different amount of CdSe nanoparticles tested at room temperature. We observe that the I–V curves are linear for all samples as shown in Fig. 2. The conductivity σ values are calculated from the current I via

$$\sigma = \frac{s\,I}{d\,l\,V}, \tag{1}$$

where s is the width between the electrodes, V is the applied voltage between the electrodes, d is the thickness of the sample, and l is the length of electrode.

Figure 3 illustrate the relationship between the amount of CdSe Nanocrystals (NCs) (25, 50 and 75 wt%) and the conductivity of hybrid films. The conductivity of the hybrid films increases with increasing CdSe content, and then decreases with excess CdSe content. The adding of CdSe might encourage the creation of a more effective network for charge transport in the POT matrix, resulting in higher conductivities [21].

CdSe nanoparticles perform as electrons acceptors and electrons can simply pass through the POT due to the creation of the band cascade rising the overall material's conductivity, which provides an indication of charge transfer complex (CTC) formation [22]. It is identified that the electrical conductivity of the hybrid material depends on two factors, one is the interfacial polarization between the NPs and polymer chain and the other is the uniform dispersion of inorganic nanoparticles [23]. The interfacial contacts would upsurge the nanoparticles orientation within the POT and, in this manner, the quality of the electrical network formation will improve. It only means that the interfacial interaction is better at H2 thin film where the conductivity reaches an optimum value. This result is consistent with the SEM micrograph where the distribution of (50%) H2 nanoparticles is more uniform than that of other weight ratios [22].

The decrease in conductivity for a high percent of CdSe in the hybrid film H3 could be due to the aggregation of CdSe nanoparticles, which can interrupt the ordering of POT chains and increase of the film resistance [24]. It turns out that the presence of CdSe aggregates not only disrupts the crystallization of POT, and hence the mobility of holes is reduced, but also decreases the surface area of nanocrystals, decreasing the efficiency of exciton dissociation [25].

The dependence of dark electrical conductivity (σ_d) of thin layers as a function of temperature is shown in Fig. 4 for a measurement at 5 V. The conductivity increased with increasing temperature, which is a characteristic semiconductors behavior [26]. All hybrid films followed the model of Arrhenius which can be described by the relation [27]

$$\sigma_d = \sigma_0 \, \mathrm{e}^{-\Delta E_a/(k_B T)}, \tag{2}$$

where E_a is the activation energy, σ_0 is the pre exponential factor, k_B is Boltzmann constant and T is temperature. From Fig. 4 we can conclude that conduction occurs through an activated process with a single activation energy. The activation energies and σ_d values of all samples are given in Table II.

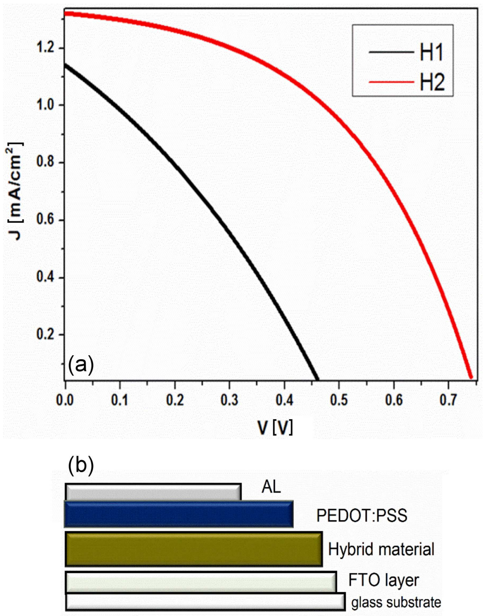

Fig. 5. (a) The J–V characteristic of POT/CdSe solar cell. (b) The structure of bulk heterojunction solar cell.

TABLE II

Variation of optical energy gap (E_g), activation energy (ΔE_a) and DC conductivity (σ_{DC}) with different concentration of CdSe in POT/CdSe thin film.

Sample	Conductivity [S/cm]	ΔE_a [eV]
POT–CSA	0.3	0.2878
H1	0.33	0.27
H2	1.00997	0.17
H3	0.11689	0.23

