

**Федеральное государственное бюджетное
образовательное учреждение высшего образования
«Московский государственный университет имени М.В. Ломоносова»**



**Сборник тезисов докладов
I МОСКОВСКОЙ ОСЕННЕЙ МЕЖДУНАРОДНОЙ
КОНФЕРЕНЦИИ ПО ПЕРОВСКИТНОЙ ФОТОВОЛЬТАИКЕ
(MAPPIC-2019)**

14-15 октября 2019 года

г. Москва

Lomonosov Moscow State University



Moscow Autumn Perovskite Photovoltaics

International Conference

(MAPPIC-2019)

Book of abstracts

October 14-15, 2019

Moscow, Russia

ОРГАНИЗАТОРЫ



**МГУ имени
М.В. Ломоносова**



**Факультет наук о
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**Конференция проводится при финансовой поддержке РФФ
(проект № 19-73-30022)**

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Функциональные материалы на основе гибридных перовскитов в последнее десятилетие привлекают внимание научного сообщества благодаря своим уникальным физическим свойствам и огромному потенциалу для применения в солнечных элементах, светодиодах, фотодетекторах и материалах для генерации лазерного излучения.

МАРРИС-2019 – международная конференция, организованная МГУ имени М.В. Ломоносова (Факультет наук о материалах, Лаборатория новых материалов для солнечной энергетики). Основными задачами конференции являются установление контактов и обмен опытом между промышленностью, исследовательскими институтами и молодыми исследователями, работающими в области современных фотоэлектрических и светоизлучающих материалов.

В рамках конференции выступили с пленарными докладами ведущие ученые в области солнечной энергетики:



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I Московской осенней международной конференции по перовскитной фотовольтаике (MAPPIC-2019). – М.: «КДУ», «Добросвет», 2019. – 51 с. – doi: 10.31453/kdu.ru.91304.0073.

ISBN 978-5-7913-1112-1

В сборнике напечатаны тезисы докладов участников I МОСКОВСКОЙ ОСЕННЕЙ МЕЖДУНАРОДНОЙ КОНФЕРЕНЦИИ ПО ПЕРОВСКИТНОЙ ФОТОВОЛЬТАИКЕ (MAPPIC-2019) (14-15 октября 2019 года). Тезисы приведены в редакции авторов.

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факультет наук о материалах
МГУ имени М.В. Ломоносова, 2019.

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Полиiodовисмутаты гидроксипиперидинов

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В настоящее время для создания фотоэлементов активно применяются гибридные йодоплюмбаты, обладающие структурой перовскита [1]. Тем не менее, ведется поиск других соединений, которые можно также использовать в солнечных батареях без существенной потери эффективности. В качестве таких альтернативных соединений интерес исследователей привлекали гибридные йодиды висмута (III), основным структурным блоком анионной подструктуры которых являются октаэдры BiI_6 . Как правило, в йодовисмутатах ширина запрещенной зоны составляет 1.8-2.2 эВ [1,2]. Однако было показано, что увеличение количества слабых контактов, таких как $\text{N-H}\cdots\text{I}$, $\text{O-H}\cdots\text{I}$ или $\text{I}\cdots\text{I}$, и/или встраивание дополнительных мостиковых элементов, вроде молекул I_2 , позволяет уменьшить ширину запрещенной зоны до 1.2 эВ [3].

Наша работа связана с изучением систем, в которых можно ожидать образования большого количества слабых межмолекулярных взаимодействий между катионной и анионной подструктурами, а также с получением соединений, содержащих дополнительные связи между элементами анионной подструктуры посредством I_2 или I_3^- . Гидроксипроизводные пиперидина представляют интерес с точки зрения образования связей $\text{O-H}\cdots\text{I}$ и $\text{N-H}\cdots\text{I}$. Было получено четыре новых соединения, два из которых являются йодовисмутатами 3- и 4-гидроксипиперидиниев и два – полиiodиды данных катионов. Для йодовисмутата 3-гидроксипиперидина анионной подструктура сформирована анионами $[\text{Bi}_2\text{I}_9]^{3-}$, связанными мостиковыми I_2 с образованием бесконечных цепей, в случае 4-гидроксипиперидина в структуре присутствуют октаэдры BiI_6^{3-} и молекулы I_2 . Полученные образцы были охарактеризованы методами РФА РСА и КР. Наличие мостиковых молекул I_2 подтверждено КР спектроскопией.

Данная работа выполнена при поддержке гранта РФФИ №19-73-30022.

Литература

- [1] N.A. Yelovik, A.V. Mironov, M.A. Bykov, A.N. Kuznetsov, A.V. Grigorieva, Z. Wei, E.V. Dikarev, A.V. Shevelkov, *Inorg. Chem.*, 55(9), (2016), 4132-4140.
- [2] T. Li, Y. Hu, C. A. Morrison, W. Wu, H. Han, N. Robertson, *Sustainable Energy & Fuels*, 1, (2017), 308-316.
- [3] Т.А. Шестимерова, N.A. Golubev, N.A. Yelavik, M.A. Bykov, A.V. Grigorieva, Z. Wei, E.V. Dikarev, A.V. Shevelkov, *Crystal Growth & Design*, 18(4), (2018), 2572-2578.

Исследование влияния технологических особенностей синтеза на фотолюминесцентные свойства галоидных перовскитных нанокристаллов

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За последние несколько лет гибридные органо-металлические перовскитные материалы на основе галогенидов свинца привлекли широкое внимание исследователей ввиду превосходных фотофизических характеристик. Недавно, были продемонстрированы лабораторные образцы перовскитных солнечных элементов с КПД, превышающим 23%. Помимо этого, активно проводятся исследования по использованию галоидных перовскитных квантовых точек и пленок в качестве активного слоя в светоизлучающих устройствах. В работах исследователей сообщалось о достижении значения квантового выхода светодиодов на основе перовскитных слоев, превышающего 20% [1]. Однако, использование перовскитных материалов до сих пор ограничено из-за постепенной деградации вне инертной атмосферы (присутствие влаги в окружающей среде). Помимо этого, квантовый выход фотолюминесценции перовскитных квантовых точек, содержащих анионы хлора, сильно уменьшается из-за появления дефектных состояний внутри запрещенной зоны, и как следствие, приводит к наличию безызлучательных переходов.

В работе исследуется возможность перестройки длины волны фотолюминесценции органо-неорганических перовскитных квантовых точек системы «метиламмоний-свинец-бром» путем манипуляции технологических параметров синтеза материалов. Синтез перовскитных квантовых точек произведен согласно протоколу, изложенному ранее [2]. Отличием являлось то, что в процессе синтеза изменялось количество поверхностно-активного вещества - октиламина. Изменение объема лигандов от 20 до 80 мкл (шаг 20 мкл) приводило к формированию нанокристаллов, в которых наблюдалась перестройка длины волны фотолюминесценции в коротковолновую область (при увеличении концентрации октиламина). Так, для объема добавляемых лигандов в 20 мкл, длина волны составила 528 нм, для 40 мкл – 482 нм, для 60 мкл – 474 нм, для 80 мкл – 471 нм. Изменение длины волны связано с модификацией формы нанокристаллов: увеличение количества лигандов приводит к формированию различных квантово-размерных структур – квантовых точек, квантовых нитей или квантовых ям. В спектрах поглощения, при увеличении концентрации лигандов, более отчетливо наблюдаются экситонные состояния.

Таким образом, в работе продемонстрирована возможность изменения длины волны фотолюминесценции перовскитных нанокристаллов системы «метиламмоний-свинец-бром». Необходимо отметить, что с повышением количества лигандов уменьшается стабильность нанокристаллов и, соответственно, происходит постепенная деградация квантовых точек. Данную проблему возможно решить, если подобрать оптимальные режимы очистки нанокристаллов от избыточного количества лигандов и прочих полярных растворителей, присутствующих в растворах.

Литература

1. Lin K. et al. Perovskite light-emitting diodes with external quantum efficiency exceeding 20 per cent //Nature. – 2018. – Т. 562. – №. 7726. – С. 245.
2. Zhang F. et al. Brightly luminescent and color-tunable colloidal CH₃NH₃PbX₃ (X= Br, I, Cl) quantum dots: potential alternatives for display technology //ACS nano. – 2015. – Т. 9. – №. 4. – С. 4533-4542.

Исследования Дубненской физико-химической научной школы в области гибридной органо-неорганической перовскитной фотовольтаики

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В докладе дается обзор проводимых Дубненской физико-химической научной школой исследований в области гибридной органо-неорганической перовскитной фотовольтаики. В двух монографиях опубликованы главы, посвященные современным проблемам перовскитной фотовольтаики и дан прогноз наиболее перспективных направлений исследований в этой области [1, 2]. Признано, что при создании фотоэлектрических преобразователей на основе гибридных органо-неорганических перовскитов с уникальными физическими свойствами, важно обеспечить разработку устойчивых неорганических р-буферных слоев, отказавшись при этом от фотодеградируемых органических материалов. Другим важным направлением является отказ от дорогостоящих электродных материалов (золото, серебро и др.) в пользу дешевых углеродных материалов. При этом необходимо обратить внимание на возможность создания перовскитных солнечных элементов без специально вводимых р-буферных слоев, что существенно упрощает архитектуру, удешевляет гибридные органо-неорганические перовскитные солнечные элементы и увеличивает перспективы их широкого практического использования. В связи с этим в экспериментальных исследованиях помимо исследования различных методов формирования органо-неорганических перовскитных пленок и n-буферных слоев основное внимание было уделено совершенствованию методов синтеза и исследованию свойств р-буферных неорганических пленок закиси меди Cu_2O , тиоционата меди CuSCN и йодида меди CuI , а также исследованию перовскитных солнечных элементов с углеродными анодами без р-буферных слоев. Учитывая важность и огромный потенциал для применения в солнечных элементах и других устройствах высокоэффективных перовскитных систем целесообразно создать российскую программу, координирующую проведения исследований перовскитных и других вспомогательных материалов для данных фотовольтаических систем.

Литература

1. Perovskite Solar Cells: Properties, Application and Efficiency Series: Renewable Energy: Research, Development and Policies Murali Banavoth, PhD (Editor) 2019 Nova Science Publishers Inc.
Chapter 1. Hybrid Organo-Inorganic Perovskite Solar Cells: Architecture Evolution, Materials of Functional Layers, Photoelectric Characteristics, Properties, and Efficiency P.P. Gladyshev, M. Banavoth, T. Swetha, N. Bingwa, Ya.B. Martynov, T.Yu. Zelenyak, V.A. Kinev and R.G. Nazmitdinov
Chapter 3. Perovskite: Material and Device Optimization for Solar Cell Applications Antonio Frontera, Yaroslav Martynov, Rashid Nazmitdinov and Andreu Moïa-Pol,
2. Органические и гибридные наноматериалы: получение и перспективы применения: Монография / под редакцией В.Ф. Разумова и М.В. Ключева.- Иваново : Иван. Гос. ун-т, 2015. – 676 с.
Глава 10. Гибридные органо-неорганические перовскитные структуры и фотоэлектрические преобразователи на их основе: физические и химические проблемы, Гладышев П.П., Юшанхай В.Ю., Сюракшина Л.А. с. 426 – 556.

Дырочно-проводящие материалы на основе оксида меди (I) для перовскитных солнечных ячеек

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Использование неорганического дырочно-проводящего буферного слоя на основе Cu_2O в органо-неорганических перовскитных фотоэлектрических преобразователях (ФЭП) позволяет снизить стоимость ФЭП и улучшить его эксплуатационные характеристики. Прекурсоры этого материала доступны, а наноструктурированные покрытия оксида меди получают по простой технологии и не подвергаются деструкции под влиянием внешней среды. Cu_2O – устойчивое соединение обладающие высоким коэффициентом поглощения ($\alpha \sim 10^5 \text{ см}^{-1}$), широким спектром поглощения (от УФ до ближнего ИК диапазона) [1] и высокой подвижностью дырок ($1\text{--}10 \text{ см}^2/\text{В}\cdot\text{с}$) [2]. Методом жидкофазного ионного наслаивания SILAR были сформированы слои оксида меди (I) на проводящих стеклянных подложках (стекло/FTO) и проведены исследования их оптических свойств. Для синтеза тонких пленок оксида меди (Cu_2O) использовалось взаимодействие комплексной соли $3\text{Cu}_2\text{S}_2\text{O}_3 \times 2\text{Na}_2\text{S}_2\text{O}_3$ и 1М NaOH. Количество циклов ионного наслаивания составило 3 и 6. Полученные пленки имели желтый цвет. Измерение спектров поглощения полученных образцов проводились при комнатной температуре на спектрофотометре УФ (190–1100 нм). Было установлено, что с увеличением количества циклов ионного наслаивания растет оптическая плотность пленки, но при этом количество циклов не влияет на вид спектра (рис.1). При помощи формулы Планка рассчитывалась ширина запрещенной зоны E_g , которая составила 2,17 – 2,2 эВ в зависимости от количества циклов.

