Solution-processed intermediate-band solar cells with lead sulfide quantum dots and lead halide perovskites

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The intermediate-band solar cell (IBSC) with quantum dots and a bulk semiconductor matrix has potential for high power conversion efficiency, exceeding the Shockley-Queisser limit. However, the IBSCs reported to date have been fabricated only by dry process and their efficiencies are limited, because their photo-absorption layers have low particle density of quantum dots, defects due to lattice strain, and low bandgap energy of bulk semiconductors. Here we present solution-processed IBSCs containing photo-absorption layers where lead sulfide quantum dots are densely dispersed in methylammonium lead bromide perovskite matrices with a high bandgap energy of 2.3 eV under undistorted conditions. We confirm that the present IBSCs exhibit two-step photon absorption via intermediate-band at room temperature by inter-subband photocurrent spectroscopy.
intermediate-band solar cells (IBSCs) have strong potential for high power conversion efficiency (PCE), exceeding the Shockley-Queisser limit. The IBSC has an intermediate-band (IB) between the valence band (VB) and conduction band (CB), within the bandgap of bulk semiconductor in a photo-absorption layer. The IBSC provides two-step photon absorption (TSPA) from the VB to IB and from the IB to CB, in addition to the bulk absorption from the VB to CB. Quantum dots (QDs) incorporated into the bulk matrix have been considered as one of the most promising candidates to realize the IBSCs. Presently, such IBSCs have been fabricated only by dry process such as the molecular beam epitaxy (MBE) and metal organic chemical vapor deposition (MOCVD). However, it is generally difficult to improve the PCE in dry-processed IBSCs, because restrictions on the materials that can be used make it difficult to increase in the particle density of QDs and in the bandgap energy (E_{BG}) of bulk in the photo-absorption layer of the IBSC.

Results
Design and fabrication. Taking into account the solution process, we have selected a perovskite compound as the bulk material and the colloidal QD as the QB-IB material. Lead (Pb) halide perovskite and lead sulfide (PbS) QDs were chosen from the viewpoint of lattice-matching. The optimized band structure by the solution process has been proposed as a means to fabricate the IBSC. The colloidal QDs have been reported to date. Here, we create IBSCs containing photo-absorption layers where QDs are densely dispersed in a bulk matrix with a high E_{BG} under undistorted conditions by the solution process. The IBSCs are confirmed to exhibit TSPA via IB at room temperature by inter-subband photocurrent spectroscopy.

Structural characterization. Figure 2 shows X-ray diffraction (XRD) patterns of the photo-absorption layers on mesoporous TiO_2 (mTiO_2) layers. The hybridization of the PbS QDs with the perovskite did not change the XRD peak positions of the perovskite. No peak due to PbS at 2θ = 25 degree was detected. The XRD results revealed that CH_3NH_3PbBr_3 perovskite with undistorted lattice was the main component of the photo-absorption layers.

Optical properties. No change in the perovskite absorption peak of 530 nm was observed even after hybridizing the PbS QDs (Fig. 5), indicating that the perovskite E_{BG} of 2.3 eV was constant. Near-infrared (NIR) photoluminescence (PL) spectra excited at 785 nm exhibited emission peaks of the PbS QDs at 1210 nm (Fig. 5). Although the emission intensity increased with increasing content of the PbS QDs, the peak wavelength remained constant. Thus, the E_{BG} of PbS QDs in the photo-absorption layers was determined to be 1.0 eV. It has been reported that PbS QDs with E_{BG} of 1.0 eV have a mean particle diameter of 4 nm.

Note that NIR emission of the PbS QDs was observed even by exciting the perovskite (excitation wavelength of 532 nm, Supplementary Fig. 1a) in the photo-absorption layers. This result indicates that a part of the charged-carriers photogenerated in the perovskite transfers to the PbS QDs, due to the fact that the VB maximum and the CB minimum of PbS QDs exist within the bandgap of the perovskite (Fig. 1a). The carrier transfer from the perovskite to PbS QDs was also supported by experimental results that emission intensity and lifetime of the perovskite decreased with the small amounts of the PbS QDs (Supplementary Fig. 1b, c), while the decrease in the emission intensity and lifetime of the perovskite may be partly attributed from the lower crystallinity of the perovskite (Supplementary Fig. 2).

