Review

Waseem Raja, Michele De Bastiani, Thomas G. Allen, Erkan Aydin, Arsalan Razzaq, Atteq ur Rehman, Esma Ugur, Aslihan Babayigit, Anand S. Subbiah, Furkan H. Isikgor and Stefaan De Wolf*

Photon recycling in perovskite solar cells and its impact on device design

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Abstract: Metal halide perovskites have emerged in recent years as promising photovoltaic materials due to their excellent optical and electrical properties, enabling perovskite solar cells (PSCs) with certified power conversion efficiencies (PCEs) greater than 25%. Provided radiative recombination is the dominant recombination mechanism, photon recycling – the process of reabsorption (and re-emission) of photons that result from radiative recombination – can be utilized to further enhance the PCE toward the Shockley–Queisser (S-Q) theoretical limit. Geometrical optics can be exploited for the intentional trapping of such re-emitted photons within the device, to enhance the PCE. However, this scheme reaches its fundamental diffraction limits at the submicron scale. Therefore, introducing photonic nanostructures offer attractive solutions to manipulate and trap light at the nanoscale via light coupling into guided modes, as well as localized surface plasmon and surface plasmon polariton modes. This review focuses on light-trapping schemes for efficient photon recycling in PSCs. First, we summarize the working principles of photon recycling, which is followed by a review of essential requirements to make this process efficient. We then survey photon recycling in state-of-the-art PSCs and propose design strategies to invoke light-

trapping to effectively exploit photon recycling in PSCs. Finally, we formulate a future outlook and discuss new research directions in the context of photon recycling.

Keywords: light-trapping; perovskites; photon recycling; photovoltaics; solar cells.

1 Introduction

Perovskite solar cells (PSCs) have become a leading technology in the photovoltaic (PV) research community owing to the remarkable optical and electrical properties of metal halide perovskites such as a large absorption coefficient, sharp absorption edge, long carrier diffusion lengths, as well as tunable bandgap [1–3]. Owing to these favorable optoelectronic properties, the power conversion efficiency (PCE) of lab-scale PSCs has exceeded 25%, approaching the record PCE for crystalline silicon (c-Si) solar cells, currently at 26.7% [4, 5]. Notably, after c-Si and gallium arsenide (GaAs), metal halide perovskites are only the third PV material class to obtain a PCE over 25%, and the first polycrystalline thin-film material to reach this milestone (albeit on a smaller active area). Nevertheless, in addition to overcoming challenges in scaling up this technology and demonstrating the stability required for market adoption, further improvements in the PCE of PSCs are required to bring its projected levelized cost of electricity generation (LCOE) to a competitive level [6]. Besides continuous device optimizations, unlocking the potential of photon recycling is one possible path to improve the PSCs' performance. Optical device design, aimed at exploiting the photon recycling phenomenon, has been crucial for GaAs solar cells to bring their PCE to 29.1%, which is the current record for single-junction solar cells [7–9], thanks to a significant enhancement in open-circuit voltage (V_{oc}) [5, 10, 11].

Photon recycling is the physical process that occurs in semiconductors when photons emitted via radiative recombination are reabsorbed by the semiconductor itself, possibly in a repeated process. This event is most efficient

*Corresponding author: **Stefaan De Wolf**, King Abdullah University of Science and Technology (KAUST), KAUST Solar Center (KSC), Physical Sciences and Engineering Division (PSE), Thuwal, 23955-6900, Kingdom of Saudi Arabia, E-mail: stefaan.dewolf@kaust.edu.sa.
<https://orcid.org/0000-0003-1619-9061>

Waseem Raja, Michele De Bastiani, Thomas G. Allen, Erkan Aydin, Arsalan Razzaq, Atteq ur Rehman, Esma Ugur, Aslihan Babayigit, Anand S. Subbiah and Furkan H. Isikgor, King Abdullah University of Science and Technology (KAUST), KAUST Solar Center (KSC), Physical Sciences and Engineering Division (PSE), Thuwal, 23955-6900, Kingdom of Saudi Arabia. <https://orcid.org/0000-0002-3121-7355> (W. Raja)

in highly luminescent materials such as GaAs, resulting in an effective increase in quasi-Fermi level splitting ($\Delta\mu$) within the material, and hence a possible increase in the V_{OC} of the device. Although there are essential differences in the structural properties of GaAs and lead halide perovskites, PSC research can benefit from the recent progress in GaAs solar cells and apply that understanding to further improve device performance.

To observe significant effects of photon recycling, a thin-film absorber material must (i) display a high photoluminescence quantum efficiency (PLQE), implying that radiative recombination is the dominant recombination process (compared to Shockley–Read–Hall (SRH) and Auger recombination), thereby favoring materials with low defect densities and a high absorption coefficient; (ii) manifest a minimum Stokes shift, i.e. the energetic difference between the maximum position of absorption and emission spectra should be small (~ 4 meV), [12–14]; and (iii) efficient light management [15–17]. Light-management strategies for conventional solar cells, such as crystalline silicon (c-Si), are usually aimed at enhancing the absorption of external photons due to silicon's relatively low absorption coefficient, resulting from its indirect bandgap. In the c-Si case, relatively thick wafers (>100 μm) are used, yielding increased light absorption in the wafer [18]. In addition, by texturing the c-Si front surface (often also its rear), using a (random) micron-sized pyramid structure [19, 20] with a typical feature size of few microns, combined with dielectric surface coatings, one can decrease the reflectivity and also randomize the light propagation directions inside the c-Si solar cell. This increases the optical path length inside the active material and substantially enhances the absorption of photons with energies close to the c-Si bandgap. Geometrical or ray optics is used to study light propagation in this type of solar cell. However, this strategy is not suitable for thin-film solar cells, where the absorber thickness is usually comparable to or even smaller than the wavelength of the incident light [21]. Thin-film solar cells, therefore, can benefit from photonic structures on the wavelength scale, such as diffraction gratings [22], plasmonic structures [23], and nanoscale structured surfaces [24] for light-trapping.

Light propagation within such nanoscale devices is explained by wave optics rather than ray optics. In particular, wave optics explain phenomena such as waveguiding (light propagation in a specific direction), diffraction, and plasmonic effects, which cannot be accomplished through ray optics. Another advantage of employing nanoscale features in devices is the possibility

to tune the feature geometry to reduce the dependence of light absorption to the incident angle of incoming light [25]. Therefore, nano-photonic structures may be considered as an effective means to enhance light-trapping in the sub-wavelength regime via spatially trapped resonant optical modes [26–28], and can aid in exploiting photon recycling to enhance device performance.

In this article, we review the current progress in photon recycling in PSCs. First, we describe the general working principle of photon recycling, followed by its impact on the PCE. We also discuss the primary requirements for efficient photon recycling, with a focus on photon management in PSCs. We then review the recent literature related to photon recycling in PSCs and go on to analyze various light-trapping strategies and device architectures that could yield efficient photon recycling in PSCs. We conclude by providing an outlook and suggesting future research directions.

