Narrow Band Gap Lead Sulfide Hole Transport Layers for Quantum Dot Photovoltaics

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ABSTRACT The band structure of colloidal quantum dot (CQD) bilayer heterojunction solar cells is optimized using a combination of ligand modification and QD band gap control. Solar cells with power conversion efficiencies of up to $9.33 \pm 0.50\%$ are demonstrated by aligning the absorber and hole transport layers (HTL). Key to achieving high efficiencies is optimizing the relative position of both the valence band and Fermi energy at the CQD bilayer interface. By comparing different band-gap CQDs with different ligands we find that a smaller band gap CQD HTL in combination with a more p-type-inducing CQD ligand is found to enhance hole extraction and hence device performance. We postulate that the efficiency improvements observed are largely due to the synergistic effects of narrower band-gap QDs causing an upshift of valence band

position due to 1, 2-ethanedithiol (EDT) ligands and a lowering of the Fermi level due to oxidation.

KEYWORDS quantum dot, solar cell, band alignment optimization, surface treatment, band gap control

INTRODUCTION

Solar cells based on lead sulfide colloidal quantum dots as the absorber have the potential to provide cheap, flexible, and highly efficient photovoltaic devices.¹⁻² Lead and sulphur are both abundant, low cost materials that can be synthesized into nanocrystal colloids which absorb across the solar spectrum.³⁻⁴ These colloids can be solution-processed into thin films with controlled semiconductor properties suitable for optoelectronic devices. Since the first report of a Schottky junction solar cell in 2005,⁵ power conversion efficiencies (PCE) have increased from less than 1% to 11.3%.^{1, 6-7}

To be a viable solar energy technology improvements in fill factor (FF) and open circuit voltage (V_{oc}) are still required. Recent device improvements have focused on carrier mobility and recombination using a variety of treatments including solid or liquid state ligand exchange,⁸⁻¹¹ surface passivation,¹²⁻¹⁴ and band alignment engineering^{2, 15-19}. It is accepted that the chemistry at the CQD surface determines carrier properties as much as the QD's bulk properties.²⁰⁻²¹ For example Tang et al.¹² showed that single halide atom passivation reduces the number of trap sites, and lowers the recombination rate of electrons and holes, compared to organic-only counterparts e.g. EDT. Ip et al.¹⁴ further introduced a hybrid passivation method using atomic and organic ligands together, efficiently reducing the number of trap energy levels in the band gap.

The alignment of the conduction and valence bands and Fermi level at interfaces is also critical to device performance. Chuang et al.² showed that replacing two layers of tetrabutylammonium iodide (TBAI)-modified PbS with EDT-modified PbS acts to block electrons at the cathode, resulting in a certified efficiency of 8.55%. Brown et al.¹⁵ tabulated the effects of various ligands on the Fermi levels and valence band positions. Besides different ligands,^{2, 15-16} different size QDs^{17-18, 22} also lead to changes in band alignment effects. Hyun et al.²² reported that changing the QD size also changes the energy level of the conduction band. However, the performance enhancement mechanism of band alignment in solar cells is still open to debate. Ning et al.⁸ suggests that it is a result of an extended depletion region, while Chuang et al.² ascribes it to the formation of an interface dipole.

This paper focuses on controlling the coupling between QDs using a combination of QD band gap and surface chemistry to create an optimized band. Kramer et al.¹⁸ reported a similar quantum funnel CQD solar cell using large band gap PbS as a blocking layer at the rear contact with PCE of 2.7%. In this design there was good conduction band alignment but poor valence band alignment as the large band gap PbS gave rise to a deeper valence band position.²² In this work a thin PbS layer with a smaller band gap is inserted between the PbS absorber and the gold cathode to act as a hole transport layer using a combination of different band gaps and ligand treatment to optimize band alignment as shown in Figure 1. This paper optimizes both absorber and HTL layers devices to improve PCE.

Figure 1a) The architecture of colloidal quantum dot solar cells used in this work. b) Cross-sectional SEM images of the optimized device. c) Cross-sectional SEM images of the reference device. The thickness for each layer is 210 nm for ITO, 150 nm for ZnO, 290 nm for PbS-TBAI, 70 nm for PbS-EDT, and 50 nm for Au.