As the excitation power density increased, the NIR emission intensity linearly increased and the emission peak wavelength blue-shifted (Fig. 6, Supplementary Fig. 3), confirming electron coupling between the PbS QDs, i.e., the IB formation in the photo-absorption layers with the PbS QDs and the perovskite. The emission peak shift was nearly saturated at about 1.058 eV when...
excited at the excitation density of 1226 W cm$^{-2}$. The blue-shifted energy was calculated to be 0.02 eV, which corresponds to the width of their IB. In summary, the band structure of the photo-absorption layer prepared was identified as designed (Fig. 1a).

Solar cell properties. External quantum efficiency (EQE) values in the visible light region from 400 nm to 550 nm (Fig. 7a) were decreased by hybridizing the PbS QDs, while EQE values in NIR light region from 600 nm to 1250 nm (Fig. 7b) were increased with the PbS QDs. The EQE onset wavelengths (550 nm and 1250 nm) were consistent with $E_{\text{BG}}$ of the perovskite (2.3 eV) and the PbS QDs (1.0 eV), respectively. Thus, the EQE values in the visible and NIR light regions are derived from the charged-carriers photogenerated in the perovskite and the PbS QDs, respectively. Consequently, the decrease of EQE in the visible region for the cells with PbS QDs should be explained in terms of the carrier transfer from the perovskite to the PbS QDs as described above. As a result, PCE values were decreased by hybridizing the PbS QDs (Supplementary Fig. 4). The changes in the solar cell properties by the PbS QDs are similar to those by InAs QDs in dry-processed IBSC. However, the NIR EQE due to the PbS QDs (0.1 to 0.2% at 1000 nm, Fig. 7b) was much lower than that in the dry-processed IBSC (6% at 920 nm)\textsuperscript{8}, suggesting that thermal excitation from the IB to the perovskite CB may be suppressed because of the larger $E_{\text{IC}}$ (0.8 eV) in the present IBSCs.

The values of $\Delta$EQE using IR bias light with more than 1319 nm (less than 0.94 eV) increased with the PbS QDs (Fig. 7c, d). In the visible light region (Fig. 7c), $\Delta$EQE spectra steeply increased at 550 nm which was consistent with $E_{\text{BG}}$ of the perovskite (2.3 eV). Consequently the $\Delta$EQE spectra between 500 nm and 550 nm are derived from the photo-excitation of the perovskite.
Taking into account the fact that the perovskite cell without the PbS QDs has no IB, the ΔEQE spectrum of the perovskite cell, which was almost independent on the IR bias light energy (Supplementary Fig. 5, 6) should arise from the photo-excitation of shallow-trapped electrons on defects of the perovskite.\(^\text{32}\) In contrast, the ΔEQE values of the hybrid cells with the PbS QDs fell by the decrease in IR bias light energy from less than 0.94 eV to less than 0.83 eV (Supplementary Fig. 5, 6), indicating the narrow energy distribution of the IB (0.02 eV, Fig. 6) with the \(E_{\text{IC}}\) of 0.8 eV (Fig. 1a). Thus, the ΔEQE spectra between 500 nm and 550 nm of the hybrid cells with the PbS QDs should be explained in terms of the TSPA of the IB electrons transferred from the perovskite CB, since the carrier transfer from the perovskite to the PbS QDs\(^\text{25–27}\) has been supported by the emission behavior (Supplementary Fig. 1) and the cell characteristics (Fig. 7a, Supplementary Fig. 4). In the NIR light region (Fig. 7d), the hybrid cells with the PbS QDs exhibited ΔEQE spectra with the onset at around 1250 nm and the rising at around 850 nm in contrast to the perovskite cell with ΔEQE = 0%. The wavelengths of the onset and the rising were consistent with the \(E_{\text{BG}}\) of PbS QDs (1.0 eV) and the \(E_{\text{VI}}\) (1.5 eV), respectively (Fig. 1a). Consequently, the ΔEQE spectra between around 850 nm and around 1250 nm can be attributed to the TSPA where electrons photo-excited from the PbS QD VB to the IB (PbS QD CB) are...
further photo-excited to the perovskite CB. The ΔEQE spectra ranging from 600 nm to around 850 nm should be partly due to the TSPA of the IB electrons photo-excited from the perovskite VB. Thus, the hybrid cells with the PbS QDs exhibited the TSPA via the IB, confirming that they were functioning as the IBSCs at room temperature.

