Lead-free perovskite LEDs powered by cyanuric acid

Yuxuan Xiao,[1] Qin Xue,[2] Xiaoke Liu,[3,*] Feng Gao,[3,*] and Guohua Xie[1,*]

[1]The Institute of Flexible Electronics (Future Technologies), Xiamen University, Xiamen 361005, China

[2]Department of Physical Science and Technology, Central China Normal University, Wuhan 430079, China

[3]Department of Physics, Chemistry and Biology, Linköping University, 58183 Linköping, Sweden

*Correspondence: xiaoke.liu@liu.se (X.L.); feng.gao@liu.se (F.G.); ifeghxie@xmu.edu.cn (G.X.)

Received: October 6, 2023; Accepted: December 7, 2023; Published Online: January 2, 2024; https://doi.org/10.1016/j.xinn.2023.100553

Citation: Xiao Y., Xue Q., Liu X., et al., (2024). Lead-free perovskite LEDs powered by cyanuric acid. The Innovation **5(1)**, 100553.

Metal halide perovskites have been considered as one of the emerging light emitters due to their unique properties, e.g., adjustable band gap, high mobility, high photoluminescence quantum yield, low cost, and solution processability.[1,2] However, lead (Pb)-based perovskites can degrade into harmful elemental Pb and Pb^{2+} compounds, which can cause significant damage to the environment and human body.

Tin (Sn) is considered as an ideal substituent element for Pb due to its similar ion radius and valence electron arrangement. However, the electroluminescent performance of Sn-based perovskite light-emitting diodes (PeLEDs) lags far behind that of lead-based PeLEDs. This is mainly because Sn^{2+} features more severe electron delocalization, making it more prone to oxidation.[3,4] After oxidation, Sn^{2+} vacancies would be generated, leading to severe p-doping and further limiting device performance. Therefore, it is challenging to maintain the stability of Sn^{2+} in Sn-based PeLEDs.

TAUTOMERIC CYANURIC ACID

Many attempts and endeavors have been devoted to improving the performance of Sn-based PeLEDs. Sargent's group introduced valeric acid (VA) to $(PEA)_2SnI_4$ (PEA = phenethylammonium). VA showed strong interactions with Sn^{2+}, which slowed down the crystallization process and further effectively improved the morphology of the film. Moreover, VA feasibly protected Sn^{2+} from oxidation during the film formation process.[3] The passivated deep-red PeLEDs reached a maximum external quantum efficiency (EQE) of 5%. In addition, at an initial luminance of 20 cd/m^2, a half-life over 15 h was achieved. Later, Wang et al. found that the formation of defects in Sn-based PeLEDs mainly occured in the initial growth process, confirmed by *in situ* spectroscopy.[4] When adding vitamin B1 to the precursor solution, the rapid aggregation of perovskite grains was inhibited. This reduced luminescence quenching centers during crystal growth, which resulted in high-efficiency near-infrared PeLEDs with a maximum EQE of 8.3%.

From the perspective of the extranuclear electron arrangement, a molecule that could form a strong interaction with Sn^{2+} should be acidic since Sn^{2+} is more stable under acidic conditions. Moreover, molecules with lone-pair electrons tend to coordinate with Sn^{2+}. Based on this concept, Wang and co-workers screened out cyanuric acid (CA), of which the tautomeric dimers and trimers can spontaneously form a quasi-vertical superstructure on the perovskite surface (Figure 1).[5] Interestingly, such a superstructure not only localized the electrons of Sn^{2+} coordinated with CA but also extended to the adjacent Sn^{2+} ions. Eventually, CA hindered the oxidation of Sn^{2+}.