EXPERIMENT

Synthesis of colloidal PbS QDs. Oleic-acid-capped PbS QDs were synthesized using Schlenk line techniques following the methods reported elsewhere.^{13, 23} 1.30 eV PbS was synthesized as follows. Lead oxide (0.46 g) was dissolved in the mixture of 1-octadecene (10 g) and oleic acid (OA, 1.5 g) by stirring. The solution was degassed at 105 °C under vacuum until the solution was totally clear and without bubbles. Separately, hexamethyldisilathiane (210 μL) and 1-octadecene (5 g) were mixed as the sulphur precursor, which was injected rapidly into the lead precursor solution under Argon. After 30 s, the reaction was cooled down in a water bath to room temperature. PbS QDs were precipitated by adding acetone, followed by centrifugation. Next, a methanol and hexane mixture was used to wash the QDs twice, and the QD precipitant was finally dissolved in octane (50 mg mL⁻¹). Different band gap PbS QDs were synthesized in the same way by varying the injection temperatures and amount of oleic acid used.²⁴

Synthesis of ZnO nanoparticles. The synthesis of ZnO nanoparticles was adapted from the literature.²⁵⁻²⁶ Zinc acetate dehydrate (2.95 g) was dissolved in methanol (125 mL) by stirring at 60 °C. Potassium hydroxide (1.50 g) dissolved in 65 mL methanol was added, dropwise, into the zinc acetate dihydrate solution. The solution was stirred at 60 °C for 2 h, then washed using dispersion and centrifuge induced precipitation with methanol three times. Finally, the ZnO nanoparticles were dissolved in a chloroform-methanol mixture at a concentration of about 100 mg mL⁻¹.

Device fabrication. Indium tin oxide (ITO) coated glass substrates were cleaned by sonication in Decon-90, deionized water, acetone, and isopropanol, followed by an oxygen plasma treatment for 3 min. The substrates were coated with ZnO on a spin coater at 2000 rpm. Subsequently PbS QD layers were spin-coated at 2000 rpm layer-by-layer using the solid state ligand exchange developed by Chuang et al². 15 mg/mL TBAI-methanol solution was coated on the PbS film for 1 min before spinning, which was subsequently washed away by 5 drop methanol. EDT-acetonitrile solution was dropped while the film was spinning, followed by 5 drop acetonitrile to rinse it. The thickness of each TBAI and EDT layer is 29 nm and 35 nm respectively as determined by using cross-sectional SEM images as can be seen in Figure 1 b&c. The combination of band gaps from absorber table (1.52 eV, 1.37 eV, and 1.30 eV) and HTL table (1.38 eV, 1.20 eV, 1.12 eV, and 1.00 eV) were conducted. The optimized device was fabricated with 10 TBAI layers with 1.38 eV PbS in the front, and 2 EDT layers with 1.12 eV PbS at the back. The reference device was built up with only 1.38 eV PbS in both TBAI and EDT layers for the same thickness (290 nm + 70 nm). Au electrode evaporation was conducted on the films in a glove box at 0.1 nm/s until reaching a thickness of 50 nm.

Optoelectronic characterization. All solar cell devices were loaded into a sealed testing chamber with N₂ continually purged through testing. I–V curves were measured using a Keithley 2400 Source Meter. An AM 1.5 solar spectrum illumination was produced by a Newport solar simulator (model 67005) with an AM 1.5 filter. The power density of the light source was calibrated with a calibrated Si reference cell from ABET Technologies (model 15151). Backward voltage scan data between 1 and -0.4 V was used in this paper. To avoid overestimation of performance due to edge effects, a slightly smaller mask (1.28 mm²) than the actual area of the cathode and anode (2.00 mm²) was used when testing the I-V curves. EQE was tested with an Oriel 1/8 m monochromator coupled to a quartz tungsten halogen lamp. 410 nm, 600 nm, and 1000 nm filters were used to remove second order grating effects. Calibrated photodiodes from Newport (818-UV and 918-IR) were used to measure photon flux at the device. The beam was chopped at a frequency of 220 Hz by a Bentham 218 chopper controller and a Xenon lamp simultaneously shone on the devices. Solar cell devices were placed under constant N₂ flow and connected to a Bentham 227 pre-amplifier, a Bentham 225 lock-in amplifier, and a Keithley 6485 picoammeter. Open circuit voltage decay was used to determine the carrier lifetime by applying a LED pulse on the devices and recording the V_{oc} decay on an oscilloscope.²⁷

