VIPERLAB

FULLY CONNECTED **VIR**TUAL AND **P**HYSICAL **PER**OVSKITE PHOTOVOLTAICS **LAB**

D7.6 Update to D7.3, taking into account the latest advances in related fields

DELIVERABLE REPORT

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FULLY CONNECTED VIRTUAL AND PHYSICAL PEROVSKITE PHOTOVOLTAICS LAB VIPERLAB

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D7.6 UPDATE TO D7.3, TAKING INTO ACCOUNT THE LATEST ADVANCES IN RELATED FIELDS

Project References

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DISCLAIMER

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EXECUTIVE SUMMARY

This report presents an overview of the current advancements in the field of photovoltaic (PV) technologies, with a special focus on perovskite-based systems. These materials have shown promising potential across a range of applications, including solar cells (PV), light-emitting diodes (LEDs), and detectors. In the realm of PV technologies, perovskite quantum dots (PeQDs) have been utilized to enhance the efficiency of solar cells, demonstrating notable records in performance. However, there are still some challenges, such as the need for ligand exchange processes and the choice of solvents, which need to be addressed for their wider implementation. For LEDs, perovskite materials have demonstrated high external quantum efficiency (EQE) for red, green, and near-infrared emissions. Still, blue-emission efficiencies remain a challenge due to their sensitivity to sub-bandgap defects and the instability of the necessary perovskite formulations. Perovskite detectors have also shown promise, particularly in the detection of high-energy radiation such as X-rays and gamma rays. Interestingly, the research in this field is contributing to the exploration of lead-free inorganic perovskite materials, expanding the possibilities for PSC.

Moving away from perovskite-based systems, we discuss the developments in other emerging PV technologies such as antimony chalcogenides, CZTSSe and $BaZrS_3$ solar cells. These emerging technologies, while not as efficient as perovskite-based systems, provide valuable insights for further improving perovskite solar cell performance.

The document concludes with an outlook on the continuous advancements in thin-film technologies and highlights the importance of ongoing research to exceed the performance of single junction cells. Comparative meta-studies and technological "openness" are encouraged for strategic advantage in future PV research and provide valuable insights for decision-makers in the PV technology field, detailing the progress in perovskite-based systems and other emerging PV technologies.

1 UPDATES ON SI, CIGS, AND ORGANIC PV

This task entails actively monitoring the latest scientific and technological advances in photovoltaic (PV) research, specifically targeting silicon (Si), copper indium gallium selenide (CIGS), and organic solar cells (OSCs).

The objective is to identify innovative fabrication routes, particularly those that facilitate large-area coatings and meet industrial requirements, along with advancements in materials and processing techniques that enhance device performance and stability through a bibliographic search. The field of research in photovoltaic (PV) technologies is thriving, with thousands of publications released annually[1]. Each technology is at a distinct stage of development, reflecting the dynamic and evolving nature of this sector, see Figure 1.
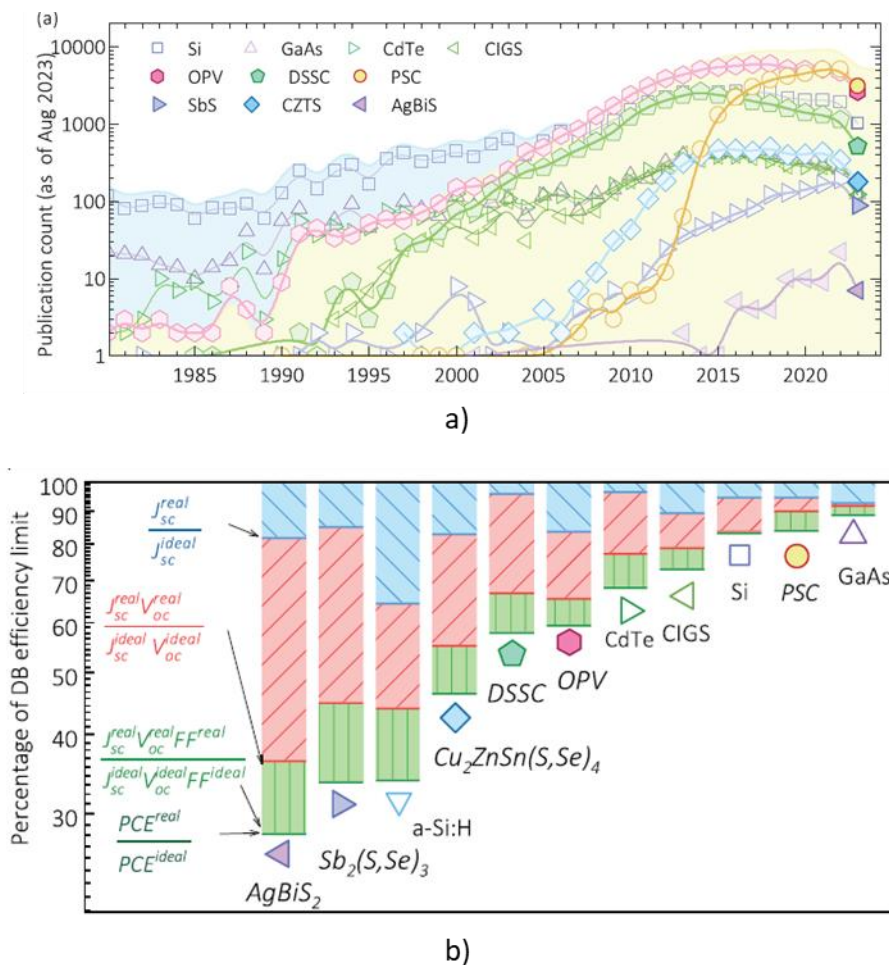

a)

b)

