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Quantum Dot Sensitized Solar Cell: Introduction

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Abstract: Quantum Dots Sensitized Solar Cell (QDSSC) recently has become a potential source to provide an alternate way to harvest the solar light for the energy conservation. Since the quantum confinement effect of the QDs result in unique optoelectronic properties of the metamaterials, it is playing an important role in designing of smart photodetectors, light-emitting diodes and solar cell in the recent years. The semiconductor materials (chalcogenides) have gained a significant ground for the fabrication of QDSSC. The main advantage is their large industrial production with tunable band gap, which helps in fabrication of cost-effective, but, high performance QDSSC devices. The efficiency of QDSSCs depends upon the fabrication method of QDs, which refines the morphology and physico-chemical properties of the desired material. Thus, it is important to engineer the QDs in such a way, so that after optimization of fabrication method, they can be used for the improvement of QDSSC performances. Although large variety of solar cell technologies are being developed, which also include dye sensitized nano crystalline solar cells, depleted heterojunction solar cells, hybrid organic-inorganic solar cells and bulk heterojuncion solar cells. However, the recent focus is on the fabrication of QDSSC, where the dye is replaced by nano sized inorganic particle that enhances the performance of QDSSC.

Keywords: QDs, QDSSC, optoelectronics

1. Introduction: Quantum dots (QDs) have become an important platform for the development of numerous optoelectronics applications *viz*, photovoltaic solar cells, light emitting diodes and photodetectors **[1-6]** in the recent years. Quantum dots (QDs) are nano sized semiconductor particles, specifically having their size reduced from three dimensional to zero dimensional nanomaterials. The reduction in the diameter of the particle approaches the Bohr exciton diameter **[7]** having charge carriers confined to three dimensions. This phenomenon is known as quantum confinement which causes continuous band of bulk to split into discrete quantized levels. There are two fundamental factors due to which the properties of QDs differ from their bulk counter-parts. It is observed that a particle in nano dimension possesses a larger surface to volume ratio imparting novel properties to the nano particles compared to the bulk solids. Besides, QDs have a tunable band gap due quantum confinement, resulting in a widening of band gap with a decrease of size of QDs, creating tremendous potential for them in sensitization of solar cells. Quantum Dot Sensitized Solar Cells (QDSSC) has been identified as potentially applicable components for 3rd generation solar cells, specifically because of its excellent light harvesting capability due to its optoelectronic properties. The process of light harvesting capability of such metamaterials has been observed to be commercially cost effective and thereby economically viable. QDSSCs reveal structure and working principles similar to those of Dye Sensitized Solar Cells (DSSC), although the size of the QD is much larger as compared to a dye molecule. In recent years,

capping ligand induced Quantum Dots Self-Assembly Deposition (QDSAD) technique have made its impression for immobilizing the QDs on a TiO_2 electrodes, as a result of series of new power conversion efficiencies data have been achieved based sensitization route. Till date, enormous developments have been boosted upon this high-end technological concept from Schottky QD solar cell to multiple-junction QD solar cell. During this series of up gradation of processes, it is found that both p-n junction materials can be achieved for the same QD with the changing of surface ligand. This may solve a serious issue of surface trap states (hole trap) because in both sides of the junction similar and different band gap with the same material can be applied as thin films. This advantage can be implemented in the multiple-junction solar cell technology to achieve device efficiency (η) more than single junction Shockley-Queisser limit (31 %). QDs have an additional important capacity to handle the hot-electron transfer process without using a concentrator. This is as crucial as MEG because practically it can enhance the efficiency of the cell by not allowing the electron to transfer/lose its energy. It is due to the lacking of available energy states within a QD by which the highly energized electron can lose its energy. In a nutshell, these crucial advantages are still so far to be explored fully in devices to achieve a future dream solar cell, in which abundant solar spectrum can be utilized for clean and green energy. In this review, we shall discuss the working principle of DSSC and the present scenario of quantum dot sensitized solar cells (QDSSC) as well as advantages-disadvantages of them.

