# New concepts of solar cells

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## 1. Introduction

The photovoltaics is one of the most promising renewable energy technology which can contribute substantially to our future energy needs. Solar energy can meet our energy needs completely. In just one hour of solar radiation reaching the surface of the earth (4.3 × 1020 J) is greater than the energy consumed throughout the year (4.1 × 1020 J) by our planet.

The efficiency of solar cells produced today is limited by Shockley-Queisser limit (detailed balance limit) to 31 % under 1 sun illumination and 40,8% under maximal concentration of sunlight (46 200 suns) for an optimized band-gap of 1.3 eV and 1.1. eV, respectively. The laboratory record of conversion efficiency of silicon solar cell with *PERC* structure equal to 25% was obtained at the University of New South Wales in Australia. This is probably the efficiency limit for industrial silicon solar cells. The 90% production of PV modules today is based on the crystalline silicon solar cells called the first generation solar cells. The price of that modules is dominated by the Si wafers and other materials used for the modules encapsulation. The thin films solar cells called the second generation of photovoltaics are less expensive because they do not use the wafers but the price of the thin films is also limited by the cost of materials used for encapsulation. Therefore, there is need to increase considerably the efficiency of solar cells and reduce the cells price by developing new concepts of solar cells. The emerging photovoltaics contains several promising new concept of solar cells, which are presented in this article.

## 2. Three generation of solar cells

The third generation (3G) of solar cells was defined by M. Green [1]. These solar cells are those which are characterized by both a relatively high efficiency (≥20 %) and low cost (approximately ≤ $\$200/m^2$) or the price of the 1Wp is lower than 0,5/Wp (Fig.1).

Cost of currently produced first generation solar cells is limited to about $ 1/Wp. This is a result of Shockley-Queisser (S-Q) limit efficiency and high costs (> $\$ 200 /m^2$) mainly related to the cost of producing silicon wafers. Thin film cells are characterized by potentially lower cost (≤ $\$ 120/ m^2$) but produced today cells have a lower efficiency (<15%). The 1G solar cells are based on the bulk materials that are subsequently cut into wafers and single p-n junction. The second generation of solar cells are thin films solar cells based on amorphous-silicon, poly-crystalline-silicon or micro-crystalline-silicon (a-Si, p-Si and mc-Si), cadmium telluride (CdTe) or copper (gallium) indium selenide/sulfide. The 3G solar cells are thin films solar cells as well, but they differs from 2G solar cells by higher efficiency.

From Fig. 1 it is seen that the solar cells of 3G concepts can be divided by two group.

The first group are solar cells (not realized yet) with efficiency higher than present S–Q theoretical limit (30-40%) and the second with efficiency lower than this limit.

The first group includes the new concepts of solar cells introduced firstly by M. Green and co-workers.

The second group includes new concepts of thin films solar cells which can be very cheap and have moderate efficiency. They include the cells from colloidal quantum dots, organic solar cells, DSSC and perovskites solar cells. Professor Ravi Silva distinct this group among the cells as 4G solar cells [3], but this is not commonly accepted by the PV community, yet.
This kind of cells belongs to the emerging photovoltaics, regardless of whether we classify them into 3G or 4G photovoltaics.