Литература

1. Кудряшов Д. А. и др. Наноразмерные пленки Cu_2O : формирование методом ВЧ-магнетронного распыления, исследование структурных и оптических свойств //Физика и техника полупроводников. – 2017. – Т. 51. – №. 1. – С. 111-115.
2. Chen, L.-C. (2013). Review of preparation and optoelectronic characteristics of Cu_2O -based solar cells with nanostructure. *Materials Science in Semiconductor Processing*, 16(5), 1172–1185. doi:10.1016/j.mssp.2012.12.028

Синтез и исследование неорганических буферных слоев CuI, CuSCN для перовскитных фотоэлектрических преобразователей

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В настоящее время активно исследуются солнечные элементы на основе гибридных органо-неорганических перовскитов. Эти материалы имеют потенциал, чтобы быть идеальными для недорогих и высокоэффективных солнечных элементов [1]. Однако для эффективной работы солнечных элементов необходимо подобрать оптимальные буферные слои.

Наиболее часто используемым материалом для транспортировки дырок в перовскитных солнечных элементах является *spiro*-OMeTAD (КПД свыше 22% [2]). Однако его стоимость остается, высокой в основном из-за его длительного и сложного синтеза, к тому же он не стоек к различным внешним воздействиям. Поэтому стало необходимым разработать более экономичные альтернативы *spiro*-OMeTAD, такие как неорганические буферные материалы CuI и CuSCN [3]. В связи с неорганической природой данных соединений, они обладают высокой стойкостью и низкой стоимостью синтеза. При этом перовскитные солнечные элементы с неорганическими буферными слоями показывают достаточно хорошую эффективность [4].

В рамках данной работы были синтезированы тонкие пленки неорганических дырочно-проводящих буферных слоев CuSCN и CuI различными мокрыми методами на стеклянных подложках. При этом предпочтение было отдано методам спин-коатинга и спрей-пиролиза. Полученные тонкие пленки CuI и CuSCN были охарактеризованы методами спектrophотометрии и профилометрии. На основании исследований спектральных характеристик тонких пленок были выявлены основные закономерности светопоглощения пленок CuI и CuSCN. Из спектров поглощения были определены значения ширины запрещенной зоны полупроводников.

Литература

1. Gladyshev P.P., Banavoth M., Swetha T., Bingwa N., Martynov Ya.B., Zelenyak T.Yu., Kinev V.A., Nazmitdinov R.G. Hybrid Organo-Inorganic Perovskite Solar Cells: Architecture Evolution, Materials of Functional Layers, Photoelectric Characteristics, Properties, and Efficiency // *Renewable Energy: Research, Development and Policies. Perovskite Solar Cells: Properties, Application and Efficiency*. – 2019. – P. 1-75.
2. Jeon N. J. et al. A fluorene-terminated hole-transporting material for highly efficient and stable perovskite solar cells // *Nature Energy*. – 2018. – V. 3. – №. 8. – P. 682.
3. Matebese F., Taziwa R., Mutukwa D. Progress on the Synthesis and Application of CuSCN Inorganic Hole Transport Material in Perovskite Solar Cells // *Materials*. – 2018. – V. 11. – №. 12. – P. 2592.
4. Martinez S. et al. Micro-combined heat and power systems (micro-CHP) based on renewable energy sources // *Energy Conversion and Management*. – 2017. – V. 154. – P. 262-285.

Перовскитные фотоэлектрические преобразователи без дырочного проводящего слоя

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Исключительные фотовольтаические свойства гибридных органо-неорганических свинцово-галоидных перовскитов (например, $\text{CH}_3\text{NH}_3\text{PbX}_3$, $\text{X} = \text{Cl}, \text{Br}, \text{I}$), привлекли огромное внимание со стороны ученых всего мира. Гибридные органо-неорганические свинцово-галоидные перовскитные солнечные элементы (ПСЭ) быстро вышли на передний край фотоэлектрических технологий и достигли сертифицированной эффективности 22,1 % [1].

В типичных ПСЭ используют конфигурацию устройства TiO_2 /перовскит/ДПМ/Ау, в которой в качестве буферного слоя с дырочно-проводящим материалом (ДПМ) применяются *spiro*-OMeTAD или РТАА (политриариламин) [2]. Однако высокая стоимость *spiro*-OMeTAD и РТАА и их нестабильность под воздействием атмосферного воздуха и солнечной радиации становятся серьезной проблемой для развития ПСЭ [3]. К счастью, перовскит, такой как $\text{CH}_3\text{NH}_3\text{PbI}_3$, обладает высокой подвижностью носителей заряда, поэтому он сам может служить в качестве переносчика дырок, что делает излишним использование дополнительного материала для их транспортировки [4]. Для создания простого и недорогого фотогальванического устройства были предложены ПСЭ не содержащие буферный слой ДПМ с углеродными анодами [5]. Углеродные материалы, особенно графит, углеродная сажа и углеродные нанотрубки, обладают такими характеристиками, как низкая стоимость, высокая электропроводность, доступность, контролируемая пористость, химическая стабильность и экологичность. Исходя из этих преимуществ, данные углеродные материалы считаются одними из наиболее перспективных анодных электродных материалов для ПСЭ.

В докладе представлены основные типы структур углеродсодержащих перовскитных солнечных элементов без буферных слоев и разработанные авторами различные методы формирования углеродных контактов для данных устройств.

Литература

1. Yang W.S., Park B.-W., Jung E.H., Jeon N.J., Kim Y.C., Lee D.U., Shin S.S., Seo J., Kim E.K., Noh J.H. Iodide management in formamidinium-lead-halide-based perovskite layers for efficient solar cells, *Science* 356 (2017) 1376-1379.
2. Gratzel M. The rise of highly efficient and stable perovskite solar cells, *Acc. Chem. Res.* 50 (2017) 487-491.
3. Berhe T.A., Su W.-N., Chen C.-H., Pan C.-J., Cheng J.-H., Chen H.-M., Tsai M.-C., Chen L.-Y., Dubale A.A., Hwang B.-J. Organometal halide perovskite solar cells: degradation and stability, *Energy Environ. Sci.* 9 (2016) 323-356.
4. Xu L., Xiong Y., Mei A., Hu Y., Rong Y., Zhou Y., Hu B., Han H. Efficient Perovskite Photovoltaic-Thermoelectric Hybrid Device, *Advanced Energy Materials* 8(13) (2018) 1702937.
5. Kinev V.A., Gladyshev P.P., Ibrahim M.A. Prospects for the Use of Carbon-based Perovskite Solar Cells, *Egyptian Journal of Chemistry* 62 (2019) 89-97.

Формирование тонкопленочных структур на основе оксида меди (Cu_2O) методом ионного наслаивания для перовскитных солнечных батарей

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Оксид меди (Cu_2O) является полупроводником p-типа с шириной запрещенной зоны 2 - 2,17 эВ [1], обладающим большим коэффициентом поглощения ($\alpha \sim 10^5 \text{ см}^{-1}$) [2], что позволяет использовать его в качестве фотоэлектрического материала в фотовольтаики. Cu_2O играет роль, в перовскитных солнечных батареях (ПСБ), дырочно-проводящего материала (ДПМ). Задача данного слоя в ПСБ заключается в блокирование переноса электрона на анод, извлечении дырок из перовскита и транспортировку зарядов на катод и предотвращение прямого контакта перовскита с электродом. По сравнению с органическими дырочно-транспортными материалами, неорганические полупроводники p-типа Cu_2O представляют собой идеальный материал, т.к. он стабилен, прост в получении, а также из-за его низкой стоимости и экологичности.

Оксид меди получали методом ионного наслаивания SILAR (Successive Immersion Layer Adsorption Reaction). В качестве подложек использовались проводящие стекла (стекло/FTO). Для осаждения пленок p- Cu_2O методом SILAR использовали двойную соль $3\text{Cu}_2\text{S}_2\text{O}_3 \times 2\text{Na}_2\text{S}_2\text{O}_3$ и 2М NaOH. Двойную соль получали из 1М раствора $\text{CuSO}_4 \times 5\text{H}_2\text{O}$ и 1М раствора $\text{Na}_2\text{S}_2\text{O}_3$ который подливали к раствору $\text{CuSO}_4 \times 5\text{H}_2\text{O}$ [3]. Метод заключается в формировании тонких пленок полученных повторением циклов, состоящих из последовательных погружений в растворы и адсорбции ионов на подложке. SILAR метод позволяет получать тонкие пленки контролируемой толщины. Метод не требует сложных дорогостоящих реактивов и оборудования.

Литература

1. Hossain M.I., Alharbi F.H., Recent advances in alternative material photovoltaics, Mater. Technol. Adv. Perform. Mater. 2013. 28. 88-97.
2. Кудряшов Д. А. и др. Наноразмерные пленки Cu_2O : формирование методом ВЧ-магнетронного распыления, исследование структурных и оптических свойств // Физика и техника полупроводников. – 2017. – Т. 51. – №. 1. – С. 111-115.
3. Э.Н. Заманова, Л.А. Алиева. Структура и оптические свойства пленок закиси меди p Cu_2O , полученных низкотемпературным химическим осаждением. // FIZIKA. 2008. №3.

Установление влияния обработки парами йода на люминесцентные свойства пленок перовскита состава $\text{CH}_3\text{NH}_3\text{PbI}_3$

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Плёнки гибридных органо-неорганических перовскитов, используемых в качестве светопоглощающего слоя в перовскитных солнечных элементах, получают растворными методами в существенно неравновесных условиях, что обуславливает высокое содержание дефектов в материале. Непрерывно ведутся поиски методов постобработки, которые эффективно улучшали бы кристалличность. Одним из новых и, как следствие, малоизученных является обработка парами йода.

Недавно было установлено, что обработка перовскита парами йода приводит к его химическому связыванию и образованию реакционного полийодидного расплава (РПР), который способствует рекристаллизации данного материала, однако детальных исследований данного подхода проведено не было.

Люминесцентная спектроскопия чувствительна к превращениям, сказывающихся на кристаллической и зонной структуре полупроводниковых материалов, поэтому может быть использована для отслеживания эффектов, вызываемых пост-обработкой.

Целью работы является установление взаимосвязи люминесцентных свойств пленок гибридного органо-неорганического перовскита $\text{CH}_3\text{NH}_3\text{PbI}_3$ (МАРІ) и режима их постобработки парами йода.

В качестве объектов исследования были использованы тонкие пленки и монокристаллы МАРІ, которые были получены методом кристаллизации из раствора. Пленки МАРІ подвергали обработке парами йода в течение различного времени, после чего проводили термическую обработку для удаления связанного йода.

Методом рентгенофазового анализа было установлено, что обработка перовскита в условиях малого давления паров йода (порядка 0,32 мбар) не приводит к изменению фазового состава. Данные растровой электронной микроскопии указывают на то, что в таких условиях происходит рекристаллизация, приводящая к росту зёрен.

Были записаны спектры люминесценции серий образцов, прошедших различные режимы постобработки. Выявлены следующие тенденции изменения характеристик люминесценции, по мере увеличения длительности выдерживания перовскита в парах йода: смещение максимумов эмиссионных полос ФЛ в длинноволновую область, увеличение полуширин полос и увеличение интенсивности люминесценции.

Важным результатом представленной работы является демонстрация взаимосвязи длительности обработки перовскита парами йода и люминесцентных свойств материала. Полученные экспериментальные данные свидетельствуют о положительном влиянии постобработки парами йода свойства поликристаллических пленок гибридных органо-неорганических перовскитов, поэтому изучение потенциала предложенного метода – важная задача, которая носит фундаментальный и прикладной характер и способствует развитию перовскитной фотовольтаики.

