# Perovskites: The Emergence of a New Era for Low-Cost, High-Efficiency Solar Cells

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ABSTRACT: Over the last 12 months, we have witnessed an unexpected breakthrough and rapid evolution in the field of emerging photovoltaics, with the realization of highly efficient solid-state hybrid solar cells based on organometal trihalide perovskite absorbers. In this Perspective, the steps that have led to this discovery are discussed, and the future of this rapidly advancing concept have been considered. It is likely that the next few years of solar research will advance this technology to the very highest efficiencies while retaining the very lowest cost and embodied energy. Provided that the stability of the perovskite-based technology can be proven, we will witness the emergence of a contender for ultimately low-cost solar power.
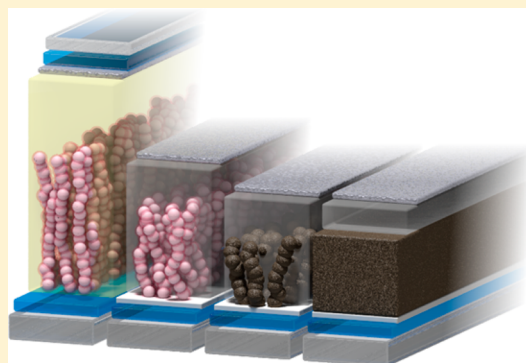
Sunlight is arguably the most abundant clean source of energy that is capable of enabling "indefinite" and sustainable economic growth, with minimum detrimental impact on the environment. Crystalline silicon solar cells have been continuously advancing in efficiency and reducing in cost of fabrication over the last 40 years,[1,2] and in some locations in the world at the current prices, they are capable of producing electricity from sunlight at a comparable cost to the price of electricity generated from fossil fuels.[3] There are many other newer solar cell technologies that promise even lower cost solar power, and these range from thin-film vapor-deposited semiconductor-based solar cells, for example, CdTe or CIGS,[4,5] to solution-processed solar cells based on organic semiconductors, hybrid composites, or inorganic semiconductors,[6–11] often referred to as second- and third-generation photovoltaics (PVs), respectively. The third generation, or "emerging technologies", has attracted a massive increase in research effort over the last 10 years, which has led to tremendous advances in efficiency, reproducibility, and stability, and the first commercial products are being sold for niche markets to power consumer electronics and low-power applications in buildings (www.g24i.com). However, to compete for the larger power markets and indeed drive the adoption of solar cells for utility-scale power generation, a significant increase in efficiency is required for these emerging technologies. Stemming from research in solution-processable semiconductors, a relatively old family of materials[12] has emerged as a serious contender for utility-scale solar power.[13–15] Solar cells based on perovskite absorbers promise to break the prevailing paradigm by combining both ultimately low cost and high efficiency. In this Perspective, the emergence of perovskite solar cells is discussed, highlighting the key steps that have led to the exciting new PV technology, and likely technological evolutionary paths are proposed. This is not a

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comprehensive review of all of the literature on the subject but simply reflects the author's perspective.

Perovskite Phenomena. "Perovskites" is the nomenclature for any materials that adopt the same crystal structure as calcium titanate, namely, ABX_3. There are hundreds of different materials that adopt this structure, with a multitude of properties, including insulating, antiferromagnetic, piezoelectric, thermoelectric, semiconducting, conducting, and, probably most famously, superconducting.[16] Traditionally, perovskites are fabricated by solid-state synthesis of the constituent elements or compounds containing the constituents at high temperature (>1300K).[17] Perovskites can also be fabricated from dried solutions of precursor salts, and those that result in semiconducting perovskites are extremely interesting for printable electronic applications.[18,19] In the early 1990s, Mitzi, Era, and co-workers undertook extensive investigation of the optoelectronic properties of organic–inorganic perovskites. Their research focused on layered organometal perovskites that exhibit strong excitonic features and demonstrated good operation in transistors and light-emitting diodes.[20,21] Peculiarly, to the best of the author's knowledge, no thin-film solar cells were reported. Ammonium trihalogen plumbates

exhibit increasingly large exciton binding energies going from a three-dimensional ABX_3 structure ($R\text{-}NH_3PbI_3$) to a layered ($R\text{-}NH_3$)$_2PbI_4$ structure with perovskite sheets sandwiched between organic planes, and exciton binding energies ranging from 45 to 300 meV have been estimated.[21] It may have been the historic focus on the layered "excitonic" materials that was partly responsible for the lack of solar cell development. However, whether these layered materials are less effective in PV applications remains to be seen.

