Quantum Dot-sensitized Solar Cells: A Review

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ABSTRACT
Quantum dot-sensitized solar cell (QDSSC) has an analogous structure and working principle to the dye sensitizer solar cell (DSSC). It has drawn great attention due to its unique features, like multiple exciton generation (MEG), simple fabrication and low cost. The power conversion efficiency (PCE) of QDSSC is lower than that of DSSC. To increase the PCE of QDSSC, it is required to develop new types of working electrodes, sensitizers, counter electrodes and electrolytes. This review highlights recent developments in QDSSCs and their key components, including the photoanode, sensitizer, electrolyte and counter electrode.

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1. INTRODUCTION
Presently, the world has been facing lots of environment problems such as overpopulation, climate changes, natural resource depletion, deforestation, global warming, and ozone layer depletion [1]. Out of these problems, one of the main problems is depletion of natural resources that makes us to think about renewable energy sources. Renewable energy plays an important role in reducing greenhouse gas emission. To reduce the demand for fossil fuels, renewable energy sources are supposed to be focused [2], [3]. Many renewable energy sources have been reported like hydropower, wave power, photovoltaic cell and wind turbine. Out of these sources, solar cells can be considered as a enormous source of renewable energy [4], [5]. Sunlight is the most abundant, cleanest, cheap and safe energy source [6], [7].

The conversion of sunlight into electrical signal is known as photovoltaic effect. It was first renowned in 1839 by French Physicist A.E. Becquerel. In 1983, Charles Fritts built first photovoltaic cell by using selenium semiconductor coated with an extremely thin layer of gold to form the junctions. There after various changes have occurred in mechanism of solar cells. PV cells are basically classified in three classes depending on their technology. First generation solar cell is based on single- and poly- crystalline silicon [8]. Second generation PV cells are based on amorphous silicon [9], CdTe [10], Cu(InGe)Se2 [11] and III-V semiconductors thin film [12]. Second generation PV cells have lower cost than first generation PV cells; but their efficiency is lower than previous ones. Research on third generation PV cells is essential to achieve solar cells, which have higher power conversion efficiency with lower fabrication cost. Much new kind of solar cells has been proposed like Dye-sensitizer solar cells (DSSCs) [13], organic solar cells [14] and Quantum dots- sensitizer solar cells (QDSSCs) [15]. DSSCs have poor conversion efficiency because of poor optical absorption of sensitizers. The dye molecules generally degrade with the exposure of infrared and ultraviolet radiations, exposure to air; water, UV light, heat and other chemicals can lead to degradation over time which leads the instability of DSSCs [16]. Quantum dots-sensitizer solar cells (QDSSCs) are considered
Quantum Dot-sensitized Solar Cells: A Review (Pooja Bhambhani)

as an alternative of DSSCs which have been studied extensively over the past two decades because of exception optical properties of quantum dots [17]-[20].

2. SPECIAL FEATURES OF QUANTUM DOTS

Quantum dots (QD’s) are semiconductor nanomaterials having size less than 10 nm. Structural, electrical, mechanical and optical properties of bulk material depend on type of material only even these properties of QD are function of material as well as shape and size also, hence by altering the shape and size of nanostructures, their properties may be altered in accordance with application. There are two basic reasons because of that, properties of nanostructures change with their shape and size: quantum confinement effect and increment of volume to surface area ratio [21]. Various QD’s such as CdS [22], CdSe [23], PbS [24], PbSe [25] have been used as sensitizer in QDSSCs. QDs have special features like Multiple exciton generation (MEG) of carrier [26], tunable optical band gap and broad optical absorption regions of solar spectrum [27], Hot electron injection [28].

