Rational Ligand Design for Enhanced Carrier Mobility in Self-Powered SWIR Photodiode based on Colloidal InSb Quantum Dots

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1. Materials and Methods

1.1 Reagents and Materials: Indium (III) bromide (99.999% trace metal basis), Lithium triethylborohydride (LiEt₃BH, 1.0 M solution in THF), Dioctyl ether (DOE), Formamide (>99.5%), N,N-dimethylformamide (anhydrous, 99.8%), Sodium sulfide, Butylamine (BTA) were purchased from Sigma-Aldrich. Antimony (III) bromide (99.9%), Toluene (99.5%, Deoxydized, 1-ppm<O₂, 10-ppm<H₂O), Hexane (99.6%, Deoxidized, 1-ppm<O₂, 10-ppm<H₂O), Methanol (99.8%, Deoxydized, 1-ppm<O₂, 10-ppm<H₂O), Ammonium acetate (AA) and Tetrachloroethylene (TCE) were purchased from Fujifilm WAKO chemical corp. Oleylamine (OLA, 80-90%) was purchased from Kanto-Kagaku. **1.2 Preparation of precursor solution:** 0.22 mmol (0.078 g) of InBr₃ and 0.2 mmol (0.071 g) of SbBr₃ were dissolved together in 10 mL OLA, which was preliminarily degassed in vacuum overnight, in a rubber stopper plastic sealed glass bottle inside of a glovebox filled with Ar. Then the sealed glass bottle was heated overnight at 50° C on top of an oil bath.

1.3 Preparation of reducing agent solution: 2.5 mL of LiET₃BH (Super-hydride, SH) solution was mixed with 2.5 mL of DOE, which was preliminarily degassed under vacuum overnight, in a 25 mL two-neck flask connected to an air-free Schlenk line, followed by evacuation at room temperature overnight to remove THF, yielding DOE solution of SH. Because SH is highly reactive and sensitive to air, we treated SH in a controlled glove box where water and oxygen were kept below 1 ppm.

1.4 Synthesis of OLA-capped InSb QD and Size selective precipitation: InSb QDs were synthesised by hot-injection method by following our previously reported method with modification with the amount of precursor and reaction solvent.¹ First 6.5 ml of

degassed OLA was injected in a three-neck flask under continuous Ar flow. Then the temperature was increased up to 240°C. Soon after reaching the reaction temperature 2.5 ml of SH solution was added in OLA, within 1 min solution becomes yellow. After waiting for 5 mins, 6.5 ml of precursor solution was injected drop-by-drop. Upon injection of precursor, solution turns darked brown. Then the solution was kept at the same condition for 45 mins to complete the reaction. After completion of reaction heater was removed and solution was mixed with super hydrated Toluene.

A schematic image of size separation was shown in Scheme 1. The solution mixture was separated in two centrifuge tubes capped with the septa for further separation. In the first set centrifugation was performed for 5 min at 8000 rpm which yielded black precipitated samples (sample A) and with dark brown supernatant. Further 2 ml of methanol was added in the solution and centrifuged for 10000 rpm for 10 mins to obtain sample B. This cycle of addition of methanol (4 ml and 5 ml) and centrifugation was repeated further to separate two more samples C and D.

1.5 Sulfide ligand exchange procedure: Solution process ligand exchange was followed with modification of the report by Kagan et. al.² InSb CQDs dissolve in octane at 30 mg/mL were mixed with 20 mg/ml of Na₂S in Formamide (FA) (solution mixing ratio is 1 ml:1 ml). Then the solution was vortex for 10 min and CQD phase was changed from octane to FA. Then centrifuge at 4000 rpm for 5 mins to precipitate. After discarding the transparent solution 1 ml super hydrated Hexane was added and vortex for 5 mins and then centrifuged again at 4000 rpm for 5 mins to precipitate, this step has been done one more time. Then precipitated sample was dissolved in 1 ml of super hydrated Hexane and 1 ml of super hydrated Methanol was added and centrifuged at 6000 rpm for 10 mins to get the exchanged ligand sample. After 2 hr. of drying in a vacuum, the sample was

dissolved in Butalamine (BTA) + anhydrous N,N-dimethylformamide (DMF) in a ratio of 2:1 for fabrication at a concentration of 100 mg/mL.

