Four-Terminal Tandem Solar Cell with Dye-Sensitized and PbS Colloidal Quantum-Dot-Based Subcells

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ABSTRACT: In this work, high-performance four-terminal solution-processed tandem solar cells were fabricated by using dye-sensitized solar cells (DSSCs) as top-cells and lead sulfide (PbS) colloidal quantum dot solar cells (CQDSCs) as bottom-cells. For dye-sensitized top-cells, three different dye combinations were used while the titanium dioxide (TiO2) scattering layer was removed to maximize the transmission. For the PbS bottom-cells, quantum dots with different sizes were compared. Over 12% power conversion efficiency has been achieved by using the XL dye mixture and 890 nm PbS QDs, which shows a significant efficiency enhancement when compared to single DSSC or CQDSC subcells.

KEYWORDS: PbS, quantum dot solar cell, dye-sensitized solar cell, solution-processed, four-terminal tandem

Colloidal quantum dot (CQD)-based materials have an excellent potential for many different optoelectronic applications, such as solar cells,2,3 light-emitting diodes,4 gas sensors,5,6 and photodetectors.7,8 CQDs have attracted a lot of attention because of the tunable band gap, low-cost earth-abundant materials, and possibility for solution-based preparation processes. A PbS colloidal quantum dot solar cell (CQDSC) was first reported in 2005,9 and it achieved over 1% power conversion efficiency (PCE) in 2008 by K. W. Johnston.10 After a decade, the efficiency of the PbS CQDSC is beyond 12% by using a solution-phase ligand exchange method, and the efficiency was stable for over several weeks under ambient conditions without encapsulation.11 Moreover, the PbS CQD also offers a possibility to fabricate other advanced photovoltaic devices, such as flexible solar cells,12 semitransparent devices,13 as well as hot-carrier or multiple excitation generation devices.14

The dye-sensitized solar cell, DSSC, has attracted researchers’ attention since the early 1990s due to low-cost materials, a simple fabrication process, low toxicity, and excellent ambient light harvesting ability.15 Around 12% PCE under AM 1.5 condition has been achieved for DSSCs, and over 28% under ambient light condition,16 but the large band gap of the most efficient DSSCs may be a drawback to achieve a higher performance because the photons with energy lower than the band gap are wasted. Therefore, it is important to find a way to take advantage of those photons with lower energy to generate more power.

Multijunction solar cells, or tandem solar cells, have been shown to be an effective way to harvest light from a large part of the solar spectrum. It has been proven that increasing the number of junctions in a multijunction device is an efficient way to overcome the Shockley–Queisser limit, which is 33% PCE for a single junction device.17 The PbS CQD has shown an excellent ability of harvesting the near-infrared spectrum, which allows researchers to use this material to fabricate bottom-cells for tandem structure devices. Within the
literature, researchers have combined different top-cell materials with PbS subcells. For example, the CdTe/PbS tandem solar cell has achieved over 9% PCE,20 the PbS/PbS tandem structure approaches 9% by using the PbS CQD with a different band gap as subcells, 21,22 while a theoretical simulation has shown that a perovskite/PbS tandem structure can achieve 43% PCE.19,23 Also, a tandem structure DSSC has been proven as a reliable tandem structure photovoltaic device in recent years.24–27 However, to the best of our knowledge, the DSSC/PbS tandem structure has not previously been investigated.

This work investigates the possibility of making a four-terminal tandem solar cell by using a DSSC and PbS CQDSC as the top-cell and bottom-cell, respectively. We comprehensively test and analyze the combination of three different dye mixtures (Y123, XY1, and XL) and three different sizes of PbS CQD (absorbance peak 790, 890, and 940 nm) in tandem solar cells under one-sun conditions.

The four-terminal tandem system contains a DSSC as the top-cell and a PbS CQDSC as the bottom-cell. For the DSSC, we fabricated the cell with a structure of FTO/c-TiO2/mp-TiO2/dye with a redox electrolyte and PEDOT/FTO back-contact. The PbS CQDSC was fabricated with the ITO/AZO/PbS–PbI2/PbS-EDT/Au structure. The PbS–PbI2 layer was deposited by a one-step method after solution ligand exchange. The schematic of the four-terminal tandem solar cell is shown in Figure 1a. Usually DSSCs are fabricated with a TiO2 light scattering layer to improve the absorption of light in the devices. However, the scattering layer reduces the light transmission because it is not transparent. To improve the transmission of light to the PbS-based bottom-cell, we removed the TiO2 scattering layer, and the transmission was increased from less than 30% to over 40%, which was mainly due to the reduction of reflectance (see Figure 1b). However, the overall transmission was still low when compared with top-cells with other materials, e.g., perovskite.28,29 The main transmission loss was due to poor transmission of the PEDOT back-contact, which caused over 30% optical losses. It should also be noticed that the reduction of transmission of light through the DSSC without a scattering layer after 700 nm was

Figure 1. (a) Schematic of the four-terminal tandem structure based on the DSSC and CQDSC. (b) Transmission, reflectance, and absorption spectra for XL DSSCs with and without the scattering layer. (c) UV−vis−NIR absorbance for different dye mixtures and quantum dots with different sizes.

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due to the light absorption and reflection from the FTO front contact.

