Minireview Article

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Research Development and Future Aspects of Quantum dot and Perovskite Sensitized Solar Cells

ABSTRACT

The sustainable development of human depends upon the clever use of natural resources. In this regard the renewable energy resources are very important regarding to fulfill our energy demand. Various research groups are engaged to innovate the efficient, economic and easy practicable solar energy harnessing devices. The use of solar cells are commercially encouraged in all over world. Although, silicon based solar cells are commonly in use but they have some draw backs associated to them regarding with cost and manufacturing processes. In the present time, dye sensitized solar cells (DSSC), perovskite sensitized solar cells (PSSC) and quantum dot solar cells (QDSSC) are new techniques which have some advantages over silicon based solar cells. Although, there are some limitations also associated with them. The present paper deals with the historical context, present development , structural informations, working mechanism, limitations, advantages and future research trends of quantum dot and perovskite sensitized solar cells.

Key words: Graphene, quantum dots, perovskite, exciton , photovoltaic.

1. Introduction

As advances in optoelectronics, the researchers have been focused to develop efficient techniques and methods for trapping and conservation of solar energy. Starting from first generation solar cells involving silicon based solar cells,[1-3] second generation thin layer semiconductor based solar cells[4-6] and third generation solar cells[7-9] like DSSC (organic and inorganic as well as hybrid DSSC), perovskite solar cells[10-12] and quantum dot solar cells,[13-15] there is a long journey. The traditional semiconductor based solar cells have limitations. The photons having energy less than the band gap of semiconductor material cannot be absorbed and those who have higher energy can get thermalize to the band gap edge[16]. In this way, there is reduction in current and decrease in voltage respectively. The thermodynamic calculation of entire processes show that maximum efficiency obtained only up to 33% for normal semiconductor (with band gap 1.34eV) while it is up to 66% in quantum dot solar cells.[17] Although, at laboratory level it is low. The quantum dots have special feature to tune the band gap. Lead sulfide quantum dots can be used in the infrared frequencies also.[18] Manufacturing process of quantum dot solar cells is also simple and involve either manual or automatic spin coating or by roll printing.[19] Perovskite solar cells involve perovskite material in their structure. The lead or tin halide based perovskite with hybrid organic-inorganic nature solar cells are common.[20] Simple printing methods are used for their manufacture. At the laboratory level the efficiency reaches up to 25%. These cells are very light-weight and also useful in wireless electronic systems. This review is an effort to throw light on various aspects of the development of scientific view on molecular advanced material perovskite and nano-dimensional material[21] quantum dot, in the field of photo voltaics.

2. Quantum dot sensitized solar cells

The use of nano dimensional advanced materials in the field of intelligent electronics[22], nonlinear optics[23], photovoltaics, fluorescence sensing optoelectronics,[24,25] chemo therapy of cancer[26] etc. have been reported. In this part of the review we have focused our attention on the use of quantum dots in photovoltaic field. Quantum dots can be defined as nano sized material with narrow band gap. Therefore, they are important in the application of photovoltaic field as absorber in the visible region they can be used as replacement for dye in Gratzel's Dye sensitized solar cell[27]. Nowadays,

researchers oriented towards the performance improvement in these QDSSCs. The scope of QDSSCs[28] are: (a) There are two electron hole pairs for each photon (b) QDs can also reduce the dark current and can improve the efficiency (c) Optical band gap of QDs is tunable. (d) The QDs have high value of extinction co-efficient. (e) Carrier multiplicates to impact of ionization show very high value of theoretical efficiency (44.4%). (f) Inorganic QDs like CdSe, CdTe, CdS and their alloyed compounds etc. are used as sensitizer, TiO_2 as one of the photoanode,[29] polysulfide redox mediator as electrolyte and noble metals, carbon based materials and metal chalcogenides are used for the construction of QDSSCs[30]. (g) The mechanism of photovoltaic function shown in figure-1 which is similar to the dye-sensitized solar cells. Due to 'quantum size effect' the quantum dot show characteristic properties which are different from the bulk materials. Historical background of photovoltaic cells starts since 1839, in which Edmond Becquerel built the first photo voltaic cell the historical events on photovoltaics can be summarized in the table 1.

