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CONDENSED MATTER PHYSICS

# Modeling and Simulation of Experimentally Fabricated QDSSC Using ZnS as Light Absorbing and Blocking Layer[1]

**Masood Mehrabian[a]* and Sina Dalir[b]**

[a] *Department of Physics, Faculty of Basic Science, University of Maragheh, P.O. Box 55136-553, Maragheh, Iran*

[b] *Department of Materials Engineering, Faculty of Engineering, University of Maragheh, PO Box 55181-83111, Maragheh, Iran*

**e-mail: masood.mehrabian@yahoo.com, masood.mehrabian@maragheh.ac.ir*

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**Abstract**—Two main factors which limit the power conversion efficiency of solar cells are light absorption and recombination processes. In photovoltaic (PV) devices, low energy photons cannot be absorbed and excite electrons from valance band to conduction band, hence do not contribute to the current. On the other hand, high energy photons cannot be efficiently used due to a poor match to the energy gap. Existence of charge recombination in PV devices causes the low conversion performance, which is indicated by the low open-circuit voltage ($V_{OC}$). Using a blocking layer in system could effectively reduce the recombination of charge carriers. In this study, we simulated a solar cell with ITO/ZnO/P3HT&PCBM/Ag structure. To prevent the charge recombination, a ZnS QD layer was used which acts as a light absorbing and a recombination blocking layer in the ITO/ZnO film/ZnS QD/P3HT&PCBM/Ag structure. The simulated $J-V$ characteristics of solar cells showed a close match with the experimental results. Simulate data showed an increase of conversion efficiency in ZnS QDSSC from 1.71 to 3.10%, which is relatively 81.28% increase.

**Keywords:** simulation, synthesis, SILVACO, ZnS, photovoltaic.

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## INTRODUCTION

In recent years, increasing global requisition for energy and limited fossil fuels require development of green and renewable energy sources. Solar energy is the most favorable natural resource to resolve the energy crisis using photovoltaic (PV) effect. In a PV device, the electric energy is transformed directly from sunlight. This phenomenon occurs in materials which capture photons and emit electrons from valence band to conduction band.

Inorganic semiconductor nanoparticles (Quantum Dots) are promising materials for new generation solar cells due to size dependent absorption. QDs utilize hot electrons and generate multiple excitons (electron-hole pairs) with one single photon through the impact ionization effect [1].

Organic solar cells based on the blend of regioregular poly(3-hexylthiophene) (P3HT) and phenyl-C61-butyric acid methyl ester (PCBM) are one of the most promising structures which have attracted considerable attention of researchers in the field of solar cells.

The structure of the cells considered in this study is presented in Fig. 1 in our case (ITO/ZnO) and Ag forms the front and back contacts, respectively. Each contact has its special work function (WFs) value. The difference of WFs sets up an electric field (potential slope) in the system which helps electrons and holes separate. P3HT is a p-type semiconductor polymer ($E_g = 1.95$ eV) which acts as active layer in the cell with ITO/ZnO/P3HT&PCBM/Ag structure (Fig. 1a).

When exposed to sunlight, P3HT absorbs photons having energy greater than 1.95 eV, some excitons (electron–hole pairs) will be generated through this layer.

The work function value of ITO (modified by ZnO) and silver are 4 and 4.8 eV, respectively. The potential created by the different work functions (4 and 4.8) helps to separate these excitons, pulling electrons to the positive electrode (ITO) and holes to the negative electrode (Ag), therefore, a photocurrent is created [2]. This created photocurrent is directly proportional to the number of absorbed photons.

Short-circuit current ($J_{SC}$), Open-circuit voltage ($V_{OC}$), Fill factor (FF) and Power conversion efficiency ($\eta$) are four basic parameters for PV systems.