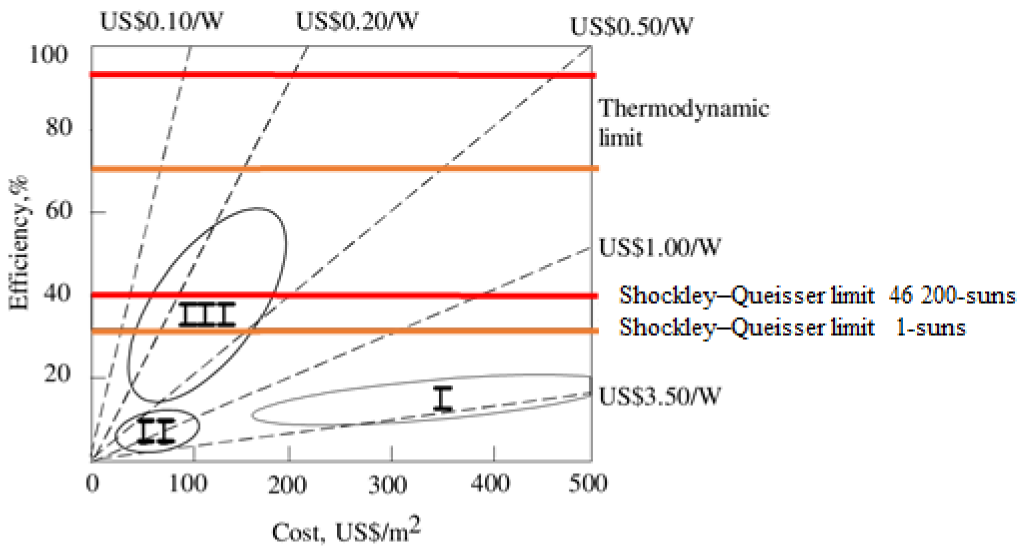


**Figure 1**. Efficiency-cost trade-off for the three generations of solar cell technology; wafers, thin-films and advanced thin-films [Green 2003, 2]

### 3. Concepts of 3G cell with an efficiency higher than S-Q limit.

The Carnot limit efficiency is equal to about 95 % for Sun with 6000K and the cell with 300K temperatures [2]. The low value of Shockley-Queisser (S-Q) limit in comparison with Carnot limit is caused mainly by two factors:

- photons with smaller energy than energy gap $E_g$ are lost;
- exited carriers by high energetic photon ($E_{ph} > E_g$) give excess energy to phonons due to thermalisation process.

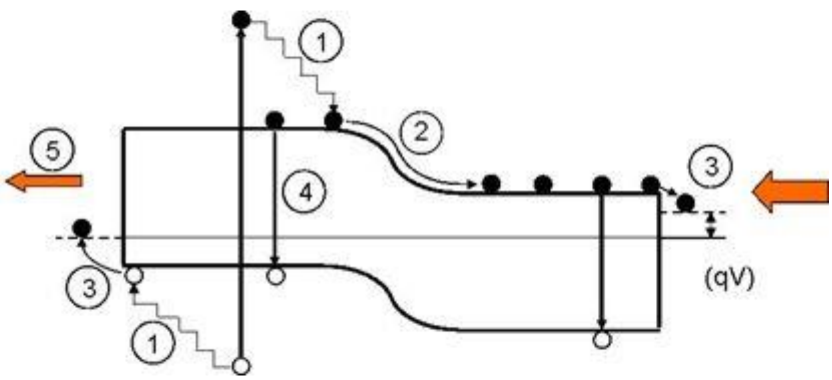


**Figure 2**. Energy losses in a standard solar cell: (1) thermalisation loss; (2) junction voltage loss; (3) contact voltage loss; (4) recombination loss; (5) optical loss arises from photons not absorber by the cell [2].

The aim of new concepts of very high efficiency solar cells is reduction these two loses and by this way to increase the efficiency. There are three approaches : 1) increasing the number of band-gaps, 2) multiple carrier pair generation per one high energy photon or one pair carrier generation by two or more low energy photons, or 3) collecting carriers before thermalisation [3]. One of the main approaches is tandem solar cell which is composed from many cells with different bandgaps. In the limit of an infinite number of cells the theoretical efficiency for concentrated sun light is about $\eta_{max}$ = 86.8 % and for one-sun intensity 69 % [3]. Usually, tandem cell is limited to 2- or 3 cells. The efficiency limit is 42.5% and 48.6 % for non-concentrated sun light for 2- and 3-bandgaps tandem cells, respectively [3].

*Multi-junction cells* consist of a number of cells present in order of the cell with the largest band gap (radiation incidence side) to the smallest. The base material of solar enabling the formation of the structure of the desired width of band gap is silicon in the form of quantum dots arranged in a dielectric layer of $SiO_2$, $Si_3N_4$ and SiC forming the so-called quantum – super lattice. Engineering the energy bandgap of such material involves the formation of silicon quantum dots of a certain size, uniformly distributed in the dielectric and a predetermined distance between them.

In the simplest case of tandem cells the two-junction are considered, consisting of an ordinary silicon cell and the second cell with silicon quantum super-lattice with band gap of 1.7 eV (Fig. 2). The diameter of Si QDs should be 2 nm in this case. These two cells are connected in series by tunnel junction. In the case of a tandem cell made up of three cells, the upper cell is composed of super-lattice quantum with the bandgap energy of 2 eV, the middle cell of the quantum super-lattice with band gap of 1.5 eV and the bottom cell is an ordinary silicon cell. These cells are connected by tunnel junctions from quantum well super-lattices [4].