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Perovskite-Sensitized Solar Cells. Solar cells employing perovskite absorbers have emerged from the field of dye-sensitized solar cells (DSSCs).[8,22] DSSCs are composed of three main components, mesoporous n-type TiO_2 that is sensitized with a light-absorbing dye and filled in with a redox-active electrolyte. The porous TiO_2 is required to deliver sufficient internal surface area to adsorb sufficient dye in order to absorb most of the incident sunlight. However, with the original embodiment of the DSSC, films as thick as 10 μm are required to enable close to complete light absorption over the absorbing region of the dyes.[8] This is impractical for solid-state DSSCs (ssDSSCs), where a number of factors collude to limit the thickness to less than 2 μm.[23] As an alternative approach, inorganic absorbers, such as quantum dots or extremely thin semiconductor absorber layers, should enable complete light absorption in much thinner films and may in addition open possibilities for pushing the photoactivity further into the near-infrared (NIR).[24−28] It is this motivation, to find more advanced absorbers than conventional dyes, which led T. Miyasaka and co-workers to report the first perovskite-sensitized solar cells between 2006 and 2008. They employed $CH_3NH_3PbI_3$ and $CH_3NH_3PbBr_3$ absorbers with either an iodide triiodide redox couple or a polypyrrole carbon black composite solid-state hole conductor and measured full sun power conversion efficiency varying between 0.4 and 2% for solid-state and liquid electrolyte cells, respectively.[29,30] The first peer-reviewed journal publication of a perovskite-sensitized solar cell came in 2009, where the $CH_3NH_3PbI_3$ absorber resulted in a 3.5% efficient sensitized solar cell employing the iodide/triiodide redox couple.[14] A schematic of the perovskite-sensitized titania and the spectral response of the ensuing solar cells is shown in Figure 1.

N. G. Park and co-workers improved on this further via optimization of the titania surface and perovskite processing, reporting a 6.5% $CH_3NH_3PbI_3$ liquid electrolyte solar cell.[31] However, the "Achilles' heel" of these electrolyte-based perovskite-sensitized cells is that the perovskite absorber dissolves or decomposes in the electrolyte, and the cells rapidly degrade within a few minutes.[14,31] The solution was to optimize the perovskite absorber with a solid-state hole conductor, as Miyasaka and co-workers had initially attempted in 2008.[30] Fortuitously, the methylammonium trihalogen plumbates, which crystallize from precursor salts, are relatively insoluble in nonpolar organic solvents, making first perovskite sensitization and subsequent infilling with the organic hole conductor
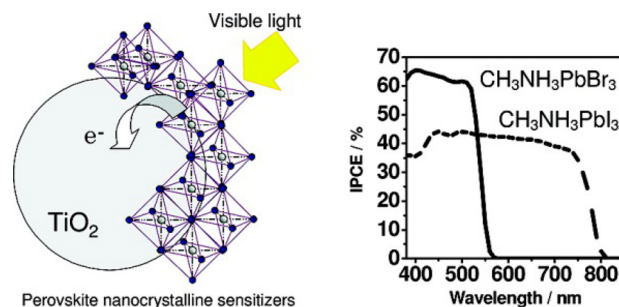

Figure 1. A schematic illustration of perovskite-sensitized TiO_2 undergoing photoexcitation and electron transfer (left). The incident photon-to-electron conversion efficiency (IPCE) spectra for perovskite-sensitized solar cells. Reproduced with permission from Kojima et al.[14] Copyright 2011, American Chemical Society.

facile. Concurrently, we ourselves in collaboration with T. N. Murakami and T. Miyasaka and N. G. Park in collaboration with M. Grätzel and co-workers developed solid-state perovskite solar cells employing $(2,2(7,7)\text{-tetrakis-}(N,N\text{-}$dipmethoxyphenylamine)9,9(-spirobifluorene)) (spiro-OMe-TAD) as the hole transporter[32] and presented maximum full sun power conversion efficiencies of between 8 and 10% employing $CH_3NH_3PbI_{3-x}Cl_x$ mixed halide perovskite and $CH_3NH_3PbI_3$, respectively.[13,15] For solid-state sensitized solar cells, this represented a step change in performance in comparison to the best-reported ssDSSCs, which exhibit just over 7% efficiency.[33] The primary advantage that the perovskite absorbers have over the dyes is that they are much more strongly absorbing over a broader range, enabling complete and broader light absorption in films as thin as 500 nm. This is specifically advantageous for the solid-state cells, where thickness limitations of around 2 μm have historically limited the light absorption and photocurrent generation.[23]