Figure 1 (a) Annual academic research publications over time in the absolute count for several photovoltaic technologies, as indicated and (b) Comparison of the experimental data to the corresponding theoretical limit in the detailed balance (DB) model Reproduced from[2].

During these latest years, 2021 to 2024, some review publications have summarized the main achievements of these technologies[2,3,4,5,6] and record efficiencies[7].

In the following sections, some of the key areas of focus for each one of the technologies are highlighted.

1.1 Si PV

Silicon continues to dominate the PV market due to its established technology and efficiency. In 2023 and 2024, notable advancements have been made in increasing the efficiency of monocrystalline and bifacial silicon solar cells. Researchers focused on optimizing cell architecture in silicon heterojunction by lower resistance loss and higher current by replacing the conventional front and rear amorphous doped silicon layers with nanocrystalline layers.

The trend goes to architectures approaching the theoretical efficiency limit of c-Si cells by

- Reducing surface recombination in silicon through advanced low-cost surface passivation and lowering recombination losses at metal contacts through novel passivating contacts and novel heterojunctions.
- Maximizing light trapping in silicon through nanophotonic structures maximizes absorption and minimises reflection, enabling reduced silicon consumption and higher efficiencies. This is also complemented by innovative texturisation§ and light-trapping concepts for thin and ultrathin c-Si solar cells[8,9,10]
- Low-cost and reduced Ag-content metallisation, using abundant materials. Innovative contacts for Si are also considered.
- Direct bandgap architectures for very high efficiencies and/or thinner cells.
- Last but not least, advanced concepts are also investigated for the implementation of solar cells.[11,12]

To reduce the impact of end-of-life photovoltaic modules, many researchers are dedicated to studying rational recycling and utilization of photovoltaic modules. Furthermore, developments in large-scale manufacturing processes, such as improved ingot growth and

wafer-cutting techniques, are being implemented to reduce costs and enhance production scalability.

Latest announcements:

- LONGi announced a major breakthrough in the development of its silicon-perovskite tandem solar cells, reaching an efficiency of 34.6%. They optimized the deposition process of the electron transport layer film, introduced high-efficiency defect passivation materials, and designed and developed high-quality interface passivation structures.

- A team of researchers from the Fraunhofer Institute for Solar Energy Research ISE and NWO-Institute AMOLF (Amsterdam) has fabricated a multijunction solar cell with an efficiency of 36.1 percent, the highest efficiency ever reached for a solar cell based on silicon and combining a state-of-the-art "silicon TOPCon" solar cell with two semiconductor layers composed of GaInP and GaInAsP and a metal/polymer nanocoating designed at AMOLF.

- Silicon heterojunction solar cells achieving a record 26.6% efficiency on commercial-size p-type silicon wafers employing a phosphorus diffusion gettering pretreatment on the wafers and pioneering the development of carrier-selective contacts using nanocrystalline silicon (nc-Si:H) [13].

As of November 2022, the certified highest PCE for single-junction silicon solar cells has achieved 26.81 %, utilizing the back junction HJT structure with improved back contacts consisting of p-type doped nanocrystalline silicon and a transparent conductive oxide with a low sheet resistance, developed by LONGi.[14]. The implementation of p-nc-Si:H together with a modified TCO greatly reduced the contact resistivity from >100 mΩ cm^2 to <5 mΩ cm^2. The total series resistance of the solar cell was reduced from the original 0.37 to 0.2 Ω cm^2, yielding a record FF for a single-junction silicon solar cell. Soon enough, they improved the PCE to 27.30 % by combining the HJT with an interdigitated back-contact (IBC) structure, also known as heterojunction back-contact (HBC) solar cells[13].

1.2 CIGS PV

Researchers at Uppsala University and First Solar achieved a world-record efficiency of **23.64%** for CIGS solar cells. This breakthrough resulted from optimizing the silver alloy composition and refining the gallium gradient in the back contact layer, which enhanced internal electric fields and reduced recombination losses[13].

CIGS is a mature and commercially available thin film technology which benefits from superior low-light behaviour and a low-temperature coefficient compared to that of Si wafer-based modules. Lightweight and flexible photovoltaic $Cu(In,Ga)Se_2$ (CIGS)-based modules are explored technologies that may result in the broader applications usage range.[15]

The improved efficiency positions CIGS as a competitive technology for both standalone applications and tandem configurations, especially when combined with perovskite layers, to achieve even higher efficiencies. Efforts are being directed towards making CIGS fabrication processes more compatible with industrial requirements, including the development of roll-to-roll coating techniques that allow for the efficient production of large-area modules. Research is also underway to improve the stability of CIGS cells, addressing issues related to moisture sensitivity and thermal degradation.