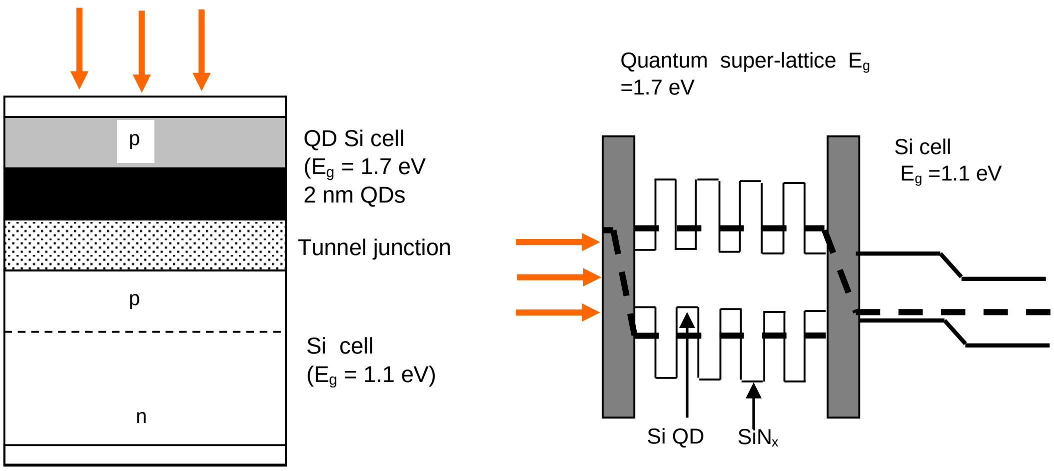


**Figure 3**. (a) Diagram of a two-junction silicon cell. The upper cell is composed of a quantum super-lattice with a band gap of 1.7 eV, and second cell is a classic silicon cell. These cells are connected by tunnel junction, (b) Schematic of the relative energy levels [4].

*Hot carrier* cells are another concept of high efficiency 3G cells. The idea of this cells is to collect the hot carriers generated by a high energy photon energy $E_{ph}$> $E_g$, before being cooled by interaction with phonons. [4-6]. If the base material is composed with low-dimensional structures, in particular quantum dots, the interaction of hot carriers with the phonons may be limited due to the discrete energy levels. For this type of cell maximum theoretical efficiency rate $\eta_{max}$ = 85% for the concentrated light and 65% for the light non-concentrated.

A third example of concepts are *IBSC* cells (*Intermediated-band solar cells*). These cells have additional bands in the band gap energy. Inserting one or more bands (to the bandgap of the semiconductor base) can increase the efficiency of the cell [7]. These additional bands may be a mini-bands in the quantum superlattice. Limit efficiency is 63.2% for the concentrated light for this type of cell. The width of the energy gap is 1.95 eV and there is an additional band in the band gap which creates two sub-bands, one with a width of 1.24 eV above the valence band and the second with a width of 0.71 eV below the conduction band [8].

The another concepts of high efficiency solar cells are based on *multiple carrier pair generation* per one high energy photon. One of this concepts is use the impact ionization process in the quantum confined nanostructures (QDs). This process called *multiple exciton generation* (MEG) was first proposed by Nozik [9]. The enhancement of MEG in QDs is due to relaxed conservation crystal momentum in QDs. This phenomenon was observed for the first time in PbSe QDs by Schaller and Klimov [10].

Another type of concepts in order to multiple carrier pair generation per one high energy photon or one pair carrier generation by two or more low energy photons are *down- converter (DC)* and *up-converter (UC)*. The both converters modify the incident spectrum: DC convert high energetic photon (at least twice the bandgap energy) into two photons incident on the cell and UC convert at least two below-bangap photons into one above–bandgap photon. The DC is placed in the front a standard cell, and the UC on the back of the cell. The limit of up-converter is 48% for a solar cell with $E_g$ = 2eV under non- concentrated AM1.5 spectrum [6].

The limit for down-converter cell is 36.7% under 1-sun illumination and for optimal bandgap close to Si bandgap.

## 4. The solar cells of emerging photovoltaics

Despite intensive work carried out for more than 10 years, the ideas of 3G cells with efficiency higher than limit S-Q have not been realized, yet.

The solar cells of emerging photovoltaics, like organic cells, DSSC cells, quantum dots solar cells and perovskite cells (Figure 4) have efficiency considerably lower than S-Q limit. These cells are produced from solutions at low temperature processes and using simple techniques such as printing or spin-on, thus potentially can be very cheap.