2.1. Multiple Exciton Generation (MEG)

Material can absorb only fixed amount of energy from incident photon. If a photon having energy more than energy band gap of semiconductor is incident on that semiconductor then excess energy is lost in the form of heat. The conversion efficiency of traditional solar cells is less because of lost of excess energy in form of heat. MEG in QDs is the one way by which power conversion efficiency of QDSSCs can be enhanced. The production of two or more electron-hole pairs by one photon excitation is known as MEG effect. In conventional case, only one electron-hole pair produces by one photon excitation irrespective to energy of photon whereas in case of QDSSC, if energy of incident photon is $E_g$, $2E_g$ or $3E_g$ then one, two or three electron-hole pairs, respectively, produce [Figure 1] because MEG takes place in QDs. A photon with energy at least twice the energy band gap of QDs is required for MEG. Nozik has predicted that the theoretic power conversion efficiency of QDSSCs to be as high as 42% [29], which is higher than the Shockley-Queisser efficiency limit of 31%, for the conventional single junction solar cell [30]. MEG effect can be observed in bulk semiconductor also but the required threshold energy of photon for bulk semiconductor is much higher than that for QDs. The threshold energy of photon for bulk PbSe is 6.5 $E_g$ whereas that for PbSe QD is 3.4$E_g$ ($E_g$ is the energy band gap of PbSe). The basic concept of MEG in QDs is shown in Figure 2.

![Figure 1. (a) Traditional solar cell and (b) Multiple excitons generation](image-url)
Figure 2. Enhanced photovoltaic efficiency in QDSSC by Multiple Exciton Generation (MEG) [29]

2.2. Size-dependant Band Gap

QDs are used as sensitizer in QDSSC because of their specific optical characteristic that is size-dependant energy bang gap. If the size of QDs has been changed, light harvesting energy can be controlled [32]. Along with it, an effective charge separation is also possible by tuning the size of QDs. quantum confinement effect of QDs is the main reason of size dependency of band gap [33]. If the size of quantum dot is smaller than the critical characteristic length, called the Bohr exciton radius, strong confinement effect takes place. Nonocrystals behave differently from their corresponding bulk material because of quantum confinement effect. The Bohr exciton radius of most of the semiconductor is in the range of 1~10 nm, for example it is 2 nm for ZnO [34], 3 nm for CdS [35], 5.3 nm for CdSe [36]. However, some semiconductors have large Bohr exciton radius like it is 18 nm for PbS [37], 46 nm for PbSe [38] and 65.6 nm for InSb [36]. Strong confinement effect can be easily achieved in those semiconductors which have large exciton radius. Energy band gap (Eg) of QD increases with reduction in their size [39]. Eg can be explicated by Eg α 1/r², where r is the radius of QD. If the energy band gap of QD increases, it will absorb photon of higher energy (lower wavelength) to be excited. It means that the range of optical absorption wavelength can be tuned by altering the size of QD. Lee et. al. [40] has reported that energy of bottom of conduction band (Ecb) of QD moves up with the QD size reduction due to the quantum confinement effect. Figure 3[41] shown the strong significance of quantum confinement effect on performance of QDSSC.

Figure 3. Schematic illustration of the modulation of energy levels of PbS by particle size [41]

As shown in Figure 3, the Ecb of bulk PbS is -4.74 eV, which is lower than that of TiO₂ (-4.21 eV), hence movement of electron from conduction band of PbS to that of TiO₂ is not possible. As the size of PbS reduces, bottom of conduction band move to higher energy. When the size of PbS QD is 5 nm, its Ecb is at -4.1 eV, hence the transfer of electron from conduction band of PbS QD to that of TiO₂ is easily possible.

BEEI, Vol. 7, No. 1, March 2018 : 42 – 54
short, quantum confinement effect is must for QDSSC. Different photovoltaic parameters of QDSSC with the QDs of different diameter are summarized in Table 1.

