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Published in:
Advanced Photonics Research

DOI:
10.1002/adpr.202100326

Published: 01/01/2022

Document Version
Publisher's PDF, also known as Version of record

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Please cite the original version:
Furasova, A., Voroshilov, P., Sapori, D., Ladutenko, K., Barretin, D., Zakhidov, A., di Carlo, A., Simovski, K., & Makarov, S. (2022). Nanophotonics for perovskite solar cells. Advanced Photonics Research, 3, 1-20. [2100326]. https://doi.org/10.1002/adpr.202100326
Nanophotonics for Perovskite Solar Cells

Aleksandra Furasova, Pavel Voroshilov, Daniel Saporı, Konstantin Ladutenko, Daniele Barettn, Anvar Zakhidov, Aldo Di Carlo, Constantin Simovski, and Sergey Makarov*

Solar photovoltaics based on synthetic halide perovskites have revolutionized solar energetics in the last decade. Since 2009 the overall efficiency of the sunlight-to-electricity conversion in perovskite solar cells increases from 3.8% up to 25.5% (for thin-film single-junction perovskite solar cells) and more than 30% (for affordable tandem solar cells with top photovoltaic layer of halide perovskite). On the other hand, nanophotonics has made a huge progress in the direction of light manipulation at nanoscale, which is highly important for various thin-film technologies. In this review, implementation of various nanophotonic designs for improvement of perovskite solar cells efficiencies is discussed. In particular, different methodologies are covered for devices nanopatterning, nanotexturing, and nanostructuring of perovskite solar cells. Moreover, how these changes in the solar cell architecture would not only affect optical properties, but also modify charge carriers transport and harvesting are discussed. Finally, recent progress in machine learning for the perovskite solar cells design optimization is overviewed.

1. Introduction

Halide perovskites are extremely prospective semiconductor materials for various applications, where light absorption or emission is required.[1–13] Among these applications, one of the most important branches is photovoltaics.[14] For the first time solar cells, where a perovskite was used as a dye sensitizer in a solid-state dye-sensitized solar cell, appeared in 2009.[15] Though the overall efficiency (also called photovoltaic conversion efficiency and defined as the electric output power per unit area of the solar cell normalized to the power flux of normally incident sunlight) of these solar cells was as low as 3.8%, such advantages as low fabrication cost, absence of toxic waste accompanying the fabrication, and interesting electrophysical properties of halide perovskites stimulated the studies of the photovoltaic potential of these materials. In a few years after, thin-film solar cells were developed in which a halide perovskite was a submicrometer active photovoltaic layer sandwiched between the electron- and hole-transport layers connecting the perovskite to the electrodes.[16–18] Bulk heterojunctions of dye-sensitized solar cells were replaced in these works with a flat heterojunction of p–n or n–p type. After realizing great potential of the halide perovskites for photovoltaics, the race for further optimization has been started.[19–28] where all available approaches were employed including perovskite material’s properties optimization, transport layers optimization, and, finally, optical design optimization in which overview is the main goal of this work.

1.1. Comparison of Perovskite and Silicon-Based Solar Cells

The best known thin-film solar cells competing with the newly suggested perovskite solar cells (PSCs) were in 2014–2016 those based on amorphous silicon (a-Si) with a polished electrode on the rear side. Due to the use of the polished metal, operating as a mirror for the sunlight transmitting through a-Si, these solar cells are not flexible. Such hard solar cells manifested in 2014–2016 the record overall efficiency of the order of 10%.[28] Meanwhile, for the PSCs in the same time the photovoltaic conversion efficiency 18% was obtained.[17,21,30] This amazing progress has been explained by excellent optoelectronic properties of perovskites discussed in detail in
various review articles[21,31,32] and high absorption.[31,33,34] Nowadays, the overall efficiency of perovskite thin-film solar cells equals to 25.5%,[14,35,36] being achieved together with the flexibility. The requirement of flexibility decreases the overall efficiency of a-Si solar cells nearly twice. For halide perovskites it is not the case. They are flexible due to their clay-like composition that allows different cations and anions for mixing. Thus, without a damage for flexibility, the overall efficiency has been raised from 3.8% to 25% in one decade. The ultimate efficiency of PSCs is now rather close to the general Shockley–Queisser limit estimated for arbitrary perfect single-junction solar cells as 30–35%.[36–38] The progress in the efficiency of PSCs was accompanied by the development of the fabrication techniques suitable for their mass production.[19,40] Note that in the most popular crystalline silicon solar photovoltaics, the same progress was achieved in seven decades. Finally, despite a number of successful demonstrations,[28,41–43] it turned out to be more difficult to integrate nanophotonic designs to silicon-based solar cells as compared with perovskite ones because halide perovskites are softer, more flexible, and more tolerant to defects formed after the integration with nonperovskite nanostructures.

1.2. Tandem Solar Cells with Halide Perovskites

The implementation of halide perovskites allowed researchers to create affordable tandem solar cells[44,45] in which different compositions of perovskite layers were utilized for effective splitting of the absorbed solar spectrum. In tandem solar cells, different bands of the solar radiation are absorbed by different photovoltaic layers. It offers a drastic reduction to the relaxation loss of photoinduced carriers. The same effect was achieved earlier for multijunction solar cells which are nowadays still used in spacecrafts. Unlike these expensive solar cells, neither rare materials such as GaAs nor expensive and challenging fabrication techniques are needed for tandems PSCs. In these tandems, a monolithic implementation (when a tunnel junction is formed between adjacent photovoltaic layers of a multijunction cell), a simple electric connection of different layers in the so-called three-terminal or four-terminal configurations, has been utilized. Later, a good electric contact of perovskite and crystalline silicon granted the affordable design solution also for hybrid tandem solar cells where a submicrometer layer of perovskite is placed on top of a silicon plate.[46] In this work, the overall efficiency 35% was achieved that makes such tandems comparable in their efficiency with the satellite solar cells whose fabrication costs are higher by orders of magnitude. In this tandem, the nanolayer of perovskite is not sandwiched between the electron- and hole-transport nanolayers, as in conventional PSCs. Such a perovskite tandem cell is free of the main drawback of conventional PSCs making their overall efficiency lower than the ultimate (Shockley–Queisser) value. This drawback is a set of parasitic shunts formed across a perovskite layer due to the diffusion of the ionized molecules from the charge-transport layers into the perovskite. The overall efficiency of the tandems in which this drawback is absent is much higher, and still there is room for its further improvement without an obvious increase of the cost.[46]

1.3. Stability Issues in PSCs

An exceptionally rapid progress, especially striking in contrast with the modest progress in the other branches of solar photovoltaic engineering, has attracted to PSCs an unprecedented attention. Probably, the most keen topic for PSCs is stability of their properties, which was a difficult problem for both halide perovskites and suitable hole-transport materials.[47–50] Their stability implies a long lifetime (more than a year without a drastic degradation of the solar cell efficiency) in the presence of the thermal variations (±50 °C), humidity (up to 100%), and UV exposure typical for outdoor conditions. In this general view, the issue of stability was very well reviewed in 2016 in the study by Matteocci et al. [51] Since that time some technical solutions improving the stability of the PSCs without a damage for their photovoltaic properties were found.[40,52–54] In particular, the issue of stability of a hole-transport material has been practically resolved.[55] Though the lifetime of PSCs is still limited by the robustness of solid perovskites to listed outdoor conditions, this robustness has been enhanced since 2009 with the same growth rate as that of the overall efficiency. In a recent review,[56] an optimistic forecast for PSCs was done, related to the improvement of the perovskite crystallinity. Generally, it is clear that the present situation leaves no doubts about the bright future of the perovskite solar photovoltaics.

However, we would like to focus on additional degree of freedom for PSCs optimization.

In this article, we overview the recent progress in those PSCs where the nanophotonic approaches were used. Namely, we consider nanostructured PSCs comprising arrays of emerged nanoparticles (NPs), nanopatterned interfaces, and nanotextured layers. We also cover the cases of the multiphase content of submicrometer layers forming a PSC because any heterogeneity on the submicrometer level makes the structure a subject of nanophotonics. However, our main attention is paid, namely, to NPs. For example, arrays of Ag and Au NPs exploiting the plasmon resonance phenomenon were previously used for the improvement of such photovoltaic devices as amorphous silicon solar cells, organic solar cells, and light-emitting diodes.[16,57,58] It is not surprising that such NPs may have a potential also for perovskite solar photovoltaics. Next, all-dielectric nanophotonics have recently opened new doors to perovskite-based photodiodes, lasers, and light-emitting diodes.[7,8,59–64] The nanophotonic approaches in this area of perovskite photovoltaics were reviewed in our previous work.[7] In the present article, we do the same for PSCs. We point out the effects related with both photonic and electrophysical properties of these nanostructured PSCs. The systematization of various approaches would help one to select the best strategy to improve PSCs using the achievements of nanophotonics.