Band position characterization. The band gap of CQDs colloids and thin films was determined using a Cary Varian 4000 UV-vis-NIR spectrophotometer. Fermi level position was measured using a KP Technology Scanning Kelvin Probe System 2001. For each sample, 25 measurements were taken at 3 arbitrarily chosen points on the sample. The instrument was calibrated using aluminum and gold thin films. The conduction band

edge positions of different PbS QD films was determined by cyclic voltammetry in a double Faraday cage with an Autolabpotentiostat (Metrohm-Autolab BV, Netherlands) using a three electrode system at 298 K. PbS QD films spin-coated on ITO were used as the working electrodes, while Ag/AgCl in saturated KCl was used as the reference electrode and a platinum foil the counter electrode. All the measurements are carried out in acetonitrile (99.9%, Sigma Aldrich) with 0.1M Bu₄NClO₄ (Fluka) as the supporting electrolyte. Before the measurements, the solution was degassed with a N₂ flow for 5 min to remove O₂, and atmosphere of N₂ was maintained during the experiment. Valence band edge positions was calculated based on the optical band gaps from absorbance. Scanning range is between -2.0V to 1.4V at a scan rate of 100 mV s⁻¹. The applied potential starts from 0.0V and follows a negative-going direction at first.

RESULTS AND DISCUSSION

A series of devices were first fabricated to optimize the absorbers' band gap using 1.52 eV, 1.37 eV, and 1.30 eV CQDs modified by TBAI as absorbers respectively, with 1.20 eV CQDs modified by EDT as hole transport layers as shown in Table 1. The 1.37eV/1.20eV (absorbers/HTL) CQD device demonstrated the best device performance. Table 1 Absorber band gap optimization: devices presented with mean and standard deviation.

Absorber/HTL Band gap	J _{sc} (mA cm ⁻²)	V _{oc} (V)	FF	Efficiency
1.52 eV/1.20 eV	21.73±1.51	0.58±0.004	0.51±0.02	6.47±0.54%
1.37 eV/1.20 eV	24.65±3.09	0.60±0.008	0.60±0.05	8.97±0.56%
1.30 eV/1.20 eV	26.97±0.38	0.49±0.004	0.56±0.02	7.58±0.41%

The optimum absorber band gap was found to be 1.37 eV. The EDT-modified HTL's band gap was next optimized. Devices with absorber/HTL combinations of 1.38eV/1.38eV, 1.37eV/1.20eV, 1.38eV/1.12eV, and 1.38eV/1.00eV were fabricated and compared, as Table 2 shows. With the HTL band gap decreasing, the PCE peaked at 1.12 eV with champion efficiency of 9.33±0.50%.

Table 2 HTL band gap optimization: devices presented with mean and standard deviation.

Absorber/HTL Band gap	$J_{sc}(\text{mA cm}^{-2})$	$V_{oc}(\text{V})$	FF	Efficiency
1.38 eV/1.38 eV	31.68±4.51	0.59±0.008	0.48±0.06	8.86±0.26%
1.37 eV/1.20 eV	24.65±3.09	0.60±0.008	0.60±0.05	8.97±0.56%
1.38 eV/1.12 eV	25.30±2.11	0.59±0.007	0.63±0.02	9.33±0.50%
1.38 eV/1.00 eV	21.49±0.47	0.53±0.010	0.53±0.01	6.03±0.40%

To understand why the optimized 1.38eV/1.12eV device achieved the highest PCE its optoelectronic properties are now compared to a reference device's with an absorber/HTL combination of 1.38eV/1.38eV. The effect of different QD sizes and ligands on band gap was determined using UV-visible absorption spectroscopy and is presented in supplementary information (Figure S 1).