Meso-superstructured Solar Cell (MSSC). While investigating the charge-transport properties of the perovskite-sensitized solar cells, we noticed that the charge extraction rates were significantly faster for the perovskite-sensitized in comparison to conventional DSSCs. This could have been due to either the perovskite having an influence upon the surface states, and hence trap site density in the TiO_2, or a significant fraction of the long-range electron transport occurring through the perovskite phase itself. The latter, fast electron transport through the perovskite, was not intuitively expected because the perovskite absorber coated upon the internal surface of the mesoporous TiO_2 was not expected to be continuous to sustain long-range electron transport. Specifically, in previous reports of perovskite-sensitized solar cells, the perovskite absorber has been shown to be in the form of isolated quantum dots[14,31] and is indeed still classified by many as a quantum-dot-sensitized solar cell.[28] However, we constructed solar cells where the mesoporous TiO_2 was replaced with insulating mesoporous Al_2O_3, with a very similar meso-morphology, with the primary intention to study and elucidate whether electron transport occurs through the perovskite phase and whether we require the mesoporous TiO_2 at all. The results took us by surprise; not only was the charge transport faster and the photocurrent unaffected when the TiO_2 was replaced by the insulating Al_2O_3, but for a like-to-like comparison, the open-circuit voltage increased by 200 to 300 mV, leading very quickly to a 10.9% efficiency solar cell. Technically, the interesting aspect of this discovery is that the fundamental loss in energy, which can be

quantified as the difference between the optical band gap of the absorber and the open-circuit voltage generated under full sun illumination,[34] is extremely low, which gives great promise for significant future increases in efficiency. Concerning the nature of this technology, there no longer remain any of the original components of the DSSC; therefore, we can consider this an "evolutionary branching point", where a new technology has emerged that we have termed a meso-superstructured solar cell (MSSC), due to the presence of the mesoporous scaffold acting as a superstructure, upon which the photoactive layer is coated. A schematic illustration of the operating principles of a TiO_2-based perovskite-sensitized and alumina-based MSSC along with the current voltage curve for our highest published efficiency of a MSSC are shown in Figure 2.
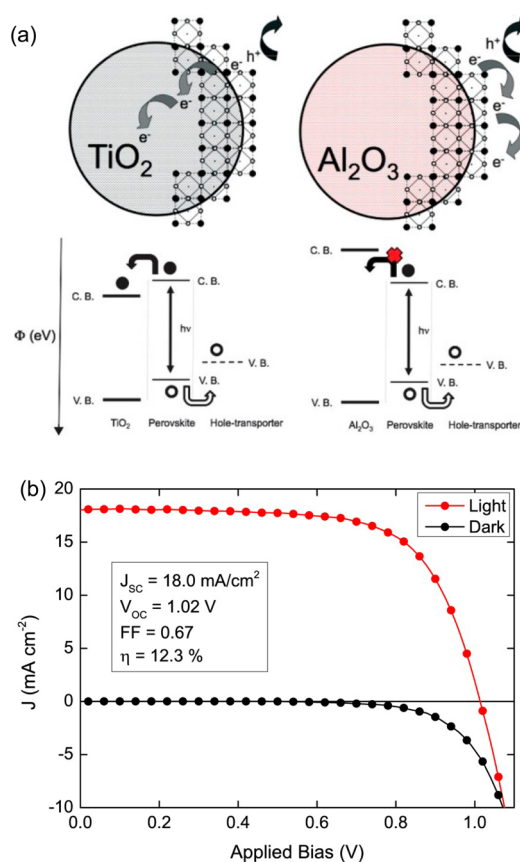

Figure 2. (a) Schematic of perovskite-coated TiO_2 and Al_2O_3, illustrating electron and hole transfer. (b) Current voltage curve for the highest reported efficiency MSSC, measured under simulated AM1.5, 100 mW cm^{-2} sunlight. Reproduced with permission,[35] copyright 2013.

