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Type III solar cells based on quantum dots

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Abstract

In this thesis the extensive study of possible and surly optimal materials for Quantum Dot Solar Cells (QDSCs) will be provided to the reader. One will have the opportunity to develop a rather current image of the necessary parts in their architecture which will be supported with an abundant description of the important aspects in engineering a photovoltaic device. With an introduction of its kind we will try to convey a basic but sufficient knowledge of standard terms, light with matter interaction, light spectrum analysis, quantum dots description with their behaviour and a photovoltaic device operation theory with certainly needed quantities that one has to find in order to properly describe a solar cell. In many parts we will try to outline possible enlargement of that information. With the objective of creating a possibly competitive QDSC the description of methods that we used will be included with a related to them characteristics. One will also be able to use this paper as a review of today's development phase and current technological state of the other scientific groups all around the world. After a successful development of a solar cell the analyse and comparison will definitely be provided.

Contents

Abstract.....	1
Contents	2
1. Introduction.....	3
2. Theory	5
2.1. Classical theory of light and light with matter interaction	5
2.2. Introduction to quantum description of light	5
2.3. Quantum dots and nanostructures.....	5
2.4. Theory of photovoltaic devices	7
2.5. Solar cell parameters.....	7
2.6. Third generation solar cells, QDSCs and review.....	7
3. Cell architecture.....	11
4. Device depositions and parameters	11
5. Results analysis.....	11
6. Future possibilities.....	11
7. Conclusion and outlook	11
8. References.....	11
9. Images.....	16
10. Tables.....	16
11. Attachment.....	16

1. Introduction

We, as a society nowadays, are in constant demand for energy. Although, even with the development of calculating, conducting and studying it, we don't really know what the energy is, we are depending on that abstract quantity. One might probably say that to study physics is to endure to study energy in its every possible form. There's a brilliant quote from Bill Bryson that: "Energy is liberated matter, matter is energy waiting to happen." What might be incredible is that from this strictly mathematical quantity we can deduct anything. And what's also important it is as arbitrary as it gets, depending only on one's reference. From energy we can create few more important quantities such as *power* P , which is simply the energy provided per unit time, so:

$$E = \int P(t)dt$$

The energy will be represented in J (Joules) or eV (*electron volt*), which directly describes energy of elementary charge body ($e \approx 1.602 * 10^{-19}C$) in 1V (Volt) potential.

$$1eV = 1.602 * 10^{-19}J$$

Power will be then represented in W (Watts)($W = \frac{J}{s}$).

The rise of energy consumption has proven that in the future we will almost certainly require even more. From Global Energy Perspective paper [1] we can learn that:

- Global energy demand will reach plateau at around 2035 despite strong population expansion and economic growth thanks to emphasis on renewable sources, more efficient service industries or more efficient industrial regions
- The energy demand and economic growth became "decoupled" for the first time in history
- Renewables will provide more than half the electricity after 2035

The reader is strongly recommended to take a look at the document.

With saying that we can produce energy there's a slick trick given with the phrase. Energy cannot be simply created, it is just converted from another source so nothing is ever lost or miraculously made. The problems we need to struggle with are then being able to obtain as much energy from the energy source as it is possible and of course, as humankind society is governed by money, keep the cost lowest. There are plenty of different energy sources that we learned to receive energy from. In (Figure 1) we can see the most vivid ones nowadays. But with the human demand fulfilment come great damages and soon depleting resources of many energy sources such as fossil fuels.

Global primary energy consumption

Global primary energy consumption, measured in terawatt-hours (TWh) per year. Here 'other renewables' are renewable technologies not including solar, wind, hydropower and traditional biofuels.

