

Room Temperature Synthesis of Lead-Free Stable FASnI₃ Perovskite Nanoparticles

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Abstract— We report a room temperature synthesis of FASnI₃ nanocrystals which exhibited long term stability against oxidization from Sn²⁺ to Sn⁴⁺ because of the thermodynamic stability of this compound. X-ray diffraction peaks were obtained from both precipitates and particles in the supernatant. The XRD spectra taken several times over two months so far show no degradation at all, which is very significant for the Sn-based perovskites. We attribute such a stability to the thermal stability of FA-based Sn-perovskite and to the ligands used that shield the core nanocrystals. The PL measurement showed the PL maximum around 830 nm, which corresponds to an energy of 1.49 eV, which is slightly higher than the band gap of the bulk form of this compound. This could be due to the particle size of the nanocrystals which were around 10 nm according to the images obtained by transmission electron microscopy (TEM) imaging.

Keywords—lead-free perovskites, FASnI₃, room temperature synthesis, Sn-based perovskites, perovskite nano-crystals

I. INTRODUCTION

In recent years, nanostructure halide perovskite materials have become the rising star in the field of electronics and photonics for applications such as solar cells, light emitting diodes, photodetectors, solid-state lasers, and optical cooling systems [1]. The perovskite nanocrystals show tunable optical properties by tailoring the halide composition, stoichiometry, shape and size. As the size of the nanocrystals gets smaller, the quantum confinement effects come into play leading to unique optical properties. The nanocrystals have exhibited bright exciton triple states [2], superfluorescence [3], defect tolerance and enhanced phase stability compared to bulk counterpart [4], [5], versatile surface chemistry and promising performance in devices. Besides, their outstanding photoluminescence quantum yields (PLQY) of up to 100% makes the perovskite nanocrystal materials more attractive [6].

The general chemical formula of metal halide perovskites is ABX₃, where A represents nonbonding univalent cations, which can be organic cations, such as methylammonium (MA: CH₃NH₃⁺), formamidinium (FA: HC(NH₂)₂⁺), or inorganic cation Cs⁺, etc., B-site can be occupied by an octahedrally coordinated bivalent metal ion, and X is monoanionic halide ion Cl, Br, or I. Despite the state-of-the-art Pb-based perovskite-based devices show outstanding performance, the use of toxic Pb raises a significant concern, which may hinder its commercialization prospect. Several lead-free ions have been considered as a replacement of Pb. Sn and Ge are first

candidates because they both fulfill the ion size, coordination, and charge balance prerequisites to form a stable perovskite structure [7]. Tin (Sn)-based perovskites were first explored to replace lead, because Sn possesses more similar radius (110 pm) to Pb (119 pm) than Ge (73 pm), and also Sn-based perovskite showed lower bandgap (1.2-1.4eV) and higher charge carrier mobility (10² to 10³ cm²/V.s) in addition to similar binding energy (2-50 meV) compared to Pb-based perovskites [8], [9]. Based on the properties of bulk materials, MASnI₃ seems to be an optimal compound since it has a similar absorption across the whole visible spectrum with high absorption coefficient and lower charge carrier recombination rate compared to MAPbI₃ [8]. However, MASnI₃ has lower formation energy of Sn vacancy and higher oxidation rate of Sn²⁺ than FASnI₃. On the other hand, although all-inorganic CsSnI₃ perovskite shows better thermal stability than organic-inorganic FASnI₃ and MASnI₃, it is a phase-change material that exhibits four polymorphs. It's in the black orthorhombic phase only at room temperature, whereas for FASnI₃, it has a stable phase over a broad range of temperatures up to 200 °C [8]. Besides, FASnI₃ compound was discovered to exhibit better stability against oxidization from Sn²⁺ to Sn⁴⁺ related to the thermodynamic stability of the corresponding oxidized products [7].

Herein, we demonstrate the synthesis of colloidal FASnI₃ lead-free perovskite nanocrystals at room temperature for the first time. A series of characterizations, which include photoluminescence (PL), UV-VIS, X-ray diffraction (XRD) and Transmission Electron Microscopy (TEM) were used to demonstrate the crystal structure, stability, optical properties, and nanocrystal sizes.

