A Short Overview on Recent Progress in Semiconductor Quantum Dot-Sensitized Solar Cells

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The past few years have been great years for semiconductor quantum dot-sensitized solar cells (QDSSCs). For the first time, efficiency exceeding 15% has been reported. This has narrowed the gap with other emerging solar cell technologies such as dye-sensitized solar cells and thin film solar cells. In this miniperspective, the reason for such improvement is briefly reviewed.

Few advancements have been identified that are responsible for the performance breakthrough in QDSSCs. These included better performance of sensitizer materials used, the use of doping agents, and surface passivation strategy.

1. Introduction

The progress of the third-generation solar cells has been encouraging over the past few years. Although there are various types and variants of solar cell architecture in this category, one cannot dismiss the great potential of this emerging solar cell technology. The progress of the third-generation solar cells was made possible with the introduction of dye-sensitized solar cells (DSSCs) in the early 90s [1]. This was followed by the introduction of organic solar cells in the late 90s [2]. Subsequently, a few variants were introduced, namely, quantum dot-sensitized solar cell (QDSSC), colloidal quantum dot solar cells, and lately the high-performing perovskite solar cells [3, 4]. The high performance of perovskite solar cells, which has a certified efficiency of over 20%, has overshadowed its predecessor, i.e., sensitizing-type solar cells [5]. Although perovskite solar cells have made a dramatic progress within a short span of time, QDSSCs have also progressed well lately. The latest research effort has yielded an efficiency of 15%, which is better than the DSSCs [6]. In this miniperspective, the recent developments of QDSSCs for the past few years in which the authors deem to have significant impact to the future works are briefly discussed and reviewed. This article is by no means to be comprehensive but serves as a guideline and forward-looking trend. The intention is to provide a snapshot on the recent works that have yielded improved performances of QDSSCs, which could be beneficial for designing better QDSSCs. For in-depth review on QDSSC subject, readers are encouraged to explore the literature elsewhere [7–12].

2. Fundamental Working Mechanism and Its Drawbacks

QDSSC works in a similar way like DSSC [7, 13]. Figure 1 illustrates the basic architecture and the electron movement path of a QDSSC. The main differences between QDSSC and DSSC are the light absorber material and the electrolyte system. In general, QDSSC works upon light illumination, where the light absorber material will respond to a specific wavelength range of the visible light spectrum by releasing its electrons from the valence band to the conduction band.
In this phenomenon, the electrons within the light absorber material are said to have been “excited.” The excited electrons are then percolated through the network of wide band gap oxide materials. Eventually, the excited electrons reach the conducting substrate and finally to the external circuit where electricity is used by the load. At the same time, as the electrons have been “excited,” the light absorber material itself is being oxidized. In other words, it is deficient in electrons. Thus, it requires supplementary electrons in order to stabilize its state. As a result, the electrolyte system will donate its electrons to the light absorber material to fulfill the electron requirement. When the electrons that are traveling on the external circuit reach the counter electrode side, they are quickly salvaged to the electrolyte system so that the electrolyte system achieves a stable state too. And the whole process will continue as long as there is light illumination.

From the working mechanism, we can deduce that there are few factors that can affect the performance of a typical QDSSC. The main factor is the electron or charge kinetics. For a high-performance solar cell, electrons should be readily available for transportation. This includes facile electrons released by the light absorber materials upon light illumination. Apart from that, the “excited” electrons should be able to move across the internal network and the external circuit smoothly. As such, any barriers or internal resistances within the system are not welcome. In practice, the internal resistances are present; thus, recombination of electrons is unavoidable. In the past few years, the reported low efficiency of the QDSSCs was mainly due to these two main factors: low electron generation and high electron recombination rate [14, 15].

The remedies for these problems are better light absorber materials with fast charge separation and enhanced solar cell architecture layers for reduced electron recombination rate. The goal is to increase QDSSC performance and stability, which can be achieved via better QD sensitizers and high QD loading [16]. These solutions appear to be easy but in reality, it took the research community several years to establish convincing results.