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Perovskites Exhibiting Ambipolar Transport of Electrons and Holes. As well as behaving as an n-type component in the MSSC, perovskites have more traditionally exhibited p-type behavior. Kantadis and co-workers demonstrated efficient ssDSSCs, replacing *spiro*-OMeTAD with $CsSnI_3$.[36] In addition, Etgar et al. have demonstrated that a simple two-component $TiO_2-CH_3NH_3PbI_3$ solar cell can indeed function well, delivering 5% efficiency under simulated full sunlight, employing a Au cathode.[37] The latter embodiment is a very similar configuration to PbS/Se nanocrystal solution processed thin-film solar cells.[38] Notably, for these last two examples of perovskite-based solar cells, the open-circuit voltages are lower because they still incorporate the mesoporous TiO_2, which through the MSSC work has been identified to be directly responsible for significant voltage loss.

In the work of Lee et al., we showed that a solid thin-film perovskite device, in the absence of mesoporous alumina, could still operate with up to 2% power conversion efficiency in a thin-film positive (p)−intrinsic (i)−negative (n) architecture.[15] More recently, we have demonstrated that solid thin films of perovskite absorber, on the order of 300 nm in thickness, can generate and transport both electrons and holes to the collecting contacts with close to unity efficiency.[13] As an ultimate demonstration of ambipolar transport, we have also constructed planar heterojunction perovskite solar cells via vapor deposition, which show extremely high efficiencies of over 15%.[39] This finally demonstrates that the perovskite semiconductors can exhibit sufficiently good ambipolar charge transport and assume all of the principal roles of PV operation, light absorption, charge generation, and transport of both electrons and holes. Controlling the specific nature of the contact of the perovskite absorber to the p- and n-type materials will be central to maximizing the performance of the p−i−n heterojunction perovskite solar cells.

Comparison to Other Technologies. The most striking aspect of the perovskite technology is the high open-circuit voltage that the cells can generate under full sun illumination. A solar cell has to absorb light and convert the solar energy to electrical power. For the broad spectrum sunlight irradiating the solar cell, photons with lower than band gap energy are not absorbed; all of the photoexcited electrons from the above band gap excitations relax down to the conduction band, losing their excess energy as heat. The maximum voltage that the solar cell can generate, the open-circuit voltage, reflects the maximum energy that can be extracted from any absorbed photon, and the difference between the potential of the lowest-energy absorbed photon that generates charge and the open-circuit potential under full sunlight can be considered a simple measure of the fundamental energy loss or "loss-in-potential" in a solar cell.[34] Due to thermodynamic constraints, this minimum loss in energy is on the order of 250−300 meV (depending on the band gap), following the Shockley−Queisser treatment.[40] The lowest-energy absorbed photon that can contribute to free carrier generation can be determined from the onset of the IPCE spectrum, which for the $CH_3NH_3PbI_{3−x}Cl_x$ perovskite is approximately 1.55 eV (800 nm), and the open-circuit voltage of the best perovskite cells can be greater than 1.1 V, giving a loss-in-potential as low as 450 meV. In Figure 3, the open-circuit voltage versus the optical band gap (estimated from the IPCE onset for all technologies) for the "best-in-class" of most established and emerging solar technologies is shown. This helps us to compare the fundamental losses of a broad range of technologies with different absorber band gaps. With this
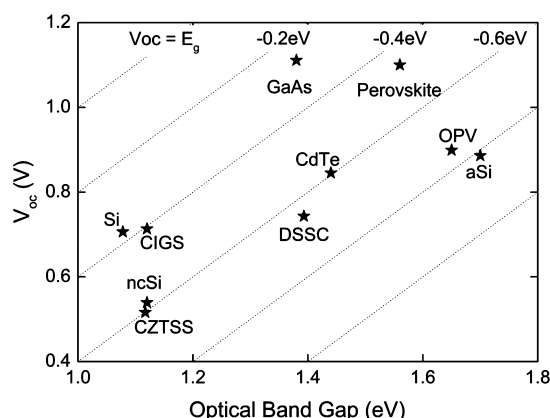
Figure 3. Open-circuit voltage (V_{oc}) versus optical band gap (E_g) for the best-in-class solar cells for most current and emerging solar technologies. All of the data for the GaAs, Si, CIGS, CdTe, nanocrystalline Si (nc-Si), amorphous Si (a-Si), copper zinc tin sulfide/selenide (CZTSSe), organic photovoltaics (OPVs), and DSSCs were taken from the solar cell efficiency tables of Green et al.[1] The optical band gaps have been estimated by taking the onset of the IPCE for all technologies in order to make a fair comparison.

