Effect of the shell material and confinement type on the conversion efficiency of core/shell quantum dot nanocrystal solar cells

Mehmet Sahin

Department of Material Sciences and Nanotechnology Engineering, Abdullah Gül University, Sümre Campus 38080 Kayseri, Turkey

E-mail: mehmet.sahin@agu.edu.tr and mehsahin@gmail.com

Received 22 January 2018, revised 23 March 2018
Accepted for publication 4 April 2018
Published 20 April 2018

Abstract
In this study, the effects of the shell material and confinement type on the conversion efficiency of core/shell quantum dot nanocrystal (QDNC) solar cells have been investigated in detail. For this purpose, the conventional, i.e. original, detailed balance model, developed by Shockley and Queisser to calculate an upper limit for the conversion efficiency of silicon p–n junction solar cells, is modified in a simple and effective way to calculate the conversion efficiency of core/shell QDNC solar cells. Since the existing model relies on the gap energy \( E_g \) of the solar cell, it does not make an estimation about the effect of QDNC materials on the efficiency of the solar cells, and gives the same efficiency values for several QDNC solar cells with the same \( E_g \). The proposed modification, however, estimates a conversion efficiency in relation to the material properties and also the confinement type of the QDNCs. The results of the modified model show that, in contrast to the original one, the conversion efficiencies of different QDNC solar cells, even if they have the same \( E_g \), become different depending upon the confinement type and shell material of the core/shell QDNCs, and this is crucial in the design and fabrication of the new generation solar cells to predict the confinement type and also appropriate QDNC materials for better efficiency.

Keywords: detailed balance model, Shockley–Queisser limit, quantum dot nanocrystal solar cells, multi-exciton generation

((Some figures may appear in colour only in the online journal)
fundamentally established depending on the band gap ($E_g$) variation, has been modified [13] in a different manner to calculate the efficiency of new generation QDNC solar cells [14]. These important modifications are basically related to the MEG in QDNCs [15–17]. In addition to the MEG, some other modifications, such as free carrier absorption, Auger recombination, etc., have been realized by some authors [19, 20]. The essential aim of these modifications is to execute more realistic efficiency calculations and to understand the fundamental physics of the devices, and, as a result, to suggest much better QDNC solar cell designs. In some studies, the carrier multiplication phenomena and, in addition to this, photon up- and down-conversion processes, have been investigated in detail in order to understand the limitation of the high conversion efficiency of QDNC solar cells [21–26].

As is well known, the detailed balance model assumes that all photons coming from the sun with energies equal to or greater than $E_g$ are absorbed and form electron–hole pairs (excitons). In this idealized model, the sole loss mechanism is the radiative recombinations of the excitons [9, 12]. Since the model is based on $E_g$ only, the efficiency of any photovoltaic device is equal to that of another one with the same $E_g$. For example, the efficiency of a QDNC solar cell with $E_g = 1.1$ eV is almost completely the same as that of a bulk silicon solar cell. Similarly, according to the original detailed balance model, the efficiency of solar cells with type-I QDNC is identical to the efficiency of solar cells with type-II QDNC if their $E_g$ values are the same [16, 17]. A number of theoretical studies have been reported in the literature related to the conversion efficiency of QDNC-based solar cells, and the calculations have been performed in the framework of the original detailed balance model in all these studies [11, 12, 16–19].

Nevertheless, essentially it is not possible to have the same efficiency values for all types of QDNC solar cells, even if they have the same $E_g$, owing to other material properties of the solar cells, such as the effective masses of the carriers, the dielectric properties of the materials, the size of the QDNCs, confinement type, etc, and all these properties are very important in terms of the carrier dynamics in solar cells. On the other hand, the recombination probability is so high in type-I structures, and also, in practice, collecting the carriers from type-I QDNCs is not easy because both the electron and hole are confined inside the core when compared to type-II QDNCs.