Discussion
We prepared the photo-absorption layers by the solution process of spin-coating from the DMF dispersions containing the PbS QDs with the size of 4 nm and the perovskite raw materials (PbBr₂, CH₃NH₃Br). The structural and spectroscopic characterizations of the photo-absorption layers indicated that the PbS QDs with the E BALL of 1.0 eV were densely dispersed in CH₃NH₃PbBr₃ perovskite matrices with the E BALL of 2.3 eV under undistorted conditions as designed in Fig. 1. The blue-shift in NIR PL with increasing excitation density (Fig. 6b) confirmed IB formation in the photo-absorption layers. The cells with the photo-absorption layers exhibited the TSPA via the IB at room temperature by the inter-subband photocurrent spectroscopy as shown in Fig. 7c, d. Thus, we can conclude that a solution process was a powerful tool to fabricate IBSCs without limitations often reported for dry-processed IBSCs.

As shown in Supplementary Fig. 4, the PCE values of the present IBSCs with the PbS QDs and the perovskite were low because of some factors such as the carrier transfer from the perovskite to the PbS QDs and poor film quality. However, an incorporation of a tunneling barrier with CB minimum above that of the perovskite into the interface between the PbS QDs and the perovskite may block the carrier transfer from the perovskite to the PbS QDs, leading to high PCE. And also, the carrier transfer may be suppressed by control of their energy levels like type-II structure which can be realized by hybridizing a QD material with VB maximum below that of the perovskite. In addition, the TSPA process should be enhanced by increasing the lifetime of carriers in the intermediate state with photon ratchet and in type-II structure. Further investigations are currently underway to enhance the solar cell performance by suppressing the carrier transfer and by improving the film quality. The present results pave the way towards not only high PCE but also low cost, flexible IBSCs.

Methods
Synthesis of PbS quantum dots (QDs) Oleate-capped PbS quantum dots (QDs) were synthesized according to a previously published method. A mixture of 0.45 g of lead oxide (99.999%), 10 g of 1-octadecene (ODE, more than 95%), and 1.34 g of oleic acid (more than 90%) was degassed at 353 K for 2 h. The obtained solution was heated to 383 K and kept for 30 min under N₂, followed by rapid injection of an ODE solution (4 mL) of 1,1,3,3,3-hexamethyldisilathiane (0.21 mL). After injection, the obtained colloidal solution was allowed to cool down to room temperature, and PbS QD solid was separated by adding acetone and centrifugation. The oleate-capped PbS QDs were characterized by inductively coupled plasma (ICP) analysis, X-ray photoelectron spectroscopy (XPS), proton nuclear magnetic resonance (¹H NMR) spectroscopy, X-ray diffraction (XRD), absorption and photoluminescence (PL) spectroscopies, as described below. The weight concentrations of Pb and oleic acid in the oleate-capped PbS QD solid were measured to be 55 wt% and 28 wt% by ICP analysis and ¹H NMR spectroscopy, respectively. The molar ratio of oleate to Pb (oleate/Pb) could be calculated to be 0.37. The atomic ratio of Pb/S/I/N was determined to be 1/0.58/0/0 by using XPS. The crystalline size of the oleate-capped PbS QDs was estimated to be 3.0 nm by XRD. The bandgap energy (E BALL) of the oleate-capped PbS QDs was estimated to be 1.2 eV from absorption onset wavelength (1050 nm) and emission peak wavelength (1040 nm) excited at 800 nm.