difference in energy as the only performance metric, the new perovskite technology is very well positioned in fourth place out of all solar technologies, behind GaAs, crystalline silicon, and copper indium gallium (di)selenide (CIGS). Remarkably, the fundamental losses of the perovskite cells are already lower than CdTe, with losses of approximately 0.59 eV, which has been the most commercially successful thin-film technology to date, with a record cell efficiency of 19.6%.[41] It is important to note that the most relevant voltage to consider for maximum efficiency in a working solar cell is the voltage at maximum power point (V_{mpp}).[42] However, V_{mpp} is strongly influenced by imperfections in the solar cell manufacture that can lead to high series resistance and/or low shunt resistance. Thus, it is expected that V_{mpp} will improve considerably with solar cell optimization and, as such, may not be such a good metric for comparing a range of technologies at different stages of development.

Future Direction and Prospects. Where the perovskite solar cell technology will end up, both in terms of physical structure and performance, is difficult to predict, but it certainly has all of the "right ingredients" to deliver the very highest efficiencies at the lowest possible cost. Considering the device architecture, if we look at the "technological ancestry", then a clear evolution is apparent, and this helps to predict where it may evolve to going forward. In Figure 4, schematic illustrations of electrolyte DSSCs, ssDSSCs, extremely thin absorbers (ETAs), or quantum-dot-sensitized solar cells to the MSSC are shown. If physical structure is all that the mesoporous alumina scaffold is delivering, then it appears that the porous alumina is purely a remnant of its ancestry. Therefore, moving forward, we may expect the scaffold to disappear altogether. This however leads to a further possible branching point in the evolution where in one instance, we can move to porous perovskite films infiltrated with a transparent charge transporter. A second direction will move to solid thin-film perovskite solar cells, most likely in the form of a p–i–n heterojunction, where uniform thin-film processing and balanced electron and hole collection is achieved. The thin-film approach has already delivered extremely efficient solar cells via vapor deposition.[35,39,43] However, the insulating scaffold may prove to be useful for

solution processing and could have other electronic advantages. The scaffold may act as a buffer layer, minimizing short circuits, or additionally, the presence of the porous scaffold may be advantageous for perovskite crystallization or film formation. There may also be additional electronic functions to which we are currently naïve. If the insulating scaffold does have certain advantages, then it would seem unnecessary to limit the MSSC technology to perovskites, and indeed, any suitable semiconductor that can be deposited to form a conformal coating upon the internal surface of a porous alumina or other oxide scaffold should function effectively in this configuration. This latter approach, to broaden the materials base for the MSSCs, may open many new possibilities for solution-processed thin-film solar cells. There are many other ways in which the perovskites could be incorporated into solar cells, such as bulk heterojunctions both hybrid and all inorganic, and we will see over time what additional interesting concepts emerge with this versatile family of photoactive materials. It is interesting to note that DSSCs emerged from flat junction photoelectrochemical cells,[44−48] and if the thin-film perovskite solar cells finally end up dominating, this generic chemically processed solar technology will have gone full circle. It is also important to note that although this Perspective has focused on the technological evolution of perovskite solar cells, the perovskite-sensitized TiO$_2$ cell concept, considered here to be following the ETA approach, is still progressing rapidly with efficiency of over 15%, also reported.[49] We can expect all of the embodiments of perovskite solar cells to continue to attract research attention over the next few years.[35,49−56]

> **Three key strategies are likely to push the absolute power conversion efficiency toward that of CIGS (20%) and then toward and beyond that of crystalline silicon (25%).**