The main aim of this study is to modify the original detailed balance model in order to calculate the structure-dependent upper limit for the conversion efficiency and to investigate the effects of shell materials and confinement types of QDNCs on the efficiency of solar cells using the modified model. With this modification, the model can estimate an upper limit for the conversion efficiency of QDNC solar cells based on the material properties and confinement types of the QDNCs. In the modification, without making drastic changes to the original model, the quantum mechanical oscillator strength effect is taken into account in the radiative recombination current calculations. As is well known, the oscillator strength is an important and unitless parameter in determining all the optical properties of quantum mechanical systems from atoms to solids. The radiative recombination phenomenon in photovoltaic devices is also an optical process, and the oscillator strength must be taken into account in the conversion efficiency calculations. As we will see later on, the oscillator strength is basically dependent on overlaps of the wavefunctions of the electron and hole as well as the transition energy of the exciton and Kane energy of the materials. All these quantities rely on the crystal structure properties, confinement regime, effective masses of the carriers, and dielectric properties of the QDNC materials. In the next step, the conversion efficiencies of the solar cells based on type-I and type-II QDNCs with different shell materials are calculated by using both the original and modified detailed balance models. The results are presented comparatively and probable physical reasons are discussed. We see that the modified model can estimate appropriate materials and the confinement type of the QDNCs that will be used in the design and fabrication of more efficient solar cells.

**Model and theory**

In the original detailed balance model, the photogenerated current density is given by [13]

$$J_{bg} = q_e \int_{E_g}^{\infty} QY(h\nu, E_g) \phi(h\nu) d(h\nu),$$

(1)

where $q_e$ is the electronic charge, $\phi(h\nu)$ is the photon flux density of the sun [27], and $QY(h\nu, E_g)$ is the quantum yield of the absorbed photon, dependent on both photon energy $h\nu$ and gap energy $E_g$. The $QY(h\nu, E_g)$ is actually external quantum efficiency (EQE) and it contains $\text{EQE}(h\nu) = C(h\nu)(1 - R(h\nu))a(h\nu)$ where $C(h\nu)$ is the collection probability of the excited carriers, $R(h\nu)$ is the reflectivity of the incident photons and $a(h\nu)$ is the absorptivity of incident photons. In ideal conditions, there is no reflectance, i.e. $R(h\nu) = 0$, and all photons with equal or higher energies than $E_g$ are absorbed, i.e. $a(h\nu) = 1$, and hence $C(h\nu)$ becomes equal to $QY(h\nu, E_g)$.

The MEG is integrated into the detailed balance model by favour of the $QY(h\nu, E_g)$ as

$$QY(h\nu, E_g) = \sum_{m=1}^{M} \theta(h\nu, mE_g).$$

(2)

Here, $\theta(h\nu, mE_g)$ is the Heaviside step function and $M$ is an integer, $M = \frac{h\nu_{\text{max}}}{E_g}$. Where $QY(h\nu, E_g)$ is fixed to unity, the MEG will become absent. The recombination current density in the original model is given by

$$J_{rc} = \frac{2\pi q_e^2}{h^2 c^2} \int_{E_g}^{\infty} \frac{QY(h\nu, E_g)^2}{\phi(h\nu)\nu \frac{\nu}{\nu_{\text{max}}} - 1} d(h\nu),$$

(3)

where $h$ is Planck’s constant, $c$ is the light speed in the vacuum, $k$ is Boltzmann’s constant, $T$ is temperature and $V$ is the applied voltage to the cell, and it is also taken into consideration as a constant quasi-Fermi level separation and its value is determined by a numerical search as it will maximize the efficiency of the solar cell. Here, the relation between the
As for QDNCs, there are different recombination mechanisms depending on the confinement regimes. In the type-I confinement regime, seen in the middle panel of figure 1, unlike bulk materials, since there are confinement potentials in both the conduction and valence bands, the electron and hole cannot move like free particles. Therefore, the recombination probability of an exciton in type-I structures can be very high depending on the size of the nanocrystal and the confinement potential depth, even if there is an external electric field. Also, the attractive Coulomb potential between the electron–hole couple becomes predominant because of the confinement when compared to bulk semiconductors. In type-II QDNCs, shown in the bottom panel of figure 1, while one of the carriers is confined in the core, the other one is confined in the shell region, and so the carriers are separated spatially in contrast to the type-I confinement regime. Consequently, it can be said that the recombination probability in type-II structures is smaller than that in type-I structures, and therefore the probability of the contribution of the carriers to the photocurrent in type-II structures will be higher.

