

Solution-processed solar cells with nanostructured hybrid materials

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Abstract

Solution-processed solar cells constructed with colloidal quantum dots and ZnO nanowires were verified to work in a wide range of solar spectrum spanning from 300 nm to 2000 nm, and yielded high external quantum efficiency in the short-wave infrared (SWIR) region. A series of experimental results open up an opportunity to develop colloidal quantum dot-based multi-junction solar cells with solution-based technologies.

1. Introduction

Efficient utilization of a wide range of solar spectrum is essential to construct ultra-high efficiency solar cells. So far, several different concepts for ultra-high efficiency have been proposed, which use multiple exciton generation (MEG), hot-carrier extraction, photo-carrier generation via intermediate bands, multi-junctions and so forth [1]. Most of them are, however, still under fundamental investigation. Multi-junction solar cells based on III-V semiconductors have been successfully implemented in the practically-used ultra-high efficiency solar cell technology. Although the multi-junction solar cells have achieved a power conversion efficiency well over the single-junction limit (~30% under one-sun illumination), these solar cells rely heavily on high cost solar cell technology, which makes it difficult for the solar cells to be used widely. If multi-junction solar cells could be constructed with cheaper technologies such as solution-based one, then a drastic reduction in the cost of power generation and an expansion of the areas to which it could be applied could be achieved.

In this respect, organic photovoltaics made up of conjugated small molecules and/or polymers, and perovskite solar cells composed of organometal halide perovskite compounds (e.g. $\text{CH}_3\text{NH}_3\text{PbI}_3$) are promising candidate solar cells since the solar cells are low-temperature, solution-processable.

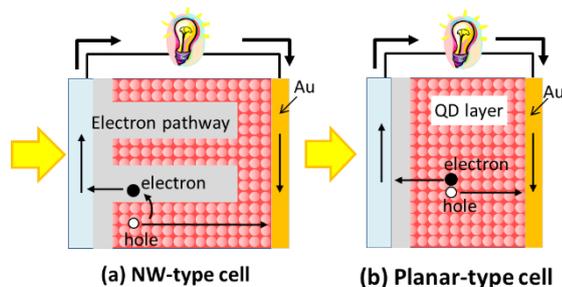


Fig. 1 Two different PbS QD/ZnO solar cells. (a) NW-type solar cell, (b) planar-type solar cell

These types of solar cells capture visible and near-infrared photon energy efficiently and are suitable for the top and/or middle cells of multi-junction solar cells [2, 3]. This means that there are a wide range of options for the top and/or middle subcells. However, there are few materials to choose from for the bottom cells, as few materials harvest solar energy below energies of about 1240 nm (1.0 eV). The development of low cost and efficient short-wave infrared solar cells is therefore essential for the development of ultrahigh efficiency solar cells. Lead chalcogenide colloidal quantum dots (CQDs), such as PbS and PbSe, are materials that seem to be promising for use as the middle and/or bottom cells of multi-junction solar cells. This is because the absorption bandgap of bulk PbS is located in the infrared region (3100 nm) and can be readily tuned by controlling quantum dot synthesis conditions [4]. Furthermore the assembly of colloidal QDs gives rise to semiconducting behavior, which could result in relatively high carrier mobility [5]. Most importantly, all of these properties can be obtained with low-temperature solution-based technologies.

We have focused on CQD/ZnO nanowire (NW) structures (NW-type), with the aim of simultaneous enhancement in carrier transport and light harvesting efficiency (Fig.1 (a)). We also used PbS CQDs with the first exciton absorption peak position in the near infrared region. The morphology of ZnO NW arrays was systematically investigated. Our recent study revealed that NW-type solar cells give a carrier diffusion length of over 1 μm , which is longer by a factor of two than that of the best performing conventional planar-type one (Fig. 1 (b)) [6 - 8].

In this presentation, we investigate the performance of PbS QD/ZnO NW solar cells using PbS CQDs absorbing photons in a wide range of solar spectrum, and discuss the potential for low-cost multi-junction solar cells with PbS CQD/ZnO NW hybrid structures.

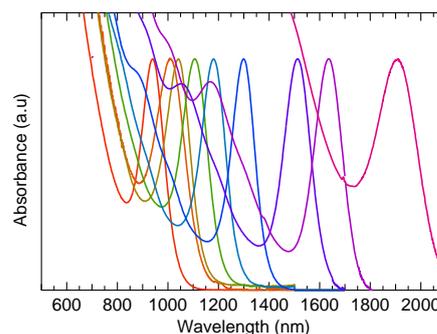


Fig. 2 Absorption spectra of PbS CQD octane solutions used in the present study

2. Results and Discussion

Colloidal PbS quantum dots producing different first exciton absorption peaks were synthesized using a method that had been reported in an earlier paper. The NW-type solar cells were constructed using a layer-by-layer deposition method. PbS CQD / ZnO NW hybrid structures were formed on FTO (F-doped SnO₂) substrates so that the first exciton absorption peak from visible light to SWIR light (from 300 nm to 2000 nm) could be obtained (Fig. 2).

