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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.

MAPPIC – 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 с приглашёнными докладами выступили ведущие ученые в области солнечной энергетики из разных стран мира:

Prof. Juan Bisquert	Impedance spectroscopy of memory effects in halide perovskites: Control of hysteresis in solar cells and memristors	Jaume I University, Spain
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Гибкие перовскитные солнечные элементы с дырочным транспортным слоем электроосажденного поли(3,4-этилендиокситиофена)

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Одним из актуальных направлений расширения функциональных и потребительских качеств солнечных элементов (СЭ) становится разработка устройств на пленочной основе. Достоинством таких СЭ вместе с механической гибкостью является малый вес.

На гибкие подложки из лавсана, покрытые проводящим слоем ИТО, электрохимически были осаждены тонкие слои поли(3,4-этилендиокситиофена) (ПЭДОТ) в присутствии сульфокислотных полиэлектролитов различной структуры в гальваностатическом режиме. Для электросинтеза слоев ПЭДОТ были использованы Na^+ -соли гибкоцепных полиэлектролитов: поли-2-акриламидо-2-метил-1-пропансульфоновой кислоты и полистиролсульфоновой кислоты, а также жесткоцепного полиэлектролита: поли-4,4'-(2,2'-дисульфокислоты)-дифенилентеревфаламида. При электрохимическом осаждении ПЭДОТ полимеризация и осаждение происходят в одну стадию. Этот метод обеспечивает высокую воспроизводимость свойств слоев благодаря точному контролю параметров синтеза, не приводит к значительным отходам материала и может использоваться на изогнутых подложках большой площади, что делает эту технологию совместимой с крупномасштабными приложениями.

Полученные слои ПЭДОТ были использованы в качестве дырочно-транспортных слоев (ДТС) в перовскитных солнечных элементах (ПСЭ). Фотоактивный слой ПСЭ толщиной 400 нм формировали из металлоорганического соединения $\text{CH}_3\text{NH}_3\text{PbI}_3$ одностадийным методом. Проведено сравнительное исследование стабильности параметров ПСЭ во времени. ПСЭ со слоями комплексов ПЭДОТ, осажденными электрохимическим методом, показали высокую стабильность в течение трех недель.

Сравнительное исследование перовскитных квантовых точек на основе компонентов CsBr·PbBr₂

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Перовскитные квантовые точки являются одним из наиболее перспективных полупроводниковых наноматериалов благодаря своим уникальным оптическим и электронным свойствам. В первую очередь, их преимуществом является Стоксов сдвиг: разница между длинами волн пика поглощения и пика фотолюминесценции, благодаря которому можно избежать перепоглощения материала. Квантовые точки используются в качестве сцинтилляционных материалов, полупроводниковых слоев в светодиодах и солнечных батареях [1], а также в настоящее время рассматривается возможность использования их в качестве биометок для медицинской диагностики [2].

В данной работе сравниваются два метода синтеза квантовых точек на основе неорганической перовскитной композиции CsBr·PbBr₂. Принципиальным отличием является выбор стабилизирующих агентов (лигандов): бромид октиламмония [3] и олеиновой кислоты [4]. В работе сравниваются оптические характеристики продуктов синтеза в зависимости от метода и используемых лигандов. Полученные вещества были охарактеризованы методом спектрофлуориметрии, просвечивающей микроскопии.

Квантовые точки с использованием бромид октиламмония не нуждаются в очистке в отличие от квантовых точек с оболочкой из олеиновой кислоты, что облегчает процесс получения готового для использования продукта. Этот фактор особенно важен для последующего применения продукта синтеза, например в качестве пленок. Также у композиции с бромидом октиламмония положение пика фотолюминесценции смещено в УФ область, относительно композиции с олеиновой кислотой. Это указывает на значительное влияние на размер синтезируемых частиц при использовании октиламмония бромид. Метод позволяет получать тонкие пленки контролируемой толщины. Метод не требует сложных дорогостоящих реактивов и оборудования.

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Разработка технологии создания преобразователей излучения оптического датчика искры на основе нанокристаллов неорганических перовскитов

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Оптический датчик позволяет детектировать электрическую искру по одной или двум координатам, в зависимости от расположения входных торцов оптических волокон или оптических жгутов. В качестве спектрального преобразователя УФ излучения искры использованы нанокристаллы свинцово-галогенидных перовскитов CsPbBr₃. Они характеризуются высоким квантовым выходом, благодаря размерным эффектам, и широкой полосой поглощения вплоть до 500-505 нм, что позволяет захватывать и преобразовывать практически весь спектр электрической искры.

Interface engineering through 2D-transition metal dichalcogenides for reliability enhancement in perovskite solar cells

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The generation of energy with a minimum carbon emission from renewable energy sources could be a possible way forward to the present energy crisis due to unending technological development. Perovskite solar cells (PSCs) are an emerging photovoltaic (PV) technology, yielding an unparalleled power conversion efficiency (PCE), which is on par with those of mature technologies. Since PSCs are composed of several layers in a sandwich structure, interfaces have a crucial role in the operation of devices, ultimately determining the overall performance and stability. A deep understanding of physical processes including photo-induced charge transfer dynamics at perovskite/charge transport interfaces is paramount for the investigation of PSCs. Interfacial engineering is one of the promising approaches to overcome energy level mismatch, undesirable charge transfer, and moisture corrosion, which have a great impact on overall electrical performances and device stability.

Recently 2D materials have been demonstrated as an interfacial layer in PSCs to enhance PV performances and long-term stability. 2D transition metal dichalcogenides (TMDs) are a promising class of direct bandgap semiconductors for PV applications including PSCs due to their outstanding chemical, physical and electronic properties which can be further tuned by their synthesis route. Among the different synthetic protocols, Li⁺ intercalated liquid-phase exfoliation of layered materials is a promising approach that offers high yield, simplistic method, up-scalability, and cost-effectiveness. In contrast, the utilization of 2D-TMDs as an interfacial layer between the active and charge transport layers led to significantly improved PV performance with an extended lifetime.[1-2] The non-covalent interactions and the danglingbond-free nature of 2D-TMDs could aid in further stabilizing the active layer from hygroscopic additives in charge transport materials.

We will report our findings on the successful implementation of Li⁺ intercalated liquid-phase exfoliated 2D-TMDs as an interfacial layer on organic-inorganic hybrid perovskite, leading to a significantly enhanced PCE and an extended lifetime. We noted that the 2D-TMDs as an interlayer could diminish the surface traps and interfacial charge recombination at the perovskite/HTM interface through the aligned energy level, subsequently boosting the PCE owing to the boosted open-circuit voltage (V_{OC}) and fill factor (FF).

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Broad-range spectroscopy of a single crystal of hybrid perovskite MAPbBr₃

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Currently, one of the most promising materials for using in solar cells and other photovoltaic devices is hybrid metal-organic perovskite (MOP) [1, 2]. Investigation of the phonon spectrum features and electron-phonon interaction of the MOP makes it possible to explain the nature of many photoelectric properties. In particular, the vibrational structure of MAPbBr₃, namely the multiphonon excitation of the crystal lattice, has not been fully understood yet.

In this work the spectroscopic study is presented for the wide frequency (1800 - 12000 cm⁻¹) and temperature (5 - 300 K) ranges. The single crystal was synthesized at the A.V. Rzhanov Institute of Semiconductor Physics in Novosibirsk [5]. For optical measurements and the study of temperature dependences a high-resolution Fourier spectrometer Bruker IFS 125HR was used. The spectra presented in this work were measured with a resolution of up to 0.2 cm⁻¹.

Analysis of the obtained absorption spectra showed the presence of several types of splittings: Davydov splittings, inversion splittings, tunneling between two or more states upon freezing the orientation of MA⁺ ions. There are groups of vibrations associated with torsional, stretching, deformation and pendulum vibrations, as well as their combinations.

At temperatures of 152 K and 148 K, structural phase transitions occur from tetragonal phase I to tetragonal phase II and from tetragonal phase II to orthorhombic, respectively. The rearrangement of the structure is clearly reflected in the absorption spectra: the parameters of many spectral lines change, and new vibrations also appear.

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11-aminoundecanoic acid: new cation for 2D layered perovskites and efficient passivator improving photostability of 3D perovskites

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Despite the significant progress achieved in increasing the stability of hybrid halide perovskite materials, their degradation under exposure of light and heating is still one of the main problems of modern perovskite photovoltaics. One of the reasons for low stability is claimed to be a high concentration of surface defects participating in surface-mediated degradation reactions.

In recent years, a large number of works have demonstrated the possibility of a significant increase in the efficiency and stability of devices after the post-treatment of the perovskite surface by various alkylammonium halides, thus passivating surface and grain boundary defects. However, for most relatively small alkylammonium cations, gradual diffusion from surface into the bulk of the 3D perovskite layer is possible, which leads to deterioration of the properties of the bulk material. This is why it is still urgent to search for new organic ions, the structure and size of which hinders their migration from the interface.

In this work, protonated 11-aminoundecanoic acid (AUDA⁺) was tested as a passivator. The presence of a carboxyl group is necessary for the correct orientation of the molecules and the formation of a passivating layer between the light-absorbing perovskite layer and the oxide layer, which is known for the case of protonated 5-aminovaleric acid (AVA⁺), widely used as a modifying additive. The advantage of AUDA⁺ over AVA⁺ is the longer carbon chain, which prevents the diffusion of molecules into the perovskite layer.

