

Energy Spotlight

Halide Perovskites Continue to Shine Brightly

Cite This: *ACS Energy Lett.* 2021, 6, 2635–2637

Read Online

ACCESS |

Metrics & More

Article Recommendations

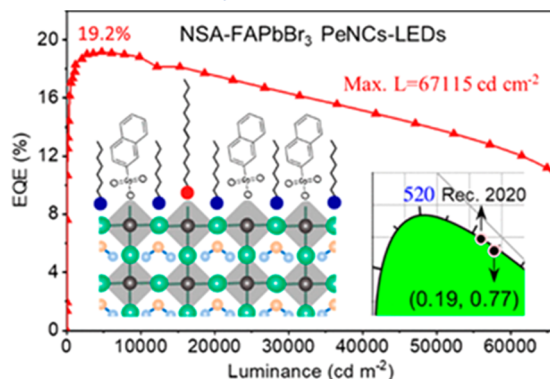
Four articles recently published in *ACS Energy Letters* are featured in this Energy Spotlight. These highlights include bright light-emitting diodes based on FAPbBr₃ perovskite nanocrystals, an ACS Editors' Choice Article of this month (highlighted by Tae-Woo Lee); reversible p-doping of CsPbBr₃ nanocrystals via electrochemical hole injection (highlighted by Csaba Janáky); and managing surface defects to improve the perovskite solar cell performance (highlighted by Filippo De Angelis). These and other articles included in this issue provide exciting new advances in energy conversion and storage processes.

■ HIGH-BRIGHTNESS PEROVSKITE LIGHT-EMITTING DIODES BASED ON FAPbBr₃ NANOCRYSTALS WITH RATIONALLY DESIGNED AROMATIC LIGANDS

Haifeng Zhao, Hongting Chen, Sai Bai*, Chaoyang Kuang, Xiyu Luo, Pengpeng Teng, Chunyang Yin, Peng Zeng, Lintao Hou, Ying Yang, Lian Duan, Feng Gao*, and Mingzhen Liu*

ACS Energy Lett. 2021, 6 (7), 2395–2403 (ACS Editors' Choice Letter)

DOI: 10.1021/acsenerylett.1c00812



Light-emitting diodes (LEDs) using metal halide perovskite nanocrystals (PNCs) are of great interest because they provide high color-purity and external quantum efficiencies (EQEs). However, they suffer from poorer charge injection/transport characteristics compared with the LEDs using perovskite polycrystalline films because the long insulating organic ligands can impede the charge injection/transport for efficient electron–hole recombination in the PNCs. To overcome this problem in PNC LEDs, researchers of the typical skill in the

field have tried to perform ligand engineering in order to exchange the conventional insulating long alkyl ligands (i.e., oleic acid) with a short ligand that surrounds the PNCs. These postsynthesis ligand treatment strategies have been very critical because they can affect the ligand binding properties significantly because of highly dynamic ligand binding properties on PNCs that have an ionic crystal nature. Therefore, ligand exchange approaches with a short ligand that improve the charge injection/transport and stabilize the ligand binding with PNCs at the same time could be ideal for achieving bright, efficient, and stable PNC LEDs.

Gao, Liu, and co-workers report a promising ligand exchange strategy that uses a short aromatic sulfonic acid (i.e., 2-naphthalenesulfonic acid (NSA)) in FAPbBr₃ PNCs instead of an insulating, nonaromatic carboxylic acid ligand (i.e., oleic acid), and they finally achieved high brightness (~67115 cdm⁻²) and high EQE (19.2%) in pure green (532 nm) PNC LEDs whose Commission Internationale de l'Éclairage (CIE) coordinate of (0.19, 0.77) is very close to that of the Rec. 2020 green primary color.

First, the NSA molecules improve the colloidal stability and photoluminescence quantum yield (93%) of PNC dispersions because (1) they can bind with the uncoordinated Pb atoms in PNCs and passivate the surface defects, (2) the ligand compensation is more effective than oleic acid when the ligands are desorbed from the surface of PNCs during purification process, and (3) NSA can have stronger interaction with PNCs than oleic acid.

In addition, PNCs capped with an NSA ligand shell provide an assembled light-emitting layer which possesses much better charge transport characteristics than the films of PNCs capped with oleic acid because the ligand is short and the aromatic nature enables strong electron resonance delocalization at the surface of PNCs.

This work on a ligand engineering strategy using a short aromatic acid may be useful in providing insights for developing efficient and stable PNCs and may also be useful

Received: June 25, 2021

Accepted: June 25, 2021

for other optoelectronic devices such as solar cells and photodetectors.