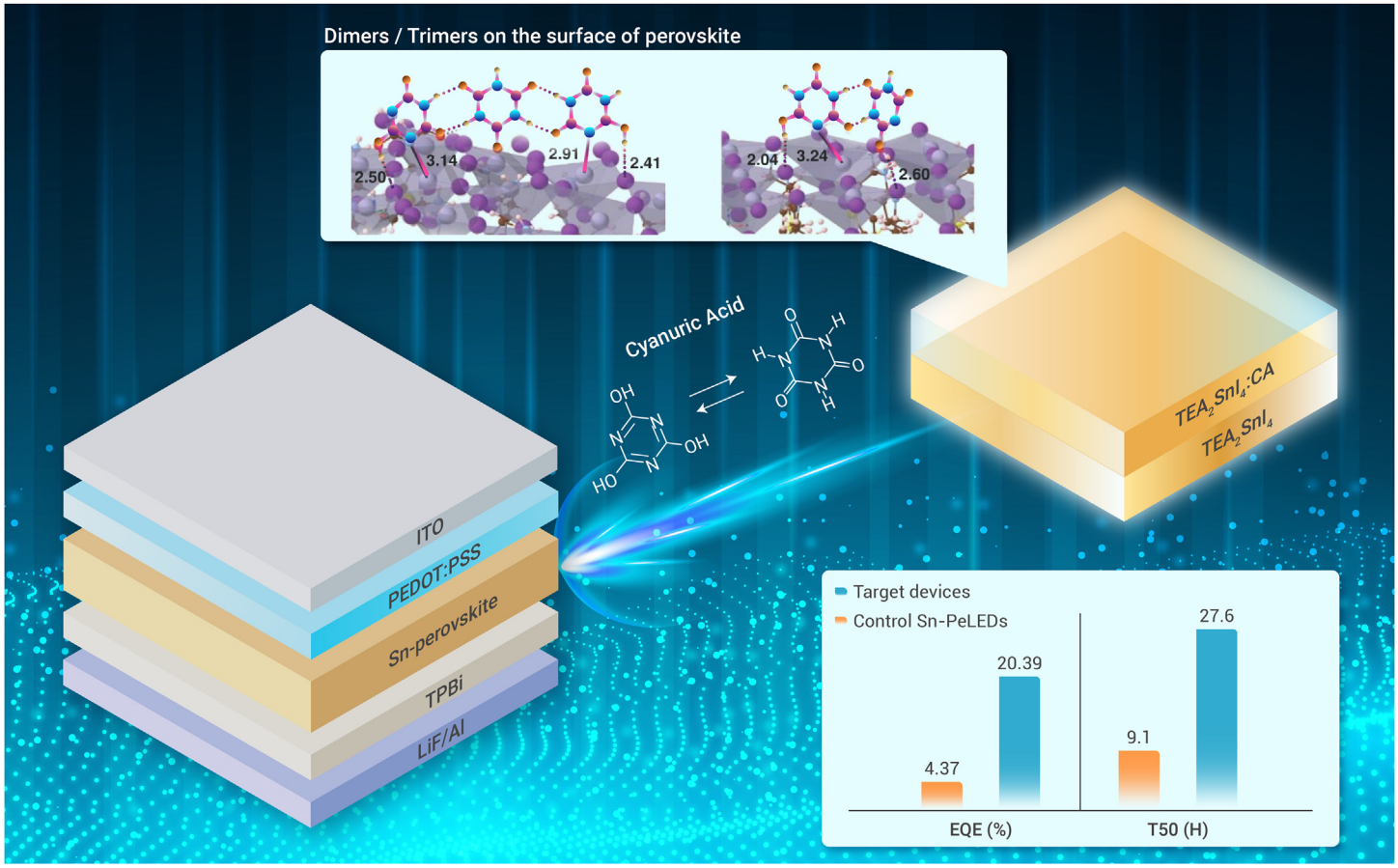

Figure 1. Chemical structure of cyanuric acid and its hydrogen-bonded tautomeric dimer and trimer superstructures as well as the device structure and the electroluminescent performance of Pb-free PeLEDs