2. Nanostructures for PSCs Coloration

The general formula for the family of halide perovskites (named after the Russian mineralogist Lev Perovskij) is ABX₃, where cation “A” stands for such ammonium-based cation as methylammonium and formamidinium, or for just inorganic cations like cesium; “B²⁺” stands for the second cation being usually lead or...
tin; “X-“ is halogen being usually iodide, bromide, or chloride. Such variety regarding the perovskites composition results in a tunability of their optoelectronic properties. For example, the bandgap of halide perovskites can be varied via halogen substitutions in methylammonium lead halide MAPb(I1-xBrx)3, where 0 ≤ x ≤ 1 depends on relationship between I and Br ions. In previous studies, the bandgap variation from 1.2 to 3.1 eV was achieved in this way completely covering the visible and near-infrared ranges. Though for the most part of PSCs the operation band is basically the visible range, the possible bandgap variety points out a straightforward way to obtain colorful PSCs—bandgap engineering via chemical management. Here, it is worth to explain why colorful solar cells are needed.

A solar cell covered with an ideal antireflector would absorb all the incident light and would look black at any angle. Advanced silicon solar cells utilizing all-angle light trapping are almost black and this is the prerequisite of their high optical efficiency exceeding now 90%. However, these solar panels are dedicated mainly for the use in solar power plants. In the domestic application, they are placed either on a roof of a building or in a backyard. PSCs due to their light weight, low cost, and flexibility are widely thought promising for the large-scale utilization in the cities. These solar panels will be placed not only on the roofs, they will cover also the facades of buildings in a form of architectural glazing. Therefore, they should not be black or dark-brown (natural color of a conventional PSC, bare one, or covered with a front glass). A part of their amazingly high overall efficiency may be sacrificed in favor of their aesthetic looking. This point of view is adopted in the so-called building-integrated photovoltaics (BIPV) whose concept was suggested in previous studies. This makes the color customization an important feature of PSCs dedicated for BIPV.

There are several ways to obtain colorful PSCs. The first way is the aforementioned bandgap engineering. In this way, the color of a PSC taken without an antireflecting coating can be tuned from dark brown (x = 0) to brownish-red and, finally, to yellow (x = 1), as shown in Figure 1. This process is accompanied by the structural transition of perovskite from a tetragonal to cubic phase which has a linear dependence on the content of Br. In the cubic phase, the perovskite absorbs in a minor part of the solar spectrum. In Figure 1, one can see a rather modest color gamut achieved by a very heavy damage for the overall efficiency. Namely, for x = 1.0 the photovoltaic absorption decreases nearly four times compared to x = 0. Respectively, the photocurrent also reduces four times. The overall efficiency of such solar cells does not exceed 4%.

The second way is cosensitizing the perovskite layer with different colorful substances (organic dyes) filling its nanopores. Here, the color tuning results from the frequency selectively absorption of sunlight. As the range of sunlight experiencing the parasitic absorption in the dye is narrow, the optical efficiency of the PSC drops only by 20%, and the internal quantum efficiency does not suffer at all. Thus, due to this coloration the overall efficiency decreases also by 20%. However, in this way one can

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**Figure 1.** a) Absorption spectra and b) J–V characteristics of a perovskite-based solar cell. c) Pictures of TiO2-perovskite bilayer on FTO substrate for different content of Br in the composition MAPb(I1-xBrx)3 from ref. [65]. Schematics of various color-filtering techniques based on optically resonant nanostructures reported for PSCs. d) Transmitting Fabry–Pérot cavity. e) Reflecting cavity with a top transparent nanolayer. f) Bragg reflector. g) Nanopatterned layer with resonant reflectance. h) Inverse moth-eye antireflective coating. i) Plasmonic metasurface. (a,b,c) Reproduced with permission. Copyright 2013, American Chemical Society. (d,e) Reproduced with permission. Copyright 2016, American Chemical Society. (f) Reproduced with permission. Copyright 2017, Royal Society of Chemistry. g) Reproduced with permission. Copyright 2019, Springer Nature; (h) Reproduced with permission. Copyright 2019, Springer Nature; (i) Reproduced with permission. Copyright 2017, Nature Publishing Group.
only increase the absorption in a given spectral range (up to nearly 100%), whereas the absorption at other wavelengths is also quite high. Its difference from 100% is determined by the imperfectness of the antireflecting coating. Practically, the optical absorbance of a PSC in the visible range without addition of the dye is as high as 70–80%. Therefore, the injection of dyes though enriches the color gamut results in a quite dull coloration of a PSC. In order to make the coloration brighter, one also needs to engineer the frequency dispersion of the optical transparency of perovskite changing its structural phase. The perovskite crystal structure can transit from the widely used corner-sharing octahedral phase, exhibiting quite uniform optical absorption coefficient in the visible range, to the orthorhombic phase which absorption coefficient is lower and more dependent on the incident light wavelength. This approach to the coloring of inorganic cesium lead halides was suggested in the study by Lin et al.\textsuperscript{[71]} The frequency dispersion of the refractive index of the perovskite results in the enhanced frequency selectivity of its absorption whose integral value (over the visible range) reduces. Respectively, the reflectance in presence of a simple antireflective coating becomes higher and more frequency selective. The most intensive coloration is achieved when the perovskite layer thickness is intentionally reduced so that not to fully absorb the transmitted light. In this design, the bottom electrode is performed of a highly transparent conductive oxide, and the colorful solar cell turns semitransparent \textsuperscript{[61,72]} Such PSC looks brightly colored in both reflected and transmitted light. Though this approach implies a twofold or even triple decrease of the solar cell optical efficiency sacrificed for its coloration, it has two advantages. First, the color gamut of such solar cells enriches drastically varying from brown to blue and these colors are bright. Even the deep blue color was implemented within the framework of this approach applying a special electrochromic nanolayer.\textsuperscript{[70]} Second, such a semitransparent solar panel, unlike a conventional PSC, can be used as a window glass. A twofold and even a threefold reduction of illumination is typical for stained window glasses. As to the overall efficiency of such PSCs (5–6%), it is still high compared to previously known design solutions for transparent solar cells.\textsuperscript{[74]} Note that the transparency of a solar cell can be also useful for optoelectronic devices for which the solar cell is a power source.\textsuperscript{[74]}

Another powerful approach to simultaneously tune the color and enhance the photons conversion into photogenerated charge carriers in PSC was demonstrated recently by using the ionic gating of porous semitransparent carbon nanotube (CNT) electrodes (both SWCNT and MWCNT) in ionic liquids.\textsuperscript{[73]} The effect of coloration change via doping is achieved in ionically gated planar PSC with ultrathick fullerene (both C60 and C70) electron-transport layers (ETLs) with porous SWCNT electron collector on top of it. Perovskite photovoltaic devices usually have undoped electron transport layer, which is typically very thin like 20–30 nm of C60 due to its high resistance and optical absorption. Ionic gating of top CNT cathode in ionic liquid by small gate voltage tunes the Fermi level of CNTs by electric double-layer charging, and causes lowering of the barrier at C60/C70 ETL. Moreover, at higher gating voltage ions further propagate into fullerene ETL and change its color by electrochemical n-doping, modulating its optical transmission that increases dramatically PSC performance by raising significantly the external quantum efficiency (EQE) additionally to two other key parameters: $I_{sc}$ and fill factor (FF), resulting in PCE efficiency raised from 3% to 11%. EQE spectra shift upward with bigger gain at 1.00–2.00 V gate bias for the C60 sample and have less response to gate voltage for the C70 cell. In the maximum point of spectra for 200 nm C70 cell, EQE was achieved at 80%, and that is 40% higher than EQE of solar cells at initial conditions without ionic liquid gate, respectively, for C60 ETL devices; the maximum was achieved at 65%. In general, the growth of the EQE spectra follows the trend of $I_{sc}$ changes of solar cells during gating in other types of organic devices: both in polymeric\textsuperscript{[76,77]} and small molecule solar cells,\textsuperscript{[78,79]} and further confirms improvement of charge photogeneration and collection via gating-induced doping.

