New Hole Transport Materials via Stoichiometry-Tuning for Colloidal Quantum Dot Photovoltaics

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***Abstract*—Colloidal quantum dots (CQDs) are of interest for photovoltaic applications such as flexible and multijunction solar cells, where solution processability and infrared absorption are crucial; however, current CQD solar cell performance is limited by the hole transport layers (HTLs) used in the cells. We report on a method to develop new HTLs for the highest-performing PbS CQD solar cell architecture by tuning the stoichiometry via sulfur infiltration of the p-type CQD HTL to increase its doping density and carrier mobility. Using SCAPS simulations, we predict that increased doping density and mobility should improve the performance of the solar cells. We show that sulfur doping of the current HTL is a facile and effective method to boost the performance of CQD photovoltaics.**

***Keywords*—colloidal quantum dots, hole transport materials**

I. INTRODUCTION

Lead sulfide (PbS) semiconductor colloidal quantum dots (CQDs) are of interest for photovoltaic applications because of their tunable optical and electronic properties [1], their infrared absorption, their basis in earth-abundant materials, and their range of low-cost solution-processed fabrication methods. However, photovoltaics (PV) made from CQDs are limited in efficiency compared to non-solution-processed technologies. A critical component in CQD solar cells is the hole transport layer (HTL), whose function is to efficiently transport holes to the cathode and block electrons with the goal of minimizing leakage and recombination in the device [2]. There is preliminary evidence that the HTL is a limiting factor in the performance of CQD solar cells due to the low carrier mobilities and doping levels in the most commonly used HTL materials. Current state-of-the-art CQD solar cell architectures with the highest efficiencies use a thin (<100 nm) layer of PbS CQDs with ethanedithiol (EDT) ligands as the hole extraction layer [3]. In this work, we seek to improve the performance of PbS CQD-based solar cells via stoichiometry control of the EDT-PbS layer. We focus on introducing additional sulfur into the EDT-ligated CQD films as alternative HTL materials to increase their p-type character [4] and improve CQD photovoltaic efficiencies. We use solar cell capacitance simulator (SCAPS) simulations [5] to study the performance of our PbS CQD solar cells as a function of the HTL doping density and carrier mobilities. We also use characterization techniques including space charge limited current (SCLC) measurements, to acquire carrier mobilities, capacitance–voltage (Cap-V) measurements to obtain doping densities, and current density–voltage (J–V) measurements under simulated solar illumination for solar cell device performance parameters. The improvement of the HTL that we demonstrate could have immediate applications in CQD PV and other optoelectronic devices.

II. EXPERIMENTS AND RESULTS

A. SCAPS Simulations

To determine the most important properties of the HTL with regards to CQD solar cell performance, we use SCAPS [5], a 1D solar cell simulator that takes materials properties as inputs and uses the Drift-Diffusion and Poisson's equations to calculate J-V characteristics. We use materials parameters based on literature values for CQD solar cells[6]. Using SCAPS, we varied the HTL doping density, hole mobility, and electron mobility by three orders of magnitude; the results are shown in Tables I, II, and III respectively. We found that the HTL doping density and, counterintuitively, electron mobility had the largest effect on CQD solar cell PCE. We attribute the electron mobility effects to significant photogeneration in the HTL.

B. Device Fabrication and Sulfur Doping

Our CQD solar cell device architecture consisted of a bottom transparent substrate, a transparent electrode (fluorine-doped tin oxide), an electron-extracting wide-bandgap n-type semiconductor (ZnO), the bulk absorbing PbS CQD film with PbX_2 (X = Br, I) ligands, a thin hole extracting p-type PbS CQD layer with ethanedithiol (EDT) ligands, and a top evaporated gold contact [7 – 9] . To tune the stoichiometry of the hole transport layer, with the goal of increasing p-type doping density

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and carrier mobility, we used varying effective thicknesses of elemental sulfur (1, 3, 6, 9, and 15 Å), which were deposited onto the PbS-EDT film using an electron beam evaporator.

TABLE I. SCAPS RESULTS FOR THE EFFECT OF HTL DOPING DENSITY ON SOLAR CELL PERFORMANCE

Doping Density [cm^{-3}]	PCE [%]	Voc [V]	Jsc [mA cm^{-2}]	FF
1 * 10^{16}	9.81	0.58	27.97	55.94
1 * 10^{17}	10.37	0.58	27.94	67.89
1 * 10^{18}	11.54	0.58	27.81	70.54

[a] Calculations done with constant hole and electron mobilities of 5 x 10^{-3} cm^{2} V^{-1} s^{-1}

