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Maximum Absorption in Quantum Dot Solar Cell with Hyperbolic Band Model

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Abstract: In recent times a steady decrease in fossil fuel calls for urgent replacement of conventional energy sources. Thus solar cells that utilizes sun light as its source of energy often considered as one of the best options available. But solar cells have certain limitations. A photon of energy ($=E_g$ eV) can excite only one electron from valance band to conduction band but if photon has energy ($h\nu$) greater than the band gap value (E_g) of the material, then excess energy will generate heat instead of generating extra electron-hole pairs (EHPs). Thus the overall efficiency is limited and it is known as Schockly and Queisser limit, which gives the maximum efficiency at 31%. Hence recently semiconductor quantum dots have been incorporated in them to overcome this low efficiency problem. In this paper, we give an introduction to Quantum Dot Solar Cells (QDSCs) and its working principles at the beginning. The quantum effects found in QDSCs like quantum confinement and MEG is also explained. The relation between absorption coefficient (α) and wavelength (λ) is established and α v/s λ curve is plotted for different materials (GaAs, InP, InSb, CdSe and ZnS). The wavelength at maximum absorption peak is used to determine the corresponding QD band gap. Finally, using the QD band gap value corresponding to maximum absorption, the QD sizes for the considered materials are determined using Hyperbolic Band Model.

Keywords: Solar cell; quantum dot; quantum dot solar cell; quantum confinement; electron-hole pairs (EHPs); hyperbolic band model.

1 INTRODUCTION

Solar cell is a device that converts light into electricity. There are mainly two steps of operation of solar cell are-photo generation of charge carriers (electron and holes) in a light absorbing material. And the separation of charge carriers is to a conductive contact that will transmit electricity [1]. But solar cells have certain limitations. A photon of energy ($=E_g$ eV) can excite only one electron from valance band to conduction band. But if photon has energy($h\nu$) greater than the band gap value (E_g) of the material , then excess energy will generate heat instead of generating extra electron-hole pairs(EHPs). Thus the overall efficiency is limited and it is known as Shockly and Queisser limit which limits the maximum efficiency at 31%. Hence recently semiconductor quantum dots have been incorporated in them to overcome this low efficiency problem.

Quantum dots (QDs) are three dimensions confined system whose size is ideally not greater than 100nm. Due to this small dimension the energy levels in QDs get splitted (called quantization effect) into discrete quantized energy levels. The properties of Quantum dot include increase in bandgap (E_g) of the material. In bulk semiconductor solar cell, high energy EHPs converts their excess energy to heat energy through phonon emission. The electron generated due to light absorption loses energy while moving within the crystal lattice. The time scale of relaxation in bulk semiconductors is of the order of sub picosecond [2]. But in QD the generated EHPs are bound to each other or, correlated to each other due to strong quantum confinement. In other words we can say that as in QDs the motion of electrons is confined in all three directions hence energy loss due to phonon emission is less. Hence power conversion efficiency is high.

QDSC is a derivative of dye sensitized solar cell [3]. Here low band gap semiconductor QDs like CdS, CdSe, PbS, etc are used, as low band gap materials absorbs more photons, as the light absorbing material in solar cells. QDSCs provides several advantages over conventional solar cells like a tunable band gap (E_g increases as size of QD decreases also QDSCs have a longer extinction coefficient and a higher stability towards water and oxygen. Multiple excitons generation effect (MEG) is another very important property of QDSCs that helps to increase the overall efficiency of QDSC. Theoretical conversion efficiency of QDSC is 42%, which is about 11% more than that of the available photovoltaic solar cells [4].