Different kind of semiconductor QDs can be used in different cells architectures: CdS, CdSe, CdTe, $CuInS_2$, $Cu_2S$, PbS, PbSe and organo lead halide perovskite, as well. However, the cells based on QDs have small efficiency today (4-6%), there is possibility to exceed the S-Q limit due to multiple exciton generation (MEG) process [9].

Among these cells, it seems that perovskite cells are the most attractive. Hybrid organic–inorganic perovskites $CH_3NH_3PbI_3$ were first demonstrated in 2009. Cells based on such materials increased power conversion efficiency from about 10% in mid-2012 to 21 % at present. There are two different structures of solar cells with the perovstites material. In one structure, the perovskite material is deposited on the mesoporous (mp) metal oxide like $TiO_2$, $Al_2O_3$ or ZnO. In Fig. 5 it is shown one of the perovskite cell structures. The perovskite $CH_3NH_3PbI_3$ is deposited on the top of the mp-$TiO_2$ film. The pores of the mp-$TiO_2$ film are infiltrated with perovskite and partly the perovskite cover the top of the mp-$TiO_2$ film. On the top of the perovskite film the organic hole-transport materials (HTM) is deposited. Commonly HTM small molecular hole conductor 2,2,7,7-tetrakis-(N,N-di methoxyphenylamine) 9,9-bifluorene (spiro-OMeTAD) is used. The good results were obtained for poly-triarylamine (PTAA) as HTMs layer [11]. The back electrode is gold evaporated on the HTM surface. The front electrode is FTO (fluorine doped thin oxide) deposited on the glass.

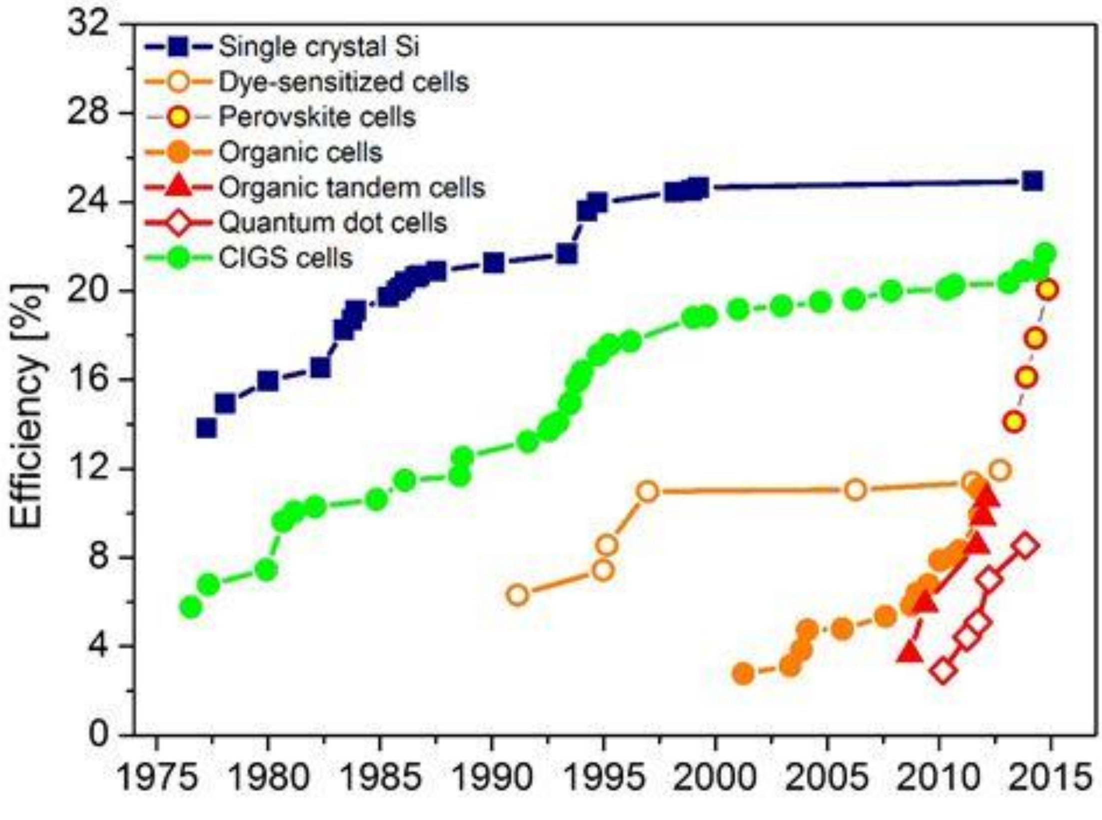


**Figure 4**. The best laboratory solar cells of emerging photovoltaics (organic, DSSC, peorovskite and QDs) compared with single crystal Si (1G) and CIGS cells (2G) (based on the data from latest chart on record cell efficiencies from National Renewable Energy Laboratory, Golden, CO (http://www.nrel.gov/ncpv/images/efficiency_chart.jpg ).