$J_{SC}$, $V_{OC}$, $FF$, and $\eta$ are current through the solar cell when the voltage across the device is zero, the voltage provided by an illuminated solar cell when no external load is connected, the ratio of

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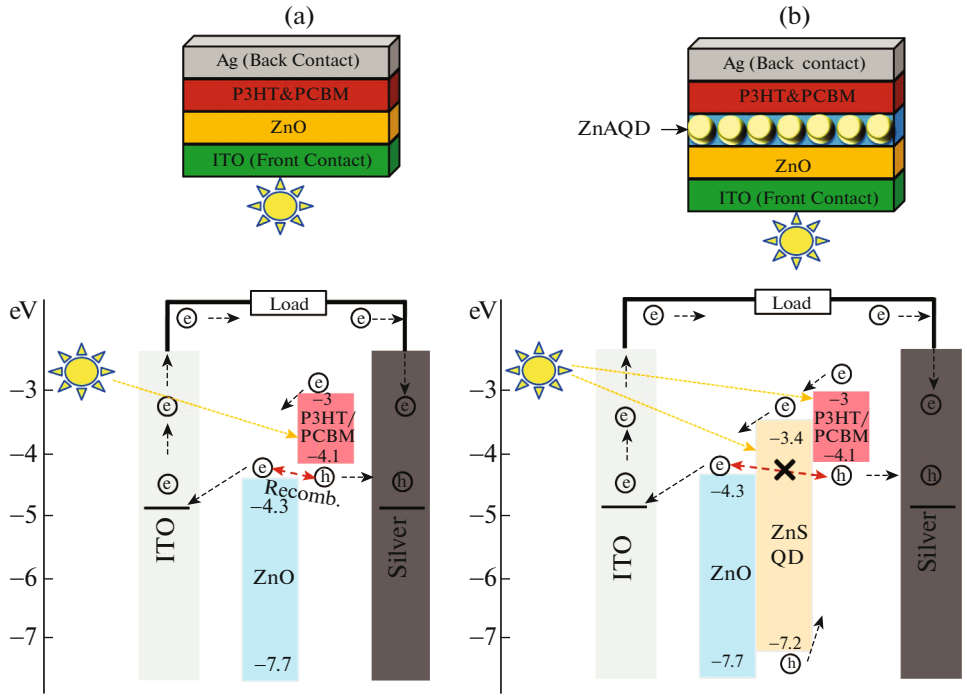


**Fig. 1.** Schematic diagram and energy level position of layers in (a) OPV, (b) ZnS QDSSC. The probable recombination is passivated with ZnS QD layer.

the actual power a solar cell can supply to the maximum predicted by the product of its $J_{SC}$ and $V_{OC}$, and the ratio between the maximum electrical power generated ($P_{max}$) and the incident optical power ($P_{light}$), respectively. The power conversion efficiency is defined as:

$$\eta = \frac{FF \times J_{SC} \times V_{OC}}{P_{light}}.$$

These parameters describe the current that flows in a PV device when illuminated and its electrodes are connected.

Naturally, solar cells exhibit a nonlinear current density–voltage ($J$–$V$) characteristic which their performance could be estimated from its ($J$–$V$) diagram.

## MODELING

Modeling of solar cells is performed using the ATLAS simulator by Silvaco which allows to numerically solving the Poisson's equation coupled with continuity equations for both electrons and holes under steady state conditions.

In this work, the performances of an OPV and ZnS QDSSC have been compared to experimental data.

Figure 1 shows the schematic structure of the organic photovoltaic (OPV) device and ZnS QDSSC.

The simulator should allow the definition of standard solar spectra. Along this work, we used a standard terrestrial solar spectral irradiance distribution, Air Mass 1.5 (AM 1.5) for simulating. AM1.5 spectrum has an integrated power of 1000 W/m$^2$ (100 mW/cm$^2$), and its graph resulted from simulation is shown in Fig. 2d. All simulations were performed at room temperature (27°C) and AM1.5. The different physical

**Table 1.** Simulated OPV and ZnS QDSSC specifications

| Parameter | Value | |
|---|---|---|
| | ZnS | P3HT&PCBM |
| $N_C$, 1/cm$^3$ | $6.35 \times 10^{18}$ | $1 \times 10^{19}$ |
| $N_V$, 1/cm$^3$ | $6.03 \times 10^{19}$ | $1 \times 10^{19}$ |
| Mobility of electrons $\mu_e$, cm$^2$ V$^{-1}$ S$^{-1}$ | 165 | $2 \times 10^{-3}$ |
| Mobility of holes $\mu_h$, cm$^2$ V$^{-1}$ S$^{-1}$ | 5 | $2 \times 10^{-3}$ |
| Relative permittivity $\varepsilon_r$ | 8.3 | 4 |
| Electron affinity $\chi$, eV | 4 | 4.02 |
| a.singlet | 3.8 | 1.1 |
| s.binding, eV | 0.034 | 0.2824 |