The third way to engineer the desirable color of a PSC is the use of color-filtering schemes illustrated by Figure 1. Here, the coloration is achieved mainly due to the frequency dispersion of the solar cell reflection loss (a parasitic frequency selective absorption may be also involved but it is an auxiliary mechanism in this approach). The resonant reflectance was achieved in semitransparent PSCs employing an optical Fabry–Pérot cavity.\textsuperscript{[71,80]} In these works, an optical filter operated as a mirror for the most part of the sunlight spectrum except a narrow frequency range, where the Fabry–Pérot resonance made it transparent. The cavity comprised an optical spacer sandwiched between two nanolayers of Ag (each of them thinner than the skin depth of Ag in the visible range but total thickness of Ag was larger than this skin depth). One of this silver layers was also the bottom electrode of the PSC, as shown in Figure 1d. The thickness of the perovskite in these structures was insufficient for the complete absorption of sunlight after one passage through the solar cell but sufficient to absorb the light after the two passages (the second one holds after the light reflection from the cavity). It is clear that the most part of the solar spectrum is absorbed in this case except a narrow range which is half-transmitted through the solar cell. This PSC, which also replaces window glass, is brightly colored in transmitted light and appears dark in reflected light, making the window opaque from the outside. Another implementation of an optical microcavity resulting in bright coloration of the PSC in the reflected light was suggested in previous studies.\textsuperscript{[81,82]} Here, the cavity comprises the photovoltaic layer and is formed between two nanolayers of transparent conductive materials—PEDOT:PSS on the top and conductive oxide on the rear side, as shown in Figure 1e. The optical contrast of these materials is sufficient for a cavity regime with a reflectance enhanced in a narrow band. Here, the top layer of the cavity serves also a top electrode and an antireflector, whereas the bottom layer (TCO) serves a bottom electrode. In this way, the vivid colors are achieved via the resonant reflectance controlled by the thicknesses of both top electrode and HTL material. The allowed damage for the optical efficiency due to the reflection loss is adopted on the level of 20%, and the overall efficiency of this PSC dedicated for building facades or roofs is triply higher (about 18%) than that achieved for the window PSC.

A reflecting Fabry–Pérot cavity with enhanced frequency selectivity can be alternatively implemented using either periodic or aperiodic multilayer dielectric mirrors. Such mirrors utilized for a PSC were reported in previous studies.\textsuperscript{[83–85]} For example, a dielectric mirror may consist of alternating SiO$_2$ and TiO$_2$ films...
of nanometer thicknesses, as shown in Figure 1f. This stacking filter can be attached to the back electrode of a semitransparent solar cells. Similarly, to the design with a bilayer of Ag reviewed above, a noticeable portion of light in the given spectral range is transmitted through the whole structure, while a broad range of wavelengths is reflected back to the active layer and absorbed in the second passage through it. As the dielectric (unlike metal) does not bring the parasitic absorption and as the filtering properties of a multilayer structure are much better than those of a bilayer of Ag, this semitransparent PSC having nearly the same bright coloring and overall transmittance of the sunlight has much higher efficiency. Namely, in this case the reduction of the optical efficiency (defined as the ratio of both absorbed and transmitted power to the incident power) is as small as 10%, and the overall efficiency for a blue PSC equals 19%—an amazing value for a semitransparent solar cell. However, the integral transparency of the PSC in this case is low—about 10%.[83]

Another implementation of the filtering functionality using a multilayer dielectric structure was suggested in the study by Zhang et al.[86] Here, a porous photonic crystal structure is formed with dense TiO2 and porous SiO2 by means of liquid processing techniques and directly integrated in a solar cell. In this case, the efficiency of the blue PSC is reduced (about 9%), but the transparency turns higher (within 20–40% for all colors). Note that in both implementations the efficiency is maximal, namely, for the blue PSCs and nearly twice lower for the red one.

Color filtering can also be achieved by the nanopatterning/nanotexturing of the perovskite layer, the charge-transport one, or, simply, the antireflective layer. For instance, a 2D inverted opal structure for the perovskite layer was implemented via template-assisted spin coating technique in the study by Meng et al.[87] In previous studies,[88,89] the so-called doctor blade technique was used to create a nanopattern of the perovskite film in a form of a polygon array (with concentric rings in the study by Liu et al.[89]). Also, a bowl-like array structure of electron transport layer (TiO2), as shown in Figure 1g, was reported in the study by Wang et al.[90] In Deng et al.,[91] the nanograting pattern of TiO2 scaffold was implemented using the nanoimprint technique. An inverted moth-eye patterned polydimethylsiloxane (PDMS) film operating as an antireflector was applied to the front glass surface of PSC in Adjikatse et al.[6]—this structure is depicted in Figure 1h. Such nanostructures allow the color tunability through the frequency selectivity of reflection determined by the nanopatterned/nanotextured layers. Due to rather high optical contract of the nanostructured layers and their small thickness compared to the wavelength in free space in all these works, these nanolayers represent so-called all-dielectric metasurfaces (see, e.g., ref. [92]).

However, the metasurfaces in these works have not been optimized in respect to the trade-off between coloring and absorption efficiency, which are mutually contradictory, especially for the obliquely incident light. The main drawback of these PSC is, namely, the strong efficiency reduction versus the angle of incidence θ that holds even for the inverted moth-eye structure. It implies a nearly twofold decrease of the mean overall efficiency (that averaged over all angles of incidence corresponding to the daytime) compared to that measured for the normal incidence. Therefore, metasurfaces designed specially for wide-angle operation are needed for PSCs.

In Lee et al.,[93] a metasurface of thin silver nanostraps located on a glass substrate, as shown in Figure 1i, was suggested. Such strips experience the resonance of the localized surface plasmon in the visible wavelength range. The resonance wavelength depends on the ratio between the strip width and thickness. This effect results in a bright coloration due to a sharp reflection peak at a specific wavelength and grants the angular robustness of the efficiency that keeps practically unchanged up to θ = 60°. This design, however, suffers from parasitic losses because at the plasmon resonance the electric field is locally enhanced in the vicinity of the metal particle and inside it. Thus, the parasitic absorption also increases in the plasmon resonance range. The resonant reflection due to the enhancement of the polarization of strips at the resonance and the resonant absorption due to the local field enhancement are competing processes. As a result, the band of the resonant absorption is narrowing the resonant reflection range in the wavelength axis. The resonant absorption and the resonant reflection form a rather broad band of the resonant optical losses, and the optical efficiency of such the PSC drops nearly twice due to the presence of the metasurface. The overall efficiency is proportional to the optical one and is reduced similarly. For the red color the mean overall efficiency of this opaque solar cell equals 10%; for the blue one it is equal to 7.7%. Expectations of higher efficiencies for similarly bright coloration in the reflected light are related with the development of all-dielectric metasurfaces, for which the resonant losses are much lower than for plasmonic metasurfaces. Note that the uncertain terminology results in misinterpretations in the available literature on PSCs. For example, in Liu et al.[94] the reflecting Fabry–Pérot cavity formed by the perovskite layer and the bottom metal electrode performed of a polished metal is called as “a planar metasurface.” In fact, it is a standard optical filter consisting of an optically thin semiconductor layer, dielectric spacer of resonant thickness, and a metal substrate. This filter operates like its analogues reviewed above.

To conclude this section, it worth noticing that the nano- and microstructured antireflective coatings of PSCs can offer better angular stability to the overall efficiency of the PSC and an additional functionality—that of self-cleaning—to its surface.[33,34,95]

3. Nanostructuring for Efficiency Enhancement

3.1. Numerical Models: Multiphysical Approach

Nanophotonic approach to the architecture of a solar cell unlocks the hidden potential of photovoltaic materials, and in particular, grants the increase to the overall efficiency.[96,97] In order to implement this approach in practice, prior to the fabrication of an experimental sample one needs, besides a fruitful governing idea, also a suitable tool for numerical simulations. Most accurate and reliable simulation results can be obtained using multiphysics models which consider not only the electromagnetic linear light–matter interaction,[98] but take into account the charge carrier transport, the structural modifications in the active material such as defects, and the chemical interactions of this material.[22] Nowadays, many research groups prefer to use coupled optoelectronic approach for simulations of nanostructured PSC which takes into account the following factors: photon
absorption, electron–hole pair formation, and charge carriers collection by the electrodes.

Spectrum of the absorbed power (P_{abs}) in the active region (V) can be calculated as follows:

$$P_{abs}(\omega) = \frac{\omega_0 e^\prime}{2} \int \int |E(\omega)|^2 d\omega$$

(1)

where \(\omega\) is the angular frequency, \(\varepsilon_0\) is the vacuum permittivity, \(e^\prime\) is the imaginary part of the complex dielectric permittivity of the active layer, and \(E\) is the local electric field produced by the incident plane wave of unit amplitude.

Generation rate (G), which shows how many electron–hole pairs are generated in each point of the solar cell when the incident light is absorbed, can be found using the following formula

$$G = \int P_{abs} \cdot \frac{J_{AM1.5} \lambda}{h c} d\lambda$$

(2)

Here, \(J_{AM1.5}\) is the intensity of sunlight at a given wavelength on the sea surface; \(h\) is the Planck constant.

Transport of charge carriers \(\nabla \cdot j_n\) and \(\nabla \cdot j_p\) can be calculated by using a drift-diffusion model which couples the continuity and Poisson equations

$$\nabla \cdot j_n \equiv \nabla \cdot (\mu_n n \nabla \phi_n) = -R + G$$

(3)

$$\nabla \cdot j_p \equiv \nabla \cdot (\mu_p p \nabla \phi_p) = R - G$$

(4)

$$\nabla \cdot (\varepsilon \nabla \phi - \mathbf{P}) = \rho$$

(5)

where \(\varepsilon\) is a permittivity of a material, \(\mathbf{P}\) is a polarization field, and \(\rho\) is a total density including free carrier densities, distribution of trap states, and ionized donors and acceptors.

