Theoretical Models and Technologies for Quantum Dots Based Third Generation Solar Cells

H. I. Ikeri, A. I. Onyia, V. M. Adokor

Abstract— **Theoretical models and technologies for efficient design of high performance quantum dots (QDs) based solar cells are presented. The obtained models indicate that QDs exhibit bandgap tunability, discrete electronic state and large surface area to volume ratio due to the confinement of photo excited carriers which permit the engineering of their optical and electro-optical responses. These novel properties expanded dramatically absorption of light over a broad spectrum of solar radiation wavelengths in contrary to bulk materials and have paved way for state–of–the-art solar cell technological design architectures via intermediate band, multiple exciton generation and multiple junction solar cells. These mechanisms have been shown to drive quantitative gains in the efficiency of energy conversion scenarios to surpass the Shockley and Quisser limit imposed on conventional cells. Intermediate band solar cell allows for the sub bandgap photons absorption that are loss in the conventional device, thus photon energy less than the fundamental band gap energy can be used to promote charge carriers through the artificially generated optical transition pathways. The multiple exciton generation allows for absorption and utilization of supra bandgap photons that would otherwise be dissipative losses to generate more carriers thereby minimizing the hot carrier thermerlization that characterized the conventional device. Multiple junction solar cells enhance absorption of solar energies over a wide range for full spectrum solar cell through stacking of QDs of appropriate sizes. These exciting advances produce significant increase in solar to electricity conversion efficiencies in the form of increased photo generated currents and voltages.**

***Index Terms*— quantum dot, intermediate band, multiple junction, multi exciton generation, quantum confinement, solar cells, solar energy.**

I. INTRODUCTION

The growing concerns over the depletion of fossil fuels and the associated carbon emissions have prompted demands for renewable, sustainable and green energy. It is now widely accepted that climate change is greatly influenced by the increase in the atmospheric concentrations of greenhouse gases such as CO_2, which is a by-product of fossil fuels exploitation responsible for the global warming. Renewable energy technology is proposed as an alternative solution to realize the required green energy sufficient enough to satisfy the inevitable rise in global energy demand that is completely devoid of greenhouse gases. Solar energy has emerged among all other renewable energy sources as the most viable energy source to meet this goal due to the sheer abundance of solar radiation reaching the earth's surface. However, the solar energy spectrum is broad and contains photons with energies ranging from ultraviolet through visible to the infra-red as shown in Figure 1 (Ikeri and Onyia, 2019).

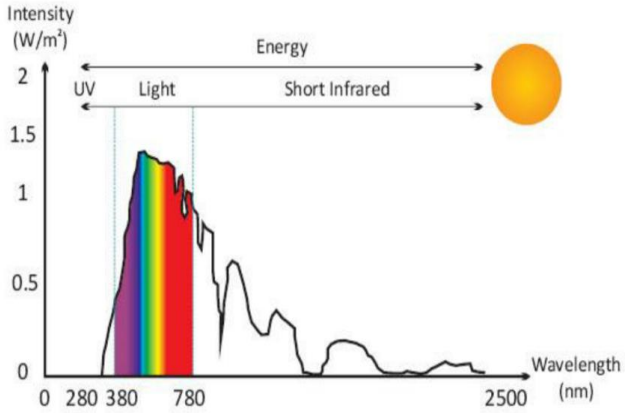

Figure 1: The Solar Energy Distribution Spectrum (Ikeri and Onyia, 2019).

A solar cell is a device that converts the solar energy into electrical energy through photovoltaic PV effect without moving parts or polluting by-products. The photovoltaic effect is the generation of power from electromagnetic radiation separating positive and negative charge carriers in an absorbing material which is capable of producing a current across an external circuit. A better understanding of the processes that govern the operation of solar cells is crucial and has significant technological implication on the power conversion efficiencies. Solar cells transform the solar energy into usable electrical energy using N-type and P-type semiconductor material. When solar radiation incident on these materials electrons are knock loose from their atoms allowing them to flow through the material to produce electricity as shown in Figure 2 (Jabbour and Doderer, 2010).

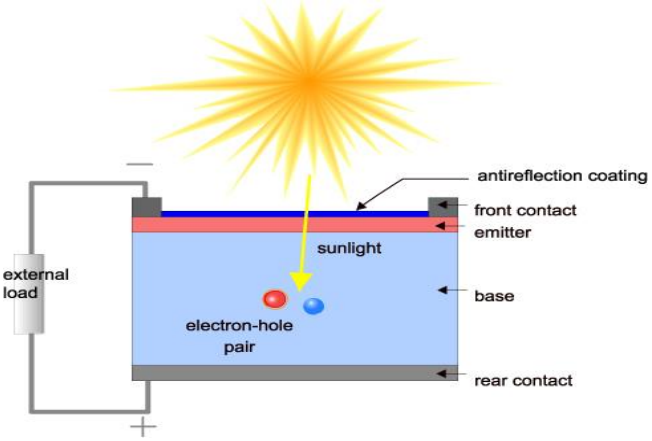

Figure 2: Diagram Showing the Basic Operation of Solar Cell (Jara, 2014)

The greater the amount of solar energy absorbed the greater the efficiency of solar to electricity conversion. The power generated by a solar cell is determined by the product of the number of photogenerated electrons (current) and the energy donated by each electron (voltage) and these parameters are

determined by band gap of semiconductor used in the solar cell.

Semiconductors play as significant role in power generation device application in the form of solar cells which absorb solar radiation and convert it into electrical energy. In semiconductors fundamental band gap energy govern their optical and electronic behaviors and arguably the most critical parameter for almost all applications involving photon absorption and emission and hence play vital roles in the range of photons a solar cell can absorb from the solar spectrum and subsequent conversion of solar energy into electrical energy (Jara, 2014). Sunlight is a form of electromagnetic radiation, which is composed of particles called photons. Each photon is associated with a particular wavelength and energy given by:

$$E_{photon} = \frac{hc}{\lambda} \quad (1)$$

where, E_{photon} is the photon energy, h is the Planck's constant, c is the speed of light and λ is the wavelength of light. For an absorbed photon to generate charge carrier (electron and hole) it has to transfer its energy to the charge carrier by exciting an electron from the valence band to the conduction band. When light is incident on a semiconductor, only solar photons with a very specific bandgap characteristic of semiconductor material can be absorbed and used to produce electricity. In other word, $E_{photon} = Eg$ is the balanced condition for excitation of charge carrier in solar cells. Consequently, energy photons below the material band gap $(E_{photon} < Eg)$ cannot promote charged carriers to conduction bands and do not contribute to photo generated current thus leading to transmission loss (Emin et al, 2011) while photons having energies greater than the material band gap $(E_{photon} > Eg)$ are utilized to generate electrical energy but the excess energy is given as $(E_{photon} - Eg)$ (Geoffrey et al., 2004). In the conventional single junction solar cells these excess energies of the photo generated electrons and holes given by the difference between the photon energy and the semiconductor band gap are in the form of kinetic energy and these charge carriers are termed hot carriers because their energies are higher than the energies of thermally equilibrated electrons and holes that exist within kT of their respective band edges.