With low fundamental losses, there are clear directions that will allow this technology to advance in efficiency. Three key strategies are likely to push the absolute power conversion efficiency toward that of CIGS (20%) and then toward and beyond that of crystalline silicon (25%). The technology, as it stands, is suboptimal, primarily resulting from large-scale inhomogeneity in film uniformity and layer thicknesses. It is remarkable that perovskite cells already deliver over 15% efficiency, but as a continuing strategy, optimization through better control over all of the processing parameters should push the efficiency of the CH$_3$NH$_3$PbI$_{3−x}$Cl$_x$ perovskite cells closer to 20%, for example, by achieving J_{sc} of 22 mA cm^{-2} with a V_{oc} of 1.1 V and a FF of 0.8. Because a capping layer of the hole transporter appears to be important in the highest-efficiency cells in order to prevent contact between the perovskite and the metal anode, it may be necessary to employ higher-mobility hole transporters than *spiro*-OMeTAD in order to achieve the highest fill factors (FFs). Better choice of both the p- and n-type charge collection layers may also lead to improved FFs. As a second strategy, to increase the efficiency further, a narrower band-gap perovskite, which absorbs out toward 940 nm, would increase the efficiency by a further few percent. As a third strategy, a simple and well-proven route for enhanced solar cell performance is to adopt a multijunction approach. In a single-
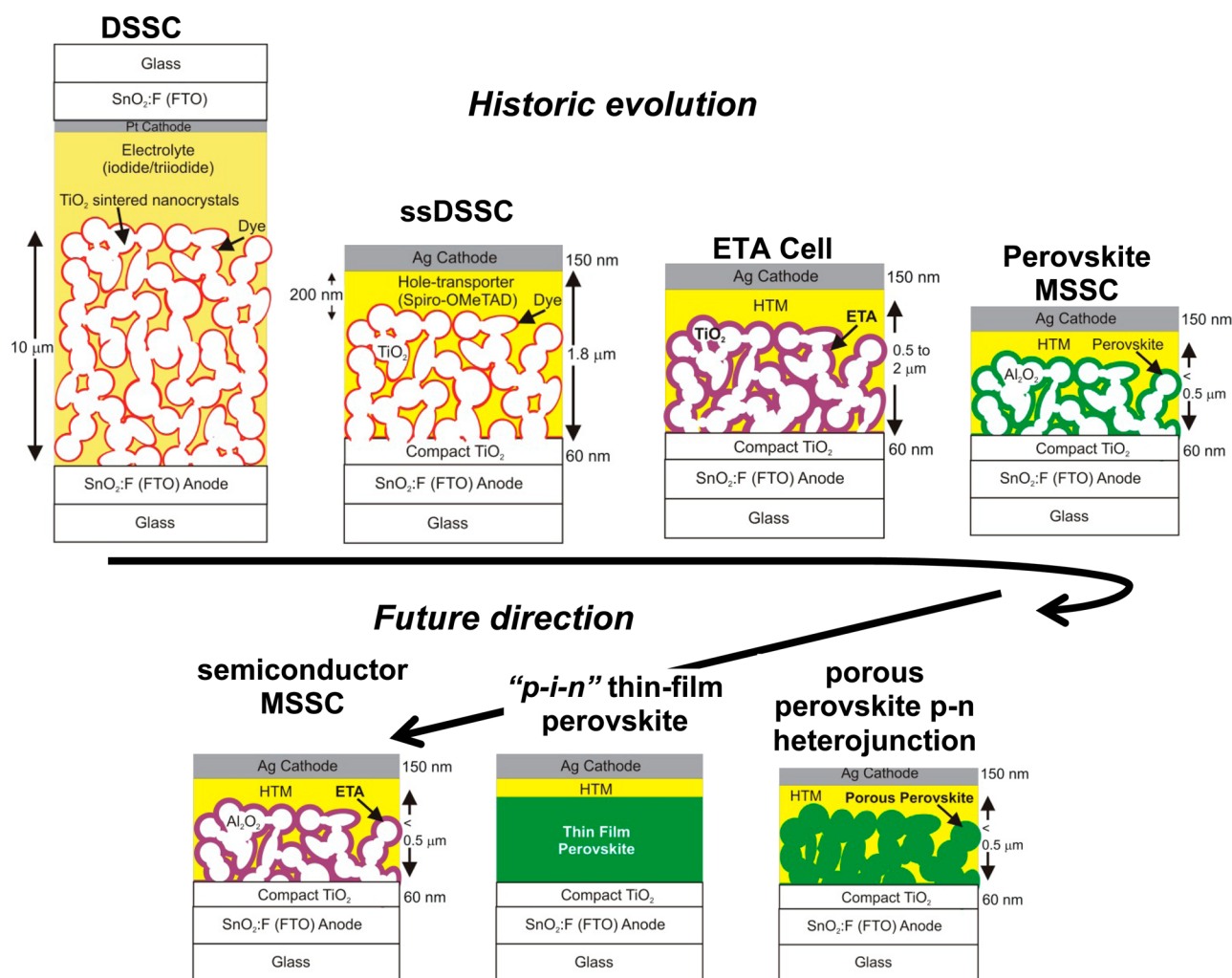
Figure 4. Historic evolution of the solar cell technology, starting from the electrolyte-based mesoscopic DSSC,[8] the ssDSSC where the electrolyte is replaced with an organic p-type hole conductor,[32,57] the ETA cell where the dye is replaced with an ETA semiconductor layer,[27,58] to the MSSC,[15] where the ETA is replaced with a perovskite absorber and the n-type TiO_2 is replaced with a porous insulating scaffold. Three likely future directions for the perovskite technology are indicated: (i) porous perovskite distributed p−n heterojunction solar cells, where the Al_2O_3 is removed but the perovskite is directly structured to give a porous film subsequently filled in with a charge conductor, (ii) thin-film p−i−n perovskite solar cells where no porosity is required and the device takes on the structure of an intrinsic, or at least ambipolar, thin perovskite film sandwiched between p- and n-type charge-extracting contacts, or (iii) semiconductor MSSCs, where any solution-processed semiconductor, such as SbS,[27] can be structured by the porous scaffold to deliver a MSSC.