Figure 2a compares the current–voltage (I–V) curves of optimized and reference devices. The mean PCE is 9.33% with standard deviation of 0.50% for the optimized devices while the reference's mean PCE is 8.86% with standard deviation of 0.26%. With prolonged exposure in an air atmosphere both optimized and reference performance become stable after the first 10 days. As previously reported,² the TBAI/EDT device

structure is air stable. After three months of storage in the air and in the dark (Figure 2c), the PCE did not show any obvious decrease. Besides PCE, the open circuit voltage (Figure S 2b) and fill factor (Figure 2b) are also higher in the optimized device than that of the reference. However, the short circuit current (J_{sc} , Figure S 2a) in the optimized device is lower.

Figure 2 Optimized and reference devices' photovoltaic performances: a) I-V curves, b) Variation of fill factor and c) PCE over 80 days

We hypothesize that the higher V_{oc} and FF observed is related to the different band structures which result from different QDs' size and ligand modification for the absorber and HTL which results from using TBAI and EDT respectively. To test this a combination of Kelvin probe and cyclic voltammetry is used.

Figure 3a shows the position of conduction and valence bands for the different sized PbS with different ligands. Comparing the 1.36eV-TBAI PbS and 1.36eV-EDT PbS it is clear that EDT modification raises the band gap position relative to the vacuum. As observed by Chuang et al.², this blocks the flow of electrons and enhances hole extraction at the positive electrode. By decreasing the HTL PbS band-gap the conduction band

becomes deeper and the valence band shallower. Thus further enhancing the hole extracting properties of the EDT layer.

Fermi level position measured by Kelvin probe is presented in Figure 3c&d. It is clear that the 1.38 eV -EDT PbS thin film has a deeper Fermi level (-4.84 eV) than 1.38eV-TBAI (-4.79 eV) layer. This indicates more p-type behavior relative to the valence band position. If a smaller band gap 1.12 eV EDT layer is used, the Fermi level is further lowered to -4.87 eV indicating even more p-type layer, considering its valence band position changes to be shallower as shown in Figure 3a.

When the absorber and HTL layers are combined together as shown in Figure 3d, the combined layers' fermi level lies between the original isolated TBAI layers' and EDT layers' fermi levels because of the fermi level equilibrium of these two layers, as can be seen in Figure 3d and Table S 3. Thus the optimized layers have a deeper fermi level than the reference layers, and also a more p-type character. As open circuit voltage is significantly influenced by the quasi-Fermi level differences between the ZnO and PbS layers, the deeper Fermi level in the PbS layers leads to larger V_{oc} as can be seen in Figure S 2b.^{13, 28}

Combining the fermi level and band edge structures analysis, the full device band structures can be seen in Figure 3b. When comparing the 1.38eV-EDT and 1.12eV-EDT HTL layers, the latter showed better valence band offset and deeper fermi level without losing the advantages of blocking electrons, resulting in better HTLs here.

Figure 3 Band structures from cyclic voltammetry and fermi level measurements using Kelvin probe on different films: a) band structures of different PbS films, b) isolated materials' band structures in the reference and optimized devices, c) fermi levels of six layer PbS films with only one ligand (TBAI: 174 nm, and EDT: 210nm), and d) fermi levels of 8 layer PbS films (244 nm) consisting of 6 TBAI layer (174 nm) and 2 EDT layer (70 nm).

There is a trade-off between gaining valence band alignment advantages and losing conduction band alignment advantages as shown in Figure 3a. Therefore, careful selection of band gap and Fermi level combination is required to optimize devices. Compared to the 1.37eV/1.20eV device, V_{oc} for the case of a smaller absorber band gap (1.30eV/1.20eV) is lower due to a small quasi fermi level difference of PbS and