The distribution of the excess energy above the bandgap between the electron and hole is expressed as

$$\Delta E_e = (hv - E_g)\left[1 + \frac{m_e^*}{m_h^*}\right]^{-1} \quad (2)$$

and

$$\nabla E_h = (hv - E_g) - \nabla E_e \quad (3)$$

where me∗ and mh∗ are the electron and hole effective masses respectively, ΔEe is the energy of the electron relative to the CBM, and ΔEh is the hole energy relative to the VBM . At later times within the picoseconds timescale the excess kinetic energy of hot carriers is converted into heat as they relax to the conduction and valence band edges via carrier-phonon scattering as shown in Figure 3. This process produces carrier cooling often called thermalization and heating of the lattice until carriers and lattice temperature equilibrate (Fu, 2017).

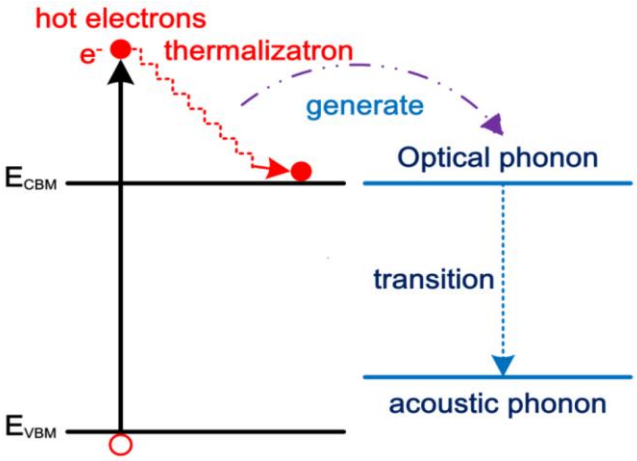

Figure 3: Thermerization of Hot electrons

Equilibration of the hot carriers with the lattice (hot carrier cooling) is achieved through carrier-phonon scattering, at high hot-carrier energies, the cooling involves longitudinal optical (LO) phonons and at lower carrier temperatures, acoustic phonons are involved.

The inherent mismatch between the incident solar spectrum and the optical band gap of the absorber material due to non absorption of sub bandgap photons and thermerlization of supra bandgap photons are the two fundamental losses that have imposed strong limitation on the performance efficiency of 31% for conventional devices based on thermodynamic detailed balance analysis of the solar irradiance by Shockley and Queisser (1961). An earnest desire to circumvent these problems necessitated for a study on the alternative pathway of light energy absorption and conversion by controlling the spatial distribution of optical energy using a number of promising optimizing routes which paved way for third generation solar cells, with a novel photo absorber material capable of utilizing the unused regions in the solar spectrum. Therefore, studies targeted at the search for suitable semiconductor absorbing material that offers these characteristics (i) tunable band gap to better match the solar spectrum (ii) increased surface area to boost the absorption spectrum and (iii) the phonon bottleneck to slow the hot carrier cooling, has led to emergence of QDs (Jun et al., 2014). The choice for QDs currently is explained by their unique physical properties and the possibility of modifying them by varying the dot's shape and dimensions. All QD-based solar cells are known as third generation cells. The term third generation solar cells refer to all novel solar cells design to overcome the Shockley-Queisser (SQ) single band gap limit usually at a low cost. QDs are particles with physical dimensions smaller than the exciton Bohr radius (Kayanuma, 1998). The small size of QDs leads to "quantum confinement". The quantum confinement effects occur when size of QD is comparable to bulk exciton Bohr radius (the average distance between the excited electron in the conduction band and the hole it leaves behind in the valence band) (Masumoto and Sonobe, 1997).

The quantum confinement means that the motion of charge carriers is restricted in all the three spatial dimensions such

that the energy levels that the carriers inhabit become discrete, with a finite separation between them (Segets et al., 2012). The discrete electronic states in QDs is a replica of atomic energy spectra which often gives them the moniker "artificial atoms" (Onyia and Ikeri, 2018). This behavior is in sharp contrast to the bulk semiconductor whose electronic energy levels are distributed in continuous bands. The emission and absorption wavelength of QDs corresponds to their band gap energy (Madan, 2018), this further makes QDs viable and suitable candidate for high efficient solar cells as their band gap can be engineered to desirable energies to better match the solar spectrum (Halim, 2012). The possibility to modulate the spatial probability of the photo-excited carriers (electron and hole) in QDs allows the absorption bandwidth of QDs to be tuned in a broad range wide enough to increase photon absorption. Thus QDs emit and absorb light at specific wavelength that depends on dots size. The smaller dots are closer to the blue end spectrum while larger dots to the red spectrum as shown in Figure 4 (Ikeri and Onyia, 2019), as a result the bandgap energy is broaden leading to a blueshift in the bandgap absorption and emission spectra.

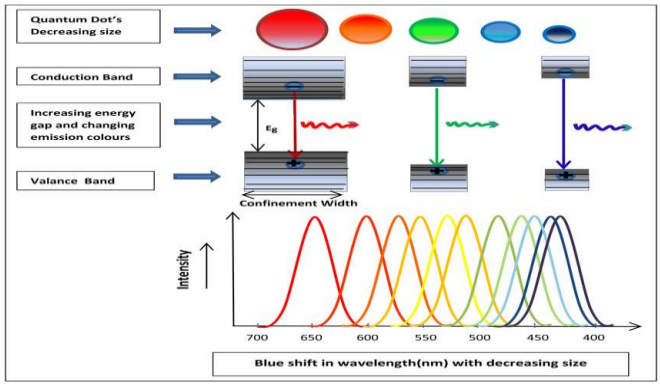

Figure 4: Optical Spectra of Quantum Dots with Decreasing Size (Ikeri and Onyia, 2019).

The size dependent excitation spectrum and the discrete quantized electronic states of QDs represent a promising route to enhance the solar to electricity conversion efficiencies in the third-generation solar cells via the following design architectures; multi junction solar cells, intermediate band solar cells and multiple exciton generation solar cells. Multi-junction solar cell uses multiple materials of different band gaps to best match the broad solar spectrum for high efficient solar cells as shown in Figure 5.

