

Dye Enhanced Quantum Dot Sensitized Solar Cell

Shawqi Al Dallal¹, Khalil E. Jasim^{2,*}

Third generation solar cells, such as dye and quantum dot sensitized solar cells are attracting attention of many research groups. In this investigation we explore the role of dye extract on the enhancement of the photovoltaic properties of quantum dot sensitized solar cells (QDSSCs). Lead sulfide quantum dots of different sizes have been used to sensitize a nanostructured titanium oxide electrode. We compare the open circuit voltage, the short circuit current, and power conversion efficiency of QDSSCs with the same quantities as obtained for dye-enhanced system using pomegranate dye extract. An open circuit voltage of 166 mV, a short circuit current of 0.1 mA, and an efficiency of 0.32% were obtained for 2.4 nm radius lead sulfide quantum dot sensitized solar cells. Using pomegranate dye extract reveals a considerable enhancement of the above characteristics. The combined dye-quantum dot system produces an open circuit voltage of 300 mV, a short circuit current of 0.55 mA, and an efficiency of 3.4%. For 3.2 nm radius QDs, the efficiency is substantially higher, reaching about 7%. A model describing the structure and processes leading to the above enhancement of the assembled solar cell characteristics is presented. In this model we explain the interplay between the transfer of electrons between the dye, quantum dots, and subsequent injection in the wide band gap titanium dioxide semiconductor.

Introduction

For many decades amorphous silicon and its alloys have been considered among the best candidates of low-cost photovoltaic or solar cells [1-3]. These devices are based on p-n junction or heterojunction structures. With the advent of nanotechnology, new types of low-cost solar cells are developed. One of the most promising of these cells was proposed by Brian O'Regan and Michael Grätzel in 1991 [4]. His pioneering work involves developing low-cost photo-electrochemical photovoltaic cells. The structure of these cells consists of a transparent conductive electrode, a dye, an electrolyte, and a transparent counter electrode. The operation of these devices is based on the injection of electrons in a high band semiconductor [5-9]. The first of these devices was studied by Gerischer and Tributsch. They utilized zinc oxide (ZnO) electrode sensitized by organic dyes such as rose bengal fluorescein and rhodamine [10, 11]. The next major step in the development of efficient sensitized solar cell was the recognition of high performance nanoporous titanium dioxide (TiO₂) thin layer coated conductive electrodes. Using nanocrystalline TiO₂ electrodes, solar energy efficiencies of 11% under AM1.5

irradiation have been realized [12]. A key concept in developing photoelectrochemical photovoltaic cells is based on injection of electrons in a wide band gap semiconductor photoelectrode [5,6,12-14].

In this paper we investigate two independent approaches to inject electrons in a wide band gap semiconductor, and subsequently we examine the enhancement achieved by combining both injection processes. In the first part of this investigation, we use PbS quantum dots (QD) as a source of electrons (sensitizer). QDs are semiconduction nanocrystals revealing high degree of confinement, and very sharp density of states. They have a remarkable property that their energy gap, and consequently their absorption edge, is a function of their sizes [15,16]. The band gap energy of PbS can be driven from 0.41 eV in the bulk to 2.3 eV in the nanostructured size scale. The strong confinement regime in QDs creates quantized energy levels and could be a source of a wide range of physical phenomena such as bottle neck effect, efficient charge carrier multiplication, and spin blockade [17,21]. Other potential sources of electron injection in a wide gap semiconductor are dyes [5,6]. Pomegranate was used in this work as an efficient dye to enhance the injection process. The optical properties of dye enhanced solar cells depends on dye concentration and QDs size.