The first stage of research was to study the effect of the deposition of 11-aminoundecanoic acid iodide (AUDAI) on MAPbI₃ and (FA_{0.75}MA_{0.25})PbI₃ thin films. The combination of the optimal deposition conditions, such as solvent, AUDAI concentration, temperature, and duration of post-annealing, allows to increase optical properties, as well as photo- and thermal stability of perovskite. It was also shown that there are no low-dimensional phases in the case of low concentrations of AUDAI post-treatment solution, however they are inevitably formed and deteriorate photostability at higher ones.

To study these new perovskite-like phases, we produced thin films and single crystals with the stoichiometry of $n=1$ (AUDA₂PbI₄) and $n = 2$ (AUDA₂MAPb₂I₇ and AUDA₂FAPb₂I₇, where MA⁺ is the methylammonium cation, FA⁺ is the formamidinium cation). The parameters of the crystal structures of the obtained compounds were determined by XRD and agreed with the proposed composition. We also carried out a comprehensive characterization of the optical properties of the new layered perovskites using absorption spectroscopy, diffuse reflection spectroscopy, time-resolved and steady-state photoluminescence spectroscopy at various temperatures. As a result, the optical band gap, the exciton binding energy, the nature of optical transitions, and the charge carrier lifetimes (τ) were determined for each phase.

As shown, the deposition of AUDAI can greatly improve both the optical properties (PL intensity, τ) of the perovskite layer and its photostability, which suggests the prospects for application of AUDAI as a passivator in perovskite solar cells.

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Adapting the geometry of Bi polyhedra in hybrid halobismuthates to weak interactions

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The chemistry of organic-inorganic halometallates attracting the increasing interest of researchers. The interest is concerned with valuable luminescent, thermochromic, photocatalytic and especially photovoltaic properties. One of the prominent representatives of this class are hybrid halobismuthates - promising candidates for solar energy. At the moment, halobismuthates with linear 1D anions $[\text{BiX}_5]_n^{2n-}$ in their crystal structure are known to have low band gap values and probably be able to provide a sufficient charge carrier diffusion. Thus, the crystal engineering of halobismuthates to prepare the substances with given anion seems to be the highest priority. In this regard, it was important to reveal the possibility of targeted production of halobismuthates with a given anion structure.

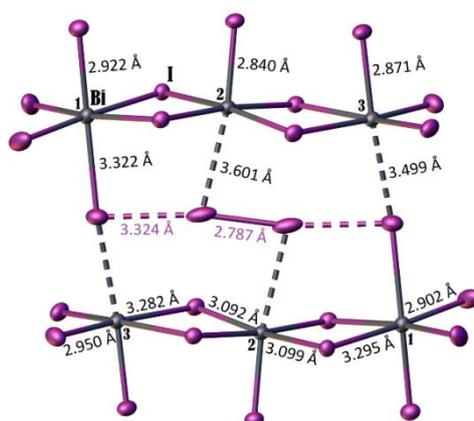


Figure 1. $[\text{Bi}_6\text{I}_{26}]^{6-}$ anion within the structure of 1,4'-bipyridine halobismuthate.

In this work, we report the synthesis and crystal structure of organic-inorganic hybrid 1,4'-bipyridine halobismuthate $[\text{PyPy}]_2[\text{PyPyH}]_2\text{Bi}_6\text{I}_{26}$. The novel anion $[\text{Bi}_6\text{I}_{26}]^{6-}$ (Figure 1) was discovered in the structure. The DFT calculation of the crystal structure and electron density distribution analysis within the QTAIM framework made it possible to calculate energies of all Bi-I bonds. The considerable range of Bi-I bond lengths (2.8 to 3.6 Å) allowed us to construct an equation relating Bi-I bond length (r) to its energy (E) ($R^2 = 0.9993$).

$$E(r) = 40352 \cdot e^{-2.683 \cdot r}$$

Using this correlation, the statistical analysis of Bi-I bond energies in 262 iodine-bismuthate anions found in the CCDC database (ver 5.40 September 2019) was performed. Analysis of these crystal structures revealed that the average binding energy of Bi polyhedra is highly conserved at 64.4 kcal/mol with the standard deviation of only 1.6 kcal/mol (Table 1). The average value and standard deviation are also very stable in the subsets of the crystal structures corresponding to

particular structural motifs, or different temperatures at which the structure was studied with XRD. Moreover, our statistical analysis confirms conservation of net energies of trans-{I-Bi-I} bond pairs at 21.5 ± 1.1 kcal/mol, which corresponds to 1/3 of the total energy of Bi-I bonds within Bi polyhedra.

Table 1. Mean values of Bi polyhedra energies for halobismuthate structures of different composition and different temperatures. All energies are given in kcal/mol.

Subset of structures	$\langle E \rangle$	σ	min	max	Total count
All structures	64.4	1.6	55.6	72.9	262
$[\text{BiI}_4]_n^{n-}$	64.7	0.7	62.5	66.1	33
$[\text{BiI}_6]^{3-}$	63.1	2.2	55.6	68.1	31
$[\text{Bi}_2\text{I}_9]^{3-}$	64.2	1.5	59.3	69.2	53
$[\text{Bi}_2\text{I}_{10}]^{4-}$	63.9	1.1	61.5	66.2	25
trans- $[\text{Bi}_3\text{I}_{12}]^{3-}$	65.1	1.2	62.5	67.2	24
150K	64.3	1.2	60.2	66.1	51
295K	64.1	1.6	55.6	69.2	128

Thus, the energy of iodobismuthate crystal structure weakly depends on the stability of the Bi polyhedron. The order of magnitude of energy variations upon changing Bi polyhedra corresponds to that of weak non-covalent interactions in the second coordination sphere. So, the main factor affecting the formation of the final structure of hybrid iodobismuthates is not the energy benefit of the formation of one form or another of a bismuth-containing anion, but a combination of weak intermolecular interactions, such as electrostatic, van der Waals, intermolecular hydrogen and halogen bonds – they should receive special attention in future modeling of these compounds.

New Fullerene-Based Electron Transport Materials for p-i-n Perovskite Solar Cells with Improved Efficiency and Stability

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In this contribution, we report on the synthesis of a series of fullerene derivatives and their systematic investigation as promising ETL materials for p-i-n perovskite solar cells. Devices fabricated using new fullerene derivatives F5-F10 demonstrated power conversion efficiencies up to 19.0%, which are higher than the reference cells assembled using PC61BM, which is a benchmark ETL material (14.0%). The improved photovoltaic performance of the devices incorporating new fullerenes derivatives originated from the decreased nonradiative recombination at the Cs_{0.12}FA_{0.88}PbI₃/ETLs interface, efficient electron extraction, and full coverage of the perovskite absorber layer. Furthermore, our unencapsulated devices based on F6, F8, and F9 exhibited long-term stability under 1 sun for ~1300 h, whereas the initial PCE of PC61BM was degraded to ~ 40 % after 200 h under the same aging conditions. These obtained results feature new functionalized fullerene derivatives as promising ETLs for efficient and potentially stable perovskite solar cells.

Passivating strategy in p-i-n planar perovskite cells for scale-up

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Halide perovskites (HP) is emerging thin-film photovoltaic technology and demonstrates high output performance of the solar cells (power conversation efficiency (PCE) >25% [1] with cost-effective solution processes for the fabrication. On the other hand, crystallization of the HP films tends to the formation of various structural defects interstitials, dislocations, grain boundaries, which could act as a trigger for the degradation of functional films [2]. P-i-n structured perovskite solar cells (PSCs) with NiO_x hole transporting layer were considered as promising architectures for hysteresis-free performance. However, such type of heterostructures suffers from chemical instability caused by interaction of the non-stoichiometric oxides with mobile charged defects migrating from the perovskite absorber. In order to passivate the NiO_x/perovskite interface [3], we designed PSCs with buffer based on wide bandgap polymer layer – polymethyl methacrylate (PMMA). The use of polymeric interlayer allows to reduce the impact of non-radiative recombination losses and trapping at the interfaces, suppress the current leakage, and maximize the open circuit voltage (VOC) of the PCSs [4]. In this work, we applied PMMA as insulating buffer to suppress decomposition of perovskite at grain boundaries and improve adhesion of thin films at NiOX/perovskite interface. PSCs based in MAPbI₃ and CsFAMAPb(I_{3-x}Br_x)₃ with PMMA interlayer showed improvement of PCE in comparison to the non-modified devices from 15.2 to 17.9% for single cation perovskite and from 17.0 to 18.4 % for triple cation composition. The approach was successfully upscaled for the minimodules which reached the PCE level at 14.4 % (S=2.3 cm²) and 8.0 % (S=10.0 cm²). Remarkable effect was obtained for the stabilization of the output performance for PCSs with PMMA buffer. Passivated devices showed more stable and higher performance during thermo-test (T=80°C, air) and light-soaking aging (LED source, 65 °C, air). PSCs showed more than 140 hours (MAPbI₃) and 630 hours (CsFAMAPb(I_{3-x}Br_x)₃) of sustained test research under illumination where losses of PCE were less than 20 %.