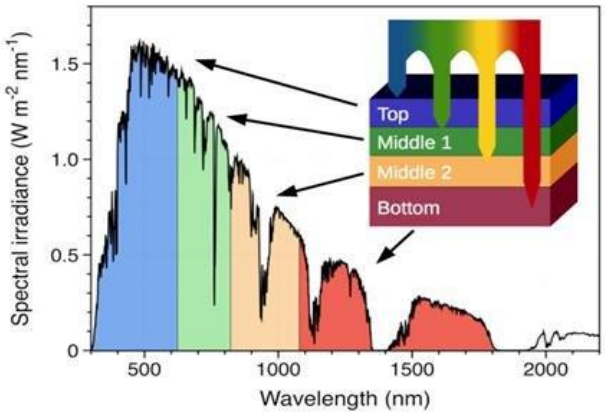

Figure 5: Multi Junction Solar Cell (Singh and John, 1997)

The next approach for high performance solar cell and most widely employed scheme to reduce the thermerlization losses from hot exciton cooling is through carrier multiplication. Carrier multiplication is an optical process in semiconductors whereby more than one carrier can be simultaneously generated upon absorption of a single high energetic photon through impact ionization, (that is, inverse Auger process) (Beard et al., 2008). In QDs the electron-hole pairs exist as exciton and thus the carrier multiplication is referred to as multi exciton generation MEG as shown in Figure 6.

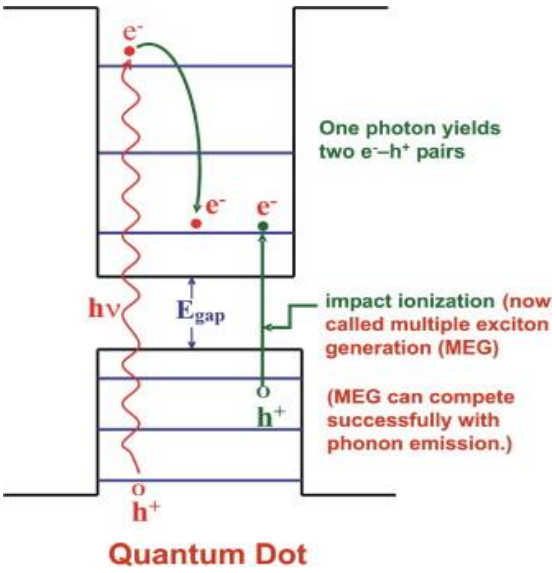

Figure 6: Multiple Exciton Generation (Nozik, 2008)

Lastly, is the intermediate band solar cell. The intermediate band solar cells consist of intermediate band IB to tackle the problem of transmission losses associated with photon energies below the material band gap (Ekins and Schmidt, 2008) and can be realized in periodic structure known as QD superlattice SL (Bimberg, 1999). Intermediate band solar cell (IBSC) consists of multiple band gaps aimed to cover the whole solar spectrum. In such "full spectrum" solar cells, the transmission loss is much less than that of a single junction cell (Luque et al., 2005). IBSCs use the IB(s) as a stepping stone to promote electrons to conduction band (CB). In the first step, an electron is launched from the valence band (VB) to the intermediate band (IB), while in the second step, another electron is pumped from the IB to the CB in addition to conventional valence to conduction bands transitions (Luque and Martin, 2010) as shown in Figure 7.

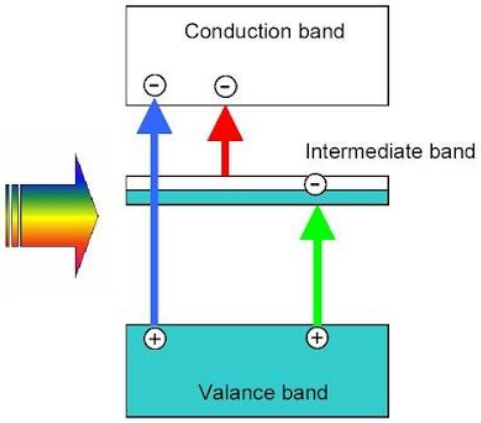

Figure 7: Intermediate Band Solar Cell (Luque and Martin, 2010)

In this research we have formulated theoretical models which have significant implications for improving performances in multiple exciton generation, multiple junction and intermediate band solar cells device applications.

II. Theoretical Models

A. *Exciton in a Quantum Box Model*

Semiconductor quantum dots are two particle system comprising an electron and hole confined in a quantum box bounded by infinite potential walls as shown in Figure 8. Due to the opposite polarity charges that exist between these charged particles there is an attractive connection between them and the particles interact through the electrostatic potential to form a quasi bound state called exciton. Thus, a good approximation of an exciton behavior in QD is that of particle trapped in an infinite potential well in which QD was approximated as quantum box and the exciton as a confined particle. This scenario is presented when the semiconductor is reduced to the nanoscale range where quantum confinement effects are used to describe the system behavior. Quantum confinement effects are observed when the generated excitons are restricted to smaller spatial volumes than they would occupy in the bulk matter. The natural spatial range over which the confinement emerges is described by the material natural exciton Bohr radius of the bulk matter.

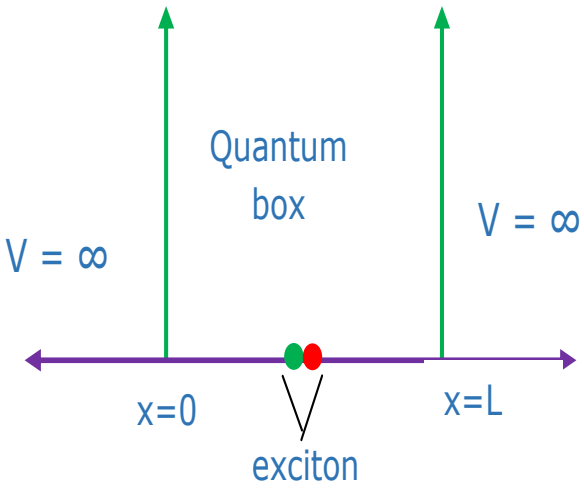

Figure 8: Exciton in the Quantum Box Mode l (Ikeri and Onyia, 2020)