1.6 Device Fabrication Process: ITO-coated glass substrate was cleaned with sonication in acetone, ethanol and IPA for 15 min each and transfer to VUV Ozone cleaner chamber (Ushio Inc., Japan, UER20-172V; λ = 172 nm and 10 mW/cm²). The substrate was further cleaned for 30 min under continuous flow of N₂ under pressure of 10³ Pa.

First, spin coating of PEDOT : PSS was performed at 3500 rpm for 35 sec, then dried on top of hot plate for 15 min at 120°C. Then, ligand exchanged InSb CQD of 90 mg/ml Sulfide-capped in BTA+DMF solution was spin coated at 1000 rpm for 60 sec. Then QD layer was dried on hot plate for 20 min at 80°C. This step was repeated for 10 times to thicken the CQD layer. After that ZnO was spin-coated on top of QD layer at 2500 rpm for 45 sec. Further the layer was dried by following heat treatment for 15 min at 120°C. Top electrode of Aluminium was deposited by thermal evaporation with a shadow mask by tuning the current with controlling the evaporation by 3-4 Å/s range.

1.7 Material Characterization: X-ray powder diffractometer Mini-Flex 600, Rigaku, Japan was used for XRD measurement. V-770 spectrophotometer (JASCO, Japan) was used for measuring optical absorption spectra for both solution and thin film form. 200 kV JEM 2100 manufactured by JEOL Ltd was used to capture HR-TEM images of QDs. IRAffinity-1S manufactured by Shimadzu was used to acquire ATR-FTIR spectra. XPS sample was prepared in glovebox by spin coating QD layer in Si substrate, while the sample handling process was on air before transferring to XPS system. XPS was measured by Quantum-2000 by ULVAC Faye Corp using AlK α (E = 1486.6 eV) radiation. The X-ray source was operated at 50 W and 15 kV. The core-level signals were obtained at a photoelectron take-off angle of 45° (with respect to the sample surface). The

BE scales were referenced to 285.0 eV as determined by the locations of the maximum peaks on the C 1s spectra of hydrocarbon, associated with an adventitious contamination. Ultraviolet photoelectron spectroscopic (UPS) spectra were measured by SigmaProbe (Thermo Fisher Scientific, USA).

1.8 ICP-OES Sample Preparation: The whole of sample was transferred into a quartz beaker, and then 5mL of H_2SO_4 and a few drops of HNO_3 were added. The sample was decomposed by heating until white smoke is occurred. After cooling, the solution was poured into a 100 mL of volumetric flask and 10 mL of 20 mg/L Mn standard solution was added into the flask as internal standard for ICP-OES. 20 mL of HCl was added into this flask and the solution was diluted to the marked line with Milli-Q water.

1.9 SWIR Device Characterization: All devices were characterized at room temperature in ambient air. The data for the photocurrent density–voltage (J-V) characteristics were obtained using Keithley 2425 source meter. A 400 W halogen lamp (W-M10UN, BUNKOUKEIKI, Co., Ltd., Japan) equipped with a monochromator and a 300 W Xenon lamp were used for illumination. Power density of the incident light was measured using PD-300IR (Ocean Photonics, Co. Ltd., Japan). In the J-V measurement, three devices on one glass substrate were measured individually and each device was characterized under SWIR light irradiation (1000 – 1500 nm) and under dark conditions without light. The results for responsivity were obtained on a home-built setup using a same incident light. The anode and cathode of the device were connected to a 1 G Ω load resistor and connected to a DS-5624A oscilloscope (Iwatsu Electric Co., Ltd) to record the modulation changes of the photovoltage under open circuit conditions. The frequency response of the photocurrent was displayed as a fast Fourier transform by the oscilloscope. The response time was calculated using the rise and fall times between 0.1 and 0.9, with the background

of the waveform displayed on the oscilloscope as 0 and the maximum photocurrent as 1.

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Scheme S1. Schematic representation of the post-synthesis size selection procedure to reduce the polydispersity from the initial ensemble.





Figure S1. (a) HR-TEM photograph, (b) NIR absorption spectrum and (c) room temperature PL spectrum of the sample D of OLA-terminated InSb CQDs. (d) HR-TEM photograph, (e) NIR absorption spectrum and (f) temperature-dependent PL spectra of the sample B of OLA-terminated InSb CQDs.