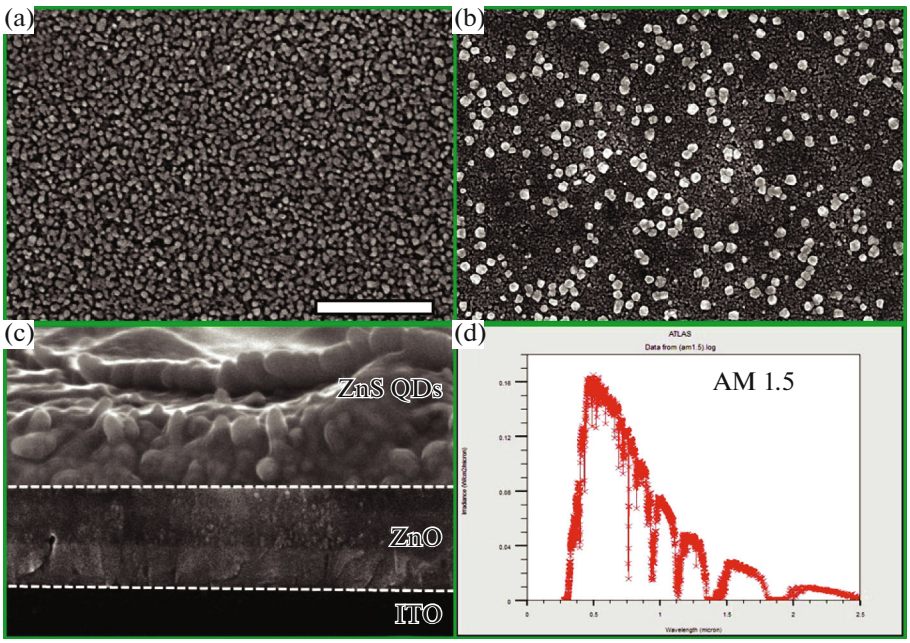


**Fig. 2.** SEM images of (a) ZnO film, (b) ZnS QD layer, (c) Cross sectional view of ITO/ZnO/ZnS QD layers, and (d) air mass spectrum 1.5 used to illuminate the model. Scale bar: 1 μm.

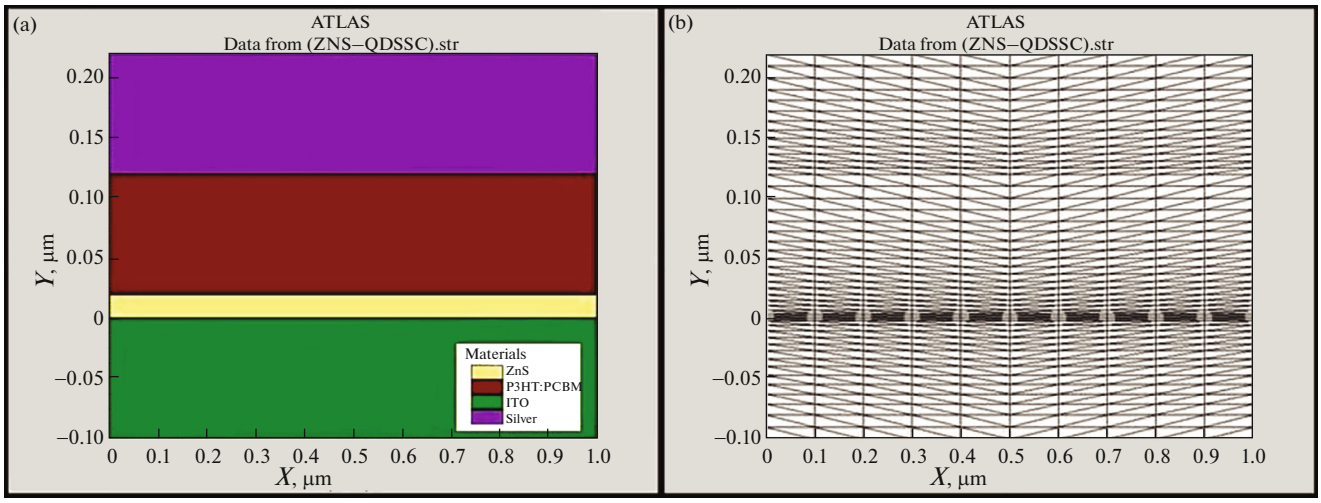


**Fig. 3.** (a) ZnS QDSSC structure, (b) 2D meshing of ZnS QDSSC.

parameters used in modeling of OPV and ZnS QDSSC are listed in Table 1.

