

## THESIS FOR THE MASTER DEGREE IN SIENCE

# "ORGANIZING MOLECULAR MATTER PROGRAMME"

### LUND UNIVERSITY

# Quantum Dots Sensitized ZnO Nanowires Solar Cells

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#### **Abstract**

In this project, solar cell based on CdSe quantum dots sensitized onto ZnO nanowires was well fabricated. The following quantum dot-nanowire linker molecules were used: 3-mercaptoproponic acid (3-MPA) and 2-mercaptoproponic acid (2-MPA). The best solar cell efficiency was observed with 3-MPA linker molecule. Solar cell efficiency for different lengths of ZnO NWs and different sensitization times was also investigated.

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## **List of Symbols**

QD	Quantum Dot.	7
MEG	Multiple Exciton Generation.	7
CdSe	Cadmium Selenide.	8
ZnO	Zinc Oxide.	8
QDSSCs	Quantum Dot Sensitized Solar Cells.	8
E	The Photon Energy.	9
h	Plank's Constant.	9
C	Speed of Light.	9
λ	Wavelength.	9
$a_B$	Exciton Bohr Radius.	10
E	Dielectric Constant.	10
Е	Electron Charge	10
$m_{e}^{*}$	Effective Mass of Electrons.	10
$m_h^*$	Effective Mass of Holes	10
E(R)	The First Excitonic Transition Energy.	10
$E_g$	Bandgap Energy.	10
R	The Radius of the Nanoparticle	10

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#### 1. Introduction

#### 1.1 Solar Cells

In the previous century, the world consumption from the non-renewable energy increase with high degree. So, the world should search for another source of energy that can meet their needs. The most renewable, clean, and cheap energy source is the sunlight that can be transferred into electricity through the photovoltaic cells or solar cells devices. A solar cell is a photovoltic device that can convert the sunlight into electricity; it contains a semiconductor material that by absorption of sunlight ejects electron from the valence band to the conduction band forming electron-Hole pair "exciton" (section 2.2). The ejected electron moves into an external circuit, produces a flow of current and then dissipates its energy and comes back to the solar cell. The main components of a solar cell are described in figure (1).

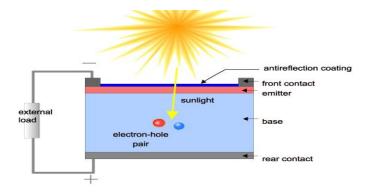


Figure (1), the main components of a solar cell.

#### 1.2 Types Of Solar Cells

There are several types of solar cells in an attempt to increase its power conversion efficiency that until now not reached the acceptable level. And not only the power conversion efficiency of solar cell is important, but also the cost of fabrication that facilitate its market entry. Solar cells can be classified as follows.

#### 1.2.1 Thin-Film Solar Cells

In thin film solar cells, a thin film of the semiconductor material which absorbs light and ejects electrons is deposited onto a substrate surface coated with transparent conducting oxide (TCO) layer by plasma enhanced chemical vapor deposition (PE-CVD) or other techniques. This substrate can be glass, plastic, or metal. The most common thin-film solar cells are amorphous silicon, microcrystalline silicon, polycrystalline silicon, and copper indium diselenide solar cells [21].

#### 1.2.2 Polymer Solar Cells

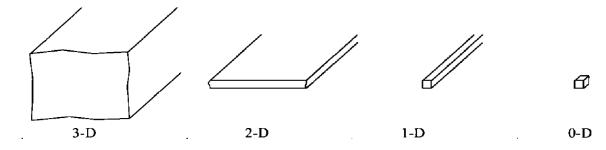
Conducting polymers was first discovered by Heeger, MacDiarmid, and Shirakawa which make them received the Nobel Prize in Chemistry in the year 2000. The conjugated conducting polymers have high delocalized  $\pi$ -electrons; enable them from absorption of visible light and electrical charge transport. These properties make the conducting polymers have important role in solar cell application.

#### 1.2.3 Dye Sensitized Solar Cells

In dye sensitized solar cells, a charge transfer dye is used as harvesting light energy material (sensitizer) which is sensitized into a wide bandgap semiconductor surface like  $TiO_2$ , ZnO, or  $Nb_2O_5$  to eject electron into the conduction band of this oxide. Then, the generated electron moves into an external circuit to produce current. The most common dyes are ruthenium and osmium complexes [20].