2. Dye sensitized solar cell (DSSC): DSSC works as the similar mechanism of photosynthesis with respect to Chlorophyll **[8]**. Infect, the first ever DSSC was fabricated (1972) as Chlorophyll sensitized metal oxide (ZnO) cell **[9]**. The dye molecule in a DSSC acts as the absorbing/sensitizing material, which is capable enough to absorb the sunlight, especially in the visible region. The work mechanism of a dye in DSSC is to excite an electron by absorbing electromagnetic waves of the solar radiation and the electron is get transferred to the wide band gap semiconductor layer deployed in the cell. Another important advantage of DSSCs is they are better than organic thick film solar cells in terms of low mobility of charges and less extinction diffusion lengths **[10]**. The primary component of a DSSC is the dye molecule. Choice of a dye molecule is essentially very important for the better efficiency of the solar cell in the primary step. An organic dye molecule can be natural or synthetic one. Primarily, natural dye molecules, extracted from plants, were used, however, they are not found to be suitable of expected efficiency. Hence, the concept of Ruthenium based synthetic dye molecules has come to play, which are found to be better light harvesters by 13 % with a current density of 20 mA cm^{-2} **[11]**. Noteworthy, whenever the dye molecule is the introduction of an inorganic molecule, known as quantum dot, these solar cells are termed as quantum dot sensitized solar cell (QDSSC).The thickness in terms of layer of dye molecules is indeed an important parameter for the cell, to avail better efficiency. It is recorded that when the layer of dye molecule is a single one, then the efficiency of the cell is limited up to 1 % **[12]**, although a major breakthrough was achieved of 7.1 % in 1991, with the conversion of 80 % of photons to electricity **[8]**.

2.1 Working principle of DSSC: The working principle of DSSC follows redox mechanism. A typical DSSC has three primary components, which are - sensitizer (dye molecule), semiconductor metal oxide layer (generally TiO_2) and transparent conducting oxide (TCO). The transfer of hot electron is dealt between the first two components. The dye molecule can promote its valence band electrons (or highest occupied molecular orbital, HOMO) to the conduction band (or lowest unoccupied molecular orbital, LUMO) with the help of absorbed photon, received from the sunlight. Then it transfers the excited electron to the semiconductor metal oxide layer. The TiO_2 has two layers. One layer is mesoporous (thickness ~ 20-30 nm), which is below the other layer, and is with direct attachment of the dye layer **[11]**. The above layer of TiO_2 is employed to block the recombination process of electrons.

2.2 A dye molecule must possess the following features to act as better photon absorber:

a) Should able to absorb the whole sunlight which is necessary for the production of photocurrent.

b) The dye molecule should possess efficient linking group/linking mechanism with the TiO_2, so that the excited electron can easily be transferred to TiO_2 from LUMO of dye molecule **[11]**.

3. Quantum Dot Sensitized Solar Cell (QDSSC):

3.1 Synthesis of Quantum Dots: Recent literature reveals that Colloidal Quantum Dots (CQDs) can be synthesized using various methods [*viz*, metal organic chemical vapor deposition (MOCVD) **[13]**, vapor phase epitaxy (VPE) **[14]**, electron beam lithography (EBL), molecular beam epitaxy (MBE) **[15]** radio frequency sputtering (RFS), quenching methods, ball milling, optical ablation, reduction with microorganisms or plants **[16]** and chemical method **[17-24]**. However, solution based chemical methods are adopted most widely. It is because of the advantageous parameters of this method which includes, application dependent synthesis of tunable size and shaped QDs, industrial based large production, comparatively easier to handle and most importantly cost-effectiveness. The chemical methods are basically divided in two broad categories, i.e. Aqueous and Non-aqueous methods. In the recent years, aqueous synthesized methods are in the limelight over non-aqueous methods due to their eco-friendly nature without compromising the productivity and quality of these dots **[25]**. Incorporation of surface functionalizing agents as capping agent is a much necessary process during the synthesis, as retention of size of QDs is an inevitable process. Another important parameter is the monodispersity or narrow size distribution of the dots, which is a little tricky but, can be achieved only with the appointment of suitable capping agent along with proper stoichiometric ratio of the precursors.

4. Optoelectronic properties of QDs in the colloidal domain: The tunable band gap property of QDs offers the electrons to absorb various energized photons of various wavelength of light of the solar spectrum. Since the VIBGYOR ranges from 400 nm to 800 nm, it is this range, where maximum conversion of electricity from light can take place. This becomes essential to produce the QDs of various sizes as it will give the access to the whole cited region with variation in band gaps. Secondly, the generation of multiple excitons (MEG) from single photon absorption is another advantage of QDs, as it has been observed to enhance the efficiency of the solar cell immensely **[26]**. The utilization of thin films of QDs in the solar cell as the p/n type QDs material can have millions of particles of different shape and size, which practically allows the cell to absorb more photon and can help in the generation of huge quantity of electrons.