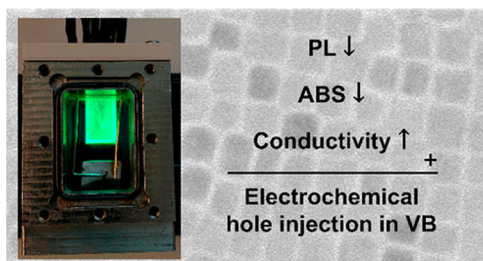
Tae-Woo Lee

■ ELECTROCHEMICAL p-DOPING OF CsPbBr₃ PEROVSKITE NANOCRYSTALS

Jence T. Mulder, Indy du Fossé, Maryam Alimoradi Jazi, Liberato Manna, and Arjan J. Houtepen*

ACS Energy Lett. 2021, 6 (7), 2519–2525

DOI: 10.1021/acsenerylett.1c00970 (Letter)



In most of the optoelectronic studies on lead halide perovskites, light excitation is solely responsible for charge carrier generation. This always results in an equal density of electrons and holes, which means that it is difficult to establish the contribution of electron- or hole-injection selectively. In contrast, upon employing electrochemical charge carrier injection, the effect of one type of charge carrier (i.e., electron or hole) on the materials properties can be probed selectively. Despite the technical difficulties (e.g., sensitivity to most commonly applied solvents and corrosion), electrochemical studies on lead halide perovskites are gaining momentum.

Using spectroelectrochemistry and electrochemical transistor measurements, Houtepen et al. demonstrate in their new study that CsPbBr₃ nanocrystals can be successfully and reversibly p-doped via electrochemical hole injection. They have presented how the emission quenches, how the band edge absorbance bleaches, and how the electronic conductivity quickly increases upon electrochemical hole-injection into the valence band. Contrastingly, n-doping was not possible because of the facile reduction of Pb²⁺ ions. By combining experimental results with DFT calculations, it was also shown that the stability of the p-doped material is limited because of Br⁻ oxidation. An especially notable feature is that the authors use a cross-linking agent (1,8-octanedithiol) to adhere the CsPbBr₃ nanocrystals on interdigitated electrode surfaces. With this method, the nanocrystalline/nanoparticulate nature of the perovskite is preserved even after the electrode preparation. Importantly, the electrodes prepared in this manner retain the luminescent properties of the perovskite nanocrystals, which allows the investigation of the effects of charge injection (p, n-doping) on the spectroelectrochemical properties of nanocrystalline CsPbBr₃. The authors found stark differences among samples prepared with different synthesis methods: in some cases a sequence of degradation processes occurs instead of p-doping. This highlights the importance of surface termination in perovskite nanocrystal-derived electrodes.

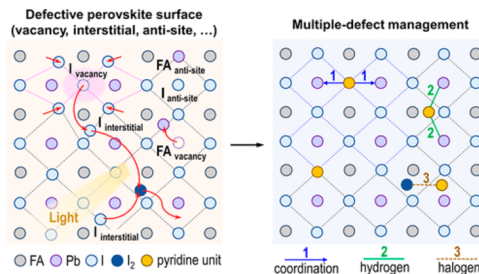
Csaba Janáky

■ MULTIPLE-DEFECT MANAGEMENT FOR EFFICIENT PEROVSKITE PHOTOVOLTAICS

Xiaoyu Yang*, Yue Ni, Yuzhuo Zhang, Yanju Wang, Wenqiang Yang, Deying Luo, Yongguang Tu, Qihuang Gong, Haifeng Yu*, and Rui Zhu*

ACS Energy Lett. 2021, 6 (7), 2404–2412

DOI: 10.1021/acsenerylett.1c01039 (Letter)



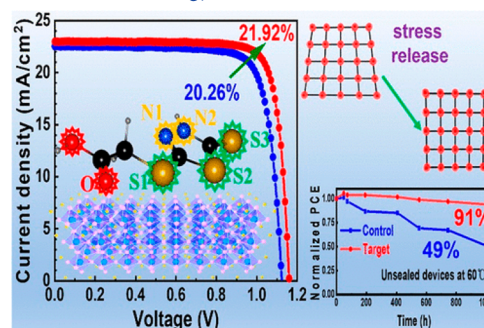
and

■ INTERFACIAL DEFECT PASSIVATION AND STRESS RELEASE VIA MULTI-ACTIVE-SITE LIGAND ANCHORING ENABLES EFFICIENT AND STABLE METHYLAMMONIUM-FREE PEROVSKITE SOLAR CELLS

Baibai Liu, Huan Bi, Dongmei He, Le Bai, Wenqi Wang, Hongkuan Yuan, Qunliang Song, Pengyu Su, Zhigang Zang, Tingwei Zhou*, and Jiangzhao Chen*

ACS Energy Lett. 2021, 6 (7), 2526–2538 (Letter)

DOI: 10.1021/acsenerylett.1c00794



Metal-halide perovskites (MHPs) have long been considered to be defect-tolerant (if not defect-free) semiconductors because of the resilient material behavior toward imperfections in polycrystalline thin films made by solution-based techniques.