## RESULTS AND DISCUSSION

Both devices are irradiated from ITO side. In OPV, incident light generates excitons in P3HT&PCBM active layer. These photo generated excitons can become dissociated with electrons moving to ITO electrode through ZnO electron transport layer (ETL), while holes are extracted by silver electrode.

The favorable pathway for nonradiative recombination process of the electrons from conduction band of ZnO with holes from P3HT&PCBM in OPV is shown in Fig. 1a which plays a major role in the low efficiency (in fact, low FF) obtained for such system [3–6].

To form a ZnS QDSSC, we use a ZnS QD layer between ZnO and P3HT&PCBM (Fig. 1b). The surface morphology characterization of ZnO and ZnS QD layers is carried out on synthesized samples using scanning electron microscopy (SEM), as shown in Fig. 2.

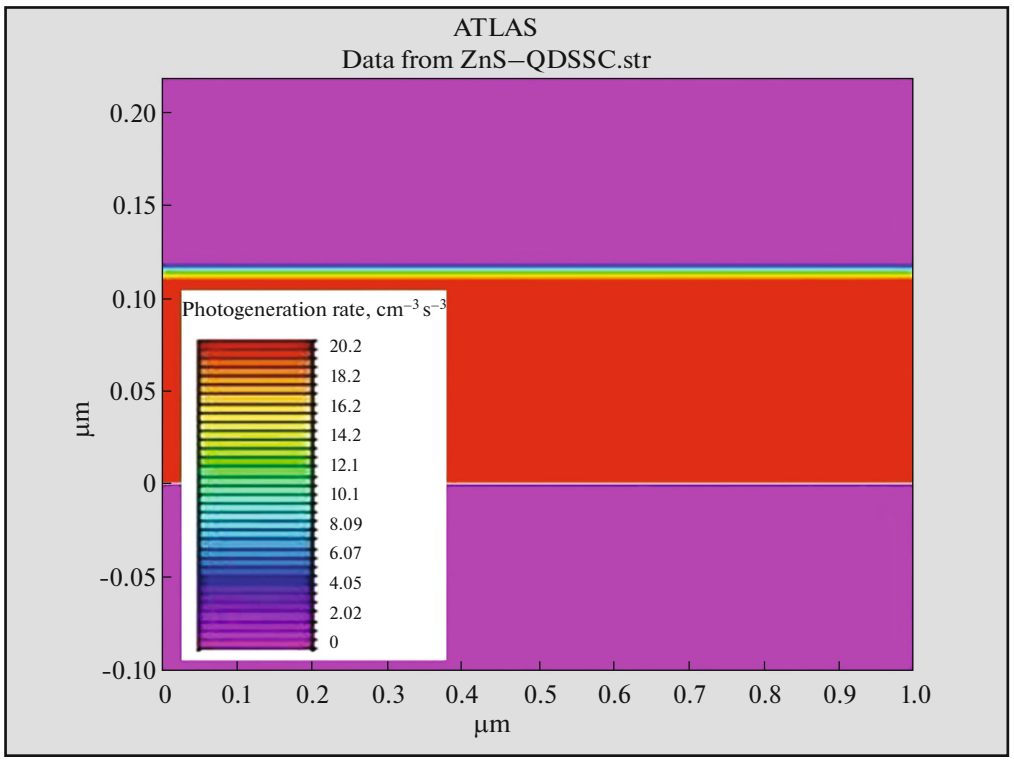


**Fig. 4.** Photo-generation rate obtained from simulation.

The mesh is very important in simulation to obtain accurate results and should be dense near regions such as junctions, material boundaries, or electrodes. Otherwise, the results will not be accurate. The 2 dimensional (2D) mashing of device structure along with its layers is shown in Fig. 3.

Langevin, S.Dissoc and pfmob are the physical models that have been used for this simulation.