We recall that the confinement energy of the particle confined in 1D well of width L is expressed as

$$E = \frac{n^2h^2}{8mL^2} \quad (4)$$

In a quantum dot, the charge carriers are confined in all three dimensional potential well and by approximation the photo-excited carriers (electron and hole) may be treated as particles in a spherical potential well. Putting $m = m_e^*$ into equation (14) for a spherical QD of radius R yields the electron confinement energy E_{en} as:

$$E = \frac{n^2h^2}{8m_e^*R^2} \quad (5)$$

Similarly, putting $m = m_h^*$ the hole confinement energy E_{hn} is obtained as:

$$E = \frac{n^2h^2}{8m_e^*R^2} \quad (6)$$

We introduced the concept of effective mass expressed in units of mass of electron to account for the interaction with the periodic potential. Therefore the total confinement energy of the confined electron and the hole (exciton) is expressed as

$$E = \frac{n^2h^2}{8m_e^*R^2} + \frac{n^2h^2}{8m_e^*R^2} \quad (7)$$

To model the two particles exciton such as electron and hole, we introduced an electronic interaction energy to account for the Columbic attraction between the negatively (electron) and positively (hole). According to Coulomb's law, the electrostatic interaction energy is on the order of;

$$E = \frac{-\beta e^2}{4\pi\varepsilon_0\varepsilon_r R} \quad (8)$$

We multiply the Coulomb interaction effect by a coefficient β which arises as a result of wave function overlap between the electron and hole in QD and it is approximately 1.8 in the first excited state. The minus sign indicates that two particles (electron and hole) are of opposite charges. Finally, exciton is not confined in an empty space but rather inside a host semiconductor crystal, thus bulk semiconductor material energy band gap was added as baseline energy to the system. The minimum energy needed to excite the quantum dot is thus made up of three main energy contributions given as

$$E_{g(QDs)} = E_{g(bulk)} + E_{confinement} + E_{exciton} \quad (9)$$

Then, by inserting equations (3.18) and (3.19) into equation 20, we obtain

$$E_{g(QDs)} = E_{g(bulk)} + \frac{nh^2}{8\mu R^2} - \frac{1.8e^2}{4\pi\varepsilon_0\varepsilon_r R} \quad (10)$$

Equation 3.20b is a simple model for exciton excitation energy of the QDs.

where; $E_{g(QDs)}$ is the energy band gap of QDs, $E_{g(bulk)}$ is the band gap of the bulk semiconductor, ε_0 is the permittivity of free space, ε_r is the dielectric constant of the material, e is the electronic charge, μ is the exciton reduced mass, h is the plank constant, R is the QD radius, n is the quantum number that labels the different confined energy levels of exciton within QD structure. The Simple model shows that electronic states of the exciton in the QDs are quantized and therefore have discrete excitation spectrum. Also in addition, excitation energy exhibits an inverse quadratic dependence on the dot size which permits the tuning effect. Thus tunable bandgap energies with respect to changes in dot size allow the engineering of bandgap to have desired of optical responses for technological applications.

B. Impact of Quantum Confinement on Optical Wavelengths and Multiple Junction Solar Cell

The results indicate that absorbance wavelength of QDs shows positve correlation with the dot size. As the confinement dimension increases in size, absorption edge shifts towards longer wavelengths (red shift) which demonstrate size dependent absorption and fluorescence spectra. Thus tuning the size of semiconductor QDs means tuning the wavelengths of absorption and fluorescence by the nanocrystal, which in turn means same material emits different colours at various crystallite size and are being studied as alternative active material for optoelectronic devices. Thus when dot sizes become smaller the optical wavelength becomes shorter yielding to an absorbance shift towards the blue spectrum and the degree of the blue shift is larger for smaller QDs as shown in Figure 9 below.

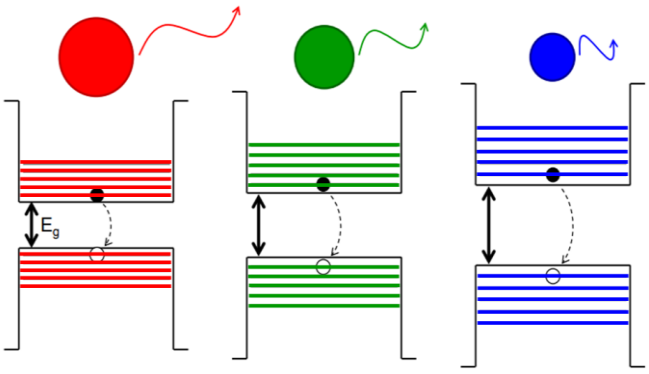

Figure 9: Optical Blue Shift Spectrum with Decreasing Size

The bandgap modulation by quantum confinement effect is a very unique characteristic that makes QDs a perfect candidate for the high efficiency solar cells, because in principle it is possible to use QDs to build absorber with any desired electronic band-gap to better match different parts of the sunlight spectrum as shown in Figure 10.

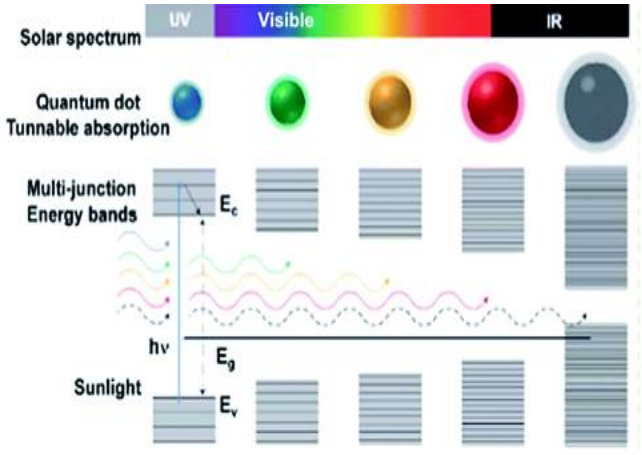

Figure 10: Quantum Dot Multi Junction Energy Band

In this way higher-energy photons are absorbed in the higher-band gap (lower sized) semiconductors and lower-energy photons in the lower-band gap (bigger sized) semiconductor.

C. Multiple Junctions Solar Cell

In multiple junction cells, different band gap materials are combined in order to maximize the amount of the sun light that can be converted into electricity. Therefore, stacking QDs of appropriate sizes onto one another in orderly manner, multi junction solar cell which enables absorption and utilization of solar energies over a wide range are produced as shown in the Figure 11. The ordering of the layers of multi junction solar cells are determined by the wavelengths the materials will absorb. The material with lowest wavelength is placed on top while the subsequent layers are then positioned in ascending order. Incoming photons will be transmitted by QDs with larger band gaps until they reach a layer with a band gap optically match their energy.

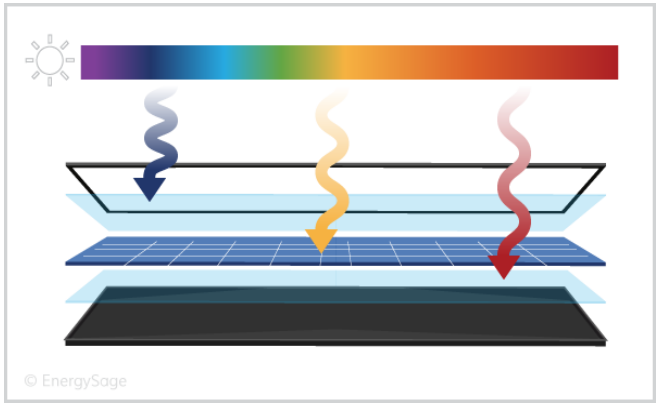

Figure 11: Multi Junction Solar Cell

Accordingly, the UV to blue photons are absorbed by the top layer and the lower layers capture the red to infra-red photons.