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Structures and optical properties of low-dimensional phases in MAX-FAX-PbX₂ system (X = I, Br)

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Small cations such as guanidinium and cesium can act as templating cations to form low dimensional perovskite-like phases (2D, 1D, 0D) in the case of excess of organic halides. However, such phases with the widely used formamidinium (FA⁺) cation have not been re-ported so far. In this study, we discovered two novel low dimensional phases of layered (2D) perovskite-like formamidinium bromoplumbates (FA₂PbBr₄, 2 polymorphs) and similar iodoplumbate phase (FA₂PbI₄), chained (1D) perovskite-related phases (FA₃PbBr₅ and FA₃PbI₅), and A_{1.5}PbI_{3.5} “hollow”-perovskite with A = FA⁺/MA⁺.

We found that both phases of FA₂PbBr₄ have the structure of (110) layered perovskite but are represented by two different polymorphs with “eclipsed” and “staggered” arrangement of adjacent layers. The prerequisites of their formation upon crystallization of FABr-excessive solutions of FAPbBr₃ were thoroughly investigated. It was shown that FA₂PbBr₄ phases usually exist in a labile equilibrium with FAPbBr₃ 3D perovskite and can form composites with it. The optical properties of both polymorphs were comprehensively studied by means of absorption spectroscopy, diffuse reflection spectroscopy and photoluminescence spectroscopy. DFT calculations were applied to investigate the band structure of the FA₂PbBr₄ and to corroborate the conclusions on their optoelectronic properties. As a result, we found that FA₂PbBr₄ phases irradiated by UV can exhibit effective green photoluminescence due to a transfer of excitation energy to defective states or 3D perovskite inclusions [1].

Also, in the present work, equilibrium phases for the formamidinium iodide-enriched (FAI) region of the FAI-MAI-PbI₂ phase diagram (MA + - methylammonium) were identified for the first time. The formation of a number of new phases (FA₂PbI₄, FA₃PbI₅, as well as mixed-cationic A_{1.5}PbI_{3.5}) with a reduced dimension of the inorganic substructure was established, and the structures of the resulting phases were determined. Relevant structural models were proposed describing the influence of the organic cation shape (A⁺) and the [A⁺]/[Pb²⁺] ratio on the dimension and distortions of the inorganic framework to predict the structure and properties of haloplumbates with specified optical and electronic properties.

The optical properties of the discovered phases were investigated by diffuse reflection spectroscopy and photoluminescence spectroscopy for thin films. Based on the results obtained, the optical bandgap values were compared to the open phases (approximately 2.16, 2.3, and 2.6 eV for the “hollow”, 2D, and 1D perovskite phases, respectively) and the characteristic positions of the photoluminescence maxima were determined. As a general trend, one can distinguish an increase in the optical band gap and a shift of the luminescence peaks towards higher energies with increasing x in the series of perovskite-like phases (FA_yMA_{1-y})_xPbI_{x+2}, while a change in the FA⁺/MA⁺ cation ratio has a relatively weak effect on the optical properties.

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Mie-Resonant electron transport layer for light harvesting by perovskite PV devices

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Lead halide perovskites show a great potential for the modern PV technology due to their unique physical properties such as direct and chemically tunable band gap, high absorption coefficient, defect tolerance, high carrier mobility and long carrier diffusion length. Besides, the fabrication of perovskite solar cells (PSC) is cheap and simple, and uses mostly chemical methods. Despite that, the experimentally achieved PSC performance is still far from the theoretical efficiency limit, which is the result of charge recombination and insufficient light management that potentially can be solved by integration of nanophotonic structures.

To solve this problem, we have decided to improve the optical properties of a mesoporous electron transport TiO₂ layer (ETL) commonly used in PSCs by inclusion of Mie-resonant silicon nanoparticles (NPs). These nanoobjects can efficiently enhance and scatter the incident light, and the average distance between the nanoparticles defines the scattering radiation pattern created by the interaction of electric and magnetic multipoles. The provided numerical calculations show that the concentration of incident light in perovskite layer reaches maximum when the average distance between the Mie-resonant NPs is comparable with their size. Moreover, NPs located in the ETL prevent parasitic charge recombination by the integrated material. The presented multi-physical calculations are in a good agreement with experimental characteristics of the PV devices.

Besides the expected enhancement of photoluminescence signal, the efficiency of n-i-p MAPbI₃-based PSCs with a Mie-resonant ETL show a certified performance of 21.1 %, while the bare cells have achieved only 18 % in literature, and the external quantum efficiency is increased in the whole MAPbI₃ operation range.

The proposed simple method of PSCs improvement can be easily adopted for other approaches of cell fabrication (slot-die, blade-coating, etc.), and even for upscaling techniques.

Evidence for polarization-induced phase transformations and degradation in $\text{CH}_3\text{NH}_3\text{PbI}_3$

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Compositional and structural stability of hybrid halide perovskites is the major source of concern for commercialization of perovskite solar cells and the lack of understanding of underlying mechanisms driving this degradation impedes further progress.

In this study we use nanoscale EDX mapping and in-situ nanofocus X-ray diffraction to reveal electric field-induced transformation of light-absorbing α -MAPbI₃ into metastable δ -MAPbI₃ polymorph which is caused by the alignment of polar organic cation with the electric field.

The report will examine the localization of δ -MAPbI₃ in the inter-electrode space, reversibility of α -MAPbI₃ \leftrightarrow δ -MAPbI₃ transition and its implications towards degradation. Also, based on the results of high-resolution TEM-EDX mapping, the controversy regarding the possibility of migration of MA⁺ cation in perovskite solar cells under typical operating voltages will be resolved.

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Single source chemical vapor deposition (ssCVD) for highly luminescent inorganic halide perovskite films

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Recent studies of lead halide perovskites demonstrate outstanding optoelectronic properties for thin-film semiconductor device application. Perovskite photovoltaic and light-emitting diodes are on the way to the mass production and spread in commercial semiconductor devices. The lab-to-fab transition of perovskite devices requires adaptation of perovskite deposition methods to industrial semiconductor fabrication standards.

Chemical vapor deposition [1] (CVD) is a widely used industrial method to produce high quality [2], high-performance, semiconductor materials [3-5]. At the same time, CVD [6] is the industrial deposition of choice for LEDs [7] and several thin-film solar cell technologies [8,9]. In CVD chemically reacting volatile compounds are deposited on a substrate to produce atomistically defined nonvolatile solid.

In this work, we demonstrated the formation of highly luminescence perovskite films by single-source chemical vapor deposition (ssCVD). Several stoichiometry compositions were prepared from inorganic precursors of CsBr and PbBr₂ by dry mechanochemical synthesis with following evaporation. The combination of mechanochemical synthesis and ssCVD is an attractive approach due to the ability to scale up to industrial level and the precise control over the evaporation rate with a single source. Among all compositions CsBr:PbBr₂ we show that CsPb₂Br₅ maintains phase composition and photoluminescent properties for powder and film. This work provides comparative study of evaporated film properties (PL, XRD, TEM) and modeling calculations of interphase optical transitions.

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CsMX₃ (M=Pb, Sn, Ge, and X= Cl, Br, I) halide perovskites as potential absorber candidates for photovoltaic applications

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Silicon has already shown its potential in photovoltaic (PV) applications and is widely used in both large scale and distributed applications. However, the Si-based PV technology is plagued by complex materials processing and high cost associated with Si solar cell fabrication. Thus, it becomes essential to explore alternative materials. The solid state perovskites with formula AMX₃ are recently gaining attention as a potential alternative to the existing Si PV with a possibility of higher efficiency in a single cell configuration. Organic cation like methyl ammonium (MA) and inorganic cation like Cs are at the forefront of perovskite based solar cell research. In this mini review, we report Cs based single cation perovskites with different M site cations and X site anions. Lead (Pb), tin (Sn) and germanium (Ge) elements lying below Si from carbon group in periodic table have been considered at M site. The well-known halogen group elements- chlorine (Cl), bromine (Br) and iodine (I) play the role of X site anions in AMX₃. The choice of Cs as A site cation is due to its capability to form cubic 3D AMX₃ structure performing better than 2D perovskites for solar cell application. [1] The importance of 3D CsMX₃ is therefore still retained in view of the recent advancements in modified perovskites structures. Herein, we report theoretical studies on CsMX₃ based on density functional theory (DFT). The light-matter interaction in case of these perovskites can be studied by computing electronic and optical properties which, in this study, are carried out by employing suitable exchange-correlation (XC) functional. The computational results obtained using mBJ XC functional are in agreement with experimentally available reports on some of these systems. However, the same XC functional is resulting in relatively lower bandgap values with respect to the experimentally available bandgap values for some systems. The promise of these systems as potential photovoltaic absorber is discussed herein with respective electronic and optical properties. This mini review thus may help in understanding the materials' properties towards developing efficient optoelectronic devices such as photovoltaic, thermoelectric, and even photodetectors.

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P-i-n perovskite solar cells for indoor and BIPV applications

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Today perovskite materials are perspective for the photovoltaic industry due to the appropriate electrophysical properties such as the high mobility, absorption coefficient, long-range ambipolar charge transport and the small nonradiative recombination rate [1-3]. P-i-n perovskite solar cells (PSC) demonstrate high-efficiency free-hysteresis output characteristics under low light. So, PSCs can be used as a power source for indoor gadgets (IoT) or be integrated into a building in the form of BIPV as well inside as outside [4-5].

Most of the research works presented thick perovskite films (> 400 nm) as well for 1 Sun as indoor and BIPV conditions. However, BIPV and indoor conceptions require finding the balance between the thickness of the perovskite layer and the efficiency of PSCs [5].