#### 1.2.4 Quantum Dots In Solar Cells

The physical dimensions of a semiconductor material play an important role in determining its electronic properties. If the carriers are confined in one dimension, this results in formation of a semiconductor material which is known as quantum wire. While if the carriers are confined in zero dimension, this results in the formation of what is called quantum dot [8] as described in figure (2).



(a)Bulk semiconductor (b) quantum well (c) quantum wire (d) quantum dot Figure (2), the forms of a semiconductor material depending on its physical dimension [8].

Quantum dots (QDs) become to have an influential role in Solar Cell application due to their size dependent bandgap which enable us from harvesting solar light in both the visible and infrared regions. Moreover, by using QDs as light harvesting material the quantum efficiency of the solar cell can be increased due to its multiple exciton generation (MEG) and collection [16]. The operating mechanism of quantum dot sensitized solar cells (QDSSCs) can be described as follows. When the quantum dots absorbs the solar light energy, electrons are excited from the valence band to the conduction band of QDs leaving empty holes in the valence band which can be considered as positive particles. Then the excited electrons of QD are transferred into the conduction band of a large bandgap semiconductor such as TiO<sub>2</sub> or ZnO. But unfortunately until now the power conversion efficiencies of quantum dot sensitized solar cells is below 5% [6,15], so a lot of research groups are concerned with how to increase the power conversion efficiency of QDSSC and what are the factors affecting light harvesting.

In this project work, we used cadmium selenide (CdSe) as the semiconductor quantum dot and zinc oxide (ZnO) nanowires as the large bandgap semiconductor. ZnO semiconductor material was used due to its high electron mobility than TiO<sub>2</sub> and its ease of synthesis [7]. The factors studied in this work were, the effect of the linker molecule between the CdSe QDs and ZnO nanowires, effect of the ZnO nanowires length, and the effect of different sensitization times. Figure (3) illustrates the configuration of QDSSCs.

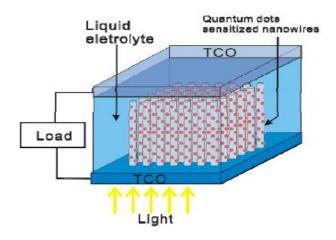


Figure (3), the configuration of QDSSCs.

#### 1.3 Nanomaterials Synthesis

There are two methods for nanomaterials preparation namely "Bottom-Up and Top-Dawn" methods. In the Bottom-Up method atoms, ions, and molecules are deposited into the growth surface one after another like in colloidal synthesis and electrochemical deposition. While in the Top-Dawn method the growth surface is etched with a certain etching solution like in the lithography. In general the Bottom-Up method gives a nanomaterial with fewer defects than the Top-Dawn method this is due to the Top-Dawn method like lithography can make a crystallographic damage to the substrate [1].

#### 2. Theory

#### 2.1 Semiconductors

A semiconductor is a substance that can conduct electricity and its electrical conductivity is intermediate between metals and insulators. The semiconductor material can be a single material like silicon (group IV), or combination between groups III-V (called III-V semiconductors like GaAs), or combination between group II-VI (called II-VI semiconductors like CdSe). Semiconductor materials have a lot of modern applications like diodes, transistors, lasers, and solar cells which is our topic [8].

A semiconductor structure is composed of individual atoms that held together in a periodic structure to form a crystal lattice in which each atom is surrounded by eight electrons through covalent bonds. At very low temperature like at or near to absolute zero temperature all

electrons in the semiconductor structure are strongly bonded together, so, the semiconductor behaves as insulator. However, when electrons absorb enough energy they can escape from their bonds and promote to higher energy state, thus participate in conduction. So, electrons can be at low energy state or at high energy state therefore the semiconductor structure consists of two distinct energy states [10].