D. Impact of Quantum Confinement on Multiple Exciton Generation Solar Cell Mechanism

A simple obtained model show that kinetic energy of the charge carriers exhibit an inverse quadratic dependence on the confinement dimension. With decreasing dot size the kinetic energies become larger by the factor 1/R2 which signifies an increase in the energy levels. Thus energy level spacing increases sharply with decreasing size. The high kinetic energies observed in some QD materials imply higher energy levels sufficient enough to inhibit hot carrier cooling rate in semiconductors and therefore can be considered as new materials to realize high efficiency multiple exciton generation for exploitation of hot carriers. Also dependence of kinetic energy on the effective mass strongly indicate that lighter carriers exhibit large energy levels and will have longer lifetime than heavy charge carriers. This in turn means that light and heavy hole states possess different energy levels in contrast contrary to bulk matters and will therefore thermalise at different rate. In addition, confinement also increases the proximity electron and hole charge distribution and hence Coulomb interaction which enhances the inverse Auger process of multiple exciton generation.

The simple model shows that the energy bands become quantized with widely spaced energy levels with decreasing dot sizes as illustrated in Figure 12.

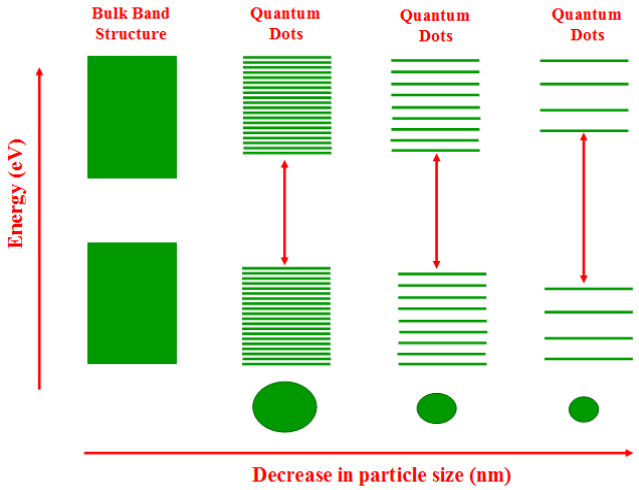

Figure 12: Energy Levels of QDs with Decreasing Size

Also, the proximity of the electron and hole resulting from quantum confinement the Coulomb interaction between them that drives carrier multiplication is greatly enhanced in QDs. Furthermore, besides electronic band structure the quantum confinement effect is also able to change the phonon band structure of the material, the wide separation between the quantized energy states in QDs can greatly exceed the longitudinal optical phonon energy ELO and therefore gives rise to significant reduction in the carrier-longitudinal optical scattering rates that dominate energy relaxation process of the bulk whose energy level coincides with longitudinal optical phonon energy as illustrated in Figure 13. Consequently, substantial increase in the optically excited hot exciton cooling time is expected in QDs in contrast to sub-picoseconds carrier relaxation timescale reported for the parental bulk.

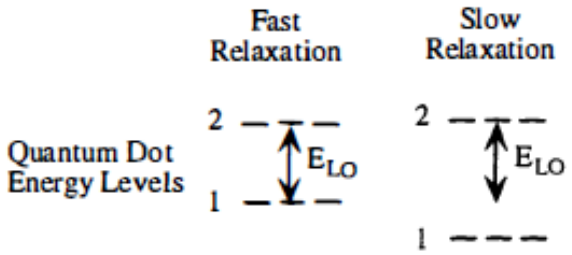

Figure 13: Optical phonon scattering process in bulk and the quantum dot

The slow hot exciton cooling dynamics called phonon bottleneck is attributed to the potential mismatch between the wide electronic energy states and phonon energy. Thus phonon mediated hot carrier cooling can be dramatically suppressed in the QDs, making it possible for the rate of impact ionization (inverse Auger effect) and hot carrier extraction to compete favorably with the rate of hot carrier cooling. The hot carrier thus has life time that is strongly dependent on the confinement strength, the stronger the confinement the greater the energy levels and the longer the thermerlization time constant. As a matter of fact, the rate of carrier cooling is much longer in QDs than in the bulk a phenomenon known as the phonon bottleneck and hence results in dramatic reduction in carrier phonon scattering which offers significant reduction of the energy losses due to ultra fast thermerlization of hot carriers. In principle these novel optical properties allows for exploitation of hot carriers that are loss by phonon emissions in conventional devices in which huge amount of high energy photons are wasted as heat. The emergence of QDs opens a lot of opportunities for new design architecture leveraging on slowed carrier cooling due to quantization effects such as hot carrier solar cell and the carrier multiplication solar cell models to minimize the thermerlization losses and remarkably improve solar to electricity conversion efficiencies.

E. Multiple Exciton Generation Solar Cell

The carrier multiplication solar cells are photovoltaic devices designed to enhance solar to electricity conversion efficiencies by utilizing the excess energy in the absorbed energetic photons that would otherwise fizzle out as heat via carrier-phonon scattering. Carrier multiplication in QD is known as multiple exciton generation (MEG) because electron–hole pairs exist as excitons due to 3D spatial confinement of charge carriers.The results obtained strongly reveal that multiple exciton generation is more efficient in QDs specifically because of the enhanced Coulomb interaction between the carriers and slow hot carrier cool. The creation of additional carriers significantly mitigates the spectral losses due to thermalization which characterized the conventional device thus making it possible for the exploitation of supra band photon energies suitable for high efficient carrier solar cells. It is essentially a process in which hot carrier created by absorption of solar photons higher than the fundamental bandgap energy is utilized to promote two or more charge carriers before they are cool to band edge through phonon emission. Thus an electron from valence band, promoted by absorption of energetic photon makes a transition to a high level in the conduction band and generates one charge carrier but the excess energy which is at least twice the bandgap energy would posses high kinetic energy that can be released to promote a second carrier through impact ionization. In this way one photon generates two charge carrier as shown in Figure 14