As the electron and hole move like free particles in bulk semiconductors, the recombination current mechanisms expressed by equation (3) in the original detailed balance model works well for solar cells like silicon p–n junctions. On the other hand, in QDNC solar cells, the recombination current density is larger due to higher recombination probabilities, and hence this higher recombination probability should be added into the recombination current density. Here, it should be noted that the oscillator strength will not be taken into account in the calculation of the photogenerated current, because, according to detailed balance limit assumptions, all photons with equal to or higher energies than $E_g$ are absorbed. On the other hand, the recombination current density is calculated statistically by basically using the Planck distribution function, and it is strongly dependent on the radiative recombination oscillator strength; hence, the oscillator strength must be taken into account in the calculation of the recombination current density. Now, equation (3) can be modified as follows: The EQE given in equation (4) can be rearranged to include the recombination probability. When we focus on equation (4), we see that, in detailed balance limit and assumptions, $R(h\nu) = 0$, $\epsilon(h\nu) = 1$ and $C(h\nu) = QY(h\nu, E_g)$. Here, the $C(h\nu)$ is strongly dependent on the overlap of electron–hole wavefunctions and this effect must be inserted into equation (4). Therefore, it can be written as $C(h\nu) = fQY(h\nu, E_g)$, and, in the calculation of the recombination current density for a QDNC solar cell, employing the following expression instead of equation (3) is more reasonable:

$$J_{rc} = \frac{2\pi q_e}{\hbar^2 c^2} \int_{E_g}^\infty \frac{fQY(h\nu, E_g)(h\nu)^2}{e^{(h\nu-E_g)/kT} - 1} d(h\nu),$$

where $f$ is the recombination oscillator strength and it is given by [28]

$$f = \frac{E_p}{2E_x} \left| \int \psi_e(r)\psi_h(r) d^3r \right|^2.$$

Here, $E_p$ is the Kane energy and $E_x$ is the exciton transition energy. $\psi_e(r)$ and $\psi_h(r)$ are the electron and hole wavefunctions. The energy states and the corresponding wavefunctions of the electron and hole are determined by solving

\[ \begin{align*}
E_c & \quad \text{valence band (VB)} \\
E_v & \quad \text{conduction band (CB)} \\
E_g & \quad \text{minimum of the conduction band (CMB)} \end{align*} \]

\[ \begin{align*}
\psi_e(r) & \quad \text{electron wavefunction} \\
\psi_h(r) & \quad \text{hole wavefunction} \\
\epsilon & \quad \text{emissivity} \\
\eta & \quad \text{efficiency} \\
\eta & = \frac{J_{net}V}{P_{in}}, \quad (5)
\end{align*} \]

\[ \begin{align*}
\text{Figure 1. Schematic representation of the exciton forming in bulk semiconductors (top panel), in type-I QDNCs (middle panel), and in type-II QDNCs (bottom panel).}
\end{align*} \]
the Poisson–Schrödinger equations self-consistently. In the calculations, excitonic effects (i.e. Coulomb interactions between the electron and hole) on both energy states and wavefunctions have been taken into account. All details of the electronic and optical property calculations can be found in [28, 29].

In equation (7), the Kane energy is strongly dependent on the crystal properties of QDNC materials, and the wavefunctions involve the penetration effect to the barrier region, and so the electron and hole energy states are affected by the penetrations. That is, when we take an overall glance of the last two equations, we see that the recombination current density includes these material dependent parameters and it has been transformed into a material dependent form.

**Results and discussion**

In this study, both type-I—InP/ZnS and InP/GaP—and type-II—InP/GaAs and InP/GaSb—QDNC structures have been taken into consideration. In all the structures, the core material is chosen as InP while the shell materials are different. Therefore, not only the confinement types but also the effects of the shell materials can be evaluated more effectively. In addition, the results of the modification on the original detailed balance model can be seen more clearly. The potential profiles of both type-I and type-II structures can be seen in figure 2. The band offsets have been determined by using the electron affinity values of the materials [28]. The confinement potentials in the conduction bands, $V_{0c}$, are 0.60 eV and 0.75 eV for InP/ZnS and InP/GaP QDNCs, respectively, while the valence band confinements, $V_{0v}$, are 1.73 eV and 0.16 eV, respectively. In the type-II structures, the conduction band offsets are 0.35 eV and 0.20 eV, and the valence band offsets are 0.27 eV and 0.92 eV for InP/GaAs and InP/GaSb QDNCs, respectively. In the calculations, the shell thickness is taken as constant, 10 Å. All the material parameters used in the electronic structure calculations are listed in table 1.