Table-1: Some historical events in solar cell research.

Year	Discovery	Scientist
1839	First Voltaic cell	Edmond Becquerel
1839	Perovskite materials	Gustav Rose
1883	First solid state selenium Photo voltaic cell	Charles Fritis
1954	First practical photo voltaic cell	Bell Labs
1980	DSSC	M.Gratzell
1983	Quantum dots	Alexey Ekimov
1984	Colloidal Quantum dots	Louis Brus
1993	Colloidal CdX (X=S, Se, Te) Quantum dot applications	Louis Brus
2009	Perovskite solar cells	Tsutomu Miyasaka

The principle of quantum dot solar cells in mainly based on quantum confinement.[31] The meaning of quantum confinement is the confining an exaction to the dimension smaller than it's Bohr radius (Exciton = Bound state of an electron-hole pair). The motivation of quantum dot solar cells is the multiple exciton generation (MEG), versatility and its reduced cost.

2.1 Construction of QDSSCS-

The construction of QDSSCs involve following steps :

(i) Preparation of optically transparent electrode of appropriate size.

(ii) Conductive compact layer deposition.

(iii) Preparation of active layer.

(iv) Scattering TiO_2 layer application.

(v) Preparation of photo anode for the purpose of sensitization.

(vi) Photo anode sensitization by using different quantum dot solution.

(vii) Preparation of ZnS blocking layer.

(viii) Counter electrode preparation with reduced grapheme oxide and copper. (Cu-RGO →Cu_2S-RGO)

(ix) Assembling of over all solar cell.

(x) Finally, the QSSCs testing is the last step of it's making.

2.2 Different Components of QDSSCs:

i) Photo anode: It involves a wide band gap semiconductor layer, mostly TiO_2.[32]It is notable that in QDs chalcogenides are used as sensitizer. The efficiency of QDSSC can be tuned by use of better band gap species, CdS, CdSe, and CdTe (Table 2).

Table 2:The chalcogenides with different band gaps.

S. No.	Chalcogenide	Band Gap (eV)	Absorption (nm)
1	CdS[33]	2.3	~540
2	CdSe[33]	1.7	~T31
3	CdTe[34]	1.4	~887

Lee et al reportedan efficient quantum dot-sensitized solar cell based on co-sensitization of CdS/CdSe. Use of combination of quantum dot sensitizers for efficient redistribution and shifting of the band edge via "Fermi level alignment" has also been reported by the work of Mc Elory et al.[35] Highly efficient CdTe/CdS[36]. QDSSC fabrication by one-step linker assisted chemical bath deposition was reported by Yu and his co-workers[37]. For the increase in the efficiency of QDSSCs, the band gap tuning with size of QDs is important feature but it was observed that this may cause problem related with the stability of solar cell. Bailey et al[38] proposed the use of alloyed semiconductor quantum dots for tuning of optical property of QDSSCs without changing the particle size. Alloyed chalcogenides ($Zn_xCd_{1-x}Te$) have been reported to show 9 and 9.4%.