In the work, we fabricated MAPI-based PSCs with different thickness of absorber (200 nm, 430 nm, 600 nm) for indoor and BIPV applications and showed the correlation between output maximum power of PSCs and the color temperature of LED sources ((2700 – 6500) K). The obtained devices showed the champion value of maximum power (PCE) – 19.6 $\mu\text{W}/\text{cm}^2$ (30.1 %) and 103.2 $\mu\text{W}/\text{cm}^2$ (31.8 %) under 200 lx and 1000 lx, respectively. The 200 nm perovskite-based PSCs showed the close values of parameters, maximum values were 18.5 $\mu\text{W}/\text{cm}^2$ (28.4 %) and 93.6 $\mu\text{W}/\text{cm}^2$ (28.8 %) under 200 lx and 1000 lx, respectively.

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Simulation of solar cell devices for lowering recombination

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We numerically perform structural engineering for lowering interfacial recombination, and enhancing efficiency of CZTS solar cells. Structural modification of controlling carrier density profile at CZTS/CdS interfaces, CZTS absorber surface region carrier density, CZTS surface region bandgap modification, Fermi level pinning and tunneling at the CZTS/CdS junction are studied for their impact on device performance. We observed that the lowering of hole concentration and widening of the bandgap of CZTS in the vicinity of the CZTS/CdS junction, lower interface recombination and improved performance. Fermi level pinning near to the conduction band edge at the CZTS/CdS interface showed lower recombination as compared to the case where the Fermi level is pinned at the mid-gap at the CZTS/CdS interface. Donor defects from the buffer layer pin the Fermi level near the conduction band and acceptor defects from the absorber CZTS layer pin the Fermi level near the mid-gap at the CZTS/CdS interface. Intra-band tunneling through the high conduction band offset barrier maintains performance for up to 0.5 eV spike barrier. High hole density profile at the CZTS/metal lower back contact interfacial recombination. These structural engineering numericals performed here, present a bright aspect for improving the efficiency of CZTS solar cells.

All-slot die printed inverted perovskite solar cells and mini-modules

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One of the key challenges for the development of perovskite photovoltaics is scalable fabrication in spite of their impression improvement in power conversion efficiency (PCE) with current record >25 % [1] for solution processed devices during last decade. The Lab-to-Fab transition requires the study of large-area deposition methods in combined printing cycle for perovskite absorbers and charge transporting films. Herein, we demonstrate the slot-die fabrication and upscaling for p-i-n perovskite solar cells (PSCs) in ambient conditions with four printed layers in the device structure - NiO_x (HTL)/perovskite (absorber based on CsFAPbI₃)/PCBM – BCP (ETLs). We found that, the pre-heating temperature of the substrate plays a critical role in the printing process of NiO_x layer from the solution precursor. With changes of the substrate temperature from 85 to 105 °C, the thickness of the NiO_x film was varied from 12 to 20 nm and determined shunt properties of the PCSs. The accurate balance between drying processes for the wet film and rapid annealing for the formation of NiO_x from the decomposed precursor required precise temperature and timing control. The vacuum assisted solution process (VASP) [2] was used as post-treatment for the non-(anti)solvent crystallization of perovskite thin film in air. Notably, adding small amount of Cl - containing additive (FACl) to perovskite precursor solution in combination with vacuum quenching was found can improve the device output parameters via enhancing the film morphology. The use of 10 % FACl additive increased the average grain size of printed CsFAPbI₃ from 120 up to around 420 nm. In addition, VASP also demonstrated effective treatment for the formation of thin electron transporting layers – PCBM/BCP out of glove-box without appearance of the coffee rings on the printed films.

Finally, 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 power conversion efficiency of the all-printed PSCs was recorded > 17 % for small device (active area – 0.14 cm²) and reached 14.9 % for mini-modules with two connected cells (total active area – 2.1 cm²). The obtained results clarified that the slot-die printing and VASP can be effectively used for the upscaling of the p-i-n devices in ambient environment.

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Auger recombination in CdSe and CsPbBr₃ 2D colloidal nanoplatelets

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Two-dimensional (2D) colloidal nanoplatelets (NPLs) are an emerging class of quantum well materials that exhibit many unique properties, including uniform quantum confinement, narrow thickness distribution, large exciton binding energy, giant oscillator strength effect, long Auger lifetime, and high photoluminescence quantum yield. These properties have led to great potentials in optoelectrical applications, such as lasing materials with a low threshold and large gain coefficient. Many of these properties are determined by the structure and dynamics of band-edge excitons in these 2D materials. Motivated by both fundamental understanding and potential applications, the properties of 2D excitons have received intense recent interests. We have carried out a series of recent studies on fundamental exciton properties in 2D NPLs, including lateral size of the 2D exciton (i.e. exciton center-of-mass coherent area); exciton in-plane transport mechanism; size and thickness dependence of bi-exciton Auger recombination rate, and optical gain mechanism and threshold. In this talk I will focus on the size, thickness and material dependence of bi-exciton Auger recombination rates. We show that in CdSe NPLs, the biexciton Auger recombination lifetime does not depend linearly on its volume, deviating from the “Universal Volume” scaling law that has been reported for 0D quantum dots. Instead, the Auger lifetime scales linearly with the lateral size, and the Auger lifetime depends sensitively (nonlinearly) on the NPL thickness. In CsPbBr₃ 1D nanorods and 2D NPLs, the biexciton Auger lifetimes increase linearly with the rod length and NPL lateral areas, respectively, and the lifetimes are much shorter than CdSe nanocrystals with similar volume. These observations can be explained by a model in which the Auger recombination rate for 1D nanorods (NRs) and 2D NPLs is a product of binary collision frequency in the non-quantum confined dimension, and Auger probability per collision. The former gives rise to the linear dependence on the lateral areas in 2D NPLs and rod length in 1D NRs. The Auger recombination probability per collision depends on material property and the degree of quantum confinement, which gives rise to nonlinear dependence on the thickness of NPLs and diameter of NRs, as well as material dependent Auger lifetimes. Thus, the Auger lifetimes of 2D NPLs and 1D nanorods deviate from the volume scaling law because of the different dependences on the quantum confined and non-confined dimensions. We believe that this model is generally applicable to all 1D and 2D materials.

Realtime suppression of interfacial trap states in perovskite solar cell using external doping of electron transport layer

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We applied an equivalent diode circuit model to an ionically gated perovskite solar cell with a porous cathode of carbon nanotubes and C60 fullerene as the electron transport layer (ETL) for simulation of the solar cells J-V curves. Experimental results showed a significant enhancement in solar cell characteristics like V_{oc} , J_{sc} and FF by doping of ETL layer through the ionic liquid and increasing of gate voltage at the cathode. Simulation results show that reproducing of experimental results is not possible except by introducing a current sink in parallel to photo-generated current in the diode circuit model. To understand the origin of such a current sink, we applied a one-dimensional drift-diffusion model on the perovskite solar cell and solved the problem numerically using the finite element method. Numerical results show the reduction of energy offset between ETL and cathode Fermi level by increasing gate voltage that leads to changing of S-shape J-V curve to a normal diode J-V curve. Moreover, we showed that at higher gate voltage while ions penetrate inside the ETL layer and reach the perovskite/ETL interface they suppress the trap states at the interface that results in a considerable increment in J_{sc} and FF.

Effect of acid additives on the intrinsic photostability of MAPbI₃ thin films

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Since the first report on PSC, the certified efficiency of perovskite solar cells (PSC) have surpassed 25% [1,2]. This increase in efficiency is indeed significant to current photovoltaic technology, indicating that PSCs could be used commercially. This is mostly due to the benefits of PSC fabrication technique, which is simple and low-cost. Unfortunately, perovskite absorber materials deteriorate in the presence of moisture, air, high temperatures, and light. In practice, these circumstances are unavoidable for the operation of solar cells. As a result, achieving high absorber layer stability has been proved to be quite challenging [3]. Scientists have proposed a variety of techniques to resolve these stability issues. Using additives in perovskite precursors is one of them [4].

Following the notion, we investigated the influence of acid additives in MAPbI₃ precursor solution on the photochemical stability of MAPbI₃ thin films. In this study, we investigated five additives named Acetylcysteine (NAC), Mercaptosuccinic acid (MSA), Lipoic acid (LA), Mercaptoundecanoic acid (MUA) and SHS-35. Our investigation revealed that the addition of NAC enhances intrinsic photostability of the absorber layer that remains stable over 1000 h under the light intensity of 70-80 mW cm⁻² at 50-60 °C.

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Quantitative descriptor for classification of layered hybrid halide perovskites and relationships between distortions of inorganic framework and band gap

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The unprecedented structural flexibility and diversity of inorganic frameworks of layered hybrid halide perovskites (LHHPs) rise up a wide range of useful optoelectronic properties thus predetermining the extraordinary high interest to this family of materials.

In this work, we introduce a new, universal and quantitative, Layer Shift Factor (LSF) [1] for a quantitative comparison and univocal classification of LHHPs and developed simple based Python algorithm for its calculation. The crystal structures of the known layered hybrid perovskites for the suggested analysis were taken from our recently published database of 2D perovskite-like materials [2]. We demonstrate that most of the structures among (100) and (110) hybrid perovskites are not “pure” DJ and RP phases or “eclipsed” and “staggered” conformations. Moreover, we show that layer shift factor strongly influence on the band gaps of layered perovskites with relatively small interlayer distance.