The first two equations are the continuity equations for the electron and hole currents, with \(n\) and \(p\) electron and hole densities, \(\mu_n\) and \(\mu_p\) electron and hole mobility, \(\phi_n\) and \(\phi_p\) electron and hole quasi-Fermi levels, and \(G\) and \(R\) generation and recombination rates, respectively. The recombination loss \(R = R_{SRH} + R_0\) includes nonradiative Shockley–Reed–Hall \(R_{SRH}\) and radiative direct recombination \(R_0\), which are given, respectively, by

$$R_{SRH} = \frac{np - n_i^2}{\tau_e (p + p_i) + \tau_h (n + n_i)}$$

(6)

$$R_0 = k_0 (np - n_i^2)$$

(7)

where \(\tau_e\) and \(\tau_h\) are lifetime of electrons and holes, \(n_i\) and \(p_i\) are density of electrons and holes in an intrinsic specimen, and \(k_0\) is the radiative recombination coefficient.

3.2. Nanoparticles in PSC

The resonant NPs incorporation in a thin film SC could be considered as one of the most popular techniques of light trapping in the absorption layer,[16,17,69–100] nevertheless, the overall efficiency of improved devices could be much more higher due to following physical effects: 1) resonant local field enhancement around NPs (if a NP is incorporated into an absorption layer, it can result in resonant enhancement of generation rate); 2) diffusive light scattering by NPs (the type of light trapping that can result in a broadband enhancement of useful absorption); and 3) the charge carriers transport improvement.

Two first effects refer to the so-called light or photon management of a solar cell, and the third mechanism takes part in the separation of the photoinduced carriers by the cell layers and, therefore, refers to the charge management. Here, it is worth noticing that the dielectric NPs emerged into the perovskite layer obviously intersect with its pores and may decrease the harmful molecular diffusion across the perovskite layer. This effect is, unfortunately, not studied well in the available literature.

Perhaps, it could be a reason because the average length of the nanopenes in a perovskite layer is of the order of 100 nm, and the parasitic shunts are rarely formed if the thickness of the perovskite layer sandwiched between the charge-transport ones exceeds 350 nm. However, 400 nm is commonly adopted as the optimal thickness of the perovskite layer in the absolute majority of available articles which is justified by the charge diffusion length in perovskites.[103]

For higher thicknesses, the ohmic resistance starts to rapidly grow due to the charge transport component, and the power conversion efficiency drops.[104] However, the maximal internal quantum efficiency of the PSC corresponds to thinner perovskite layers. If we forget on the optical efficiency of the PSC and neglect therefore mentioned parasitic shunts in the nanopenes, the optimal thickness of the perovskite layer turns out to be equal 200 nm. This optimal value was theoretically obtained in Hima et al.[105] and it fitting the experimental data of Lee et al.[106] obtained for a crystalline perovskite. For such thicknesses of the perovskite layer, the impact of the NPs to the parasitic shunts may be significant and such a study would be actual. In this section, we consider the introduction of metallic, high refractive index dielectric, and low index dielectric nanostructures as well as their influence on light distribution, charge transport properties, and stability of PSC.

3.2.1. Plasmonic NPs

As to the studied impact of NPs, the most part of these studies concern the light management. Here, the highest impact corresponds to plasmonic NPs. Ag and Au NPs grant the extreme light localization at different wavelengths depending on their shape. This light localization implies a very high local field enhancement and holds in the band of localized plasmon resonance. This effect is the most popular mechanism of light trapping in PSCs because the light with locally enhanced intensity is absorbed better than a propagating plane wave in the active layer. Practically, the light in the range of the plasmon resonance is fully absorbed in the layer and does not propagate further. Initially, plasmonic NPs were used to enhance the thin-film-based a-Si solar cells, as mentioned in the Introduction. Later, they were employed in dye-sensitized solar cells of the so-called Grätzel type.[107] For PSCs, the use of plasmonic NPs was suggested in the study by Zhang et al.[107] Later, the light management caused by different plasmon NPs with various distance to the incident light source was studied in detail.[108–110]

In addition to local enhancement of the optical field (Figure 2), plasmonic NPs also enhance diffuse scattering, when their size...
becomes comparable to the order of the light wavelength.[121]

Then, the part of the light transmitted into perovskite propagates along the perovskite layer; a larger amount of light can be absorbed by a thin perovskite layer. If this layer is not thick enough to completely absorb a normally incident plane wave after two passages back and forth (between top and back electrodes), it may be thick enough for almost full absorption when most of the light experiences diffusive scattering on the nanoparticles. The lateral scattering by plasmonic NPs can dominate over the forward scattering, if the radius of the metal nanosphere is larger than the skin depth.[122] This depth for Ag and Au in the most part of the visible range is equal to $\lambda/20-25$ nm.

Despite the parasitic plasmonic losses discussed above, core–shell NPs with a plasmonic core of radius 40-50 nm and a dielectric shell of thickness 10-20 nm grant the enhancement of the average optical efficiency of a PSC. Keeping the same thickness of all layers and emerging the NPs near the boundary of the top charge-transport layer and the perovskite one can increase the overall efficiency up to 40–45% (Table 1).[108,123] This improvement is achieved because the thickness of the perovskite layer sufficient for the nearly complete absorption of the plane wave per two passages (350 nm in absence of resonant nanostructures) becomes smaller and approaches to the electrophysical optimum of 200 nm, whereas the absorption of sunlight keeps nearly complete.[124] The maximal known (45%) improvement of the optical efficiency of a PSC with a perovskite layer of thickness 250 nm was obtained in Luo et al.[108] For a so small thickness, nearly one half of the incident power would be lost in the absence of NPs. In their presence, if the fraction of NPs is optimal, both light-trapping effects—local field enhancement and scattering—are coupled. This case is illustrated by Figure 2a. Note that this strong light–matter coupling regime is utilized for optical heating of NPs by the laser light propagating in the dielectric ambient.[125]

It worth noticing that metal NPs can be utilized for injection of additional electrons into the photovoltaic layer (this effect is referred as hot electrons photovoltaics).[126] However, in this case

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**Figure 2.** Numerical calculations provided for the optically active NPs: plasmonic, Mie-resonant and with a low refractive index placed in a hole-transport layer, perovskite, and in a hole-transport layer of solar cells. Optical electric enhancement by a) gold, b) silicon, and c) silicon dioxide NPs at the certain wavelengths when they are located in perovskite. (a) Adapted with permission.[124] Copyright 2020, Royal Society of Chemistry. (b,c) Adapted with permission.[132] Copyright 2018, The Optical Society. The calculated generation rate map by MAPbI$_3$ PSC with d–f) gold NP, g–i) silicon NP and m) with SiO$_2$ NPs (j–l) with respect to the reference cell and (n–q) corresponding current density maps. The current density distribution in perovskite layer where the particles are in the photoactive perovskite. The size of the unit cell is 500 nm.
the NPs in the photovoltaic layer should be bare (without a dielectric shell) that results in rather high parasitic losses in the metal at the plasmon resonance and for PSCs may result in a degradation of perovskite due to the diffusion of the metal ions and, in general, due to catalytic properties of the noble metals.\cite{127} Therefore, for the use in PSCs metal NPs must be of the core–shell type.\cite{128} In Saliba et al.\cite{129} it was shown that the dielectric nanoshell not only positively influences the photon management and preserves the perovskite of destruction, but it also plays a positive role in the charge management. In all available works, where the enhancement of the overall efficiency due to plasmonic NPs was reported, these NPs were core–shell ones.

Remarkably, core–shell NPs can result in electronic bands engineering in the active layer, which results in dramatic variation of local transport and recombination processes. Namely, radiative recombination rate in perovskite can be enhanced by orders after the core–shell NPs incorporation, which is beneficial for light-emitting designs\cite{130} and, potentially, for light-emitting solar cells.\cite{131} At the same time, an array of core–shell NPs incorporated into the perovskite is a more expensive design solution than an array of bare metal NPs. Thin-film solar cells enhanced by core–shell NPs, in spite of their advantages, are hardly compatible with the idea of cheap solar electricity.

### 3.2.2. Dielectric NPs

An important alternative to plasmonic NPs is represented by solid dielectric NPs. Unlike bare metal NPs silicon, GaP and other high-RIs dielectric NPs are chemically inert to halide perovskites at normal conditions that is important for the internal stability of PSCs. These nanostructures can be divided into two main groups: NPs whose refractive index (RI) is lower than that of the ambient, and NPs with higher RI. For lead halide perovskites RI \( \approx 2.3 \)–2.7 in the visible range, therefore, to achieve nonresonant scattering by low index materials, such as chemically inert silica with RI \( \approx 1.45 \), can be used. These NPs work as voids in the perovskite devices and cause the diffusive scattering (Figure 2g).\cite{132,133} Such low-RIs nanostructures can reduce optical losses or reduce the optimal perovskite layer thickness from the usual 400 to 250–300 nm.