#### 2.2 Electron-Hole Pair Generation

A semiconductor is composed of a highest filled band which is called a valence band and a lowest empty band which is called the conduction band separated by band gap. When a photon has energy equal to or higher than the energy difference between the conduction band and the valence band (i.e. band gap), it can be absorbed by an electron causing the electron to be promoted from the valence band to the conduction band. Leaving behind a vacant position in the valence band which makes the covalent bond to move from one electron to another through the crystal lattice which is considered as a positive particle called a hole. This electron-hole pair is called an exciton and the distance between the electron and the hole is defined as the Exciton Bohr Radius"  $a_B$ ". The number of electrons in the conduction band or holes in the valence band (number of carriers) is affected by the band gap of the semiconductor material and the temperature. When the band gap is large, the number of electrons that can be promoted to the conduction band is low and vice versa. While if we increase the semiconductor material temperature the number of promoted electrons increases.

#### 2.3 Recombination Process

The electron in the conduction band is in unstable state and needs to loss its gained energy to return to its original state and to do so it will recombine with the created hole in the valence band in a process called recombination [8].

#### 2.4 Photovoltaic Effect

The photon spectrum coming from the sun consists of a range of energy. If the photon energy is greater than the energy difference between the valence band and the conduction band of a semiconductor material, then the electrons in the valence band will excite and promoted to the conduction band. This process creates a voltage or electric current in the exposed material due to the transfer of electrons between bands, resulting in the creation of a voltage between two electrodes. This process is known as the photovoltaic effect that was discovered by Becquerel in 1839[8]. The photon energy can be calculated from the following formula [2],

$$E = hc/\lambda$$
 (1)

where the photon energy E, is inversely proportional to the wavelength  $\lambda$ , of the incident light, h is Planck's constant and c is the speed of light.

#### 2.5 Quantum Confinement In Semiconductors

As stated, after excitation of the electron an electron-hole pair is formed and there are attractive coulomb interactions between the electron-hole pair. So, the Wannier exciton is formed which is a state similar to the hydrogen atom and can be described by a two particle Hamiltonian. The Bohr radius,  $a_B$ , for the bulk exciton is given by the following formula [2].

$$a_B = \frac{\hbar^2 \varepsilon}{e^2} \left[ \frac{1}{m_e^*} + \frac{1}{m_h^*} \right] \tag{2}$$

where  $m_e^*$  and  $m_h^*$  are the effective masses of the electrons and holes respectively, and  $\epsilon$  is the dielectric constant.

If the nanostructure like quantum dot has a radius which is smaller than the exciton Bohr radius  $a_B$ , then the electrons crowding and according to the Pauli Exclusion Principle this will lead to splitting of continuous energy bands into discrete levels as in figure (4). The effect of the quantum dot size on the first excitonic transition energy E(R), can be observed from the following relation [2].

$$E(R) - E_g = \frac{\hbar^2 \pi^2}{2R^2} \left[ \frac{1}{m_e^*} + \frac{1}{m_h^*} \right] - \frac{1.8e^2}{\epsilon R}$$
 (3)

where  $E_g$  is the bandgap energy, and R is the radius of the particle.

From equation (3), the band gap of the quantum dot increases with the decrease of the particle size due to the quantum confinement effect. If the quantum dot has a radius which is smaller than the exciton Bohr radius, then it will be in the strong confinement regime. Figure (4) describes the energy levels diagram for bulk semiconductor and quantum dot.

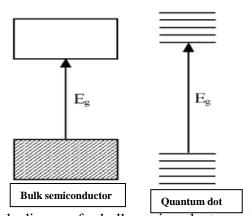


Figure (4), energy levels diagram for bulk semiconductor and quantum dot [5].

#### 3. Experimental Section

#### 3.1 Materials

All chemicals were purchased from Sigma Aldrich. For the preparation and purification of CdSe quantum dots the chemicals used were Cadmium Oxide (CdO 99.5%), Selenium Powder (> 99.5), Oleic Acid (> 99%), Trioctylphosphine (TOP > 90%), also 1-Octadecene ( 90%), Hexane (HPLC,97%), Methanol (HPLC,99.9%), Acetone (HPLC,99.8%), and Toluene (HPLC,99.9%) as solvents. For ligand exchange the chemicals used were 3mercaptoproponic acid (3-MPA ≥99%), 2-mercaptoproponic acid (2-MPA ≥95%), and Tetramethylammoniumhydroxide (TMAOH, 25% wt. in methanol). For the synthesis of ZnO precursors used were zinc nitrate hexahydrate hexamethylenetetramine (>99%). For the fabrication of solar cell, fluorine-doped tin-oxide conducting glass plates (FTO), FTO coated with 200Å Platinum works as a cathode, and thermal-plastic film 25  $\mu m$  all were purchased from Solaronix.