1.3 Organic PV

New records have been recently achieved with this technology driven by the development of new donor-acceptor materials and advanced charge transport layers[13], achieving a certified power conversion efficiency of up to 19.2%. This advancement has been demonstrated with a double-fibril network based on a ternary donor-acceptor morphology with multi-length scales constructed by combining ancillary conjugated polymer crystallizers and a non-fullerene acceptor filament assembly. This strategy leads to an enhanced exciton diffusion length and a reduced recombination rate, hence minimizing photon-to-electron losses in the ternary devices as compared to their binary counterparts.[16] On a smaller scale and uncertified, even up to 20.8% efficiency has been reported by going to a layer-by-layer fabrication method. This fabrication method leads to both effective exciton dissociation at the mixing zone between the p-type and n-type semiconductors and efficient carrier

transport with pure semiconductors. Further improvements in photocurrent come from light management through a patterned surface, which results in reduced reflection losses as well as an increased optical path for the photons.

Innovations in material formulations aim to enhance charge mobility and minimize recombination losses.Combining different strategies, such as new non-fullerene electron acceptors with high absorption in the solar spectrum, minimal loss in the driving force during charge separation, film shape, interfacial layer, and device engineering. The addition of a third component in the active layer in comparison with the binary OSCs contributes to improvements in the energy level cascade and charge transport between the device's layers, which jointly result in a PCE higher than the binary OSCs.[17]

Plasmons can broaden the absorption range to cover the entire solar spectrum and enhance absorption efficiency while maintaining a relatively thin active layer. Carbon nanotubes (CNTs) and graphene have been investigated as alternatives to fullerenes (electron acceptors) and/or transparent electrodes. Organic solar cells utilizing CNT/polymer nanocomposites are anticipated to lead the next generation of solar cell materials[18].

Organic solar cells face challenges in terms of efficiency, durability, and competition from established renewable energy technologies.[19]

Research is also focused on scalable technologies relying on abundant elements with low toxicity and short energy payback, positioning OPV as a green PV technology of the future. OPV cells have the potential to offer a sustainable and eco-friendly alternative to traditional solar cells, with low production costs and design flexibility. Organic photovoltaic (OPV) module fabrication involves precise laser scribing (P1, P2, and P3 patterns) for cell interconnection, with advancements achieving geometric fill factors (GFF) over 95% by minimizing dead zones. Large-area thin-film printing techniques, such as blade coating, slot-die coating, and gravure printing, enable scalable production, with roll-to-roll (R2R) processes offering high throughput and uniformity. Enhancing film morphology, optimizing drying kinetics, and improving material solubility are critical for achieving high efficiency and uniformity in printed modules. Encapsulation remains a challenge, with glass-to-glass encapsulation unsuitable for flexible devices. Thin-film encapsulation using materials like PET and PEN, supplemented with inorganic barriers, is advancing to improve moisture and oxygen resistance, although durability under sunlight requires further research[20].

Two major challenges are still an object of research in this technology: first, preparing high-quality flexible transparent electrodes with low resistance, high transparency, smooth surface, and superior mechanical properties such as ITO/Ag mesh/ITO, AgNWs:AZO-SG, and Ag-grid/PH1000[21] or silver nanowire (AgNW) [22] and, second, the scalable fabrication of thickness-insensitive photoactive layers with low-cost materials.[23]

The challenge of stability remains, as OSCs typically have shorter lifespans compared to silicon and CIGS cells. Recent innovations in encapsulation materials and deposition techniques are being explored to enhance the durability of OSCs, enabling their application in flexible and large-area installations, such as building-integrated photovoltaics (BIPV) One of the major focuses in 2023 and 2024 is improving the long-term stability of OSCs, as these cells are generally less durable compared to silicon and CIGS technologies. Researchers are exploring advanced encapsulation techniques and novel polymer blends that can provide better resistance to environmental factors, thereby extending the lifespan of OSCs[24]. Furthermore, scalable production techniques such as inkjet printing and slot-die coating are being refined to enable the manufacturing of OSCs suitable for large-area applications, thus promoting their integration into flexible and lightweight PV systems.

Stretchable organic photovoltaics have recently garnered significant attention as promising power sources for wearable electronic systems. Especially, research on intrinsically stretchable organic photovoltaics (IS-OPVs) has been accelerated[24] Additionally, plant-based materials are being explored for their technical potential in photovoltaic (PV) technologies, offering functionalities such as light absorption, charge transport, and encapsulation[25].

Recently, wearable electronic devices have been drawing considerable interest because of their versatility in a wide range of applications, including motion detection, smart clothing, and health surveillance. Maintaining an adequate power supply is a critical factor in ensuring the continuous operation of wearable electronics. Organic solar cells (OSCs), with advantages that include high flexibility, portability, and low-cost solution-based processing, have achieved power conversion efficiencies of more than 20% and can thus serve as self-powered sources for sustainably powered wearable electronics[24].