Organic semiconductors are well known as low mobility materials. Electrons and holes move slowly in such mediums. Therefore, the recombination of electrons with holes is probable in organic layers. The Langevin describes the theory of such process.

$$R_{\mathrm{L}}(n,p) = r_L \frac{q[\mu_{\mathrm{n}}(E) + \mu_{\mathrm{p}}(E)]}{\varepsilon_{\mathrm{r}}\varepsilon_0}(np - n_{\mathrm{i}}^2),$$
$$n_{\mathrm{i}}^2 = n_0 p_0,$$

where $r_{\mathrm{L}}$ is the Langevin recombination rate coefficient and $q$ is the magnitude of the charge on an electron. $\mu_{\mathrm{n}}$, $\mu_{\mathrm{p}}$, $E$, $\varepsilon_{\mathrm{r}}$, $n$, and $p$ are the mobility of electrons and holes, local electric field, relative permittivity, electron and hole concentrations, respectively. Therefore, the Langevin recombination model is enabled by the LANGEVIN parameter in the model statement.

Once electrons and holes were dissociated, they experience built-in electric fields. They are then separated and detected at the electrodes. To enable dissociation process, we specify S.DISSOC on the MODELS statement.

We used also Poole–Frenkel mobility modeling. In organic materials, the Poole–Frenkel effect occurs when the Columbic potential barrier is lowered due to the electric field ($E$).

However, the Poole–Frenkel effect assumes an electron in the Coulomb potential of a positively charged (trap) state. By applying an electric field, the effective barrier for leaving this potential is reduced which could be calculated as the maximum of the superposition of the two potentials:

$$V = -\frac{e^2}{2\pi\varepsilon_0\varepsilon_{\mathrm{r}} r} - eFr,$$

$$dV/dr = \frac{e^2}{4\pi\varepsilon_0\varepsilon_{\mathrm{r}} r^2} - eF = 0 \rightarrow r = \sqrt{\frac{e}{4\pi\varepsilon_0\varepsilon_{\mathrm{r}} F}}$$

$$\rightarrow (\Delta\phi)_{\max} = -\sqrt{\frac{Fe^3}{\pi\varepsilon_0\varepsilon_{\mathrm{r}}}}.$$

Therefore, we enabled also Poole–Frenkel mobility model by specifying PFMOB on the MODEL statement.