2 Theory of photon recycling

In an ideal semiconductor (i.e., one where recombination only occurs radiatively) under thermal equilibrium and steady-state illumination conditions, a detailed balance exists between photon absorption (resulting in electron-hole generation) and radiative emission (due to band-to-band recombination). Inside the semiconductor, depending on its absorption properties, emitted photons can potentially be reabsorbed and re-emitted. This iterative reabsorption/re-emission process is known as photon recycling [29, 30] and is sketched in Figure 1. Photons will continue repeating the internal reabsorption/re-emission events until they are internally re-emitted at an angle within the semiconductor's escape cone (i.e., a reduced solid angle determined by the refractive index difference between the absorber and its surroundings), resulting in their outcoupling without further recycling [32]. In this way, photon recycling enhances the effective density of charge carriers within the absorber layer, resulting in a larger $\Delta\mu$ within the absorber. In a solar cell featuring external contacts, this increases the V_{OC} , and hence the PCE [11, 14, 32, 33].

On thermodynamic grounds, Smestad et al. [34] estimated the concentration ratio C , quantifying the increase in the number of incident photons when a light concentrator system is employed. By analogy, a solar cell employing light-trapping features essentially also behaves as a concentrator system, where the voltage gain corresponding to an increased photon absorption can be expressed as function of the concentration ratio C [35]:

Figure 1: Schematic design of photon recycling under thermal equilibrium in a semiconductor slab. Following radiative recombination, photon recycling may occur due to direct reabsorption or photons emitted outside the escape cone due to total internal reflection (TIR). Re-emitted photons may lie within the escape cone leaving the slab without further recycling. Re-emitted photons could also be absorbed parasitically into another layer without generating any electron-hole pair. Figure 1 is adapted from Ref. [31].

$$\Delta V = \left(\frac{k_B T}{q} \right) \ln(C) \quad (1)$$

In this, k_B , T , and q , are the Boltzmann constant, absolute temperature, and elementary charge respectively. Hence, using Eq. (1), the net enhancement in V_{OC} by photon recycling (ΔV_{oc}^{PR}) is expressed by the equation [12, 36]:

$$\Delta V_{oc}^{PR} = \left(\frac{k_B T}{q} \right) \ln(4n^2) \quad (2)$$

In this, n is the refractive index of the absorber. Here, it is assumed that the device is optically thin and features Lambertian light-trapping, no external reflection losses, and a perfect back mirror. In such a case radiative recombination is the only energy loss mechanism. Under these assumptions the maximum path length enhancement of light is $4n^2$ [37], which is known as the Yablonovitch limit. Assuming a refractive index of 2.6 near the lead-halide perovskite band edge [38], this implies that a ΔV_{oc}^{PR} of 83 mV may be obtained, with perfect photon recycling of internally re-emitted photons. These calculations indicate that photon recycling may be a strategy to further enhance the V_{OC} of PSCs. However, the $4n^2$ limit can be further increased by utilizing advanced light-trapping structures which can alter the acceptance angle and exploit photon recycling, as discussed in Section 5 below.

3 Key requirements for efficient photon recycling

As mentioned above, there are three essential requirements to be implemented to achieve efficient photon recycling in thin-film direct-bandgap semiconductors: i) a

high radiative emission yield; ii) high reabsorption (i.e., a minimum Stokes shift); and iii) efficient light management. Here, we briefly investigate each of these requirements in more detail within the context of PSCs.

3.1 Radiative emission yield

The primary necessity for efficient photon recycling is a high radiative emission yield. This implies that photo-generated carriers recombine radiatively rather than via competing SRH or Auger recombination processes. A high radiative emission implies that noncollected electron-hole pairs predominantly recombine radiatively, potentially setting off reabsorption/re-emission cycles. The total charge-carrier recombination in a perovskite layer under open-circuit conditions is quantified by the general rate equation [39]:

$$\frac{dn_c}{dt} = G_{ph} - k_1 n_c - k_2 n_c^2 - k_3 n_c^3 = G_{ph} - nR_T(n_c) \quad (3)$$

In this, G_{ph} is the carrier generation rate by absorbed photons, k_1 , k_2 and k_3 are rate constants associated with SRH recombination, band-to-band radiative recombination, and Auger recombination, respectively, and R_T is the total charge recombination rate; n_c is the charge carrier density.

SRH recombination refers to nonradiative recombination caused by defect states which can be present in both the bulk and at the surfaces. Here, we consider the k_1 factor to be associated with bulk SRH recombination [Figure 2(a)]. Bresnes et al. [32] showed from device simulations that perovskite films need to have a k_1 value lower than $1 \times 10^4 \text{ s}^{-1}$ to truly benefit from photon recycling to increase the V_{OC} and thus PCE on the device level, as shown in

Figure 2: (a) Schematic diagram of nonradiative recombination (bulk and interfaces) in PSCs. Simulated current density-voltage (J - V) curve of PSCs of 1.6 eV bandgap, including and excluding photon recycling (PR) for SRH recombination constants (b) $k_1 = 1 \times 10^4 \text{ s}^{-1}$, (c) $k_1 = 2 \times 10^5 \text{ s}^{-1}$ and (d) $k_1 = 3 \times 10^6 \text{ s}^{-1}$. (e) Efficiency (η) and (f) V_{OC} as function of SRH carrier lifetime τ_{SRH} (s) with and without photon recycling for perfectly passivated PSCs. (g) and (h) panels show the same results as (e) and (f) but include the effect of surface recombination ($S > 0 \text{ cm s}^{-1}$) with and without photon recycling in PSCs. Here, the authors in their calculation assumed that $S_1 = S_2$ at each interface. (i) Schematic depiction of defects at the surface and bulk of perovskite and the various passivation strategies using functional groups. Figure (b)–(d) are adapted with permission from Ref. [32], Figure (e)–(h) are taken with permission from Ref. [40] and Figure (i) is adapted from Ref. [41].

Figure 2(b). If k_1 increases, the presence of photon recycling starts to diminish and becomes insignificant upon reaching the value of $3 \times 10^6 \text{ s}^{-1}$, as depicted in Figure 2(b)–(d). Furthermore, Bresnes et al. [32] also demonstrated the sensitivity of k_2 on photon recycling, indicating that a value of $k_2 = 9.2 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$, as measured in state-of-the-art PSCs devices, may be sufficient [42]. Auger recombination is also associated with nonradiative recombination, however it does not play a significant role in PSCs since it is only significant at extremely high carrier injection levels ($>10^{18} \text{ cm}^{-3}$) while being negligible at 1-sun equivalent carrier densities [43]. We note that k_1 can be engineered by defect passivation strategies [44] whereas k_2 and k_3 are intrinsic material properties. Simulation results revealed that photon recycling only becomes significant if the SRH lifetime, τ_{SRH} , is more than 300 ns which is the typical

transient photoluminescence lifetime value of perovskite films on glass [40]. Here, the model was assuming perfectly passivated interfaces (expressed by the surface recombination velocity, $S = 0$) and used the bulk lifetime as the main parameter (Figure 2(e) and (f)). For lower values of τ_{SRH} , photon recycling is hardly present and does not influence the V_{OC} of the device.

