

Luminescent Tin-Halide Perovskite Materials

Adding an aliphatic carboxylic acid can decrease the defect density of the tin perovskite and thereby improve the luminescent property of tin-halide perovskite nanoplates.

In recent years, the efficiency of power conversion (PCE) of perovskite solar cells (PSC) has increased rapidly up to 22%, which opens a new window for a novel recipe of developing solar cells. Research groups in increasing numbers have therefore devoted much effort to the investigation of PSC, which replace dye-sensitized solar cells (DSSC) and organic photovoltaics (OPV) to become the main stream for the next generation of solar-cell development. Basically, a PSC is a hybrid organic-inorganic material, having an octahedral structure with general formula ABX_3 . In this crystal structure, an A-site ion, at the corners of the unit cell of the lattice, is typically an alkaline-earth or rare-earth element; B-site ions, at the center of the unit cell, might be 3d-, 4d- or/and 5d-transition-metal elements, and X is halogen. The conventional material of a PSC is methylammonium lead trihalide ($MAPbX_3$) having an optical band gap between 1.5–2.3 eV depending on the halide content, but the content of the toxic lead in $MAPbX_3$ hinders the large-scale commercial production for PSC. The task of replacing the toxic lead with a non-toxic metal, such as tin (Sb), for perovskite-based material hence attracts much attention in the development of these PSC. $MASbX_3$ is, however, unstable because of the oxidation of Sn^{2+} to Sn^{4+} that increases the defect density. The control of the luminescent properties of tin perovskite-based nanomaterials was recently successfully demonstrated first by Jellicoe *et al.*¹; they mixed halides of two types and altered the ratios of halide components of the $CsSnX_3$ nanocrystals, but a small photoluminescence quantum yield (PLQY < 0.14%) and a broad emission bandwidth (FWHM > 100 nm) were observed. Subsequent work, such as on replacing Cs^+ cations with butylammonium (BA) or octylammonium and using 2D nanoplates with a double-layered structure were investigated to improve the quantum yield.² Although the photoluminescent quantum yield improved up to 2.6%, the reality of using perovskites as a luminescent emitter is still far away.

To improve the optoelectronic device performance, strongly coupled 2D perovskite nanoplates are required to realize a small density of crystal defects and a large yield of photogenerated carriers. A research group from National Taiwan University led by Ching-Wen Chiu, Hao Ming Chen and Pi-Tai Chou synthesized a 2D single-layered nanoplate with chemical formula PEA_2SnI_4 ($PEA = C_6H_5(CH_2)_2NH_3^+$) that attained PLQY 2.7%, with an emission at 640 nm in toluene.³ Furthermore, adding aliphatic carboxylic acids with one methyl branch at the β -position with PEA effectively prevented the transformation from Sn^{2+} to Sn^{4+} during the nucleation, thereby leading to strongly coupled 2D nanoplates with a defect-free nature to boost the emission quantum yield. They tested numerous aliphatic carboxylic acids and determined 3-methylbutanoic acid to be superior among all tested additives, as it required only 2% by volume in toluene to enhance the emission yield of tin perovskite nanoplates from 2.70% (without additive) to as much as 6.40%.

This group showed also how the absorption and emission spectra of putative PEA_2SnX_4 nanoplates varied with halide composition and optimal 3-methylbutanoic acid content on varying in halide composition as shown in **Fig. 1** and **Table 1**.

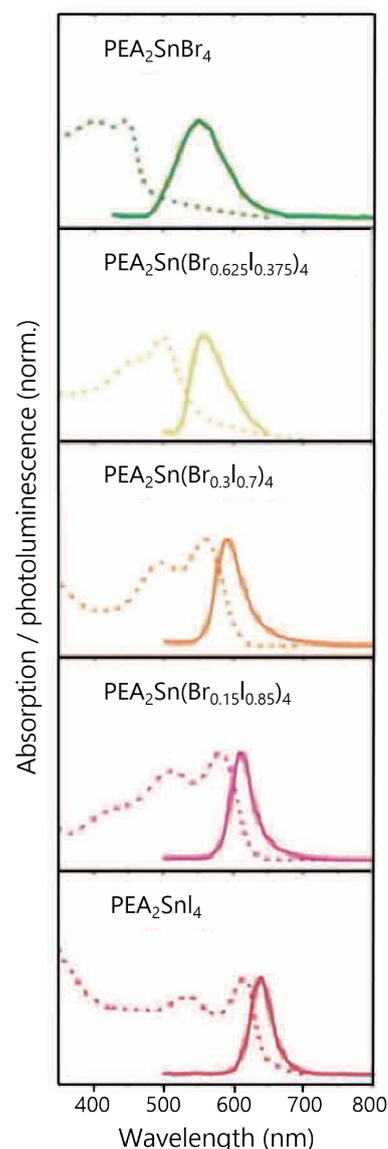


Fig. 1: Absorption (dashed line) and photoluminescence spectra (solid line) of the corresponding PEA_2SnX_4 nanoplates in toluene. [Reproduced from Ref. 3]