3. Recent Advances in QDSSC

It is without doubt that materials in small scales of sizes play an important role in achieving high-performance solar cell devices [17]. Here, the preferred size of the materials is in the nanometer range, typically less than 20 nm. The types of materials used as light harvesting materials are also critical to the performance of the solar cell. It is due to the unique properties and characteristics of the inorganic semiconductors used as sensitizers (or light harvesters) that enable the QDSSC to be advantageous than DSSC. Some of the notable advantages of QDSSC are tunable bandgap of the semiconductor via its nanosize, rapid charge separation (as a result of large intrinsic dipole moment), and possible multiple charge carrier generation from a single photon [18].

In the early years, QDSSC research was centered around PbS as the quantum dot (QD) sensitizers [19]. Later on, more semiconductor materials were introduced where cadmium-based QDs were the focus of the research [7]. To date, QDSSCs with CdS and CdSe as sensitizers have been widely reported. The increase in the research reports could be due to the easy fabrication of CdS QD and the high performance of CdSe QD. Although the best efficiency of QDSSC using single CdSe as a sensitizer is around 2%, the cell’s performance increases when multilayers of QDs are used [20, 21]. Such technique is termed as cosensitization. There are also other new types of semiconductors being proposed to be used as sensitizers in QDSSC although some may not perform well in the device level [22–25].

CdS and CdSe have gained much research interest in QDSSC. However, one should not dismiss the potential of CdTe as a sensitizer. Unfortunately, CdTe has been reported to have poor performance when used as a sensitizer in QDSSC with polysulfide electrolyte [26]. However, when CdTe was cosensitized with other semiconductors or
blended to form a ternary compound, a significant improvement was observed as reported by Wei et al. [27]. In their work, CdSeTe$_{1-x}$ QDSSC with SiO$_2$-modified electrolyte produced an efficiency of 11.23%. This result (and other earlier results not reported here) marks improved performance of QDSSC beyond the binary QD compound. The better performance exhibited by QDSSC with ternary QD compound is largely due to the band gap tunability, improved surface chemistry, and efficient exciton generation [28]. Further analysis revealed that the improvement is related to the increased charge mobility, longer electron lifetime, high QD loading rate, and widening of light conversion range [27, 28]. Figure 2 illustrates the performance improvement attributed to ternary QD structure.

Since ternary QD compound has shown good performance in QDSSC, the next logical move is to assess quaternary QD compound as a sensitizer. Higher reported efficiencies of QDSSC to date consist of ternary compound CdSe$_{1-x}$ QDs and quaternary compound Zn-Cu-In-Se and Cu$_2$ZnSnS$_4$ QDs [27, 29–32], where efficiency around 10% was observed. Improvement observed in quaternary QD like Zn-Cu-In-Se and Cu$_2$ZnSnS$_4$ is attributed to the improved optical properties of the compound when Cu element is alloyed within it at an appropriate ratio. For example, efficiency of 12.57% was reported in Zn-Cu-In-Se QDSSC when the QD compound was fabricated in a nonstoichiometry state [33].

Other alternative QD sensitzers included Pb-Cd-S as reported by Yuan et al. [34]. Apparently, nonstoichiometry ternary Pb$_{0.54}$Cd$_{0.46}$S and Pb$_{0.31}$Cd$_{0.69}$S QDs were reported to have improved photocurrent compared to single CdS or PbS QDs. Efficiency as high as 3.2% was achieved with such QDs in a cell architecture without a surface protection layer. Although the efficiency is inferior to that of other Cu-based ternary and quaternary QD compounds, the fabrication of nonstoichiometry compounds could set as the base for new QD compounds.

With the introduction of quaternary QD compound in QDSSC, attempt to assess more complex QD compound has started. Song et al. have reported QDSSC with QD consisting of Zn-Cu-In-S-Se, with treatment with Mg ion [35]. Song et al. demonstrated that by applying secondary deposition on top of primary deposited QD layers, higher QD loading was achieved. The cell produced the efficiency of 15.31% which is the highest reported so far. With the untreated QD, efficiency of 13.54% was obtained, which is higher than the common DSSC. Such improvement is largely to due improved QD loading coupled with reduced charge recombination due to surface treatment with metal ion.

One of the promising strategies of improving charge collection is by introducing metal ion dopants into the photoanode active layer. Typically, transition metal ions are used for doping with QDs in order to enhance the photophysical properties of the photoanode. This effect was first reported by Santra et al. where Mn-doped CdS/CdSe QDSSC has shown efficiency above 5% for the first time [36]. Since then, studies on the doping effect have been carried out by various groups as this method is able to improve the charge collection and charge transfer process.