2 STRUCTURE AND WORKING PRINCIPLES OF QDSC

Fig. 1(a) shows the structure of a typical $TiO_2 - ZnO$ QDSC. It consists of a wide band gap mesoporous oxide film (a photo electrode like TiO_2 or ZnO , QDs (sensitizer), an electrolyte and a counter electrode. Steps of operation are as follows: firstly, the QD absorbs photon gets energized and it injects charge into the oxide (TiO_2). On the next step the TiO_2 generates excitons that are separated as electrons and holes at the junction of QD and oxide. After the electrons and holes gets separate then the electrons jumps to oxide i.e the collecting electrode surface, while holes are transferred to the redox couple. The final step includes recombination of electron from QD and oxidized form of redox couple and interfacial recombination of electron from TiO_2 oxidized form of redox couple. Thus the whole path of current flow is completed as shown in Fig. 1(b).

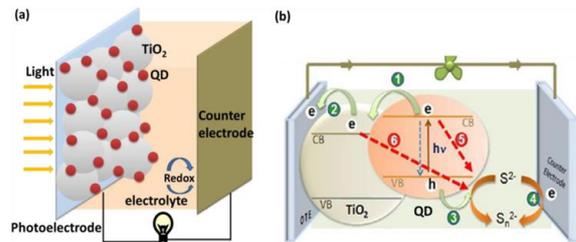


Fig. 1(a). QDSC structure and (b) Current path in a QDSC.

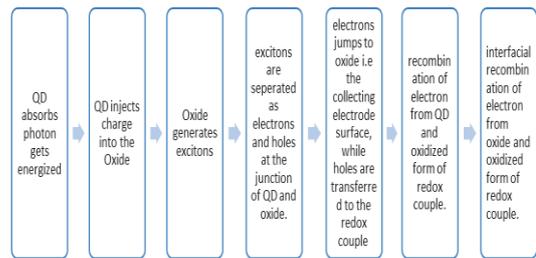


Fig. 2. Steps of operation of a QDSC.

2.1 Main Sections of QDSC

Photodiode: For the QDSCs, the photoelectrodes are generally either adsorbed or deposited in form of a monolayer of the QDs on the surfaces of a wide-bandgap semiconducting photoelectrode. The films act as conducting medium for the transport electrons toward collection electrode [the transparent conducting oxide (Tco)]. When sunlight falls on it, electron-hole pairs are generated in the QDs, which results in injection of electrons from CB, excitonic states, or trap states of the QDs into the CB of the wide band gap photoelectrode, while the oxidized QDs are recharged by the redox electrolyte. Theoretically,

electrons moves faster if the photoelectrode has a higher degree of order [like nanowires and nanotubes as shown in Fig. 3(b)-(d)], than that made of a nanoparticles network [8]. Thus using a nanowire or nano tube can achieve a high photovoltaic efficiency. But it is also to be noted that faster electron transport can also reduce the recombination process. Thus a balance between recombination and light harvesting is needed to maximize the performance of the QDSCs.

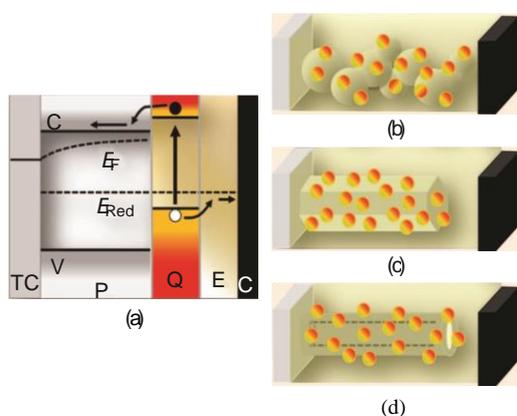


Fig 3(a). A schematic representation of electron generation-injection of typical QDSSCs. The energy band diagram shows the CB and valence band (VB) edges of the wide-bandgap semiconducting photoelectrode, the ground and excited level of the QD, and the redox potential E_{redox} . Upon illumination, electrons are injected from the excited QD state into the wide-band-gap semiconducting photoelectrode, while the oxidized QD is recharged by the redox electrolyte. The different morphologies of photoelectrodes for the QDSSCs are (b) mesoporous, (c) nanorods or nanowires, and (d) nanotubes [8].