The first attempt to incorporate SiO\(_2\) into PSCs was done in Hwang et al.\cite{138} where SiO\(_2\) NPs were too small so that to grant the noticeable light trapping effect, and only their positive role in the charge management was shown. However, this impact is quite minor, i.e., restricted by the wide bandgap of the perovskite.\cite{138} Larger than 50 nm low-RI NPs may grant a noticeable light management. In Aeineh et al.\cite{134} the effect of enhanced lateral scattering for silica NPs was studied theoretically using the Mie theory, and proved experimentally. According to this work, NPs of radiuses 25-50 nm distributed randomly with the optimal fraction ratio close to 0.1 scatter the light in the lateral directions quite efficiently. Figure 2c shows that the incident red light is scattered by the SiO\(_2\) particle and propagates further along the perovskite layer. This optical phenomenon underlies the current density distribution behavior expressing in the numerical calculations of the current density distribution onto perovskite layer (Figure 2p). Being incorporated into the 200 nm-thick layer of electron-transport material they grant the 20% enhancement to the overall efficiency of a PSC with a perovskite layer of thickness 300 nm. Richter et al.\cite{133} claim that SiO\(_2\) submicrometer spheres placed in perovskite thin films improve the EQE of photoluminescence in two times of MAPb(I\(_3\)Cl\(_{2}\))\(_3\) perovskite compared with the planar film. At the same time, these nanostructures are not involved in a PV process due to their large bandgap and low charge mobility.

For a more significant reduction of the perovskite thickness (below 200 nm), one needs a stronger light-trapping effect than that granted by low-RI NPs. NPs with intermediate RI, such as TiO\(_2\) and Al\(_2\)O\(_3\), are worse than the low-RI ones due to their lower optical contrast with both perovskite and charge transport layers.\cite{132}

High RI and quite low losses in the visible range are offered by some semiconductors, such as silicon, both crystalline and amorphous phase (except the blue-violet band, where a-Si has high losses), GaAs, and GaP. These NPs are widely used in modern nanophotonics.\cite{135,138} In contrast to plasmonic NPs, where resonances are limited to electric multipoles (mainly the electric dipole), high-RI dielectric NPs support both electric and magnetic multipolar modes. Their interference at the same wavelengths leads to interesting resonant effects, such as resonant control of scattering efficiency and directionality.\cite{139}

High-RIs NPs may grant both strong near-field enhancement and scattering as shown in Figure 2c. This type of NPs demonstrates almost similar strength of these properties as compared to plasmonic NPs, but does not have their main drawback of high dissipative losses.\cite{140}

According to the Mie theory,\cite{141} the light scattering efficiency spectrum strongly depends on the size of the NPs and their RI. It means that incorporating high-RI NPs with different sizes into a perovskite film the whole visible range will be covered by the resonances in scattering. It grants the light trapping in the whole operation band of PSCs.\cite{142} Low losses in silicon grant the high quality to these Mie resonances. The local field enhancement is, therefore, accompanied by a rather minor dissipation. Low losses implies that the radiative Purcell factor prevails over the dissipative modes. In other words, the external quantum yield of a perovskite film increases due to the presence of the silicon NPs. The balance between the radiative and nonradiative recombination changes in favor of the first one.\cite{133,134,144} It grants the photon recycling (because the re-emitted photons are absorbed in the same area) and effectively increases the carriers recombination pathways.\cite{133,134,144} As a result, both photocurrent and the open-circuit voltage grow.\cite{142}

Figure 2 illustrates the difference between spatial distributions of the optical electric field in the perovskite devices containing the following components: plasmonic NPs (a), usual low-RI NPs (b), and high-RI NPs (c), all located at the interface between the perovskite and the hole-transport layer (HTL) of a PSC. The modeling of hole current density (Figure 2n-q) in the color map (bottom panel) was performed with finite elements method (FEM) using Numerical DEVICE software following the approach in Furasova et al.\cite{145} Both gold and p-type silicon inclusions in HTL accelerate hole extraction to the top electrode that may improve \( V_{OC} \). Wide bandgap particles like SiO\(_2\) block the photo-current behind it but increase it aside. The best operation in this sense corresponds to high-RI particles. Figure 2d shows that the optimal location of NPs is, namely, on the interface of the HTL.
and perovskite—then both light-trapping effect and transport enhancement are combined. This conclusion is confirmed experimentally, where Si NPs were incorporated into TiO2 HTL.

### 3.3. PSCs with Nanotextured Interfaces

Nowadays, for thin-film photovoltaics, the Shockley–Queisser (SQ) limit remains still unachievable due to two main physical restrictions: weak light absorption and charge recombination on defect states. In case of PSCs, where the most of defect energy levels is close to the valence and conduction bands, that does not significantly effect on PV performance, the efficient light absorption remains unsolved problem for flat solar cells. A large part of the incident light is reflected from the flat surface or can be absorbed by transport materials. Moreover, for thin-film devices, where thickness of photoactive layer is comparable to the optical wavelength, the part of the incident light can be transmitted by PV layer, reflected from the back electrode, and transmitted again. To minimize these optical loses, solar cell design can be modified by nanostructuring. With periodic surface patterning the incident light changes the path angle and traps in the photoactive medium. As a result, the light path length is enhanced and absorption is increased (Figure 3).

Besides the increase of absorption, the effect from nanostructuring of perovskite film can be characterized by increase of external quantum yield of luminescence as compared with smooth surfaces. Indeed, recently the improvement of PSCs characteristics after their nanopatterning was reported by several researchers. In Table 1, we summarized the most prominent examples of PSCs improved by nanostructures.

| Nanophotonic designs | Efficiency change | References |
|----------------------|-------------------|------------|
| Au@TiO2, nanospheres (80 nm) in m-ETL or MAPbI3 | From 12.59% to 18.24% | [108] |
| Au@SiO2, nanospheres (14 nm) between compact and m-ETLs in MAPbI3 | From 16.18% to 17.55% | [109] |
| Au@SiO2, nanorods (15 x 37 nm) between hole transport layer (HTL) and MAPbI3 | From 13.5% to 17.6% | [110] |
| Au@TiO2, nanorods (5 x 40 nm) in ETL of mixed PSCs | From 15.76% to 16.35% | [112] |
| Au (40 nm) between m-ETL and MgO of MAPbI3 | From 15.1% to 16.1% | [113] |
| Au@TiO2, (60 nm) on TiO2 nanofibers of MAPbI3 | From 10.27% to 14.37% | [114] |
| Ag@TiO2, (40 nm) between m-ETL and MAPbI3 | From 11.4% to 13.7% | [129] |
| Au nanostars, (30 nm) in HTL of MAPbI3 | From 8.3% to 8.8%, from 12.5% to 14% | [116] |
| Au@SiO2, (100 nm) in m-ETL of MAPbI3 | From 10.7% to 11.4% | [17] |
| Moth-eye m-TiO2 layer of MAPbI3 | From 15.3% to 16.9% | [149] |
| Ag NPs in TiO2 compact layer of MAPbI3 | From 4.6% to 6.15% | [216] |
| Ag@TiO2@Pa in MAPbI3 | From 18.4% to 20.2% | [217] |
| Ag@SiO2 in m-TiO2 of MAPbI3 | From 12.23% to 14.61% | [218] |
| Au@SiO2 in m-TiO2 of MAPbI3 | From 12% to 13.9% | [219] |
| Ge NPs in m-TiO2 of MAPbI3 | From 16.2% to 18.6% | [143] |
| Au@Ag@SiO2 in MAPbI3 | From 15.4% to 17.4% | [220] |
| Au nano-bipyramids in VO2 of MAPbI3 | From 16% to 18.8% | [221] |
| Ag NPs and nanostructured FTO of MAPbI3 | From 9.3% to 14% | [222] |
| Au@SiO2 between PEDOT: PSS and MAPbI3 | From 11.44% to 14.57% | [223] |
| AuAg@AuAg into PEDOT:PSS of MAPbI3 | From 13.1% to 16.8% | [224] |
| AgAl@Au NPs in LiF of MAPbI3 | From 15.2% to 16.9% | [225] |
| Au@TiO2, NPs (0-20 nm) in c-TiO2 of FAMAPbI3 | From 17.19% to 20.31% | [226] |
| Si, NPs (100-200 nm) in m-TiO2 of MAPbI3 | From 18% to 21.1% | [146] |
| Al-Si, NPs (100-200 nm) in SPIRO-MeOTAD of MAPbI3 | From 18.2% to 18.7% | [145] |
| Si, NPs (100-200 nm) between ETL and MAPbI3 | From 17.7% to 18.8% | [142] |
| AgOx@Ag, NPs (40-80 nm) of MAPbI3 | From 17.8% to 20.33% | [227] |
| Randomly nanotextured Au interface of MAPbI3 | From 19.3% to 19.8% | [150] |
| Nanostructured MAPbI3 | From 16.7% to 19.7% | [151] |
| Nanostructured/ moth-eye back electrode of MAPbI3 | From 14.3% to 15.5%/16.3% | [215] |
| Nanocone substrate for MAPbI3 | From 12.06% to 13.14% | [33] |
| Nanocone substrate for MAPbI3 | From 8.3% to 11.3% | [228] |
| Nanobowl TiO2 layer in MAPbI3 | From 8.8% to 12% | [229] |

aETL, electron-transport layer; HTL, hole-transport layer.
The positive impact of the nanotexturing was shown for the p–i–n, n–i–p, and tandem architectures of the PSC.[14]