2 PEROVSKITE QUANTUM DOTS PV, LED AND DETECTORS

2.1 Perovskite Quantum dots (PeQD) PV

Perovskite Quantum Dots (PeQDs) display unique properties compared to their bulk counterpart mainly due to the fact that excitons are confined in all three spatial dimension. Tunable band-gap, multiple excition generation (MEG), high photoluminescence quantum yield (PLQY) and high colour purity make these materials promising for many different applications such as, photovoltaic, LED, lasers, detectors[26] and recently also in realizing WORM memory devices for data storage (Write-Once-Read-More memory devices),[27] in this last case taking advantage from the migration of mobile ionic halide vacancies, that is usually considered detrimental to the performance and stability of perovskite optoelectronic devices.

Inorganic $CsPbI_3$ is the most widely studied PeQDs, due to its increased surface strain ascribable to quantum size effect confinement that stabilize the perovskite black phase, it was possible to reach 16% efficiency in solar cell devices; nevertheless its intrinsic soft lattice and narrow bandgap (<700nm) limits the further improvements in terms of efficiency and durability.[26] The introduction of organic cation (FA, MA) can help in obtaining preferable Goldschmidt factor and ideal E_g, improving efficiency and crystal stability of PeQDs Solar Cells. In this sense it is important to have a fine control over the synthetic procedure to tune the perovskite stoichiometry avoiding to alter the delicate colloidal surface equilibrium, as demonstrated by the use of an antisolvent-assisted cation exchange technique, throught which it was possible to obtain different stoichiometry $FA_xCs_{1-x}PBI_3$ PeQDs with efficiency as high as 17.29% and good PeQDs-Solar Cell stability (see Figure 1).[28]

Similarly, the substitution of Cs^+ ion with MA^+ by adopting an alkyl ammonium-iodide ligand exchange strategy, allowed the organic PeQDs Solar Cells to reach the highest efficiency so far equal to 18.1%, also showing remarkable stability under stress test (1.200-h under illumination at open-circuit conditions and 300-h stability at 80 °C).[29]
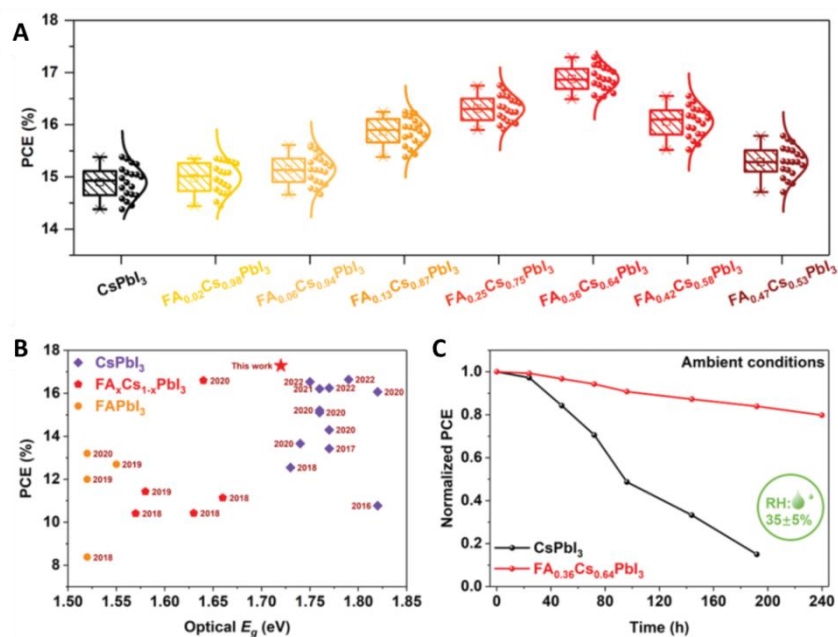
Figure 2 Variation of PSCs efficiency as funtion of FA content (A). Comparative PCE values (B). Stability test for pure CsPbI$_3$ and FA$_{0.36}$Cs$_{0.64}$PbI$_3$ PSCs. Graphs reproduced from reference [28]

The chemical strategy used to govern the perovskite stoichiometry showed in the previous examples can be taken as inspiration to translate a similar approach also in the bulk PSCs to further tailor the band-gap and stabilty of the final device. By a general point of view, the commercialization of devices based on PeQDs is strongly hampered by two main factors: a synthetic approach capable to give high reaction yield for mass-production, and the loss of colloidal stability and structural integrity arising from the easy desorption of surface capping molecules during isolation, purification and device realization steps. If the synthetic issue concerning low PeQDs reaction yield can be addressed by using solvents commonly adopted also for traditional semiconductor QDs, such as trioctylphosphineoxide (TOPO) capable to afford an almost quantitative reaction yield,[30] the stability issue of PeQDs requires a very deep knowledge of reaction mechanisms so that it is possible to adopt the right surface passivating agent in order to improve both properties and stability of PeQDs colloidal suspension and this is particulary true in the optimization of PeLEDs production (see next section).