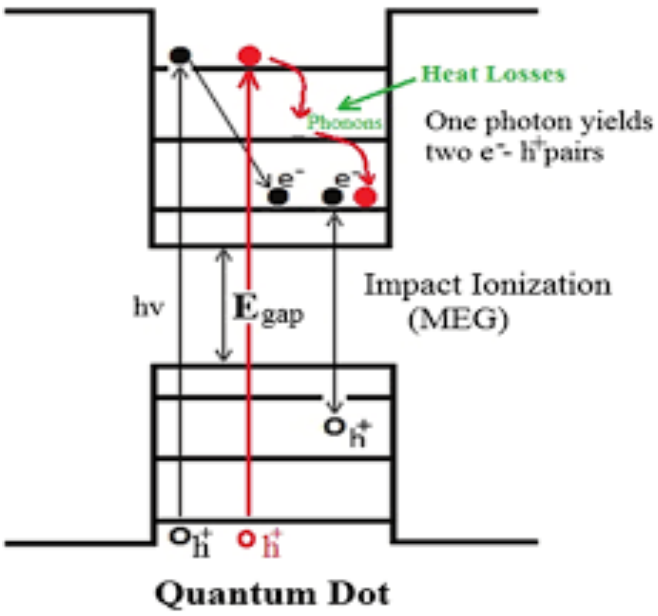

Figure 14 : Multi Exciton Generation Mechanism

III. InAs/GaAs Quantum Dot Superlattice Model

The QD essentially comprised multiple arrays of alternating semiconductors with different band gaps periodically in space (Sabeur, 2015). The superlattice assumed in this model is a cubic InAs QDs embedded in a matrix of GaAs semiconductor. The model consists of an infinite periodic array of QDs and barriers in space to form an artificial 1D crystal as shown in Figure 15 with potential variation that matches well with the analytical Kronig Penney model who assumed a rectangular potential as an approximation of crystal potential of a single electron moving in 1D crystal and by this analogy we modeled the electronic band structure of the QDSL by Kronig-Penney model.

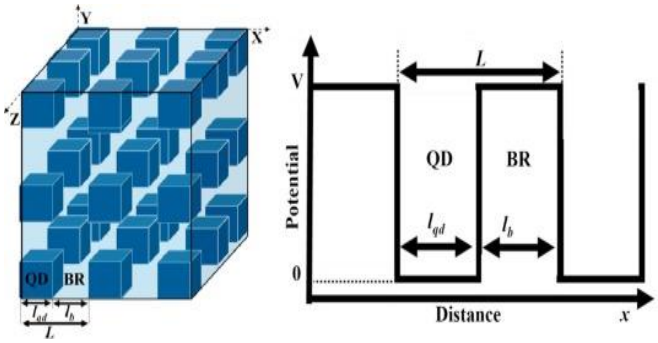

Figure 15a: Quantum Supper Lattice Diagram

Comparing with kronig penney model we obtained

$$\left(\frac{k_B^2 - k_Q^2}{2k_B k_Q}\right)\sinh(k_B L_B)\sin(k_Q L_Q) + \cosh(k_B L_B)\cos(k_Q L_Q) = \cos kL = z \quad (11)$$

The simplified equation becomes

$$P\frac{\sin(K_Q L_Q)}{K_Q L_Q} + \cos(K_Q L_Q) = \cos(kL_Q) \quad (12)$$

We define P a dimensionless parameter of the model measuring the strength of potential barrier as

$$P = \frac{mL_Q V_o L_B}{\hbar^2} \quad (13)$$

It implies P is a measure of how strongly an electron is bounded in a crystal. Thus, a large value of P implies that electron is strongly bounded to its parent atom and represents physical scenario that an electron is in the constant potential. Also, small P means that an electron is a completely free particle. We therefore deemed it necessary to obtain the expression for energies of an electron for these two limiting cases of P.

i. Limiting case in which P → 0

The energy of electron becomes

$$E = \frac{h^2 k^2}{2m} \quad (14)$$

This expression corresponds to Drude Lorentz model and represents the energy of a free electron in which all energies are allowed. Thus the electrons propagate through the system with no restriction by any potential. we have free particle dispersion relation in which there is no limit (gap) on the allowed particle energy as shown in the energy continuum in Figure 16a. The dispersion relation here is parabolic as shown in Figure 16b and thus supports the classical free electron theory.

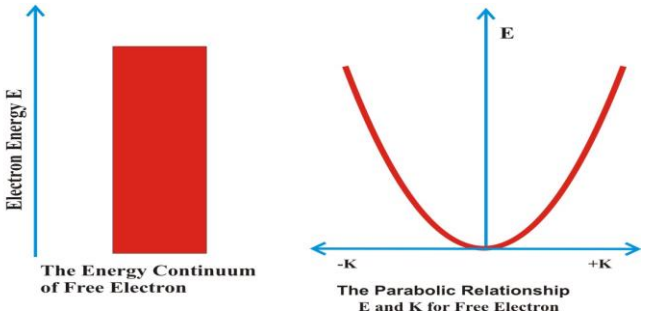

Figure 16: (a) Energy Continuum for Free Electron and (b) Dispersion Relation

ii. Limiting case in which P → ∞

The energy of electron becomes

$$E = \frac{n^2 h^2}{8mL^2 Q} \quad (15)$$

The energy spectrum consists of discrete electronic states which is consistent with the Sommerfeld free electron model which expresses the energy of electron moving in a constant potential. It is understandable fact because very large P signifies that the potential barrier strength is strong enough that electron is trapped and cannot escape from an isolated potential well in which case there is no dispersion of the corresponding energy band. we have the expression for sharp energy levels in an infinite potential well. Hence there will be discontinuity (gap) in the free particle dispersion relation at the boundaries $k_Q = \frac{n\pi}{L_Q}$ and this manner we get series of discontinuities in the dispersion relation for all other k values as shown in Figure 17

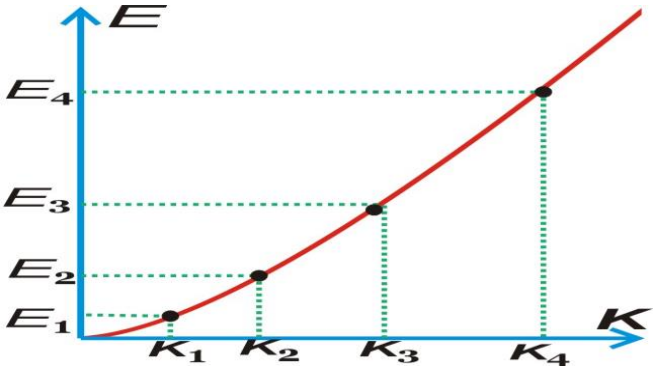

Figure 17: Dispersion Relation of Confined Electron and Free Electrons

The black dots represent the energy of particle in a box and the red line the free particle energy.

In the general case the simplified model for dispersion equation of an electron in the SL which relates the energy (through k_Q) on the left hand side (LHS) and wave vector k on the right hand side (RHS) is:

$\frac{p}{k_Q L_Q}\sin(k_Q L_Q) + \cos(k_Q L_Q) = \cos(kL_Q)$. The LHS of the equation can be express as $f(E)$, then we have $f(E) = \cos kL_Q$. It is clear from the equation if $|\cos kL_Q| \leq 1$ the Schrodinger equation for the SL has a proper solution and we have real values k. The energies E corresponding to these k values is allowed (i.e., we are in the energy band). In other words, if $|\cos kL_Q| > 1$ there are no real values of k and hence no proper solution, in which case there will be bandgap (energies for which there is no propagating solution) in the spectrum of energies (i.e., we are in the forbidden region). This solution results in *complex band structure* consisting of dispersion with *real* components of Bloch wave vector *k* and dispersion with pure *imaginary* components of Bloch wave vector *k*. The corresponding real band structure describes *delocalized propagating electron states* in the crysta and the imaginary band structure describes *localized non-propagating electron states, i.e. forbidden region*. A typical plot of $f(E)$ as a function of energy E for P = $\frac{3\pi}{2}$ is shown in Figure 18.