In realistic devices surface recombination is likely to occur, which – as stated – is predominately caused by SRH processes [40]. Figure 2(g) and (h) shows the effect on V_{OC} and PCE as function of the bulk lifetime (τ_{bulk} , denoted as τ_{SRH} in the figure taken from Ref. [40]), and the impact of S on photon recycling. We can see that above $S = 10^2 \text{ cm s}^{-1}$, the V_{OC} and PCE considerably decrease, even with high values for τ_{bulk} , illustrating that both bulk and surface passivation of metal halide perovskite defects play a

crucial role for enhancing photon recycling and thus, considerably impacts the efficiency potential of PSCs. The surface recombination velocity S influences the effective lifetime τ_{eff} which is also influenced by τ_{bulk} (combining the effects of SRH, radiative, and Auger recombination), the diffusion coefficient D and the film thickness W , as:

$$\frac{1}{\tau_{\text{eff}}} = \frac{1}{\tau_{\text{bulk}}} + \frac{2}{\frac{W}{2S} + \frac{1}{D} \left(\frac{W}{\pi} \right)^2} \quad (4)$$

It should be noted that, under low excitation intensity, τ_{bulk} for lead halide perovskites is primarily determined by τ_{SRH} , due to bulk and grain boundary defects [45]. To increase τ_{eff} , the surface recombination velocity should be decreased and the τ_{SRH} of perovskite films should be increased. To achieve this, several passivation strategies have been reported [44], as summarized in the sketch in Figure 2(i). After implementing these passivation strategies, contemporary state-of-the-art PSCs exhibit experimental values of k_1 between 1×10^5 – $1 \times 10^7 \text{ s}^{-1}$ with a trap density of 10^{15} – 10^{17} cm^{-3} [12, 39, 46]. Comparing these values with those mentioned earlier suggests that a further reduction of nonradiative recombination losses is required to reduce k_1 in order to observe a substantive impact of photon recycling in PSCs. In the context of surface passivation, Yang et al. [45] reported a value of $S \sim 10^2 \text{ cm s}^{-1}$ for polycrystalline halide perovskite films coated with polymethylmethacrylate (PMMA). Moreover, Staub et al. [33] demonstrated the utility of combining time-resolved photoluminescence (TRPL) measurements with analytical models to determine values for S . For materials with high purity and good surface passivation, the estimated S values are in the order of $\sim 10 \text{ cm s}^{-1}$ for typically observed perovskite TRPL lifetimes (few hundred nanoseconds). Meanwhile, Krogmeier et al. [47] obtained $S \approx 200 \text{ cm s}^{-1}$ for the interface between the halide perovskite film and PCBM. Recently, Wang et al. [48] determined S values in the range of 10^{-1} – 10^4 cm s^{-1} using TRPL for various electron/hole transport and polycrystalline halide perovskite interfaces, values that may be suitable to enable photon recycling, if combined with sufficiently high τ_{bulk} values.

In the context of devices, the requisite high radiative yield for effective photon recycling can be expressed by the need for high internal (Q_i) and external (Q_e) photoluminescence quantum efficiencies [35, 36, 49], determined at open-circuit conditions. Q_e is the ratio of the emitted photons per absorbed photons in the material, whereas Q_i is the ratio of the radiative recombination rate to the device's total (radiative and nonradiative) recombination rate [50]. Q_e is an important parameter affecting the V_{OC} and thus PCE. If $Q_e = 1$, the V_{OC} is equal to the radiative

open-circuit voltage ($V_{\text{OC, rad}}$). The total recombination current (expressing the loss in charge carriers per unit time via radiative and nonradiative processes) increases in case of any additional nonradiative recombination, reducing the V_{OC} and Q_e [40]. Similarly, failure to achieve a high Q_i is an indicator for high nonradiative recombination losses [36]. To estimate the influence of radiative and non-radiative recombination on device performance, Q_e and Q_i values should be known. Simulations by Kirchartz et al. [51], revealed that both a high Q_e and Q_i are critical parameters in the context of photon recycling and therefore the V_{OC} of the device. The relationship between Q_i and Q_e can be expressed using the following equation [51]:

$$Q_e = \frac{p_e Q_i}{1 - p_r Q_i} \quad (5)$$

Here, p_e stands for the probability of emission or out-coupling of photons, $p_r = 1 - p_e - p_a$ is the reabsorption probability in the perovskite, and p_a is the probability of parasitic absorption, most prominently via free-carrier absorption within the contact layers of the device. Given that in the case of photon recycling, photons may undergo multiple reabsorption and re-emission events within the absorber and may bounce back and forth many times within a thin-film solar cell, the optical design must play a vital role in curtailing parasitic absorption [52]. Figure 3 clearly shows how Q_e depends on Q_i and p_a , assuming $p_e = 12.7\%$ for flat PSCs [55]. From Eq. (5), it is clear that Q_e increases with the higher $p_r Q_i$ and thus increased photon recycling. Conversely, an increase in p_a results in a substantial decrease in Q_e , as shown in Figure 3(a). A reduced Q_i directly lowers Q_e and hence the $\Delta V_{\text{oc}}^{\text{PR}}$ as depicted in Figure 3(b). Q_i can be calculated with the help of the experimentally given Q_e , through rearranging Eq. (5) and assuming that there is no parasitic absorption ($p_a = 0$) [56]:

$$Q_i = \frac{Q_e}{p_e + p_r Q_e} \xrightarrow{p_a=0} \frac{Q_e}{p_e + (1 - p_e) Q_e} \quad (6)$$

As introduced by Abebe et al. [31], a significant enhancement in photon recycling only occurs for very high Q_i and p_r as per the following equation:

$$\Delta V_{\text{oc}}^{\text{PR}} = \frac{kT}{q} \ln \frac{1}{1 - p_r Q_i} \quad (7)$$

Hence, based on Eqs. (6) and (7), specific knowledge of p_e is required to define Q_i and thus minimize the non-radiative recombination in PSCs and evaluate the potential for ($\Delta V_{\text{oc}}^{\text{PR}}$) in PSCs. Moreover, Figure 3(d) displays the increase in photon recycling ($\Delta V_{\text{oc}}^{\text{PR}}$) over Q_i for various p_r . For low $Q_i \lesssim 40\%$, $\Delta V_{\text{oc}}^{\text{PR}}$ is low and similar for all p_r , while for

Figure 3: Simulation results illustrating the importance of Q_i and parasitic absorption probability (p_a) for (a) Q_e and (b) ΔV_{oc}^{PR} of PSCs.

Calculations are based on Eq. (5) with $p_e = 12.7\%$, associated with the flat PSCs. (c) Relationship between Q_i and Q_e for various photon escape probabilities (p_e) and assuming no parasitic absorption $p_r = 1 - p_e - p_a \xrightarrow{p_a=0} = 1 - p_e$ losses. Dotted line with $Q_e \sim 50\%$ (highest reported value for perovskite films [53, 54]) and Q_i of 80% corresponds to $p_e \sim 24\%$. This analysis shows the importance of p_e to achieve the Q_i value that is derived from the experimentally determined Q_e value. (d) Relationship between Q_i and ΔV_{oc}^{PR} for various photon reabsorption probabilities p_r .

higher Q_i , the value of ΔV_{oc}^{PR} more sensitively depends on p_r . Hence, the above calculation demonstrates the dependence of Q_i on Q_e and also highlights the importance of accurately determining p_e . In recent reports, p_e values are reported between ~ 5 and 13% for planar perovskites films [31, 36, 49, 52, 56]. Employing such values in Eq. (7), the noticeable value of $\Delta V_{oc}^{PR} = 30$ mV can be achieved for $Q_i \sim 90\%$ ($Q_e \sim 40\text{--}50\%$) in PSCs as shown in Figure 3(c) and (d). The recent advancements in passivation strategies for perovskite absorbers enable lower nonradiative recombination and defect densities, allowing for internal Q_i values above 90% [57]. These results underline the promise for realizing photon recycling in practical applications.