Structure and operation principles of dye enhanced QDs solar cell

The structure of dye enhanced QD solar cell is shown schematically in Fig. 1. In this system, both QDs and dye

¹College of Graduate Studies and Research, Ahlia University, P. O. Box 10878, Bahrain

²Department of Physics, College of Science, University of Bahrain, P. Box 32038, Bahrain

*Corresponding author:

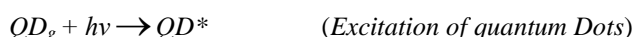
E-mail: kejasim@uob.edu.bh; Tel: (+973) 39921144

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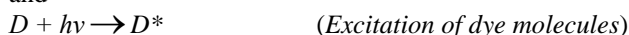
molecules work in tandem to inject electrons in the wide band gap nanostructured TiO₂ semiconductor. The cell consists of a transparent conductive electrode, a carbon coated counter-electrode, a layer of nanostructured TiO₂ layer, dye molecules, and electrolyte. Efficient sensitization of the TiO₂ thin film is obtained by adhering the QDs to its surface. The operation of the cell involves a series of processes, impacting both QDs and dye molecules, leading to the injection of electrons in the nanostructured TiO₂ conduction band. The following steps describe the processes involved in solar cell operation:

(I) Excitation process

A QD is excited from the ground state (QD_g) to any of its higher energy states (QD*) via absorption of a photon, in a similar way dye molecule get excited from its highest occupied molecular orbitals (HOMO) state (D) to the lowest unoccupied molecular orbitals (LUMO) states (D*). These processes can be described by the following equations



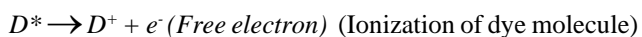
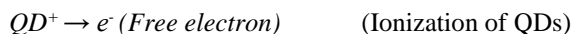
and



The small energy difference between HOMO and LUMO states guarantees the absorption of longer wavelength (lower energy) photons. In fact, the injection of electrons in the nanostructured TiO₂ layer conduction band becomes more effective when the energy of the LUMO state coincides with that of the nanostructured TiO₂ conduction band.

(II) QD exciton dissociation

The absorption of photons by the QDs results in the formation of bound electron-hole pair in the form of exciton. As a matter of fact, if thermal energy exceeds its binding energy, exciton dissociates.



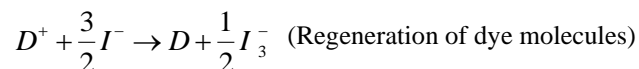
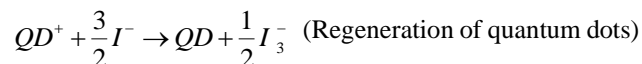
(III) Electron injection in the TiO₂ layer

Electrons from dissociated excitons and from ionized dye molecules are injected into the TiO₂ layer. The injected electrons are then transported between the TiO₂ nanoparticles and transferred to the load where the work done is supplied as electric energy.

(IV) Regeneration of QDs and dye molecules

The electrolyte used in the cell contains I⁻/I₃⁻ redox ions. These ions play the role of electron mediator between the TiO₂ photoelectrode and the counter-electrode. The ionized sensitizer (QD⁺) or dye molecule (D⁺) are restored by accepting an electron from the oxidized I⁻ mediator. This process will regenerate the ground state of both the QD and

dye molecules, as well as leading to the conversion of the I⁻ ions to the oxidized state I₃⁻.



(V) Electron capture

The I₃⁻ ion diffuses to the counter-electrode (C.E) and replaces the internally donated electron with that from the external load, and therefore it becomes reduced back to the I⁻ ion state.

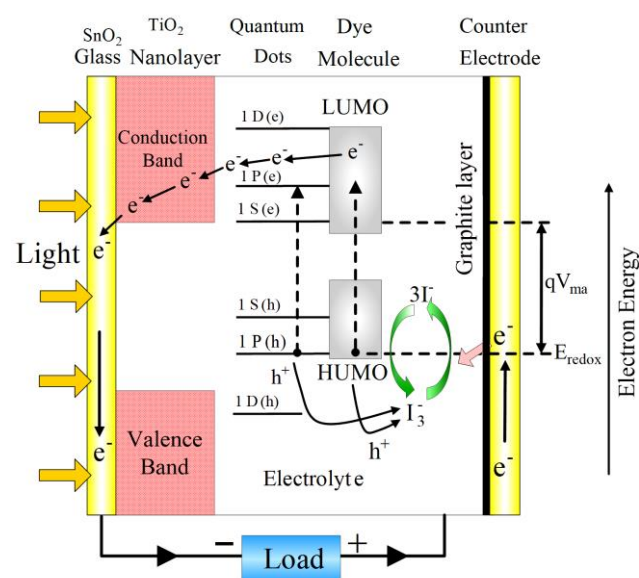
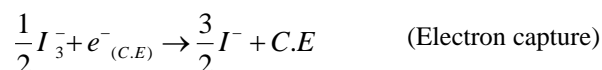


Fig. 1. Schematic diagram of the structure and operation of dye enhanced QD solar cell.