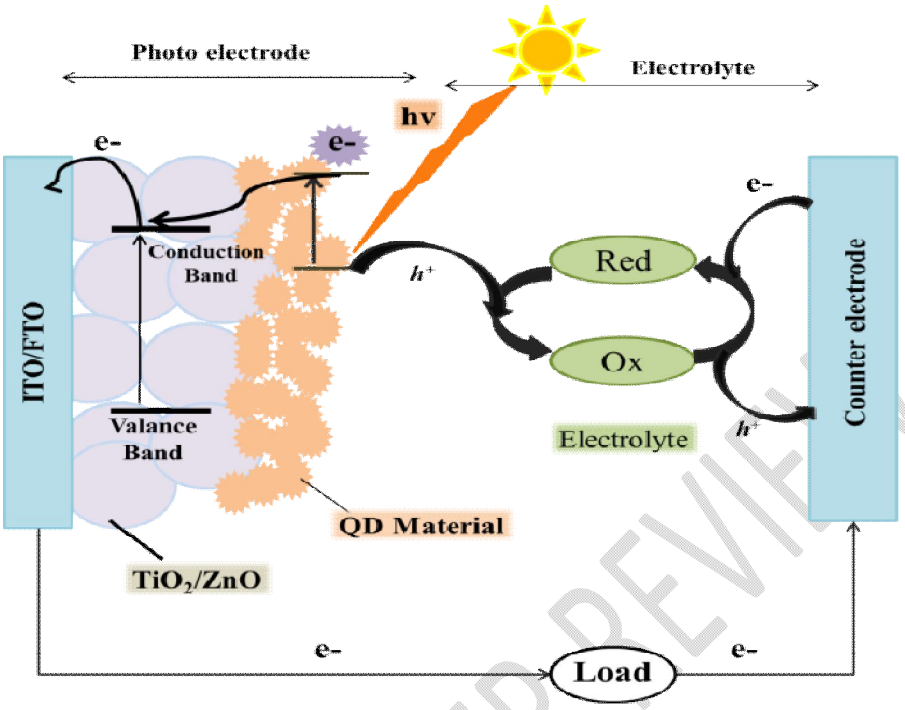
Passivation layer:

When we compare the performance of QDSSCs with the DSSCs, it was found the efficiency of QDSSCs is much lower than the DSSC.[39] This is due to the fact in photovoltaic mechanism the excited electron in quantum dots involve recombination process with redox mediator ions in the electrolyte which decreases the performance of QDSSCs.[40] The solution of this problem is the application of passivation layer am-TiO_2/ZnS/SiO_2 and ZnS layer as a passivation layer to the CdSeTe quantum dots to achieve 9.0 & 9.41 % efficiencies.

Another disadvantage of QDSSCs are it's toxicity Cd, Se, Te based quantum dot solar cells are lightly toxic and require stable polymers.[41] Cd and Se ions have been known to use in core of quantum dots. Accumulation of quantum dots in kidney, spleen and liver is harmful. In UV and aqueous condition degradation may be enhanced.

ii) Electrolyte in QDSSCs:

Just like DSSC, in QDSSCs also involve the use of redox mediator for the purpose of conduction of electron from the photo anode to the counter electrode. Most commonly used electrolytesare S^{2-}/S_x^{2-}[r] Enhancement of V_{oc} and FF by the use of chemical additive as NaOH into polysulfide electrolyte was reported by Park and his co-workers.[42] To replace the liquid electrolyte due to leakage and easy vaporization the use of solid polymer electrolyte has been proposed by Duan and co-worker[43] in QDSSCs, but low ionic conductivity limits their performance. Again, gel polymer electrolyte (GPE) has been introduced and CdSe/CdS GPE based QDSSCs have been reported upto 45% efficiency.
Fig.-1 Working Scheme of Quantum dot solar cell.



iii) Cathode

In QDSSC, the counter electrode of platinumis not suitable because of its reaction with sulfur and and also it is non catalytic to sulfide in as well as it restrain charge transfer to polysulfide ions. The use of noble metal and chalcogenide are suitable for cathode in QDSSCs.[44]

2.3 Mechanism of QDSSCs

It involve the following steps :

1. Absorption of photons by quantum dots sensitized which are absorbed on the photo anode. This results in the excitation of electrons into it conduction band.
2. The electron from conductor band of sensitizer will be transferred to the conduction band of the semiconductor (TiO_2).
3. Again quantum dots receive electron from sulfide ions of electrolyte and regeneration.
4. From conduction band of TiO_2/ZnO, electrons will be transferred to the external circuit and to the cathode. The schematic diagram of working mechanism of QDSSC is shown in fig.1.

3. Perovskite Sensitized Solar Cells

Perovskites are a class of materials that show a very many fantastic properties like femo electric behavior, super conductivity, charge ordering, giant magnets resistance, catalytic properties and also optoelectronic properties. Metal halide perovskites act as semiconductor.