ZnO layers (Figure 4b&c). J_{sc} and FF are comparable to the 1.37 eV/1.20 eV case. Comparing 1.52 eV/1.20 eV with 1.37 eV/1.20 eV the V_{oc} is comparable, but FF and J_{sc} are reduced because of the poorer conduction band alignment which blocks electrons between the two PbS layers, leading to increased recombination (and hence slightly depressing V_{oc} too). Therefore, an appropriate band gap combination is necessary for high PCE. In combinations of 1.37 eV/1.20 eV, EDT modification results in a shallower conduction band edge position in the rear PbS-EDT layer, which creates an energy barrier to block electron transport to the Au electrode. Therefore, such an optimally aligned band structure for optimizing absorbers (Figure 4b) formed with the contribution by both different ligand modification and different quantum confinement effects on band alignment. Further optimization on HTL layers was conducted, the diagram of which is shown in Figure S 3, and the best device 1.38 eV/1.12 eV was demonstrated.

Figure 4 Band diagram of devices for absorbers' band gap optimization: a) 1.52 eV/1.20 eV, b) 1.37 eV/1.20 eV, and c) 1.30 eV/1.20 eV.

This better band alignment in the optimized device can also be implied by its longer carrier lifetime in measurements in the decay of open circuit voltage. Under different

light density, the optimized device's carrier lifetime is always longer than in the counterpart reference devices as shown in Figure 5a. Under air mass (AM) 1.5, the optimized device's carrier lifetime is 4.6 μs , while that of the reference device is just 2.8 μs . The better band alignment structure lowers the barrier for carrier transport and hence reduces the probability of carrier recombination.

Furthermore, the incident light intensity dependence of short circuit current was studied (Figure 5b).

$$J_{sc} \propto I^\alpha$$

If J_{sc} is observed to change linearly with incident light intensity, it can be said that the electron and hole extraction are balanced.²⁸⁻²⁹ Deviation of α from 1 implies the formation of space charge depletion region.²⁹⁻³⁰ For the optimized device and reference device, both α values are near 0.90, indicating that there is a small, but similar, space charge limiting effect in both cases. This similarity in the quality of the devices makes the electrical property comparison more meaningful.

Figure 5 Optimized and reference devices' electrical performance comparison: a) carrier lifetime, b) light density dependence of J_{sc} , c) EQE, and d) UV-vis light absorption.

To research whether there is more light absorption contributing to the PCE enhancement, external quantum efficiency (EQE) and UV-visible absorption (UV-vis) measurements were conducted on the optimized and reference devices and films. In Figure 5c, it can be seen that the reference showed higher EQE than the optimized device, and the same peaks are found in both. The integrated J_{sc} from EQE (22.4 mA cm⁻² for optimized devices; 26.3 mA cm⁻² for reference devices) is a bit lower than that derived from I-V curves (25.3 mA cm⁻² for optimized devices; 31.7 mA cm⁻² for

reference devices in Table 2). UV-vis curves also showed less absorption on the optimized device than reference. Only a small peak around 1100 nm corresponding to the small band gap PbS was found in the optimized device's curve (Figure 5d), but this contributes so little that it cannot be seen on EQE. When increasing EDT layer thickness, the PCE even becomes lower (Figure S 4). Although the band gap distribution in the optimized device is more aligned with the light wavelength distribution across the solar cell, it seems the absorption depth for the infrared is beyond the active layer thickness. This further means that it is the optimal band alignment that is mainly responsible for the performance enhancement, rather than any additional absorption by smaller band gap layers.

CONCLUSION

The band gaps of Absorber and HTL layers of CQD solar cells have been optimized. It was found that a small band gap HTL layer with a more p-type-inducing ligand (EDT) resulted in the best devices (1.38eV/1.12eV) with efficiency of $9.33 \pm 0.50\%$. The reason for higher efficiencies is mainly improved band alignment at the interface between the absorber and HTL, which results from an upshift of valence band position due to narrow band gap CQDs and EDT ligands, and a lowering of the Fermi level due to oxidation. Improvements by further optimization of band gap combinations, layer thickness control, and ligand selection are expected further optimize the device so that it has more balanced hole and electron transport as well as better light absorption.

ASSOCIATED CONTENT

Supporting Information. UV-vis results, description for detailed testing conditions, cyclic voltammetry tests, and supplementary characterization results. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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