#### 3.2 Preparation of the Photoanode

#### 3.2.1 CdSe Quantum Dots Synthesis

CdSe quantum dots capped with oleic acid can be synthesized by the hot-injection method [3]. In the preparation of CdSe quantum dots, the Cd<sup>2+</sup> source solution was prepared according to the following procedure. In a three necked flask, 0.51 gm CdO, 70 ml 1-octadecene, and 5.54 gm oleic acid were mixed together at temperature of 180 °C under N<sub>2</sub> atmosphere. While the Se<sup>2-</sup> source solution was prepared as the following, 0.1 gm selenium powder dissolved in 10ml 1-octadecene, and after fifteen minutes 0.5 gm trioctylphosphine was added with stirring for one hour. When the Cd<sup>2+</sup> precursor solution appear to be clear, the Se<sup>2-</sup> precursor solution was quickly injected to it, the temperature of the Cd<sup>2+</sup> precursor solution is raised to 200 °C, and after two minutes the reaction was stopped to get the CdSe quantum dots with size of 2.9 nm as described in figure (5).

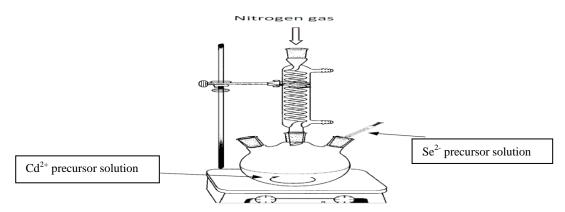


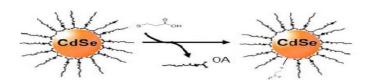
Figure (5), the experimental setup for CdSe QD synthesis.

After synthesis of CdSe quantum dots, a mixture of acetone and methanol was used to precipitate the CdSe QDs, and then dissolved in toluene after centrifugation.

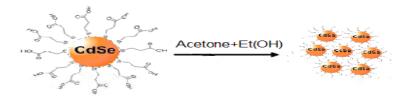
#### 3.2.2 Ligand Exchange

The obtained CdSe quantum dots are capped with oleic acid which is a mono-functional compound. And in order to sensitize the CdSe QDs into the ZnO nanowires structure a bifunctional compound must be used. In this work, two ligands were used 3-MPA and 2-MPA all have the same procedure in ligand exchange. For 3-MPA, 1 ml CdSe QDs capped with oleic acid was mixed with 0.1 ml 3-MPA and 1 ml acetone with stirring for 30 minutes. After that 0.5 ml ethanol was added and then wait for another 15 minutes. Centrifuge with a speed of 3500 r.p.m for 5 minutes then, dry the resulting powder with N<sub>2</sub> gas. Dissolve in 10 ml ethanol and use the shaker and ultrasonic to disperse it. Finally, a few drops of TMAOH were added until a clear solution was obtained as described in figure (6).

a) Exchange with bi-functional linker molecule containing S-H group.



b) Extraction of QDs.



c) Obtaining of a monodisperse QDs.

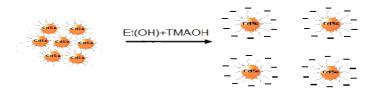


Figure (6), steps of ligand exchange

#### 3.2.3 ZnO Nanowires Synthesis

ZnO nanowires (NWs) were synthesized according to the hydrothermal method [4]. Using a spin coater at speed of 1000 r.p.m for 30 seconds a thin layer of a seed solution containing 50 mM solution zinc acetate dehydrate and ethanolamine in 2-methoxyethanol was coated into the fluorine-doped tin-oxide (FTO) conducting glass surface. Then sintered in the oven at 350 °C for 30 minutes. After that using a water bath at 92.5 °C the ZnO nanowires were grown by adding an aqueous solution containing 20 mM HTMA and zinc nitrate to the seeded FTO substrate for four hours then refresh the solution again for another four hours. Finally

after the growth, the samples were rinsed with de-ionized water and dried at 100 °C. Following this procedure, the obtained ZnO nanowires have  $2\sim3$  µm in length and  $40\sim60$  nm in diameter as indicated by SEM, figure (7).