Исследование выполнено за счет гранта Российского научного фонда (Проект № 18-73-10224).

Nickel oxide thin films produced via rf-sputtering method. Structural and lattice effects investigation

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In the past ten years, it has seen high grown rate of organic photovoltaic devices efficiency such as perovskite solar cells (PSC). PSC have very attractive features such as long carrier free path in comparison with all-organic SC, high sun power absorption, and low-cost precursors to synthesis PSC as well as simplicity of the fabrication. The high interest among scientists has evolved into a significant efficiency increase in past ten years from 3.8 to 24.2% for single-junction PSC [1]. Generally, typical perovskite-based SC is a multilayer structure include the photoactive layer consisting of MAPbPbX₃ solid solution (where X = Br⁻, Cl⁻, I⁻ etc.) embedded located between the hole and electron transport layers.

Organic transport layers limit the stability and lifetime of PSC due to oxidation between photoactive layer and transport layers thereby destruct solar cell [2]. Transition metal oxides thin films are supposed to be used as transport layers for perovskite solar cells because it provides better chemical stability. Transition metal oxides are perspective materials for construct transport layers in perovskite solar cells for better energy-level alignment [3]. Moreover, these compounds increase device's service life.

In the work polycrystalline non-stoichiometric nickel oxide (NiO) thin films had deposited by an RF magnetron sputtering process in different gas compositions – mixtures of nitrogen, oxygen, and argon. The x-ray diffraction and Raman scattering were measured. The texture Harris coefficients and dependencies of the spectral properties on proportions of gases mixture were studied. The evolution in spectra with increasing of substrate temperatures were investigated.

Study of the NiO thin film properties was carried out for further fabricating effective non-organic transition metal oxide hole transport layers for perovskite solar cells by magnetron sputtering method.

The reported study was funded by RFBR, project number 19-38-90149. The authors acknowledge support from the Ministry of Science and Higher Education of the Russian Federation (RFMEFI61619X0115).

REFERENCES

- [1] NREL Research-Cell Efficiency chart.
- [2] Ishii, H. et. al. Energy level alignment and interfacial electronic structures at organic metal and organic organic interfaces. *Adv. Mater.* 11, pp. 605–625, (1999).
- [3] Shrotriya, V. et. al. Transition metal oxides as the buffer layer for polymer photovoltaic cells. *Appl. Phys. Lett.* 88, 073508, (2006).

Ternary solar cells based on double-caged fullerene derivatives with long alkyl moiety

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Toward efficient polymer solar cells several key challenges have to be resolved, including improvement of light absorbance, management of transport properties of free charge carriers, and nanomorphology of bulk heterojunction. Ternary systems, including the D1:D2:A system and D:A1:A2 system, is regarded as prospective approach to address these issues [1].

We previously reported novel highly soluble double-caged fullerene acceptors (dFR) providing enhanced charge transport and molecular ordering in binary systems with P3HT as a donor component.ii Here we report fabrication, optimization, and testing of related photovoltaic devices with ternary active layer based on P3HT, dFR, and third component comprising a low band gap donor polymer or small-molecule/fullerene acceptors. Optimization of the fabrication protocol for ternary solar cells includes variation of donor/acceptor/third component ratio, thickness of photoactive layer, annealing temperature, and used solvent(s). Electronic properties of individual compounds as well as the active layer, including the HOMO and LUMO levels, the charge carrier mobility as well as the nanomorphology of photoactive layer will be discussed. The experimental composition-structure-property relationships for a representative series of ternary photovoltaic devices makes possible to reveal correlation between the molecular and electronic features of components of the active layer and its photovoltaic characteristics.

This work was supported by RFBR (project № 18-33-00670).

REFERENCES

[1] Huang H., Yang L., Sharma B., *J. Mater. Chem. A*, 2017, 5, 11501. ii Brotsman V.A. et al., *Chem. Asian J.*, 2017, 12, 1075.

Photostimulated defect formation in pristine and doped halide perovskites

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We report the results of experimental studies of the processes of photostimulated defect formation in pristine and doped halide perovskites by diffuse reflectance spectroscopy. Absorption spectra of photoinduced defects and kinetics of their formation under irradiation within fundamental absorption spectral range will be presented in details. Based on the kinetic analysis it is suggested that both mechanisms of defect formation which are typical for the photoresistant and photosensitive solids, can be observed in halide perovskite. Particularly, a formation of new types of defects through excitonic dissipation is characteristic for Ag-doped halide perovskites.

In addition, the effect of photostimulated defect formation on photoluminescence of halide perovskites will be also demonstrated and discussed in terms of competing relaxation pathways through exciton and defect states. The observed effects may play a significant role in terms of photostability of halide perovskites for their application in photovoltaics and optoelectronics.

Monoalkylammonium polyiodides: structure, physical properties and application for synthesis of hybrid perovskites

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We have shown recently that methylammonium and formamidinium polyiodides can serve as facile precursors for a completely new solvent – free scalable approach of hybrid halide perovskite film processing based on their interaction with the metallic lead thin layers; as a proof of concept, high-efficiency perovskite solar cells were fabricated using these new precursors [1].

On the other hand, these polyiodides are responsible for perovskite solar cells degradation [2]. The dual character of such compounds, either as a facile precursor for perovskites in solar cells or corrosive products of photodegradation, is governed by their unique feature to occur as a liquid at room temperature. This inevitably raises the demand of complex investigation of such polyiodides and building up their preliminary phase diagram.

As a result, we identified and refined four new methylammonium polyiodides with complicated crystal structures, namely, MAI₂, MA₃I₈ (MAI_{2.67}), MAI₄, MA₂I₁₁ (MAI_{5.5}). The performed DFT calculations revealed the crucial role of entropy contribution to the formation of higher methylammonium polyiodides which is in a good agreement with experimental data. On the basis of a set of techniques, we investigated phase relations in the system MAI-I₂ and built up a first phase diagram of the system MAI-I₂ characterized by unprecedented (for known polyiodide systems) phase diversity. The formation of observed peculiar structures and unusually low melting points of the observed compounds are determined by conjoint presence of small polar amphiphilic cation, highly polarized catenating anion and the competition between H-bonds and halogen bonds. Overall, there are deep reasons to believe that the MAI-I₂ system is the first but quite characteristic representative of the new class of compounds which we suggest to name as “monoalkylammonium polyiodides” [3].

The set of properties of alkylammonium polyiodides made them nearly ideal candidate to realize the reactive flux approach for a directed synthesis of ternary and more complex metal halide perovskite-like compounds. Therefore, an understanding of the unique distinguishing features of MAI-I₂ system can greatly promote the development of hybrid polyiodide fluxes assisted synthetic approaches. Research was financially supported by the Russian Science Foundation (Project № 18-73-10224).

REFERENCES

- [1] I. Turkevych, S. Kazaoui, ..., S.A. Fateev, A.A. Petrov, E. A. Goodilin, M. Graetzel and A.B. Tarasov, *Nature Nanotechnology* (2019), 14, 57–63.
- [2] N.N. Shlenskaya, N.A. Belich, M. Grätzel, E.A. Goodilin and A.B. Tarasov, *Journal of Materials Chemistry A* (2018), 6, 1780–1786.
- [3] A. A Petrov., S. A. Fateev, ..., E. A. Goodilin & A. B. Tarasov, *The Journal of Physical Chemistry Letters* (2019), 10, pp. 5776-5780

Iodine bismuthates, iodides and polyiodides of phenyldiammonium and its derivatives: synthesis, structure and properties

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The discovery of photovoltaic efficiency of various inorganic and hybrid haloplumbates has led to the increasing in activity in the scientific community and boost the research into synthesis and properties of various complex halides of mainly metals of fourth and fifth groups, including bismuth(III). Such interest is caused by the need to search lead-free perovskite-like materials. One of the most significant problems is to find lead-free halide semiconductors demonstrated high photovoltaic efficiency and also high stability. Due to the structural diversity polyhalide complexes of bismuth(III) are also interesting as objects of fundamental research [1].

We consider some optical properties, crystal structure and thermal stability of compounds, formed during to interaction of bismuth(III) iodide with phenyldiammonium derivatives in presence of hydroiodic acid. A number of halide complexes with the similar crystal structure $[C_6H_4(NH_3)_2][Bi_2I_{10}] \cdot nH_2O$ ($n=0,4,6$) was obtained by varying synthesis conditions in well-known literature method. $[C_6H_4(NH_3)_2][BiI_4]_2(I_2)$ was formed when we used fourfold excess of iodine in the same conditions. The crystal structure of new complex consist of anionic chains $[BiI_4]_{\infty}^-$, connected by bridging I_2 molecules through weak $I \dots I$ interactions. The cations and I_2 molecules alternate along the axis forming a supramolecular arrangement running parallel to the $[BiI_4]_{\infty}^-$ chains [2].

Presence of acetone in the stock solution leads to cation conversion and crystallization of new complex - $[C_6H_4(CNH(CH_3)_2)_2][BiI_4]_2$, composed of the same anionic chains which are connected to pseudo-three-dimensional structure only by hydrogen bonds. [3] The new complex with discrete tetra-core anions - $[C_6H_4(NH_3)_2]_2[Bi_4I_{18}]_4^-$ was formed in presence of copper(I) iodide. All compounds, formed in the system $BiI_3 - C_6H_4(NH_2)_2 - HI$ demonstrated thermal stability in the air. For each of them band gap value was obtained. The most interesting value for us was illustrated by $[C_6H_4(NH_3)_2][BiI_4]_2(I_2)$ ($E_g=1.45$ eV) Complexes with $[BiI_4]$ chains were also obtained in the same conditions when we changed cation to N,N-dimethylphenyldiammonium. A number of compounds with interesting structure such as $[C_6H_4(NH_3)(NHMe_2)]_3[BiI_6](I_3)$, $[C_6H_4(NH_3)(NHMe_2)](I_3)I$ were formed by varying synthesis conditions.

Работа выполнена при финансовой поддержке РФФ (проект №19-73-30022).

REFERENCES

- [1]. S.A. Adonin, M.N. Sokolov, V.P. Fedin. Polynuclear halide coplexes of Bi(III): From structural diversity to new properties. // J. Coordination Chemistry Reviews, 312, (2016), 1-21
- [2]. T.A. Shestimerova, N.A. Golubev, N.A. Yelavik, M.A. Bykov, A.V. Grigorieva, Z. Wei, E.V. Dikarev, A.V. Shevelkov. Role of I_2 Molecules and Weak Interactions in Supramolecular Assembling of Pseudo-Three-Dimensional Hybrid Bismuth Polyiodides: Synthesis, Structure, and Optical Properties of Phenylenediammonium Polyiodobismuthate(III). // J. Crystal Growth & Design, 18(4), (2018), 2572-2578.
- [3]. T.A. Shestimerova, N.A. Golubev, A.V. Mironov, M.A. Bykov, A.V. Shevelkov. Synthesis, structure, and properties of Schiff base iodobismuthate and its alteration in DMSO solution. // Russian Chemical Bulletin, 67(7), (2018) 1212–1219.

Improvement of morphology and crystallinity of hybrid perovskite thin films via novel gas-treatment approach

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Recently our group has developed a new strategy of perovskite thin film fabrication using novel reactant compounds, reactive polyiodide melts – the so-called RPM-process [1] that was proved to be applicable to fabrication of high-performance large scale perovskite solar cells [2]. The RPMs can be easily obtained from solid I₂ and MAI, exhibit very low melting points and high chemical activity. They are liquid at room temperature, readily react with lead-containing compounds to form the hybrid perovskite CH₃NH₃PbI₃ and do not require the use of any solvent.

We found that perovskite can chemically bind iodine to form RPM. Once being formed, RPM acts as a liquid medium that facilitates the recrystallization of perovskite grains. Furthermore, under proper conditions (iodine vapor pressure and time of exposure) this process is reversible and, once excess of iodine is liberated from the system, the target perovskite structure is formed again with no signs of PbI₂ or other decomposition products. Using scanning electron microscopy, x-ray diffraction, time-resolved luminescence spectroscopy we showed that iodine treatment is beneficial for the overall quality of perovskite thin films that were fabricated by means of classical solution-based approaches and result in the increase of the average grain size, crystallinity, lifetime of charge carriers.