Quantum dots-dye molecules interaction

In the above model, we considered QDs and dye molecules as separate entities contributing separately to the injection mechanism in the nanostructured TiO₂ layer. However, once a QD is ionized, it can receive an electron from an excited dye molecule and returns back to its ground state. Likewise, an ionized dye molecule can receive an electron from an excited QD and returns back to its ground state. These processes combined can lead to a suppression of electrons available for the injection process in the nanostructured TiO₂ layer, thus lowering the efficiency of the system. However, the nanostructured TiO₂ layer provides a much larger surface area for capturing dissociated electrons from dye molecules and QDs. Therefore, electrons are injected preferentially in the TiO₂ layer.

As a matter of fact, generation of electric power in a dye enhanced quantum dots solar cell produces no permanent chemical transformation.

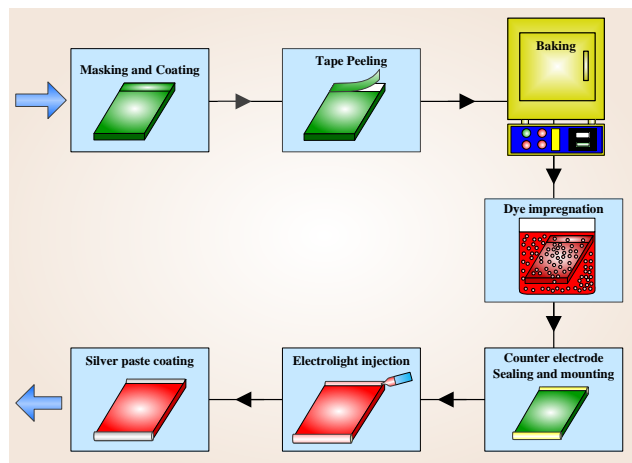


Fig. 2. Steps for preparation of dye enhanced QDs solar cell.

Experimental

Nanostructured TiO₂ layer is prepared according to the preparation methodology described in [4-6] and shown in Fig. 2. According to this method, TiO₂ suspension is acquired by adding 9 ml of nitric acid solution of PH 3-4 (1 ml/increment) to 6 gm of colloidal P25 TiO₂ powder in motor and pistil. During the grinding process, a white-free flow paste is obtained after adding 8 ml of deionized water. Finally, a drop of transparent wetting agent, such as clear dish detergent is added in 1 ml of distilled water. This step is essential to guarantee the uniformity and adhesion to the transparent conducting electrode. The cell operation is usually affected by the ratio of nitric acid solution to the colloidal P25 TiO₂ powder. If this ratio exceeds a certain threshold value, the TiO₂ layer becomes thick and has the inclination to peel off. Conversely, lower ratio reduces substantially the efficiency of light absorption.

Doctor blade method is utilized in the deposition of the TiO₂ suspension uniformly on a cleaned (rinsed with ethanol) transparent electrode plate. The TiO₂ layer was allowed to dry for few minutes and then annealed at 450 °C for about 15 minutes to form a nanoporous layer of TiO₂. The annealed plate is allowed to cool slowly to room temperature to remove thermal stresses and prevent cracking of the glass or detaching of the TiO₂ layer. The formation of the nanoporous TiO₂ layer was confirmed by a scanning electron microscopy (SEM) and X-ray diffraction (XRD) measurements, as depicted in Fig. 3. Finally, the nanoporous TiO₂ layer is coated with PbS QDs suspended in toluene. But the counter electrode is coated with graphite layer that acts as a catalyst in redoxing oxidized QDs.