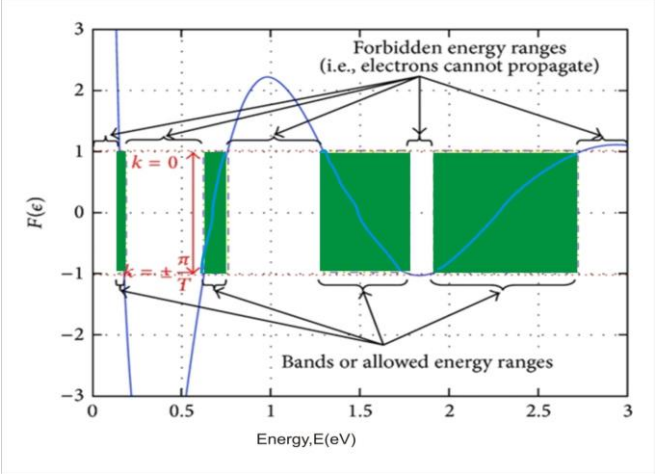

Figure 18: ($f(E)$ *versus* E) showing Electrons and Energy Band Structure in Superlattic

Following the fundamental relation $F(E) = \cos kL_Q$, we generated a vital figure known as dispersion diagram showing the energy versus wave number (E vs k) in Figure 19.

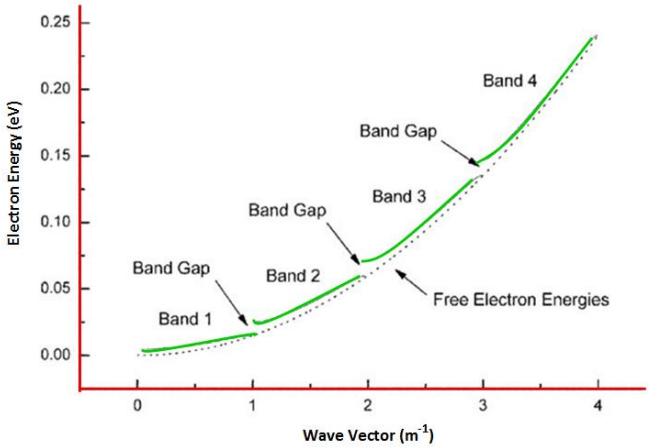

Figure 19: Energy Versus Wave Vector Showing the Gaps that appear when ka = $n\pi$.

A. *Intermediate Band Solar Cells IBSCs*

IBSCs are novel concept in solar cell technology in which sub band gap energy photons can promote electron to conduction band using intermediate band IB structure as a ladder.

B. *One Intermediate Band Solar Cell*

This is a solar cell that uses one intermediate band IB in between the band gap region of semiconductor to produce 3 bands semiconductor structure. By careful observations we have ascertained from this work that if there are n intermediates bands the total upward energy transitions T in the IBSC is calculated using the combination statistical relation T = ${}^{N}_{n}C$ where n is total number of IB(s) and N the sum of valence band, conduction band and intermediate band(s). Thus, for one intermediate band the total upward energy transition is calculated as:

$$T = \frac{3!}{(3-1)!1!} = 3 \qquad (16)$$

It means for one IB there will be three optical upward energy transitions which are transitions from VB to IB, from IB to CB and the conventional VB to CB. The first sub band gap photons with energy, $E = \hbar\omega_1$ which usually transmitted in the conventional device are absorbed through transition from valence band to intermediate band (which has an empty state to receive this electron), and the second low energy photons $E = \hbar\omega_2$ are also absorbed through transition from intermediate band (which also has filled state to supply electron) to conduction band and the third conventional solar photons $E = \hbar\omega_3$ which further causes a direct transition from valence band to conduction band shown in Figure 22. In this way the solar photons which have low energy to pump electrons from the valence to the conduction band, can use this intermediate band concept as a stepping stone (ladder approach) to optically generate electron hole pair.

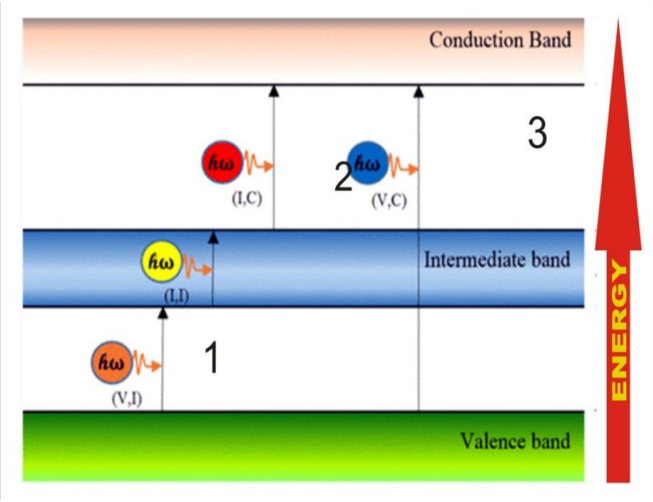

Figure 22: One Intermediate Band Solar Cell Mechanism with the possible Electronic Transitions

C. Two Intermediate Bands Solar Cells

These are solar cells characterized by the existence of a two IBs located in the forbidden region of semiconductor. In this way 4-band semiconductor structure is formed and the total number of upward energy transitions in this device based on the above model, is calculated as:

$$T = \frac{4!}{(4-2)!2!} = 6 \quad (17)$$

This means in an IBSC made up of two IBs there are six upward energy transitions which are E_1: transition from VB to IB_1, E_2: transition from IB_1 to IB_2, E_3: transition from IB_2 to CB, E_4: transition from IB_1 to CB and the conventional VB to CB (bandgap) transition which also implies six optical absorption possibilities as shown in Figure 23. It follows that increase in the number of IBs increases the absorption possibilities which in turn provides significant increase in the conversion efficiencies through increase in the photo generated current.