<table>
<thead>
<tr>
<th>Quantum Dots</th>
<th>Diameter of QDs (nm)</th>
<th>Jsc (mAcm⁻²)</th>
<th>Voc (V)</th>
<th>PCE (%)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdS</td>
<td>4.4</td>
<td>3.519</td>
<td>0.41</td>
<td>0.66</td>
<td>[42]</td>
</tr>
<tr>
<td>CdS</td>
<td>4.9</td>
<td>4.519</td>
<td>0.44</td>
<td>0.85</td>
<td>[42]</td>
</tr>
<tr>
<td>CdS</td>
<td>5.9</td>
<td>6.694</td>
<td>0.48</td>
<td>1.29</td>
<td>[42]</td>
</tr>
<tr>
<td>CdS</td>
<td>6.2</td>
<td>5.494</td>
<td>0.51</td>
<td>1.05</td>
<td>[42]</td>
</tr>
<tr>
<td>CdSe(I)</td>
<td>2.5</td>
<td>2.25</td>
<td>0.59</td>
<td>0.86</td>
<td>[43]</td>
</tr>
<tr>
<td>CdSe(II)</td>
<td>3.5</td>
<td>3.23</td>
<td>0.64</td>
<td>0.86</td>
<td>[43]</td>
</tr>
<tr>
<td>CdSe(I)/CdSe(II)</td>
<td>2.5/3.5</td>
<td>3.41</td>
<td>0.66</td>
<td>1.26</td>
<td>[43]</td>
</tr>
<tr>
<td>CdSe/N719</td>
<td>2.2</td>
<td>2.37</td>
<td>0.75</td>
<td>0.71</td>
<td>[44]</td>
</tr>
<tr>
<td>CdSe/N719</td>
<td>2.5</td>
<td>6.42</td>
<td>0.78</td>
<td>3.31</td>
<td>[44]</td>
</tr>
<tr>
<td>CdSe/N719</td>
<td>3.3</td>
<td>6.95</td>
<td>0.81</td>
<td>3.65</td>
<td>[44]</td>
</tr>
</tbody>
</table>

Jung Sung Woo et al. [42] reported that Photocurrent increases with the size of CdS QD because CdS QD-assembled TiO₂ films were fully covered by large CdS QDs, which reduces recombination between TiO₂ and electrolyte whereas with the increase of QD size, electron transfer rate reduces, hence the size of QDs should be optimized for better performance. In order to increase the power conversion efficiency of QDSSC, band structure of QD should be matched with that of oxide film and optical absorption wavelength range should be wide.

Under such consideration, construction of rainbow solar cell is an approach towards high efficient QDSSC. In rainbow solar cell, QDs with two or more different sizes are employed instead of single-sized QD. Chen et al [43] has reported efficiency of QDSSC with two different sized QD (1.26%) is higher than that with single-sized QD (1%). As white light is incident on cell, smaller sized QDs (larger energy band gap) absorb smaller wavelength region (blue region) of white light, light with longer wavelength (red region) which is transmitted through initial layer is absorbed by subsequent layer of bigger sized QDs. By using different sized QDs, optical absorption wavelength range can be enhanced.

3. STRUCTURE OF QDSSC

The basic structure of QDSSC is shown in Figure 4.

The typical QDSSC has four major parts:
1) Photoanode
2) Sensitizer (Quantum dots)
3) Electrolyte
4) Counter electrode

3.1. Photoanode

Photoanode usually consists of semiconducting metal oxide deposited on a transparent conducting oxide (TCO) substrate, typically fluorine-doped tin oxide (FTO) glass. TCO substrate in QDSSC supports the...
semiconductor layer and works as a current collector. For an idea TCO substrate, optical transparency should be high and electrical resistivity should be low. Transmission of sunlight through substrate become smooth without any unwanted optical absorption due to high transparency of substrate and to facilitate the charge transfer process and to reduce energy loss, low electrical resistivity of TCO substrate is must [45].

Photoanode is an important part in QDSSC because it works as a matrix for QD adsorption and provides a charge transport medium for transportation of electrons from sensitizer to TCO substrate. To achieve better QD adsorption and smooth transportation of electrons from sensitizer to TCO substrate without undergoing recombination, photoanode should have following characteristics:-

a. High electron mobility to achieve smooth electron transport.

b. High surface area for maximum QD loading, hence effective light absorption takes place.

c. High transparency to reduce unwanted adsorption of incident photon.

d. Does not react with redox electrolyte to reduce recombination rate.

