Supporting Information

Red Luminescent Water stable Lead-Free 2D Tin Halide Perovskite Nanocrystal for Photodetector

Bharat Lal,^a Praveen Kumar,^b Sumit Kumar,^a Ankush Saini,^b Monojit Bag*^b, and Prasenjit Kar*^a

^aDepartment of Chemistry, Indian Institute of Technology Roorkee, Uttarakhand-247667, India

^bDepartment of Physics, Indian Institute of Technology Roorkee, Uttarakhand-247667, India

Corresponding Email address: kar.prasen@gmail.com, prasenjit.kar@cy.iitr.ac.in

SI.No.	Contents	Page No.
1.	Experimental section	S3
2.	Characterization techniques	S3 – S4
3.	Structure of the 2D perovskite material (Fig. S1)	S4
4.	Time depemdent PL spectra in water (Fig. S2)	S5
5.	In Fig. S3 (a) Photoresponsivity, (b) XPS fresh sample, (c) XPS analysis after 6 days of $(Oleylamine)_2SnI_4$.	S5
6.	TGA Analysis (Fig. S4)	S6
7.	TEM Elemental mapping (Fig. S5)	S6
8.	Chronoampereometry of the photodetector under chopped light of 385 nm UV LED at power density 15 mW/cm ² in (Fig. S6).	S7
9.	TEM-EDX Analysis (Table. S1)	S7
10.	Resultant table for the rise and fall time of (oleylamine) ₂ Snl ₄ (Table. S2)	S7

Experimental Section

Chemical Reagents

All the chemicals are Tin (II) oxide (SnO, Alfa Aesar 99%) and Oleylamine (Sigma Aldrich 70%), Hydrogen iodide (HI, Himedia,59%), and Hypo phosphorous acid (H_3PO_2 , Avra 50%) were purchased from a local vendor.

Synthesis of (Oleylamine)₂Snl₄

We synthesized here perovskites nanomaterial (Oleylamine)₂SnI₄ by the reported method of $(OCTAm)_2SnBr_4$ synthesis methods¹. Here we used (0.101 gm) Stannous oxide with 2.5 ml HI solution sonicated for some time in a round bottom flask until stannous oxide dissolved completely in hydroiodic acid after some time of sonication a yellow colored solution was obtained. After that 15 ml of hypophosphorous acid (H₃PO₂) was added into the Precursor solution to reduce Sn²⁺ to Sn⁴⁺ oxidation and then in this solution, 475 micro Litre Oleylamine, after mixing immediately this solution converted into a red precipitate solution. This solution is heated at 80 °C for 40 minutes in an oil bath with vigorous stirring until it is converted into a colorless solution. This colorless solution cools down in an ice bath for 4 to 5 hours, and then a red precipitate solution is obtained and gives bright red fluorescence under the U.V. Chamber. Finally, after the filtration process of this solution, we received our desired product.

Characterization techniques-

1. Absorption, excitation, and emission spectroscopy

Ultra Violet-Visible (UV-Vis) absorbance was measured on a Shimadzu UV-Vis 2600 spectrophotometer in the range of 200-800 nm. Photoluminescence spectra were recorded in the Cary eclipse fluorescence spectrophotometer. The emission spectra were recorded in the range of 300-900 nm wavelengths, while the excitation spectrum was recorded between 350-420 nm wavelength. The slit widths and step size of excitations and emissions were 2.0, 2.5, and 1.0, respectively.

2. Powder X-ray Diffraction (P-XRD) measurement

Thin film XRD was performed on a Rigaku Smart Lab automated multipurpose X-ray diffractometer with a wavelength of 0.154 nm (Cu K α) and an accelerating voltage of 9 kW in the range of 2 to 50.

3. Field Emission Scanning Electron Microscopy (FE-SEM)

FE-SEM Carl Zeiss ultra was used to analyze the surface morphology of perovskite materials. The sample was gold-coated with an operating voltage of 20 kV.

4. Transmission Electron Microscopy (TEM)

TEM images were collected by using M/S JOEL JEM 2100. A drop of diluted samples was deposited on a carbon-coated copper grid. Again, a drop was added before drying it, and drying was carried at room temperature.

5. X-ray photoelectron Spectroscopy (XPS)

Surface analysis of the material was carried out on XPS with model no. PHI 5000 Versa Probe III. Step width – 0.05 eV, Temperature - 19-21 °C, Vacuum – 10^{-7} Pascal, Pass Energy – 55 eV, Sweep 8 cycle, Source 1.48 Kev, Neutralizer 1.5 volt 20 μ A, Beam diameter 100 micrometer.

6. Thermo-gravimetric analysis (TGA)

Thermal analyses were performed on SII 6300 EXSTAR. The sample was heated in a temperature range of 0- 800 $^{\circ}$ C at a 10 $^{\circ}$ C/min heating rate under a nitrogen atmosphere.