Figure S2. HR-TEM photograph, the enlarged HR-TEM image and size distribution of the sample A of OLA-capped InSb CQDs.



Figure S3. Bandgap energies (E_g) plotted versus diameters of InSb CQDs reported in literatures. The solid curve shows the theoretical relationship between the values of E_g and CQD diameter using effective mass approximation (EMA):

$$E_g = E_{g0} + \frac{h^2}{8m_0 R^2} \left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right)$$

where E_{g0} is the bulk bandgap energy, R is the radius of QD, m_e^* (= 0.25m₀) and m_h^* (= 0.014m₀) are electron and hole effective masses, respectively.²

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Figure S4. XPS spectra of sulfide capped InSb CQD of (a) S2p (b) Na1S region. (c) Raman spectra of sulfide capped InSb CQD.



Figure S5. GI-XRD data of InSb with OLA-, bromide-, and sulfide-capped CQDs in 2θ. (b) q values of InSb CQD films with OLA and bromide ligands.

Sample preparation: InSb QD in DMF with concentration of 80 mg/ml was spin coated on top of Si substrate with 500 rpm for 30 sec, followed by heat treatment at 120 °C for 15 min.

20 value was converted with Braggs formula:1

 $q = 4\pi/\lambda(sin\theta)$

Here, $\lambda = 1.54$ Å, 2 θ is the scattering angle. Here, d is Particle-to-particle distance calculated from following formula:¹ $d = 2\pi/q$ Adjacent distance between particle (edge-to-edge of particle) was calculated by following formula:¹

D=2R-d

Here, R is average diameter of QDs.

Reference:

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Figure S6. HR-TEM images in other areas of InSb CQD (a) before (OLA capped), (b) after (sulfide capped) and (c) after (bromide capped) ligand exchange.



Figure S7. Absorption spectra of the Na₂S treated CQD in DMF solution.



Figure S8. Cross-sectional SEM and EDS mapping of the QPD.



Figure S9. Energy band diagram of InSb CQD terminated with sulfide or bromide ligand depicted by the results obtained from UPS measurement.



Figure S10. Normalized photocurrent response of the QPDs with (a) sulfide- and (b) bromide-capped InSb CQDs under white light illumination with an optical power density of 80 mW/cm^2 .

NOTE:

The sulfide-capped QPD's rise and fall time were approximately 5.5 ms and 9 ms at 0 V, whereas bromide-capped QPD's rise and fall time were approximately 17 ms and 62 ms at 0 V. The rise and fall time of the sulfide-capped QPD responded 3.0 and 6.8 times faster than those of bromide-capped QPD.



Figure S11. (a) and (b) multiple Na_2S treated QPD's fresh devices were subjected to air exposure for a duration of 30 to 45 days at room temperature, conducted in a non-cleanroom environment.

Specific Detectivity (D* in Jones):

$$D^* = \frac{R}{\sqrt{\frac{2eI_{dark}}{A}}}$$



Figure S12. Specific detectivity at -1 V of different wavelength under a constant light intensity of 1 mW/cm^2 .

The Space-Charge-Limited-Current (SCLC):

The SCLC model was carried out to calculate estimated electron and hole mobility and trap density of InSb QD with bromide- and sulfide-capped ligands. Figure S5 shows the I-V curve of electron-only and hole-only devices. Mott-Gurney formula was used to calculate carrier mobility:¹⁻³

$$J = \frac{9}{8} \varepsilon_r \varepsilon_0 \mu \frac{V^2}{d^3}$$

Where J is the current density, \mathcal{E}_r and \mathcal{E}_0 are the relative dielectric constant of InSb in bulk and the permittivity of free space, respectively. μ is the field independent carrier mobility, d is the thickness of the QD layer. Here, \mathcal{E}_r and \mathcal{E}_0 are set to be 16.8 and 8.85×10^{-14} F cm⁻¹⁷. The thickness of QD films is about 100 nm.