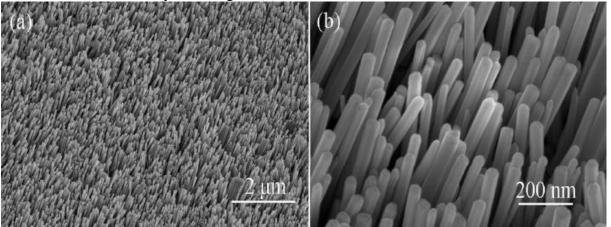


Figure (7), SEM image of ZnO nanowires prepared by hydrothermal method.

#### 3.2.4 CdSe QDs on ZnO Nanowires Sensitization

The synthesized ZnO nanowires were heated at 70  $^{\circ}$ C for 10 minutes then, immersed directly into the QDs solution and kept in a dark place for different sensitized times 1 and 12 hours. After the sensitization process the samples were rinsed with ethanol and dried in  $N_2$  gas atmosphere.

#### 3.3 Fabrication of QDSSCs

After preparation of the photoanode, the photoanode was scratched to the required area of about  $0.250~\text{cm}^2$ . The electrolyte solution was prepared as 1M Na<sub>2</sub>S and 1M S in Milli-Q water. Then, by using the FTO glass coated with 200Å Platinum (cathode) and thermal-plastic film with thickness of 25  $\mu$ m, the QDSSCs was fabricated as in figure (8).

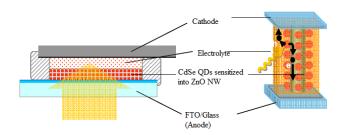


Figure 8, schematic configuration of the QDSSCs [12].

#### 4. Characterization

The UV-Vis absorption spectra of the CdSe QDs solution were measured by using Agilent spectrophotometer in a wavelength range of 200-1100 nm. The solar cells were characterized with a Keithley 2400 source meter under simulated AM 1.5 solar illumination (100 mW/cm<sup>2</sup>). IPCE was measured under short-circuit condition with Oriel Merlin digital lock-in radiometry under illumination of monochromatic light.

#### 5. Results and Discussion

#### 5.1 Effect of Linker Molecule

Two linker molecules were used; 3- mercaptoproponic acid (3-MPA) and 2-mercaptoproponic acid (2-MPA) to link the CdSe QDs onto ZnO nanowires. Figure (9), shows the effect of the linker molecule on the current-voltage (I-V) curve for 12 hours ZnO nanowires growth and 12 hours sensitization time.

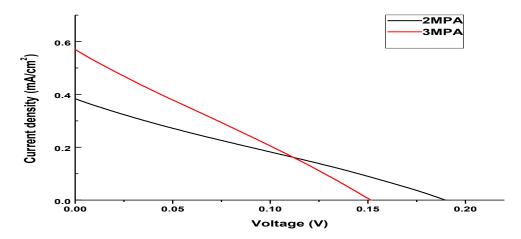


Figure (9), the current-voltage (I-V) curve for 3-MPA and 2-MPA linker molecules.

From figure 9, the higher value for the open circuit voltage ( $V_{oc}$ ) was obtained for 2-MPA linker molecule and appears at 0.189 V. While the higher value for the short circuit current density ( $I_{sc}$ ) was obtained for the 3-MPA linker molecule which appears at 0.566 mA/cm<sup>2</sup>. Table 1, summarizes the results that were obtained for the 3-MPA and 2-MPA linker molecules.

Table (1), Summarizes the results obtained from the I-V curve by using these two linker molecules to link the CdSe QDs onto ZnO nanowires where the measured parameters were, the open circuit voltage ( $V_{oc}$ ), short circuit current density ( $I_{sc}$ ), the fill factor (F.F.), and the effeciency ( $\eta$ ) for a cell area of 0.250 cm<sup>2</sup> and visible light intensity of 1000 W/m<sup>2</sup>.