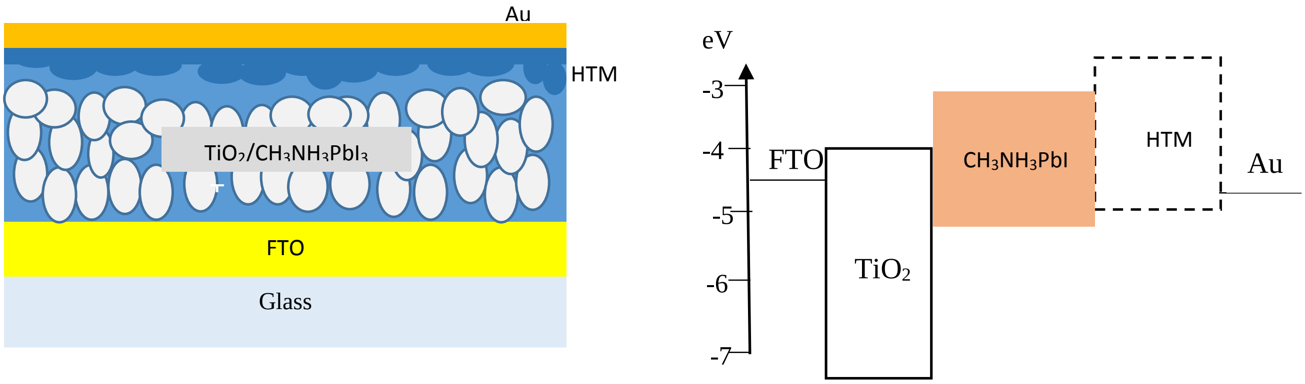


**Figure 5**. Schematic of device architecture with $TiO_2/CH_3NH_3PbI_3$ composite and the HTM layer - next-generation of dye-sensitized solar cells (a). Schematic of the relative energy levels of each layer (b). FTO - fluorine doped thin oxide, HTM- hole transport material. The efficiency 12 % for AM1.5 was obtained for poly-triarylamine (PTAA) as HTMs layer [11].

In the other kind of perovskite cell structure, the perovskite is in the form of the planar film. Recently, Olga Malinkiewicz showed the solar cells with thin film (285nm) planar perovskite deposited in the typical organic cell structure (Fig.6) [12]). In this cell the perovskite film $CH_3NH_3PbI_3$ was deposited by vacuum evaporation from two sources $PbI_2$ and $CH_3NH_3I$. The efficiency of that cells was 12% for AM1.5 and 100 mW/cm$^2$ illumination. Advantage of this new cell structure is that it can be produced at low temperature and can be applied on the flexible substrates.