Research was financially supported by the Russian Science Foundation (Project № 18-73-10224).

REFERENCES

- [1] Petrov AA, Belich NA, Grishko AY, Stepanov NM, Dorofeev SG, Maksimov EG, Shevelkov AV, Zakeeruddin SM, Graetzel M, Tarasov AB, Goodilin EA. A new formation strategy of hybrid perovskites via room temperature reactive polyiodide melts. *Materials Horizons*. 2017;4(4):625-32.
- [2] Turkevych I, Kazaoui S, Belich NA, Grishko AY, Fateev SA, Petrov AA, Urano T, Aramaki S, Kosar S, Kondo M, Goodilin EA, Graetzel M, Tarasov AB. Strategic advantages of reactive polyiodide melts for scalable perovskite photovoltaics. *Nature nanotechnology*. 2019 Jan;14(1):57.

Exceptional Long Electron Lifetime of Methylammonium Lead Iodide Perovskite Solar Cell Made from Aqueous Lead-Nitrate Precursor

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Studies on photoelectronic properties of perovskite solar cells (PSC) made from non-PbI₂ precursors are seldom reported. In this study, a series of transient techniques are applied to investigate the charge recombination and trap distribution in a highly efficient PSC fabricated using a low-toxicity Pb(NO₃)₂/water protocol. A device with identical conversion efficiency fabricated using a conventional PbI₂/DMF protocol is also studied for comparison. Transient photovoltage and time-resolved photoluminescence analysis revealed that the Pb(NO₃)₂/water-based device exhibits a long lifetime in both bimolecular and trap-assisted recombination. However, differential capacitance and differential charging analysis indicate that there are more charges storing in the Pb(NO₃)₂/water-based perovskite layer, which stretches the energy tail from band edge to mid-band and should provoke serious trap-assisted recombination. The exceptional long electron lifetime of Pb(NO₃)₂/water-based is explained by a benign defect inactivation which is originated from water and NO₃⁻ residues left from the aqueous precursor solution. Consequently, despite the perovskite film made from Pb(NO₃)₂/water protocol possesses high trap density, its photovoltaic device still exhibits long electron lifetime and superior photovoltaic properties.

Ambipolar perovskite light emitting diodes

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Perovskite light-emitting diodes (PeLEDs) have recently attracted great research luminescence at room temperature in interest for their narrow emissions and solution processability. Remarkable progress has been achieved PeLEDs in recent years [1]. Here we present the new configuration of ambipolar transparent perovskite light emitting device. The combination of voltage induced p-i-n formation and ionically doped carbon electrodes and allows electroluminescence in forward and reverse bias. For this experiment PeLEDs were assembled using a glass substrate with ITO stripes as bottom electrode; spin-coated CsPbBr₃/I₃:PEO composite as emissive layer [2]; single wall carbon nanotubes (SWCNT) deposited by a simple press transfer process at room temperature as top electrode, that were produced by the aerosol (floating catalyst) chemical vapor deposition (CVD) method [3]. SWCNT has a sensitive response of electrical properties to doping, due to having only one graphene layer. Any changes on the external graphene layer leads to sensitive response of SWCNT properties. In direct mode on PeLED device (+ITO/pero/SWCNT-) positively charged ions coat SWCNT. P-type doping leads to downshifting and change in the Fermi level, that helps to holes injection from SWCNT instead of ITO. Changing the direction of the electrical field coats the surface with oppositely charged ions. We demonstrate a concept of stacked multicolor tandem pixel. Stack of transparent light emitting units might allow fine color tuning in parallel tandem connection without segregation compared to mixed halide perovskites. This configuration conforms pixel downsizing and make to fabrication of emissive multijunction pixels in a stack. Stacked pixel designs have potential application in head-up displays and augmented reality technologies, due to smaller pixel area compared to conventional display with active matrix.

Free and self-trapped excitons in low-dimensional halide perovskites

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Many halide perovskites are direct-gap semiconductors. This allows one to observe excitons in them –quasiparticles, consisting from an electron and a hole. Free excitons have a narrow optical resonance and high nonlinearity, which is important for various optoelectronic applications. In halide perovskites, it is also possible to observe self-trapped excitons with broadband emission, which makes them an attractive material for white light phosphors. The optoelectronic properties of halide perovskites are determined ultimately by the metal-halogen sublattice. The choice of the A-cation allows one to control the crystal structure, including the synthesis of low-dimensional perovskites. Here we report various quasi-1D and 2D halide perovskites obtained by the liquid-phase synthesis. Crystallography and optical properties of APbX₃ halide perovskites with pyridine and substituted pyridine in A-position will be discussed. It will be shown that the edge-sharing of PbX₆ octahedrons in quasi-1D (PyOH)PbBr₃ and quasi-2D (PyCN)PbBr₃ favors formation of self-trapped excitons, whereas octahedrons face-sharing motif in quasi-1D PyPbI₃ makes free excitons stable at temperatures below 70 K.

Lateral photodetector based on organic-inorganic halide perovskite single crystal

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Nowadays scientific community has shown the growth of interest in organic-inorganic halide perovskites as an absorbing layer of photovoltaic devices. Moreover, recent studies demonstrated that this type of perovskite is prospective material for the technology of photon detection with high performance and cheaper fabrication process in comparison to silicon and III-V photodetectors. This class of semiconductors has unique optoelectronic and electrophysical properties for application in the field of imaging, optical communication and medicine. Perovskite single crystals are appropriate material for the future studies due to the high carrier lifetimes (to 15 μs) and diffusion length (to 175 μm) as a sequence of lack of surface defects on interface and grain boundaries. Also, a high absorption coefficient leads to high photosensitivity and response speed. However, the growth process required high temperatures and lots of time (about two weeks) and consequently, there were only a few investigations in this area. This problem was solved in 2015 when Saidaminov et al. demonstrated retrograde solubility of perovskites in organic solvents (DMF, DMSO, etc.). So, the growth process can be provided in 50-110°C and with time spent about 5-6 hours which is extremely cheaper than traditional semiconductor materials technology. In this work, photodetector based on perovskite single crystal was fabricated and studied. Perovskite single crystal was grown with inverse temperature crystallization method and optimal parameters for this process were selected. Calculated from J-V measurements photosensitivity was 0.023 $\text{A}\cdot\text{W}^{-1}$. The mobility of photogenerated carriers was measured using the time-to-flight technique. The measured value was 2 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$.

Environmental Stability under Operational Conditions of Perovskite Solar Cells

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Perovskite solar cells (PVs) are very promising due to their high efficiency and low manufacturing cost, but their stability and toxicity remain key challenges. In particular, mixed APbX₃ perovskite consisting of A cations (Cs, FA, MA) and B anions (I, Br) have attracted much attention due to their higher efficiency and greater thermal stability compared with MAPbI₃. However, the question regarding their stability to various environmental stresses such as oxygen (O₂) and humidity (H₂O) at moderated temperature (T~60°C) under 1 sun continuous illumination and under load (maximum power point) has not been fully addressed. Here, we shall address these issues, discuss the mechanisms and suggest strategies for improving their environmental stability.

Films of $\text{Cs}_{1+x}\text{CuI}_{3+x}$ ($x=0, 2$)

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In the last 10 years rapid growth of the perovskite solar cells efficiency occurred (from 3.8 to 25.2%) [1], [2]. Main component of such solar cell are complex halides with perovskite structure ($\text{CH}_3\text{NH}_3\text{PbI}_3$ and other). These halides were also studied as a material for photodetectors and light – emitting diodes [3]. At the same time their usage is limited because of due to many factors [4]. For that reason study of the optical properties of other halide compounds are carried out. These compounds should be more stable and have potentially acceptable optical and conductive characteristics. Also investigation of the luminescent properties of that type of materials and analysis of their perspectives as an inorganic luminophores. One of the promising but weakly studied materials are cesium iodocuprates ($\text{Cs}_3\text{Cu}_2\text{I}_5$ и CsCu_2I_3). In recent papers was demonstrated the possibility of light – emitting diodes [5] and photodetectors [6] development.

In our previous research we studied structural, optical and luminescent properties of cesium iodocuprates powders. Crystal lattice parameters were refined. Also melting point was determined and thermal stability was studied as well as width of band gap and photoluminescence peaks positions.

We obtained thin transparent films of CsCu_2I_3 by spin – coating. Their width was determined by step – profilometry and was about several hundreds of nanometers. Phase composition was refined by XRD which did not show impurities in the film. Also directed growth along [020] was found with the help of the XRD. Investigation of the luminescent properties revealed the difference between spectra obtained on the films and on the powders. This difference is related to directed growth of the films.

The work was supported by the Russian Foundation for Basic Research grant No. 19-03-00849.

REFERENCES

1. Akihiro Kojima, Kenjiro Teshima, Yasuo Shirai and T.M. Organometal Halide Perovskites as Visible- Light Sensitizers for Photovoltaic Cells // *J Am Chem Soc.* 2009. Vol. 131, № October. P. 6050–6051.
2. <https://www.nrel.gov/pv/assets/pdfs/best-research-cell-efficiencies.20190703.pdf>
3. Zhang Q. et al. Efficient metal halide perovskite light-emitting diodes with significantly improved light extraction on nanophotonic substrates // *Nat. Commun.* 2019. Vol. 10, № 1. P. 1–9.
4. Domanski K. et al. Systematic investigation of the impact of operation conditions on the degradation behaviour of perovskite solar cells // *Nat. Energy.* 2018. Vol. 3, № 1. P. 61–67.
5. Jun T. et al. Pb-free Blue-emitting 0D $\text{Cs}_3\text{Cu}_2\text{I}_5$ with High PLQY of ~ 90 %. 2019. Vol. 1. P. 1176–1178.
6. Cu L.C. et al. Sensitive Deep Ultraviolet Photodetector and Image Sensor Composed Sensitive Deep Ultraviolet Photodetector and Image Sensor Composed of Inorganic Lead-Free $\text{Cs}_3\text{Cu}_2\text{I}_5$ Perovskite with Wide Bandgap. 2019.

Toward large scale fabrication of perovskite solar cells by applying slot-die printing technology

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Halide perovskite photovoltaics is promising thin-film technology that demonstrated unprecedented progress in the growth of power conversion efficiency during the last decade with a current record of 25.2 % for small area devices ($<1 \text{ cm}^2$). Typically spin coating method of deposition is used as the main route for the fabrication of lab-scale perovskite solar cells (PSCs). However, spin-coated PSCs are limited in small-size by the spatially inhomogeneous nucleation due to the radial gradient of oversaturation by dropping anti-solvents in the centre of film during coating. Slot-die printing is known as one of the most promising printing methods for industrial manufacture of PSCs. In this work, we present the application of the slot-die coating technology on the fabrication of hole transporting (HTL) and absorbing layers (AL) with vacuum-assisted solution process (VASP) without using toxic anti-solvents. Developed deposition routes were used for the fabrication of planar p-i-n perovskite solar cells including ITO/NiO/MAPbI₃/PCBM/BCP/Al. The NiO HTL was printed on ITO glass from the water solution of tris(ethylenediamine) nickel acetate with replacing of ethylene glycol as a solvent of the spin coating route to stabilize meniscus during head motion over the substrate and obtain continuous thin film. For the vacuum-assisted perovskite deposition, we found an optimal mixture of solvents with DMF:NMP (vol. ratio: 4:1) that gives excellent reproducibility and long operation window in the ambient conditions. The AL was slot-die printed on NiO-coated ITO glass with coating speed of 30mm/s. Then the wet printed films were kept in vacuum chamber for a few minutes before being annealed at 100°C in 10 min to completely remove all remaining solvents. PCBM and BCP layers were deposited by spin coating, and finally, a 100nm-thick Ag electrode was thermally evaporated. For the comparison, we fabricated fully spin-coated devices as reference (AL was done with solvent engineering methods) and configurations with printed HTL/spin-coated AL (p-s devices); printed HTL/printed AL (p-p devices). To estimate the output performance of the fabricated devices we measured JV curves at standard conditions 1.5 AM G light spectrum with calibrated 100 mW/cm² intensity. The p-s devices had an efficiency around 15%, 1.01-1.05 V of V_{oc} and highest J_{sc} 19.67 mA/cm², all output parameters were obtained at the same level as for reference device. The efficiency of p-p devices was about 7% with 1.00V of V_{oc} and 15mA/cm² of J_{sc} . The reduced performance of the p-p devices was affected from high leakage current caused by not uniform coverage and film morphology of the perovskite layer and can be improved with special additives of chlorines and thiocyanates of organic cations for stabilization of crystallization rates during VASP treatment. PSCs with slot-die printed HTL and AL were successfully fabricated. The obtained results clarified that the slot-die printing and VASP methods can be effectively used for the upscaling of the devices with p-i-n planar structure including ITO/NiO/MAPbI₃/PCBM/BCP/Ag.

