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Emerging Photovoltaic Technologies and Eco-Design—Criticisms and Potential Improvements

Nicole Mariotti, Matteo Bonomo and Claudia Barolo

Abstract

An efficient waste management for emerging photovoltaic (PV) technologies is not mature yet. The problematic aspects along with the possible failure's identification have a pivotal role in modelling the future end-of-life management strategies. The identification of substances of concern (e.g. high cost, low availability, and high toxicity) and valuable materials is a key point to better define the research priorities to improve the eco-design of these technologies. The ultimate goal is to promote the disposal processes which enhance the repair, refurbishment, and recover opportunities and so the profitability of recycling. These studies can also prompt the investigation of innovative materials which are more cost-effective and/or coming from renewable resources or secondary raw materials. Forecasting the waste management technologies for the emerging photovoltaics is highly challenging. In this context, our purpose is to provide an overview of the critical elements and understand the appropriate corrective improvements towards more sustainable technologies.

Keywords: sustainability, environmental impact, emerging photovoltaic technologies, life cycle assessment, recycling, disposal, organic photovoltaics, dye-sensitised solar cells, perovskite solar cells

1. Introduction

We must recognise that overpopulation is the main environmental issue, the main cause of the unsustainable depletion of our planet. The correlation between overpopulation and environmental concerns can be completely understood through the definition by Ehrlich et al. [1].

When is an area overpopulated? When its population cannot be maintained without rapidly depleting non-renewable resources (or converting renewable resources into non-renewable ones) and without decreasing the capacity of the environment to support the population. In short, if the long-term carrying capacity of an area is clearly being degraded by its current human occupants, that area is overpopulated.

Recently, some studies [2, 3] confirmed that human population planning (anti-natalist policies) cannot stop the enormous environmental crisis that we are facing

nowadays. Indeed, a prompt and effective solution should be found in technology and through the improvement of resources and waste management.

Energy production is for sure at the top of the list of the most polluting activities in the whole planet. For this reason, environmental concerns are strengthening the interest in the alternative energy research field that started already during the 1970s energy crisis. The energy transition should intimately deal with the implementation of new infrastructures, the promulgation of adequate policies and the gradual conversion of a system that has been based on oil for more than 150 years [4].

In the context of energy production, one of the most promising alternative sources to fossil fuels is solar energy. Indeed, the energy supplied by the sun irradiation over 1 year is roughly 10,000 times higher than the world's current rate of energy consumption [5]. Starting from the first photovoltaic (PV) technologies based on silicon, the researchers developed a plethora of different materials and devices looking for higher efficiencies and performances. Nevertheless, the design of a new technology cannot be set up only on efficiency and performance improvements but also the sustainability of the product must be considered. Starting from this assumption, it becomes more and more important to examine the following aspects when a new technology is studied: (i) the energy consumed for its production, (ii) the kind of resources and materials exploited, (iii) the waste produced during the production and use phases, (iv) the energy produced/energy consumed ratio and (v) the end of life of the product. It is worth mentioning that these aspects are not only strictly related to environmental issues but also to the high dependency of countries on resources, the critical problem of waste accumulation and the increasing cost of waste disposal—these are also economic and sociologic issues to be seriously addressed. The increasing demand for raw materials and the waste accumulation can be partly mitigated through the recycling and the identification of secondary raw materials. This is particularly important for those materials defined as Critical Raw Materials (CRMs), that is, materials that are characterised by supply risk and economic importance (Figure 1).

A very powerful tool to analyse how sustainable is a product or a service is the *Life Cycle Assessment (LCA)*; this helps to evaluate the environmental impacts of a