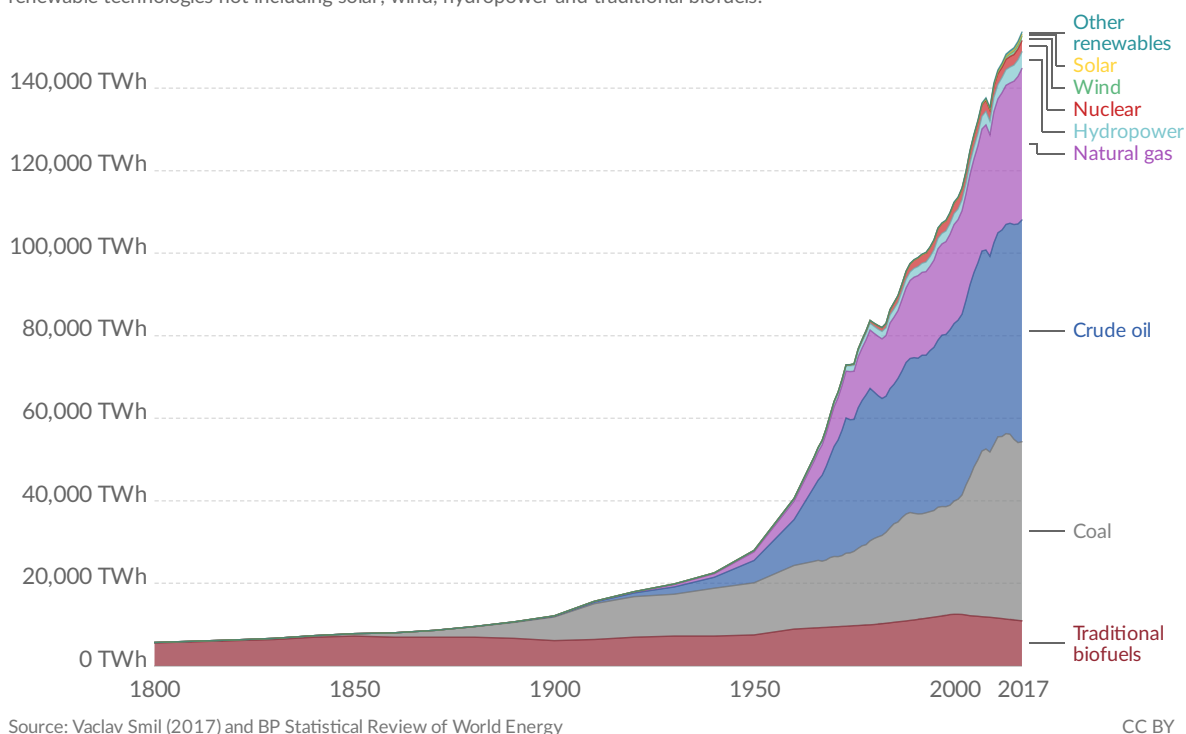


Figure 1. Energy sources contribution in world scale [97]

The necessity of searching new possible ways to harness it through renewable sources has become a global issue. Our concern of the environment had never been that serious before. Not only the change of methods for energy production must be enhanced because of this demand but we need to be strictly aware of the world's urging trepidation of Global Warming of which evidence is provided for example here [2] .

With conventional methods still being the vast majority, the new approaches that might solve most of our problems, are arising to become significant. There are for example:

- hydroelectric farms that use to convert potential energy from water sources and create electrical energy from it with usage of water turbines
- wind mills that convert kinetic energy of air flow
- tidal energy plants

Among all of the ideas created in a past few decades, solar energy is believed by many to be the most reliable and promising. It can be directly converted into electricity, heat or chemical energy and our only star seems to be an infinite power resource for us. In the last ten years the world solar PV electricity production has grown impressively, being almost three times bigger in 2016, than in 2010 [3]. In theory, the Sun has the potential to fulfil earth's energy demand if it is not for the technology. Annually, nearly 10^{18} EJ of energy reaches our planet and of that 10^4 EJ is claimed to be harvestable. The possibility of converting the solar energy into electric

energy has been studied since discovery of the basic photovoltaic effect and the development of semiconductor technologies.