P-doped resonant silicon nanoparticles for light management and efficiency improvement of perovskite solar cells

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Nowadays resonant semiconductor nanoparticles (NPs) are promising tool for light trapping and scattering improvement and were recently proposed for a number of applications [1,2], therefore, they can be employed for perovskite based solar cells (PSCs) efficiency enhancement [3]. In particular, Mie resonant silicon nanoparticles are able to refine not only the optical optimization of solar cells, but also, being doped by elements of III/V groups, influence on the carrier management of devices.

Here we show for the first time theoretically and experimentally, that the doped and resonant silicon nanoparticles can boost the efficiency of n-i-p based PSCs being in hole transporting layer [4]. We choose the well-studied material MAPbI₃ based perovskite to avoid any influence of material's composition. We achieved the PSC enhancement of efficiency up to 18.7% by incorporation of Al-doped resonant silicon nanoparticles into hole transporting layer of the devices. The efficiency boost of PSCs with p-Si NPs is caused by photocurrent and fill factor enhancement.

Our theoretical analysis includes a comprehensive multiphysics modeling of interacting optical and electrical effects produced by Si NPs. This approach gives us a physical insight into the phenomena under consideration. We revealed a resonance behavior of silicon inclusions that contributes to enhanced generation rate. Also, we investigated charge carrier transport properties of our solar cell for different architectures. Our results are of high importance for further optimization of perovskite-based devices containing nanophotonic elements.

REFERENCES

- [1] A. Kuznetsov et al, *Science* 354, (2016)
- [2] S. Makarov et al, *Adv. Opt. Matter.* 7, (2018)
- [3] A. Furasova et al, *Adv. Opt. Matter.* 6, (2018)
- [4] A. Furasova et al, *Energy Technol.* (accepted)

**Semi-empirical modeling of disordered mixed-halide hybrid perovskites
CH₃NH₃Pb(I_{1-x}Br_x)₃: prediction of thermodynamic properties, phase stability
and deviations from Vegard's law**

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In the present study, we suggest a novel effective approach on computational investigation of thermodynamic properties of the CH₃NH₃Pb(I_xBr_{1-x})₃ solid solution using the semi-empirical method combining with an effective configurational space study of disordered halide sublattice [1]. We developed a new model of interatomic potentials for CH₃NH₃Pb(I_xBr_{1-x})₃ solid solution. The calculated Gibbs free energy values were found to be in a perfect agreement with experimental data and deviation from the starting geometry of cells is no more than 1%, which confirms the transferability of our computational scheme between the phases with different composition. In our approach we used disordered halide sublattice (I⁻ and Br⁻). For the first time the representative disordered configurations within supercells, imitating infinite crystal, was determined by analyzing a set of random configurations for the deviation from the ideal statistical histogram of the frequency of occurrence of dissimilar second neighbors for each composition.

The developed model predicts tetragonal to cubic phase transition at Br content of ~0.2 and a large immiscibility gap at R.T. and lower temperatures. We performed a corresponding experiment with single crystals of mixed halide perovskites and observed phase segregation at room temperature, therefore proving the prediction of the model. Using our approach we clearly demonstrate a positive deviation from the Vegard's law for the CH₃NH₃Pb(I_xBr_{1-x})₃ disordered solid solution which is consistent with experimental data and can be explained by the local structure of the solid solution.

The proposed semi-empirical approach predicts with high accuracy the thermodynamic properties and phase stability hybrid perovskites with mixed halide composition. Therefore our transferable model of potentials provides the way to further theoretical study of hybrid halide perovskites of more complex composition and predicting their physical properties.

This work was financially supported by Russian Foundation for Basic Research (RFBR), project number: 19-33-70077.

REFERENCES

1. Marchenko, E.; Fateev, S.; Petrov A.; Goodilin E.; Eremin N.; Tarasov A. Transferable Approach of Semi-Empirical Modeling of Disordered Mixed Halide Hybrid Perovskites CH₃NH₃Pb(I_{1-x}Br_x)₃: Prediction of Thermodynamic Properties, Phase Stability and Deviations from Vegard's Law. *J. Phys. Chem. C*. Just Accepted Manuscript. 2019. DOI: 10.1021/acs.jpcc.9b08995.

Perovskite photovoltaic element with zero built-in voltage

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Rapid progress in efficiency of photovoltaic elements, based on hybrid organic-inorganic perovskites (PPE), attracts a tremendous experimental as well as theoretical attention. In particular, it was reported recently on the power conversion efficiency (PCE) around 22% [1]. We show that PCE of PPE can be further improved not only by purification of photoelement crystal structure or some light-trapping technique but also by contacts tailoring. We make use of the effect that photovoltage can be generated in illuminated p-i-n heterostructure with zero built-in voltage.

The PCE of PPE is proportional to the open-circuit voltage that is the maximum voltage obtained under sunlight. On the other hand, open circuit voltage in p-i-n or in p-n photodiode is the increasing function with the total recombination rate R decrease. R can be defined as $R = N_{mn} \cdot La / \tau$ (1). Where N_{mn} - is the mean (over absorber thickness) injected carrier concentration under forward bias, τ - is the carrier recombination lifetime and La - is the absorber thickness. So the decrease of the absorber thickness must cause the increase of open circuit voltage and at the same time the decrease of the short circuit current. Since we can keep short circuit current nearly constant with some kind of the light-trapping technique we can expect from (1) the efficiency increase with a) absorber purification - increase of the carriers life time τ , b) absorber thinning - decrease of the La , c) contact barriers tailoring - decrease of the carrier concentration injected into the absorber N_{mn} .

The influence of τ and La on the power conversion efficiency of the perovskite photovoltaic element have been shown in previous works [2,3] and in this contribution we shall deal with contact tailoring.

The increase of contact barriers height not only decrease injected carrier concentration under forward bias and hence open circuit voltage and PCE but also increase crystal field on the perovskite boundaries and make it possible to create a photovoltaic cell with zero built-in voltage.

REFERENCES

1. Yang W.S., Park B.-W., Jung E. H., Jeon N. J., Kim Y.C., Lee D.U., Shin S.S., Seo J., Kim E.K., Noh J.H., Seok S. I., Science 2017, 356, 1376-1379.
2. Martynov Y.B., Nazmitdinov R.G., Moia-Pol A., Gladyshev P.P., Tameev A.R., Vannikov A.V., Pudlak M. „On efficiency limit of ZnO/CH₃NH₃PbI₃/CuI perovskite solar cells”, Phys.Chem.Chem.Phys. 2017, 19, 19916-19921.
3. F. Bonnin-Ripoll, Y. B. Martynov, G. Cardona, R. G. Nazmitdinov, R. Pujol-Nadal «Synergy of the ray tracing+carrier transport approach: On efficiency of perovskite solar cells with a back reflector», Solar Energy Materials and Solar Cells, 200 (2019) 110050.

Improvement of the solar cell based on a perovskite-polymer compound due to its memristive properties

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Organometal halide perovskites (OHP) have emerged 10 years ago as a family of materials prospective for optoelectronics and photovoltaics. From this point, OHP attracted tremendous attention from scientific community since new material demonstrate many interesting properties like high absorption, high exciton energy at room temperature, lasing and many more. The record efficiency of perovskite solar cells (PSC) reached more than 23%. Simultaneously with the development of PSC, scientists revealed hysteresis phenomena of the J-V characteristics, which are associated with the phenomenon of ion migration in perovskite.

Memristor is a nonlinear, bipolar, passive circuit element capable to change its resistance depending on the charge flowing through it. After power off, the memristor remembers its last state, that can be used as a non-volatile memory cell. Usually, memristors consists of two layers e.g. with high and low oxygen concentration. The resistance changes under applied external voltage due to ion migration inside these two layers. And the resistance change can be controlled by value and sign of the applied voltage.

The presence of ion migration opens the way for the implementation of perovskite-based memristors. However, to implement such a device, it is necessary to resolve a number of problems, one of which is the backward ion migration in the absence of a restraining voltage. We added a small amount of polyethylene oxide (PEO) into the perovskite layer. PEO is an ion conducting polymer. It fills the space between the perovskite grains in the film and restrain ions as they move between grains, slowing down the migration.

The solar cells devices had the structure: ITO / PEDOT: PSS / MAPbBr₂I:PEO / C60 / LiF / Ag. The J-V characteristics of the devices were obtained by the AM1.5G irradiation (100 mW/cm²). Before hysteresis measuring the J-V characteristics, the devices were biased at small forward voltage. Immediately, after the voltage soaking at high voltage device has p-i-n structure, and low resistance. With decreasing the voltage, we observe state switching, that is probably associated with backward ion migration in the film. With increasing voltage, ions become able to migrate through PEO to boundaries, that forms p-i-n structure and switches device to on state. This hysteresis dependence forms a hysteresis loop that is very similar to J-V of a memristor.

The study of morphological changes in hybrid perovskite thin films with various composition under light irradiation

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At the moment, stability of hybrid perovskites (HPs) is the most critical problem in the field of perovskite solar cells (PSCs). A huge amount of research is dedicated to the study of HPs degradation mechanisms from various factors – humidity, oxygen, elevated temperatures, light irradiation. The latter is one of the most inevitable factors in photovoltaics, therefore, overcoming of light instability will pave the way to commercialization of PSCs. Hybrid perovskites undergo reversible and irreversible changes in morphology, phase composition, optical properties, etc. under exposure to light. While light-induced variations of optical properties have been widely studied, corresponding morphological changes were usually ignored. Especially, scarce information about light-induced changes in HPs with various cation composition is published.

In the current study we try to fill this gap and investigate the features of morphological changes in perovskite thin films with different cation composition: MAPbI₃, FA_{0.85}CS_{0.15}PbI₃ and MA_{0.15}FA_{0.85}PbI₃ (MA = CH₃NH₃⁺, FA = CH(NH₂)₂⁺) under light irradiation (white and blue LEDs) with power density ≤ 400 mW/cm². All thin film samples were spin-coated from the mixtures of DMFA/DMSO solvents in the inert glove box. Thin films were exposed to light in heptane environment. This substance selectively dissolves the iodine – one of perovskite degradation products, heptane is inert to hybrid perovskite (unlike toluene, isopropyl alcohol, etc.), and it also enforces the heat dissipation from HPs films. Morphology was studied by scanning electron microscopy (SEM) including electron probe microanalysis (EPMA) method. Crystal structure and its modifications were studied by X-ray diffraction (XRD), while optical properties were analyzed by UV-vis absorption spectroscopy.

We have shown that perovskite films with different composition demonstrate different stability under the same light irradiation: MAPbI₃ first undergoes irreversible degradation, while FA_{0.85}CS_{0.15}PbI₃ perovskite stays stable at the same exposure time. MA_{0.15}FA_{0.85}PbI₃ shows an intermediate stability comparing to above samples. MAPbI₃ perovskite completely degrade under white light irradiation with the formation of PbI₂ crystallites which was supported by EPMA, XRD, and UV-vis spectroscopy data. Another behavior demonstrates FA_{0.85}CS_{0.15}PbI₃, thin films of which save grain structure even at longer irradiation times, but a large number of pores (10-15 nm in diameter) are observed on the film surface. Optical absorption of this perovskite gradually decreases in time without formation of PbI₂ absorption edge. MA_{0.15}FA_{0.85}PbI₃ in its turn undergoes both – pore appearance and grain destruction. Therefore, considering the equal amount of the more stable FA⁺ cation in MA_{0.15}FA_{0.85}PbI₃ and FA_{0.85}CS_{0.15}PbI₃, we can assume the presence of MA⁺ cation reduces HPs stability. In all samples EPMA reveals gradual decrease of I:Pb ratio with increase of irradiation duration.