After computation of the energy levels and corresponding wavefunctions of the QDNCs, the photovoltaic efficiencies are calculated by using the original and modified detailed balance models, and the results are plotted as a function of the $E_g$ of the QDNCs. The results of the original detailed balance model are given in figure 3. The top panel of the figure shows the efficiency values for type-I—InP/ZnS and InP/GaP—and the bottom panel demonstrates the efficiency values of type-II—InP/GaAs and InP/GaSb—QDNC solar cells. As seen from the top panel, in larger core radii which correspond to smaller $E_g$, the efficiency values of the type-I QDNC solar cells are very high and decrease with an increase in the $E_g$ values of the QDNCs. Here, it is important to emphasize that there is no indication of the effect that the shell material has on the solar cell efficiency because the original detailed balance model depends only on the $E_g$. When the MEG is considered in the calculations, the efficiency values become larger in the case of $E_g < 2E_g$, as expected and reported in previous studies [16, 17]. It should be noted that the QY($h\nu, E_g$) is taken as a maximum of two when the MEG is taken into consideration in the calculations because there is a maximum of two carriers in the ground states of the QDNCs for selected materials.

When we look at the bottom panel of figure 3, we see that the
Figure 3. Efficiency values of QDNC solar cells for type-I—InP/ZnS and InP/GaP—(top panel), and type-II—InP/GaAs and InP/GaSb—(bottom panel). The results are obtained using the original detailed balance model.

maximum efficiency values are slightly greater with respect to the type-I structures because of the smaller $E_g$ values of the type-II QDNCs. Also, the general behaviour of the efficiency values are the same as studies reported in the literature. As can be seen from the figure, the shell material has no effect on the solar cell efficiency in type-II structures also. After this overall glance, when we focus on both panels of figure 3, we see that the efficiency values are almost the same in both type-I and type-II QDNC solar cells for the same $E_g$ values. In addition, the results are the same as the p–n junction solar cell efficiency values reported in the literature. We can conclude that since the original detailed balance model gives an upper limit for the efficiency values of the solar cells depending on $E_g$ only, it does not provide any information about the effects of shell materials and/or the type of the QDNCs on the efficiencies of QDNC solar cells.

However, the shell material and/or the confinement type of the QDNC must actually have a significant effect on the electronic and optical properties of QDNCs, such as overlaps of the wavefunctions, recombination oscillator strength, etc., depending on the penetration of the wavefunctions to the shell regions, as well as other material parameters, such as effective masses, dielectric constants, etc. Thereby, the recombination current density and so the efficiency of the QDNC-based solar cells must be strongly dependent on these QDNC properties. The oscillator strength (OS) contains all these effects and it must be taken into consideration in the recombination phenomenon, as mentioned before. Figure 4 shows the OSs of the type-I (top panel) and type-II (bottom panel) QDNCs as a function of the core radii. Here, at the same time, the gap energies, corresponding to each core radius, are given on the bottom axes of the graphs. It should be noted that the gap energies are calculated by means of $E_g = E_g(\text{bulk}) + E_e + E_h$, where $E_g(\text{bulk}) = E_g$ for the type-I, and $E_g(\text{bulk}) = E_g - V_h$ for the type-II structures, $E_e$ and $E_h$ are the single particle energy states of the electron and hole, respectively. These single particle energy values are strongly dependent on the effective masses of the electron and hole and the penetration of the wavefunctions to the barrier regions, as mentioned previously, and hence the same core radii may correspond to different gap energies depending on the shell materials. When we look at both panels, we see that the behaviours of the OSs are completely different in the type-I and type-II structures. The OS in type-I QDNCs increases with an increase in the core radius (decreasing $E_g$) while it decreases in type-II QDNCs. At the same time, the shell material effects on the OS are seen clearly in all QDNCs. In the type-I structures, the OS values of InP/ZnS are smaller, especially at a smaller core radius, when compared to that of InP/GaP QDNC, and their values increase with an increase in the core radius and become close to each other at larger core radii. This is because the overlaps of the electron and hole wavefunctions are larger in larger core radii. This results in higher recombination probabilities. Also, the overlapping is bigger in InP/GaP QDNC than in InP/ZnS. As for the type-II QDNCs, the OS values are almost the same and bigger at smaller core radii (higher $E_g$ values) and decrease with an increase in core radii. This is because both the electron and hole localize to the vicinity of the core region at smaller core radii. When the core radius increases, the strong confinement regime relaxes and the overlapping of the wavefunctions decreases with an increase in the spatial separation of the carriers. So the lifetime of the carriers becomes longer and the recombination probability becomes smaller.