Linker molecule	V <sub>oc</sub> (V)	$I_{sc}$ (mA/cm <sup>2</sup> )	F.F.	η (%)
3-MPA	0.152	0.566	0.257	0.022
2-MPA	0.189	0.382	0.252	0.018

Table (1), results obtained for different linker molecules.

From table 1, there is no significant difference in the fill factor for the linker molecules. But the higher value for the open circuit voltage ( $V_{oc}$ ) was 0.189 V which belongs to the 2-MPA linker molecule, while the lower one was 0.152 V which belongs to the 3-MPA linker molecule. And the short circuit current density ( $I_{sc}$ ) for 3-MPA was 0.566 mA/cm<sup>2</sup> which is higher than that of 2-MPA which was 0.382 mA/cm<sup>2</sup>. And the higher value for the solar cell efficiency was obtained for 3-MPA which was 0.022 %. Also from the IPCE measurements for 3-MPA and 2-MPA linker molecules, figure 10, it is evidence that the short circuit current density for 3-MPA is higher than that for 2-MPA.

Figure (10), shows the incident photon to current conversion efficiency (IPCE) for the 3-MPA and 2-MPA linker molecules and the absorption spectrum for CdSe QDs with 3-MPA in solution.

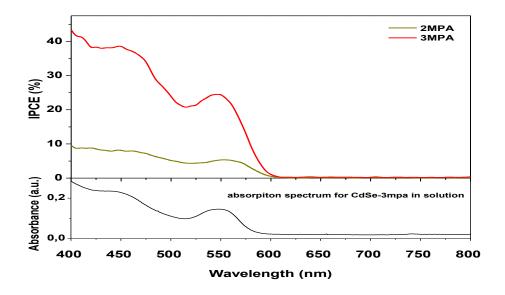


Figure (10), IPCE spectra for the solar cell using 3-MPA and 2-MPA linker molecules.

The incident photon to current conversion efficiency (IPCE) was evaluated by changing the incident light wavelength and determining the corresponding short circuit current through the following relation,

IPCE % = 
$$(1240/\lambda)$$
 ( $I_{sc}/I_{inc}$ ) 100

From figure 10, the photoanode response is below 600 nm which confirms that the source of the current is the CdSe QDs [9]. The peak for 3-MPA in the IPCE spectra appears at about 550 nm that match with the first excitonic transition peak in the absorption spectrum for CdSe in ethanol solution. The first excitonic state in the IPCE spectra for 3-MPA, and 2-MPA were

24.5%, and 5.34% respectively at wavelength of 550 nm which indicate to the higher short circuit current value obtained for 3-MPA.

The higher solar cell efficiency for using 3-MPA linker molecule than 2-MPA linker molecule can be attributed to the presence of methyl group in 2-MPA linker molecule which is an electron donating group (figure 11). And according to the inductive effect this methyl group decreases the rate of electron injection from the CdSe QDs into ZnO NWs, resulting in lower short circuit current and then lower solar cell efficiency.

Figure 11, chemical structures of 3-MPA and 2-MPA.

#### 5.2 Effect of ZnO nanowires growth time

Two nanowires growth times were used in the synthesis of ZnO nanowires which were 4 hours (about 600 nm ZnO NWs length) and 8 hours (about 1 $\mu$ m ZnO NWs length) with using the 3-MPA as the linker molecule between the CdSe QDs and ZnO nanowires. Figure (12), shows the current-voltage (I-V) curve for two different nanowires growth times.

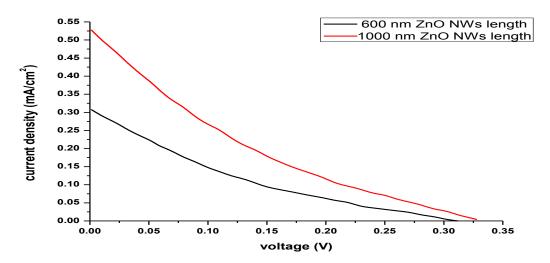


Figure (12), the current-voltage (I-V) curve for 4h and 8h ZnO nanowires growth times.

From figure 12, the higher results for the open circuit voltage ( $V_{oc}$ ) and short circuit current density ( $I_{sc}$ ) obtained for 1000 nm ZnO NWs length which were 0.330 V and 0.528 mA/cm<sup>2</sup> respectively. Table 2, summarizes the results that obtained for the two growth times.