Fresh pomegranate seeds (100 g) were smashed to produce dye extract. Optical characterization of the filtered extract is achieved by dual beam spectrophotometer (Shimadzu UV-3600 double beam spectrophotometer). By clamping both photo and counter electrodes together and adding a drop of electrolyte- to fill the clamped cell- the solar cell is cleaned and ready to be tested using solar

simulator. We used iodide electrolyte in this study (0.5 M potassium iodide mixed with 0.05 M iodide tri-iodide I⁻/I₃⁻ couple).

A hand-made solar simulator is used to measure both the open circuit voltage (V_{OC}) and short circuit current (I_{SC}) of the assembled cells. To eliminate or prevent over-heating of the tested cell; a 2-mm thick glass sheet has been placed above the cell. Also, no antireflection coating on the photoelectrodes has been applied.

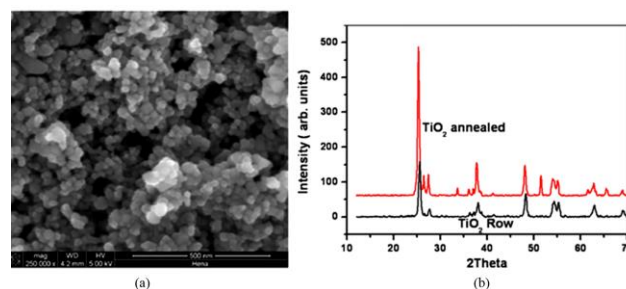


Fig. 3. (a) Scanning electron micrograph (SEM) image of nanostructure TiO₂ layer and (b) X-ray diffraction (XRD) before and after annealing.

Results and discussion

Optical measurements were carried out to assess the effectiveness of sensitizing TiO₂ nanoporous layer using different sizes of PbS QDs. After the TiO₂ layers annealed, scanning electron microscope (SEM) is used to image the formation of nanostructure properties. The morphology of the nanostructured TiO₂ layer is shown in Fig. (3a), and the X-ray diffraction spectrum (XRD) is presented in Fig. (3b). A quantity of prime importance is the incident photon to current conversion efficiency (IPCE) defined as

$$IPCE = \eta_{LHE} \Phi_{inj} \eta_c$$

where η_{LHE} is the light harvesting efficiency ($\eta_{LHE} = 1 - 10^{-A}$), where A is the spectral absorbance), Φ_{inj} is the quantum yield of electron injection, and η_c is the collection efficiency of injected electrons at the back contact. If both Φ_{inj} and η_c are in close proximity to 100%, then the IPCE is equal to η_{LHE} . However, this situation is far from being reached. In fact, due to the electron transfer dynamics, if the electron injection rate in the semiconductor is comparable to, or slower than the relaxation time of the dye/QD system, then $\Phi_{inj} \ll 100\%$. This is obvious from the definition of the quantum yield

$$\Phi_{inj} = \frac{k_{inj}}{k_{inj} + k_{rad} + k_{nrad}}$$

where k_{inj} is the electron injection rate from both quantum dots and dye molecules, k_{rad} and k_{nrad} are the radiative and non-radiative rates respectively.

Absorbance of quantum dots and dye molecules

Fig. 4 shows the absorbance wavelength dependence of pomegranate dye extract. Wavelengths in the UV and