3.2 High reabsorption: minimum Stokes shift

Improving only the radiative emission yield is insufficient to observe photon recycling. The increase in ΔV_{oc}^{PR} is only obtained by reabsorbing internally emitted photons, resulting in an increased carrier concentration within the absorber. If the emitted photon energy is smaller than the perovskite bandgap, or, more specifically, is emitted at a

photon energy that corresponds to a negligible absorption coefficient, the emitted photon is unlikely to be reabsorbed. Hence, to enable photon recycling, understanding the reabsorption mechanism is as essential as increasing the radiative emission yield.

The Stokes shift is a useful figure of merit to estimate the influence of reabsorption on photon recycling, and is defined as the energy difference between the maximum positions of the emission and absorption spectra as sketched in Figure 4(a) [12]. To effectively reabsorb the re-emitted photons (a necessary condition for photon recycling), the Stokes shift must be minimal. In other words, a significant overlap between the absorption/emission spectra is essential for the reabsorption mechanism to occur [59]. Lee et al. [12] demonstrated that ΔV_{oc}^{PR} decreases exponentially with increasing Stokes shift, as shown in Figure 4(b). In Table 1, we summarize the reported Stokes shift in GaAs and perovskites. For GaAs, the Stokes shift is quite small (4 meV) compared to perovskites. A small Stokes shift implies that the bandgap of the absorber is direct. In addition, Wong et al. [60] demonstrated that the smaller the Urbach energy (γ) of a semiconductor, the smaller the Stokes shift, where the Urbach energy is extracted from the logarithmic slope of the absorption

Figure 4: (a) Schematic diagram representing emission, absorption, reabsorption spectra, and Stokes shift (ΔE_{stokes}). The overlap is essential between emission and absorption spectra as it increases the reabsorption and consequently enhances the $\Delta V_{\text{OC}}^{\text{PR}}$. (b) Calculated $\Delta V_{\text{OC}}^{\text{PR}}$ as a function of (ΔE_{stokes}) in perovskite films. The table shows the Stokes shift in GaAs and perovskites, as reported in the literature. (c) Effects of Urbach energy (γ) on absorption and emission (photoluminescence) spectrum; Normalized photoluminescence (PL, dashed line), absorbance (Abs, solid line) spectrum and distribution of band gaps (dotted line) of solar cell with increasing γ . (d) Schematic diagram of density of states (DOS) with excitation and recombination of carrier. Figure (a)–(b) are derived from Ref. [12] and Figure (c)–(d) are taken with permission from Ref. [60].

Table 1: Reported values of Stokes shift.

Materials	Calculated Stokes Shift in meV
GaAs	4.0 [58]
MAPbI ₃	89.41 [12]
CsPbBr ₃	42.0 [59]

coefficient below the band edge and is indicative of the material's static and dynamic disorder. In the case of $\gamma < kT$, the absorption and emission spectra are overlapping and this leads to a minimal Stokes shift. However, in the case of $\gamma > kT$, the emission spectra are notably broadened and move away from the absorption band edge, resulting in a larger Stokes shift as shown in Figure 4(c). With the

presence of deeper, yet nonlocalized bandedge states, radiative recombination of electrons and holes populating these deeper states results in a redshifted emission of photons with energies below the absorption band edge [Figure 4(d)].

Practically, at room temperature, γ is about 15 meV for lead-halide perovskites, compared with GaAs = 7 meV [61], which likely explains also the difference in Stokes shift for these materials. It is of note that the Urbach energy scales with temperature [62]. Therefore, with increasing temperature the Stokes shift will also increase, likely impairing photon recycling. This further underlines the importance of addressing parasitic heating of solar cells; the hotter the devices, the less photon recycling will be present, due to the increased Urbach energy [63]. Overall, γ can be used as

be metric for the material's high structural quality, with small values leading to a smaller Stokes shift [61]. We note that different perovskite compositions and the use of various additives may be explored to improve the material's quality, expressed through γ and ΔE_{Stokes} , which may aid in enhancing photon recycling in these materials.

3.3 Efficient light management

Apart from radiative emission and reabsorption, light management also plays an essential role in thin-film solar

cells for effective photon recycling. Figure 5(a), shows the optically ideal structure for photon recycling which minimizes the escape-cone angle from the front side of the cell and increases the photon concentration by perfectly internally reflecting all the emitted photons that reach the rear side of the device. In particular, following Snell's law, the large refractive index contrast between the absorber and free space leads to a narrow escape cone angle [64]. To analyze the impact of optical design on photon recycling in PSCs, Abebe et al. [31] discussed three types of light interaction with semiconductors [Figure 5]. The first possible light interaction is perfect incoupling of light (ideal case of

Figure 5: (a) Schematic diagram of optically ideal solar cell structure for efficient photon recycling with no optical loss (No reflection from the front side and perfectly reflected from the back side). Photons are trapped due to the narrower escape-cone angle and reabsorbed and re-emitted within the active layer. Moreover, when the escape-cone angle is narrower than the emission angle, the emitted photons will be reflected from the cell's front surface. (b) Schematic representation of layer stack [ITO(150 nm)/TiO₂(20 nm)/CH₃NH₃PbI₃(300 nm)/Spiro-OmeTAD(250 nm)/Au(60 nm)] of PSCs considered in the photon recycling calculation by Abebe et al. [31]. θ_{in} is the incident angle of incoming light and θ_{out} is the angle relative to the surface normal i.e., defined as the escape-cone angle. (c) Schematic illustration of perfect incoupling of incoming light and a perfect back reflector with no light-trapping. The absorbance is calculated through Beer-Lambert law which assumes zero front reflection. (d) Schematic depiction of a planar stack of PSC for which the absorption is calculated using the transfer matrix method (TMM). (e) Schematic design of front side Lambertian scatterer to consider optimum light-trapping in solar cell. (f) Absorption spectrum of PSCs with a Lambertian front texturing, perfect ARC (Beer-Lambert Law) and planar stack of PSCs. (g) Calculated V_{OC} and (h) $\Delta V_{\text{OC}}^{\text{PR}}$ as function of Q_i for Beer-Lambert, or wave optics, or Lambertian light-trapping angle-independent absorption response of PSC for $\theta_{\text{out}} = 90^\circ$. All plots are plotted for cases with and without parasitic absorption in other layers of PSCs. (i) Calculated $\Delta V_{\text{OC}}^{\text{PR}}$ as function of parasitic absorption probability (p_a) in supporting layers of PSCs at $Q_i = 1.0$ and for various escape cone angles (θ_{out}). Figure (f)–(i) are taken with permission from Ref. [31].

a perfect antireflective coating, ARC), where the absorption response is based on the Beer–Lambert law but without considering light-trapping effects [Figure 5(c)]. A second interaction is light propagation in a multilayer medium where constructive and destructive interference effects occur. The interference effect is produced only if each layer's (optical) thickness in the thin-film stack is on the order of the wavelength of light. In general, the transfer matrix method (TMM) is used to model such structures. The TMM relies on wave optics, in which a matrix represents the propagation of the electromagnetic field (light) through each layer of the device. The matrices associated with each layer are multiplied together to achieve a global matrix and is used to calculate the electromagnetic field on each side of the layer that allows to calculate reflection and transmission coefficients [65]. Essentially, with the TMM, the absorptance of a planar experimental solar cell device can be calculated [Figure 5(b) and (d)].