Table (2), Summarizes the results obtained from the I-V curve by using the two different ZnO nanowires growth times for a cell area of 0.250 cm<sup>2</sup> and visible light intensity of 1000 W/m<sup>2</sup>.

ZnO NWs length	$V_{oc}(V)$	$I_{sc}$ (mA/cm <sup>2</sup> )	F.F.	η (%)
600 nm	0.312	0.308	0.158	0.0152
1000 nm	0.330	0.528	0.159	0.0277

Table (2), results obtained for different ZnO nanowires growth times.

From table 2, there is also no significant difference in the fill factor for the two ZnO NW growth times. But as stated, the higher values for the open circuit voltage ( $V_{oc}$ ) and short circuit current density ( $I_{sc}$ ) were obtained for 8 hours ZnO nanowires growth time. And the higher efficiency value was obtained for 8 hours ZnO nanowires growth time which was 0.0277 %.

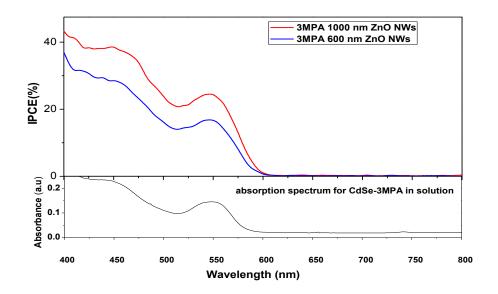


Figure (13), the IPCE for two different ZnO nanowires lengths.

Figure (13), shows the incident photon to current conversion efficiency (IPCE) for other two different ZnO nanowires growth times 4 and 8 hours with the absorption spectrum for CdSe QDs with 3-MPA in solution.

From figure 13, the peaks for 3-MPA with 4 and 8 hours NW growth time in the IPCE spectra appears at about 550 nm that match with the excitonic transition peak in the absorption spectrum for CdSe-3MPA in ethanol solution. The IPCE spectra for 3-MPA with 8 hours NWs growth time was 24.5% which is higher than that for 3-MPA with 4 hours NW growth time which was 16.8% at wavelength of 550 nm in an indication that the short circuit current ( $I_{sc}$ ) for 8 hours ZnO NWs growth time is higher than that for 4 hours ZnO growth time.

The effect of increasing the solar cell efficiency with increasing the length of ZnO NWs is due to with increasing the length of the nanowires, the surface area of the NWs increases which means more CdSe QDs loaded onto the ZnO nanowires. Which result in increasing the numbers of electrons sources (QDs) and hence promoting the solar cell efficiency.

#### 5.3 Effect of the sensitization time

Two sensitization times were used one and twelve hours with 3-MPA as the linker molecule with 600 nm ZnO NWs length. Figure (14), shows the current-voltage (I-V) curve for the two different sensitization times.

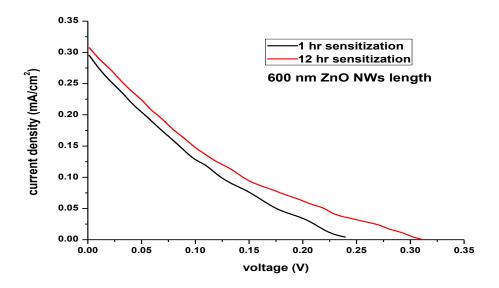


Figure (14), the current-voltage (I-V) curve for the two different sensitization times.

From figure 14, the higher values for the open circuit voltage ( $V_{oc}$ ) and the short circuit current density ( $I_{sc}$ ) were obtained with 12 hour sensitization time which were 0.312 V and 0.308 mA/cm<sup>2</sup> respectively. Table 3, summarizes the results that were obtained for the two sensitization times.

Table (3), Summarizes the results obtained from the I-V curve by using the two different sensitization times for a cell area of  $0.250 \text{ cm}^2$  and visible light intensity of  $1000 \text{ W/m}^2$ .

Sensitization time	$V_{oc}(V)$	$I_{sc} (mA/cm^2)$	F.F.	η (%)
1 hr	0.245	0.296	0.182	0.013
12 hr	0.312	0.308	0.158	0.015

Table (3), results obtained for different sensitization times.