Besides the absorption boost caused by increase of interaction length of photons in nanotextured perovskite films, the photon recycling plays an important role in the final PCE performance. In general, photon recycling is a physical process of reabsorption of photons which occurs from radiative recombination.[133] The main aim of the perovskite film nanostructuring is transmission and reflection suppression. Thus, photon recycling must depend on nanostructuring indirectly. Initially, the nanostructuring implies a flat film with deformation which should not produce additional harmful defects on the surface or inside the perovskite film. Generally, to avoid additional defects of perovskite films after nanostructuring, it is better to provide the surface passivation[157] of the perovskite. Provided we do not produce additional defects in the film after nanostructuring involved in the emergence of new nonradiative losses, we can say that this approach increases also the surface area between a perovskite and a charge transporting layer that improves the charge extraction. Taking this assumption into account, one can expect both Voc and Jsc growth.

The most widespread nano- and microtextured PSCs possess the following architectures: cone/triangular, moth eye, or rectangular shapes illustrated in Figure 4a–c. These geometries can be applied either to the interface of the perovskite layer with the electron-transport layer (top panel in Figure 4a–c) or to its interface with the hole-transport layer (bottom panel). To provide high throughput surface texturing of soft materials, a nanoimprint lithography[158] can be applied. Indeed, this method is adopted well for a large-scale manufacturing, where a mold with desirable morphology for a perovskite thin film undergoes external mechanical pressure forming a negative replica on the film. Flexibility and entire softness of halide perovskite films make this method suitable for thin-film PSCs. Also, nanopatterning was successfully applied for perovskite based photodetectors,[159] surface coloration,[160] perovskite antireflective coating,[161] nonlinear metasurfaces,[162,163] and perovskite photonic crystals.[164,165]

Also, a polymer-based (PDMS) mold once obtained with a silicon stamp is feasible for multiple replication of the nanopatterning in the perovskite layers.[155] This approach promises cheap mass production of nanostructured PSCs. In Kang et al.,[149] a PDMS mask was applied to m-TiO2 electron transport layer just after spin coating procedure before the solution evaporation. As a result, they could achieve the light absorption boost by 5% in 550–750 nm range. Also, an easily reproducible method was proposed in Wang et al.,[151] where the interface was textured using a commercial optical CD or DVD disks. This approach was later employed for the significant improvement of photodetectors.

Figure 3. Optical electric field distribution at different textured interfaces: a) rectangular back charge transporting layer, b) rectangular top charge transporting layer, c) moth-eye textured top contact with in respect to the according references in red wavelength range. (a) Reproduced with permission.[91] Copyright 2019, John Wiley and Sons. (b) Reproduced with permission.[15] Copyright 2018, John Wiley and Sons. (c) Reproduced with permission.[21]
and terahertz radiation sources.\cite{166} In the original work, it was, however, used, namely, for texturing the interface of perovskite with a HTL in a PSC. The improvement of all basic photovoltaic parameters due to this texturing was demonstrated.\cite{151} Importantly, the PSCs nanopatterning results in the improvement of absorption for the broader range of incident light angles Figure 4e. To achieve high PCE by PSC nanostructuring, it is necessary to use careful indentation and impurity free stamps to avoid an interface contamination and additional geometry defects generation. Moreover, the further surface passivation is desirable to decrease the interface recombination on traps. Therefore, this nanopatterning approach is usually more technologically complicated than the incorporation of resonant NPs.

### 4. Light Management in Perovskite-Based Tandem Solar Cells

As presented before, halide perovskites exhibit several important properties: they possess a direct bandgap that can be tuned, they are low cost, as well as easily and all-solvent processable. Therefore, they are ideal candidates to produce competitive tandem solar cells and are implemented generally as high-bandgap absorber. Several configurations with c-Si, CIGS, organics or CdS absorbers, and even all-perovskite tandem are today already demonstrated. Nevertheless, the most accomplished combination is perovskite/silicon (PK/Si)-based tandem solar cells with an actual record certified of 29.8% reported by the Helmholtz-Zentrum Berlin, higher than the silicon-based cell record.
efficiency of 26.7% obtained by Kaneka Corporation,\textsuperscript{35,167} showing the great potential of perovskite to increase silicon solar cell efficiencies beyond their theoretical limit. In addition, this development of perovskite silicon tandem could benefit from the existing industrial production of silicon solar cells: its deployment would be facilitated if seen as an upgrade of actual production line by addition of few equipment to deposit perovskite layers. In the following we will focus on Si/PK tandem as being the actual most advanced technology.

In tandem solar cell, light management is by far more complex than in single-junction solar cell. Instead of having one photoabsorber, two photoabsorbers are combined to improve the utilization of the solar spectrum: wide and low bandgap materials that absorb the high and low energy photons, respectively. Because of the penetration depth of photons in materials, light is first crossing the wide bandgap top cell before to reach the low bandgap subcell.\textsuperscript{148} As a result, the top cell should have a high-transmittance in the NIR and the visible region absorbed by the bottom cell. Producing semitransparent PSCs is challenging because of the addition of a transparent electrode. Its deposition may be destructive for the layers underneath, especially the top transport material layer. For this reason, a buffer layer such as SnO\textsubscript{2} is usually deposited to prevent any damages.\textsuperscript{44,168} The transparent electrode should have a high transparency, high conductivity, and low sheet resistance to transport carriers to the metal electrode.

Moreover, in the case of a monolithic integration, the situation is even more delicate because of the current matching condition. Indeed, in such case, both subcells are interconnected in series and the photocurrent is, therefore, determined by the smaller photocurrent generated by each subcell. Consequently, when designing the structure, one must pay attention about the absorption balance and ensure an equal distribution of the photogenerated carriers in each subcell: the maximum efficiency is expected when both subcells photogenerate the same current, while minimizing reflectance and parasitic absorption.

In the case of 4 and 3-terminal (4T and 3T) tandem solar cells, the device operation is not subjected to this current matching condition. If 4T tandem presents also the advantage that both cells can be prepared independently leading to more flexibility for the design, choice of materials, and processes, they have serious disadvantages: additional parasitic absorption losses due to the two more transparent electrode to collect carriers and more complex and costly electrical management at the module level. Regarding 3T tandem, they can be processable monolithically as 2-terminal tandem. Despite a first proof of concept with a remarkable efficiency of 17.1% reported by Tockhorn et al.,\textsuperscript{169} they are more complex to fabricate and also to handle electrically at the module level.

Several light management strategies employed in single-junction solar cells can be easily integrated into tandem devices. To reduce reflection losses at the front, ITO/air interface, antireflective coating such as lithium fluoride (LiF)\textsuperscript{168,170} and MgF\textsubscript{2}\textsuperscript{44,171,172} can be easily implemented. In addition, the rear-side of the silicon subcell can be textured to increase its infrared response, as it is frequently done for single-junction silicon solar cell such SHJ\textsuperscript{168,172–174}. In fact, the main concern comes from the additional interface located between the two subcells. Its optical management is already complex as one wants the light absorbed by the perovskite material to be confined in the top cell and the light absorbed by the silicon layer to be transmitted without any losses and be confined in the bottom cell. And in addition, the top cell integration raises practical difficulties that need to be solved. Hence, the challenge is to achieve the integration of the top cell while having an optimal light management at the interface. In the two next subsections, we will discuss about two strategies currently considered: achieving the perovskite subcell integration while keeping the front textured interface of the silicon subcell, or implementing alternative light management strategies to reduce reflection losses when integrating the top cell on a flat front-surface silicon precursor.