Yearly sum of Global Horizontal Irradiation (GHI)

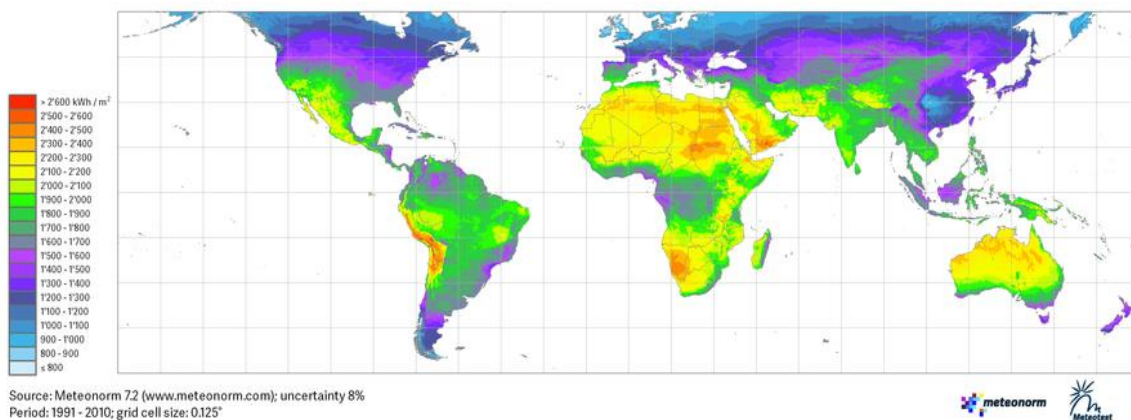


Figure 2. Annual yearly sum of Global Horizontal Irradiation [110]

2. Theory

2.1. Classical theory of light and light with matter interaction

2.2. Introduction to quantum description of light

2.3. Quantum dots and nanostructures

2.3.1. Colloidal Quantum Dots

CQDs are semiconductor crystals of the nanometre-scale size, with the diameter of less than twice the Bohr radius size, which are restricted with surfactant molecules and deployed in a solution. They have manifested to provide a development of numerous types of optoelectronic devices including photodiodes and PV devices. The properties of CQDs are easily adjusted by changing the volumetric features of nanoparticles similarly to metallic nanoparticles in plasmonic transport. [4] [5]

a) Quantum dot size.

With changing the size of the nanoparticle we can control the band gap over significant range of spectrum. Yet, practically, the width of the nanoparticle is estimated from the energy band gap. [6]

b) Quantum dot shape

The geometry in physics plays an important role, there is no question about that. It is obviously not different for Quantum Dots. The quantum confinement strongly depends on the shape and dimensional geometry. The ability to control the growth of certain form allows the nanoparticles to exhibit a variety of properties.

As it is the introduction part we will proceed to investigate different forms later.

2.3.2. Chemical properties controlling.

a) Ligand exchange

While long-chain surfactants enable us to have a firmly stable CQD solution they are an insulating medium as well. [7] [8] To achieve massive improvements in film properties shall we partially or fully exchange the initial ligands in solution. The first studies of reactions to exchange the ligands were based on replacing the long-chain ones with organic short molecule structures (butylamine or pyridine [9] [10]) Also, the metal chalcogenide complex for these cases were tested widely and also quite successfully deployed. [11]

b) Alloying and Doping.

The inner relationship between the band gap and fraction of nanocrystal particles in solution gives nonlinear characteristics and shall be studied to definitely provide the optimum. The distribution can determine precisely if the alloy is graded or homogeneous. [12]

Doping CQDs with other nanoparticles can also allow different strategic fabrication of PV structure than using single type of CQDs. An example of such behaviour can be PbS CQDs doped with silver, which has led to increasing the solar cell efficiency via introducing an extra charge carrier in the film [13].

c) Core/Shell Quantum Dots.

Easy desorption of the ligands from the surface can be limited by more convenient surface passivation through the introduction of extra material shell- a core/shell structure. It can provide an isolation that would allow the core atoms to last significantly longer than without it.

Again, the detailed part shall be provided in the next chapters.

d) Fully inorganic solar cells.

Between all of the examples shown above, a new idea of using all-inorganic CQD Photovoltaics has marked its' extraordinary intro. The approach to brand new CQDs films production based on the replacement of organic ligands with halide anions has become the new track for scientist. There are some advantages of using such a method of omitting redox reactions, with reducing the inner density of trap states within the bandgap among them. The so-called ligand passivation can be a strategy to ultimately enhance device performance. [14] Shall we ponder only the working principles, by many means the scheme isn't much different from other approaches, but it could remind us more about the original, first generation PV devices rather than organic ligand-based ones.