Sensitization materials and methods: Semiconductors used as sensitizer material are Cadmium Sulfide (CdS), Cadmium Selenide (CdSe), Cadmium Telluride (CdTe), Copper Indium Di-Sulfide ($CuInS_2$), Lead Sulfide (PbS), Lead Selenide (PbSe), Indium Phosphide (InP), Indium Arsenide (InAs), Silver Sulfide (Ag_2S), Bismuth Sulfide (Bi_2S_3), and Antimony Tri-Sulfide (Sb_2S_3). Especially, CdS, CdSe, and PbS are mostly used in QDSCs [9]. Linker molecules can be used in a sensitization method, the chemical nature of the bi-functional molecular linkers effects the charge separation and power conversion efficiency of the solar cells. After surface modification, the sensitized photoelectrodes are by immersing it into the QDs dispersion solution [10]. The bi-functional molecular linker contains the structure as (COOH)-R-SH, where R is the organic core. The carboxyl group i.e ; COOH is attached to the photoanodes, while the thiol i.e. SH remains free to connect to the QDs shown in Fig. 4. Thus the injection

efficiency of the photoelectrons generated is determined by the linker molecules. It should be noted that in case of directed attachment (DA) as the QDs are attached directly to the surfaces of the photoelectrodes hence the electrons transfer is faster. But in this case there is a possibility of recombination of the photo generated carriers if the sensitization process takes too long.

Two methods are generally used for the in-situ sensitization process, namely, Chemical bath deposition (CBD) and successive ionic layer adsorption and reaction (SILAR). The schematic diagram is shown in Fig. 5. CBD is done by immersing the wide band gap nanostructured electrode into a solution of cationic and anionic precursors [9]. For selenides, Na_2SO_3 is commonly used. In case of SILAR technique, the cationic and anionic precursors are dissolved in two different solutions. The electrode is first dipped into the solution containing the metal cations and then into the second solution containing the anions. The QD size is controlled by the number of deposition cycles. This method is generally used to prepare metal sulfides, but, recently, metal selenides and tellurides have also been prepared by this method [9].

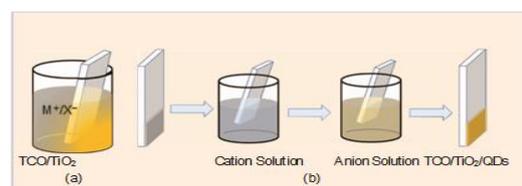


Fig. 5. A schematic illustration of the bench top approaches of depositing a QD suspension on electrode surfaces: (a) CBD and (b) SILAR.

Holes transport media: The most common electrolytes used in the QDSCs are aqueous polysulfide and organic electrolyte with $i2/i3$ -redox couple. The Fe^{3+}/Fe^{2+} and the $Fe(Cn)_{63-}/Fe(Cn)_{64-}$ redox system, both in aqueous solution, have also been tested with CdS based QDSCs. Recently, a cobalt complex redox couple was proposed to employ in the system of CdSe, PbS, and CdS sensitized solar cells [9]. In addition to liquid electrolyte, like spiro-MeOTAD and $CuSCn$, have also been used to replace the liquid electrolyte recently. Long-term sealing of solid-state QDSSCs is much easier compared to solar cells with liquid electrolyte. But, a problem of solid-state hole conductive materials is penetration into the QD-nanostructured film, which limits the thickness of the mesoporous film and can result in incomplete photon absorption. Also the addition of ionic

species to spiro- MeOTAD can have a strong positive impact on the photovoltage [11].