4.1. Textured Front-Side Monolithic Tandem Solar Cells

Silicon and PSCs present several design differences owing to their intrinsic properties. Because of its indirect bandgap, about hundreds of μm, typically 160 μm, is needed for silicon to achieve a near-complete absorption of sunlight. On the contrary, thanks to its high absorption coefficients, only hundreds of nm, typically 300–400 nm, are enough for halide perovskite materials. The perovskite subcell is therefore about 500 times thinner than the silicon one. This leads to compatibility issues when integrating perovskite layers on top of the silicon subcell, especially when the front surface is textured. Indeed, light management in silicon solar cells is generally achieved by an antireflective coating like ITO and SiN\textsubscript{x}\textsuperscript{175} and by light-trapping through a random pyramidal texturing of the silicon surfaces.\textsuperscript{176} Therefore, achieving a conformal deposition of tens or hundreds nanometer thick layers on several μm width and height pyramid is origin of difficulties (Figure 2b). In addition, usual solvent-based deposition techniques used for perovskite layer deposition such as spin coating are not well adapted for such conformal deposition. For this reason, first silicon perovskite tandems were reported using CMP polished silicon precursor.\textsuperscript{170} Nevertheless, use of polished surface is detrimental for the device light management due to reflectance losses.\textsuperscript{170}

To achieve a conformal deposition on structured silicon precursors, a solution was reported by Sahli et al. using a hybrid sequential method to deposit the perovskite: the inorganics PbI\textsubscript{2} and CsBr were first deposited by evaporation followed by the deposition by spin coating of the organohalides FAI and FABr.\textsuperscript{44} In addition, others layers as transport materials were deposited using thermal evaporation, sputtering, or atomic layer deposition\textsuperscript{177} allowing a conformal deposition of the textured precursor as well. Furthermore, they point out also the complexity of conformal depositions even using this protocol: they show that if the deposition of the HTM spiro-RRB was conformal on the ITO recombination layer, after the perovskite annealing step, it detaches from the ITO. Fortunately, this was not observed for the nc-Si:H recombination junction leading to a high efficiency of 23.2% and a notable current of 19.5 mA cm\textsuperscript{-2}. The cumulative current measured by EQE was 40.4 mA cm\textsuperscript{-2} which compare well with the FF obtained by the best both sides contacted silicon solar cells.\textsuperscript{178} However, the FF of only 73.1% leaves room of improvement if we adapt the target value of the FF about 78–80% obtained for flat front-surface tandem.\textsuperscript{168,179,180} The reduced FF may be explained not only by the increased contact...
surface between the perovskite and the transport material leading to more detrimental recombination but also by a noncompletely perfect conformity of the layers on the texture surface.

Later, use of solvent-based techniques on texture substrate has been solved: the idea was to produce thick film of perovskite to recover the pyramid. Hou et al. achieved μm-thick film that could cover pyramids by spin coating concentrated perovskite precursor solution. A higher efficiency of 25.7% was obtained thanks to a higher FF of 75.36% despite a lower current of 19.1 mA cm$^{-2}$. A lower efficiency of 23.8% was obtained by Subbiah et al. by depositing a thick layer but using the upscalable slot-die technique. To facilitate the layer coverage, one may play on the texture design, for example, reducing the pyramid size. Chen et al. realized submicrometer pyramid texturing of silicon surface, called planarized surface, with a mean pyramid height of 0.43 and maximum of 0.83 μm. Both PTAA as HTM and perovskite layers were deposited by blade coating. To achieve a conformal deposition of PTAA, the substrate was heated at 7 °C during deposition to accelerate the solvent evaporation. Solvent engineering was then employed for the deposition of perovskite to avoid void between the perovskite film and the pyramids. Besides, they capped the tandem with a textured PDMS layer to reduce reflection losses at the front interface leading to an increase of the $J_{SC}$ generated by the top cell limiting subcell of 1.7 and of 0.7 mA cm$^{-2}$. The use of PDMS light management foil will be more discussed in the next section. Finally, an efficiency of 26.2% was obtained with an FF of 75.3% and a $J_{SC}$ of 19.2 mA cm$^{-2}$ in reverse scan.

Another approach is to achieve the top cell integration by mechanical stacking (Figure 5c). This way has the advantage to produce both subcells independently which allow to free from limitations regarding deposition methods and conditions such as choice of temperature and solvent. Lamanna et al. reported a 26.3% efficient two-terminal perovskite silicon tandem solar cell produced by mechanical stacking. Thanks to this method, they could demonstrate a tandem that displays both c-TiO$_2$ and meso-TiO$_2$ as ETM and a-Si as passivation layer for the silicon subcell. Indeed, the process temperature 45 °C needed for deposition of TiO$_2$ transport material is too high regarding the stability of a-Si (maximum 20 °C).

### 4.2. Light Management in Flat Front-Side Tandem Solar Cells

Despite the best silicon and perovskite based tandem solar cells were so far obtained with front flat surface, they are not optically optimal. Indeed, methods used to produce the best single junction PSCs are more adapted to a flat substrate than to a textured one. In addition, high efficiencies could be obtained thanks to the implementation of light management strategies to reduce reflective losses as it will be discussed below.

Even if the front-side is flat, having a rear-side textured compared to a dual-side flat tandem strongly reduces losses through a better collection of the NIR in the bottom cell. Nevertheless, the flat front surface may lead to reflection losses in the region of 600–900 nm and light management strategies have to be considered.

A solution is to add an interlayer with adequate optical properties in between the two subcells to improve light transmittance (Figure 2d). Santerbenget al. et al. proposed the incorporation of an interlayer with an intermediate refractive considering the refractive index of the ETM and the a-Si and with a low parasitic light absorption for wavelengths absorbed by the bottom subcell. They calculated an optimum of $n = 2.7$ and a thickness of 90 nm. Later, Mazzarella et al. demonstrated the use of nanocrystalline silicon oxide as an interlayer in tandem. Through oxygen content tuning, the refractive index and the thickness of the nc-SiO$_2$:H spacer was optimized to 2.6 and 110 nm. Reducing the reflectance losses, they obtained a $J_{SC}$ gain of 1.4 mA cm$^{-2}$ compared to the reference structure consisting of 20 nm of standard nc-Si: H layer and achieved for the best cell a certified efficiency of
25.43% and a $J_{SC}$ of 19.02 mA cm$^{-2}$. The sum of the photogenerated current reached 38.7 and was 1.8 mA cm$^{-2}$ lower than the one obtained by Sahli et al.

Using same strategy, Köhnen et al. achieved a higher efficiency of 26%, $J_{SC}$ of 19.22 mA cm$^{-2}$, and total photogenerated current of 39.46 mA cm$^{-2}$ with IZO as top TCO layer.[186] Reducing the thickness of IZO, the authors even increased $J_{SC}$ and total $J_{SC}$ to 19.72 and 40.04 mA cm$^{-2}$, respectively, yet leading to a higher sheet resistance and thus a lower FF.

Another approach then having the front texture from the silicon precursor is to introduce the texture surface when the device is completed by applying a textured light management (LM) foil (Figure 2e). The random pyramid texturing of silicon solar cell surfaces can be easily reproduced using UV Nanoimprint Lithography and a textured silicon wafer.[180,187] In addition to the moth-eye effect of the optical index gradually varying from that of the air to that of the TCO layer, which is granted by texturing, LM foil enhances light trapping in the solar device, reducing the reflectance at the interface between subcells.[188] Interest of use of LM foil has started with first reports of perovskite silicon tandem, showing significant enhancement of spectral response in each subcell.[170,174,189] Using a pyramidal texture LM foil, Jost et al. reduced greatly the reflectance losses for wavelengths lower than 1000 nm: the overall reflective loss was reduced from 6.13 to 2.48 mA cm$^{-2}$ leading to an increase in $J_{SC}$ of 2.27 and 0.92 mA cm$^{-2}$ for the top and the bottom cells, respectively.[180] 25.5% efficiency was hence demonstrated with a $J_{SC}$ of 18.5 mA cm$^{-2}$, a total $J_{SC}$ of 39.01 mA cm$^{-2}$, and an FF of 78.5%. Doing optical simulation of their device, they showed that the use of the LM foil led to a reduced reflectance loss in the 800–1050 nm range absorbed by the silicon subcell compared to the use of a planar ARC LiF. However, interestingly, after optimization of layer thicknesses and properties, the advantage was not significant anymore for the LM foil. It is worth noting that the device also displayed the interlayer nanocrystalline silicon oxide reducing reflectance losses at the interface between the two subcells.

Nevertheless, they exhibited another great advantage of textured LM foil: the use under nondirect illumination like diffuse light: in such case, LM foil devices outperformed devices with simple planar ARC. Best optimization for front flat surface tandem would be the combination of the intermediate optical index layer and an LM foil.

Another interesting feature of LM foil has been reported by Zheng et al.; they introduce fluorescent downshifting material into the PDMS foil leading to an increase in the device response in the UV region.[190] The concept has also the advantage to reduce the UV irradiation of the perovskite layers which are known to be detrimental for device stability.

Finally, nanophotonic designs can be implemented in the perovskite layers as well to enhance light confinement inside the perovskite and light in-coupling into the silicon subcell (Figure 2f). For example, the use of nanostructures of perovskite layer[191] or the nanotexturing of the perovskite layer[192] have been numerically simulated but not yet demonstrated experimentally as being complex to fabricate.