Summing up, hybrid perovskite composition plays an important role not only in material stability, but also in the morphological changes during light-induced degradation. We discovered pore formation over all FA_{0.85}CS_{0.15}PbI₃ thin film surface which wasn't reported earlier.

The reported study was funded by RFBR according to the research project № 19-53-53028.

How to measure the solar cell performance?

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During the last decades, intensive research in photovoltaics has led to appearance and substantial development of novel solar cell families. The power conversion efficiency (PCE) of a solar cell is the main driver of the field; therefore, an accurate and proper estimation of PCE is crucial for scientific and technological progress in the field. Furthermore, an accuracy estimation is necessary to compare various cells measured in various laboratories. However, there are rising concerns about correctness of PCE values presented in literature [1-3]. To tackle this issue, Nature group released a checklist for PV publications [4].

In the review part of the talk, we discuss the main pitfalls in laboratory characterization of the various type of emerging solar cells. The main difficulty is correct determination of the solar cell current. We analyze how masking of the solar cell active area and the transient behavior (because of an intrinsic slow process or/and degradation) impact the measured solar cell current and its hysteretic behavior. Meanwhile, the most complicated issue leading to under/overestimation of the solar cell current is a practically unavoidable mismatch between the solar spectrum and the solar simulator spectrum. Usually, this mismatch is taken into account with the use of a reference solar cell, whose normalized spectral response, ideally, should be equal to that of the solar cell under test. A reference cell-based PCE measurement method is widespread across the community: in this approach, the solar simulator intensity is adjusted to the current of the reference cell. This technique has been adopted from the silicon photovoltaics and implies a good spectral correspondence between the photocurrents of the reference and test cells. Unfortunately, this correspondence is not easy to achieve for novel materials (organic, hybrid, perovskites), whose absorption spectra strongly differ from that of the test cell (usually a silicon cell with an appropriate color filter).

In the original part of the talk, we present a laboratory measurement technique for PCE evaluation — the spectral technique — and demonstrate its applicability for advanced solar cells [5]. In contrast to commonly used methods, the spectral technique provides estimation of accuracy in PCE. Using as examples, organic and perovskite solar cells, we show that the reference cell-based technique either over- or underestimates PCE. Nevertheless, the spectral technique delivers the PCE values with a guaranteed accuracy (4% in our realization), independent from the type and spectral properties of the test cell. The spectral technique allows reliable evaluation of PCE and its measurement inaccuracy, which are independent from the spectral properties of a studied cell type or a solar simulator used. We anticipate that the spectral technique will facilitate easier comparison of the results across the community and between various solar cell technologies contributing to credibility of photovoltaic research and development.

REFERENCES

- [1] H. J. Snaith, Nature Photonics 2012, 6, 337-340.
- [2] Nature Photonics 2014, 8, 665.
- [3] R. B. Dunbar et al., Journal of Materials Chemistry A 2017, 5, 22542-22558.
- [4] Nature Photonics 2015, 9, 703.
- [5] A. Gavrik et al., Solar Energy Materials & Solar Cells (to be submitted).

Crystallization of hybrid perovskites from aprotic solvents: new intermediate phases

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Solution processing is the most common method to produce films of perovskite as a cheap and simple deposition approach. So far, dimethylformamide (DMF), dimethyl sulfoxide (DMSO) and γ -butyrolactone (GBL) are found to be almost unique solvents used for hybrid perovskites processing. The chemical origin of solvents strongly influences the process of perovskite crystallization because of the formation of intermediate adducts with different structures and morphology.

A variety of adduct phases of MAPbI₃ and DMF or DMSO has been recently reported [1,2]. In contrast, there is a common belief that the perovskite does not form adducts with GBL and there is a lack of understanding about crystallization pathways of perovskite from it.

In this study we for the first time showed that GBL in fact does form adducts [3]. Three types of adducts were obtained upon crystallization of perovskite solution from GBL: (MA)₂(GBL)₂Pb₃I₈ and two cluster adducts with ordered and semi-ordered (MA)₈(GBL)_x[Pb₁₈I₄₄] structure. The structure of the first adduct is analogous to the adducts (MA)₂(DMSO)₂Pb₃I₈ and (MA)₂(DMF)₂Pb₃I₈, while the cluster adducts are made of unique superoctahedral building blocks.

Raman spectroscopy studies of perovskite solutions in DMF, DMSO and GBL showed that this variety of adducts reflect the form of iodoplumbates in the solutions. At high concentration of iodide ions [PbI₃]⁻ prevail in the solution, while at low concentration coordination strength of a solvent start to play a crucial role. DMF and DMSO strongly coordinate Pb²⁺ and form only coordination complexes, whereas GBL leads to formation of clusters in the solution.

Based on these results, we concluded that undesired adduct formation can be avoided during perovskite thin films fabrication from either hot or iodide-excessive GBL solutions containing lead predominantly in the form of small coordination complexes such as PbI₃⁻. The obtained perovskite films are presented in Fig 1.

The research was financially supported by the Russian Science Foundation (Project No. 18-73-10224). Synchrotron radiation measurements were performed at the unique scientific facility Kurchatov Synchrotron Radiation Source.

REFERENCES

- [1] J. Cao et al. *J. Am. Chem. Soc.* (2016), 138, 9919–9926.
- [2] A.A. Petrov et al. *J. Phys. Chem. C* (2017), 121, 20739–20743.
- [3] S.A. Fateev, A.A. Petrov et al. *Chem. Mater* (2018), 30, 5237–5244.

Development of organic semiconducting materials for organic and hybrid photovoltaic devices

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Organic semiconductors are very important type of functional materials, which find their application in various devices of organic and hybrid electronics, including organic photovoltaics (OPV), dye-sensitized solar cells (Graetzel cells) and perovskite solar cells. They are small molecules, oligomers and polymers, which consists of π -conjugated aromatic and/or heteroaromatic fragments, with efficient light absorption in the visible and/or IR spectral range. In this lecture historical overview of the development of several generations of organic semiconductors used in different photovoltaic devices will be considered. Recent advances in organic and hybrid photovoltaics accelerated by the appearance of novel highly efficient organic semiconducting materials will be highlighted. Examples of novel donor-acceptor organic semiconductors developed in ISPM RAS, as well as their application in OPV [1-4] and perovskite optoelectronic devices will be discussed [5].

This work was made in the framework of Leading Science School NSh-5698.2018.3 and supported by Russian Science Foundation (grant 19-73-30028).

REFERENCES

1. J. Min, Y.N. Luponosov, C.Cui, B. Kan, H. Chen, X. Wan, Y. Chen, S.A. Ponomarenko, Y. Li, C.J. Brabec, *Adv. Energy Mater.*, 2017, 7(18), 1700465
2. O.V. Kozlov, Y.N. Luponosov, A.N. Solodukhin, B. Flament, O. Douheret, P. Viville, D. Beljonne, R. Lazzaroni, J. Cornil, S.A. Ponomarenko and M.S. Pshenichnikov, *Org. Electron.*, 2018, 53, 185
3. A.N. Solodukhin, Y.N. Luponosov, M.I. Buzin, S.M. Peregudova, E. A. Svidchenko and S. A. Ponomarenko, *Mendeleev Commun.*, 2018, 28(4), 415-417
4. A.N. Solodukhin, Y.N. Luponosov, A.L. Mannanov, P.V. Dmitryakov, S.M. Peregudova, S.N. Chvalun, D.Yu. Parashchuk, S.A. Ponomarenko, *Mendeleev Commun.*, 2019, 29(4), 385-387
5. C.-Y. Chang, A.N. Solodukhin, S.-Y. Liao, K.P.O. Mahesh, C.-L. Hsu, S.A. Ponomarenko, Y.N. Luponosov, Y.-C. Chao, *J. Mater. Chem. C*, 2019, 7, 8634-8642

Large-scale fabrication of hybrid perovskites in films by conversion of metallic lead with polyiodide-based reactive inks

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Hybrid halide perovskites with a general formula ABX_3 ($A=CH_3NH_3^+$, $CH(NH_2)_2^+$, $X=Cl, Br, I$) are considered to be highly promising materials for the light-absorbing layers of next-generation solar cells. The main synthesis approaches are based on the use of toxic lead salts dissolved in polar aprotic solvents such as DMF, DMSO and GBL that makes them unsuitable for industrially scalable perovskite solar cells production. Thus, new techniques to form perovskite layers with high uniformity are required. It is important also that such new methods should be applicable to form the perovskite layers at a large scale. Earlier the opportunity of one-step conversion of metallic lead into perovskite with reactive polyiodide melts (RPM) AI_n ($n=3-4$) was demonstrated. In theory, such approach allows to obtain large-scale perovskite films. However, there are number of technological difficulties in uniform RPM distribution and control of reaction stoichiometry.

The main purpose of the work is to develop the technique of hybrid halide perovskite films obtained with improved morphology and optoelectronic properties by the conversion of metallic lead with reactive polyiodide melts for scalable perovskite solar cells production. To achieve the goal we need to find conditions for perovskite films synthesis, investigate their microstructural, optical and optoelectronic properties and to fabricate solar cells to prove their power conversion efficiency.

Here, we use spin coating of RPM solution in isopropyl alcohol for uniform deposition of reactive polyiodide melt onto metallic lead surface. The perovskite films are investigated by XRD, SEM, EDX, TRPL, luminescence spectroscopy. Solar cells based on obtained films are fabricated, their IV-characteristics, power conversion efficiency and stability are determined. We have studied phase formation during the conversion of metallic lead into perovskite with different composition of RPM solution. According to the XRD data, the use of stoichiometric composition MAI_3 does not lead to single-phase perovskite formation without residue of MAI and metallic lead, whereas the use of enriched by I2 (MAI_4) and iodine deficient (MAI_x , $x<3$) composition, with subsequent post-treatment under particular temperature and gaseous environment, allows to obtain single-phase compact films with a thickness of ~500 nm and perovskite crystallites 200-500 nm in size. According to time-resolved photoluminescence data, estimated lifetimes of charge carriers are 45-50 ns. The opportunity of the $MA_xFA_{1-x}I_{3-x}Br_x$ films formation has been demonstrated. Moreover we have fabricated solar cells based on obtained films and measured their IV-characteristics.

Thus, the technique of hybrid halide perovskite films of different composition obtained by the conversion of metallic lead with reactive polyiodide melts has been developed. The solar cells with power conversion efficiency more than 15% have been demonstrated.

The work was supported by Russian Science Foundation (project RSF-19-73-30022).

Non-Planar Polyenes: a Circuit Boards with Tunable Electronic Properties

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Bowl-shaped polycyclic aromatic hydrocarbons (PAH) or buckybowls are pyramidalized polyenes composed of fused hexagons and pentagons, which can be considered as substructures of fullerenes. Buckybowls demonstrates superior acceptor properties as compared to planar PAH consisted of fused hexagons [1]. Recently reported efficient strategy for the direct synthesis of functional buckybowls [2] significantly broaden scope of synthetically available buckybowls with desired carbon frameworks and side chains [3] which opens a highway to the broad spectrum of derivatives with fine-tuned physicochemical properties with preserved electron accepting properties (due to low disturbance of π -conjugated system), which are essential for fabrication of efficient buckybowls-based organoelectronic devices.

Here we report the features of molecular and electronic structures of indaceno[3,2,1,8,7,6-pqrstuv]picene, indeno[4,3,2,1-cdef:4',3',2',1'-lmno]chrysene, extended indacenopicene and tetraindeno[1,2,3-cd:1',2',3'-fg:1'',2'',3''-jk:1''',2''',3'''-mn]pyren frameworks prepared via fluorine promoted Aryl-Aryl coupling [2,3] as well as related polyaromatic compounds. The derivatives were spectroscopically characterized; their electrochemical behavior, the reduction and oxidation potentials were measured by means of cyclic voltammetry.

The work was supported by Russian Science Foundation (project RSF-18-13-00337).