Titanium dioxide (TiO$_2$) is found most promising semiconductor material for photoanode in QDSSC, because of its specific features like wide band gap (~3.2eV) [46], low cost [47], nontoxic, high chemical stable, mesoporous nature [48, 49]. Along with these features, TiO$_2$ has higher CB edge, surface area and electron affinity, compared with other metal oxides, which make it the most suitable material for photoanode in QDSSC.

TiO$_2$ exists in three crystalline forms, namely rutile (tetragonal), anatase (tetragonal) and brookite (orthorhombic) [50]. Out of these forms, rutile is the most thermodynamically stable form. However, anatase is more preferred in QDSSC because of its better efficiency for solar energy conversion and photo-catalysis [51]. Zhang et al. [52] have reported that rutile and brookite belong to direct band gap semiconductor category, while anatase is direct band gap semiconductors. In anatase, the direct transition of photoexcited electrons from conduction band (CB) to valence band (VB) is impossible because of its indirect band gap. Consequently, the lifetime of photoexcited electrons is longer in anatase compared with brookite and rutile. In addition, the average effective mass of photoexcited electrons of anatase is also the lightest among the three forms of TiO$_2$, which results fast migration of photoexcited electrons and hence lower recombination rate in anatase compared with other two forms [52]. Park et al.,[53] reported that anatase-based solar cell has higher short-circuit photocurrent (Jsc) than rutile-based solar cell, whereas the open-circuit voltage (Voc) is the similar for both the cells. Rutile-based cell has lower photocurrent because its film has smaller surface area compared with anatase film, hence absorption of QDs is lower in rutile film.

Thin films made of sintered TiO$_2$ nanoparticles (~20 nm diameter) are extensively used as photoanode for QDSSCs due to their large surface area that is desired for the adsorption of QDs. On the other hand, there are two major drawbacks of these conventional sintered TiO$_2$ photoanode. First, the scattering of incident light is negligible because the size of the TiO$_2$ nanoparticles is much smaller than the wavelength range of the absorbed solar irradiations; hence probability of photon-QDs interaction reduces. Second, the transport of carriers through complex networks of sintered nanoparticles is not smooth because several grain boundaries between sintered nanoparticles arise that enhance recombination and very slow migration of carriers [54].

Various one-dimensional nanostructures such as nanowire [55], [56], nanorod [57], [58] and nanorod [59], [60] have been reported as photoanodes for enhancing the transport of electrons by providing direct conduction pathways with reduced recombination at the grain boundaries and trapping. However, these one-dimensional nanostructures have smaller surface area of nanoparticle which makes less absorption of QDs on photoanode, i.e. less light harvesting. To enhance light scattering and transport of charge carriers, different nanostructure of TiO$_2$ has been reported as photoanode in QDSSC. Anita Kolay et al [61] compared the photovoltaic performances of QDSSCs having different morphologies of TiO$_2$. They considered four morphologies: porous nanoparticles (PNPs), nanowires (NWs), nanosheets (NSHs) and nanoparticles (NPs).

The reported order of average magnitudes of PCEs: NWs (5.96%), NPs (4.95%), PNPs (4.85%), NSHs (2.5%). Y.B. Lu. et al. [62] reported the 1D connected TiO$_2$ nanoparticles (1D CTNPs) as photoanode sensitized solar cells. This idea combines the advantages of TiO$_2$ nanoparticles (high specific surface area) and one-dimensional (1D) nanostructures (fast transport channels) for obtaining highly efficient sensitized solar cells. To evaluate the effects of the 1D CTNPs on the performance of CdSe QDSSC was fabricated based on conventional TiO$_2$ nanoparticles (TNPs). The light-to-electricity conversion efficiency of 1D CTNP-based CdSe QDSSC (5.45%) is much higher than that of the TNP-based cell (4.00%). In addition to NWs and NPs, other morphologies, such as nanosheets (NSs), nanorods (NRs), microspheres (MSs), nanotubes (NTs), nanofibers (NFs), mesoporous (MPs), tetrapods (TPs), and nanodisks (NDs), have also been developed for TiO$_2$. Similarly, along with TiO$_2$, other materials like ZnO [63]-[65], SnO$_2$ [66], NiO [67] etc have been used as photoanode in QDSSC. Photovoltaic parameters of QDSSCs with different photoanode are summarized in Table 2.
3.2. Sensitizer (Quantum Dots)