junction solar cell, all of the photons with above band gap energy are absorbed, but the excess energy is lost as heat as the photoexcited electrons relax back down to the conduction band. By absorbing the high-energy photons in a wide-band-gap solar cell and letting the low-energy photons pass through the first cell and be absorbed in a narrow-band-gap solar cell, a higher overall voltage can be achieved and less energy lost as heat. Similarly to organic absorbers and quantum dots, the broad family of perovskite materials and the ability to tune the band gap by cation and anion choice,[59,60] in addition to quantum confinement in layered perovskites, make this multijunction approach extremely feasible. For an efficient tandem junction, there is a requirement for current matching of the front and rear cells. If this is done effectively, then the overall efficiency increases by approximately 1.3 times that of the optimum single-junction cells, leading to a possibility of achieving greater than 25% efficiency under 1 sun illumination without having to reduce the fundamental energy losses.

Hybrid Multijunction Solar Cells. An "all-perovskite" multijunction cell is very attractive; however, even without the need to develop new absorbers, the current system employing $CH_3NH_3PbI_{3-x}Cl_x$ is already very well set to match with crystalline silicon and other thin-film technologies such as CIS, CIGS, and CZTSSe, if used as a top cell in a tandem junction.[61] If we are optimistic and assume that we can achieve 20 mA cm^{-2} in the top perovskite cell with a 1.1 V open-circuit voltage and can match this with 20 mA cm^{-2} from the NIR absorption in a crystalline silicon cell, which generates a 0.75 V V_{oc},[20] then with a FF of 0.8, this would lead to a 29.6% cell (notably, in this example, the top perovskite cell would have an efficiency in a single junction of 17.6% and the bottom c-Si cell would be 23−24%). The remarkable aspect of this is that it does not require a "quantum leap" in our current technology, simply a little optimization, predominantly of FF improvement, a slight widening of the band gap, and effective integration into the tandem architecture. There are many distinct advantages of "piggybacking" on existing technologies; the continuing drop in
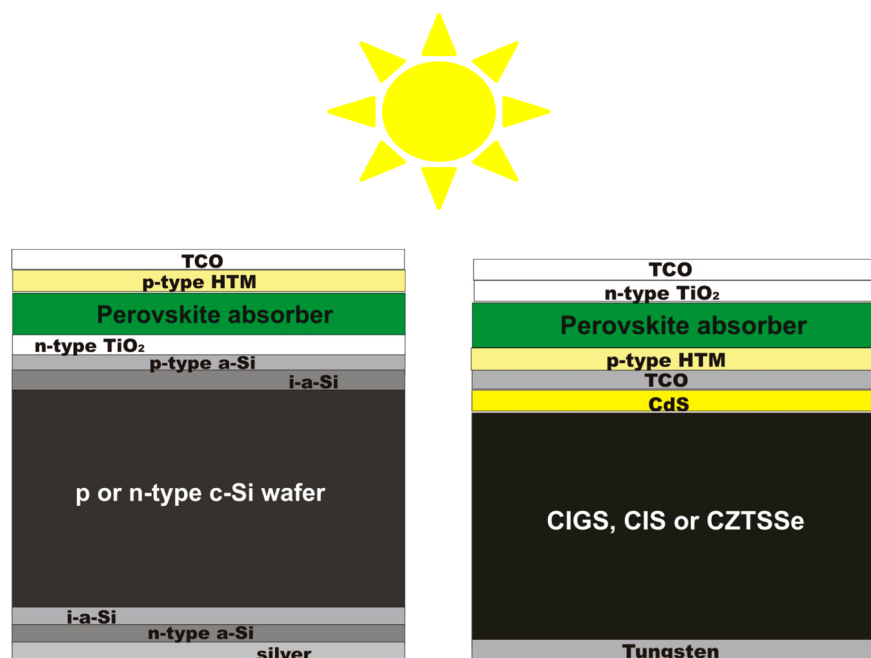
Figure 5. Schematic illustration of proposed hybrid tandem solar cell architectures, where the left illustrates a perovskite−c-Si HIT (heterojunction with intrinsic thin layer) cell tandem and the right shows a perovskite−thin film tandem, where i = intrinsic, a = amorphous, c = crystalline, and TCO = transparent conducting oxide. Notably, for the current generation of thin-film technologies such as GIGS and CdTe, there is a requirement to realize "inverted" perovskite solar cells for monolithic two-terminal tandem devices. Sunlight is incident from the top, as illustrated.