Among third generation solar cells perovskite DSSCs have been attracted very much to the scientists.The term perovskite is used for the crystal structure of the type similar to calcium titanium oxide ($CaTiO_3$) i.e. ABX_3 in which A is large cation like ($CH_3CH_2NH_3^+$), formadinium ($NH_2CH{=}NH_2^+$) and ($CH_3NH_3^+$), B is cation metal of the carbon group of periodic table, i.e. Ge^{2+}, Sn^{2+} and Pb^{2+} and X is anion of halogen family.[45]

3.1 Structure of Perovskite sensitized solar cells:

Comment [VZ2]: Check whether the explanation of properties such as ferroelectric behaviour, superconductivity, charge ordering, giant magnetoresistance, catalytic properties and optoelectronic properties is supported by recent literature.

Among the two main categories of perovskite solar cells, the first type is those in which cell constitute a mesoporous structure while the other involve the perovskite sensitized solar cells without mesoporous structure which is also called as planar structure.

In the mesoporous structure, the main components of the cells are:

- **(i)** Transparent conducting oxide layer (TCO)
- **(ii)** Over the TCO substrate there is an oxide semiconductor compact layer of mesoporous metal oxide (TiO_2, Al_2O_3etc.)[46]
- **(iii)** Perovskite sensitizer[47]
- **(iv)** Hole conductor
- **(v)** Gold conductor.

In Planar structure (fig. 2(A)), the main component of the cell does not have mesoporous metal oxide layer but rest of the components are same as mesoporous structure cell.

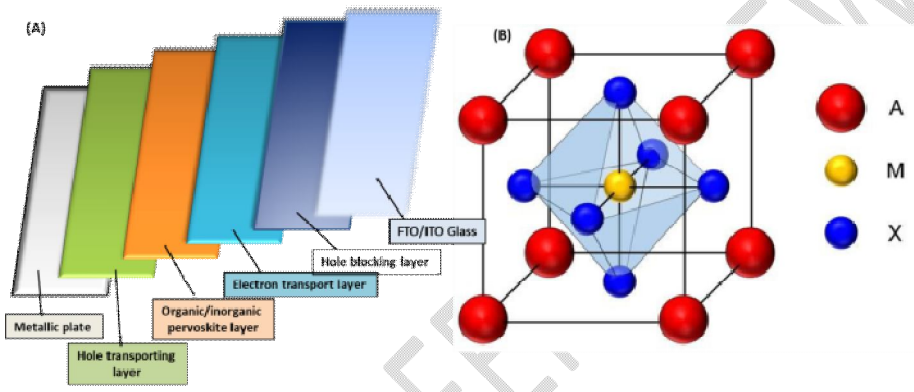


Fig.-2 (A) Layered Structure of Perovskite solar cell. (B) 3D Structure of AMX_3 perovskite.

Lee et alhave been reported organometallic halide planar structure perovskite solar cells with n-type TiO_2 $CH_3NH_3PbI_3Cl$ and p-type spiro-O-MeTAD hole conductor.[48]The efficiency was found to be increase from 7.6% to 10.9% by substitution of TiO_2 with Al_2O_3 in this cell. Proposed explanation was that injection of electron from conductor band of TiO_2 by the perovskite structure to the FTO electrode and in Al_2O_3 based cell, the perovskite layer behaves as absorber and as n-type component. It is essentially due to high range of band gap i.e.7-9 eV in case of Al_2O_3.[49] Concluding remarks given by as that the electron diffusion through perovskite is faster than in TiO_2 and therefore it results an increase in efficiency of the cell Heo et al[50] reported that those structure where perovskite filled up the pores to form a dense layer over the TiO_2 the perovskite functions as sensitizer and as a hole conductor, both.

3.2 Mechanism of function for perovskite sensitized solar cells:

Elgar et alreported mesoscopic $CH_3NH_3PbI_3/TiO_2$ heterojunction solar cells .The mechanism shown in fig. 3 involve following steps:

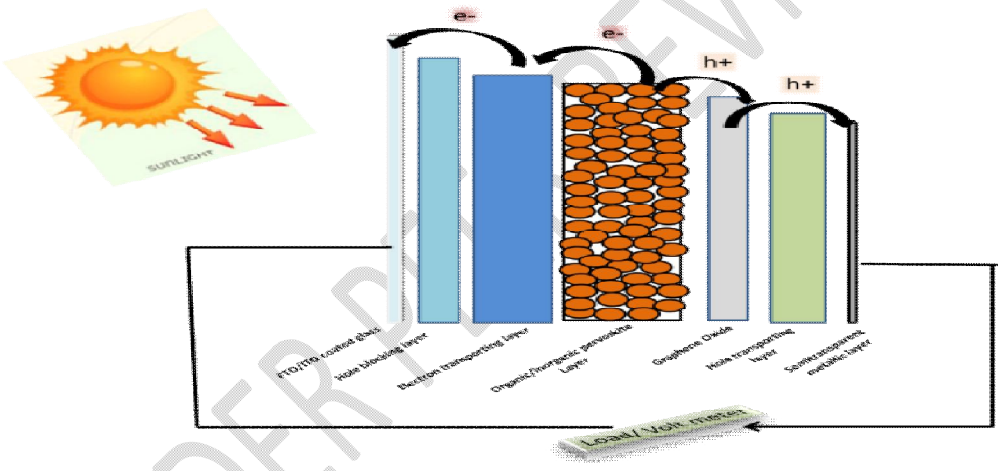
1. In the first step the sensitizer $CH_3NH_3PbI_3$ absorbs the photons and produced excitons which then dissociated via electron injection at interface of sensitizer and semiconductor.
2. The second step involves migration of electron to FTO. In this step it travels through the TiO_2 network.
3. In the third and final step the electron reaches to the Au electrode. The efficiency of TiO_2/ $CH_3NH_3PbI_3$ cells was found to be 12%.

Fig.-3 Schematic mechanism of pervoskite solar cell.

Islam and his co-workers[51] reported 15% efficiency for hybrid perovskite cell[52] of the type TiO_2 layer/ $CH_3NH_3PbI_3$/poly-triarylamine/A vapour u by blending TiO_2 nano particles with nano rods. Liu et al[53] reported the planner heterojunction perovskite solar cells by deposition method with 51.5% efficiency. Labana and coworker[54] in the same year published their work depleted hole conductor free lead halide iodide hetero junction solar cells and proposed that 8% efficiency.The increase was due to replacement of TiO_2 nano sheet with thinner planner perovskite solar cell using SnO_2 as compact layer and CuSeN as hole conductor.

3.3 Some lead free perovskite solar cells:[55]

Due to poisonous property of lead, several research groups have been worked to replace lead by some eco-friendly material.In this effort the solar cell of the composition $CH_3NH_3Pb_{1-x}I_3$ have been reported which is partially substituted by Sn in place of Pb. Other efforts in this field is reported by Hao et al[56] with composition $CH_3NH_3Sn_{0.25}Pb_{0.75}I_3$ (n=7.37%) and $CH_3NH_3Sn_3I_3$(n=5.44%). Germanium (Ge^{2+}) perovskite of the form, $CsGeX_3$ (X = Cl^-, $Br^-_{OR}I^-$) have also been reported with



efficiency 3.2%.