QDs are important part of QDSSC. To maximize the harvesting efficiency of the incident light, it should possess a high absorption coefficient and appropriate band-gap energy. The energy levels of QDs applied in QDSSCs must match those of the sensitized wide-band-gap semiconductors. If the band-gap energy of the QDs is high, although a large VOC can be achieved, the wavelength range of light absorption will be narrowed. On the other hand, low band-gap energy of QDs may contribute to a wide wavelength region of light absorption, whereas it may lead to a low VOC [75].

The QDs employed in QDSSCs as sensitizers including Ag2S [76], Bi2S3 [77], CdS [78], CdSe [79], CdTe [80], CuInS2 [81], [82], Cu2ZnSnS4 [83], InAs [84], In2S3 [85], InP [86], PbS [87], [88], PbSe [89], Si [90], graphene [91] and so on. Among these sensitizers, Cd chalcogenides QDs have drawn great attention because of their relatively high stability in QDSSCs even though they may be unstable under visible light. In addition, co-sensitization of two or three types of QDs, for example, CdS/CdSe [92], CdS/CdTe [93], CdSe/CdTe [94], [95], CdS/PbS [96], [97], CdS/CdSe/PbS [of the complementary effect of extending the wavelength range of absorbed light.

There are two fundamental techniques of fabrication of QD sensitizers: in situ fabrication and ex situ fabrication. Chemical bath deposition (CBD) [104] and successive ionic layer adsorption reaction (SILAR) [105] techniques belong to in situ fabrication whereas linker-assisted assembly (LAA) [106] is an example of ex situ fabrication technique. In situ technique is more preferable to ex situ fabrication technique because of its better performance [107]. Photovoltaic parameters of QDSSCs with different QDs are summarized in Table 3.