We present a first systematic study of the effect of the main structural parameters of LHHPs inorganic framework on their band gaps. We use six structural descriptors (interlayer distances, in-plane and out-of-plane distortion angles in layers of octahedra, layer shift factor, axial and equatorial Pb-I bond distances) to construct the design space in order to realize the inverse material design approach to search LHHPs with target values of a band gap. The proposed multi-step DFT and machine learning based approach has shown its high efficiency of the searching for a band gap minimum and, therefore, for prediction of LHHPs with a given band gap [3]. The analysis of calculated descriptor – band gap dependences for the wide range of generated model structures of (100) single-layered LHHPs results in discovery of several new structure-property correlations.

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Correlation between efficiency and device characterization in MAPbBr_3 inverted solar cells

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Metal-halide perovskites have been widely used as the light absorber of solar cells, with the highest certified power conversion efficiency has reaching 25.2 %, which is comparable to silicon-based solar cell technology. This high efficiency is inherent in perovskite's characteristics, such as high absorption coefficient, bandgap tunability, long carrier diffusion length, high carrier mobility, and compatibility with simple solution processing or vacuum evaporation. One of the effective ways to achieve reproducibly efficiency perovskite is the deposition method. In this report $\text{CH}_3\text{NH}_3\text{PbBr}_3$ light absorber materials was deposited on the PEDOT: PSS layer via one-step and two-step coating methods and their photovoltaic performance are compared. Inverted perovskite solar cells with ITO/PEDOT: PSS/ $\text{CH}_3\text{NH}_3\text{PbBr}_3$ /PCBM/Al structure have been investigated. The morphological, structural, optical and electrical properties of the deposited perovskite are found to be critical and the higher performance was obtained from two-step deposition process.

Ammonium sulfate treatment on metal oxide-based ETL prevents deprotonation of PSC's A-site organic cations in operational condition

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Titanium dioxide (TiO₂) electron transport layers (ETLs) are still widely used in perovskite solar cells (PSCs) due to their compatibility with existing printing technologies and favourable energy level alignment for efficient electron extraction. However, TiO₂ ETLs suffer from surface defects, e.g., oxygen vacancies, that are detrimental to perovskite/ETL interface stability, especially under operational conditions. Furthermore, hydroxyl groups present on the TiO₂ surface also contribute to deprotonation of acidic organic cation in PSCs. We thus hypothesize that the metal oxide surface turns chemically reactive under 1-sun illumination whereby devices are highly populated with charge carriers and experience elevated temperature (ca. 60 °C). Here, we introduced a facile incorporation of sulfate species on the metal oxide surface to minimize chemical degradation at the perovskite/ETL interface. The sulfate treatment was found to minimally influence the perovskite film morphology grown on top of the ETLs so ruling out the morphological effects and allowing us to study the perovskite/ETL interface stability. We found that sulfate treated devices exhibited enhanced operational stability under initial maximum power point voltage (VMPP) over 1800 s measurement. Sulfate treated devices retained 95 % of their initial efficiency while pristine devices already lost more than 40 % of their initial efficiency. We also thermally aged, encapsulated perovskite films coated on top of pristine and treated ETLs. We found that thermally aged perovskite films coated on pristine ETL contained perovskite hydrate species while the treated samples did not. We thus postulate that the water molecules contributing to the hydrate formation were generated solely from the ETL/perovskite interface. Lastly, a better energy alignment was also found between perovskite and sulfate-treated ETL which also contributes to the improved operational and thermal stability.

Light-trapping electrode for the efficiency enhancement of perovskite solar cells

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Organic-inorganic halide perovskites belong to the group of the most promising materials for next-generation solar cells. Rapid progress has been made since the first perovskite solar cell was reported in 2009 by Kojima et al [1]. While previous studies were mostly focused on the improvement of electrical quality of materials and interfaces, there are still opportunities for further optimization through photon management.

Light-trapping structures (LTSs) can significantly improve power conversion efficiency of perovskite solar cells by scattering the light or reducing the optical losses. Various light-trapping strategies can be aimed at the suppression of incident light reflection, increase of light absorption by the active layer, or alter the optical response of the device for specific applications. There are different types of LTSs, which include photonic crystal structures, plasmonic nanoparticles, structures with gradual refractive index, random scatterers, and microlenses [2, 3].

In this study, we present a novel LTS for perovskite solar cells consisting of arranged dielectric microspheres and metal film with an array of holes, which can significantly decrease parasitic reflection from the surface and increase useful absorption in the active layer. Moreover, our LTS can serve as a transparent electrode with better characteristics to replace ITO. We analyze the structure by numerical simulations and show that the gain in optical absorption due to the proposed light-trapping electrode can reach 9 % compared to the reference structure for conventional perovskite architecture. Another promising application of our LTS corresponds to the bifacial perovskite solar cells [4]. We demonstrate that optical absorption in the active layer of such bifacial module can be increased for both sides simultaneously using our light-trapping electrode. We believe that the present concept can be useful for the further development of high-performance perovskite solar cells.

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Sub- and supersolidus phase relations of formamidinium-cesium polyiodides

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Up to now, perovskite thin films are commonly obtained by solution techniques. In these methods, however, solution crystallization goes through formation of intermediate phases which deteriorate film morphology and impedes controllability and reproducibility of the film deposition process [1]. Moreover, there is a lack of deposition methods that can be used for obtaining large-sized solar cells and potentially trigger commercialization of PSCs.

Recently, a new scalable solvent-free approach has been proposed which is based on direct conversion of lead films by liquid methylammonium and formamidinium polyiodides, coined as reactive polyiodide melts (RPM), into target perovskite compounds with efficiencies over 17% for perovskite solar cells with MAPbI₃ and (MA,FA,Cs)PbI₃ [2]. To obtain perovskite films with a perspective composition of FA_{1-x}Cs_xPbI₃, essential information on the properties of FAI-CsI-I₂ ternary system, such as temperature and composition ranges of liquid reactive phases, is needed. Therefore, the purpose of this work is to investigate phase relations between formamidinium-cesium polyiodides in sub- and supersolidus region.

To determine melting and liquidus temperatures of the mixed-cation Cs-FA polyiodide system, we analyzed a series of compositions FA_{1-x}Cs_xI_n with different cesium content ($x = 0.1, 0.2, 0.3$) and several iodine ratios ($n = 2, 3, 4, 5$) using visual polythermal analysis in a glass thermostated cell. For AI₂ and AI₄ compositions, where A is a mixture of Cs⁺ and FA⁺ cations, melting temperatures were found to change linearly with increasing of cesium iodide quantity, whereas for AI₃ and AI₅, the dependencies exhibited extrema. Using X-Ray diffraction analysis, it was found, that compositional range of existence of mixed formamidinium and cesium polyiodide phases in the FAI-CsI-I₂ ternary system seems to be narrow and therefore leads to the appearance of a eutectic point and the extremum on the observed liquidus curves.

We also investigated the FAI/I₂ binary system using a visual polythermal analysis and thermal X-Ray diffraction using synchrotron irradiation and built a scheme of phase relations. According to the data obtained, we suggest that there are at least 3 previously unknown formamidinium polyiodides and four eutectics in the binary system with the deepest one at $0.6 < x < 0.7$ with a temperature ~ 20 °C. For one of the polyiodides with FAI₃ composition the structure was found to consists of two independent isolated triiodide ions located on inversion centers. The centrosymmetric character of I₃⁻ was additionally confirmed by the Raman scattering spectroscopy. Therefore, only centrosymmetric I₃⁻ anions are present in the structure which is rare for structures with relatively small cations such as formamidinium [3].

Additionally, the solid FAI₃ phase was found to react with metallic lead at elevated temperature below its melting point. A thin film of metallic lead was converted into primarily a-FAPbI₃ phase in 30 minutes by adjoining with a drop-casted FAI₃, suggesting that FAI₃ would play the role of a new facile precursor for FA-based perovskites.

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Atomic layer deposited Nb₂O₅ electron transport layer for efficient and stable perovskite solar cells

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Many studies are devoted to circumvent the issue of charge accumulation and recombination at electron transport layer/perovskite in PSCs. Recently, Nb₂O₅ has emerged as a promising n-type ETL in PSCs due to its wide bandgap energy, high electron mobility and improved chemical stability as compared to the TiO₂ ETL. Many reports have investigated performance of Nb₂O₅ ETL in PSCs. Notably, these studies mainly focused on preparation of Nb₂O₅ solely as an ETL, however, the utilization of Nb₂O₅ as an ETL/perovskite interface layer in PSCs has not been investigated.

In this study, we modify the surface of ms-TiO₂ by an ultrathin layer of Nb₂O₅ using ALD technique in order to fabricate efficient and less-hysteresis mesoscopic PSCs. The performance of the PSCs was optimized by adjusting the number of ALD cycles. We demonstrate that the Nb₂O₅ interface layer not only improves the morphological and optical properties of the subsequently deposited perovskite layer but also promotes the charge transfer across the interface most likely due to the suitable band alignment in the modified PSCs. The measurements of Voc as a function of light intensity and impedance spectra results demonstrate that the charge recombination in the Nb₂O₅-modified PSCs is suppressed as compared to the reference devices. Consequently, the Nb₂O₅-modified devices demonstrate improved stability after prolong exposure to high humidity, temperature and UV irradiation.