One of the most important applications of hybrid materials are solar cell devices, which rely on hybrid nanomaterials as the active material. Solar cells were investigated by varying the nanoparticle/polymer ratio. Voltage was applied from −1 to +1 V. The current density–voltage (J–V) characteristic curves and structure of solar cells are revealed in Fig. 5. Solar cell parameters cell, i.e., J_{sc}, $J_{\max}$, $V_{\max}$ and V_{oc}, η and FF have been extracted from Fig. 5 and listed in Table III. As a result, the J–V curves and the solar cell parameters for devices made from 1:1 wt% H2 showed higher photovoltaic characteristics when compared to the device made from 3:1 wt% H1. This means that the performance of organic–inorganic solar cells was found to be significantly dependent on the weight ratio of donor to acceptor electrons, which in our research is 1:1 wt%. Weizhe Xu. et al. [28] found the same results for the solar cells prepared from P3HT:CdSe and speculated that the enhancement of the solar cells came from the improvement of charge transport which might be accomplished at an appropriate weight ratio of interpenetrated donor/acceptor materials [28]. This speculation has been established by the electrical properties tests to the hybrid material in this paper, and we found that the electric conductivity has a higher value at this weight (50:50). Also, formation of a good interpenetrating network at this weight ratio will produce larger photoactive interface areas and decrease the rate of recombination of the carrier and could enhance dissociation of excitons and transport of charge carriers to their respective electrodes, which will be enhanced the efficiency of solar cells [26].

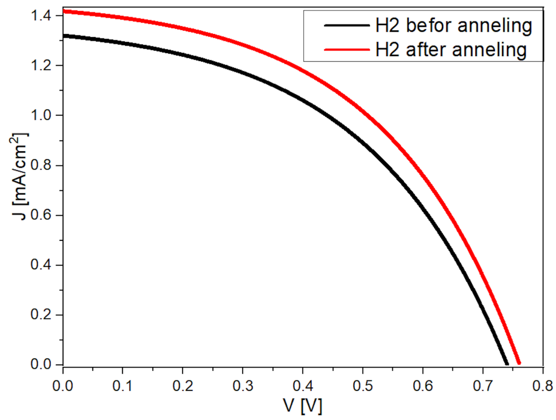

Fig. 6. The J–V characteristic of POT/CdSe solar cell for H2 active layer before and after annealing.

One reason for the absence of photovoltaic effect in devices made from 1:3 wt% H3, which contain CdSe aggregates, could be the formation of an insufficiently interpenetrating network through the photoactive layer. Such case occurs where the improvement in the properties of hybrid materials depends on the degree of dispersion and interaction of nanoparticles within the polymer matrix [29]. The dispersion and processibility of the semiconductor in the polymer at this concentration (75:25) is very poor, and the organic material is isolated from the inorganic material, which reduces the quality of the thin film. Agglomerates form and pinholes occur on the surface of the film. When aluminum electrodes are deposited, contact occurs between the AL and FTO electrode, causing shorts despite all attempts to address the problem, such as annealing the film and heating upon mixing.

Additionally, the effects of thermal annealing treatments on the device performance have been investigated. The prepared hybrid cell with POT/CdSe NPs H2 nanocomposites were annealed at 80°C for 30 min. Figure 6 shows the J–V curves before and after annealing. The performance is relatively low. Before annealing, the device had $V_{\mathrm{oc}} = 0.74$ V, $J_{sc} = 1.322$ mA/cm^2, FF = 0.47 and 0.5%. After annealing, the performance improves slightly. The increase of efficiency was attributed to an increase in current to $I = 1.42$ mA/cm^2 and voltage $V_{\mathrm{oc}} = 0.76$ V.

TABLE III

Parameters of solar cells.

Sample	$J_{\rm sh}$ [mA/cm^2]	$V_{\rm oc}$ [V]	$J_{\rm max}$ [mA/cm^2]	$V_{\rm max}$ [V]	R_s [Ω]	R_{sh} [Ω]	FF	η [%]
H1	1.14	0.46	0. 528	0.26	276	1500	0.26	0. 13
H2	1.322	0.74	0.896	0.52	180	7200	0.47	0.5
H2 annealed	1.42	0.76	0.918	0.54	167	7320	0.46	0.53

This result may be attributed to (i) better molecules organisation and (ii) polymer crystallization, resulting in an improvement of the transport properties of charges in the film. This is probably attributable to better charge transport resulting [25]. The annealing process not only causes recrystallization, but likewise decreases the free volume and density of defects at the interfaces. Recrystallization has a beneficial effect on the holes mobility [30]. The solar cells parameters before and after annealing were given in Table III.

4. Conclusions

We have studied the morphological and electrical properties of hybrid material POT/CdSe prepared by varying the content of TSC-capped CdSe. Blends of CdSe and POT have been prepared from the solution via the drop-casting method. DC conductivity measurements show that hybrid films semiconducting in nature and the optimum value of conductivity have been obtained when the percent of organic and inorganic materials are equal. Based on the improved properties of hybrid materials, good photovoltaic parameters have been obtained in the fabricated solar cell from this material. This study indicates that the POT/CdSe hybrid nanocomposite material is a promising material in bulk heterojunction solar cell applications.

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