

Solution Processed Infrared PbS Colloidal Quantum Dot / ZnO Nanowire Solar Cells

Haibin Wang¹, Takaya Kubo¹, Jotaro Nakazaki² and Hiroshi Segawa²

¹ Research Center for Advanced Science and Technology, Univ. of Tokyo
4-6-1, Comaba, Meguro-ku
Tokyo 153-8904, Japan

Phone: +81-3-5452-5140 E-mail: wanghb@dsc.rcast.u-tokyo.ac.jp

² Graduate School of Arts and Sciences, Univ. of Tokyo

Abstract

A systematic investigation into the performance of PbS quantum dot (QD) / ZnO nanowire (NW) solar cells in the near-infrared and short-wave infrared (SWIR) region was carried out. The solar cells were confirmed to convert a wide range of solar energy (0.35-2.0 μm). We found that the solar cells working in SWIR region had a high open-circuit voltage (V_{oc}). A relatively high V_{oc} of 0.25 V was achieved even in solar cells whose photocurrent onset were at approximately 0.64 eV (1.9 μm), these results indicate that solution-processed colloidal PbS QD solar cells with ZnO NWs are promising candidates for the middle and bottom subcells of multijunction solar cells.

1. Introduction

Colloidal semiconductor quantum dots (CQDs) give unique optical properties such as size dependent absorption, which makes the quantum dot promising candidate materials toward high efficiency solar cells. Most importantly, CQDs are compatible with low-temperature solution-based technologies. The performance of PbS CQD solar cells has increased in the past decade to certified power conversion efficiencies (PCEs) of approximately 12 % in 2017. The most widely studied PbS QD solar structures are based on depleted heterojunction that is formed by deposition of a QD layer on top of an electron-accepting layer such as ZnO or TiO₂. To enhance the performance of the solar cells, several strategies, which include new solar cell architectures and bandgap engineering were reported.¹ We focused on a solar cell structure composed of PbS QD / ZnO NW structures (Fig.1a) with the aim of achieving efficient carrier transport and light absorption in the near-infrared region simultaneously.² These PbS QD-based solar cells were also found with high stability under continuous light soaking.³ To clarify the exact role of the ZnO NWs in PbS QD / ZnO NW solar cells, we studied photocurrent properties of the solar cells by impedance spectroscopy, and found out that, ZnO NWs act as a very efficient transporter and collector for the photogenerated electrons in the PbS QD region.⁴ In this study, We investigate the performance of PbS QD / ZnO NW solar cells using PbS CQDs that absorb photons in a wide range of solar spectrum to examine the potential for low-cost multi-junction solar cells with PbS CQD / ZnO NW hybrid structures.⁵ To Improved performance in the infrared region, we engineering the band alignment of quantum dot through the use of different ligand treatment^{6,7} PbS QDs, a 31.5% EQE at 1550 nm has been reached, showing a EQE enhancement of 40% at the first exciton peak as compared to that of the control solar cell.

2. Experiment methods

PbS QDs based solar cells were constructed by combining ZnO nanowire arrays with a nine difference PbS CQDs, which give the first exciton absorption peak in near and short-wave infrared region (Fig.1c). The ZnO nanowire array (about 1.2 μm thick) formed on FTO (F-doped SnO₂) glass