Fig. S1. Likely structure of the 2D two-dimensional perovskite material.

The synthesis of water-stable (Oleylamine)₂Snl₄ perovskite nanoparticles following 9 days of storage in water, and the peaks remain unchanged in photoluminescence spectra presented



in Fig, S2 demonstrating that the synthesized perovskite nanomaterial is stable in water.

Fig. S2. Time-dependent PL spectra in water

The oxidation problem of Sn²⁺ is also improved significantly in the photodetector device and the stability of 1 day under continuous illumination. After 24 hours, the same device is again tested under UV (385 nm) LED. The photodetector device was still in working condition. Thus, the material is also shown in Fig. S3b for fresh and after 6 days of exposure in an open-air environment respectively. There is no extra peak obtained in the XPS graph. It is also concluded the stability of perovskite materials in Sn²⁺ is improved.



Fig. S3. (a) Photoresponsivity, (b) XPS fresh sample, (c) XPS after 6 days analysis of (Oleylamine)₂Snl₄.



Fig. S4. TGA spectra of (OleyIAm)₂SnI₄.^{2,3}

Fig. S5. (a) EDX of TEM image, Elemental mapping,(c) C, (d) N, (e) Sn, (f) I, of (Oleylamine)₂SnI₄ perovskites nanomaterial.

we have conducted chronoamperometry tests with zero external bias voltage on the device under continuous illumination of 385 nm UV LED at a power density of 15 mW/cm², alternating between ON and OFF conditions in intervals of approximately 30 seconds. Our findings indicate that after 24 hours of continuous illumination in open air environment (R.H., 40-50%), the photodetector device remains stable and operational, with a minor decrease in photoresponse. It should note that some noise was introduced into the data, likely due to instability in the electrical connections.





Fig. S6. Chronoampereometry of the photodetector under chopped light of 385 nm UV LED at power density 15 mW/cm², keeping the device area 0.04 cm².

Table S1. Elemental composition of TEM-EDX.

Element	Atomic wt %
Sn	81.9
I	18.1

Table S2. Summary of the rise/fall time of the layered structured A_2BX_4 type perovskitesbased photodetectors.

S.No.	Active Material	Rise/fall time	Reference
1.	(1,4-butyl diammonium)CdBr ₄	1.2/2.1 s	4
2.	$(C_4H_9NH_3)_2PbBr_4$ -nanobelts	340/500 ms	5
3.	$(C_4H_9NH_3)_2PbBr_4$ -microplatelates	280/550 ms	5
4.	(PEA) ₂ SnI ₄	0.37/3.05 s	6
5.	(PEA) ₂ SnI ₄	630/3600 ms	7
6.	BA ₂ Snl ₄	2.62/0.3 s	8
7.	(4-FEPA) ₂ SnI ₄	151 ms	9
8.	(OleylAm) ₂ Snl ₄	910 μs/1.28 ms	This work

References

1 A. Wang, Y. Guo, Z. Zhou, X. Niu, Y. Wang, F. Muhammad, H. Li, T. Zhang, J. Wang, S. Nie and Z. Deng, *Chem. Sci.*, 2019, **10**, 4573–4579.

2 G. T. Shechkov, I. A. Pevneva and O. A. Meshkova, Russ. J. Appl. Chem, 2003, 76, 8.

3 F. Lan, J. Bai and H. Wang, RSC Adv., 2018, 8, 16866–16872.

4 Y. Wang, C. Ji, X. Liu, S. Han, J. Zhang, Z. Sun, A. Khan and J. Luo, *Inorg. Chem. Front.*, 2018,5, 2450-2455.

5 B.-H. Zhu, Z. He, Yao, J.-S. Yao, C. Chen, K.-H. Wang, H.B. Yao, J.-W. Liu, S.H. Yu, *Adv. Opt. Mater.*, 2017, **6**(3), 1701029.

6 L. Qian, Y. Sun, M. Sun, Z. Fang, L. Lin Li, D. Xie, C. Chun Li and L. Liming Ding, *J. Mater. Chem. C*, 2019, **7**, 5353-5358.

7 L. Qian, Y. Sun, M. Wu, C. Li, D. Xie, L. Ding and G. Shi, *Nanoscale*, 2018, **10**, 6837-6843.

8 Y. Yang, H. Zhang, S. Hou, T. Wang, W. Chen, S. Xian, Z. Zhang, Y. Mao, *Appl. Phys. Lett.*, 2021, **119**, 161106.

9 C. Han, Q. Wei, X. Jiang, B. Yao, H. Li, H. Chen, B. Li, P. Fu, W. Zhou and Z. Ning, *ACS Materials Lett.*, 2022, **4**, 5, 987–994.