2.2 Perovskite LED (PeLED)

As mentioned above the PeLEDs require a very deep knowledge of the reaction mechanism for the synthesis of QDs and even larger knowledge of the molecules used as "surface passivating agent" to improve device performance and stability. The most widely adopted method for the synthesis of PeQDs for LEDs technologies is the Hot Injection method (HI), it is carried out at high temperature (180-200 °C) in order to favour the almost instantaneous formation of QDs after the introduction of the Cesium source as last reagent (or A cation of the general ABX_3 stoichiometry). It is paramount of importance to distinguish and control the kinetic of nucleation and the subsequent growth of PeQDs to avoid particles aggregation, clusterization and precipitation phenomena, that compromise the properties of the final material. The reactions are generally carried out in presence of acid and base reagents, such as Oleic Acid (OA) and Oleic Amine (OAm), that affect the nucleation and growth of PeQDs, so in principle, different K_a and K_b value can be used to discriminate between the good (nucleation and growth) and bad processes (aggregation, precipitation). The use of the stronger octanoic acid (OTAc) and octylamine (OTAm) with respect to OA and OAm, suppresses the formation of the clusters leading to green PeQDs with almost unit PLQY then used to realize a green LEDs with 24.16% of EQE and very good stability (T_{50} lifetime of 54 min at 10.000 cdm^{-2}).[31] The possibility to lower the kinetic of the nucleation process along with subsequent passivation of surface defects is a valid strategy to optimize both efficiency and stabiltiy of PeLEDs. In this direction many different additives or passivating agents can be used,[32] among all ASC18 (3-(N,N-dimethyloctadecylammonio)-propanesulfonate) and its derivatives (sulfobetaine class of compounds) are emerging as very effective bidentate ligands in both inhibition of the "*Ostwald ripening*" (uncontrolled growth of the QDs size and aggregation) and surface passivation of PeQDs.[33] ASC18 was used for-large scale production of PeQDs with uniform morphology, high crystallinity and near-unit optical properties and also to realize very stable green PeLEDs (520 nm) under UV and thermal stress conditions.[34] One of its derivatives (ASDC-12) was demonstrated to have a fine control over the morphology of $CsPbBr_3$ QDs, producing nanocrystals with highly unusual rhombicuboctahedron morphology against the cubic one when ASC-18 was used.[35]

Multifunctional additive strategy was also used to realize pure-blue and pure-red PeLEDs with high EQE as in the case of the couples TFA$^-$/PEA^{+}[36] or 2-naphthalene sulfonic

acid/ammonium esafluorophosphate.[37] In the first case, the phenylethylammonium (PEA⁺) ion with its low adsorption energy towards perovskites surface facilitates the charge transport within the perovskite films, while the interaction between the C=O group in trifluoroacetate (TFA⁻) and perovskites significantly reduces defects in the perovskite films. This double effect allowed the realization of a pure-blue led (468 nm) with $CsPb(Br_{0.55}Cl_{0.45})_3$ stoichiometry showing one of the highest EQE (11.47%) reported so far. In the second case a pure-red $CsPbI_3$ PeLED (628 nm) was realized by using the naphthalene sulfonic acid to suppress the "*Ostwald ripening*" and by employing the inorganic ligand NH_4PF_6 to replace the weak binding ligands (OA and OAm) fro defects passivation, obtaining as a final results an improved conductivity of the QDs. Red PeLEDs bearing such type of PeQDs showed near unit PLQY wtih an EQE equal to 26.04%.

Moreover, also the stabilization of the crystal lattice of perovskite is important to increase efficiency and stability of PeQDs. The halide-based perovskite still suffer from a "soft" ionic lattice that rendering them more sensitive to light, moisture and polar solvents as compared to the perovskite oxides. As an example, under continuous optical irradiation mixed halide perovskites tend to undergo severe halide phase segregation. Recently the introduction of fluoride within the perovskyte lattice was demostrated to be a valid method to increase efficiency and stability of PeQDs. Beacuase of its high electronegativity, fluoride atom generates strong ionic interactions, stabilizing the crystal lattice and also passivating the surface defects, increasing both efficiency and stability of the corresponding blue, green and red PeLED.[38]