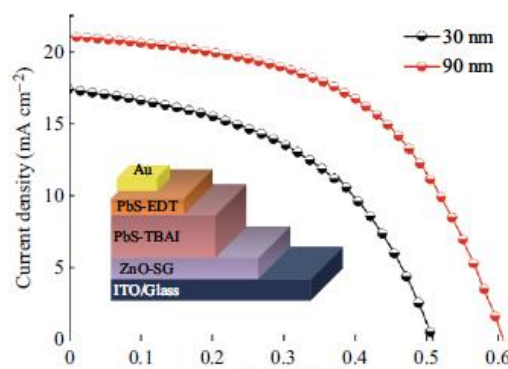


Figure 3. The structure of all-inorganic solar cell based on PbS CQDs with optimized ZnO film and its I-V characteristics for two different ZnO film thickness. [15]

Within this rather modern idea, the PbS and PbSe CQDs are commonly used. The widely explored architecture is shown in (Figure 3). A numerous researches and their record results

has shown that architecture to be very promising. [15] The passivation of ligands has been achieved by different fabrication methods, resulting in various models and their performances, yet based on the same idea. [15] [16] [17] In case of this paper we shall also investigate whether we can improve the scheme of those structures and create even more stately device prototype.

2.4. Theory of photovoltaic devices

2.5. Solar cell parameters

2.6. Third generation solar cells, QDSCs and review

2.6.1. QDSC in principle.

The great achievement of these types of solar cells is the decoupling the charge generation and its' transport to different materials- the hole and electron transport layers. The effect of such a procedure is the decrease in recombination process and reduction of production costs. Without that technique, the architecture is adequate to the standard PV solar cell device. The generation of electron-hole pairs proceeds the injection of electrons from Conduction band of light harvesting material to electron acceptor layer and holes from valence band to hole acceptor layer. We call this process a charge separation. Nevertheless, even though we do regenerate QDs in the light harvesting area after charge separation, we still have to struggle with recombination processes and consider them as the significant performance wasters. [18]

2.6.2. Materials and performance development.

a) Electron transporting materials (ETMs)

They are used to support charge separation as briefly described above. The function proceeds as a support for QD in the charge generation layer as it transports charged electrons to the conductive substrate(usually FTO) [19] [20] [21] The properties shall be as follows:

- Matching CB edge – which will determine exciton generation and partial transfer efficiency.
- High electron mobility.
- Fine surface to provide suitable loading of particles.
- Suitable technological properties, such as stability, low cost etc.

The most widely studied materials nowadays are TiO_2 and ZnO . Materials based on first compound are of such importance due to their nontoxicity, chemical stability and low cost [22] [23]. Among them (TiO_2 -NP) based mesoporous layers are studied as photoanodes [22]. The highest efficiency ever recorder were based on that material [24] [25] [26]. Unfortunately, the probability for charge recombination in that kind of films is rather unsatisfactory. Therefore, one provides one- dimensional structures such as nanorods and nanowires to improve smoother electron transport channel and decrease loses provided with recombination [27] [28] [29]. In 2007 it was shown that TiO_2 nanotubes win over nanoparticles of the same material in case of transport capacity [30] [31]. Thus, the research of such structures was accelerated and CdSe sensitisation was proposed [32]. After that, many different sensitisations were provided, in which also PbS QDs had their small part [33]. Although promising, the 1D structured TiO_2 based anodes were unsatisfactory in case of PCEs comparing to standard nanoparticles (maximum of around 6% [29]). The hypothesis was put on insufficient loading amount on 1D structured TiO_2 , therefore the focus should be put on improvement of that area. A group of

researchers has also used graphene frameworks incorporated into TiO₂ photoanode achieving 4.2% PCE for QDSSCs. [34] By using double-layered films with particles of bigger volume, there has been achieved a high PCE of 4.92%. A lot of dopants and different solutions, hybrid photoanode films with metal and non-metal ions and carbonaceous layers has been proposed to improve performance of PV devices. Also with the usage of hollow structure techniques, by creating nanotube arrays, the possibility of achieving a PCE of 6% was shown. [35] Improvement light absorbance was achieved by using microporous TiO₂ photoanode for PbS quantum dot sensitised solar cells achieving up to 3.5% PCE performance. [36]