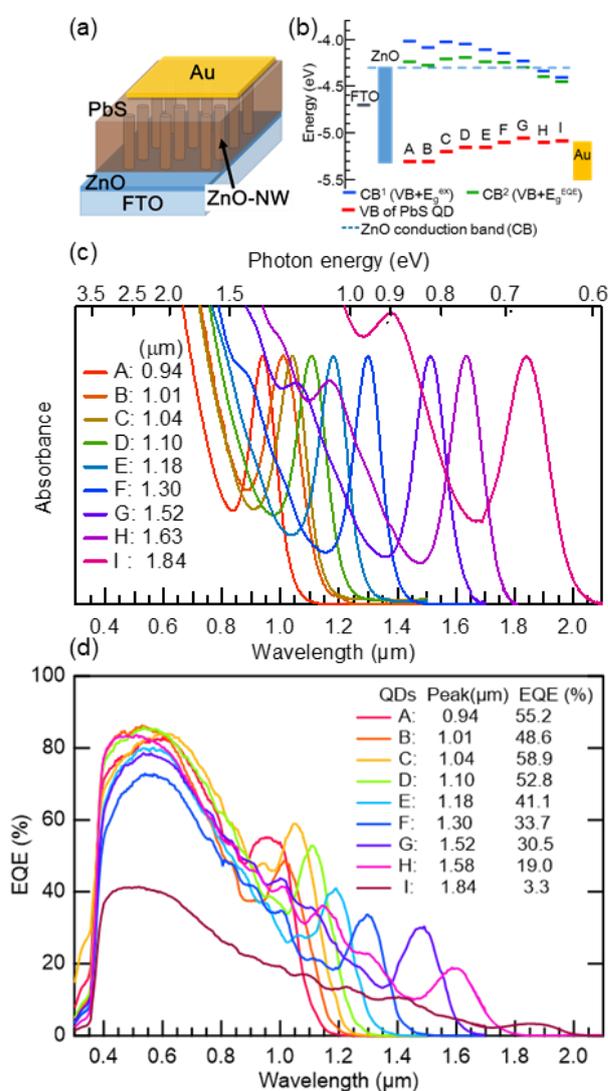


Fig.1 (a) Schematic of the structure of the PbS QD / ZnO NW solar cells. (b) Energy diagrams of the PbS QD / ZnO NW solar cells with nine difference PbS QDs. (c) Absorbance spectra of the PbS QD octane solutions with different the first exciton absorption peak. (d) EQE spectra of the PbS QD / ZnO NW solar cells with different the first exciton absorption peak PbS QDs.

Table. Solar cell performance obtained on solar cells with different the first exciton absorption peak PbS QDs

QDs	J_{sc} (EQE) (mA/cm ²)	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	PCE (%)
A	27.8	26.6	0.505	53.1	7.13
B	27.4	25.1	0.503	53.1	6.69
C	30.2	28.5	0.46	53.7	7.05
D	29.7	29.6	0.468	52.5	7.27
E	27.2	28.3	0.462	54.3	7.11
F	25.3	27.0	0.411	52.4	5.81
G	28.9	24.3	0.396	51.5	4.96
H	30.2	29.0	0.351	49.8	5.08
I	15.6	7.2	0.251	38.9	0.70

substrates by a hydrothermal method. The PbS QDs were infiltrated into the ZnO nanowire array from a PbS QD octane solution via the layer-by-layer spin-coating method. The deposited PbS-QD layer were treated with a tetrabutylammonium iodide (TBAI) methanol solution to replace the insulating oleic acid chain ligands with iodide anions (PbS-I). The substrates were then rinsed with a methanol solution to remove excess TBAI and oleic acid ligand. After the ZnO nanowire array were infiltrated with PbS QDs, an additional PbS overlayer approximately 300 nm thick was deposited by the spin-coating method. For PbS-EDT layers, an ethanedithiol (EDT) solution (0.02% vol% in acetonitrile) and acetonitrile were used. Finally, an Au layer was deposited on top of the PbS-QD overlayer by thermal evaporation to complete solar cell fabrication. Solar cell performance of the cells was evaluated by measuring current density-voltage (J - V) curves, from which open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}), fill factor (FF), and PCE were obtained. External quantum efficiency (EQE) spectra were measured from 300 nm to 1700 nm (Bunko-keiki, CEP-2000MLQ). The EQE spectra over 1700 nm were measured with a Fourier transform infrared spectrometer (JASCO, VIR-300).

3. Results and discussion

The EQE spectra of the PbS QD / ZnO NW solar cells (Fig.1d) give EQE peaks originating from the first exciton absorption in short-wave infrared region. We confirm our solar cells can convert photon energy to electricity in a wide range of the solar spectrum. However, the EQE of the spectra cells tended to become smaller at the peak position shifted to longer wavelengths. One of the reasons for this was that, in the short-wave infrared region, the free carrier absorption of transparent conductive oxide (FTO) cause a non-negligible energy loss of the incident solar energy to be absorbed by the PbS QD layer. The average visible transmittance of the FTO substrate was approximately 80%, whereas the transmittance values at 1500 nm and 1800 nm were approximately 50% and 30%, respectively. The EQE value of solar cell I was below 40% in both the infrared and visible region. The reasons for this are the conduction band edge of PbS QD I low than ZnO conduction band (Fig.1b). The solar cell performances of the solar cells are tabulated in Table 1. The best PCE of solar cell reached 7.27 % (D: J_{sc} = 29.7 mA/cm², V_{oc} = 0.468 V, FF = 0.525) under simulated one-sun illumination. Although V_{oc} of the solar cells monotonically decreases as band gap decreased. One of the interesting findings is that the solar cells operating