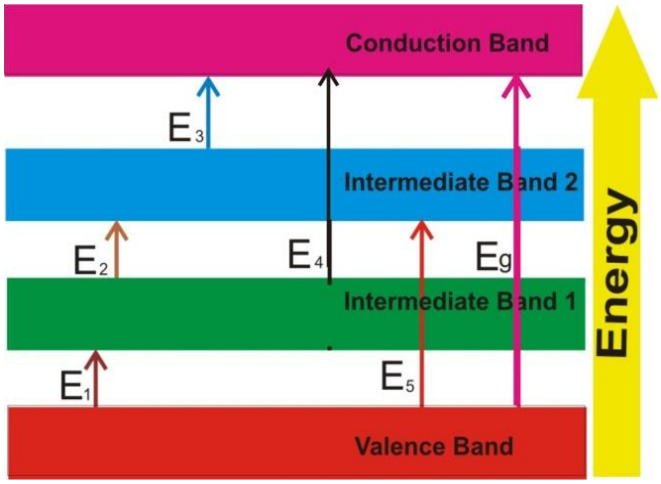

Figure 23: Two Intermediate Band Solar Cell Mechanism with the possible Electronic Transitions.

Intermediate band solar cell has shown great potential to enhance light absorption in a single junction cells.

IV. Quantum Dots Surface Area Per Unit Volume Model

The other vital characteristic of QDs responsible for their novel behaviour is the surface effect. Thus, surface area to volume ratio for a material or substance made of nanoparticles has a significant effect on the properties of the material. QDs have a relatively larger surface area when compared to the same mass of material in bulk form (Qiu and Liu, 2010). This makes them more chemically reactive (in some cases materials that are inert in bulk form are reactive in their quantum state), which has significant impact on their strength or electrical properties (Alivisatos, 2004). We considered spherical and cubic QDs geometries and applied basic mathematical formulas based on geometry to establish a fundamental surface area to volume relationship. For spherical shape semiconductor nanocrystal the equation for the surface area S of the sphere of radius r is described by:

$$S = 4\pi r^2 \quad (18)$$

Volume of the sphere V is defined as:

$$V = \frac{4}{3}\pi r^3 \quad (19)$$

Then the surface area to the volume ratio α becomes:

$$\alpha = \frac{4\pi r^2}{\frac{4}{3}\pi r^3} \quad (20)$$

$$\text{Thus } \alpha = \frac{3}{r} \quad (21)$$

$$\rightarrow \alpha \propto \frac{1}{r}$$

Similarly, for cubic shape semiconductor nanocrystal of the length of a side L the equation of the surface area S of the sphere is:

$$S = 6L^2 \quad (22)$$

Volume of the cube V is:

$$V = L^3 \quad (23)$$

Then the surface area to the volume ratio β becomes:

$$\beta = \frac{6L^2}{L^3} \quad (24)$$

Thus

$$\beta = \frac{6}{L} \quad (25)$$

$$\rightarrow \beta \propto \frac{1}{L}$$

The radius r and length L are both referred here as sizes hence surface to volume ratio for both spherical and cubic geometrical QDs indicates that the surface area increases faster relative to the volume as crystal size decreases. It means also that when a given volume of material is made up of smaller particles, the surface area of the material increases. Maximum exposed surface area signifies an improved reactivity thus greater percentage of the material atoms are exposed for potential reaction. Given equation 21 the surface area per unit volume for a sphere $\alpha = \frac{3}{r}$ and equation 25 for the cubic shape, $\beta = \frac{6}{L}$ therefore between a spherical and cubic shapes of same volume there will be larger increased surface area in the cube relative to the sphere and for this particular reason not only the size of the QD particles is vital but also their shape. Thus the shape of the QDs also plays critical role on the surface area of the material and influences their properties

Figure 24 shows surface area per unit volume for different crystal sizes both for the cubical and spherically shaped QDs. It is found that the surface area to volume ratio scales as an inverse power law. It means that the surface area to volume ratio increases as the size of the particle decreases and vice

versa. This also implies that for a given volume of material made up of smaller particles, the surface area of the material increases and thus has a relative larger surface area when compared to the same volume of material made up of larger particles. The large surface area per unit volume provided by quantum dot has significant advantage for both light absorption and charge separations which are two critical steps in solar to electricity energy conversion. The increased surface area would increase light absorption because photons would pass through more of material and would have a higher probability of being absorbed. In addition to creating a large interfacial area, this architecture would allow the electrons and holes created by photon absorption in the material to travel only a short distance before being separated. Since they travel a short distance, probability of recombination would be reduced and more of the photo generated charges can be collected. Generally, higher surface area implies higher surface atoms. Thus greater portion of their existing atoms are found at the surface. This leads to nanoscale semiconductors being more chemically reactive. As chemical reactions occur between particles that are on the surface, a given mass of nanomaterial will be much more reactive than the same mass of material made up of large particles. In general perspective physical and chemical properties of a material greatly depend on the surface atoms, and the fact that a significant number of atoms exist at the surface in nanocrystals implies tremendous effects on the reactions that occur at interface (surface) such as catalysis and detection reactions.

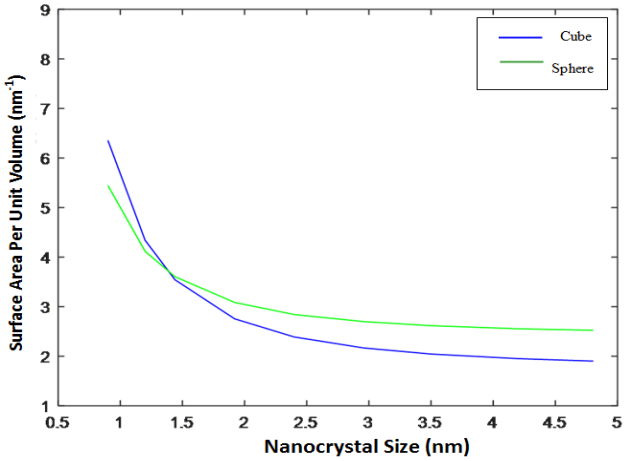

Figure 24: Surface area per unit volume versus spherical and cubic nanocrytal size

The results reveal that whenever materials are reduced to nanoscale regime the shape of the material plays critical role on the properties of the material. Given the same volume, the extent of the surface area depends on the shape of the material. A simple scenario is a sphere and a cube having the same volume. The comparison between the cubic and spherical nanocrystals demonstrates a higher surface area to volume ratio for cubic geometries. This strongly suggests that the shape of the matter influences the surface area and may have significant effect in the absorption and emission process of nanoparticles. For this particular reason not only the size of semiconductor QDs is important, but also its shape.

V. Conclusion

The enhancement pathways of solar energy absorption that confines to the concepts of third generation solar cells to realize efficient photovoltaic cells have been provided. In conclusion QDs have undoubtedly display novel optical properties and potentials to be considered as a possible alternative to bulk materials for solar cells application. The novel achievements include the use of multi junction with different QD materials of broader spectral absorption capability to better match the wide range of solar spectrum, multiple exciton generation for single photon absorption, formation of intermediate band in the bandgap regime for sub bandgap photon absorption and increase surface area per unit volume ratio which collectively provide mechanisms for increasing the efficiency beyond the Shockley and Queisser established limit of energy conversion efficiencies in the conventional solar cells..

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