Key Words: Polyenes, Electrochemistry, Spectroscopy, Electronic Properties

REFERENCES

- [1] C. Koper, M. Sarobe, L.W. Jenneskens, Redox properties of non-alternant cyclopenta-fused polycyclic aromatic hydrocarbons: The effect of peripheral pentagon annelation, *Phys Chem Chem Phys.* 6 (2004) 319–327. doi:10.1039/B312234D.
- [2] K.Y. Amsharov, M.A. Kabdulov, M. Jansen, Facile Bucky-Bowl Synthesis by Regiospecific Cove-Region Closure by HF Elimination, *Angew. Chem. Int. Ed.* 51 (2012) 4594–4597. doi:10.1002/anie.201200516.
- [3] O. Papaianina, V.A. Akhmetov, A.A. Goryunkov, F. Hampel, F. Heinemann, K.Y. Amsharov, Synthesis of Rationally Halogenated Buckybowls via Chemoselective Aromatic C-F Bond Activation, *Angew Chem Int Ed.* 56 (2017) 4834–4838. doi:10.1002/anie.201700814.

Influence of the nature of cation A on the optical properties of quasi-one-dimensional lead halide perovskite APbX₃ (A is a cyclic amine cation: piperidine, pyridine, 3-hydroxypyridine; X=Br⁻, I⁻)

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Organic–inorganic halide perovskites are a wide class of photoactive materials, which attract the thorough attention of the research community due to their unique characteristics useful for manufacturing optoelectronic, photonic and photovoltaic devices. Recently there has been an increase in the number of works aimed at obtaining low-dimensional perovskite materials, in particular, perovskites with a one-dimensional (1D) structure. Due to the quantum-size effect, 1D perovskites demonstrate specific properties of their excited states: large exciton binding energy, large oscillator strength and the related non-linear optical effects. For this reason, 1D perovskites are interesting from both applied and fundamental viewpoints.

The structure of 1D perovskites is composed of inorganic anionic chains of the octahedra [PbX₆]⁴⁻_n surrounded and isolated from each other by organic cations. There are a number of works devoted to synthesis of 1D perovskites using as organic cation - protonated molecules of cyclic amines of the saturated and unsaturated nature. The π -system of an unsaturated organic cation can interact with the electronic structure of the inorganic component and contribute to the band structure of perovskite. Therefore, the use of unsaturated compounds for the synthesis of perovskite structures is especially interesting. Our earlier study on 1D pyridinium lead trihalides [1] has shown an existence of energy levels formed from unoccupied π^* -orbitals of aromatic pyridinium cation in the these compounds' bandgaps.

In this work, a number of lead halide low-dimensional perovskites were synthesized using cyclic amines: piperidine, pyridine and 3-hydroxypyridine. Their spatial structure, spectral-luminescent properties and effect of the nature of selected amine on these properties have been studied.

This work was financially supported by RFBR, project Nr. 19-03-00836.

REFERENCES

1. N. I. Selivanov, A. A. Murashkina, R. Kevorkyants, A. V. Emeline, and D. W. Bahnemann, Dalton Trans., 2018, 47, 16313.

Famous Perovskites: Periodic Table elements chemical puzzle for modern functional materials

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Widely spread crystal lattices of the perovskite type represent a natural flexible platform for chemical design of various advanced functional materials with unique features. An interplay between chemical bonding, defects and crystallochemical peculiarities make the perovskite structure a lego designer utilising natural chemical features of chemical elements of the renown Mendeleev's Periodic Table (PTE) celebrating 150 year anniversary this year. In this minireview crystal chemistry and bonding features physical and functional properties preparation methods and tuning the properties with periodicity "tools" of the PTE will be exemplified for legendary families of high temperature superconductive cuprates colossal magnetoresistive manganites and hybrid lead halides of a new generation of solar cells.

Spray pyrolysis and chemical bath deposition of SnO₂ thin films as an electron transporting layer for perovskite solar cells

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Nowadays, solar cells based on hybrid organic-inorganic perovskites attract increasing attention due to their high efficiency (current record PCE exceeds 25%) and potentially low production costs comparing to other solar cells with equatable efficiency. Perovskite solar cells consist of several functional layers and one of the most important ones is electron transporting layer (ETL). Until recently one of the most frequently used electron transporting layers were TiO₂ films. But alternative materials as ETLs are required due to photoactivity of TiO₂, impossibility of production of flexible modules based on TiO₂ which require high temperature synthesis that leads to degradation of most of flexible substrates. Currently one of the most perspective alternatives to TiO₂ are SnO₂ films which possesses a number of suitable for ETLs properties: high light transmittance owing to wide bandgap (>4 eV) and small reflective index, high electron mobility (up to $240 \text{ cm}^2 \cdot (\text{V} \cdot \text{s})^{-1}$), chemical stability, low temperature synthesis that is required for flexible modules production.

In this work several scalable methods for SnO₂ thin films synthesis were investigated and tested, including chemical bath deposition (CBD) from diluted solution of SnCl₂·2H₂O in presence of mercaptoacetic and hydrochloric acids; spray pyrolysis (SPR) of the SnCl₂·2H₂O solution in ethanol or methanol at 400°C. Also Sb:SnO₂ films (1,2,3,4,10 mol% ratio) were synthesized (minimum of resistivity is achieved at 2% Sb – $9,48 \cdot 10^{-2} \Omega \cdot \text{cm}$, while sheet thickness reaches 67 nm). Spin-coating (SC) of SnCl₂·2H₂O ethanol solution with subsequent post annealing was used as a reference method. Homogenous films without pinholes were obtained.

Solar cells with glass/FTO/ETL/Cs_{0,05}MA_{0,2}FA_{0,75}PbI₃/Spiro-MeOTAD/Au architecture were assembled. following ETLs were used: FTO, SPR_SnO₂, TiO₂, TiO₂+SC_SnO₂, TiO₂+CBD_SnO₂, SC_SnO₂, SC(twice)_SnO₂, CBD_SnO₂, SC+CBD_SnO₂. We achieved a maximum efficiency of 16,5 +/-0,6% with “SC(twice)_SnO₂” as ETL. Solar cells with ETL synthesized by scalable method gained comparable PCE (achieving up to 16,2±0,8% for “CBD_SnO₂”).

QTAIM method for accelerated band gap prediction in perovskites

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Elaborating descriptors for fast and reliable prediction of electronic structure in semiconducting materials is of primary importance for their efficient screening for practical applications. A number of electronic properties, for non-degenerate states, has a one-to-one correspondence with the electron density, which is a function of chemical composition and crystal structure. Topological analysis of electron density within Quantum Theory of Atoms-in-Molecules (QTAIM) allows to quantify electron density features and provides descriptors, which can be further used for evaluation of electronic structure parameters. In the current work, we demonstrate that band gaps in perovskite compounds are correlated with the electron density at the bond critical points. This allows to use PBE-based descriptors for fast evaluation of quantities obtainable with more resource-demanding methods, such as hybrid functionals or GW. Moreover, observed correlations enable a direct prediction of experimental band gaps for yet unsynthesized perovskites using topological descriptors [1].

REFERENCES

1. Syzgantseva, M.A.; Syzgantseva, O.A. // *Theoretical Chemistry Accounts*. 2019, 138, 52.

Computational and Theoretical Chemistry for Hybrid Perovskite Research

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Despite a substantial progress in perovskite research for photovoltaics, there still remain phenomena, for which experimental physicochemical methods cannot provide a sufficiently full understanding, and this prevents an adequate qualification of some studied phenomena. Therefore for the successful development and expansion of perovskite research, computational modelling on supercomputers is used, that in its turn creates a need for theoretical models, adequate to experimental data. This challenge brings to the forefront the necessity of on-line collaboration between experimentalists, computational chemists and theoreticians. Such an interaction is intended to ensure a fruitful background for the research on a qualitatively new level. In this talk, some examples of this kind of interaction between experimentalists, computational chemists and theoreticians, involved in hybrid perovskite research, will be presented and some preliminary conclusions on the research potential of such interactions will be made.

Room-temperature melts based perovskite processing: polyiodide-based approach as a mirror strategy to amine-based methods

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Perovskite solar cells are one of the fastest growing classes of photovoltaic devices overcoming record efficiencies for silicon solar cells and reaching power conversion efficiencies of 24.2%. Methylamine-based approaches such as perovskite crystallization from MA-MAPbI₃ melt [1] or perovskite crystallization from a methylamine-saturated solution in acetonitrile [2] demonstrate high potential towards scalable processing of hybrid perovskites. These approaches are based on the formation of room temperature perovskite melts through a subsequent evaporation of amine resulting in formation of a pure perovskite film.

While the amine-based approaches stem from the use of perovskite (MAPbI₃) cation derivative, namely, methylamine (MA), the recently developed polyiodide approach take advantage of the anionic constituent derivative which is iodine (I₂). The reactive polyiodide melts (RPM) are liquid polyiodides which can be readily prepared by mixing powders of I₂ with organic iodides such as MAI and FAI or a mixture thereof. The reaction proceeds instantly at room temperature and results in a highly-viscous liquid [3].

Based on the interaction of RPMs with metallic lead, high-quality perovskite films with various compositions were obtained according to the following reaction: $AX_3 + Pb \rightarrow APbX_3$ (A = MA, FA, Cs; X = I, Br). Thus, RPM opened up a new formation strategy of hybrid lead halide perovskites using the polyiodide-based method. Due to its unique composition the RPM acts simultaneously as a liquid medium and a highly reactive precursor that swiftly converts metallic lead into perovskite. Using this novel approach we fabricated high-quality polycrystalline perovskite films with micron-size grains with power conversion efficiency (PCE) of over 17%. The modules with 2.45 cm² active area showed PCE exceeding 14.2% with great uniformity of the perovskite layer over the large area. In addition, we demonstrated applicability of this method for the fabrication of highly uniform perovskite films with micron-size grains over large substrates of 10x10 cm² and 20x30 cm², including flexible supports [4].

Moreover, the RPMs have been recently found to be also a highly corrosive decomposition product which forms under sunlight and cause degradation of perovskite solar cells components, including spiro-MeOTAD and gold electrode [5].

In the present study, we thoroughly investigated chemical and physical properties as well as phase equilibriums in the polyiodide systems and revealed the outstanding potential of the polyiodide melts for the improvement of the processing of hybrid perovskites.

Research was financially supported by the Russian Science Foundation (Project № 18-73-10224).

REFERENCES

- [1] H. Chen, et al. *Nature* (2017), 92–95.
- [2] N.K. Noel, et al. *Energy Environ. Sci.* (2017), 145–152.
- [3] A.A. Petrov, et al. *Mater. Horiz.* (2017), 625–632.
- [4] I. Turkevych, et al. // *Nat. Nanotechnol.* (2019), pp. 57-63.
- [5] N.N. Shlenskaya, et al. // *J. Mater. Chem.* (2018), 1780–1786.

Electrodeposited TiO₂ electron transport layer for perovskite solar module

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There has been significant progress in organometallic halide perovskite solar cell (PSC) in decade, boosting the record certified power conversion efficiency (PCE) up to 25.2%. However, the high PCEs of PSCs are almost realized on the small area device, typically around 0.1cm². The PCEs of large area PSCs, such as 1 cm² and modules, still lag behind those of small area devices considerably. The quality requirement of the films in large area PSC is more severe than that in small area device. For example, a pinhole-less and uniform electron transport layer (ETL) is regarded as one of the key factors to improve the PCE of large area PSC.

We previously developed a bottom-up deposition method to prepare TiO₂ ETL based on electrodeposition technology. This method provides controllability for the morphology and thickness of resultant TiO₂ films by simply manipulating deposition parameters. In this work, we take above-mentioned advantage of electrodeposited TiO₂ technology in preparing ETL for perovskite solar module and compare with common spin-coated TiO₂ ETL. The thickness and conditions of electrodeposited TiO₂ were comprehensively studied. Our approach is compatible with up-scalable deposition techniques and paves the way for large-scale fabrication of highly efficient large area PSC.