Thirdly, light may interact at the interface in which a Lambertian light-trapping structure is implemented, as shown in Figure 5(e). Here, the frontside-textured surface is considered to allow complete randomization of the direction of transmitted light and results in an absorptance enhancement by a factor up to the Yablonovitch limit, assuming the absorption in the active layer is weak. The absorption spectra were calculated with thickness $h = 300$ nm of the perovskite absorber at normal incidence.

To analyze the performance of these designs, Abebe et al. [31] derived an explicit expression to predict the ΔV_{oc}^{PR} . They also derived an expression to describe the dependence of ΔV_{oc}^{PR} on Q_i , the probability of parasitic absorption of radiatively emitted photons (p_a), and the escape probability of emitted photons (p_e), respectively, as defined earlier. In particular, they calculated p_e without any angular restriction ($\theta_{out} = 90^\circ$, angle-independent) while comparing the impact of the various absorption responses on photon recycling in a solar cell.

The Lambertian response leads to a higher and ideal absorption response but results in a lower $V_{oc} = 1290$ mV at $Q_i = 1$ [Figure 5(e)], and ΔV_{oc}^{PR} [green plots in Figure 5(g) and (h)] compared to the Beer–Lambert and wave-optics response [red and blue plots in Figure 5(g) and (h)]. This relates to the high escape probability of the Lambertian scheme ($p_e = 17.8\%$) as compared to the Beer–Lambert ($p_e = 5.32\%$) and wave optics ($p_e = 3.32\%$) responses. The Lambertian response shows the highest p_e due to the lack of total internal reflection inherent for such an idealized front texture. Figure 5(g) and (h) show the V_{oc} of the PSC as a function of Q_i and the obtained maximum V_{oc} of 1317 and

1305 mV for the PSCs including charge-transport layers (wave optics) and Beer–Lambert cases at $Q_i = 1$, respectively. The Beer–Lambert response leads to a higher absorption compared to the wave-optics analysis but provides less V_{oc} and ΔV_{oc}^{PR} . Following this, the authors argued that the perfect incoupling of light through the Beer–Lambert response results in a larger escape probability of re-emitted photons compared to the wave-optics analysis and hence to a less ΔV_{oc}^{PR} as shown in Figure 5(h). Indeed, the wave-optics case results in a larger V_{oc} when $Q_i > 0.95$, where the photon recycling impact is sufficiently large. Moreover, they have calculated ΔV_{oc}^{PR} based on different escape-cone angles (θ_{out}) and found that at $\theta_{out} = 2.5^\circ$, one could reach $\Delta V_{oc}^{PR} = 240$ mV, as shown in Figure 5(i). The increase in ΔV_{oc}^{PR} is mainly due to re-emitted photons having a lower escape probability due to a smaller escape cone. Note that upon introducing parasitic absorption p_a , even though Q_i approaches unity, the increase in ΔV_{oc}^{PR} substantially reduces [Figure 5(h)]. This is because the parasitic absorption probability p_a profoundly affects the probability of reabsorption of photons within the perovskite. Furthermore, parasitic absorption's unfavorable influence on photon recycling is more obvious in the case of varying θ_{out} [Figure 5(i)]. Therefore, dedicated attention must be given to light management to minimize p_a to exploit photon recycling in PSCs.

In practical terms, rugate structures could establish a narrow θ_{out} angle over a broader wavelength range [66, 67]. This structure relies on dielectric coatings, such as a solar cell with an ARC (which simultaneously may act also as transparent electrode, depending on its electrical conductivity) with a refractive index equal to the geometric mean of that of its adjacent materials, i.e. glass ($n = 1.5$) and the absorber material (the optical thickness of the ARC then dictates the minimum of reflection via quarter-wavelength conditions). The refractive index of the ARC could also be made gradual, e.g. by $\text{SiO}_2/\text{TiO}_2$ codeposition [68, 69]. However, light-trapping strategies that involve narrowing θ_{out} , compared to Lambertian light-trapping concepts, come at the cost of reducing J_{sc} of the device due to the optical reciprocity principle.

These results show the importance of photon management in PSCs toward efficient photon recycling. In addition, the authors' theoretical analysis of photon management for photon recycling has assessed only planar PSCs while the optical treatment of nanostructure-based PSCs is yet to be reported. In particular, the analysis could be extended to perform a precise photon-recycling treatment in PSC designs that feature nanoparticles, nanowires, grating structures, or nanopatterned active layers.

In recent times, similar models were also demonstrated by Kirchartz et al. [49], who studied systems in the framework of ray optics. Furthermore, several groups have also investigated both randomly-textured and planar structures to quantify the impact of photon recycling for PSCs by using both simulations (ray-optics and statistical models) and experimental analyses [70–72]. Nevertheless, Abebe et al. [31] reported that conventional light-trapping structures that are based on Lambertian light scattering will not be applicable for efficient photon recycling in PSCs. For thin-film planar stacks and nanostructured solar cells, interference and light-matter interactions at the nanoscale need to be considered. Therefore, the PSC community should explore other light-trapping strategies for excellent light-trapping in PSCs. Some potential light-trapping structures are discussed in Section 5.

4 Photon recycling in PSCs

In 2016, Pazos-Outon et al. [73] reported one of the first demonstrations of photon recycling in lead iodide-based

PSCs by studying a thin film of perovskite (~ 100 nm) on a glass substrate and measuring the spatial distribution of photogenerated emission via confocal optical microscopy [Figure 6(a)] [73].

The authors observed a change in the normalized photoluminescence (PL) spectrum while increasing the separation distance between excitation and collection lenses that probe the perovskite film, as presented in Figure 6(b). At a separation distance greater than $5\text{ }\mu\text{m}$, the PL spectrum red-shifted beyond 800 nm , accompanied by a weaker peak close to the original emission at 765 nm , as shown in Figure 6(c). The authors attributed this shift to the guided re-emitted but nonabsorbed photons scattered out from the perovskite film. The authors also fabricated an interdigitated back contact (IBC) PSC with electron- and hole-transport layers. They observed the extraction of charge $>50\text{ }\mu\text{m}$ away from the contacts as exhibited in Figure 6(d), which arises from repeated photon recycling events.

Likewise, Dursun et al. [74] experimentally demonstrated photon recycling via two photon-excitation measurements on perovskite microwires. The team observed

Figure 6: Spatial-distribution mapping of emission and photoluminescence (PL) of a perovskite film deposited on a glass substrate.

(a) Schematic diagram of confocal optical microscopy setup to measure the spatial distribution of light emission from the film, with separately controlled excitation and collection objectives. (b) Normalized photoluminescence spectra against increasing separation between excitation and collection lenses on the perovskite film. (c) Comparative analysis of PL spectra with no separation ($0\text{ }\mu\text{m}$) and separation ($5\text{ }\mu\text{m}$) between excitation and collection lenses. (d) Photocurrent mapping at the edge of an interdigitated back-contact (IBC) perovskite solar cell. The electrode moves along the lateral direction of the film. (e) The left part of the schematic design shows the linear absorption measurements using white light in individual perovskite microwires. The right part of the schematic demonstrates the two-photon excitation measurement to measure PL spectra where excitation of light is done by an 800 nm laser source on the microwire while the collection point of PL is mapped along the bottom of the microwire's surface with a separation (s) more than $\sim 100\text{ }\mu\text{m}$. (f) PL spectrum as a function of s (0 – $125\text{ }\mu\text{m}$), showing an additional peak at lower energy along with the primary PL peak emission at 530 nm . Figure (a)–(d) and (e)–(f) are taken with permission from Refs. [73] and [74], respectively.