Concernig the fabrication method of PeLEDs, it is very interesting to note the emerging of the template-assisted synthesis method, by using a pore allumina membranes with ultra-small pore size (6.4 nm) it was possible to realize Perovskite Quantum Wires (PeQWs), acting the allumina as capping material in place of organic ligands (see Figure 2). With this methodology large area PeLEDs with outstanding efficiency for blue and sky-blue were obtained (12.41% and 6.49% respectively), being remarkable also the EQE for green (26.09) and pure-red (9.97%).[39]
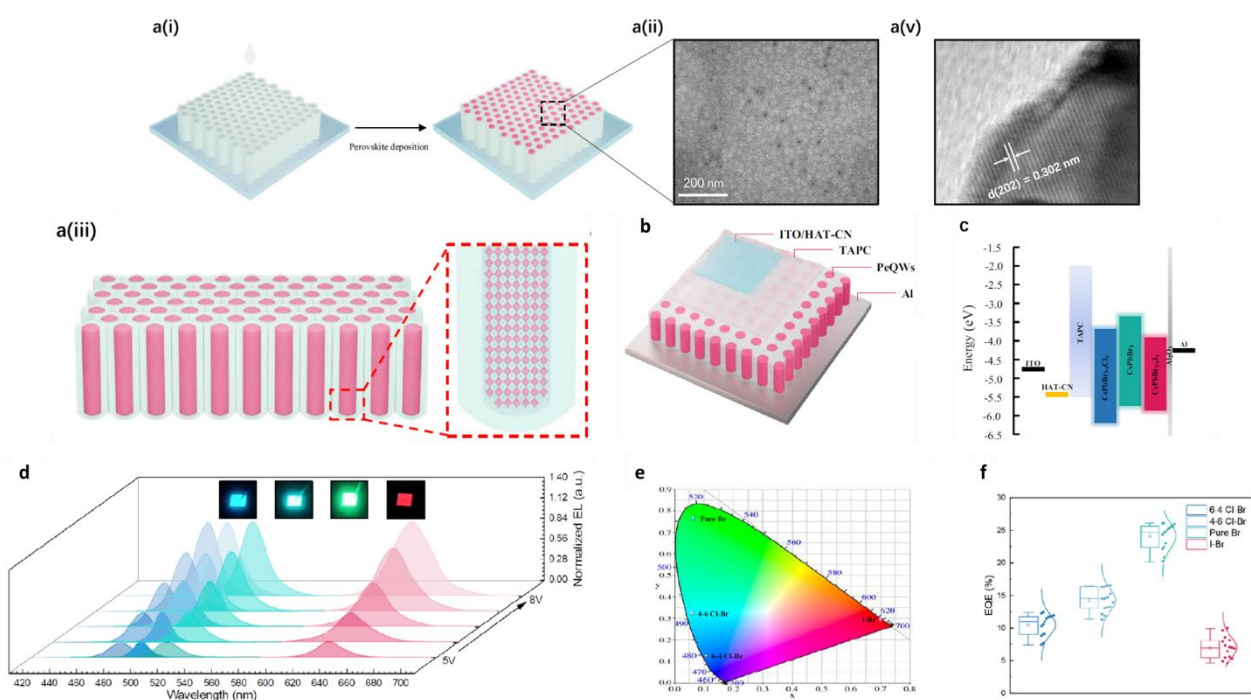
Figure 3 Graphic representation of Perovskite Quantum-Wires LEDs (a(i) and a(iii)) with respective top view SEM and cross-sectional TEM images (a(ii) aand a(v)). PeLED device stack (b) with respective energy band-gap-alignement (c). Electroluminescence spectra at different electric biases for blue, sky-blue, green and pure-red PeQWs-based LEDs (d) with the corresponding CIE coordinates (e). EQE of each device (f). Reproduced from reference [39]

In conclusion, since the kinetic and thermodynamic aspect that govern the formation of PeQDs are similar to those observed for Perovskite film and also present comparable problematic concerning the crystal stability, most of the previous discussed materials or methodologies used to increase efficiency and stability of perovskite nanocrystals could be also used and tested in the perovskite-based solar cells.

2.3 Perovskite Detectors

Undoubtedly the most relevant aspect of the Perovskite-based detector concerns the synthesis of perovskite single-crystal (Pe-SCs) scintillator for X-ray detection. The possibility of having an ordered crystal lattice of different stoichiometry with, in principle, fewer defects respect to the poly-crystalline perovskite film, is the most intriguing and interesting feature that have to be taken into consideration also for PSCs.

Nevertheless some issues have still to be solved. First of all the different synthetic methods adopted so far (temperature cooling crystallization (TCC), inverse temperature

crystallization, antisolvent vapor-assisted crystallization (AVC), solvent evaporation crystallization (SEC), liquid-diffused separation induced crystallizatio and Bridgman growth method, allowed the realization of quite large-size crystal (in the mm to cm range) expecially with the Bridgam growth method, but they are very time-consuming, and an extremely fine control over the synthetic variables (temperature-dependent solubility variation of the starting reagents, solvent evaporation and diffusion rate, temperature fluctuations) are required to obtain a good quality single-crystal.[40]

At the same time the quality of single crystal can be affected by the same intrinsic problems observed for the polycrystalline films, e.g. the intrinsic structural instability of the iodide-based perovskite soft-nature crystal-lattice and the subsequent instability towards halide migration, water sensitivity and iodide to iodine oxidation.

To fix these issues an already known strategy, also used in polycrystalline perovksite film, is the synthesis of mixed-halide perovskite, such as $FA_{0.85}MA_{0.1}Cs_{0.05}PbI_{2.55}Br_{0.45}$ SCs (FAMACs)[41] to gain in thermal stability, suppress the ion migration and reduce the trap density, but a real novelty comes from the so-called metal-free perovskite (MFPs) single crystal,[42] where the B-site metal (e.g. Pb^{2+} or Sn^{2+}) is replaced with NH_4^+ or Cs. In these structures the selection of organic cation and halide capable to strenghtening the hydrogen bond[43] and the partial or complete halide substitution with pseudohalide[44] (PF_6^-) are the new strategies adopted to obtain higher structural stability and to reduce/eliminate the halide migration respectively. These two approaches, to some extent, can be also adopted to realize perovskite single-crystal for photovoltaics.