Intermediate solvate phases in the ternary systems MAI-PbI₂-DMF and MAI-PbI₂-DMSO

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Hybrid halide perovskites with a general formula APbX₃ (A = MA⁺ – methylammonium, FA⁺ – formamidinium); X = I⁻, Br⁻) possess unique combination of optical and electronic properties and are promising materials for use in optoelectronics and photovoltaics [1]. In particular, the record values of the efficiency of solar cells based on hybrid perovskites reach 25.5%, exceeding the record values of the efficiency of cells based on polycrystalline silicon. [2].

The most common approach of obtaining thin perovskite films for solar cells is solution crystallization from dimethyl sulfoxide (DMSO) and dimethylformamide (DMF). However, despite the active use of these solvents for the synthesis of perovskites, the processes occurring during the crystallization of perovskites from such solutions are practically not studied, which complicates the development of methods for obtaining films of hybrid perovskites.

In this work, we carried out a systematic study of the crystallization of perovskite solutions depending on the cation (MA⁺/FA⁺), anion (I⁻/Br⁻) and solvent type (DMF/DMSO), as well as the ration of the precursors in the solution. It was found that crystallization of MAPbI₃ leads to formation of three types of crystal solvates: (MA)₂Pb₃I₈·2Solv, (MA)₂Pb₂I₆·2Solv, and (MA)₃PbI₅·Solv (Solv = DMF, DMSO) [3], while in the case of FAPbI₃ the phases (FA)₂Pb₃I₈·4DMF and FAPbI₃·2DMF are formed [4].

During crystallization of bromide compositions, the intermediates (FA)₅Pb₂I₉·0,5DMSO, FA₂PbBr₄, and (FA)₂PbBr₄·2DMSO are formed only in the case of an excess of organic cations in solution, in other cases perovskite phase is formed (MAPbBr₃, FAPbBr₃) [4]. Additionally, the phases formed during the crystallization of perovskites with mixed cationic and anionic composition were also determined.

Based on the solubility measurements of solutions with different ratios of the precursors and XRD analysis of the solid phases in equilibrium with solutions, phases diagrams of MAI-PbI₂-DMF and MAI-PbI₂-DMSO are built revealing the influence of the solvent type on the crystallization pathways of hybrid perovskites.

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Evaluation of front and back electrode material in lead-free double perovskite material $\text{Cs}_2\text{AgBiBr}_6$ based solar cell through numerical simulation

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Organic-inorganic hybrid perovskite solar cells (PSCs) have emerged as a game-changer photovoltaic technology owing to its recent advancement. Significantly, lead-based PSCs are becoming popular and exhibited high power conversion efficiency in a very short period. Despite, lead-based perovskite devices are still far from the commercial photovoltaic market due to environmental concerns related to the toxicity of lead and stability of the device. Therefore, it is the urgent need of the whole world to develop a lead-free PSC device to protect our environment. In this regard, it is also necessary to check all the aspects of the device to improve device efficiency. In the present work, we have investigated the effect of front and back electrode work function on device performance of lead-free double perovskite absorbing material $\text{Cs}_2\text{AgBiBr}_6$ based PSC through SCPAS-1D software. The appropriate identification of work function and selection of front and back contact material accordingly may boost up the device efficiency in the experimental counterpart.

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CsSnI₃ lead-free perovskite-based inverted perovskite solar cell with Cu₂O as HTM: The theoretical insights

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Organo-lead halide perovskites are the most studied perovskite materials for solar cell applications. However, their widely acknowledged instability led to exploring CsPbI₃ material. But the high cost and toxicity due to lead-based perovskites have been proved to be a major hurdle in the large-scale application. The search for a possible alternative to Pb has put forward Sn as the potential candidate for absorber material. The experimentally reported bandgap for cubic CsSnI₃ is ~1.3 eV [1], [2]. This bandgap value is appropriate for solar cell application following the Shockley-Queisser limit. This work investigates the CsSnI₃ absorber in inverted perovskite solar cell configuration using the SCAPS-1D tool. The device performance is simulated using Cu₂O metal oxides as hole transporting material (HTM) and suitable electron transporting material (ETM). Further, we optimized HTM/CsSnI₃/ETM device by varying electron affinity, thickness, defect density, and the absorber's carrier concentration of absorber and HTM. Moreover, we consider optimizing interfacial parameters to make the simulation results more realistic to a practical scenario. This study is expected to provide guidelines on designing and developing an efficient lead-free perovskite solar cell towards low-cost HTM with optimal performance.

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Suppressed ion migration in powder-based perovskite thick films using an ionic liquid

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While solution-processed halide perovskite thin films caused enormous attention when used in solar cells, thick films prepared by compressing perovskite powders are considered promising candidates for the next generation of X-ray detectors. However, X-ray detectors based on such powder-pressed perovskites typically suffer from relatively high dark currents, which were attributed to be caused by ion migration. Here we show that the dark current in 800 μm thick powder-pressed MAPbI_3 -pellets can be reduced by a factor of 25 when using a passivated powder. The passivation was achieved by adding 1 mol % of the ionic liquid (IL) BMIMBF_4 to the precursors MAI and PbI_2 during the mechanochemical synthesis of the MAPbI_3 powder. NMR verified the presence of the IL, and its impact on the excited state recombination dynamics was manifested in an increase in the photoluminescence (PL) intensity and a decrease in the monomolecular (trap-assisted) recombination rate, both by about one order of magnitude. By measuring the migration of a PL quenching front upon application of an electric field in a microscope, we determine an ionic diffusivity in the typical range of iodide vacancies in the non-passivated pellet. At the same time, we observe no such PL quenching front in the passivated pellet. Concomitantly, dark I–V curves are hysteresis-free, and light-soaking effects are absent, in contrast to non-passivated pellets. Thus, our work demonstrates the effect on the optical and electrical properties when passivating mechanochemically synthesized halide perovskite powders using an IL, which will facilitate the further development of powder-based perovskite X-ray detectors.

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Structure and optical properties of low-dimensional perovskite phases in FAI-MAI-PbI₂ system

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In recent years, the excellent optoelectronic properties and facile solution processing of hybrid halide perovskite-based materials have called great attention of researchers due to high perspectives for applications in thin film solar cells and LED devices. A widespread strategy to improve the luminescence properties of hybrid perovskites such as MAPbI₃, FAPbI₃ (where MA⁺ = methylammonium, FA⁺ = formamidinium) is addition of excess organic halides [1, 2]. However, there is a lack of understanding of the key dependencies between the non-stoichiometry, structure and optical properties of the hybrid halide perovskites. Under specific conditions, a formation of perovskite-like phases with partial replacement of [PbI]⁺ moieties with organic cations of appropriate size ([PbI]⁺ ↔ A⁺) can take place. In this work, we have shown this effect for the MAI-FAI-PbI₂ system and studied the structure and optical properties of new phases.

Powders of the new phases were synthesized from corresponding iodides mixed in desired ratio and reacted at 50-70 °C in toluene with a small additive of iodine acting as a mass transfer agent ($I + I_2 \leftrightarrow [I_3]^-$). Such a mild reaction conditions without usage of coordinating solvents and annealing provides the formation of equilibrium phase composition. The XRD analysis of obtained powders showed 3 new phases: “hollow” - (FA_yMA_{1-y})_{1.5}PbI_{3.5}, (0.75 ≥ y ≥ 0.6), “2D” - (FA_yMA_{1-y})₂PbI₄ (1 ≥ y ≥ 0.9), and “1D” - FA₃PbI₅. For each phase full-profile refinement was carried out (Table 1) and model structures were proposed. “Hollow”-phase has a perovskite-like structure with an ordered set of parallel empty channels without [PbI₆] octahedra. “2D” phase is a layered perovskite with LSF of (0, 0). Finally, the “1D” phase structure is linear unbranched chains of [PbI₆] octahedra bounded by vertices and tilted by 45° each other. For the “hollow” phase a decrease of cell parameters with increasing methylammonium content, which is directly related to cations size. But there is an inverse relation for the “2D” phase presumably because higher packing density of flat FA⁺ cations compared with more isotropic MA⁺ cations.

Table 1. Lattice parameters and R-factors for experimentally refined structures for MAI-FAI-PbI₂ system.

Composition	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	α, β, γ (°)	<i>R_p</i>	Space group symmetry
(FA _{0.75} MA _{0.25}) _{1.5} PbI _{3.5}	14.152	14.152	6.333	90	7.27	<i>P4/m</i>
(FA _{0.6} MA _{0.4}) _{1.5} PbI _{3.5}	14.142	14.142	6.317	90	4.58	<i>P4/m</i>
FA ₂ PbI ₄	12.690	8.941	26.887	90	5.49	<i>Pmc2₁</i>
(FA _{0.9} MA _{0.1}) ₂ PbI ₄	12.784	8.936	27.003	90	5.49	<i>Pmc2₁</i>
FA ₃ PbI ₅	17.838	17.788	12.643	$\alpha = 90$ $\beta = 90$ $\gamma = 90$	8.86	<i>P1</i>

A wide composition area ((FA_yMA_{1-y})_xPbI_{2+x} 3≥x≥1, 1≥0) is being investigated, and a corresponding phase diagram is in development. There discovered a couple of other phases, but their structure is still unknown.