The above oleate-capped PbS QD solid could be dispersed in toluene, but not in N,N-dimethylformamide (DMF), which was a good solvent for a solution of perovskite raw materials (PbBr₂, CH₃NH₃Br). Consequently iodine (I)-capped PbS QDs with high dispersibility in DMF were synthesized by ligand exchange process at room temperature. In the ligand exchange process, DMF-solvated I-ligands replace oleate ligands on the PbS QD surface. In a glovebox, 0.20 g of the above oleate-capped PbS QD solid could be dispersed in 2 mL of DMF (super dehydrated). A mixed solution of 1 mL of toluene, 0.5 mL of DMF (super dehydrated), and 0.062 g of CH₃NH₃I (MAI) was dropwise added to the PbS dispersion for 11 min without stirring. The molar ratio of MAI to Pb of oleate/Pb could be calculated to be 2. After 18 h, 5 mL of methanol (super dehydrated) was added to the PbS dispersion in order to precipitate I-capped PbS QD solid. The I-capped PbS QD solid was separated by filtration using polytetrafluoroethylene (PTFE) filters with the pore size of 0.20 μm. The weight concentrations of Pb/S/I/N were measured to be 55 wt% and 28 wt% by ICP analysis and ¹H NMR spectroscopy, respectively. The molar ratio of I/Pb was determined to be 2. The obtained I-capped PbS QDs were characterized by XPS, XRD, absorption and photoluminescence (PL) spectroscopies.

Fig. 5 Absorption and NIR PL spectra of the photo-absorption layers at room temperature. Excitation wavelength was 785 nm

Fig. 6 Excitation density dependence of NIR PL of the photo-absorption layers. a Emission intensity and b emission peak energy at room temperature. Excitation wavelength was 532 nm
concentrations of Pb and oleic acid in the I-capped PbS QD solid were measured to be 55 wt% and 1 wt% by ICP analysis and \(^1\)H NMR spectroscopy, respectively. The atomic ratio of Pb/S/I/N was determined to be 1:0.51:0.49:1 by using XPS. The crystalline size of the I-capped PbS QDs was measured to be 3.5 nm by XRD. The ratio of Pb/S/I/N was determined to be 1/0.51/0.49/1 by using XPS. The crystalline size of the I-capped PbS QDs was determined to be 3.5 nm by XRD. The absorption onset wavelength of less than 30 nm was deposited on a UV-ozone-cleaned fluorine-doped tin oxide (FTO)-coated glass substrate (Asahi Glass Co., Ltd., 25 × 25 × 1.8 mm) by spray pyrolysis at 723 K from a precursor solution of 4.04 g bis(isopropanol)bis(acetylacetone)-titanium(IV) (75 wt% in 2-propanol) in 123.24 g ethanol (super dehydrated). The amorphous TiO\(_2\) (TiO\(_2\)-a) layer with the thickness of about 200 nm was coated on the FTO substrate by spin-coating with a speed of 5000 rpm for 30 min from a diluted solution of 20 nm TiO\(_2\) particle paste (PST-18NR, JGC Catalysts and Chemicals Ltd.) with the weight ratio of TiO\(_2\) paste: ethanol of 1: 3, 5: 1, solar slit of 5.0 degree, divergence slit of 13.0 mm, scan range of 2θ = 5 to 60 degree. The crystalline size of the PbS QDs was determined to be 7.3 nm s\(^{-1}\) on top of the HTM layer under high vacuum (4 to 5 × 10\(^{-3}\) Pa).