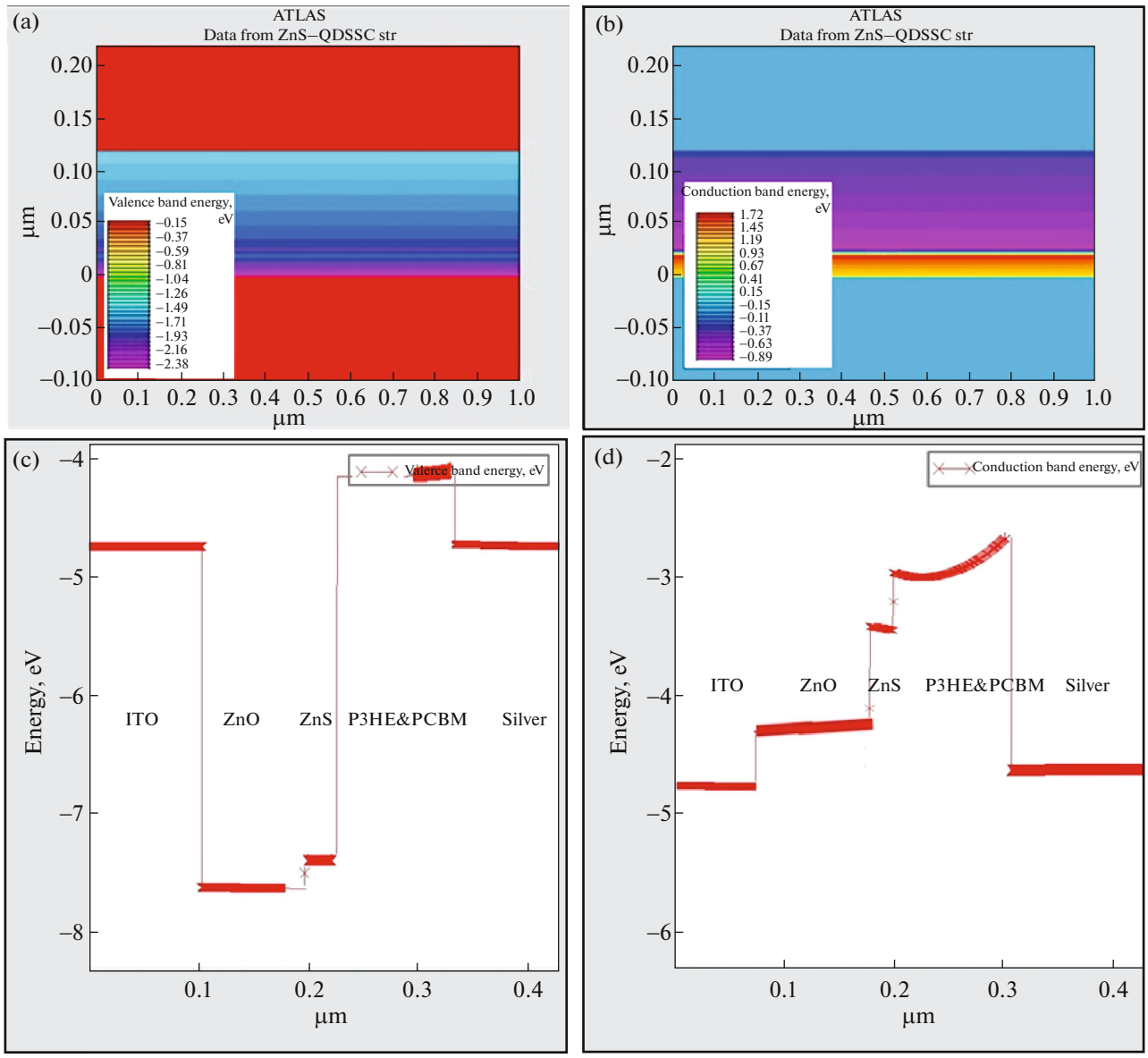


**Fig. 5.** (a), (c) The valence band energy, (b), (d) the conduction band energy diagrams of ZnS QDSSC layers.

Photo-generation rate diagram is shown in Fig. 4. In solar cells, photo-current is being produced in different wavelengths, according to the frequency response of layers. The highest photogeneration rate of 20.2 ($cm^{-3}$ $s^{-1}$) was obtained in the upper layers because they are exposed to a greater number of photons.

Band energy diagram of ZnS QDSSC with ITO/ZnO/ZnS QD/P3HT&PCBM/Ag layers is shown in Fig. 5.

**Table 2.** PV parameters obtained for simulated and fabricated OPV device with ITO/ZnO/P3HT/Ag structure

| PV parameter | Value (simulation) | | Value (experiment) | |
|---|---|---|---|---|
| | OPV | ZnS QDSSC | OPV | ZnS QDSSC |
| $V_{OC}$, V | 0.42 | 0.54 | 0.48 | 0.57 |
| $J_{SC}$, mA/cm$^2$ | 6.1 | 9.73 | 6.74 | 9.94 |
| *FF*, % | 36.95 | 48.07 | 46.47 | 47.11 |
| η, % | 1.71 | 3.10 | 1.50 | 2.72 |

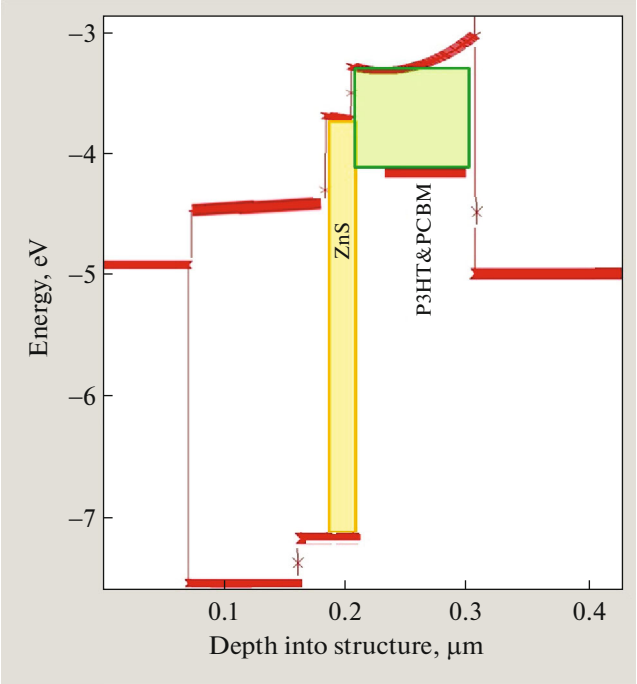


**Fig. 6.** Valence and conduction bands energies for active layers.

One of the most important parameters in a photovoltaic device is the band gap alignment. The band gap energy ($E_g$) is the difference between the conduction and valance bands, which has a great impact to the charge transport process.