II. EXPERIMENT

A. Synthesis of FASnI₃ perovskite nanocrystal

The colloidal FASnI₃ nanocrystals were fabricated following a modified ligand-assisted reprecipitation (LARP) method in the N₂ filled glove box at room temperature [10]. It is accomplished by preparing precursor solution of FAI and SnI₂ in a “good solvent” N, N-dimethylformamide (DMF) containing ligand oleylamine (OLA), and then, this precursor solution is added dropwise to a vigorously stirred “poor solvent” toluene together with ligand oleic acid (OA). After injection of precursor into the poor solvent, nonequilibrium state of supersaturation reaches, accompanied with the spontaneous precipitation and crystallization reactions until the system goes back to an equilibrium state. Since this process is carried out in the

presence of ligand, the formation of crystals can be controlled down to the nanoscale, allowing for the fabrication of colloidal nanoparticles [11]. After injecting the precursor solution, the reaction happens immediately. The purification of crude solution is carried out by centrifuging at 6000 rpm for 5 min. The precipitate is resuspended in toluene, and the supernatants are separated, and both are stored for characterizations.

B. Characterizations

The crystallographic characterization of the perovskite is performed with X-ray diffraction (XRD) on a PanAnalytical X'Pert PRO X-ray diffraction system which uses CuK α X-rays and a line-focus optics. The photoluminescence (PL) was measured using Horiba's PL measurement system with 532 nm laser and a photo-multiplier tube (PMT) detector. UV-VIS spectra were acquired by an S2 HP 8453 spectrophotometer in the range of 200-1100 nm. The size and shape of the nanoparticles were obtained by transmission electron microscopy (TEM) imaging.

III. RESULTS AND DISCUSSION

A. X-ray Diffraction

In Fig. 1, the XRD peaks indicate that both precipitate and supernatant of FASnI₃ particles exhibit perovskite structure, which crystallize in the orthorhombic structure (Imm2 space group). This is consistent with the literature results for the bulk FASnI₃ material.

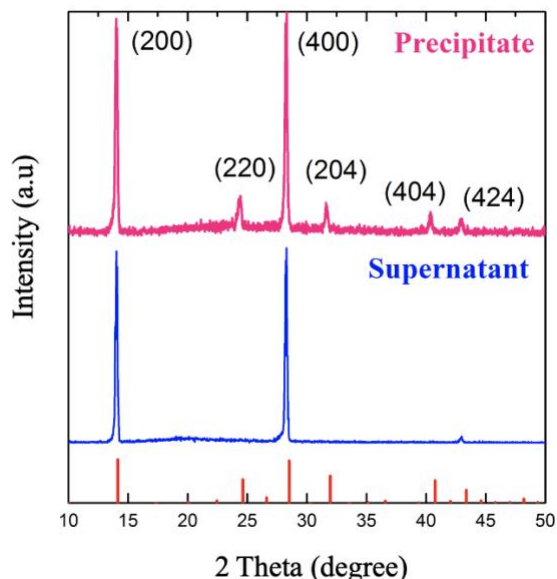


Fig. 1. XRD spectra of precipitate (TOP) and supernatant (Bottom) of FASnI₃ perovskite nanocrystals. The red line is the standard XRD spectrum in PDF # 01-084-2963 of orthorhombic FASnI₃ perovskite.

B. Optical measurements

The absorbance and PL spectra of FASnI₃ supernatant under inert atmosphere revealed optical bandgap of 1.49 eV as shown in Fig. 2. A strong and sharp PL peak was seen at 831 nm with

full width at half maximum (FWHM) < 50 nm. Compared with the bandgap of parent bulk perovskite (1.41eV) [12], the maximum PL peak position is slightly blue shifted, which could be due to quantum confinement effect [13].

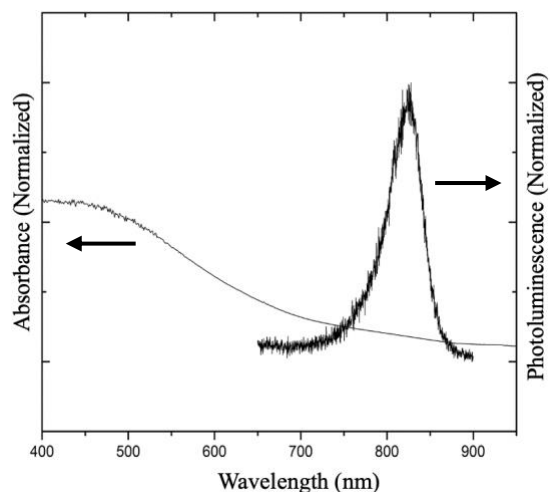


Fig. 2. Absorbance and normalized PL of supernatant of FASnI₃.

C. Stability measurements

The XRD measurements were performed on the nanocrystal thin films several times over a period of more than two months after the first synthesis.