### Structural characterization

XRD patterns were recorded on a X-ray diffractometer (Rigaku, Mini Flex600, light source CuK\(_\alpha\), tube voltage 40 kV, tube current 15 mA) under the conditions of sampling width of 0.02 degree, scan speed of 20 degree min\(^{-1}\), scan range of 2θ = 5 to 60 degree. The crystalline size of the PbS QDs was determined at cubic PbS (220) peak (2θ = 42 degree) based on Scherrer equation by using analysis software (PDQX ver.2.6.1.2).
The weight concentrations of Pb in the PbS QD solids were determined by ICP analysis of clear solutions dissolved in HNO₃/H₂O₂ mixture. The weight concentration of oleic acid in the PbQD solids were measured by HR NMR spectra with dibromomethane as an internal standard in deuterated toluene (99 atom%D, tetramethylsilane (TMS) 0.03 volume%) or deuterated DMF (99.5 atom%D). The ¹H NMR spectra in these solutions were obtained on an NMR spectrometer (Agilent, VNMRF400), operating at 400 MHz. Delay times of 60 s were used for 32 times. The atomic ratios of Pb/S/I/N in the PbS QD solids were determined from the area ratios of Pb 4f, S 2p, I 3d, and N 1s in XPS data. The XPS spectra were measured on a XPS spectrometer (Ulvac-phi, PHI Quantera SXM) using monochromatic AlKα radiation (25 W, 15 kV) under the conditions of beam size of 100 μm, area of 1 mm², pulse energy of 112 eV, step of 0.2 eV, detection angle of 45 degree, binding energy correction C1s (284.8 eV). Scanning electron microscopy (SEM) images of the photo-absorption layer surface were obtained on a field emission-scanning electron microscope (SEM, Hitachi, S-4800), operating at 10 kV. The fraction of surface coverage of the perovskite in the photo-absorption layer was calculated from SEM images. The XPS and SEM images were measured on a XPS spectrometer (Ulvac-phi, PHI Quantera SXM) and afield emission-scanning electron microscope (STEM, Hitachi, H-9500), operating at 300 kV. Using the STEM and HRTEM observations, we found that some of the PbS QDs were aggregated to form the larger particles with the size of more than 10 nm by the laser light scattering and the glass substrate for the photo-absorption layers on glass substrates were measured at 544 nm. Quantaurus-Tau C11369). Emission decay curves from 0 to 100 ns of the perovskite layers for efficient solar cells. J. Am. Chem. Soc. 137, 024301-1-5 (2015). 18. Yang, W. S. et al. Iodide management in formamidinium-lead-halide-based perovskite layers for efficient solar cells. Energy Environ. Sci. 355, 6890 (2010). 19. Nozik, A. J. et al. Semiconductor quantum dots and quantum dot arrays and applications of multiple exciton generation to third-generation photovoltaic solar cells. Science 354, 206–209 (2016). 20. Yang, W. S. et al. High-performance photovoltaic perovskite layers fabricated through intramolecular exchange. Science 348, 1234–1237 (2015). 21. Saliba, M. et al. Incorporation of rubidium cations into perovskite solar cells improves photovoltaic performance. Science 354, 206–209 (2016). 22. Tan, H. et al. Efficient and stable solution-processed planar perovskite solar cells via contact passivation. Science 355, 722–726 (2016). 23. Ryu, S. et al. Voltage output of efficient perovskite solar cells with high open-circuit voltage and fill factor. Energy Environ. Sci. 7, 2614–2618 (2014). 24. Yang, W. S. et al. High-performance photovoltaic perovskite layers fabricated through intramolecular exchange. Science 348, 1234–1237 (2015). 25. Hou, Y. et al. A generic interface to reduce the efficiency-stability-cost gap of perovskite solar cells. Science 358, 1192–1197 (2017). 26. Nozik, A. J. et al. Semiconductor quantum dot arrays and applications of multiple exciton generation to third-generation photovoltaic solar cells. Chem. Rev. 110, 6873–6890 (2010).
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Acknowledgements
We acknowledge Dr. A. Wakamiya at Kyoto University for his advice in the fabrication of solar cells. A part of this work was conducted at Kyushu University, supported by Nanotechnology Platform Program (Molecule and Material Synthesis) of the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.

Author contributions
H.H., T.S., H.S., and T.Y. conceived the design. H.H., R.T., T.S., A.O., and Y.Og. carried out the experiments and analyzed the results. H.H. and R.T. co-wrote the manuscript with input from all authors. S.H., Y.Ok., and T.Y. supervised the project.

Additional information
Supplementary Information accompanies this paper at https://doi.org/10.1038/s41467-018-07655-3.

Competing interests: The authors declare no competing interests.

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