Table 1: Photoluminescent properties of mixed-halide tin perovskite nanoplates in toluene (excitation at 400 nm). [Reproduced from Ref. 3]

| Compound | QY/Lifetime, τ_1 , τ_2 , τ_3 [%]/[ns] | FWHM [nm] | Peak [nm] |
|---|--|-----------|-----------|
| PEA ₂ SnI ₄ | 6.40 ± 0.14 (0.10/2.57/17.88) | 36.0 | 640.6 |
| PEA ₂ Sn(Br _{0.15} I _{0.85}) ₄ | 2.19 ± 0.16 (0.09/1.26/9.06) | 36.2 | 610.9 |
| PEA ₂ Sn(Br _{0.3} I _{0.7}) ₄ | 1.03 ± 0.03 (0.12/1.19/8.06) | 44.5 | 590.4 |
| PEA ₂ Sn(Br _{0.625} I _{0.375}) ₄ | 0.36 ± 0.01 (0.15/0.83/5.23) | 56.2 | 557.8 |
| PEA ₂ SnBr ₄ | 0.10 ± 0.01 (-/0.32/2.94) | 79.6 | 550.2 |

The photostability was also significantly improved for PEA₂SnI₄ prepared with 3-methylbutanoic acid. Upon irradiation of PEA₂SnI₄ at 406 nm (10 mW cm⁻²) for 120 h in degassed toluene, the emission intensity decreased only 25% compared to the original value. In contrast, under identical conditions, pristine PEA₂SnI₄ synthesized without added carboxylic acids showed a loss ≈ 77% of the emission intensity. The observed degradation of PEA₂SnI₄ was attributed to the oxidation of Sn²⁺ toward Sn⁴⁺. Taken together, upon mixing iodo- and bromo- precursors, the emission wavelength was successfully tuned from 640 nm (PEA₂SnI₄) to 550 nm (PEA₂SnBr₄), with a corresponding emission quantum yield 0.16–6.40% and FWHM 36–80 nm. The results demonstrate a major advance in the emission yield and tunability of tin-halide perovskites. (Reported by Yu-Jong Wu)

This report features the work of Ching-Wen Chiu, Hao Min Chen, Pi-Tai Chou and their collaborators published in Adv. Mater. 30, 1706592 (2018).

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- X-ray Powder Diffraction
- Materials Science

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A New Series of Tin-Based Perovskite Materials

Hybrid HEA⁺/FA⁺ organic cations can tune the optoelectronic properties and band structures on varying the HEA proportions.

Perovskite solar cells (PSC) possess the advantages of cheap fabrication, versatile configurations and large expected efficiency of power conversion, which lead them to become the most promising next-generation photovoltaic devices.¹ Conventional perovskite materials containing toxic element lead (Pb) have evoked the development of lead-free PSC and become an important issue for future commercialization of PSC. In the same group of the periodic table, tin (Sn) is hence a promising candidate to replace lead in PSC, but a problem of reproducibility was discovered for tin-based PSC in recent tests. Sn²⁺ is readily oxidized to Sn⁴⁺, which increases the density of defects. Previous investigations tried to improve the performance and stability of tin-based devices generally on

varying the B and X components of the typical formula ABX₃, in which A represents site ions on the corners of the lattice, B represents site ions on the center of the lattice and X is halogen.

A research team from National Chiao Tung University recently tried to modify the energy levels by altering A upon mixing two organic cations, formamidinium (FA⁺) and 2-hydroxyethylammonium (HEA⁺), to improve the performance and the stability of a tin-based PSC.² With chemical formula HEA_xFA_{1-x}SnI₃, the authors found that, as x increases, the crystal structure alters from orthorhombic (x = 0) to rhombohedral (x = 0.2–0.4), and then to tetragonal (x = 0.6–1.0), as shown in Fig. 1.