To date one of the main drawback of perovskite SCs is related to its use into real operating devices, to do that it is necessary to select an appropriate interface transport layers to regulate the carrier transport and suppress the reverse injected carrier, for such a reason, for the future, it is paramount of importance to monitor the developments of new manufacture techniques to integrate them onto the different functional substrates, this is the main direction to follow for possible use of perovskite-SCs also in the photovoltaic technology.

3 EMERGING PV

The increasing interest towards the chalcogenide as new materials for photovoltaic application is undoubtedly ascribable to their distinct physicochemical properties. Band-gap

tunability, higher thermal stability respect to the halide-based perovskite, resilience against advanced weathering conditions (moisture, oxygen, and UV light) and higher defect tolerance are just some examples.[45,46]

In addition to these features, the necessity to use non-toxic components and more earth abundant resources makes the chalcogenide a desirable material for the green energy production, following the criteria of the circular economy.

CdTe and Cu(In, Ga)Se$_2$ (CIGSe) has resulted in considerable advances in thin film photovoltaic performance (20-22% PCE), however, some doubts concerning toxicity and the scarcity of constituent elements in CIGSe/CdTe absorber still persist, so that materials based on less toxic and more abundant elements are emerging as appealing alternative. This is the case of chalcogenide based on Zn, Cu and Sn having kesterite structure, naming Cu$_2$ZnSn(S, Se)$_4$, (CZTSSe).[47] One of the main problem of solar cell devices realized with this material is the important V$_{oc}$ loss due to numerous secondary phases and defects. This is thought to be mainly due to the Sn loss during selenization process, so recently, by tuning the selenium partial pressure during the deposition process, it was possible control the phase evolution of kesterite obtaining high-crystallinity films with fewer defects and no secondary phase, whose use in a final device allowed to reach 13.8% efficiency.[48]
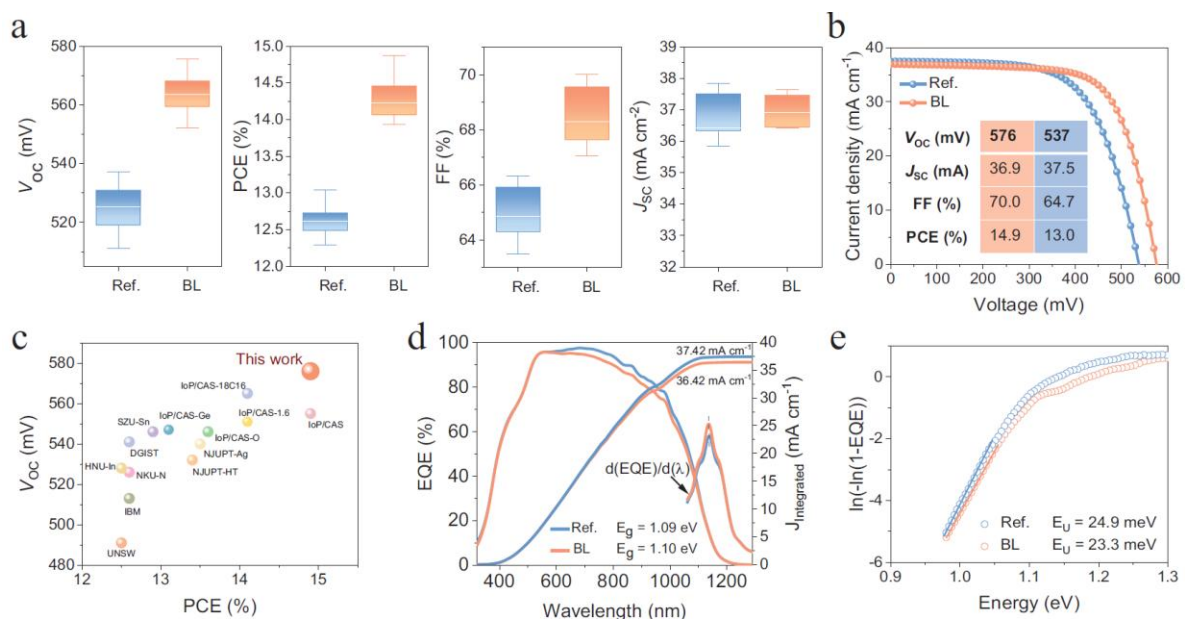

Figure 4 a) Statistical parameter box plots of the Ref. and BL devices. b) J–V curves of the Ref. and BL champion devices. c) Comparison of the state of-the-art works published in recent years. d) EQE curves, integrated JSC, and Eg of Ref. and BL devices. e) EU of CZTSSe solar cells calculated from the EQE spectra of Ref. and BL devices. Reproduced from reference [5]

In other cases, the V_{oc} loss seems to be dependent on the Cu diffusion towards $Mo(S,Se)_2$ layer, causing phases and defects. In this case, the introduction of a blocking layer allowed to reach the highest efficiency so far equal to 14.9%.[49] (see figure 4)

The interface problems of kesterite-based solar cell were also addressed by a post-treatment strategy adopting Rb^+ ion and thiourea during the chemical bath deposition (CBD) of CdS interlayer.[50] The coordination between Rb^+ ion and thiourea during CBD has the double effect to passivate the Se defect promoting a better epitaxial growth of CdS and can also improve iob-by-ion deposition of the CdS layer. The corresponding CZTSSe flexible solar cell realized in such a way showed a very high efficiency for flexible device, equal to 12.84%.