5. Architecture of different types of Quantum Dot Sensitized Solar Cell (QDSSC): In QDSSCs, the thin film of electron acceptor (e.g., TiO_2 or ZnO) is coated with colloidal QDs. The work function is similar to DSSC except the replacement of dye with QDs. QDs when subjected to band gap excitation as a result of illumination, results in the formation of electron-hole pairs in the QDs. During this process, the electrons enter into the conduction band (CB) in the QDs and the holes remain in the valence band (VB). The excited QDs inject the electrons from their CB into the CB of the wide band gap semiconductor and during the process in doing so, it gets oxidized itself with a hole, remaining in the valence band. Ejected electron from the QDs percolates through the porous semiconductor network and thereby, reaches to the conducting glass, from where; it travels through the external load leading to the completion of the circuit by entering back thorough the counter-electrode. The voltage thus generated can be perceived as an evidence of the solar energy to the electrical energy. QDs are better electron generator; therefore substitution of dye with comparatively more stable QDs is a better option. Thin films have been used in this technology vastly due to the versatility of them as a cost-effective material and large surface area provider. QDSSC works with electrolyte like polysulfide instead of Iodide base electrolytes as in case of DSSC. It is because of the corrosive nature of the Iodide electrolytes for the semiconductor material, which eventually hampers the photo electricity generation. The efficiency level of QDSSC (9 %) **[27, 28]** has *not* been yet counters the efficiency of DSSC (13 %), however the

theoretical efficiency is calculated to be 44.4 % [29]. Figure (1) shows the basic working principle of a QDSSC.

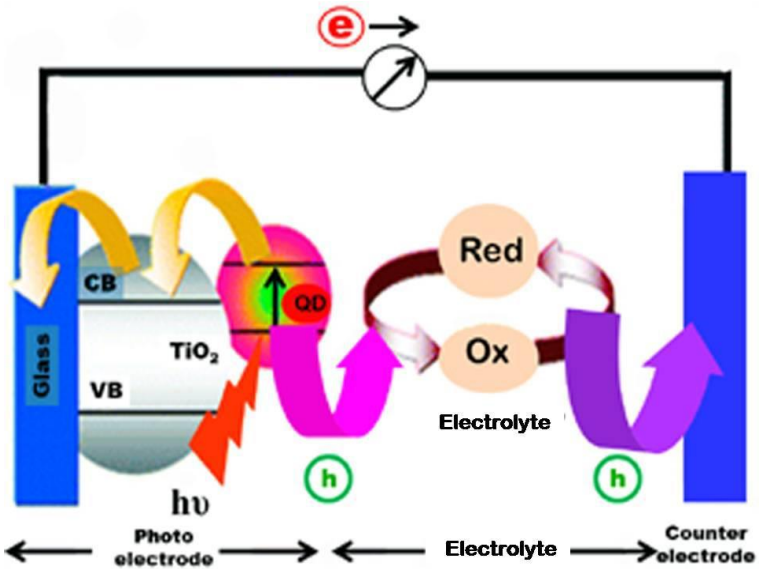

Figure (1): Schematic of the working principle of QDSSC.

6. Different types of QDSSCs: Depending upon the incorporation of type of QDs, the QDSSCs can be divided into the following categories:

(a) Schottky QDSSC: The first thin films solar cell composed of QDs as primary absorber, was reported in 2005 [30]. The fabrication of these devices was taken up based upon, the electron affinity between the Transparent Conductive Oxide (TCO) and the reflective black contact (e.g. Mg), to extract electron and holes in their directions. In these cells, PbS QDs were used along with organic polymer (poly [2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene]) to absorb photon and exciton thus generated, were separated with the offsets of conduction band [31].The impact of polymer blended with the QDs was further studied and found that polymer free QDs can separate and transport the electron-hole pair efficiently through pure thin films of QDs in the presence of an applied electric field [32]. The enhancement in performance due to the incorporation of PbS CQD/Mg interface has led to further research on Schottky-barrier based devices [33-40]. Schottky QDSSCs have proved their ease of fabrication, thus functional simplicity along with their excellent architecture. The simple Schottky cells have reported to have an optimized efficiency (η) > 4.5 %, with the selection of suitable size of CQDs [31].