visible region of the electromagnetic spectrum are greatly absorbed. The absorbance shows also a characteristic peak at 520 nm and then decreases steadily at higher wavelengths. The wavelength dependence of the absorption spectra was measured for three different sizes (radius) of QDs, as depicted in Fig. 5. The main absorption peak shifts towards longer wavelengths as the QD radius grows. For the present study, it was found that the 3.2 nm radius QDs are the most efficient for electron injection in the TiO₂ layer. This is basically because the energy levels configuration in the 3.2 nm QDs provides a more efficient injection of electrons in the TiO₂ layer. Moreover, the absorbance of the three different sizes of QDs shifts toward longer wavelengths as the size of the QDs increases, as predicted by the quantum confinement effect [16,17,21]. The peak position of the QDs is indicative of this effect. The 5 nm QD absorbance spectrum covers the useful portion of solar spectral region extending from UV to about 1.5 μm. The absorbance of the 3.2 nm QDs is the most prominent. However, it decreases sharply to a cut off value at 1200 nm. The 2.4 nm QDs absorbance peak appears at shorter wavelengths. Overall, the UV and visible wavelengths are highly absorbed by all three sizes of QDs. Fig. 6 depicts the I-V characteristics of the solar cells constructed using three different sizes of QDs without addition of dye extract. The 3.2 nm radius QD demonstrates the highest short circuit current (I_{sc}) and open circuit voltage (V_{oc}), and consequently, it produces the most efficient photovoltaic effect among the three sizes of QDs based cells. Figs. 7, 8, and 9 show the dye enhanced photovoltaic effect of the three sizes of QDs based solar cells. In all cells, the I_{sc} is appreciably enhanced, whereas the increase in the V_{oc} reaches a saturation value corresponding to the energy arrangement between the bottom of the nanostructured TiO₂ conduction band and the electrolyte oxidation potential E_{redox}, as illustrated in Fig. (1). Fig. 10 compares the I-V characteristics obtained for the three sizes of QDs solar cells enhanced by the dye molecules.

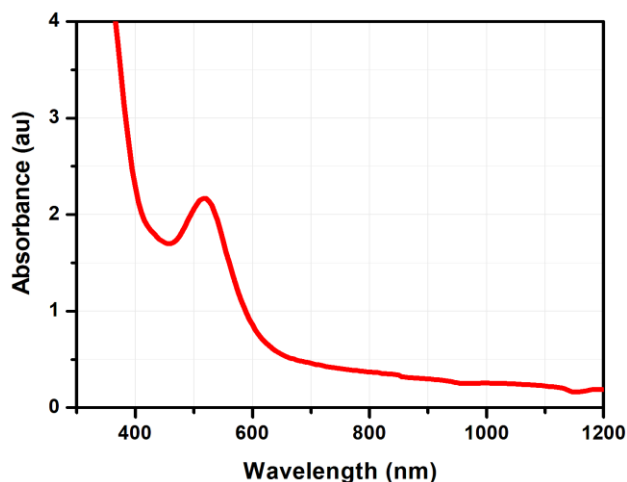


Fig. 4. Absorbance of pomegranate dye extract.

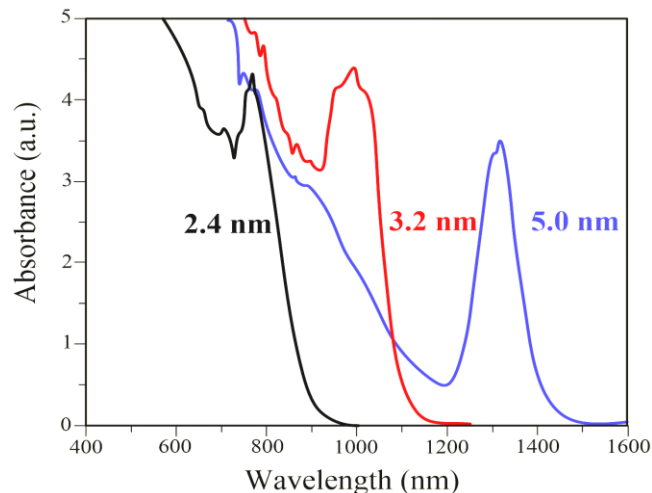


Fig. 5. Absorbance measured for different sizes (radius) of the QD solution.