In case of ZnO based photoanodes the differencing property is a higher electron mobility and better conduction band edge. With them, the achievement of higher V_{oc} is more probable [37] [38]. Unfortunately, the chemical stability of those films is significantly lower. Similarly to the former, the nanoparticles were widely studied. [39] [40] [41] [42] As an example, the CdS sensitised ZnO nanoparticles were used to construct a photoanode, which allowed the achievement of 4.46% PCE. They used TiO₂ passivation of ZnO surface to improve the PCE of same sensitized CdS/ZnO QDSCs by more than 2%, achieving 4.68%. [41] Similarly, the 1D structures for ZnO can be crystallised. The distinction from the former is the ease of its' development [39] [41]. The ZnO nanowires sensitised with CdSe constructed in 2007 were the launch of the technology development and allowed Young et al. achieve PCE of 4.15% [43] [44] [45] [46]. Many more one dimensional structures of ZnO based photoanodes were used to research maximal performance but it was shown that the problem again concerns the surface area [47]. For example, it was shown that modification of surface of ZnO NRs with TiO₂ improves PCE from 1.54% up to 3.14% [48]. The second strategy to improve the performance of such material based structures is double layer replacement with two different 1D structures such as NR on bottom and TP on top. However, the PCEs of ZnO based films still stay behind TiO₂ ones. [49] [50] The Al/Cl hybrid doping allowed to use ZnO in IR spectrum. [51]

There are other kinds of ETMs researched as well. Using big tandem structures has manifested superb PCE through simulations. [52] The doping of synergistic fullerene electro transport layer has proven to increase Solar Cell performance [53] A series of materials such as SnO₂, NiO, BiVO₄, Zn₂SnO₄, BaTiO₃, CoO has been incorporated to QDSC manifesting future potential. [35] High performance has been achieved using CdS thin films as single-source precursors to ETM layer providing over 8% PCE. [54]

All of the above materials are n-type semiconductors. Furthermore shall we proceed to introduce the p-type metal oxides and p-type Quantum dot sensitised cells. Typically, the NiO semiconductor is widely used. The promising and comprehensive material that can be implemented is CuSCN, which is an inorganic of p-type. Of course, the extraction of a hole from light harvesting layer to a redox couple will be rather slower than in case of electron. [29] [55]. Therefore, being the potential solution to this problem, the p-type semiconductor based layers are beginning to leave their mark in PV devices. As expected, the most accurate application of that type of films would be the tandem configuration construction, which contains

ETM	QDs	CE	Electrolyte	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF	PCE (%)	Ref.
TiO ₂ -NP	ZnS/CdSe	MC/Ti	Polysulfide	27.39	0.752	0.619	12.75	112
TiO ₂ -NW	CdS/CdSe	Cu ₂ S/FTO	Polysulfide	19.32	0.531	0.586	6.01	145
TiO ₂ -NT	PbS	Pt	I ⁻ /I ₃ ⁻	8.48	0.64	0.63	3.41	127
TiO ₂ -NR	PbS	—	Spiro-OMeTAD	13.56	0.52	0.579	4.10	133
TiO ₂ -NS	CdSe	Cu ₂ S/brass	Polysulfide	16.95	0.591	0.50	5.01	148
ZnO-NP	CdS/CdSe	Cu ₂ S/brass	Polysulfide	10.48	0.683	0.623	4.46	149
ZnO-NW	Zn _{0.9} Cd _{0.1} Se	Cu ₂ S/brass	Polysulfide	18.05	0.65	0.40	4.74	105
ZnO-NW	ZnSe/CdSe	Cu ₂ S/brass	Polysulfide	11.96	0.836	0.45	4.54	150
ZnO-NR	CdS/CdSe	Cu ₂ S/brass	Polysulfide	13.28	0.642	0.567	4.83	151

Table 1. Photovoltaic performance summary for QDSCs based on different Electron transport materials. [56]

both n-type and p-type QDSCs to overcome so called a Shockley-Queisser limit. However appealing, the efficiencies of p-type QDSCs are yet to be enhanced. [56]

b) Hole transporting material (HTM) layers.