Under this scenario the CZTSSe chalcogenide seems to be a very promising material to implement in heterojunction perovskite-based solar cell.

$Sb_2(S,Se)_3$ is another interesting chalcogenide largely studied for photovoltaic applications. The best efficiency obtained so far is 10.75%, it is achieved by using a novel methodology for the film deposition: the solvent-assisted hydrothermal deposition (SHD), where ethanol was used as cosolvent with water.[51] The addition of the organic solvent slows down the kinetic of the film deposition, resulting in more suitable features, such as large grain size, smooth surface, and proper bandgap, also reducing the defect density.

Noteworthy this material is also one of the first to be employed as ETL in tin-based nip type perovskite, boosting the efficiency from 6.98% to 11.78%.[52] The underperformance of nip-type tin-based perovskite solar cell is largely due to the indiscriminate use of metal oxide electron transport layers originally designed for nip-type lead-based perovskite solar cells. This low performance is caused by oxygen vacancies and deeper energy levels in metal oxide the tin-based perovskite solar cell. The use of $Sn(S_{0.92}Se_{0.08})_2$ ETL seems to circumvents the oxygen molecules desorption and impedes the Sn^{2+} oxidation boosting in such a way the device efficiency.

In conclusion, $BaZrS_3$ is another example of chalcogenide with high potentiality for solar cell application. Its band-gap (1.7 eV) is not optimal for single junction device, but Sn doping can modulate this value in structure type like $BaZr_{1-x}Sn_xS_3$, computational studies show theoretical efficiency as high as 20%.[53]

4 OUTLOOK

Notable technological advancements beyond Pb-perovskites for solar cells including other applications such as detectors and LEDs were made in the recent months and are witness to the continuous improvements in thin-film technologies. The market dominance of silicon PV is unaltered, but several companies have now started investing heavily into perovskite-based single junction and tandem devices in combination with silicon, but also perovskite-only or in conjunction with CIGS. This goes in line with many technologies having a comparable learning curve w.r.t. effort in R&D (Figure 6).
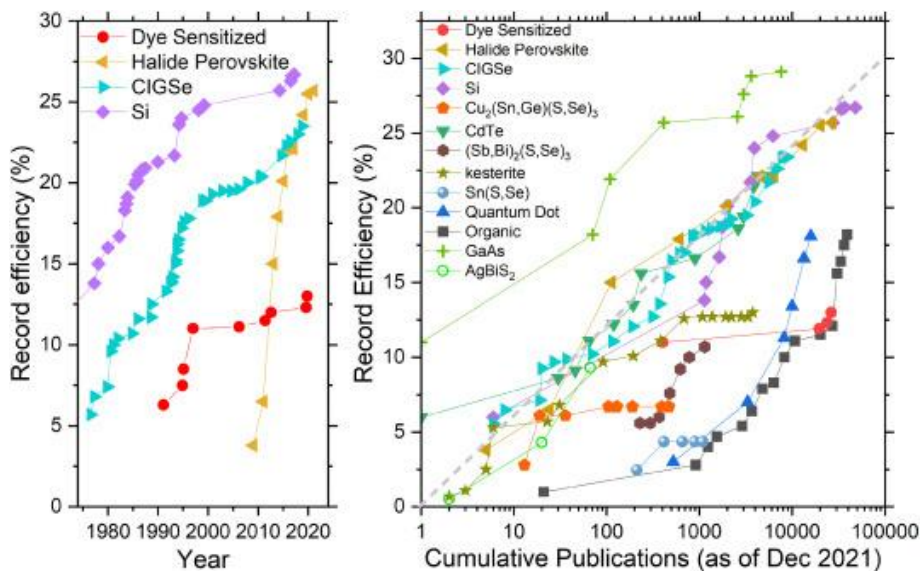

Figure 6: record efficiencies for a few selected PV technologies vs. year (left) and vs. the cumulative number of publications (right) . Reproduced from [1]

It is important to note that all the mentioned technologies that are on the brink of commercialization or already commercialized fall onto this "standard" learning curve, while other technologies, that failed in the market, usually fall below. An interesting new contendor we mentioned above are cells based on $AgBiS_2$, with a few tens of publications recorded as per end of 2021 and more since, as outlined above. With prospective higher performance than single-junctions the tandem architecture will likely penetrate mass markets in the next two decades. Projections indicate that initially perovskite/silicon tandems will dominate, leaning onto the large production capacity of silicon, where the perovskite top-cell can be considered a relatively easily adapted add-on to the production line. Despite this, the fast

development of the all-thin-film technologies in recent years may impact the composition of the market shares in the years to come and other markets in the IoT sector are offering new avenues for commercialization with less strict reliability requirements.

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