As the material and thin-film quality improved and the associated device efficiency increased, however, it became apparent that defects acting as trap states could limit both device performance and material stability. Referring to the most commonly employed lead-iodide perovskites, it was discovered that despite a relatively high defect density ($\sim 10^{14}$ cm⁻³) the apparent perovskite defect tolerance was indeed due to the peculiar iodine photoelectrochemistry leading to asymmetric electron/hole trapping and detrapping dynamics associated with long-lived trapped charges.¹ While the latter are relatively harmless to carrier dynamics (once filled they stay filled for a long time, not able to capture additional carriers), it also became apparent that the long-lived traps could promote photochemical transformations, eventually leading to molecular iodine release and thin-film degradation.²

Theoretical and experimental investigation revealed the nature of trapping defects in MHPs, which, as mentioned above, are mainly related to iodine interstitials and vacancies


and lead vacancies.¹ It also became apparent that defects mainly occurred at the surface and grain boundaries in polycrystalline MHPs film.^{3,4} In particular, surface and grain boundary-located undercoordinated lead ions were found to be defect nucleation sites.² Identification of this feature paved the way to efficient defect passivation strategies by employing Pb-coordinating ligands or optimized transporting materials functionalized by Pb-binding moieties. The multiple and sometimes complementary nature of MHPs defects, however, requires more than one type of defect or site being tackled at the same time.

In this spirit, Liu et al.⁵ employ a tailored Lewis base ligand endowed with functional N-, S-, and O-binding groups which, by a combination of theory and experiments, is shown to effectively achieve multisite passivation of MHP surface and grain boundaries and to release the associated surface stress leading to increased solar cell efficiency, due to efficient trap passivation, and long-term stability, due to inhibited trap photochemistry, in nonencapsulated devices.

Similarly, Yang et al.⁶ employ a Lewis base pyridine-containing polymeric agent which is able to achieve efficient multiple defect passivation by concomitant Pb-coordination, hydrogen bond and halogen bond, the latter suppressing molecular iodine release from the perovskite film. As a result of multisite/multibond defect passivation, high-efficiency solar cells are obtained (>23%) and long-term stability is achieved in nonencapsulated devices which retain significant performance after thousands of hours of aging in ambient conditions.

Filippo De Angelis

Tae-Woo Lee  orcid.org/0000-0002-6449-6725

Csaba Janáky, EAB, *ACS Energy Letters*  orcid.org/0000-0001-5965-5173

Filippo De Angelis, Senior Editor, *ACS Energy Letters*  orcid.org/0000-0003-3833-1975

Stress Release via Multi-Active-Site Ligand Anchoring Enables Efficient and Stable Methyammonium-Free Perovskite Solar Cells. *ACS Energy Lett.* 2021, 6, 2526.

AUTHOR INFORMATION

Complete contact information is available at:
<https://pubs.acs.org/10.1021/acsenerylett.1c01321>

Notes

Views expressed in this Energy Focus are those of the authors and not necessarily the views of the ACS.
The authors declare no competing financial interest.

REFERENCES

- (1) Meggiolaro, D.; Motti, S.; Mosconi, E.; Barker, A.; Ball, J.; Perini, C. A. R.; Deschler, F.; Petrozza, A.; De Angelis, F. Iodine chemistry determines the defect tolerance of lead-halide perovskites. *Energy Environ. Sci.* 2018, 11, 702–713.
- (2) Motti, S. G.; Meggiolaro, D.; Barker, A. J.; Mosconi, E.; Perini, C. A. R.; Ball, J. M.; Gandini, M.; Kim, M.; De Angelis, F.; Petrozza, A. Controlling competing photochemical reactions stabilizes perovskite solar cells. *Nat. Photonics* 2019, 13, 532–539.
- (3) Meggiolaro, D.; Mosconi, E.; De Angelis, F. Formation of Surface Defects Dominates Ion Migration in Lead-Halide Perovskites. *ACS Energy Lett.* 2019, 4, 779–785.
- (4) Park, J.-S.; Calbo, J.; Jung, Y.-K.; Whalley, L. D.; Walsh, A. Accumulation of Deep Traps at Grain Boundaries in Halide Perovskites. *ACS Energy Lett.* 2019, 4, 1321–1327.
- (5) Yang, X.; Ni, Y.; Zhang, Y.; Wang, Y.; Yang, W.; Luo, D.; Tu, Y.; Gong, Q.; Yu, H.; Zhu, R. Multiple-Defect Management for Efficient Perovskite Photovoltaics. *ACS Energy Lett.* 2021, 6, 2404.
- (6) Liu, B.; Bi, H.; He, D.; Bai, L.; Wang, W.; Yuan, H.; Song, Q.; Su, P.; Zang, Z.; Zhou, T.; Chen, J. Interfacial Defect Passivation and