Optical properties were studied by diffuse reflectance spectroscopy and photoluminescence (PL) spectroscopy on thin films. The optical band gap (2.16, 2.3, and 2.6 eV for “hollow”, “2D” and “1D” phases respectively) and PL maximums were defined for new phases. During the transition to lower-dimensional phases, the optical band gap increases significantly, and PL peaks are shifted to the higher energies. The MA/FA ratio has only a small influence on optical properties.

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Temperature and excitation density dependence of luminescence properties of MAPbBr₃ and MAPbCl₃ single crystals

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Methyl-ammonium lead halide perovskites are known to have a subnanosecond luminescence decay time with a relatively high light yield. Exact mechanisms and energy transfer processes in these materials under photo- and X-ray excitation require further research. Here we present luminescence spectra, light yield and decay kinetics changes with temperature and excitation density.

The crystals were grown by antisolvent vapor-assisted crystallization. The measurements were performed at P23 beamline of PETRA III storage ring (X-ray region, DESY, Hamburg) and in CELIA, Bordeaux, France (3rd harmonic of femtosecond Ti-sapphire laser) using Z-scan technique. The range of photo-created excitations varied from ~ 1017 to 1022 e-h/cm³. The trends in the temperature and excitation density dependences of MAPbBr₃ and MAPbCl₃ exciton and side band luminescence are discussed.

Changes in the luminescence spectra and kinetics with temperature and excitation density related to the changes of photo-created charge carrier mobilities derived from these experiments can assist in the understanding of properties both of luminescent materials and those for photovoltaics with requirements often contradicting each other.

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First principles simulations for solution of the PSC stability challenge

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Achieving a long-term stability of perovskite solar cells (PSC) while preserving cost-effective manufacturing procedures is a cornerstone challenge, solving which would allow for lifting the barrier towards their large-scale implementation and extensive commercialization. Among the strategies to enhance the durability of PSC is the engineering of charge transporting layers and their interfaces with perovskite light absorbers, as well as the reduction of the defect concentration within the perovskite light-harvester and their passivation at the interfaces. In the current work, the first principles simulations are employed within the quest of novel hole-transporting materials (HTM) to unveil the passivation mechanisms and purposely tune the interfacial interactions, thus facilitating an engineering of low-cost alternatives to spiro-OMeTAD enabling an enhanced durability of PSC devices [1-3], as well as to investigate the atomistic leverages for the reduction of the defect concentration and morphology improvement through the compositional tuning and the control over the crystal growth [4-5].

The research is carried out using the equipment of the shared research facilities of HPC computing resources at Lomonosov Moscow State University. The Siberian Branch of the Russian Academy of Sciences (SB RAS) Siberian Supercomputer Center is gratefully acknowledged for providing supercomputer facilities.

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Semi-transparent perovskite solar cell with Ion Beam Sputtering top-contact

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Halide perovskites (HP) are emerging technology for thin-film photovoltaics with an outstanding combination of semiconductor properties (defect tolerance [1], wide range of bandgap tunability [2], and cost-effective fabrication [3]).

Strong absorption in the visible part of the light spectrum [4] allows the use of HP as top sub-cell in multi-junction devices with Si and CIGS absorbers to improve the power conversation efficiency over Shockley - Queasier limit of 33 %. The design of efficient multijunction solar cells requires precise spectral splitting. Moreover, the fabrication of HP-based top sub-cells has several limitations of the high-temperature processing (typically below 140 °C) and use of vacuum deposition methods with plasma interaction (magnetron sputtering, etc.).

In this work we designed efficient wide-bandgap p-i-n perovskite solar cells based on multi-cation perovskite $\text{Cs}_{0.2}\text{FA}_{0.8}\text{Pb}(\text{Br}_{0.25-x}\text{I}_{0.75}\text{Cl}_x)_3$ with the bandgap (~1.73 eV) for top-sub-cell. We found that the use of Cl-based additives is essential for suppression of the phase segregation to iodine and bromide-rich domains in the perovskite absorber films and effectively improve charge transport properties. The morphology of the wide bandgap perovskite absorber was observed with the formation of wrinkled structure, although it does not affect the diode properties of the devices (via shunts etc.).

For the opaque configuration of the device with Cu cathode we achieved the output performance at the level of PCE = 15.4 %, $V_{oc} = 1.14$ V, $J_{sc} = 19.1$ mA/cm² and FF = 70 %. For the semitransparent configuration, we used the rear ITO electrode (210 nm) deposited with the ion-beam sputtering technique which allows excluding the interaction of the perovskite solar cell (PSC) structure with plasma.

The use of ZnO_x/ITO stack at the ETL side of semitransparent perovskite solar cells resulted in the following IV parameters – PCE = 11.25 %, $V_{oc} = 0.98$ V, $J_{sc} = 15.5$ mA/cm² and FF = 0.74 %. The shading of p-i-n HJT Si cell (PCE 21.2 %, $J_{sc} \sim 41.6$ mA/cm²) with semitransparent PSCs reduced the output current by 2 times at the level of ~ 21.05 mA/cm². The result of this work opens new pathways for the design of semi-transparent PSCs for tandem and BIPV applications.

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Time-resolved luminescence spectroscopy of $\text{MAPb}_x\text{Hg}_{1-x}\text{Br}_3$ single crystals

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The aim of this research was to study the effect of solid-solution formation on the luminescence properties of concentration series of $\text{MAPb}_x\text{Hg}_{1-x}\text{Br}_3$, with x takes the value 1, 0.9, 0.75 and 0.5 (MA = CH_3NH_3 - methyl ammonium) in view of their possible application as scintillators. The single crystals were grown using antisolvent vapor-assisted crystallization method. Synchrotron radiation was used for luminescence excitation at the FinEstBeAMs station of the MAXIV storage ring (UV and VUV excitation spectra, temperature range 7-300 K), Lund, Sweden, and P23 station of the PETRA III storage ring (X-Ray excitation spectra, temperature range 80-300 K) of the German center for synchrotron radiation DESY, Hamburg, Germany. Time-resolved luminescence spectra, luminescence kinetics, temperature dependences of luminescence and kinetics spectra were measured using the unique features of synchrotron radiation.

The fast luminescence band of free excitons with a maximum at ~ 2.25 eV at 80 K, was split into at least two subbands in the samples with $x = 0.9$ and 0.75. This was attributed to disorder in cation spatial distribution in these systems. On the contrary, in the spectra of MAPbBr_3 and $\text{MAPb}_{0.5}\text{Hg}_{0.5}\text{Br}_3$ a single luminescence band associated with the exciton was observed indicative of a higher ordering of the structure with the equal concentration of Br and Hg.

Comparison of the luminescence spectra upon VUV excitation and X-ray excitation made it possible to separate surface defects from the bulk ones and to reveal the role of reabsorption of exciton emission. In a series of solid solutions, a shift of the exciton peak was observed depending on the concentration of mercury in the sample by ~ 0.02 eV, which was attributed to the narrowing of the band gap with mercury content.

The kinetics of exciton luminescence was nonexponential with a high contribution of the fast component with a characteristic decay time of less than 100 ps. This fact makes the studied perovskites promising scintillators in agreement with earlier research; however, upon irradiation with high-density VUV radiation, the formation of new defects was observed. Radiation hardness of hybrid perovskites is a recognized issue and researches are working in this direction.

Nonlinear photoluminescence in halide perovskites

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Multiphoton absorption and photoluminescence are fundamentally important nonlinear processes, which can be employed for efficient light conversion from infrared into visible range. One of the most important parameters in these processes is the order of nonlinearity, which predicts output emission power. Here, we have shown theoretically and experimentally how the coexistence of excitons and free carriers affects the order of nonlinearity. Our developed theoretical model is confirmed by experiments, where we exhibit strong dependence of nonlinearity order on temperature, exciton binding energy and dimensionality.

The challenge to obtain phase-pure $\text{BA}_2\text{MA}_{n-1}\text{Pb}_n\text{I}_{3n+1}$ films by using proper additives

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In the last few years, increasing interest have been attracted to the layered metal-halide perovskites $\text{R}_{2/q}\text{A}_{n-1}\text{Pb}_n\text{X}_{3n+1}$, which are a homologous series of compounds with different thicknesses of perovskite-like layers $[\text{A}_{n-1}\text{Pb}_n\text{X}_{3n+1}]^{(2/q)-}$ divided by layers of organic cations R^{q+} (where q is the charge of the cation R). These compounds are multiple quantum wells, where layers of organic cations serve as potential barrier for charge carriers from perovskite-like layers, which makes it possible to change the exciton binding energy and the band gap by changing thickness of these layers due to the quantum confinement. This makes them promising materials for applications in thin-film LEDs and solar cells.

However, the controlled and reproducible synthesis of layered perovskites films with specified properties is one the most important problem at the moment. Films of layered perovskites obtained by solution methods contain impurities of layered perovskites with higher thicknesses of the perovskite-like layer complicating control of film properties through its composition.

One of the most effective approaches to control crystallization process of hybrid perovskites is addition of various organic and inorganic salts to the solution. This work is dedicated to the study of effect of the additives KI and $\text{C}_4\text{H}_9\text{NH}_3\text{I}$ in the solution $(\text{C}_4\text{H}_9\text{NH}_3)_2(\text{CH}_3\text{NH}_3)_{n-1}\text{Pb}_n\text{I}_{3n+1}$ ($n = 1-4$) on composition, structure and optical properties of obtained films.