The electrolyte or HTM is crucial to QDSCs as well. The properties of such film shall be:

- Low corrosivity.
- Redox potential appropriate to regenerate QDs and maintain fine V_{oc} .
- High conductivity through ions.
- Stability and transparency in visible spectrum.
- Possibility to fully regenerate. [56]

The common electrolytes:

- Liquid electrolytes
- Quasi-solid state electrolytes
- All-solid state QDSCs

were described comprehensively in the following research papers [56] [57] [58]

Although using Sb_2Se_3 as a thin light harvesting film, a group of researchers has also used PbS colloidal quantum dots as a hole transport layer achieving 6.5% certified PCE in 2017. [59] In 2016 the usage of graphdiyne (a novel large π -conjugated carbon hole transporting material) was used for an efficient hole transport layer for solar cells based on PbS-EDT colloidal quantum dots. [60] Before that, in 2015, colloidal $CuInS_2$ QDs were layered to hole transporting solution and even though the scientist did their research on Perovskite solar cell, they accomplished to get almost 8.5% PCE. [61] The extended device stability and a rise to 10.6% of PCE was certified using CQD solar cells using P3HT as a hole transport material. [55]

c) QD sensitizers

The main part of our PV device, the QDSC are QDs. The ability of harvesting interfering light is a crucial component of such device. [62] [63] Therefore, the ideal nanostructures should exhibit certain properties:

- A higher CBE than the one in the electron transport material and lower than in hole transport material to provide effective charge separation.
- Obviously, as in all semiconductor PV devices, we shall provide a material with accurate band gap, ideal for our purpose. The reason is clear, we are interested in superb absorption in wide range of solar spectrum.
- The stability is the crucial property as well.
- From the technological point of view- the simple preparation and of course low toxicity would be rather expected.

Therefore, we will now examine methods to deposit them and the differences between certain QDs materials.

Because of QDs being inorganic and possessing larger size than simple molecular dyes, they are much more difficult to tether onto metal oxide to form a high quality monolayer. Therefore high QD-loading amount is rather high to achieve. [64] We can difference the deposition

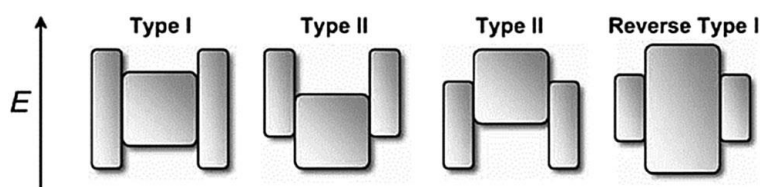


Figure 4. Schematic illustration of energy levels in different core/shell QDs types.

methods by putting them into two categories: *in situ* and *ex situ*. In the first one, the QDs are grown directly on the surface of the metal oxide substrate, being created using an ionic precursor. We can include chemical bath deposition (CBD) and successive ionic layer adsorption and reaction (SILAR) into this category. The second approach bases on pre synthesising of QDs and then depositing them onto the metal oxide. Easily processable and finely reproducible, the *in situ* method has been used more widely than its' counter. In that kind of deposition we can control not only the QD-loading amount but also size distribution. Unfortunately, the achieved density of trap states is rather high, therefore the obtained maximal PCE is about 7% [65] [66]. In this case, excluding the QDs growth process, we have to accurately deploy them onto the surface. The most common methods are: direct absorption, linker-molecule-assisted self-assembly, electrophoretic deposition. [56] [67] The ligand part in QDs is, as mentioned before, the important part of obtaining high efficiency of QDSCs. [68] The comparison of halide ligands in PbS CQDs for field effect transistors has been made by researchers in 2018. [69] The capping-ligand-induced self-assembly method was the clue for TiO₂ photoanodes. [56] Nevertheless, researchers haven't discovered a satisfying approach yet. In 2012, the deposition method were optimised through using ligand-exchange techniques. [70] [71] Thanks to that, the PCE record of 13% was achieved [72] Not only CLIS deposition has been used. The aqueous solution provided the simplification of QDs fabrication with shorter ligands. [73] Some relatively high PCEs have been achieved with that method. [56] Then, the organic molecules usage allowed scientist in 2015 to achieve 300% times PCE compared to common creation of PbS quantum dots. [74] The certified PCE of 11.21% has been achieved via so called "solvent curving", which is the simplified method of PbS QDs fabrication processing. [75] The passivation of PbS QD surface with L-glutathione was used to produce QDSCs with promising results. [76] 10.6% PCE was achieved thanks to solvent-polarity-engineered halide passivation. [77]