Figure 5 shows the efficiency values calculated using the modified detailed balance model for type-I—InP/ZnS and InP/GaP—QDNC solar cells (top panel) and type-II—InP/GaAs and InP/GaSb—QDNC solar cells (bottom panel). In the calculations, the recombination current densities are computed by means of equation (6). When we look at both panels, we can see easily that the efficiency values are smaller than the results of the original detailed balance calculations demonstrated in figure 3. This situation is very drastic and at the same time more reasonable, especially for type-I QDNC solar cells. If we focus on the efficiency values of the InP/ZnS QDNC solar cell, we see a completely different behaviour. Here, the efficiency of the InP/ZnS QDNC solar cell has smaller values for a smaller band gap and increases with an
increase in $E_g$, and, with a further increase of the gap value, they reach a maximum value, which is slightly greater than 9%. The tendency of the efficiency values is not in agreement with the result of the original model and exhibits a completely opposing characteristic to it. This can be explained with smaller OS values at larger $E_g$ energies. On the other hand, although changes in the efficiency values of the InP/GaP QDNC solar cells with the $E_g$ are similar to the original method results reported in the literature, the values are drastically smaller than the original method results. This is also due to the higher OS values. Since the OS of InP/GaP QDNC is larger than that of InP/ZnS QDNC, the efficiency values of the InP/ZnS QDNC solar cell are higher. The efficiency of the InP/GaP QDNC solar cell reaches to maximum 6% values. As can be seen from the top panel of the figure, although the core materials of the QDNCs are the same, the efficiency values exhibit completely different behaviours depending on the shell materials. Many electronic and optical properties of core/shell QDNCs, such as oscillator strength, are affected by the shell material, as expected and mentioned above. The effect of the oscillator strength on the efficiency is seen clearly in type-I QDNC solar cells. The results of the modified model are very reasonable because, until now, there have been no experimental studies related to type-I core/shell QDNC solar cells reported with higher efficiency values of more than 4% [33]. Indeed, type-I QDNCs are more compatible for LEDs rather than solar cells. It should be noted that there are many different reasons, other than OS, that make type-I QDNCs suitable for LED applications, such as confinement strength, dielectric properties of the QDNCs, defect states, etc. The illumination intensity of InP/GaP LEDs is more efficient than that

Figure 4. Oscillator strength of type-I—InP/ZnS and InP/GaP—(top panel) and type-II—InP/GaAs and InP/GaSb—(bottom panel) QDNCs.

Figure 5. Efficiency values of QDNC solar cells for type-I—InP/ZnS and InP/GaP—(top panel), and type-II—InP/GaAs and InP/GaSb—(bottom panel). The results are obtained using the modified detailed balance model.
of InP/ZnS ones [34], and this indirectly demonstrates that the efficiency of InP/GaP QDNC solar cells will be smaller than that of InP/ZnS QDNC solar cells.