From table 3, there are noticeable differences in the values of the open circuit voltage ( $V_{oc}$ ) and the short circuit current density ( $I_{sc}$ ) for the two sensitization times. The values of ( $V_{oc}$ ) and ( $I_{sc}$ ) for 12 hour sensitization time were much higher than that for one hours sensitization time which were 0.312 V, 0.308 mA/cm<sup>2</sup> and 0.245 V, 0.296 mA/cm<sup>2</sup>. Thus, obtaining the higher value for the solar cell efficiency which was 0.015 % for the 12 hours sensitization time.

Figure (15), shows the incident photon to current conversion efficiency (IPCE) for two different sensitization times with 600 nm ZnO NWs length and the absorption spectrum for CdSe QDs with 3-MPA in solution.

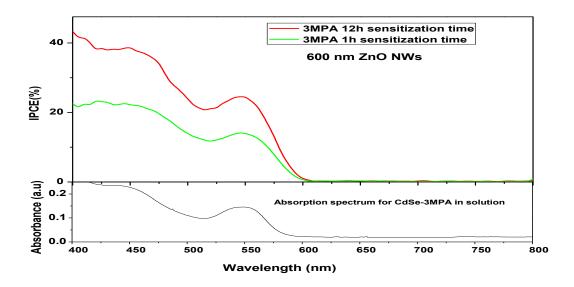


Figure (15), the IPCE for two different sensitization times.

From figure 15, the peaks for 3-MPA with one and 12 hours sensitization time in the IPCE spectra appears at about 550 nm that match with the excitonic transition peak in the absorption spectrum for CdSe-3MPA in ethanol solution. The IPCE spectra for 3-MPA with 12 hours sensitization time was 24.5% which is higher than that for 3-MPA with one hour sensitization time 14% at wavelength of 550 nm.

By increasing the sensitization time, more CdSe QDs were loaded and adsorbed onto the ZnO nanowires. Resulting in better coverage of the QDs and avoiding the back recombination between ZnO and the electrolyte.

Table 4, shows a comparison between our work and other groups work for QDs based solar cell systems and the related efficiency obtained.

Photoanode		alaatralyta	V (V)	$I_{sc}$		Reference	
QDs	NW/NP	method	electrolyte	electrolyte $V_{oc}(V)$	(mA/cm <sup>2</sup> )	η	Reference
CdSe 3-4 nm	ZnO NW 12 μm	Linker molecule MPA	$I_3^-/I^-$	0.5-0.6	1-2	IQE=50- 60%	Kurtis S,nano let.vol.7, No 6, 2007.p1793-1798
CdSe 2.8 nm	TiO <sub>2</sub> NP	Linker molecule cysteine	Na <sub>2</sub> S/NaOH/S	0.490	1.87	0.4%	Mora-Sero et al. nanotech.19(2008)424007
CdSe	TiO <sub>2</sub> NP 5 μm	- CBD 10C/600min	Na <sub>2</sub> S/S	0.600	7.56	2.04%	71: 71 HEEF 2010
3-4 nm	ZnO NW 5 μm		Na <sub>2</sub> S/S	0.812	4.44	1.63%	Zhi Zheng, IEEE,2010 978-1-4244-5892-9/10
CdSe 2.9 nm	ZnO NW 1 μm	Linker molecule TGA	Na <sub>2</sub> S/S	0.330	0.528	0.028	Ours

Table 4, comparison between different QDs based solar cells efficiencies.

Table 4, shows that QDSSCs still needs much more effort in an attempt to increase its efficiency and studying other parameters like electrolytic solution or the chemical stability of ZnO NWs in different electrolytic solutions.

#### 6. Conclusion

Quantum dots (QDs) enable us from harvesting solar light in both the visible and infrared regions. A lot of parameters need to studied and optimized in order to increase the QDSSCs efficiency. We studied the effect of linker molecule, the length of the ZnO nanowires, and different sensitization times. We found that the length of the linker molecule affect the solar cell efficiency, also by increasing the ZnO NWs length the solar cell efficiency increased. Finally with increasing the sensitization time from one hour to twelve hours this will increase the solar cell efficiency also.

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