 N_{t} is the carrier trap density of the thin film has been calculated by the following formula: $^{3\text{-}4}$

$$V_{TFL} = \frac{eN_t d^2}{2\varepsilon_r \varepsilon_0}$$

Here, e represents elementary charge, V_{TFL} known as trap filled limit voltage. V_{TFL} can be describes as the transit point between two regions: ohmic region (I \propto V), trap-filled limit region (TFL region).

Fabrication procedure: ZnO layer was spin coated with 2500 rpm for 45 sec. After that substrate was dried on top of hot plate at 120 °C for 15 min. PEDOT: PSS layer was spin coated with 5000 rpm for 35 sec, followed by heat treatment at 120 °C for 15 min. QD layer was spin coated at 1000 rpm for 60 sec, followed by heat treatment at 80 °C for 20 min. This process was repeated for 10 times to thicken the layer.

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Figure S13. (a) The hole only devices PEDOT:PSS/*InSb-InBr*₃, (b) and (c) the electron only devices $ZnO/InSb-InBr_3/ZnO$ devices. (d) and (e) is hole only devices PEDOT:PSS/*InSb-Na*₂*S*, (f) electron only devices ZnO/InSb-Na₂*S*/ZnO.



Figure S14. (a) and (c) The electron mobility from ZnO/*InSb-InBr*₃/ZnO and ZnO/*InSb-Na*₂*S*/ZnO devices respectively. (b) and (d) The hole mobility from PEDOT: PSS/*InSb-InBr*₃ and PEDOT: PSS /*InSb-Na*₂*S* devices respectively.



Figure S15. Error bar of $V_{TFL}(V)$ values of four type devices with standard deviation.

Table S1. Summary of the device performances for nontoxic SWIR photodetectors (1-2 μ m) based on InSb CQDs. PT: Phototransistor, PC: Photoconductor, PD: Photodiode, R: Responsivity, EQE: Equivalent quantum efficiency, T: Response time and λ : Incident-light wavelength.

Photoactive material	Device type	Ligand	<i>R</i> (A/W)	EQE (%)	λ (μm)	T (sec)	Reference
InSb	РТ	K ₂ S, K ₂ Te					1
InSb	PC	Na ₂ S					2
InSb:PCBM :poly-TPD	РТ	OLA	4×10 ⁻⁵		1, 1.2, 1.4	0.08	3
In(P)As	PD	MPD	0.031(-3V) 0.029(-3V) 0.007(-3V)	5(-4V) 5(-4V) 1(-4V)	1.14 1.27 1.4	1.2×10 ⁻⁶ , 8.9×10 ⁻⁶ at - 3 V under 100 mW/cm ² white LED	4
InSb	PD	InBr ₃	0.098(-1V) 8×10 ⁻⁴ (0V)	10.1(-1V) 0.008(0V)	1.2	0.55 at 0 V under 1,2 and 4 mW/cm ² SWIR from Halogen lamp	5
InSb	PD	TBAX + MAX	-	75(1V)	1.2	7.3µ and 5.4µ	6
InSb/InAs (Core-Shell)	PD	Mn ₂ Se ₂	0.078	11.4 6.3	1.37 1.52	-	7
InSb	PD	MA + TBAI	0.28	25 (-1V)	1.4	5.6µ at -1V	8
InSb/InP (Core-Shell)	PD	InI ₃	-	25(-2V) 15(1.5V) 12(-1.5V)	1.24 1.3 1.42	7 ×10 ⁻⁸	9
InSb	PD	Na ₂ S	0.18(-1V) 12×10 ⁻³ (0V)	18.52(-1V) 1.3(0V)	1.1	0.2 at 0 V under 1,2 and 4 mW/cm ² SWIR Halogen lamp 0.005 and 0.009 at 0V under 80 mW/cm ² white light Xenon lamp	This work

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Table S2. Summary of the carrier mobility and carrier trap density calculated fromSCLC from electron-only and hole-only device.

Ligand	Number of	E-only device	h-only device	
	devices	$V_{TFL}(V)$	$V_{TFL}(V)$	
	1	0.55	0.57	
InDr	2	0.48	0.59	
IIIDI'3	3	0.55	0.55	
	4	0.54	0.56	
	1	0.42	0.37	
	2	0.39	0.4	
Na_2S	3	0.37	0.44	
	4	0.37	0.44	
	5		0.44	