We first compared the performance of the DSSCs with different dye combinations and the effect of the removal of the scattering layer for the DSSCs. As shown in Figure 2, after the scattering layer was removed, the PCE of XL, XY1, and Y123 dye decreased from 10.20%, 9.0%, and 8.11% to 8.85%, 7.17%, and 7.19%, respectively. For the DSSC with Y123 dye, the main reason for the efficiency reduction is that the Y123 dye has a poor light absorption, and removing the scattering layer will therefore reduce the $J_{sc}$ dramatically. On the other hand, though XY1 dye has a better light absorption, the removal of the scattering layer reduces the fill factor (FF) significantly which causes a lower efficiency. By using the XY1 and L1 dye cocktail, the light absorption is enhanced dramatically, so removing the scattering layer will not cause a significant impact on $J_{sc}$.

We then measured the performance of differently sized PbS CQDSCs and also measured the performance for the CQDSCs as bottom-cells with an XL DSSC top-cell. As shown in Figure 3a, without the top-cell, the PCE of PbS CQDSC was 8.53%, 10.85%, and 5.23% for devices based on CQDs with peak light absorption at 940, 890, and 790 nm, respectively. Previous reports have shown that PbS CQDs with peak absorption around 900 nm result in the highest efficiency for the PbS CQD solar cells.\textsuperscript{3,30,31} When the DSSC top-cell was applied on top of the CQDSCs, the PCE of these PbS CQDSCs decreased to 3.64%, 1.82%, and 1.78%, for devices based on CQDs with peak light absorption at 890, 940, and 790 nm, respectively. The main loss of the performance was due to the significant reduction of $J_{sc}$ which is expected, since the incident-power-to-current-efficiency (IPCE) shows that the visible light blocked by the DSSC top-cell contributes to over 60% of $J_{sc}$ in the CQDSC (Figure 3b). By combining the XL DSSC top-cell and the CQDSC bottom-cell based on CQDs with peak light absorption at 890 nm, the best overall efficiency for the 4-terminal system is 11.7%, which is about a 7.4% and 41% relative enhancement when compared to the single junction PbS CQDSC and DSSC, respectively (Table 1). We can therefore observe a clear enhancement of the performance due to the better utilization of the infrared light by combining the DSSC with a CQDSC, and this first demonstration paves the way for future DSSC/CQDSC tandem cells with further improvements.

![Figure 2](https://example.com/figure2.png)  
**Figure 2.** Current–voltage ($J$–$V$) measurements under illumination (1000 W/m$^2$, AM 1.5G) for DSSCs with different dye combinations both for devices with a scattering layer (“scattering”) and for devices without the scattering layer (“transparent”).

![Figure 3](https://example.com/figure3.png)  
**Figure 3.** (a) Current density–voltage ($J$–$V$) measurements under illumination (1000 W/m$^2$, AM 1.5G) for different size PbS CQDSCs with and without the XL DSSC top-cell. (b) IPCE and calculated $J_{sc}$ of XL DSSC and 890 nm PbS CQDSC under different conditions.

| Table 1. Performance of Single Cells and of Subcells in the Four-Terminal Tandem Solar Cell, and the Total Efficiency of the Four-Terminal Tandem Solar Cell |
|---------------------------------|-----------------|---------------|-------------|
|                                  | $V_{oc}$ (mV)   | $J_{sc}$ (mA/cm$^2$) | FF (%) | PCE (%) |
| single XL DSSC with scattering layer | 1050           | 12.90           | 75.0    | 10.20   |
| single PbS CQDSC (based on CQDs with 890 nm abs. peak) | 592          | 28.33           | 64.7    | 10.85   |
| single XL DSSC without scattering layer | 1018          | 12.30           | 71.0    | 8.85    |
| PbS CQDSC as bottom-cell (with XL DSSC as top-cell) | 534            | 9.88            | 66.7    | 3.52    |
| 4-terminal tandem solar cell based on the XL DSSC (without scattering layer) and PbS CQDSC (based on CQDs with 890 nm abs. peak) | | | | 12.37 |

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improved performance. Furthermore, the rather similar currents from the DSSC top-cell and PbS bottom-cell is interesting, and gives a possibility to fabricate a two-terminal tandem structure in the future. However, to achieve very highly performing tandem cells, further work is needed on the light management to reduce the infrared light reflection and absorption within the DSSC device.

In conclusion, we have demonstrated a high-performance four-terminal tandem solar cell by applying a dye-sensitized solar cell as the top-cell and a PbS colloidal quantum dot solar cell as the bottom-cell. Three different types of dyes (XL, XY1, and Y123) and three different PbS CQDs (with absorbance peak at 790, 890, and 940 nm) have been examined. The PbS CQDSC with CQDS absorption peak at 890 nm shows the best performance, which boosts the performance of the DSSC by ~41% relative for the XL mixed dye, ~21% for XY1, and ~31% for Y123. We therefore see a clear enhancement of the performance due to the better utilization of the infrared light by combining the DSSC with a CQDSC, which shows that DSSC/CQDSC tandem cells may be a very interesting alternative for future high-efficiency devices.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/10.1021/acsaem.0c00030.

Experimental details, $J$–$V$ plot, and a summary of solar cell performance (PDF)

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