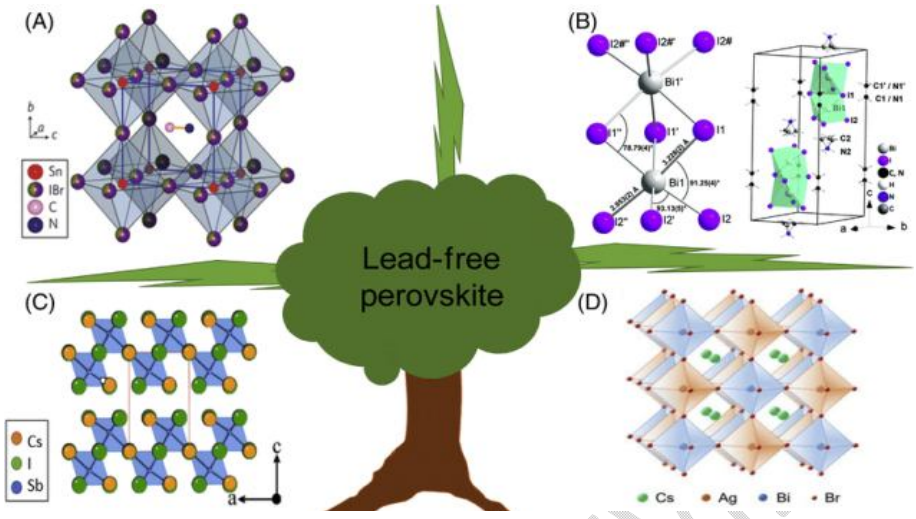


Fig.-4 Structures of Lead-Free Perovskites. (A) 3D crystal structure of $CH_3NH_3SnI_{3-X}Br$ (B) 2D layered structure of $Cs_3Sb_2I_9$. (C) Local structure of the $Bi_2I_9$3-anion(left); cation and anion positions in the unit cell (right). (D) The crystal structure of $Cs_2AgBiBr_6$. [57]

3.4 Limitations of Perovskite solar cell

1. Perovskite material is very much absorptive and moisture sensitive.
2. Stability and life-time of these cells is very low.
3. Use of lead which is poisonous in nature is also making it not eco-friendly.

3.5 Future development of PSCs[58]

Efforts to remove the limitation of perovskite PSCs-

1. Research have been not focused to improve the device stability.
2. Now, the application of grapheme and it's oxides have great considerable attention by research groups.
3. HTM (hole transport material/ETM (Electron Transport medium) layer not only could replaced by graphene or its oxide but also could be inserted between perovskite and other HTM/ETM or between HTM/ETM and metal contact.
4. Wetting transparency property of 2D graphene the perovskite decomposition maybe released.
5. Graphene Oxide would add to the perovskite decomposition reactions and could improve.
6. The perovskite inserted tandem cells have been reported to show very high efficiency (26.7%).
7. Lead toxicity is a drawback of PSSC. Now, by the use of double perovskite (Elpasolites); with the general formula : $A_2BB'X_6$ type of the type CS_2 Ag Bi Br_6 have been reported perovskite solar cell with these double perovskite also show material stability. In fig.4 some lead free pervoslite structure are shown.
8. The application of Guanidinium thiocyanate (GuaSCN)[59] to fine tune the mixture of tin and lead in the perovskite films to improve structural and opto electronic proportion have been repotted the mixed tin-lead organic inorganic perovskite material with a small amount of GuaSCN show a low band gap, long charge carrier life time.
9. The perovskite silicon tandem Oxford PV reported world record for perovskite solar cell.[60] They have achieved a certified 28% conversion efficiency, which is the highest even performing single

junction silicon solar cell validating the ability of perovskite to increase the performance of silicon based photovoltaics.

4. Conclusion

Comment [VZ3]: 1.Some statements are vague or unclear.
2.There are several grammatical errors and awkward phrases.
3. The mention of advantages of perovskite materials is not detailed or specific

By the utilization of UV light spectrum of the solar energy using quantum dots now became a very progressive approach for the photovoltaic cell research. It has lots of possibilities in future in this field for the development of efficient sensitized solar cells.

Quantum dots band gap can be tuned by changing the size or composition. Processing of quantum dots can be done with the solution by roll to roll technique. QDSSC are helpful for less expensive manufacturing the commercialization of quantum dots is not easy, but in filed of solar technology quantum dot solar cells will be an efficient and stable method for solar energy harassing processes. This technology certainly will be one of the leaders in photovoltaic filed and a promising game changes with a lots of possibilities in future.

Perovskite materials which are easily synthesized molecular materials have vibrant and versatile characteristics and they play vital role in vehicle batteries, sensors, lasers and micro-electronics. The perovskite photo voltaics have several advantage as comparison to silicon solar cells (a) Dany carrier diffusion lengths (b) Widely-tuned band gap (1.5 eV to 2.3 eV); (c) great light absorption coefficient ($>10^4$ cm^{-1}); (d) low cost and (e) easy fabrication. The vibrate increase in the efficiency of photovoltaic cells with low cost value make perovskite cells as a potential technique to achieve an efficient technology for green energy resource, to overcome the use of poisonous lead to the lead free perovskite cells are the attraction of researchers.

Ethical approval

Not applicable.

Informed Consent

Not applicable.

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