2.2 Quantum Effects in QDSCs

Quantum Confinement Effect in QDSCs

Due to small dimension (comparable to Bohr radius, 1-10nm) effect, the behavior of electron in QDs are different from the corresponding bulk material. This is called Quantum Confinement effect. Few materials have smaller bohr radius like Si (4.2 nm), CdS (3.1 nm), CdSe (6.1 nm), ZnO (2.2 nm). But Bohr radius is large for some semiconductors like PbS (20.4 nm), PbSe (46 nm), InSb (67.5 nm). A larger Bohr radius implies that it is easier to obtain quantum confinement effect. Because of QCE the bandgap energy of QD increases with decrease in particle size. Band gap energy is inversely proportional to square of the radius of QD. As E_g increases more energy needed to be absorbed by QD. Range of optical wavelength in QD is tunable with size. Thus QDSC can absorb desired wavelength. Conduction band gap energy (E_c) of bulk PbS is -4.75 eV which is less than TiO_2 (-4.21 eV). But in a QD made from PbS the value of conduction band increases to -3.7 eV. So when PbS QD is used instead of bulk material, electrons from conduction band can easily transfer from the conduction band of PbS to the conduction band of TiO_2 much more easily. Thus separation of electron and holes at the QD-oxide junction becomes easier, as shown in Fig. 6(a). The variation of band gap energy (E_g) with variation in QD size for PbS is shown in Fig. 6(b) [6].

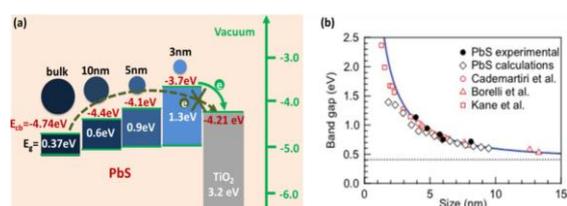


Fig. 6(a). Schematic illustration of the modulation of energy levels of PbS by particle size; and (b) relationship between the PbS E_g and particle size.

Smaller QDs are preferred for QDSCs because of two reasons. Firstly to achieve more QDs is on photo electrode film. And secondly because of the reason that small QDs show higher electron injection rate. But problem of using too small QDs in solar cell is that, as size of QD decreases, band gap increases. So the quantum confinement effect provides a tunable band gap in QDSCs. So as a result of this only higher wavelength (i.e. high energy photons) can be absorbed. Thus the spectrum shifts towards blue. This effect in QDs is termed as BLUE SHIFT. Thus too small QDs can cause too low optical absorption for photo

electrodes. Thus optimization in QD sizes is required for proper operation of QDSCs.

Multiple Exciton Generation (MEG) Effect in QDSCs: MEG is a method to enhance the power efficiency of QDSCs by utilizing the excess energy in the absorbed photons. In general one photon can produce only one EHP. But sometimes one photon can generate multiple excitons. This phenomenon is known as MEG effect. Theoretically the minimum energy required for the photons to generate multiple carrier is $2E_g$ i.e. twice the band gap of the QD. This effect is the reason for increase in power efficiency of QDSCs to 42 % (theoretically) [6]. The MEG effect is also seen in bulk materials. But energy required in case of bulk materials is much higher. The MEG effect can lead to higher efficiency limits if it is developed and improved further. It is preferable to obtain MEG by applying energy as low as possible and value should be as close to twice the band gap ($2E_g$) [7].

In a traditional photon excitation in Fig. 7A [8], one photon can generate only one pair of exciton. The excess photon energy ($\hbar\omega - E_g$) is dissipated as heat via phonon emission and therefore is wasted. In this case, the quantum efficiency (QE) of photon-to exciton conversion is zero below E_g , the energy gap, and is 100% above it [8]. This corresponds to the Shockley Queisser limitation of the maxima quantum efficiency. The number of excitons produced by a single photon is only limited by energy conservation. Photons with energies E_g , $2E_g$, and $3E_g$ produce one, two, and three excitons, respectively. The QE is increased by 100% if photon energy is increased by E_g . When $E_g = 0$ the power conversion efficiency approaches to 100% [8, 9].