Up to date, binary QDs have also been used as sensitizers. There are many examples but the most common are: InP, InAs, CdS, CdSe, CdTe, Ag₂S and with them, the most interesting one considered in our case- PbS. [78] [79] [80] [81] [82] [56] The main problem with them is to control and balance the narrower band gap and relatively high conduction band edge. For example, for PbS nanocrystals the band gap is narrow, but the conduction band edge is rather low, which causes the problem and has to be dealt with. In case of binary QDs we have to balance between the light harvesting efficiency and efficiency of charge injection. Mixing binary structures (for example PbS with PbSe) has been also proven to enhance the interesting efficiency. [83] [84] Treatment of PbS QDs with metal salts provided some advantages in CQD PV devices resulting in the increase of short circuit current and fill-factor. [85] The crucial part of success in getting high efficiency would also be suitable engineering of solvent. [86]

The other methods to use QDs as sensitizers in PV devices is creating a Core/Shell QDs. Their unique properties have been mentioned before. The alignment in these provides ability to tune the light-absorption range, recombination processes and charge separation. Usage of them in QDSCs is rather modern. The first noticed implementation was created by Lee et al. in 2009. Through SILAR method, he achieved PCE of 4.22%. [87] Yet the difficulties in creating specific materials may occur, because of inability to prepare a stable precursor for deposition

methods. Core shell QDs can be classified into three categories: type I, reverse type I, and type II structures. [88] [89] [90] A great deal of detailed information can be possessed from that review [56].

The massive perspective in PV devices has also been established by using Alloyed QDs. These allow us to create the non-linear band gap [91] [92] [93]. Stability in such materials is again much higher than in their constituents. A lot of scientific research was done in that area. The summary is satisfactorily described in publication below. [56] The review finely describes recent achievements and potential usage of alloyed QDs in the near future.

We can also include dopants to QDs. There were a handful of propositions in the former review as well. Yet, the promising idea has been introduced with the usage of metallic nanoparticles dopants by considering plasmonic physical phenomena. [94] [95] [58]

d) Counter electrode

As we may already expected, they are also playing an important role in achieving high performance of PV device. The electrodes have to catalyse reduction reaction. These shall poses properties as follows:

- Good conductivity
- High catalytic activity
- Fine stability, either chemical and physical

We can also put them into four categories:

- Noble metals
- Metal chalcogenides
- Carbon materials
- Composite CEs

Recent progress has been comprehensively described in those publications [56] [96] [57]

2.6.3. Recombination control

Non-radiative charge recombination can seriously disable any performance of PV device. Because of defects states in QDs, the recombination is more serious than in normal DSCs. The recombination processes maintain standard paths, but of course they have their own specificity. [56] Controlling of recombination processes can be either through material engineering and interface engineering. [56] More specific information shall be provided later.

2.6.4. Stability

Controlling of stability can be achieved through material design and of course temperature adjustment. More specific information is also provided with the [56] review.

3. Cell architecture

4. Device depositions and parameters

5. Results analysis

6. Future possibilities

7. Conclusion and outlook

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9. Images

Figure 1. Energy sources contribution in world scale [97]	4
Figure 2. Annual yearly sum of Global Horizontal Irradiation [110]	5
Figure 3. The structure of all-inorganic solar cell based on PbS CQDs with optimized ZnO film and its I-V characteristics for two different ZnO film thickness. [15]	6
Figure 4. Schematic illustration of energy levels in different core/shell QDs types.	10

10. Tables

11. Attachment