Manganese ion is probably the best dopant for QDSSC. In the work of Hou et al., Mn-doped CdSe QDSSC based on the ZnO layer has shown 40% increase in performance [37]. When manganese ion is doped in CdS QDSSC, the same improvement is also observed with an efficiency of at least 3% [38]. The presence of metal ion allows the formation of an intermediate band gap which ultimately facilitates the charge injection, as illustrated in Figure 3.

Although manganese ions have been frequently used as a doping agent in QDSSC, other metal ions have been reported to function well as doping agents. In the work of Gopi et al., they used nickel ions to dope into CdS QDSSC [39]. They deduced that the synthesized CdNiS QDs have better light absorption, better electron injection kinetics rate, and reduced charge recombination. The best cell had a 50% increase in efficiency compared to that without nickel ion doping. In another reported finding, Muthalif et al. demonstrated a high-performance CdS QDSSC doped with copper ion [40]. However, the effect of doping copper ions in CdSe QDSSC is not well documented. But based on the trend, it should have an improved performance. On the other hand, cobalt ion also has the potential to be used as a doping agent where in one report, efficiency increment of 25% was observed in Co-doped CdS QDSSC [41]. Although the improvement is not impressive (in terms of percentage improvement), it is still a viable strategy. The varying degrees of performances of metal ion-doped QDSSC are largely due to different concentrations of metal ion doped into photoanode, as well as the overall device architecture where different groups used different types of counter electrode and electrolyte system. Nevertheless, the concentration of the metal ion to be added into the QDSSC photoanode should not be excessive so that the impurities do not serve as recombination centers instead.

Recombination of charge carriers at the photoanode/electrolyte interfaces has posed a critical threat to the performance of QDSSC. A simple solution could be patching up any pathway for the charge to recombine at the interface. Due to low surface coverage by QDs on the wide band gap metal oxide layer, charge recombination becomes easier [42]. As such, a passivation layer is applied to cover the photoanode surface. The most popular passivation layer used is ZnS [43, 44]. The ZnS layer has proven to be very effective in suppressing the charge recombination process. The recent TiO$_2$/ZnS/CdS/ZnS QD heterostructure employing duo layers of ZnS has shown improvement of performance, although at a moderate rate [45]. Therefore, most of the high-performing QDSSC has a passivation layer or barrier layer applied on top of QD. Besides ZnS, some groups used a SiO$_2$ layer [46]. The group reported 9.48% efficiency for CdSeTe QDSSC treated with a-TiO$_2$ and SiO$_2$ layers. The layers help suppressed the charge recombination at the QD/electrolyte and TiO$_2$/QD interfaces (see Figure 4).

Other few more materials have also been reported that have a better passivating effect. Huang et al. reported the effect of different Zn chalcogenides as a passivation layer in CdS/CdSe QDSSCs [47, 48]. QDSSCs with ZnSe as a passivation layer showed a better performance compared to that using ZnS as a passivation layer where efficiency as high as
6.39% was reported (Figure 4). Such a result was not observed in the previous work, possibly due to different chemical preparation routes [49]. Aside from Zn chalcogenide, other metal oxyhydroxides have also been tested for their capability as a passivating layer. Ren et al. has used metal chlorides (NbCl5, ZrOCl2, SnCl4, FeCl3, AlCl3, CoCl2, CuCl2, MgCl2, and ZnCl2) on CdSeTe QDSSC [50]. A good efficiency of 9.73% was observed in cells passivated with the ZrOCl2 layer.

A variant of a passivation layer includes application of a light-scattering layer. Typically, such a layer is used in DSSC where TiO2-based material is frequently employed [51]. The same approach has also been applied in QDSSC. The light-scattering layer can be from nonmetallic material as in the work of Esparza et al. where they used polymer-based material containing poly [9,9-bis(3′(N,N-dimethylamino)propyl)-2,7-fluorene-alt-2,7-(9,9-dioctylfluorene)] (PFN) [52]. This new material has allowed them to achieve QDSSC with better short-circuit current compared to that without the PFN layer. Specifically, the short-circuit current value achieved was 17.6 mA/cm² for the cell configuration of TiO2/PFN/PbS/CdS/ZnS compared to that of 13.3 mA/cm² for the cell configuration without PFN coating. Such improvement is attributed to the presence of the PFN layer where it acts as a light-scattering intralayer by increasing the light absorption and provides protection to the QDs by reducing the recombination rate between the QDs and the electrolyte.