Figure 7: (a) Photograph of the image of multimetal back reflector substrate. (b) Schematic diagram of a perovskite film deposited on multimetal rear reflector for determining the internal quantum efficiency. (c) Cross-section of scanning electron microscopy (SEM) image of a perovskite/SiO_x/Au/Si sample. Measurement of internal and external luminescence efficiency of surface passivated perovskite film; (d) Spatial distribution map of optical loss factors ($L = 1 - \text{Reflectivity}$) within the quadrants (Pd, Au, Ti, Si) of the back substrate. Spatial distribution map of external luminescence quantum efficiency (η_{ext}) of (e) control and (f) TOPO-treated perovskite film deposited on the multimetal back reflector. Due to the passivated surface (TOPO treated), η_{ext} improves across the entire sample. (g), (h) η_{ext} as function of L for control and TOPO passivated film. The error bars depict 95% confidence intervals due to spatial heterogeneity, whereas the black lines are nonlinear regression fits. (The shaded regions represent 95% confidence intervals of the regression fits). We can see the advantage of the TOPO passivated film, η_{int} and η_{ext} reached a value of ~91.0 and ~36.4%, respectively. Figure (a)–(h) are taken with permission from Ref. [54].

that the PL spectrum leads to a red-shifted secondary emission peak accompanying the primary PL emission, as shown in Figure 6(e) and (f), a finding that became more apparent when the detector was further moved away from the excitation source. Similar behavior was also observed by Wang et al. [75] in perovskite nanowire arrays. Braly et al. [54] passivated polycrystalline perovskite ($\text{CH}_3\text{NH}_3\text{PbI}_3$) thin films by an electron-donating molecule *n*-trioctylphosphine oxide (TOPO) and utilized a multimetal back reflector substrate [Figure 7(a)–(f)] to experimentally evidence a Q_i of over 90% [Figure 7(g) and (h)]. These passivated perovskite films showed one of the highest $\Delta\mu$ of ~1.28 eV, approaching $97.1 \pm 0.7\%$ of the radiative limit, which is close to the best performing GaAs solar cells [13]. Since such a high Q_i implies

negligible nonradiative recombination, the authors predicted through simulation that the PCE values can be improved from 24.3 to 27.9%, which can be ascribed mainly to increases in $\Delta V_{\text{oc}}^{\text{PR}}$ (by 130 mV) and fill factor of the device.

With a similar approach, this time with superoxide ion ($\text{O}_2^{\bullet-}$) defect passivation, Brenes et al. [77] demonstrated $Q_i \sim 89\%$ and calculated a potential short-circuit current density (J_{sc}) and V_{oc} enhancement $\Delta V_{\text{oc}}^{\text{PR}}$ of 90 mV resulting in a predicted PCE increase of 1.4%.

In addition, Fassel et al. [76] developed a curve-fitting model to determine p_e accurately (and thereby Q_i) from the experimentally accessible Q_e spectrum of perovskite films, measured with the help of a confocal microscope. The PL spectra associated with photon recycling can be explained

Figure 8: (a) Schematic diagram showing the photoluminescence (PL) emission process from perovskite films. (A) Representation of the various radiative mechanisms (numbers) and PL emission paths (letters) in a perovskite film: (0) Initial source (laser) excitation; (1) isotropic internal radiative recombination (emission); (A) PL emitted within the escape cone ($\theta < \theta_c$) and collected for measurement; (2) Reabsorption and re-emission of photons, i.e. photon recycling; (B_i) and (C_i) are the PL emitted within the escape cone following (2) and at angles $\theta > \theta_c$ (photons trapped within the perovskite film by total internal reflections) and coupled out upon scattering (scattered PL). The change in the photon trajectory color from red to brown represents the increase in red-shift of PL in the perovskite film. In this analysis, it is assumed that there is a perfect back-reflector at the bottom. (b) Directly emitted internal PL spectrum (λ) (black) and absorption coefficient (λ) (gray) showing a small red-shift depends on the depth d_{ec} of the center of the emission within the perovskite film. (c) Redshift is observed in the scattered PL spectra with the increasing number of total internal reflections (j) with the entire propagation distance z . The progressive redshift in PL clearly shows the photon-recycle process in perovskite film. Figure (a)–(c) are taken with permission from Ref. [76].

by light propagation and scattering events, as shown in Figure 8(a). The authors claimed that the initially trapped photons are scattered out before being reabsorbed and re-emitted, giving rise to the red-shift in the PL spectra, indicative of photon recycling [Figure 8(b) and (c)]. Furthermore, the team pointed out that not considering the scattering events diminishes the p_e by more than 10% in absolute terms and hence overestimates the Q_i and underestimates the effect of photon recycling on the PCE of PSCs. A recent article by Wang et al. [78] introduced an analytical expression to define photon recycling in halide perovskite films. Their model has successfully quantified the increase in $\Delta\mu$ in the presence of photon recycling with a k_1 value as low as $7 \times 10^5 \text{ s}^{-1}$ in halide perovskite films. Their findings give insight into how $\Delta\mu$ depends on photon recycling, a requirement for PSCs' future developments.

Furthermore, Gan et al. [79] aimed to isolate the contributions of carrier diffusion and photon recycling to understand carrier dynamics and long-range transport in perovskite single-crystals [Figure 9(a) and (b)]. Although both mechanisms were observed to a certain extent, photon recycling seems to be the main effect responsible for the red-shifted emission and enabling long-distance transport of energy in both two-dimensional (2D) and three-dimensional (3D) halide perovskites. On similar grounds, Yamada et al. [80], showed the role of photon reabsorption and re-emission in PL spectra, using Bi^{3+} doped samples, where the Bi^{3+} ions act as a dopant resulting in a reduced photon-recycling effect. The exploitation of photon recycling may also be used to further enhance the performance of perovskite-based tandem solar cells [51, 81, 82]. Sheng et al. [83] proposed a

Figure 9: (a) Schematic representing photon recycling and carrier recycling as plausible pathways for long-range carrier dynamics in halide perovskites as discussed by Gan et al. [79], and (b) Schematic, illustrating the cleavage of MAPbBr₃ single crystals with PMMA interfaces for comparing carrier diffusion and photon recycling processes at the interfaces. PL and TRPL images of 3D MAPbBr₃ crystals before and after cleavage indicate photon recycling's central role in single crystals. Figure (a)–(b) are taken with permission from Ref. [79].

design strategy that involves integrating a low refractive index layer between the subcells of III/V tandem solar cells to trap the re-emitted photons and improve photon recycling. This strategy enabled increasing the V_{OC} and an enhancement in the overall PCE of the device. In a similar context, Steiner et al. [84] demonstrated enhanced photon recycling by implementing a low-index transparent epoxy to join the subcells of mechanically stacked multi-junction solar cells, fabricated on GaAs and InP substrates. In particular, a low-index transparent epoxy reflects a substantial portion of light toward the GaAs subcell while transmitting the rest of the sub-bandgap light.

The current literature studies imply the role of photon recycling and its impact on metal halide-based perovskite absorbers. A few reports based on simulations have gone further and investigated the potential for photon recycling to push the PCE of PSCs, and the extent of its contribution for high performing device requires further studies. More importantly, PSCs are nicely poised to exploit photon recycling with novel light-trapping strategies and which may be able to further increase their performance in the future.