A visual representation of this alignment is shown in Fig. 6a.

It could be seen that the valence and conduction band energy of ZnS and P3HT&PCBM are located at ~ −7.2, −3.4 eV and −4.1, −3 eV, related to their band gap energy of ~3.8 and 1.1 eV, respectively.

Current density–voltage ($J$–$V$) characteristics of OPV and ZnS QDSSC, obtained using ATLAS are shown in Fig. 7 and were compared to experimental data.

The performance parameters and characteristics of organic cell and ZnS QDSSC are listed in Table 2.

Using of ZnS QD layer can partially increase the light absorption (as the second active layer in QDSSC) and decrease the recombination rate leading to higher photocurrents. In ZnS QDSSC the ZnS QD layer acts as light absorber and electron–hole recombination layer, which leads to increase the photovoltaic performance.

Indeed, the ZnS QD layer enhances $J_{SC}$ by 59.5% (from 6.1 to 9.73 mA/cm$^2$), because it acts as the light absorber layer (beside P3HT). This QD layer also increases the $V_{OC}$ by 28.57% (from 0.42 to 0.54 V) since acts as blocking layer material.

## CONCLUSIONS

We fabricated and simulated an organic cell as well as a ZnS quantum dot sensitized solar cell (ZnS QDSSC) with the structure of ITO/ZnO film/ZnSQD/P3HT&PCBM/Ag. Simulation was carried out by using SILVACO TCAD software. The electron-hole recombination process from the ZnO film to the P3HT&PCBM was blocked by inserting a ZnS QDs blocking layer.

The simulated $J$–$V$ characteristics of solar cells showed a close match with the experimental results. The power conversion efficiency of 1.71 and 3.10% was obtained from simulation for organic and ZnS QDSSC, respectively. These data are in good accordance with experimental results (1.5 and 2.72%). It is

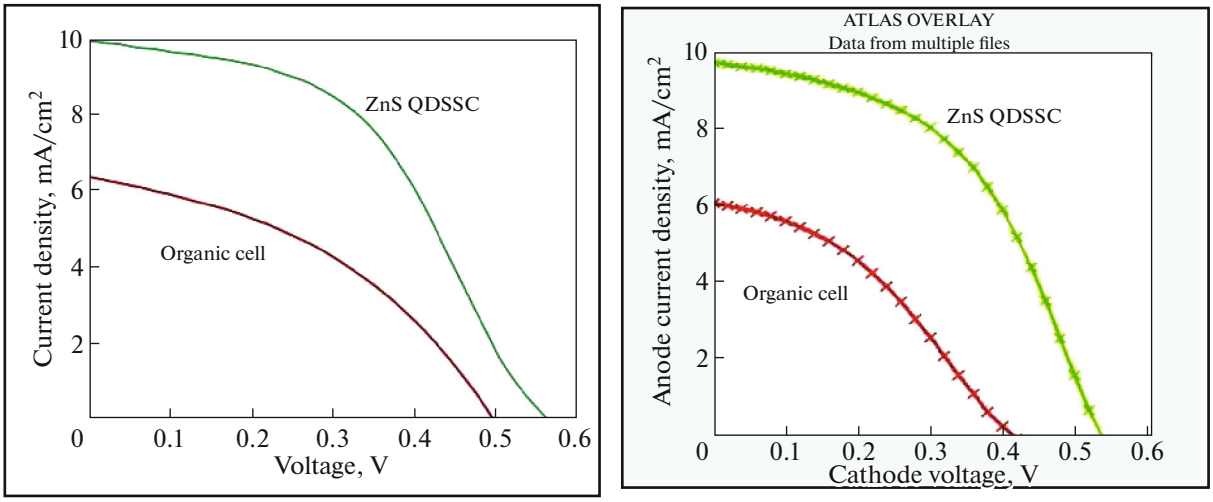


**Fig. 7.** $J$–$V$ curves of OPV and ZnS QDSSC obtained (a) experimentally, (b) from simulation.

formerly evident that a ZnS QDs layer could be successfully used in solar cells as a light absorber and a recombination blocking layer material.

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