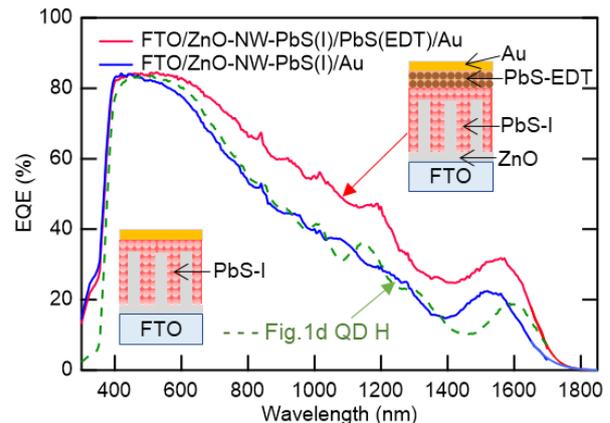


Fig.2 EQE spectra of the PbS QD / ZnO NW solar cells with and without PbS-EDT overlayer.

in infrared region (solar cells: G, H, I) produced high V_{oc} and low V_{oc} loss⁵.

To improved solar cell performance in the infrared region we use EDT treatment PbS QD overlayer, the role of the PbS-EDT layer as an electron-blocking / hole-extraction layer between the PbS-I layer and the Au anode, which leads to an improved photocurrent collection efficiency and enhanced the infrared region EQE in the PbS-I / PbS-EDT solar cell (Fig. 2). In the PbS-I only solar cell, electron flow from PbS-I to the Au anode, which is in the opposite direction to photocurrent, and interfacial recombination at the PbS / Au interface are possible loss mechanisms. In the PbS-I / PbS-EDT solar cell, the conduction band offset between the PbS-I and PbS-EDT layer provide an energy barrier that prevents photogenerated electrons from flowing to the PbS-EDT layer^{6,7}. PbS-I / PbS-EDT solar cell shown an average 10% EQE enhancement from 700 nm to 1600 nm.

These results indicate that the engineering the structures of PbS CQD solar cells with the ZnO nanowire and band edge energies of QD film through ligand exchange are promising enhancement the photocurrent collection efficiency in the infrared region.

Acknowledgements

The research work was partially supported by the New Energy and Industrial Technology Development Organization (NEDO); the Ministry of Economy, Trade, and Industry (METI) and MEXT KAKENHI under Grant No. 16H03824.

References

- [1] G. H. Carey, A. L. Abdelhady, Z. Ning, S. M. Thon, O. M. Bakr and E. H. Sargent, *Chem. Rev.* **115** (2015) 12732.
- [2] H. Wang, T. Kubo, J. Nakazaki, T. Kinoshita and H. Segawa, *J. Phys. Chem. Lett.*, **4** (2013) 2455.
- [3] H. Wang, T. Kubo, J. Nakazaki and H. Segawa, *Phys. Status Solidi RRL*, **8** (2014) 961.
- [4] H. Wang, V. Gonzalez-Pedro, T. Kubo, F. Fabregat-Santiago, J. Bisquert, Y. Sanehira, J. Nakazaki and H. Segawa, *J. Phys. Chem. C*. **119** (2015) 27265.
- [5] H. Wang, T. Kubo, J. Nakazaki and H. Segawa, *ACS Energy Lett.* **2** (2017) 2110.
- [6] C-H. M. Chuang, P/ R. Brown, V. Bulovic and M. G. Bawendi, *Nature Mater.* **13** (2014) 796.
- [7] P. H. Rekemeyer, S. Chang, C-H. M. Chuang, G.W. Hwang, M. G. Bawendi, S. Gradecak *Adv. Energy Mater.* **6** (2016) 1600848.