(b) Depleted Heterojunction QDSSC: There are two key limitations of Schottky QDSSCs, which are: a) the Fermi level imposes upper bound on the built-on-voltage due to the generation of excessive electronic trap states [41] and b) non rectified side of the device, which develops illumination. In depleted heterojunction, the introduction of highly doped n-type metal oxide in the p-n heterojunction is taking place. The traditional glass substrate is associated with TCO (ITO or Fluorine Doped Tin Oxide). The wide band gap TiO_2 or ZnO is commonly used as the n-type junction. The p-type junction is a 50-400 nm thick CQD thin film and the back reflector is commonly made of a deep work function material, Gold or heavily doped metal oxide (*viz,* MoO_3), paired with a reflective metal (*viz* Silver or Aluminum) [31]. These heterojunction cells get illuminated with the help of a wide band gap semiconductor and transparent substrate. Thus, it is overcoming one drawback of Schottky QDSSC as, now the photogeneration occurs in the close vicinity of the junction.

(c) Bulk-Heterojunction QDSSC: The minority carrier transport is a major issue in depleted heterojunction QDSSCs, which can be mitigated by the bulk heterojunction concept. In this system, the CQD thin film and the wide band gap semiconductor form an interpenetrating layer. Since it is a 3D structure **[34]**, like organic photovoltaic, hence it is referred as bulk heterojunction. The CQDs are allowed to infiltrate the structured electrodes, by which the depletion region shall become more pronounced **[42]**. Addition of more absorbing CQDs can enhance both absorbing and carrier collection simultaneously **[43]**.

(d) Bulk-Nano Heterojunction QDSSC: This kind of PV cells adopts one active bulk material (*viz* CdTe) and one quantum confined material (*viz,* CdSe), as p-type and n-type semiconductor materials **[44]**. Both the n-type and p-type materials are made interpenetrated by mixing of them with a solution phase mixture. Such a type of solar cell architecture is found to be better than the former, due to the exhibition of current collection from both the bulk and nano phases.

(e) Multiple-Junction QDSSC: In this type, the single junction QD solar cell material is replaced by multiple junctions to achieve better efficiency (η > 31 %). This multiple junction materials have various band gap materials by using different sized QDs **[45]**.

7. Advantages of QDs in QDSSC: QDs are basically inorganic metamaterials whose optoelectronic properties get enhanced drastically in the quantum confined scale. QD has short band gap, which allows the electron to be excited more easily than in case of a dye molecule **[11]**. They are resistant to photobleaching effect, more than the dyes **[46]**. Most importantly, the tunability in band gaps of every single QD is possible and multiple junction cells, which can be fabricated. The tunability in band gap by just changing the size of the dot can provide accession to the whole VIBGYOR region, which is not possible in dye molecules **[47]**. The synthesis of these QDs are easy and cost-effective, therefore, the cost of fabrication of individual solar cell is expected to be bearable price for the common users **[46]**. The surface passivation plays a significant role in these kinds of QDDSCs. The surface dangling bonds can be generated due to the unsatisfied cationic or anionic constituents, which lead to the development of additional surface trap states. This can be taken care of by incorporating suitable capping/surface passivating agents. A hot electron transfer is possible in QDs due to the presence of very less dense energy states, which provides the generation of multiple exciton generation (MEG) **[48]**. Therefore, additional luminescence solar concentrator (LSC) is not necessary in these systems. Both n-type and p-type QDs can be achieved for the same material of semiconductor QDs by changing the ligand. Therefore, there is no need of incorporation of different materials. In case of QDs, extinction coefficient is high, which reduces the dark current, hence improves the performance of the QDSSC **[49]**.

8. Disadvantages / limitations of QDs in QDSSC: The synthesis of surface passivated QD is not a very easy process, because it involves the selection of proper ligand/capping agent which can really satisfy the surface dangling bonds and not generate surface trap states. Moreover, synthesis in aqueous medium in a *greener* way is still under investigation **[50].** Moreover, toxicity of QDs can be an issue, as metal chalcogenides consist of heavy metals (*viz,* Cadmium) can be harmful for human health as well as nature, if effective surface passivation is not done **[51, 52]**.

9. Conclusions: QDSSC can be a replacement of all the renewable green energy harvesting system of today's world. However, there are a few key parameters which have to be sorted out, especially in terms of the synthesis of green, stable and sustainable QDs. The major advantage of these QDs is their Multiple Exciton Generation (MEG) and Hot Electron Transfer capability. In both the cases, it is mandatory to have a surface passivated QD because, only a surface passivated QD can practically diminish the surface trap states. Hence, MEG is possible through hot electron transfer. In a nutshell, it is

expected that, the latest development in the field of QDSSC, i.e., multiple junction QDSSC can overcome all the limitations and the world can have a better cost-effective and efficient solar cell.

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