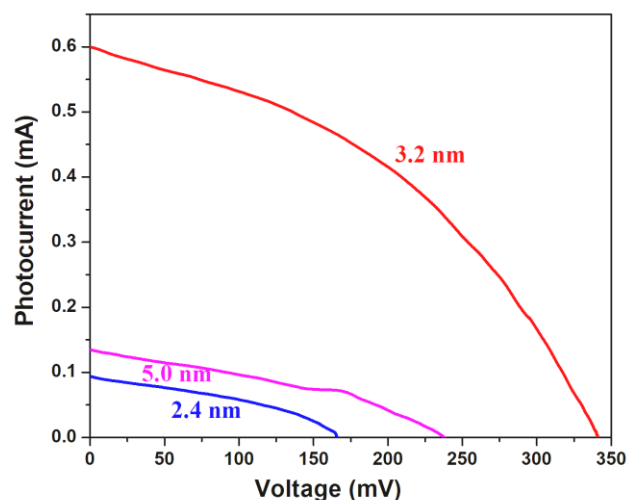


Fig. 6. I-V characteristics of different sizes of PbS QDs solar cells without dye extract.

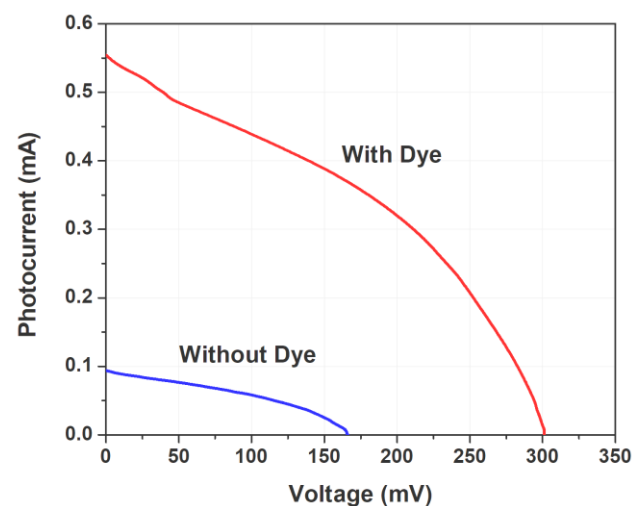


Fig. 7. I-V characteristics of PbS QD of size 2.4 nm solar cell with and without dye extract.

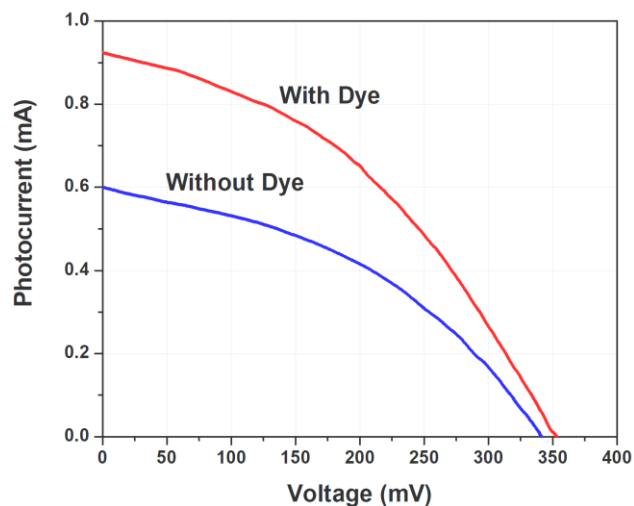


Fig. 8. I-V characteristics of PbS QD of size 3.2 nm solar cell with and without dye extract.

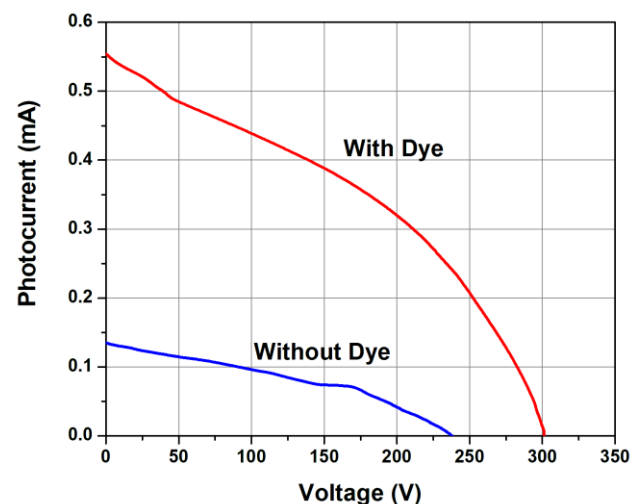


Fig. 9. I-V characteristics of PbS QD of size 5.0 nm solar cell with and without dye extract.