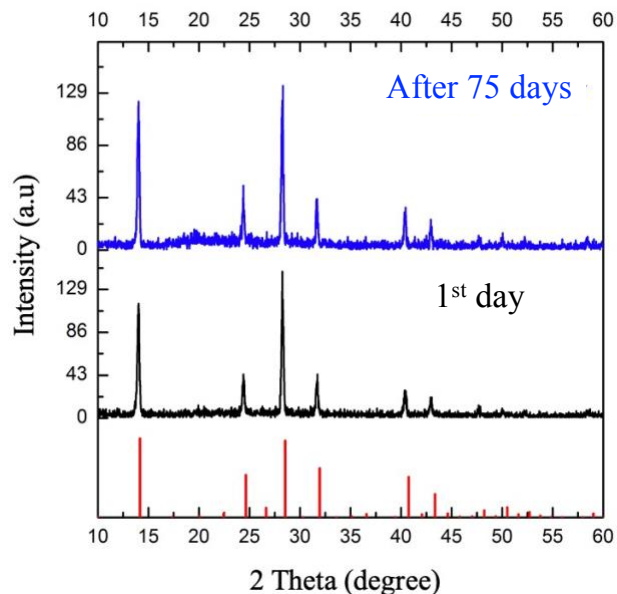


Fig. 3. The XRD peaks of the FASnI₃ nanocrystal films taken 75 days apart

After each XRD measurement, the films were kept in the glove box. The signature peak remained the same even after 75 days as shown Fig. 3 proving that the nanocrystal films are very stable. The XRD scans of the nanocrystal films will continue in the future until they degrade.

D. Nanocrystal Imaging

For comparison, the TEM images (Fig. 4 a and b) were taken of supernatant and corresponding precipitates resuspended in toluene, which showed the size of particles ~ 10 nm or less in both supernatant and precipitate solution, and also demonstrated that the nanoparticles were covered by the ligands. No significant difference was observed between the samples. In the samples containing the precipitates, however, the nanoparticles appeared to be more scattered (see Fig. 4b).

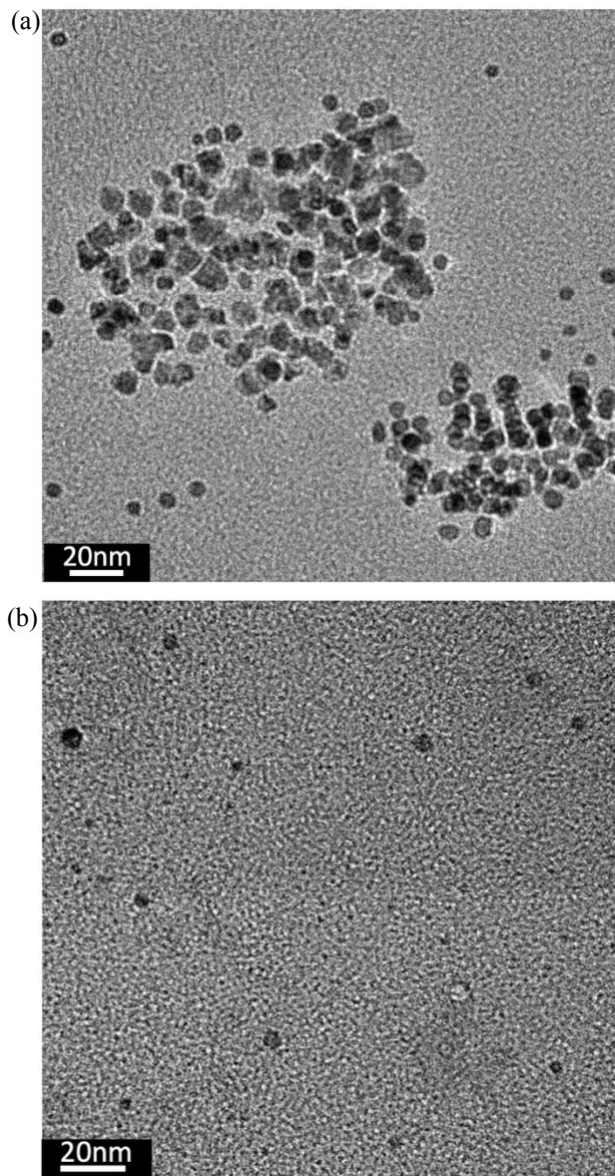


Fig. 4. TEM image of FASnI₃ (a) supernatant and (b) precipitate.