To conclude this section, light management in tandem is complex but is also essential to push the efficiency of these devices. It can be even more complex if considering bifacial tandem. It is not clear yet if the way to go is fully textured or flat front surface tandem. So far, as said above, the best tandems were obtained with flat front surface, even if fully textured tandems appear to have the best potential in theory.[186] In addition, other aspects such as the challenges of industrialization must be considered. On the one hand, it appears difficult to improve fully textured tandem devices and achieve upscalable and reproducible processes. On the other hand, the use of chemical mechanical polishing process to obtain flat precursor is not a viable solution but chemical polishing is an alternative to be considered.

5. Machine Learning for PSCs Improvement

A reliable multiphysics computer simulation of PSCs is a key to develop advanced designs with improved performance. Such models should consider both the charge carrier transport through the device and the light propagation governed by a nanophotonic design. This type of simulation requires a significant amount of computational resources[145] and thus is not directly applicable to the search of advanced PSC designs in a large parametric space. However, a similar challenge was solved for a pure nanophotonic problem[193] utilizing machine learning algorithms.

Machine learning (ML) is an emerging technology which has proved useful for various applications, such as image classification,[194,195] the generation[196] of realistic images and videos, natural language processing and translation,[197] transport routing,[198] and many others. The application of ML techniques is gaining popularity due to 1) increased accessibility to data and related computational power for data processing; 2) the availability of state-of-the-art software libraries to develop ML algorithms; and 3) the existence of multiple learning materials from leading universities and professionals.

For the readers, who lack the ML background, we would suggest considering ML algorithms as a sophisticated subset of curve fitting. The fitting process (called learning or training in ML context) typically benefits from sufficient amount of data points, provides a more reliable result when we can avoid extrapolation, and converges much better if we can exclude some nonessential behavior from the obtained data, e.g., high-frequency modulation (when we are just interested in envelope) or noise.

The improvement of PSCs is one of the many areas which can benefit from ML. However, there are several key prerequisites for the development of any useful ML algorithm, related to the amount and quality of available data. Typically, we need hundreds or thousands of data entries to lay out the problem in an unbiased and representative way, and it can be challenging to comply with these characteristics at the same time, especially in the context of scientific research.[199]

First, the amount of data for ML is often limited. On the one hand, for simulated data it may be unreasonable to use months of supercomputer time to obtain a comprehensive dataset. On the other hand, if a single simulation run is relatively cheap, other methods can often be beneficial, e.g., the parameter sweep or stochastic optimization. This way, we can investigate a class of problems which is too expensive computationally to be solved completely at the moment; however, it may be feasible to obtain some minimal dataset which is nevertheless large enough to apply ML algorithms to get partial solution.
As for experimental data, the amount of data entries needed to train ML algorithms means that we need to fabricate many samples. These should be different enough to be considered as individual data entries, and they should be supported with enough information about their fabrication and the resulting properties. Consequently, fabrication and characterization of a single sample should be relatively inexpensive, which limits the number of problems suitable for ML based on experimental data. Alternatively, obtaining the dataset could be done as part of some other research activity where ML complements a more traditional approach.

As for the next dataset requirement, it can be hard to specify the bias and to find it out whether the dataset bias is harmful or not. Moreover, as soon as our knowledge about the research object is incomplete, thus any data is biased to the domain of existing knowledge. Usually, we obtain a dataset with some method known in advance, and we focus on some known properties. This way, ML algorithms trained on this type of data are bounded to the existing knowledge. However, it still makes sense to train ML algorithms on such data, as soon as it can provide some insights about nontrivial relations between components of a known system, missed by traditional approaches.

For example, it was shown in Çağla Odabaşı and Yıldırım\(^{200}\) that high (>18%) power conversion efficiency is often related with the usage of mixed cation perovskite materials. However, if we try to perform the same type of analysis in the past, before any data on usage of mixed cation perovskite materials become available, the used ML algorithm will fail to predict any correlations due to the bias to the domain of existing knowledge, and there was just no data to come to any conclusions about the usage of such materials. Even worse, ML predictions based on biased data can lead to wrong interpretation of the analysis result. For example, it might be possible that there are several results related to some promising technology; however, due to its infant stage of development, it does not show results good enough to be favorably compared against some mature alternatives. So, if we perform a similar to Çağla Odabaşı and Yıldırım\(^{200}\) association rule mining ML analysis based on this data, it will clearly show that this new technology leads to poor results. However, it only represents the current state of technology; association rule mining does not provide any forecast. As we know, due to technology progress, it sometimes happens that new technology provides a superior result and replaces the older one. Thus, to predict technology trends, we need some other algorithms.

The last mentioned requirement of dataset is representativity, which links the dataset variety with the problem statement. Typically, we can only sample a tiny fraction of the parameter space. Therefore, we have to provide some bias to our data in such a way that it will capture the essence of the phenomenon under investigation. Without such a bias in the dataset, the ML algorithm has to struggle against additional effects, which perturbs the dataset and veils the needed relations. Thus, we need biased and unbiased data at the same time, which is similar to the bias-variance dilemma.\(^{201}\)

As an example, the conclusions obtained with the ML algorithm in\(^{200}\) are only valid under specific conditions of academic research and thus do not consider properties that are important for mass production. Thus, if you are going to launch a factory to produce PSCs, there is no need to use a whole dataset. You might want to exclude from it the part which uses an expensive fabrication process or a process, which does not scale to mass production. This will bias the dataset to the market scope, and the same ML algorithm will provide you different insights into the problem.

ML turned out to be extremely fruitful in solving the problem of discovering perspective perovskite materials suitable for PSCs. A good coverage of this topic can be found in the review article by Tao et al.\(^{202}\) Dozens of research groups were able to obtain significant results in discovering perspective perovskite materials using a vast list of ML algorithms. Therefore, we would mostly attribute this success to the used training data set, while the overall result is relatively independent on the specific ML algorithm.

Recent advances in ML for PSCs improvement are covered in review articles\(^{203,204}\) and. The majority of presented results are related to new materials and their processing; however, several authors used ML to address the problem of overall PCS performance improvement. Among them, we would like to highlight the work by Le Corre et al.\(^{205}\) where the dataset for ML training was generated with large-scale drift-diffusion simulations. We believe that simulations of charge carriers drift-diffusion combined with optical simulations of complex nanophotonic designs can provide a dataset for ML algorithms, needed to design the next generation of PSCs.

6. Conclusions and Outlook

In conclusion, we have summarized basic approaches for PSCs improvement by various nanophotonic designs: from external structures to nanostructuring of active and transport layers. We point out to the importance of separate contributions from optical and electronic effects. The main physical effects emerged after PSC nanostructuring are equally related to both improved light and carrier management.

Once nanophotonics has demonstrated outstanding abilities to improve PSCs, we anticipate further progress in the following directions: novel designs based on low-loss materials, cheap large-scale approaches, advanced tandems with nanostructures, and wide machine learning implementation. We envision that multifunctional perovskite-based devices improved by nanophotonic structures will be of a high interest in the nearest future. For example, there are several additional functionalities which were demonstrated recently with photovoltaic devices: solar cells integrated with hydrogen photocatalytic generators,\(^{206}\) light-emitting solar cells,\(^{12}\) light-emitting photodetectors,\(^{207}\) light-emitting transistors,\(^{208}\) photobattery,\(^{209,210}\) and even photonic synapses.\(^{211,212}\) They combine photocharging (photovoltaic functionality), light-emission (LED functionality), energy storage (battery functionality), and light-induced ionic current (neuron functionality), and can be in tandem with other devices in such a way when some photons work for the semitransparent perovskite devices, while the other part of the spectral range drives additional functionality.

Acknowledgements

A.F., P.V., D.S. and K.L. contributed equally to this work. The work was supported by the Russian Science Foundation (Project 19-73-30023).
Conflict of Interest

The authors declare no conflict of interest.

Keywords

charge carrier improvement, light management, machine learning, nanophotonics, perovskite solar cells

Received: October 28, 2021
Revised: April 16, 2022
Published online: May 18, 2022
Aleksandra Furasova is a junior researcher in the Laboratory of Hybrid Nanophotonics and Optoelectronics at the ITMO University. She received her double Ph.D. degree in physics at the ITMO University (St. Petersburg, Russia) and Tor Vergata University (Rome, Italy). Her research interests include perovskite nanostructures, optoelectronic device preparation and improvement as well as dielectric nanomaterials synthesis.

Aldo Di Carlo is head of the Institute for Structure of the Matter of the Italian National Research Council (CNR-ISM) and full professor at the University of Rome “Tor Vergata” (Italy). He founded the Centre for Hybrid and Organic Solar Energy (CHOSE) that involves more than 40 researchers for the development and industrialization of the organic and hybrid organic/inorganic photovoltaic technologies. Di Carlo is author/coauthor of more than 500 scientific publications on international journals, 13 patents, and several book chapters.

Sergey Makarov is a professor, dean of Faculty of Photonics at ITMO University, chief research associate, head of the Laboratory of Hybrid Nanophotonics and Optoelectronics, and director of ITMO Core Facility Center “Nanotechnologies.” His research interests include nanophotonics and optoelectronic devices based on halide perovskites.