PASSIVATION MECHANISM

Firstly, the dimer and trimer superstructures formed by the CA tautomeric mixture can passivate defects on the film surface. Secondly, the functional groups of CA could coordinate with the Sn-based perovskite emitter after the formation of dimer/trimer, which further stabilized the grain boundary and improved the crystal stability. Finally, the coordination energy of the CA tautomeric mixture led to electronic localization around Sn^{2+}, which was beneficial to obtain the more stable and ordered perovskite lattice. These led to the weaker adverse effect of Anderson localization and thus reduced the non-radiative recombination of the passivated TEA_2SnI_4 (TEA = 2-thiophenethylammonium) film by two orders of magnitude and simultaneously doubled the exciton binding energy.

DEVICE PERFORMANCE

The ultraviolet electron spectroscopy measurement showed that the Sn-based perovskite emitter with CA possessed the better energy-level alignment with the electron and hole transport layers, which was conducive to charge injection and transport. The Pb-free perovskite TEA_2SnI_4 with CA was employed to make PeLEDs (see Figure 1), which showed a narrower bandwidth of 24.9 nm and a considerably high EQE of 20.29%. This result is comparable with the state-of-the-art Pb-based PeLEDs. Moreover, the lifetime of the device at an initial luminance of ca. 30 cd/m^2 reached 27.6 h, which was three times higher than that of the control device (9.1 h). It is worth noting that this strategy could be extended to the other quasi-2D and 3D Pb-free perovskite systems.

CONCLUDING REMARKS

The interactions between tautomeric mixture and Sn induced electron localization in a quasi-2D Sn-based perovskite emitter and spontaneously formed the vertical tautomeric dimer and trimer superstructures on the perovskite surface. This amplified the electronic effects even for Sn atoms without strong bonding with CA but avoided the adverse effects caused by Anderson localization. Instead of focusing on Sn supplements and antioxidants, more attention should be paid to the oxidation principle and electronic structures of Sn-based perovskite emitters. This will inspire the molecular designs and device engineering for improving the electroluminescence of Sn-based perovskite emitters. The improvement of the chemical stability of the Sn-based perovskites guarantees the possible practical applications in LEDs, solar cells, and detectors. To overcome Sn oxidation, the following issues should be feasibly addressed: (1) analogs or similar molecules to CA with strong interactions with Sn to inhibit Sn oxidation are urgently required, (2) the fast crystallization of Sn-based perovskites should be well managed to reduce the defects, and (3) cost-effective surface and bulk passivation should be implemented to improve charge-carrier transport and radiative recombination. Alongside band-gap manipulation, more stable and efficient Sn-based PeLEDs can be anticipated.

REFERENCES

1. Cao, Y., Wang, N., Tian, H., et al. (2018). Perovskite light-emitting diodes based on spontaneously formed submicrometre-scale structures. Nature ***562***, 249–253.
2. Luo, J., Wang, X., Li, S., et al. (2018). Efficient and stable emission of warm-white light from lead-free halide double perovskites. Nature ***563***, 541–545.
3. Yuan, F., Zheng, X., Johnston, A., et al. (2020). Color-pure red light-emitting diodes based on two-dimensional lead-free perovskites. Sci. Adv. ***6***, eabb0253.
4. Min, H., Chang, J., Tong, Y., et al. (2023). Additive treatment yields high-performance lead-free perovskite light-emitting diodes. Nat. Photon. ***17***, 755–760.
5. Han, D., Wang, J., Agosta, L., et al. (2023). Tautomeric mixture coordination enables efficient lead-free perovskites LEDs. Nature ***622***, 493–498.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (nos. 52373195 and 62175189). G.X. acknowledges the funding support from the Opening Project of Key Laboratory of Optoelectronic Chemical Materials and Devices, Ministry of Education, Jianghan University (no. JDGD-202301), and the joint China-Sweden Mobility Program (no. 52211530052).

DECLARATION OF INTERESTS

The authors declare no competing interests.