### Table 2. Photovoltaic Parameters and Photoactive Materials of QDSSCs Based on Different Photoanode

<table>
<thead>
<tr>
<th>Photoanode</th>
<th>Quantum dot</th>
<th>Electrolyte</th>
<th>Counter Electrode</th>
<th>Jsc (mA cm⁻²)</th>
<th>Voc (mV)</th>
<th>FF</th>
<th>PCE (%)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂ NPs</td>
<td>CdSe/ZnS</td>
<td>S²⁺/S⁻²</td>
<td>Cu₂S</td>
<td>15.54</td>
<td>56.3</td>
<td>0.61</td>
<td>5.53</td>
<td>[69]</td>
</tr>
<tr>
<td>TiO₂ NPs</td>
<td>CdSe/ZnS/</td>
<td>S²⁺/S⁻²</td>
<td>Cu₂S</td>
<td>16.95</td>
<td>591</td>
<td>0.50</td>
<td>5.01</td>
<td>[70]</td>
</tr>
<tr>
<td></td>
<td>CdS</td>
<td>S(Se)</td>
<td>Cu₂ZnSn</td>
<td>17.5</td>
<td>563</td>
<td>0.605</td>
<td>5.96</td>
<td>[71]</td>
</tr>
<tr>
<td>TiO₂ NTs</td>
<td>CdSe/ZnS/</td>
<td>S²⁺/S⁻²</td>
<td>Cu₂S</td>
<td>10.81</td>
<td>689</td>
<td>0.62</td>
<td>4.61</td>
<td>[72]</td>
</tr>
<tr>
<td>TiO₂ NWs</td>
<td>CdSe/CdS</td>
<td>S²⁺/S⁻²</td>
<td>Pt</td>
<td>17.98</td>
<td>465</td>
<td>0.502</td>
<td>4.20</td>
<td>[73]</td>
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<tr>
<td>ZnO NWs</td>
<td>CdSe/CdSe/</td>
<td>S²⁺/S⁻²</td>
<td>Au</td>
<td>17.3</td>
<td>627</td>
<td>0.383</td>
<td>4.15</td>
<td>[63]</td>
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<td>ZnO NPs</td>
<td>CdSe/CdSe/</td>
<td>S²⁺/S⁻²</td>
<td>Cu₂S</td>
<td>9.93</td>
<td>61.6</td>
<td>0.52</td>
<td>3.14</td>
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<tr>
<td>ZnO NPs</td>
<td>CdSe/CdSe/</td>
<td>S²⁺/S⁻²</td>
<td>Pt</td>
<td>16.0</td>
<td>620</td>
<td>0.49</td>
<td>4.86</td>
<td>[65]</td>
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<tr>
<td>TiO₂ WNS-ZnO NPs</td>
<td>CdSe/CdSe/ZnS</td>
<td>S²⁺/S⁻²</td>
<td>Cu₂S</td>
<td>13.64</td>
<td>511</td>
<td>0.44</td>
<td>3.05</td>
<td>[74]</td>
</tr>
<tr>
<td>SnO₂</td>
<td>CdSe/CdSe/</td>
<td>S²⁺/S⁻²</td>
<td>Cu₂S</td>
<td>16.11</td>
<td>512</td>
<td>0.55</td>
<td>4.57</td>
<td>[68]</td>
</tr>
<tr>
<td>NiO</td>
<td>CuInS₂,S₂</td>
<td>S²⁺/S⁻²</td>
<td>Cu₂S</td>
<td>9.13</td>
<td>350</td>
<td>0.39</td>
<td>1.25</td>
<td>[67]</td>
</tr>
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</table>

### Table 3. Photovoltaic Parameters and Photoactive Materials of QDSSCs Based on Different QDs

<table>
<thead>
<tr>
<th>Quantum dots</th>
<th>Method</th>
<th>Photoanode</th>
<th>Electrolyte</th>
<th>Counter Electrode</th>
<th>Jsc (mA cm⁻²)</th>
<th>Voc (mV)</th>
<th>FF</th>
<th>PCE (%)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag₂S/ZnS</td>
<td>SILAR</td>
<td>TiO₂ NPs</td>
<td>Tl(I)</td>
<td>Pt</td>
<td>28.5</td>
<td>270</td>
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<td>CdS/Bi₂S₃/ZnS</td>
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<td>S²⁺/S⁻²</td>
<td>Cu₂S</td>
<td>9.3</td>
<td>502</td>
<td>0.537</td>
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<td>CdSe/CdSe</td>
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<td>489</td>
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<td>0.581</td>
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<td>Cd₂Se/CdSns/</td>
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<td>0.494</td>
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<td>TiO₂ NPs</td>
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<td>Cu₂S</td>
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<td>S²⁺/S⁻²</td>
<td>Cu₂S</td>
<td>19.59</td>
<td>606</td>
<td>0.569</td>
<td>6.76</td>
<td>[95]</td>
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<td>CdTe/CdSe/Te₆</td>
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<td>S²⁺/S⁻²</td>
<td>Cu₂S</td>
<td>20.19</td>
<td>610</td>
<td>0.51</td>
<td>6.32</td>
<td>[99]</td>
</tr>
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<td>Cu₂S</td>
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<td>595</td>
<td>0.642</td>
<td>7.19</td>
<td>[97]</td>
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<td>ZnTe/CdSe/ZnS</td>
<td>LAA</td>
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<td>19.29</td>
<td>640</td>
<td>0.552</td>
<td>6.82</td>
<td>[103]</td>
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</table>
3.3. Electrolyte