IV. CONCLUSION

We successfully synthesized FASnI₃ nanocrystals by using a simple method known as LARP technique for the first time and confirmed their orthorhombic crystal structure with Imm2 phase. The synthesis of FASnI₃ nanocrystal was carried out at room temperature. The produced FASnI₃ nanocrystals were 10 nm or less in size. The XRD scans taken over two months period

show that the nanocrystals are very stable, which could be due to defect-free crystals and the ligand layer acting as an encapsulant. The nanocrystals showed no degradation at all even after 75 days, which is very significant for a lead-free perovskite. Our work thus provides a new insight into the synthesis of stable Sn-based perovskite at room/low temperature. More work will be done in the future by replacing the iodide partially or completely with bromine and chlorine to achieve nanoparticles with emission in wide wavelength range. In addition, the XRD scans of the fabricated nanocrystal films will continue until they degrade.

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REFERENCES

- [1] A. Jancik Prochazkova *et al.*, "Synthesis conditions influencing formation of MAPbBr₃ perovskite nanoparticles prepared by the ligand-assisted precipitation method," *Sci. Rep.*, vol. 10, no. 1, pp. 1–12, 2020.
- [2] M. A. Becker *et al.*, "Bright triplet excitons in caesium lead halide perovskites," *Nature*, vol. 553, no. 7687, pp. 189–193, Jan. 2018.
- [3] G. Rainò, M. A. Becker, M. I. Bodnarchuk, R. F. Mahrt, M. V. Kovalenko, and T. Stöferle, "Superfluorescence from lead halide perovskite quantum dot superlattices," *Nature*, vol. 563, no. 7733, pp. 671–675, Nov. 2018.
- [4] Q. Fan *et al.*, "Lead-Free Halide Perovskite Nanocrystals: Crystal Structures, Synthesis, Stabilities, and Optical Properties," *Angew. Chemie - Int. Ed.*, vol. 59, no. 3, pp. 1030–1046, 2020.
- [5] Y. Wang, J. Tu, T. Li, C. Tao, X. Deng, and Z. Li, "Convenient preparation of CsSnI₃ quantum dots, excellent stability, and the highest performance of lead-free inorganic perovskite solar cells so far," *J. Mater. Chem. A*, vol. 7, no. 13, pp. 7683–7690, Mar. 2019.
- [6] F. Liu *et al.*, "Highly Luminescent Phase-Stable CsPbI₃ Perovskite Quantum Dots Achieving Near 100% Absolute Photoluminescence Quantum Yield," *ACS Nano*, vol. 11, no. 10, pp. 10373–10383, Oct. 2017.
- [7] W. Ke, C. C. Stoumpos, and M. G. Kanatzidis, "'Unleaded' Perovskites: Status Quo and Future Prospects of Tin-Based Perovskite Solar Cells," *Adv. Mater.*, vol. 31, no. 47, 2019.
- [8] H. Lin *et al.*, "The Low-Dimensional Three-Dimensional Tin Halide Perovskite: Film Characterization and Device Performance," *Energies*, vol. 13, no. 1, p. 2, Dec. 2019.
- [9] M. Wang *et al.*, *Lead-Free Perovskite Materials for Solar Cells*, vol. 13, no. 1. Springer Singapore, 2021.
- [10] Y. Tang, N. Yan, Z. Wang, H. Yuan, Y. Xin, and H. Yin, "Precursor solution volume-dependent ligand-assisted synthesis of CH₃NH₃PbBr₃ perovskite nanocrystals," *J. Alloys Compd.*, vol. 773, pp. 227–233, Jan. 2019.

- [11] J. Shamsi, A. S. Urban, M. Imran, L. De Trizio, and L. Manna, "Metal Halide Perovskite Nanocrystals: Synthesis, Post-Synthesis Modifications, and Their Optical Properties," *Chem. Rev.*, vol. 119, no. 5, pp. 3296–3348, Mar. 2019.
- [12] S. Kahmann *et al.*, "Negative Thermal Quenching in FASnI₃Perovskite Single Crystals and Thin Films," *ACS Energy Lett.*, vol. 5, no. 8, pp. 2512–2519, Aug. 2020.
- [13] J. K. Park, J. H. Heo, B. W. Kim, and S. H. Im, "Synthesis of post-processable metal halide perovskite nanocrystals via modified ligand-assisted re-precipitation method and their applications to self-powered panchromatic photodetectors," *J. Ind. Eng. Chem.*, vol. 92, pp. 167–173, Dec. 2020.