The external quantum efficiency (EQE) spectra of the ZnO NW type solar cells fabricated with the hybrid structures give EQE peaks originating from the first exciton absorption (Fig. 3). From the EQE spectra, we confirmed that the solar cells were able to convert photon energy to electricity in a wide range of the solar spectrum by simply tuning CQD synthesis conditions. The EQE value at the exciton peak tends to decrease as the absorption edge shifts to longer wavelengths. There are several factors to be considered. One of the clear factors is the free carrier absorption of the FTO substrate. 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. In spite of the free carrier absorption of the FTO in the SWIR region, the solar cell whose first exciton peak (1520 nm) produced an EQE of 30.5% at that peak. The internal quantum efficiency at this peak was estimated to be not less than about 60%, which indicates that an efficient carrier collection took place even in the solar cell working in the SWIR region. This is because the PbS QD/ ZnO NW hybrid structure provided spatially separated carrier pathways, which helped reduce the frequency of the recombination of the photogenerated carriers. However, the EQE values of the solar cell whose first exciton peak is located at 1840 nm remain too low to be explained solely by the free carrier absorption. Insufficient passivation of the trap states of the PbS QDs may account for such a low EQE. The optimization of QD synthesis and solar cell fabrication is expected to further improve the performance.

Solar cell performances (J_{sc} , V_{oc} , FF , and PCE) were obtained from the current vs voltage curves of the solar cells measured under quasi-one-sun illumination (Table 1). Although the J_{sc} is expected to increase with increasing $\lambda_{bandgap}$, it reaches a maximum value at a $\lambda_{bandgap}$ of 1290 nm, and then decrease as $\lambda_{bandgap}$ gets larger. This is because of the free carrier absorption of FTO. Whereas the V_{oc} monotonically decreases with

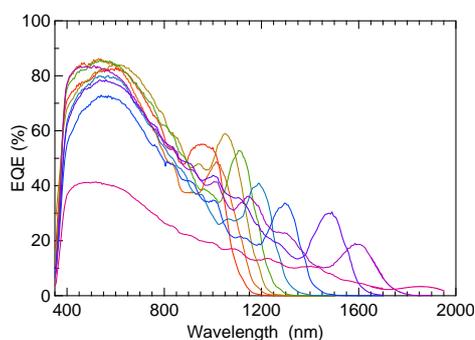


Fig.3 EQE spectra of the solar cells with different size PbS QDs.

increasing $\lambda_{bandgap}$, but keeps at approximately 250 mV even in the solar cell whose $\lambda_{bandgap}$ is 1970 nm (the first exciton peak is 1840 nm). The V_{oc} is as high as that

Table. 1 PV performance obtained on the solar cells fabricated with different size QDs

$\lambda_{excito\ peak}$	nm	$\lambda_{bandgap}$	nm*	J_{sc}	V_{oc}	FF	PCE
				mA/cm ²	mV	%	%
940		1170		25.7	510	52.4	6.87
1010		1220		24.9	505	52.8	6.62
1040		1250		28.5	464	52.8	6.98
1100		1290		28.8	463	52.1	6.94
1180		1360		27.5	457	54.5	6.85
1300		1460		26.0	420	51.3	5.60
1520		1650		24.4	394	50.9	4.88
1630		1770		27.6	351	48.6	4.70
1840		1970		6.90	253	38.9	0.67

* $\lambda_{bandgap}$: the EQE onset wavelength giving an EQE of 1%

of Ge solar cells (the bandgap is approximately 1900 nm), and such a high V_{oc} may originate from the spike-like pn-heterojunction formed at the PbS QD/ZnO NW interface [9].

3. Conclusions

PbS CQD/ZnO NW-based solar cells were constructed with nine differently sized PbS QDs, and were verified to work in a wide range of the solar spectrum spanning from the visible to short wave infrared. A theoretical calculation reveals that, to attain ultimately high efficiency over 50% under the one-sun condition, absorbers for the bottom cells of multi-junction solar cells are required to have the absorption edge about 0.65 eV (1900 nm) [1]; this value is almost the bandgap energy of the PbS QD/ZnO NW solar cells whose exciton peak appears at 1840 nm. Even though there are many issues to be solved, a series of experimental results obtained indicate that solution-processed CQD/ZnO NW solar cells have a great potential for the subcells of multi-junction solar cells.

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References

- [1] M. A. Green, *Third Generation Photovoltaics: Advanced Solar Energy Conversion*; Springer, 2003.
- [2] G. E. Eperon, T. Leijtens, K. A. Bush, R. Prasanna, T. Green, J. T.-W. Wang, D. P. McMeekin et al., *Science*, **354**, 861 (2016).
- [3] A. Guchhait, H. A. Dewi, S. W. Leow, H. Wang, G. Han, F. B. Suhaimi, S. Mhaisalkar, L. H. Wong, N. Mathews, *ACS Energy Lett.*, 807 (2017).
- [4] E. H. Sargent, *Adv. Mater.*, **17**, 515 (2005).
- [5] C. R. Kagan, and C. B. Murray, *Nat. Nanotech.*, **10**, 1013 (2015).
- [6] H. Wang, T. Kubo, T. Kinoshita, J. Nakazaki, and H. Segawa, *J. Phys. Chem. Lett.*, **4**, 2455 (2013).
- [7] H. Wang, T. Kubo, J. Nakazaki, and H. Segawa, *J. Phys. Chem. C*, **119**, 27265 (2015).
- [8] T. Kawawaki, H. Wang, T. Kubo, K. Saito, J. Nakazaki, H. Segawa, and T. Tatsuma, *ACS Nano*, **9**, 4165 (2015).
- [9] H. Wang, T. Kubo, J. Nakazaki, and H. Segawa, (submitted).