If we look at the bottom panel of figure 5, although the maximum efficiency values are in relatively good agreement with the literature [11, 12, 17], we see completely different behaviors in the efficiency values with respect to the $E_g$ when compared to the bottom panel of figure 3. When we compare the bottom panels of figures 3 and 5, we see that while the efficiency values of the InP/GaSb QDNC solar cell is higher in the first figure, the efficiency values of the InP/GaAs QDNC solar cell become robust in the second one. In figure 5, the efficiency values start from higher ones and decrease rapidly with an increase in $E_g$ in both type-II structures, similar to the reported studies. But here, the decrease continuously contrasts with the bottom panel of figure 3 and the reported studies in the literature [15–17]. In type-II structures also, the effect of the oscillator strength can be seen explicitly. If we perform an overall evaluation, we see that the efficiency values are higher in type-II QDNC solar cells when compared to the results of type-I. Also, the behavioral characteristics of efficiency with $E_g$ can be completely different in both type-I and type-II QDNC solar cells depending on the shell materials of the structures. As can be seen clearly from the results, the modified model gives an upper limit depending on the materials and the confinement type for the conversion efficiency of QDNC solar cells.

**Conclusion**

The original detailed balance model has been modified, and the upper limits for the conversion efficiency values of QDNC-based solar cells have been calculated by using both the original and modified models for core/shell type-I and type-II QDNCs with different shell materials. The modification is executed on the recombination current density. The original detailed balance model gives the same upper limit values and the same tendencies for all QDNC solar cells with the same $E_g$. That is, the original model does not provide any information about the effects of the materials and/or confinement type of the QDNCs on the solar cell conversion efficiencies. However, both the confinement type and shell material have an enormous influence on the recombination rate, and hence this must affect the recombination current density. Since the modification is taken into consideration in the recombination rate with the assistance of the oscillator strength, the modified model yields different upper efficiency values for different QDNC solar cells, even if they have the same $E_g$ values. That is, the modified model is able to estimate an upper limit for the efficiency of the QDNC solar cells depending on the material properties and confinement types. This is an extremely important result in terms of both the confinement type and the determination of the QDNC materials which will be fabricated for the solar cell applications. It is hoped that the modified model will be used to carry out more realistic efficiency calculations by including material properties, and so a better QDNC solar cell design can be realized.

**Acknowledgments**

The author is grateful to the Abdullah Gul University Foundation (AGUV) for their partial financial support.

**ORCID iDs**

Mehmet Sahin @ https://orcid.org/0000-0002-9419-1711

**References**

[1] Nozik A J 2002 Quantum dot solar cells *Physica E* 14 115–20
[2] Nozik A J 2010 Nanoscience and nanostructures for photovoltaics and solar fuels *Nan Lett.* 10 2735–41
[3] Semonin O E, Luther J M and Beard M C 2012 Quantum dots for next generation photovoltaics *Mater. Today* 15 508–15
[4] Carey G H, Abdelhady A L, Ning Z, Thon S M, Bakr O M and Sargent E H 2015 Colloidal quantum dot solar cells *Chem. Rev.* 115 12732–63
[5] Chuang C-H M, Brown P R, Bulovic V and Bowendi M G 2014 Improved performance and stability in quantum dot solar cells through band alignment engineering *Nat. Mater.* 13 796–801
[6] Green M A 2002 Third generation photovoltaics: solar cells for 2020 and beyond *Physica E* 14 65–70
[7] Akturk A, Tas H, Koksal K and Sahin M 2016 The electronic and optical properties of a triexciton in CdSe/ZnS core/shell quantum dot nanocrystals *Phil. Mag.* 96 584–95
[8] Brown G F and Wu J 2009 Third generation photovoltaics *Laser Photon. Rev.* 3 394–405
[9] Shockley W and Queisser H J 1961 Detailed balance limit of efficiency of p–n junction solar cells *J. Appl. Phys.* 32 510–9
[10] Queisser H J 2009 Detailed balance limit for solar cell efficiency *Mater. Sci. Eng. B* 159–60 322–8
[11] Leontiadou M A, Tyrell E J, Smith C T, Espinobarro-Velazquez D, Page R, O’Brien P, Miloszewski J, Walsh T, Binks D and Tomic S 2017 Influence of elevated radiative lifetime on efficiency of CdSe/CdTe Type II colloidal quantum dot based solar cells *Sol. Energy Mater. Sol. Cells* 159 657–63
[12] Tomic S, Miloszewski J M, Tyrell E J and Binks D J 2016 Design of core/shell colloidal quantum dot mesoporous solar cells *IEEE J. Photovolt.* 6 179–84
[13] Brendel R, Werner J H and Queisser H J 1996 Thermodynamic efficiency limits for semiconductor solar cells with carrier multiplication *Sol. Energy Mater. Sol. Cells* 41–2 419–25
[14] Hanna M C and Nozik A J 2006 Solar conversion efficiency of photovoltaic and photodetector cells with carrier multiplication absorbers *J. Appl. Phys.* 100 074510
[15] Beard M C, Luther J M, Semonin O E and Nozik A J 2013 Third generation photovoltaics based on multiple exciton generation in quantum confined semiconductors *Acc. Chem. Res.* 46 1252–60
[16] Binks D J 2011 Multiple exciton generation in nanocrystal quantum dot—controversy, current status and future prospects *Phys. Chem. Chem. Phys.* 13 12693–704
[17] Smith C and Binks D 2013 Multiple exciton generation in colloidal nanocrystals *Nanomaterials* 4 19
[18] Smith C T, Tyrell E J, Leontiadou M A, Miloszewski J, Walsh T, Cadirci M, Page R, O’Brien P, Binks D and Tomic S 2016 Energy structure of CdSe/CdTe type II colloidal quantum dots. Do phonon bottlenecks remain for thick shells? *Sol. Energy Mater. Sol. Cells* 158 160–7
[19] Li T and Dagenais M 2015 Modified Shockley–Queisser limit for quantum dot solar cells IEEE 42nd Photovoltaic Specialist Conf. (IEEE Conference Publications) (https://doi.org/10.1109/PVSC.2015.7355808)