the cost of existing PVs becomes advantageous, the market should be much more willing to adopt an "enhanced silicon technology" rather than an all new perovskite technology, and, last but not least, a key challenge for the broader PV community has been to develop a wide-gap top cell for silicon and thin-film technologies. This does not yet exist at suitable efficiency,[62] and the perovskite solar cells could prove to be compatible. In Figure 5, schematic illustrations of possible tandem junction device configurations are given for perovskite on c-Si and perovskite on a conventional thin film.

Clearly, for any substantial PV market, and most certainly for piggybacking on silicon, 25 years of operational lifetimes will be required. This may be delivered by the first generation of these devices; however, it is likely that significant effort will be required in this area. The "golden triangle" for a solar technology is cost, efficiency, and stability. It appears that it will be a relatively straightforward research and development challenge to increase the efficiency of the perovskite cells to the highest levels for flat plate technologies. The basic cost of the materials, which will not be discussed in detail here, is extremely low (simply as an example, $PbCl_2$ costs at the research level £52 ($82)/kg, which is enough to coat 1000 m^2 at 200 nm film thickness), and the processing methods are extremely basic; thereofre, fundamentally, this technology should be at the very lowest cost to manufacture. Hence, the real challenge to make sure that this technology has a dramatic impact on the solar industry is to focus on continually understanding and enhancing the stability. Initial results look promising; the materials appear to be stable to prolonged exposure to sunlight when sealed in an inert atmosphere,[15] and the mixed halide perovskites appear to be relatively insensitive to moisture.[15,59] However, full device stability over a broad range of conditions and testing is still to be proven. It would not be expected that this is already proven, but understanding changes that can occur during aging and developing

components and processing steps that enhance stability should be one of the key scientific goals for the field. The breadth of possible perovskite materials makes it highly likely that extremely stable absorbers will be developed.

> A new era and a new avenue of research and development for low-cost solar cells have emerged based on perovskite semiconductors.

In summary, a new era and a new avenue of research and development for low-cost solar cells have emerged based on perovskite semiconductors. If a small fraction of the current PV research community expends effort on developing this technology, we will see many transformative steps over the coming few years. There is a tangible possibility that a solar technology based on perovskite absorbers could lead to position PV solar energy as *the* lowest-cost energy source, capable of many tens of TW of power generation indefinitely into the future.

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Author Contributions
The manuscript was written, and all new figures/schematics were drawn by the author.

■ **ABBREVIATIONS**

DSSC, dye-sensitized solar cell; MSSC, meso-superstructured solar cell; ETA, extremely thin absorber

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