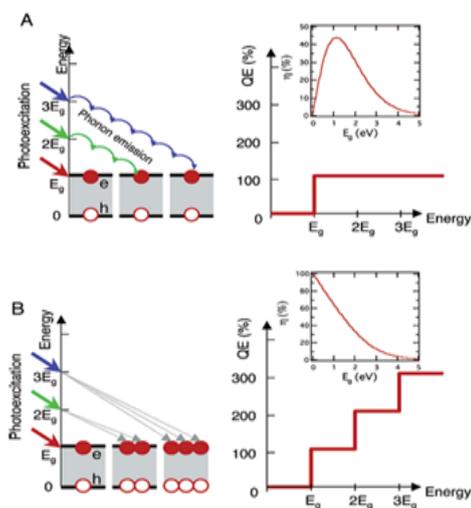


Fig. 7. (a) Traditional schematic of solar cell; (b) Multiple excitons are generated with absorption of a single phonon.

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3 CALCULATION OF QD SIZE FOR MAXIMUM ABSORPTION

3.1 Absorption Coefficient in QDSC

The light absorbing property of any material is measured in terms of its co-efficient of absorption denoted by α . It is always preferred to use material with high light absorbing property for a better performance of solar cells. The co-efficient of absorption in a material can be defined as A measure of the rate in decrease of electromagnetic radiation (here light) as it passes through a given substance; the fraction of incident radiant energy absorbed per unit mass or thickness of an absorber [10]. The units of α is per length (cm-1). The mathematical formula for absorption coefficient is

$$\alpha(\eta\omega) = \frac{\pi e^2 \eta}{\epsilon_0 n_0 c m_0^2 V_{av}} \times \frac{1}{\eta\omega} \sum_{\vec{f}} |a.P_{\vec{f}}| N(\eta\omega) \quad (1)$$

Here, V_{av} is the Average Volume, $P_{\vec{f}}$ is 2D momentum matrix element, a is polarization of light, $N(\hbar\omega)$ is the density of states. Now,

$$(a * p)_{if}^2 = \frac{2}{3} p^2_{cv} \quad (2)$$

And

$$\frac{p^2_{cv}}{m_o} = 20 \sim 24eV \quad (3)$$

Considering this values equation (1) simplifies to:

$$\alpha(E) = \frac{\pi q^2 \eta}{2n_r c \epsilon_0 m_0} \times 23eV \times \frac{N_{cv}(E)}{E \times V_{avg}} \times \frac{2}{3} \quad (4)$$

Here $N_{cv}(E)$ is given by:

$$N_{cv}(\eta\omega) = \frac{\sqrt{2}(m_r^*)^{3/2}(\eta\omega - E_g)^{1/2}}{\pi^2 \eta^3} \quad (5)$$

Putting the values of constants we obtain [22]:

$$\alpha(\eta\omega) \approx (3.5 \pm 0.5) \times 10^6 \left(\frac{mr^*}{m_0}\right)^{\frac{3}{2}} \times \frac{\sqrt{(\eta\omega - E_g)}}{\eta\omega V_{avg}} \quad (6)$$

4 WAVELENGTH AND BANDGAP RELATION

From the above plots the value of λ for maximum absorption i.e the peak values is obtained and the corresponding nano material band gap (E_{gn}) is obtained as:

$$E_{gn} = \frac{hc}{\lambda} \quad (7)$$

This relation simplifies further if the wavelength value is calculated in micro mater (μm) and band gap is given in electron volts (eV):

$$E_{gn}(eV) = \frac{1.24}{\lambda(\mu m)} \quad (8)$$

Table 1. List of materials considered with their required properties.

Material	Electron mass (m_e) kg	Hole mass (m_h) kg	Band gap at 300K (E_g)	λ for peak α value (nm)	QD Bandgap (eV)
GaAs	0.067	0.082	1.43 eV	450	2.7
InP	0.073	0.64	1.35 eV	500	2.48
InSb	0.014	0.4	0.17eV	3800	0.326
CdSe	0.13	0.45	1.74eV	350	3.5
ZnS	0.39	0.23	3.54eV	158	7.8

5 THE HYPERBOLIC BAND MODEL

The particle size of the CdSe quantum dots can be assessed from the absorption wavelength of the UV-vis spectra by using hyperbolic band model [11]. The Hyperbolic Band Model provides the relationship between the QD particle size and Bandgap. The relation is given as:

$$R = \sqrt{\frac{2\pi^2 \hbar^2 E_{gb}}{m^* (E_{gn}^2 - E_{gb}^2)}} \quad (9)$$

Where, R = quantum dot radius ($2R$ is the diameter and hence, indicates particle size), E_{gb} = bulk band gap, E_{gn} = quantum dot band gap (calculated from the absorption peak), \hbar = Planck's constant, m^* = effective mass of specimen.