[20] Tiedje T, Yablonovitch E, Cody G D and Brooks B G 1984 Limiting efficiency of silicon solar cells IEEE Trans. Electron Dev. 31 711–6

[21] Werner J H, Kolodinski S and Queisser H J 1994 Novel optimization principles and efficiency limits for semiconductor solar cells Phys. Rev. Lett. 72 3851–4

[22] Klimov V I 2006 Detailed-balance power conversion limits of nanocrystal-quantum-dot solar cells in the presence of carrier multiplication Appl. Phys. Lett. 89 125118

[23] Takeda Y and Motohiro T 2010 Requisites to realize high conversion efficiency of solar cells utilizing carrier multiplication Sol. Energy Mater. Sol. Cells 94 1399–405

[24] Alharbi F H 2013 Carrier multiplication applicability for photovoltaics; a critical analysis J. Phys. D: Appl. Phys. 46 125102

[25] Alharbi F H and Kais S 2015 Theoretical limits of photovoltaics efficiency and possible improvements by intuitive approaches learned from photosynthesis and quantum coherence Renew. Sustain. Energy Rev. 43 1073–89

[26] Shpaisman H, NishtoO, Lubomirsky I and Cahen D 2008 Can up- and down-conversion and multi-exciton generation improve photovoltaics? Sol. Energy Mater. Sol. Cells 92 1541–6

[27] http://rredc.nrel.gov/solar/spectra/am1.5/ (Accessed: 10 April 2018)

[28] Sahin M, Nizamoglu S, Kavruk A E and Demir H V 2009 Self-consistent computation of electronic and optical properties of a single exciton in a spherical quantum dot via matrix diagonalization method J. Appl. Phys. 106 043704

[29] Koc F and Sahin M 2014 Electronic and optical properties of single excitons and biexcitons in type-II quantum dot nanocrystals J. Appl. Phys. 115 193701

[30] Adachi S 2009 Properties of Semiconductor Alloys: Group-IV, III–V and II–VI Semiconductors (New York: Wiley)

[31] Vurgaftmana, Meyer J R and Ram-Mohan L R 2001 Band parameters for III–V compound semiconductors and their alloys J. Appl. Phys. 89 5815

[32] Van Stryland E W, Woodall M A, Vanherzeele H and Soileau M J 1985 Energy band-gap dependence of two-photon absorption Opt. Lett. 10 490–2

[33] Kumar S, Nehra M, Deep A, Kedia D, Dilbaghi N and Kim K-H 2017 Quantum-sized nanomaterials for solar cell applications Renew. Sustain. Energy Rev. 73 821–39

[34] Kim S et al 2012 Highly luminescent InP/GaP/ZnS nanocrystals and their application to white light-emitting diodes J. Am. Chem. Soc. 134 3804–9