It was found that films obtained from the solution of $(\text{C}_4\text{H}_9\text{NH}_3)_2\text{PbI}_4$ ($n = 1$) consist only one phase $(\text{C}_4\text{H}_9\text{NH}_3)_2\text{PbI}_4$, while using a solution with stoichiometry $n_s > 1$ leads to formation of film with impurities of layered perovskites with $n = n_s \pm 1$. The impurities are assumed to be crystallites of layered perovskite with n_s with staking faults stemming from inclusion of pieces of layered perovskites with $n = n_s \pm 1$ into the structure. Addition of KI to perovskites solution with $n = 2$ reduces concentration of the defects in the film, however the addition in case $n = 3$ and 4 increases amount of defects in films. Using addition of $\text{C}_4\text{H}_9\text{NH}_3\text{I}$, it was possible to obtain film of phase $n = 2$ without impurities. In case of $n = 3$ and $n = 4$, addition of $\text{C}_4\text{H}_9\text{NH}_3\text{I}$ makes it possible to increase content of the target phase, but it was not possible to obtain samples without impurities. X-ray diffraction revealed significant narrowing of layered perovskites peaks and increase in intensity of (001) series peaks using both additives, which indicates improvement in crystallinity of obtained materials and reduction of number of defects in the crystal structure.

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A detailed stability study of layered $\text{BA}_2\text{MA}_{n-1}\text{Pb}_n\text{I}_{3n+1}$ perovskites: new lessons learned

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Layered lead halide perovskites (2D LHPs) are attracting considerable attention as a promising material for new generation of solar cells. 2D LHPs, with a general formula $\text{A}_{2/q}\text{A}_{n-1}\text{Pb}_n\text{X}_{3n+1}$, are layered structures consisting of $[\text{A}_{n-1}\text{Pb}_n\text{X}_{3n+1}]^{2-}$ perovskite-like layers with singly ($q = 1$) or doubly ($q = 2$) charged A^{q+} organic cations in the interlayer space. The number n corresponds to the number of the inorganic layers of corner-sharing octahedra $[\text{PbX}_6]$ held together by the small A^+ cation if $n > 1$. 2D LHPs have been presented as a more stable alternative to the more widespread APbI_3 bulk perovskite materials. The high stability of integrated in perovskite solar cells (PSCs) 2D LHPs against moisture is consistently demonstrated due to the presence of hydrophobic cations in the interlayer space. However, the reported results regarding the photostability of layered perovskites still remain limited and controversial. Additionally, there is scarce information on the effect that the surrounding atmosphere (inert or oxidizing) could play during the light soaking of the material, being, on the contrary, a well-known topic in the case of 3D perovskites.

In this article, we provide a detailed photostability study of layered perovskites $\text{BA}_2\text{MA}_{n-1}\text{Pb}_n\text{I}_{3n+1}$ (BA = butylammonium, MA = methylammonium) with $n = 1 - 3$, comparing the results with the 3D parent phase MAPbI_3 . We suggest that in-situ or periodic tracking of perovskite functional properties such as photoluminescence during light or heat treatment is one of the most suitable strategies for comparative stability studies of both 3D and 2D hybrid perovskites with the control of surrounding atmosphere as an essential step preceding these experiments. We found out that the presence of molecular oxygen in the atmosphere during light-soaking tests plays a critical role affecting both photodegradation mechanism and rate of hybrid perovskites and PSCs, as especially important for 2D systems. We proved that the presence of >10 ppm O_2 during 2D-PSCs preparation and/or resource testing causes a dramatic loss of their performance. In the inert atmosphere (<10 ppm O_2) the layered perovskites become more stable to visible light irradiation and demonstrate a nonmonotonic photostability dependence on the n number as follows: $\text{BA}_2\text{MA}_2\text{Pb}_3\text{I}_{10} > \text{BA}_2\text{MAPb}_2\text{I}_7 \sim \text{MAPbI}_3 > \text{BA}_2\text{PbI}_4$. This stability trend could be explained by two factors: (1) the intensification of internal Γ/Γ^0 and $\text{Pb}^{2+}/\text{Pb}^0$ redox processes along with perovskite bandgap value; (2) the higher volatility of MA^+ in MA -abundant compositions (e.g., MAPbI_3). As a result, the family of $\text{BA}_2\text{MA}_{n-1}\text{Pb}_n\text{I}_{3n+1}$ layered perovskites demonstrates an “island of photostability” for phases with $n \geq 3$ in the inert atmosphere and this clue would be practically used in the engineering of solar cell devices.

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Full efficiency recovery in hole-transporting layer-free perovskite solar cells with free-standing dry-carbon top-contacts

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Carbon-based top electrodes for hole-transporting-layer-free perovskite solar cells (PSCs) were made by hot press (HP) transfer of a free-standing carbon-aluminum foil at 100 °C and at a pressure of 0.1 MPa on a methylammonium lead iodide (MAPbI₃) layer. Under these conditions, the perovskite surface was preserved from interaction with the solvent. Over a timescale of 90 days, HP-PSCs were systematically compared to reference cells with carbon-based top electrodes deposited by doctor blading (DB). We found that all the photovoltaic parameters recorded in HP-PSCs during time under ambient conditions settled on values systematically higher than those measured in the reference DB-PSCs, with efficiency stabilized at around 6% within the first few measurements. On the other hand, in DB-PSCs, a long-lasting (~ 14 days) degrading transient of the performances was observed, with a loss of efficiency from an initial ~ 8% to ~ 3%. Moreover, in HP-PSCs, a systematic day-by-day recovery of the efficiency after operation was observed ($\Delta \sim 2\%$) by leaving the cell under open circuit, a nitrogen environment, and dark conditions. Noteworthy, a full recovery of all the parameters was observed at the end of the experiment, while DB-PSCs showed only a partial recovery under the same conditions. Hence, the complete release of solvent from the carbon contact, before an interface is established with the perovskite layer, offers a definite advantage through the long period of operation in preventing irreversible degradation. Our findings indeed highlight the crucial role of the interfaces and their feasible preservation under nitrogen atmosphere.

Iodine solution treatment in nonpolar solvent as a facile approach to improve morphology and photostability of perovskite films

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Hybrid organic-inorganic lead halide perovskites (APbX₃, A=methylammonium(CH₃NH₃⁺), formamidinium ((NH₂)₂CH⁺), Cs; X= I, Br, Cl) are a perspective family of semiconductor materials, which received a great attention among scientists around the world, due to possible application as an absorber layer in new generation solar cells. The efficiency of such devices recently reached 25,5 % in single junction solar cell, and 29,5 % in tandem with silicon, making perovskites a strong competitor to other groups of materials. In addition, hybrid organic-inorganic lead-halides has significantly lower production cost owing to quite affordable chemical solution fabrication.

However, the quality of resulting hybrid perovskite films after solution deposition procedure is quite poor and requires additional post-treatment procedures. There were suggested several methods for improving properties of lead-halide perovskite materials such as thermal or solvent annealing treatment, which became essential for effective perovskite solar cell fabrication.

Within the framework of present research we proposed a new approach of perovskite film treatment using iodine solutions in toluene and decane, resulting in film morphology improvement, 3.5 times increase of the average grain size, enhanced optoelectronic properties and photostability. The plausible mechanism involves polyiodide formation acting as a liquid transport medium and causing the recrystallization (Figure 1). One of the advantages of such technique is the exceptional high rate of semiconductor film recrystallization. The proposed technique was successfully applied for perovskites with mixed cation and mixed anion compositions and can be further considered as a new perspective perovskite post-treatment strategy.

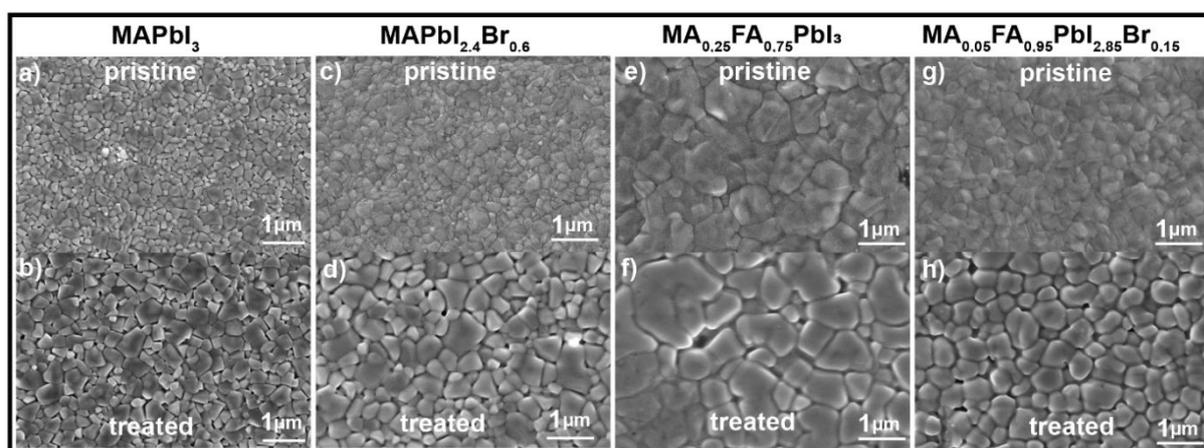


Figure 1. Perovskite films recrystallization using film treatment.

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