Redox electrolytes significantly influence both the efficiency and stability of QDSSCs. It is a medium which transfers charges between counter electrodes and photoanodes for the regeneration of oxidized QDs [108]. The most common electrolyte used in QDSSCs is the iodide/triiodide (I-3/I-2) electrolyte, which is prepared by mixing I- and I2 with other additives in suitable organic solvents [109]. Cadmium chalcogenide QD-based solar cells are unstable in the iodide/triiodide electrolyte because of photoanodic dissolution and the formation of cadmium iodide. Although, several studies have been proposed to protect the QDs from bleaching by coating them with protective layers [110], but the overall power conversion efficiency of the cell remained quite low which indicates that suitable alternative electrolytes is required to improve the performance and long-term stability of QDSSC.

Thus, a polysulfide (S2-/Sn2-) redox couple aqueous solution electrolyte is generally used in QDSSCs because it is able to stabilize the cadmium chalcogenides QDs with fine performance of the corresponding QDSSCs [111]. Still, there are some disadvantages of the polysulfide electrolyte; like, the VOC of the resultant QDSSCs is generally low because polysulfide electrode has the relatively high redox potential [112]. To optimize the polysulfide electrolyte, many works have been reported like controlling the concentration of the redox mediator [113], introducing additives e.g., SiO2 [114], poly (vinyl pyrrolidone) (PVP) [115], and guanidine thiocyanate [116], and using a modifying solvent [117]. In order to improve the photovoltaic performance, especially the VOC of QDSSCs, alternative redox couples having relatively low redox potentials, such as Mn poly (pyrazolyl) borate (PEO-PVDF) [125] have been applied in solid state QDSSCs. However, the efficiency of the solid state devices is lower than that of the liquid-junction cells.

3.4 Counter Electrode

Counter electrode (CE) plays an important role in performance of QDSSC. It transfers electrons from the external circuit into electrolyte and catalyzes the reduction reaction of the oxidized electrolytes at the electrolyte/CE interface. To achieve a superior electrocatalytic performance, CEs should possess high electrical conductivity, excellent electrocatalytic activity and great stability [126]. The most common material for CE in QDSSCs is Pt because of its good electrocatalytic ability for the reduction of iodide/triiodide electrolyte. However, when Pt CE is used with polysulfide electrolyte, the performance of resultant solar cell is poor because sulfur atoms would easily adsorb onto the Pt surface, hence conductivity of CE reduces consequently power conversion efficiency of QDSSC reduces [127]. For that reason, alternative CE materials in QDSCs have been extensively investigated, like metal chalcogenides [128-130] carbon-based materials [131-133] and various composites [134-136]. Photovoltaic parameters of QDSSCs with different CEs are summarized in Table 4.

Table 4. Photovoltaic Parameters and Photoactive Materials of QDSSCs Based on different CEs

