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Optimization of PbS Quantum Dot Hole Transport Layer Using Hybrid Ligand Treatment

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The 1,2-ethanedithiol (EDT) capped PbS quantum dot (PbS-EDT) is a common p-type material for colloidal colloidal quantum dot (CQD) solar cell devices. However, the PbS-EDT thin film suffers from low mobility compared to other ligands such as 3-mercaptopropionic acid (MPA) [1, 2]. There is an urgent need to find an alternative p-type PbS material with a higher mobility or conductivity to further raise the device thickness ceiling beyond the current limits at 200-300nm, limited due to the low diffusion length caused by low carrier mobility and lifetime of PbS CQD films. PbS-MPA is one such alternative, which has demonstrated higher conductivity and J_{SC} compared to PbS-EDT [1, 2]. However, the improvement of J_{SC} is at the expense of a poorer V_{OC} at 559 mV for PbS-MPA, while PbS-EDT devices had a V_{OC} of 623 mV[1].

The key motivation for a hybrid ligand treatment reported in this work is to combine the high J_{SC} characteristic of PbS-MPA and high V_{OC} characteristic of PbS-EDT to produce a p-type layer with improved solar cell performance. The hybrid ligand treatment procedure used in this work is a 2-step ligand treatment process that introduces both MPA and EDT ligands into the HTL. This work has demonstrated that a combination of EDT and MPA ligands is able to improve the conductivity of the device while maintaining the higher V_{OC} from EDT passivation, resulting in an improvement in power conversion efficiency (PCE) from 7.0% for PbS-EDT and 8.2% for PbS-MPA to 10.4% for PbS-Hybrid based on devices with an n^+-n-p structure as shown in Table I.

Table I. J_{SC}, V_{OC}, FF and PCE of solar cell device with different HTL as described. The values in the brackets are the results from the best performing devices.

Treatment	J_{SC} (mA cm^{-2})	V_{OC} (mV)	FF(%)	PCE (%)
MPA	23.8 ± 0.8 (24.6)	565 ± 14 (573)	57 ± 6 (60)	7.7 ± 1.2 (8.2)
EDT	21.2 ± 1.0 (21.9)	630 ± 12 (635)	49 ± 2 (51)	6.6 ± 0.5 (7.0)
Hybrid	23.2 ± 2.0 (25.3)	630 ± 2 (633)	66 ± 1 (67)	9.6 ± 0.7 (10.4)

From the IV results in Table I, it is clear that the PbS-EDT device has a superior V_{OC} at 635 mV while PbS-MPA has a better J_{SC} at 24.6 mA cm^{-2}. PbS-EDT also has a poorer fill factor (FF), and such observation matches with literature (Crisp *et al.*, 2015). The hybrid device successfully combines the higher J_{SC} and FF of PbS-MPA and the higher V_{OC} of PbS-EDT. This allows the champion device to achieve a PCE of 10.4%.

The improvement in solar cell performance is attributed the improved conductivity. Similar improvements in J_{SC} and FF of PbS-MPA over PbS-EDT were observered for heterojunctions [2]. The improvement in conductivity for PbS-Hybrid was confirmed by dark IV measurements of Schottky devices, whereby PbS-Hybrid had improved conductivity over PbS-EDT as shown in Figure 1. This improvement in conductivity is due to a reduction of the interdot distance, which was observed under the transmission emission microscope, and presence of a small amount of MPA ligands on the PbS surface, which was confirmed with the fourier transform infrared spectroscopy. The presence of a carboxylic group in MPA has been shown to improve conductivity and mobility by one order magnitude over thiols [2-4].

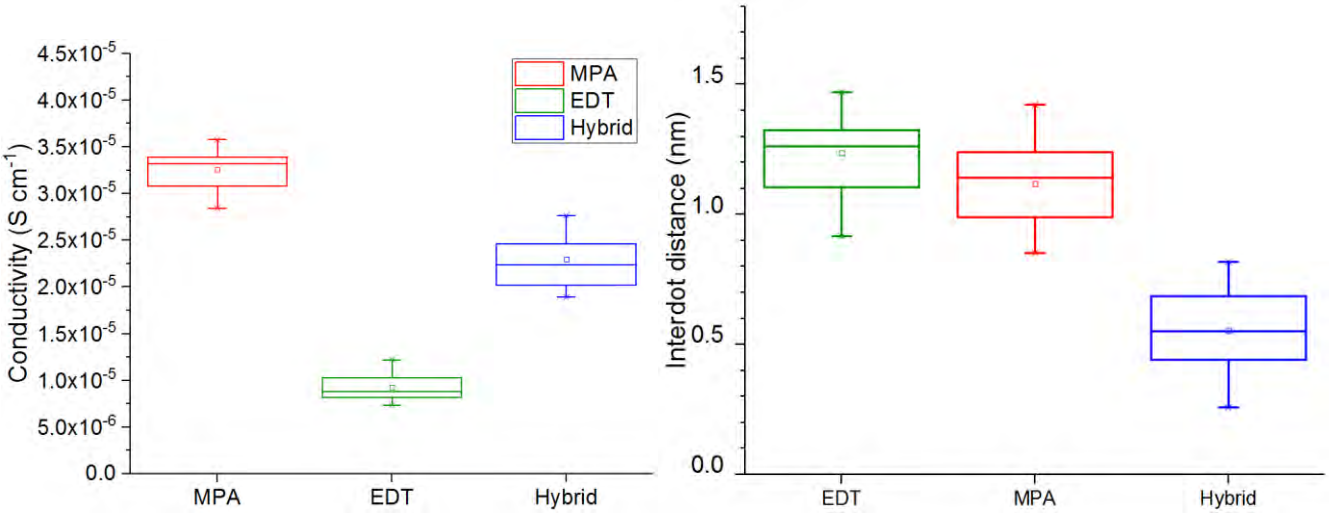

Figure 1. (LEFT) Conductivity of PbS treated with MPA, EDT and Hybrid ligands. (RIGHT) Interdot distance between PbS QDs treated with EDT, MPA and hybrid ligands.

PbS-EDT QDs show the largest interdot distance of 1.2 nm, which matches literature [5]. This value is double the molecular length of EDT due to dimerization, which is a common observation of EDT ligand treatment. MPA does not dimerize and has a slightly shorter interdot distance at 1.1 nm and also matches with literature [5]. The hybrid treatment further reduces the ligand length to 0.6 nm which is comparable to the molecular length of EDT.

During the 2-step hybrid treatment, the interdot distance is first reduced to 1.1 nm by treating the PbS CQDs with MPA ligands. The 2nd step of the treatment introduces EDT with a length of 6.1 Å to further reduce the interdot distance by displacing MPA. Unlike the direct treatment of EDT on oleic acid passivated PbS, treating PbS-MPA QDs with EDT does not lead to EDT dimerization that is responsible for the large interdot distance. This allows the QDs to directly couple by just one EDT ligand length. The reduction in interdot distance for PbS-Hybrid helps enhance interdot coupling and improves the mobility and conductivity of the film. This mobility and conductivity gains translates into the J_{SC} and FF improvements of CQD solar cell devices using PbS-Hybrid as the HTL over PbS-EDT.

References

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