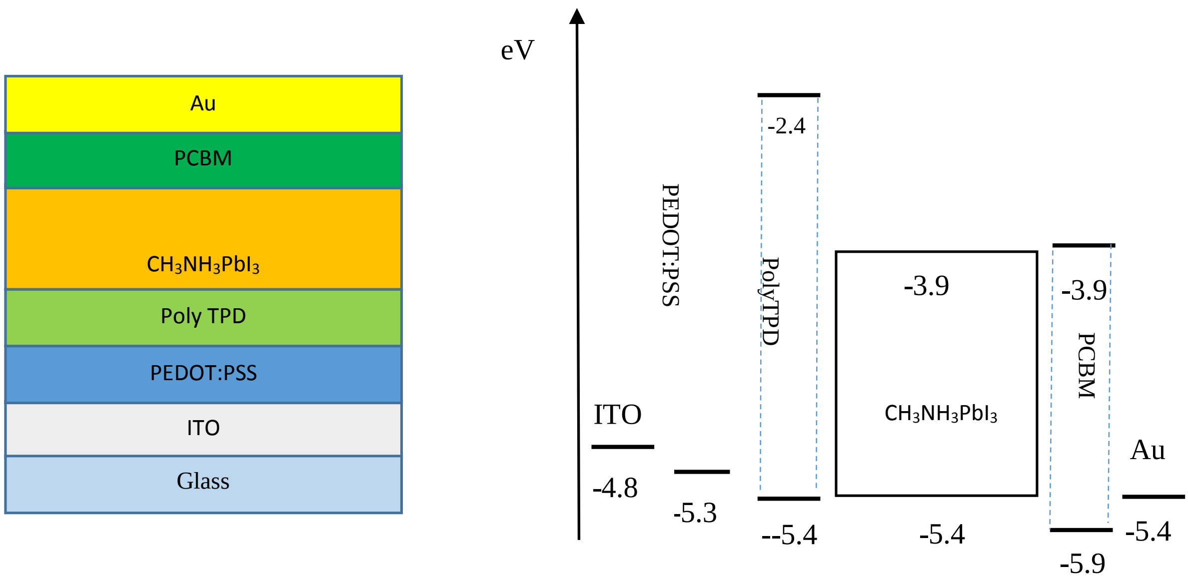


**Figure 6**. Structure of the cell with planar perovskite layer – the cell structure similar to the organic cells (a). Schematic of the relative energy levels of each layer (b). ITO- indium thin oxide, PEDOT:PSS - Poly(3,4-ethylenedioxythiophene) : Polystyrene sulfonate – conductive polymer, PolyTPD - poly(N,N′-bis(4-butylphenyl)-N,N′-bis(phenyl)benzidine) - electron-blocking layer, PCBM- C61-butyric acid methyl ester - the hole-blocking layer [12].

The QD-based solar cells with QDs as light harvesters in solar cells, can be used in different structures of QD heterojunction solar cells, QD-Schottky solar cells, QD-sensitized solar cells and in organic-inorganic perovskite heterojunction solar cells [13]. The name of QDs solar cells usually refers to the cells using inorganic quantum dots such as: PbS, PbSe. Figure 6 shows the of QDs cell structure with heterojunction. The effciecy is in the range 4-6% under AM1.5 illumination [14 -16]. The commonly used QD-Schottky cell structure is FTO(glass)/QDs/Metal. The reported efficiency of these cells is in the range of 1.8% – 2.1% under AM1.5G illumination [17 -19].

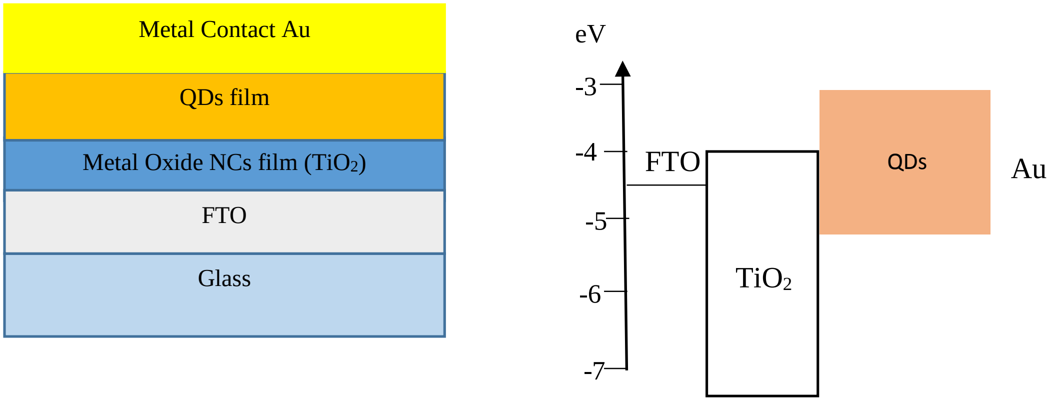


**Figure 6.** Quantum dots (QDs) heterojunction solar cell (a); Energy level diagram of QDs hetero-junction solar cell (b). The efficiency is in the range of 4-6 % [13].

## 4. Summary

The short review shows many new concepts of solar cells. The concepts of 3G solar cells with very high efficiency higher than S-H limit encountered major problems with their implementation. Despite intensive work carried out for more than 10 years, these concepts have not been realized, yet. Despite this, we can see the big progress in the organic cells, DSSC cells, quantum dots solar cells and perovskite cells. Among these cells, the perovskite solar cells are the most promising.

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