Another strategy to improve the light-harvesting performance of QDs is postheat treatment. Qiao et al. reported that a postheat treatment at 200°C for 30 minutes on the CdS/CdSe QD electrode was able to improve the cell efficiency and current density [53]. The slight improvement could be attributed to the reduced surface defects as a result of heat treatment. This stipulates that crystal structure is an important factor in influencing the performance of the QDSSC.

So far, most of the improvement was reported on QD sensitizers and their interfaces. The electrolyte and counter electrode components are also studied although the degree of improvement may not be substantial. A significant development aimed at improving counter electrodes included new materials like Cu2S/brass, graphene hydrogel-CuS/Ti, and nitrogen-doped mesoporous carbon [54–56]. For example, Jiao et al. reported efficiency of 12.45% for QDSSC using nitrogen-doped mesoporous carbon as the counter electrode [56]. Compared to those cells without nitrogen doping, the average efficiency observed was 11.44%. The improvement is attributed to the better catalytic activity of the new counter electrode material as measured with electrochemical
impedance spectroscopy and cyclic voltammogram techniques. The doping with nitrogen heteroatoms has contributed to the increased catalytic reduction of the polysulfide electrolyte.

Probably the most challenging component is the electrolyte system. Polysulfide electrolyte has been the main choice for QDSSC since it is best suited for the QD materials. The best reported efficiency also utilized polysulfide as its electrolyte [35]. However, most of the electrolyte systems used in QDSSC are in a liquid state. Recent efforts to modify electrolytes to obtain gel or solid-state electrolyte with high efficiency and stability have produced some positive results. Interestingly, Jiang et al. introduced poly(vinyl pyrrolidone) polymer as a potential electrolyte additive for QDSSC [57]. They reported an efficiency of 9.77% in cells with 20 wt% PVP added in polysulfide. More importantly, addition of PVP in the polysulfide electrolyte system brings benefit to various types of QD sensitizers used. The improvement is attributed to the inhibition of charge recombination at the TiO2/QDs/electrolyte interfaces.

Separately, Feng et al. demonstrated a high-performance QDSSC with quasi-solid-state electrolyte [58]. They used sodium carboxymethylcellulose to solidify the polysulfide solution. Their solid-state QDSSC registered an efficiency of 9.21%. Remarkably, the ionic conductivity of the gel electrolyte did not decrease much (6.9% decrement to be exact). Despite the reduction of the volume ratio of the polysulfide, the porous nature of the polymer enables the migration of ions within the electrolyte. In short, researchers tend to modify the polysulfide electrolyte system by adding additives as in the case of Wei et al. [27]. In that work, they added fumed SiO2 into the polysulfide electrolyte which yielded efficiency of 11.23%. Again, the additive serves as a barrier for the recombination in the interfaces within the QDSSC (see Figure 5).

As a conclusion, the recent years of QDSSC development have shown that higher-power conversion efficiency is still possible. The strategy of the future research and development should be aimed at improving QD loading, reducing charge recombination at the interfaces, and efficient and stable electrolyte system in a solid state as well as excellent catalytic activity of counter electrode materials (Figure 6).

4. Outlook

Based on the recent works by different groups, it can be concluded that QDSSC has the potential to be adopted as one of the mainstream solar cell technologies. However, much work is needed in order to improve the performance as well as achieve stable and reliable devices. One of the strategies is to fabricate a hybrid solar cell. QDs can be included into other high-performance solar cells for acquiring better photophysical properties. In a recent report, QD materials were mixed into perovskite-based material, paving a way for possible application in solar cells [59]. The next step would be scaling up the device to the application level. To achieve this, multidisciplinary studies which involve nanotechnology, materials science, and semiconductor physics are crucial in order to understand the working mechanism, especially the charge transport mechanism within the cell. In the next few years, efficiency exceeding 15% or even 20% should be within reach.

Conflicts of Interest

The authors declare that they have no conflicts of interest.
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