<table>
<thead>
<tr>
<th>Counter Electrode</th>
<th>Photoanode</th>
<th>Quantum dots</th>
<th>Electrolyte</th>
<th>Jsc (mA cm2)</th>
<th>Voc (mV)</th>
<th>FF</th>
<th>PCE (%)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuSNSBrass</td>
<td>TiO2 NPs</td>
<td>CdS/CdSe/ZnS</td>
<td>S2-/S2-</td>
<td>14.54</td>
<td>634</td>
<td>0.667</td>
<td>6.15</td>
<td>[128]</td>
</tr>
<tr>
<td>CuS NSs</td>
<td>TiO2 NPs</td>
<td>CdS/CdSe/ZnS</td>
<td>S2-/S2-</td>
<td>17.43</td>
<td>596</td>
<td>0.495</td>
<td>5.15</td>
<td>[129]</td>
</tr>
<tr>
<td>CuS NPs</td>
<td>TiO2 NPs</td>
<td>CdSe/ZnS</td>
<td>S2-/S2-</td>
<td>17.7</td>
<td>551</td>
<td>0.491</td>
<td>4.78</td>
<td>[130]</td>
</tr>
<tr>
<td>Carbon NPs</td>
<td>TiO2 NPs</td>
<td>CdSe/ZnS</td>
<td>S2-/S2-</td>
<td>11.99</td>
<td>620</td>
<td>0.60</td>
<td>4.81</td>
<td>[131]</td>
</tr>
<tr>
<td>Carbon NPs</td>
<td>TiO2 NPs</td>
<td>CdSe/ZnS</td>
<td>S2-/S2-</td>
<td>13.53</td>
<td>510</td>
<td>0.40</td>
<td>2.67</td>
<td>[132]</td>
</tr>
<tr>
<td>Carbon MNNs</td>
<td>TiO2 NPs</td>
<td>CdSe/ZnS</td>
<td>S2-/S2-</td>
<td>12.41</td>
<td>600</td>
<td>0.52</td>
<td>3.90</td>
<td>[133]</td>
</tr>
<tr>
<td>ITONWs/CuS NPs</td>
<td>TiO2 NPs</td>
<td>CdSe/ZnS</td>
<td>S2-/S2-</td>
<td>14.31</td>
<td>540</td>
<td>0.525</td>
<td>4.06</td>
<td>[134]</td>
</tr>
<tr>
<td>CuS NPs</td>
<td>TiO2 NPs</td>
<td>CdSe/ZnS</td>
<td>S2-/S2-</td>
<td>14.48</td>
<td>760</td>
<td>0.38</td>
<td>4.18</td>
<td>[135]</td>
</tr>
<tr>
<td>PbS NPs</td>
<td>TiO2 NPs</td>
<td>CdSe/ZnS</td>
<td>S2-/S2-</td>
<td>13.28</td>
<td>633</td>
<td>0.566</td>
<td>4.76</td>
<td>[136]</td>
</tr>
</tbody>
</table>
4. WORKING PRINCIPLE OF QDSSC

A QDSSC operates in the following processes under illumination as shown in Figure 5:

a. Upon light irradiation, the sensitizer is photoexcited.

b. The excited electrons of QDs are injected into the conduction band of the TiO$_2$.

c. The electrons penetrate through the nanocrystalline TiO$_2$ film to the back contact of the conducting substrate, and flow through an external circuit to the CEs.

d. At the CEs, the oxidized component of redox couple in the electrolyte is reduced.

e. The oxidized form of the sensitizer (QDs) is finally regenerated by the reduced component of redox couple in the electrolyte.

![Figure 5: Working principle of QDSSC [137]](image)

In this overall process, there are two major recombination loss processes that limit the total photoconversion efficiency within the QDSSCs: the photoinjected electrons in TiO$_2$ can recombine directly with the oxidized QDs or with the oxidized form of the redox couple in the electrolyte.

5. CONCLUSION

Over the past few years, QDSSCs have been the subject of extensive studies for the optimization of all the active materials relating to cell devices. However, many challenges hinder the practical application of QDSSCs, such as achieving higher power conversion efficiency, long-term stability, and large-scale production. Future works should focus on improving the power conversion efficiency of the solar cells as follows:

a. Designing new semiconductor QDs with a large wavelength range of optical absorption in terms of quantum confinement.

b. Getting MEG effect enhancement of QDs by reducing the threshold energy.

c. Constructing suitable porosity for photoelectrodes to improve the loading of QDs on photoanode to increase the light harvesting efficiency of QDs.

d. Minimizing the charge recombination taking place at the QD– and photoanode–electrolyte interfaces.

e. Increasing electron mobility and device stability.

f. Reducing fabrication costs.

Solar cells using QDs have already exhibited high efficiency of conversion of light energy into electrical energy. However, commercialization of QDSSCs in large scale has yet to be realized. With the recent advances in the study of semiconductor QDs, we expect QDSSC will compete with silicon solar cell in the future.

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