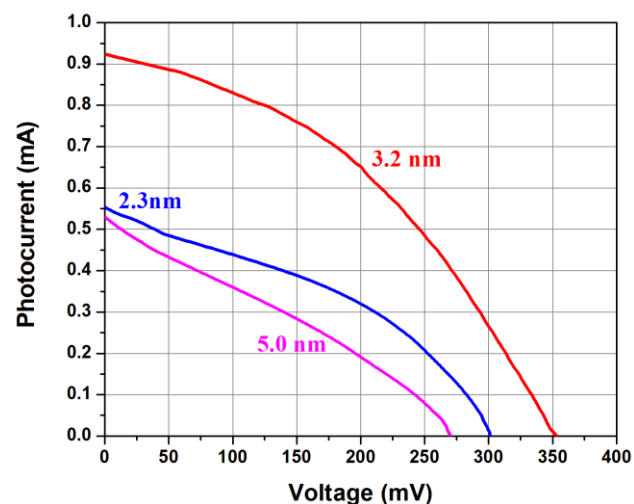


Fig. 10. I-V characteristics of PbS QD solar cells of different sizes with dye extract.

Table 1 summarizes the measured and computed parameters for the three assembled QDs sensitized solar cells and the dye enhanced solar cells using pomegranate as dye sensitizer. The maximum efficiency of the QD sensitized solar cells occurs for the 3.2 nm QDs and reaches 4.47 %. While the efficiency of the combined dye-3.2 nm QDs sensitized solar cells reaches a maximum value of 6.99%.

Table 1. Measured and calculated parameters for the three assembled QDs sensitized solar cells and the dye enhanced solar cells using pomegranate as dye sensitizer.

	QD cell without dye extract			QD cell with dye extract		
	5 nm	3.2 nm	2.4 nm	5 nm	3.2 nm	2.4 nm
V_{oc} (mV)	238.0	341.0	166.3	270.0	353.0	301.0
I_{sc} (mA)	0.135	0.600	0.093	0.530	0.925	0.554
V_m (mV)	170.3	211.0	106.7	160.0	201.0	196.0
I_m (mA)	0.071	0.397	0.055	0.267	0.651	0.327
FF%	37.6	40.9	37.9	29.9	40.1	38.4
Eff %	0.65	4.47	0.32	2.28	6.99	3.43

Conclusion

Third generation solar cells using sensitized dye and quantum dots proved to be one of the top candidates for low-cost solar cells. The role of dye extract on the enhancement of photovoltaic properties has been investigated. The Three sizes of PbS QDs used to enhance the dye action are those with radii 2.4 nm, 3.2 nm, and 5.0 nm. It was found that the 3.2 nm radius QDs are the most efficient for electron injection in the nanostructured TiO₂ layer. This is basically because the energy levels configuration for the 3.2 nm QDs provides more efficient injection of electrons in the nanoporous TiO₂ layer. In this investigation we compared the open circuit voltage, the short circuit current, and efficiency of quantum dot-sensitized solar cells with the same quantities as obtained for dye-enhanced system using pomegranate dye extract. For the 2.4 nm radius PbS QDs, an $V_{OC} = 166$ mV, a $I_{SC} = 0.1$ mA, and a power conversion efficiency of 0.32% were acquired. Upon using dye extract with the same QDs, the cell generated a considerable enhancement on the above parameters. The combined dye-quantum dot system produces an $V_{OC} = 301$ mV, a $I_{SC} = 0.55$ mA, and an efficiency of 3.43%. For 3.2 nm radius QDs, an enhanced efficiency, reaching about 7% has been obtained. Based on our presented model, the injection of charge carries in the conduction band of the nanoporous TiO₂ layer turn out mainly due the interaction between the transfer of electrons between the dye molecules and quantum dots.

Keywords: Dye sensitized solar cell, quantum dots, titanium oxide nanoparticles.

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Conflicts of interest

The authors of this work declare no conflict of interest.

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