5 Light-trapping for efficient photon recycling

The optical design of solar cells largely depends on the absorber layer's optical properties, particularly the real

and complex parts of the refractive indices. The real part directly relates to reflectance at interfaces which can be minimized by ARCs [51]. To effectively couple light into a macroscopically thick semiconductor, it may also be beneficial to use micron-scale texture, such as is the case of silicon solar cells. The refractive index contrasts at the interfaces also regulates the total internal reflection, by which the optical path length can be increased, and which holds relevance to exploit photon recycling in the case of thin-film direct-bandgap semiconductors such as lead halide perovskites. To exploit photon recycling, light-trapping should aim to keep the re-emitted photons inside the cell until they are finally reabsorbed, effectively resulting in an optical path enhancement (α_{ope}). This parameter can also be regarded as a simple metric to quantify the effectiveness of distinct light-trapping schemes [16]. Following, we discuss the three fundamentals light-trapping concepts that could be used to exploit photon recycling by maximizing the optical path enhancement of re-emitted photons.

5.1 Lambertian light-trapping

Lambertian light-trapping is based on the complete randomization of incoming light directions after entering the absorber. By definition, an ideal Lambertian scatterer works independently of the angle of incidence of incoming light [71] resulting in an upper limit of light path

enhancement to be $\alpha_{\text{ope}} = 4n^2$ for weakly absorbed light [37, 85] [Figure 5(e)], as defined above. For example, for silicon and lead halide perovskites, α_{ope} values of ≈ 50 and ≈ 21 are theoretically possible respectively.

However, the theoretical photon recycling models of Abebe et al. [31] and Kirchartz et al. [49] explained that Lambertian light trapping would undesirably improve light out-coupling (through optical reciprocity) and thereby actually reduce the amount of reabsorbed photons, and hence relatively reduce the carrier concentration and thus the V_{OC} of the device. Nevertheless, the optical benefits of Lambertian light-trapping via the increase in absorption and so J_{sc} outweigh these shortcomings. Consequently, a solar cell with a Lambertian light trapping [Figure 5(e)] structure can be of interest in those cases where the photon recycling effect is anyway relatively weak (e.g. when using an absorber with indirect bandgap or relatively large Stokes shift, possibly caused by high environmental temperatures).

5.2 Resonant light-trapping

Light-trapping structures that can achieve a larger redirection of path lengths are diffractive elements such as diffraction grating structures. A possible light path of emitted photons involving a diffraction grating in a solar

cell is shown in Figure 10(a). In principle, the grating structure, placed on the front side, diffracts the light into at least one diffraction order m ($\dots -2, -1, 1, 2, \dots$) other than the 0th order in the case where the grating period (d) is larger than the effective wavelength of light in the absorber (at normal incidence) [85]. The diffraction efficiency (the ratio between the diffracted and incident light intensity) is responsible for the amount of light energy going into a particular diffraction order m , which essentially relies on the grating structure's geometry [22, 85]. In particular, for gratings with a periodicity $d \leq \lambda_r$ (λ_r is the wavelength of re-emitted photons), internally emitted photons can couple into a particular diffraction mode in air i.e. the 0th or the principal diffraction order. As the refractive index of the absorbing medium is higher than air, re-emitted photons can couple to the available propagating diffraction modes in the absorber [86]. Hence, the re-emitted photons can couple to a higher number of propagating diffraction modes inside the absorbing medium, compared to only one diffraction mode in air. Therefore, such gratings can act as an efficient light-trapping scheme for photon recycling. However, as the number of allowed propagating diffraction orders in air increases with an increased grating period, so does the light out-coupling efficiency. Therefore, the grating design is critical for maximizing the V_{OC} improvement by photon recycling.

Figure 10: Schematic design of proposed light-trapping structure for photon recycling in PSCs.

(a) Grating coupler used as a light-trapping structure for trapping re-emitted photons through diffraction orders and waveguide modes. (b) Spherical nanoparticle array placed at the front side of the cell so that the re-emitted photons could be trapped through back scattering and waveguide modes. (c) Schematic design of angularly selective light-trapping concept. Incident light passes through the angularly selective optical filter and enters into the solar cell and randomized. In the schematic design, randomization is depicted through surface texturing (Lambertian scatterer). Re-emitted photons lying in an angle greater than the acceptance angle (θ_a) will be reflected back. (d) Double-array cone-like dielectric nanostructure, separated by an ideal reflector that facilitates re-emitted photon trapping and reabsorption within the active layer.

Peters et al. [87] derived the maximum optical path enhancement for a diffraction-based light-trapping structure to be $\alpha_{\text{ope}} = 893n$ [85]. In addition, Eq. (2), describing $\Delta V_{\text{oc}}^{\text{PR}}$ can be rewritten with the optical path enhancement of diffraction-based light structure and described as follows:

$$\Delta V_{\text{oc}}^{\text{PR}} = \left(\frac{k_B T}{q} \right) \ln(893n) \quad (8)$$

Assuming $n = 2.6$ near the perovskite band edge [38] implies $\alpha_{\text{ope}} \approx 2053$ for lead halide perovskites and that $\Delta V_{\text{oc}}^{\text{PR}}$ of 200 mV may be obtained, with perfect absorption of re-emitted photons. Thus, this approach constitutes a diffraction-based theoretical upper limit and emphasizes the higher potential to trap the re-emitted photons via diffraction gratings, compared to Lambertian trapping concepts, albeit at the cost of restricting the acceptance angle to normal incidence, which will come at the expense of the J_{sc} of the device.

In addition to diffraction gratings, in literature various other concepts are suggested based on resonant structures including dielectric [88–94] as well as metallic nanoparticle arrays for light-trapping, as shown in Figure 10(b). Utilizing metallic nanoparticles allows efficient light scattering via localized surface plasmon resonances that originate from collective oscillations of free electrons in a metal [95]. The surface plasmon resonance condition can be tuned by varying the particles' size, shape, and distribution. Although solar cell results based on plasmonic light-trapping have been reported by several research groups [96–100], the absolute PCE values are usually limited by dissipative losses, such as parasitic absorption within the metallic nanoparticle array [101]. Furthermore, parasitic absorption, i.e., photons that are absorbed within the material without resulting in collected charge carriers, can be detrimental for photon recycling. Recently, to overcome parasitic absorption and bring novel functionalities, dielectric Mie resonators can be used for photon recycling, where light can be confined via geometrical resonances [102]. However, the challenge when incorporating Mie resonators is to make their relatively narrowband resonances more broadband for covering the entire wavelength spectrum to overlap with the emission within the perovskite material's bandgap. Moreover, extensive optimization of the particle size, shape, and distribution is required to adjust the desired range of wavelength spectrum. 3D photonic crystal structures are also excellent candidates for photon recycling as they combine the properties of a grating and a mirror [67]. However, apart from the recent work of Chen et al. [103], little effort has yet been made toward using 3D photonic crystals combined PSCs, where

these challenge consists of implementing 3D photonic crystals with a photonic bandgap around the perovskite electronic bandgap.