TABLE II. SCAPS RESULTS FOR THE EFFECT OF HTL HOLE MOBILITY ON SOLAR CELL PERFORMANCE

Mobility [cm^{2} V^{-1}s^{-1}]	PCE [%]	Voc [V]	Jsc [mA cm^{-2}]	FF
5E-4	10.96	0.58	27.95	67.29
5E-3	11.07	0.58	27.94	67.89
5E-2	11.08	0.58	27.94	67.95

[b] Calculations done with constant doping density of 1*10^{17} cm^{-3}; electron mobility of 5 x 10^{-3} cm^{2} V^{-1} s^{-1}

TABLE III. SCAPS RESULTS FOR THE EFFECT OF HTL ELECTRON MOBILITY ON SOLAR CELL PERFORMANCE

Mobility [cm^{2} V^{-1}s^{-1}]	PCE [%]	Voc [V]	Jsc [mA cm^{-2}]	FF
5E-4	10.68	0.58	26.79	68.25
5E-3	11.07	0.58	27.94	67.89
5E-2	11.34	0.58	28.51	68.11

[c] Calculations done with constant doping density of 1*10^{17} cm^{-3}; hole mobility of 5 x 10^{-3} cm^{2} V^{-1} s^{-1}

TABLE IV. SUMMARY OF EXPERIMENTAL CQD SOLAR CELL PERFORMANCE WITH VARIED HTL SULFUR CONTENT

Device	PCE [%] Best (Average)	Voc [V] Best (Average)	Jsc [mA cm^{-2}] Best (Average)	FF Best (Average)
No Sulfur	9.32 (7.51±0.98)	0.57 (0.56 ±0.01)	25.98 (21.32±2.50)	0.61 (0.61±0.01)
1 Å Sulfur	9.16 (7.72±0.95)	0.58 (0.57 ±0.01)	24.97 (21.63±2.65)	0.62 (0.61±0.01)
3 Å Sulfur	9.22 (7.79±1.2)	0.58 (0.57±0.01)	23.79 (21.22±2.71)	0.64 (0.61±0.03)
6 Å Sulfur	9.80 (8.67±0.39)	0.57 (0.57 ±0.00)	25.72 (23.84±1.00)	0.65 (0.62±0.02)
9 Å Sulfur	9.97 (9.04±0.74)	0.58 (0.58±0.01)	26.21 (24.07±1.84)	0.64 (0.63±0.01)
15 Å Sulfur	10.35 (9.00±0.62)	0.57 (0.57±0.00)	26.90 (24.17±1.47)	0.65 (0.63±0.01)

[d] Measured over a total 246 solar cells; 30-59 for each row.

C. Characterization

The current density–voltage (J–V) characteristics of the CQD solar cells were measured under simulated AM 1.5G illumination (100 mW cm^{-2}), and the results are summarized in Table IV. By comparing our control (no sulfur doping in the HTL) device to the best performing sulfur-doped HTL solar cell, we see an absolute increase of 1% in the PCE of the best devices, from 9.32% to 10.35%. Using a Keithley 590 sourcemeter, we performed capacitance-voltage measurements at 100 kHz under reverse bias in the dark. Mott–Schottky plots (1/C^{2} vs. V) were obtained, and the linear regions of the plots were fit to extract doping densities. We measured an average doping density of 2 x 10^{17} cm^{-3} for the PbS-EDT HTL in our control device and an average doping density of 1 x 10^{18} cm^{-3} for the HTL with 15 Å of evaporated sulfur. We also performed SCLC mobility measurements in dark conditions under reverse bias using a Keithley sourcemeter to collect the current and voltage plots. We identifed the SCLC region of the log-log plot, where the slope of the data is equal to two, to extract the electron mobilities (using a FTO/ZnO/HTL/Au device structure) and hole mobilities (using a ITO/PEDOT:PSS/HTL/Au device structure) of the HTL. We measured a relatively constant hole mobility on the order of 10^{-2} cm^{2} V^{-1}s^{-1} and an order of magnitude increase in the electron mobility from 1.1 x 10^{-3} with no sulfur to 1.7 x 10^{-2} with the addition of 15 Å of sulfur, attributed to the passivation of surface electron trap states.

III. SUMMARY

We performed 1D SCAPS simulations to determine the effects of increasing the doping density and mobility of the p-type HTL layer in PbS CQD PV and predicted that the performance of these solar cells should improve with increases in these critical parameters. We used electron beam evaporation to systematically introduce different amounts of sulfur into the traditional PbS-EDT HTLs as a method to tune their stoichiometry towards more p-type behavior and passivate surface electron trap states. This resulted in increases in the doping density and carrier mobility in the HTLs and an absolute increase of 1% in the PCE. Future work will involve further optimizing the HTL. This study demonstrated a facile and effective method to increase the PCE in PbS CQD solar cells and identified inefficiencies with the standard HTL.

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