Photoluminescence quantum yield enhancement by Purcell effect in halide perovskite resonant nanostructures

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Recent studies demonstrated high interest in halide perovskite materials for different applications including solar cells, light emitting diodes and many others. Therefore, making photoluminescence quantum yield is one of the most important characteristics. However, the external quantum efficiency from a perovskite film is much lower than the internal one, because emitted light does not escape from the film with respect to the normal of the surface owing to strong reflection and re-absorption. One of the straightforward strategies for external quantum efficiency improvement is the enhancement of light scattering increasing probability of emission outcoupling. On the other hand, radiation recombination can be relatively enhanced via acceleration of spontaneous emission in a resonator as compared with that in homogeneous medium due to the Purcell effect. Also, it was experimentally shown that nanoparticles made of organic-inorganic (hybrid) $\text{MAPb}(\text{I},\text{Br})_3$ perovskite materials can support Mie-resonances in the visible range, thus enhancing the photoluminescence emission from the nanoantennas. In this work, influence of Purcell effect on photoluminescence quantum yield of perovskite nanostructures is studied. We theoretically demonstrate enhancement of photoluminescence quantum efficiency for a single spherical MAPbI_3 nanoparticle. Such nanostructures can be used as effective optical nanosources and promising platform for optical cooling.

Unravelling intrinsic bulk and interfacial degradation mechanisms in lead halide perovskite solar cells

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The emerging perovskite solar cells demonstrated impressive power conversion efficiencies exceeding 24%, while their practical application is restricted mainly by poor operation stability. We have reported recently that hybrid MAPbX₃ perovskites undergo facile thermal and photochemical degradation even under anoxic conditions without exposure to oxygen and moisture, while their all-inorganic counterparts CsPbX₃ proved to be significantly more stable.

Here we will discuss our the most recent results coming from a systematic study of the intrinsic stability of a broad range of materials represented by various lead-based perovskites and compare them with some lead-free complex halides of tin, germanium, bismuth and antimony. The revealed pathways of thermal, photochemical and electrochemical degradation processes will be presented and a conclusion on the potential of different groups of materials for practical application in PV technology will be drawn.

We will particularly focus on analyzing the interface degradation effects occurring between the electrodes, charge transport layer materials and the photoactive layer induced by electric field, elevated temperatures, solar light or a combination of these stress factors. Finally, it will be shown that reaching any commercially interesting operation lifetimes for perovskite solar cells requires a considerable shift from the currently used device design paradigms as well as a comprehensive multiparametric optimization of all used materials and functional components.

Hybrid materials in photovoltaics, photocatalysis and sensing

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Solar cells based on Pb-based hybrid halide perovskites demonstrated unprecedented progress of photoconversion efficiency during the past decade. This is one of the first and prominent examples when a hybrid organic-inorganic material demonstrated significantly better combination of electronic and optoelectronic properties in comparison to conventional inorganic PV materials. In my presentation I will highlight R&D activities in Japan related to the development of scalable perovskite PV technologies. In addition, I will present a perspective on application of other classes of hybrid materials in photovoltaics, photocatalysis and sensing. For a long time, hybrid materials were not considered as promising candidates for the fabrication of electronic devices. However, modern electronics requires multi-functional materials, in which certain combination of properties must be fulfilled simultaneously (for example flexibility, conductivity and transparency in flexible transparent conductive electrodes). In many cases hybrid materials may possess unique combinations of properties derived from complex interaction between inorganic and organic components. In particular, there is a tremendous progress in the development of hybrid non-halide perovskites that show a wide range of interesting electronic and magnetic properties. Furthermore, recent developments in electronically conductive metal organic frameworks (MOFs) open new horizons in the application of hybrid materials in electronic devices.

Optical tracking of photochemically formed I₂ during hybrid perovskite decomposition: a valid method for the hybrid perovskite stability investigation

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Perovskite solar cells (PSCs) have been a hot topic in the field of photovoltaics during last decade. PSCs are based on hybrid perovskites (HPs) ABX₃ (A=CH₃NH₃⁺, CH(NH₂)₂⁺, Cs⁺; B=Pb²⁺, Sn²⁺; X=I, Br⁻), acting as light harvesters in the visible spectrum (absorbance edge varies from 539 to 950 nm). This class of materials demonstrate excellent optical and charge transport properties leading to high power conversion efficiencies (>25%). However, instability of light-absorber material prevents fast implementation of perovskite solar cells to the manufacturing process. PSCs suffer from instability to moisture and oxygen but can be successfully overcome via encapsulation methods. Visible light also causes degradation of hybrid perovskite materials, however, no 100% effective approach to diminish this perovskite decomposition path has been reported so far. Moreover, in the literature there is a lack of information about standard protocols for the investigation and testing of hybrid perovskite photostability. Predominantly, light-driven processes inside HPs materials are studied by photoluminescence which is a powerful approach, but usually implemented locally. Hybrid perovskites, in turn, demonstrate heterogeneity of optical properties even from one grain to another, greatly complicating the process of obtaining reliable data by local methods.

We introduce a simple approach based on *in-situ* tracking of molecular iodine – one of the main hybrid perovskite photolysis product, during irradiation of perovskite material by light with controlled parameters. Iodine release from irradiated film is provided into nonpolar aliphatic solvent (C₇H₁₆ – C₁₀H₂₂) in a sealed quartz cuvette. Iodine solutions in non-polar solvents effectively absorb light in a green part of the visible range (absorption line maximum at 514 nm) which enables iodine concentration tracking by a photometry with green LED and photodetector. We used 450 nm laser as a light source for perovskite photolysis with a power density in 100-500 mW/cm² range. MAPbI₃ was used as the first material for this research. Time dependence of heptane absorption (proportional to I₂ concentration) shows sharp monotonic decrease with ultimate saturation at the final decomposition stage.

Corresponding evolution of film morphology was studied by scanning electron microscopy. Photolysis of MAPbI₃ thin film starts on grain boundaries which is clearly visible in SEM micrographs and can be explained by the high concentration of defects on them. Photochemical formation of I₂ in inert atmosphere under visible light can be described by the following quasi-chemical equations: $O \rightarrow h\nu + e^-$; $2I_I^x + 2h\nu \rightarrow 2I_I^x + 2V_I^- \rightarrow I_2$; $Pb_{Pb}^x + 2e^- \rightarrow Pb^0$. This process was found to be reversible in the case of heptane solution above the thin film, which can be also used for recovery of hybrid perovskite layer without illumination. Minimizing the area of grain boundaries is one of the potential ways to increase the overall HPs stability. Iodine-tracking approach allows to estimate contribution of such modifications into the material stability.

Thus, we suggested potentially standard protocol for the hybrid perovskite photostability testing, which includes ability to qualitatively and quantitatively characterize perovskite material depending on different parameters.

The reported study was funded by RFBR according to the research project № 19-53-53028.

Unraveling chemical processes driven by intensive laser irradiation of hybrid perovskites

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Laser irradiation is widely used in materials science and photovoltaics as both a non-destructive diagnostic and destructive patterning light source. The latter is a basis for the widely known laser scribing technology applied in photovoltaics for solar panels assembly. Perovskite solar modules are also processed by using this technology; however, only scarce information is known about photochemistry of hybrid perovskite interaction with intensive laser irradiation. One of the potential methods for *in situ* study of laser-driven processes in hybrid perovskites is Raman spectroscopy. A number of articles about perovskite degradation caused by Raman spectroscopy has already been published but the reported data are controversial.

In the current work, we provide a detailed study of structural changes in hybrid perovskite powders and thin films with various composition under laser irradiation in a visible range by Raman spectroscopy. We also discuss the influence of atmosphere and confined space on the degradation products, dynamics of decomposition, and morphological features of the laser scribing.

According to Raman spectroscopy results, all hybrid perovskites (MAPbI₃, MA_{0.15}FA_{0.85}PbI₃, FAPbI₃, MA_{0.25}FA_{0.75}PbI_{2.25}Br_{0.75}, FA_{0.85}CS_{0.15}PbI₃, CS_{0.05}MA_{0.15}FA_{0.8}PbI_{2.5}Br_{0.5}) undergo laser-induced degradation followed by formation of PbI₂, polyiodides and solvating iodine species. In the case of ambient atmosphere, additional formation of lead oxide (PbO_x) is observed. Partial iodine substitution with bromine slightly increases perovskite stability, but doesn't prevent material from degradation under laser beam. We consider I₂ and PbO_x as ultimate decomposition products, vibration intensity of which in Raman spectra may reflect the depth of perovskite degradation. An analysis of the I₂/I₃⁻ vibration intensities ratio revealed a monotonic increase of this value in the following sequence: MAPbI₃ < MA_{0.15}FA_{0.85}PbI₃ < FAPbI₃ < MA_{0.25}FA_{0.75}PbI_{2.25}Br_{0.75} < FA_{0.85}CS_{0.15}PbI₃ < CS_{0.05}MA_{0.15}FA_{0.8}PbI_{2.5}Br_{0.5}, which agrees well with stability issues known with respect of hybrid perovskites of different composition. We also investigated the dynamics of Raman spectra from MAPbI₃ thin films under three different conditions: open air, sealed with a glass slide, under an argon flow. The former demonstrates a strong increase of PbO_x vibration intensity in the irradiated area, the second condition leads to the accumulation of all the products (I₂, polyiodide, PbI₂, PbO_x), while an addition of argon flow allows to prevent perovskite oxidation and increase the efficiency of overall sublimation/ablation under the laser beam. Scanning electron microscopy study combined with electron-probe microanalysis revealed a tendency of a "crater" size reduction in the order: under glass > open air > Ar flow. A comparison of "craters" made with laser irradiation in MAPbI₃, MA_{0.25}FA_{0.75}PbI_{2.25}Br_{0.75}, and FA_{0.85}CS_{0.15}PbI₃ demonstrated a visible difference in the "dead area" size (area surrounding the crater with visible film destruction) with the smallest one for FA_{0.85}CS_{0.15}PbI₃ and the largest for MAPbI₃. I:Pb elemental ratios correlate strongly with the above mentioned morphological changes.

In summary, this work elucidates the chemical aspects of laser-driven hybrid perovskites degradation, including the study of the effects of perovskite composition and surrounding atmosphere on the ongoing degradation processes and the size of the formed laser-induced craters.

The reported study was funded by RFBR according to the research project № 19-53-53028.

Ion migration in the perovskite light emitting solar cell

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Organo-halide perovskites have developed very fast over the last ten years and achieved power conversion efficiencies of well-established technologies as silicon heterojunctions. Also, perovskite light emitting diodes now have efficiencies about 20%. High performance of perovskite based devices, low-cost manufacturing and their simple processing make them one of the most perspective material for developing solar cells and light emitting diodes. Despite all the attractive properties of perovskites, they demonstrate one unwanted property, which is ionic migration. Usually, ion migration leads to performance losses in perovskite based devices, halide segregation in mixed halide perovskites and hysteresis in current-voltage characteristics. Halide segregation manifest in separation of mixed halide perovskite into two mono halide phases with different band gap. Hysteresis in current-voltage characteristic lead to dependence of device photovoltaic parameters on scan direction. This causes over- or under-estimation of device parameters.

Nevertheless, ionic migration can demonstrate some positive effect for example in dualfunctional devices – light emitting solar cells. Usually, high-efficient solar cell is a non-effective light emitting diode since it is design specifically optimized for one purpose. And in the reciprocal working regime there will be a high potential barrier for charge injection between transport layers and perovskite layer. For realization of light emitting solar cell, there is a need for reversible adjustment of band diagram for specific working regime: light emitting diode or solar cell. In this case, ionic migration can aid to solve this problem due to forming of pin structure under applied voltage. Devices based on mixed halide perovskites with PEDOT:PSS and C60 transport layers capable of demonstrating low threshold voltage around 1.7 V in case of MAPbBr₂I perovskite layer. Whereas threshold voltage around 2.7 V in the case of FAPbBr₂I perovskite layer. It seems that in mixed halide perovskite there are cation and anion migration. Difference in threshold voltage justifies by dipole momentum of organic cations methylammonium (MA) and formamidinium (FA), 2.29 Debye for MA and 0.21 Debye for FA. Under applied voltage organic cations move to the electron transport layer (ETL) and form a dipole layer at the perovskite/ETL interface. This dipole layer allows to adjust device band structure for light emitting diode working regime. Since ionic migration is a reversible process, removal of external voltage leads to backward ionic migration. Which leads to device band structure adjustment to solar cell working regime. Therefore mixed halide perovskite allow developing dualfunctional devices with simple perovskite solar cell architecture based on mixed halide perovskite without using special types of transport layers.