5.3 Angular selective light-trapping

Another potentially useful light-trapping scheme consists of merging light scattering with an angularly selective optical filter [85, 104, 105]. The working principle of this concept is shown in Figure 10(c). Incoming light is allowed within the angular acceptance angle θ_a of the system. Once light enters the device, it scatters due to the surface's roughness, where isotropically scattered light is confined by total internal reflection. In particular, the scattered light is trapped in case of light incident on the optical filter with an angle larger than θ_a . This mechanism achieves $\alpha_{\text{ope}} = 4n^2/\sin\theta_a$ with a Lambertian-scatterer and an ideal mirror at the rear side of the cell. Inserting $\theta_a \sim 1^\circ$, a higher optical path enhancement can be realized; for silicon $\alpha_{\text{ope}} \approx 20,000$ and lead halide perovskites $\alpha_{\text{ope}} \approx 15,000$ is theoretically possible. In addition, Eq. (2) of $\Delta V_{\text{oc}}^{\text{PR}}$ can be rewritten with optical path enhancement of angularly limiting light-trapping structure as follows:

$$\Delta V_{\text{oc}}^{\text{PR}} = \left(\frac{k_B T}{q} \right) \ln \left(\frac{4n^2}{\sin\theta_a} \right) \quad (9)$$

Assuming a refractive index of 2.6 near the perovskite band edge [38], this implies that a $\Delta V_{\text{oc}}^{\text{PR}}$ of 240 mV may be obtained, with perfect absorption of re-emitted photons.

Angular selective light-trapping concepts restrict the escape cone angle, creating thereby a situation where the emitted photons are recycled back into the cell. Two components are required to accomplish such a system: a surface to induce a scattering mechanism and an appropriate angularly selective optical filter. Well-known possibilities to realize the first component includes the introduction of substrate roughness in the case of thin-film solar cells [106, 107] or front/backside texturing of a silicon solar cell [108, 109]. However, texturing the surface of perovskite films is not trivial [110, 111]. Since most perovskite films are deposited on glass superstrates, the best approach is to texture either the glass surface or the transparent conducting oxide (TCO) electrode or have a detached rear Lambertian reflector (like spectralon [112], or a textured Si wafer with a reflector for the relevant wavelengths on top). Recently, several works successfully explored the possibility to deposit solution-processed perovskite films on a textured TCO [113, 114]. Furthermore, vacuum-deposition approaches can also be utilized to deposit perovskite films on textured glass substrates [113]. In addition, solution-

processed perovskite films on textured silicon tandems have been successfully demonstrated, paving the way for applications on textured glass [110, 115, 116]. The challenges in realizing an angularly selective light-trapping structure lie in the second component, which is finding the appropriate optical element. Peters et al. [104] suggested that a Bragg-like filter or opal (3D photonic crystal) could be used as a suitable optical filter to restrict the angular confinement of light. However, as also noted above, reducing the acceptance angle comes at the cost of reducing the J_{sc} and hence reducing the PCE of the device. When the acceptance angle is restricted, the angles at which light can go out of the cell are also limited due to optical reciprocity. As such, this approach may be compatible with concentrated PV designs which inherently limit the incoming light to direct radiation. In these cases, combining moderate-angle restriction with moderate concentration can offer more flexibility in system design, enabling higher PCEs. Besides, this method needs a solar tracking system on to which the solar cell is installed so that light always comes within the same acceptance angle. However, the concentration or tracking systems increase the balance of the system (BOS) costs. In terms of angular restriction light-trapping structures, a low parasitic absorption probability p_a is required, i.e., at least in the range of 0–2% for efficient photon recycling [Figure 5(i)]. Achieving such low values of p_a is certainly challenging; however, devices with thicker absorber layers can usually support longer optical path lengths and offer low values of p_a [16, 31].

Based on a similar concept, Figure 10(d) illustrates the schematic design of dielectric double-array cone-like structures. In particular, the design comprises of a closely packed double array of cones set apart by a broadband band reflector shown in Figure 10(d). The radiatively emitted photons are reflected by the ideal broadband reflector. This kind of design has already been successfully implemented in GaAs solar cells to demonstrate photon recycling, inspiring its utilization in PSCs [26]. Another possible configuration to induce light-trapping is to nanopattern the active layer itself, such as by the use of cylindrical nanopatterned perovskite thin-films [28]. In this design, the light-trapping of re-emitted photons is achieved through the excitation of waveguide modes. Here, a significant portion of re-emitted photons are reabsorbed through the nanopatterned perovskite layer.

To date, there are no reports yet published that demonstrate the use of either a grating structure, a nanoparticle array or an angular-selective filter in the context of photon recycling for PSCs. However, in terms of optical path enhancement, the angular-selective light-trapping

structures outclass both Lambertian and resonant light-trapping structures. Generally, these approaches aim at elevating the device-level J_{sc} by curtailing front-side reflection losses while concurrently increasing the optical pathlengths of the weakly absorbing in-coupled photons. Analogous to c-Si devices, numerous light management strategies have also been explored for improving the performance of perovskite-based single-junction and tandem solar cells. Typically, for light management, surface corrugations or periodic features are introduced in either the device stack's supporting layers or within the photoactive layer itself. Examples of the former case include the use of fiber-array based anti-reflection electrodes which provide a lensing effect for realizing multiple reflection minima in the 360–750 nm wavelength interval [88], incorporating nanostructured frontside electrodes which address both anti-reflection and light-trapping aspects by allowing an increased number of higher order diffraction modes in the active layer while limiting those in the air [89] and the application of micro-pyramidal textured polydimethylsiloxane (PDMS) anti-reflection coating on an incident glass medium for improving the transmission to reflection ratio at the air/PDMS interface by means of multiple reflections at pyramid facets and refracting light at larger angles [90].

6 Summary and outlook

Optimizing a solar cell's design to enhance the V_{oc} is a hurdle that requires a clear and in-depth understanding of the structural and material properties of the absorber. In particular, with lead halide perovskites, nonradiative recombination losses in the bulk and at the surface have to be suppressed relative to radiative recombination for optical effects like photon recycling to manifest a significant role. The primary benefit of photon recycling as applied to solar cells is the enhancement of the V_{oc} . Such a benefit is achieved by increasing the quasi-Fermi level splitting ($\Delta\mu$) within the absorber material via reabsorption of radiatively emitted photons. The increased $\Delta\mu$ results in a higher maximum power point voltage and, therefore, a more efficient light-to-electricity conversion system. Apart from higher radiative recombination rates, a minimal Stokes shift and efficient light trapping are required to observe efficient photon recycling in PSCs. In particular, it is vital to understand the potential of light trapping to maximize light path enhancement for internally emitted photons. We have shown that light trapping in perovskite solar cells could be accomplished by following several strategies. We demonstrated three fundamental types of light-trapping

concepts and explained their potential in terms of light path enhancement. In particular, the light path enhancement by resonant and angle-selective light-trapping structures is superior to the Lambertian scattering based structures (Yablonovitch limit). Moreover, despite having the highest theoretical upper limit for light-path enhancement, the experimental implementation for angularly selective structures, suitable for concentrator applications, is still lacking. Similarly, resonant and angularly selective light-trapping structures hold promise for enhancing the path length in perovskite solar cells, but there are no reports yet published that demonstrate their use in the context of photon recycling for PSCs.

While simulations have predicted considerable potential gains in PCE for PSCs via the incorporation of photon recycling, this has yet to be demonstrated at the experimental device level. One limitation is that the phenomenon relies on high-quality perovskite films and contact interfaces. In this context, the immediate future requires further development of efficient strategies to passivate the surface and bulk defects in perovskite films. Passivation strategies based on Lewis-acid/Lewis base molecules, long-chain alkyl amines, 2D passivation, and various other additives are being explored continuously toward this purpose.

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