6 RESULT ANALYSIS

The absorption coefficient (α) with respect to wavelength (λ) for different material are shown in given bellow:

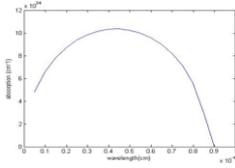


Fig. 8. α v/s λ plot for GaAs.

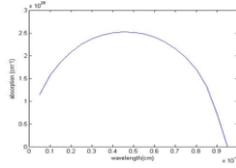


Fig. 9. α v/s λ plot for InP.

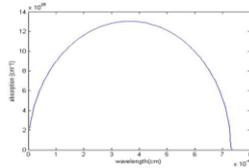


Fig. 10. α v/s λ plot for InSb.

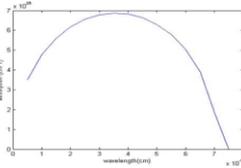


Fig. 11. α v/s λ plot for CdSe

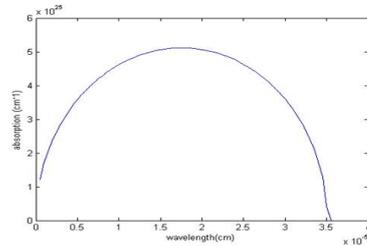


Fig. 12. α v/s λ plot for ZnS.

QD radius v/s QD-band gap plots for different materials based on hyperbolic model are shown below:

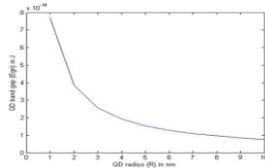


Fig. 13. E_{gn} v/s R for GaAs.

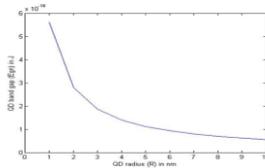


Fig. 14. E_{gn} v/s R for InP.

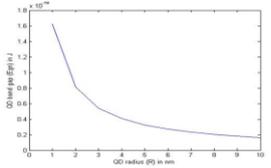


Fig. 15. E_{gn} v/s R for InSb

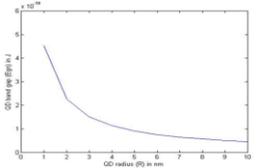


Fig. 16. E_{gn} v/s R for CdSe.

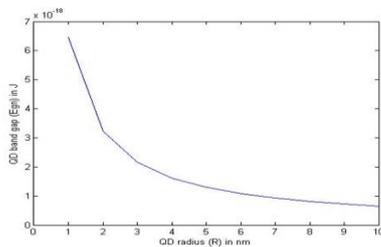


Fig. 17. E_{gn} v/s R for ZnS.

The above plots show that this model gives result consistent to the relation: $E_g \propto r^{-1/2}$. Exponential decrease in QD band gap with increase in QD size is evident from the curves.

Hence can be used to calculate the QD radius (R) corresponding to the value of QD band gap value (E_{gn}).

The QD sizes required for obtaining maximum absorption for different materials as calculated from the hyperbolic band model is given below in Table 2.

Table 2. QD radius as obtained from Hyperbolic Model relation.

QD Material	QD radius for maximum absorption (nm)
GaAs	50.91
InP	36.38
InSb	97.78
CdSe	27.5
ZnS	18.71

7 CONCLUSIONS

Thus it is concluded that using absorption formula and hyperbolic band model the QD size in QDSC for obtaining maximum photon absorption can be determined theoretically. But in this work practical effects like inter sub band tunneling, auger recombination, the effect of optimum band filling and other practical effects is not taken into account. Thus this work needs to be tested in practical QDSCs and verified with practical data.

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