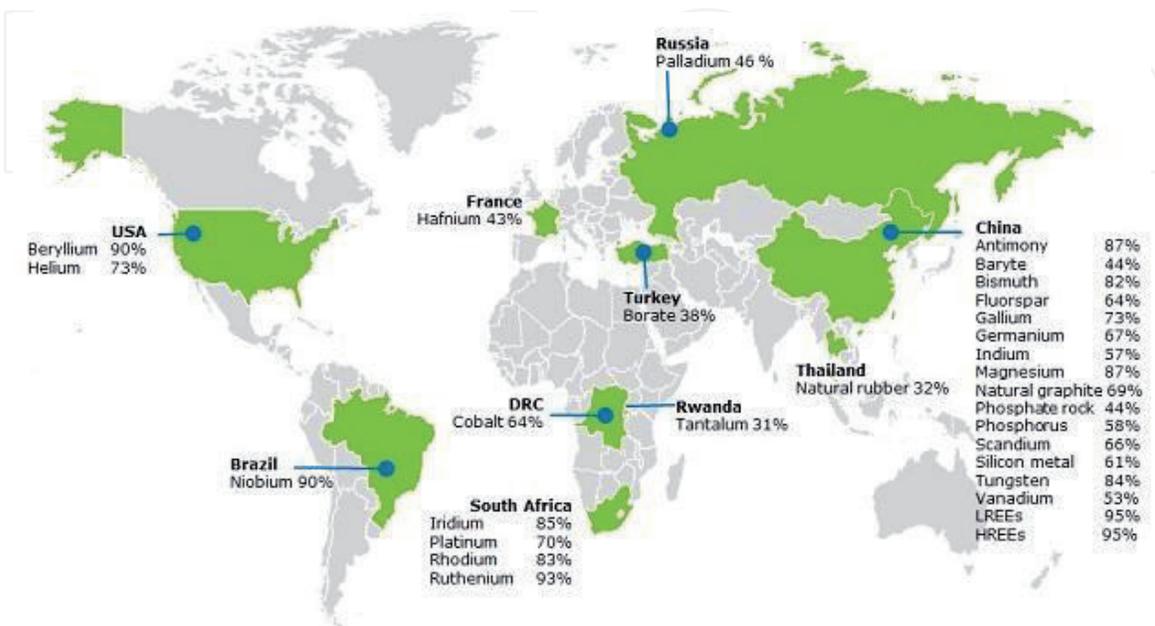


Figure 1. Countries accounting for the largest share of global supply of CRMs [6].

product life-cycle in all its parts. In early technology development stage, an LCA can give an overestimation of the energy consumed; it is important to underline that laboratory instruments are not completely conceived for a specific synthesis or process. However, it could be of great relevance—it has been indeed recognised that 70% of a product's environmental impact is determined in the design and development stage [7, 8]. The life cycle assessment can have either a cradle-to-gate or a cradle-to-grave approach. The former allows to outline the environmental profile of a product, process or service from the raw materials extraction to the factory gate (the use phase and disposal phase of the product are omitted in this case); the latter considers the whole process, from the raw materials extraction to the disposal phase [9].

In this chapter, many LCA works have been analysed to assess the sustainability of emerging PV technologies. There are many variables in life cycle assessment; any study can consider a different functional unit, a different efficiency and a different life-time of a device. Hence, it is recommended to check the referenced LCA works to have a better comprehension of the boundaries and limitations of the studies as it was not possible to give all the details in the body of this work.

2. Emerging PV technologies—critical aspects and potential improvements

Although the energy generated by silicon PVs is quickly approaching, the price of traditional sources (such as coal) and the market prices of silicon are decreasing (0.30 \$ W/peak [10]), the interest on emerging PVs is still present. These technologies exhibit a plethora of advantages: lower materials cost, easy manufacturing, flexible and light modules, less energy and mass requirement in the production with a subsequent decrease of the overall environmental footprint.

In the field of solar energy conversion, emerging technologies include Organic Photovoltaics (OPVs), Perovskite Solar Cells (PSCs) and Dye-Sensitised Solar Cells (DSSCs). In the following sections, an analysis of the critical aspects of each class of devices will be presented in order to highlight weaknesses and failures and to identify the corrective measures to apply to build more sustainable PVs. Disposal perspectives will be investigated as an efficient waste management is not mature yet. In this context, it is worth mentioning that the studies considered hereafter mainly concerns laboratory-scale device. Yet, the strategies highlighted could be feasibly extended on larger scale too.

2.1 Organic photovoltaics

Organic photovoltaics are a promising technology as it offers the advantage to have light, easily printable and scalable, thin and flexible solar panels [11].

Organic solar panels are usually structured as follows:

1. A flexible polyethylene terephthalate (PET) substrate on the light collecting side;
2. A transparent conductive oxide (TCO), usually indium tin oxide (ITO) or fluorine-doped tin oxide (FTO), as electrode
3. An active layer usually made of a [6,6]-phenyl-C61-butyric acid methyl ester:poly-3-hexyl-tiophene (PCBM:P3HT) mixture behaving as electron transport layer (ETL)

4. A hole transport layer (HTM) usually based on a PEDOT:PSS system but also MoO_3 can be used
5. An aluminium back electrode covered by a thin layer of lithium fluoride
6. Sometimes, a second PET layer could be employed to cover (and straightforwardly protect) the entire device.
7. Epoxy resins as sealant material
8. Interconnections made of a silver paste

The configuration of the devices can be of two different types: the single- and multi-junction system. The former is a single p-n junction while the latter has more than one p-n junction leading to better efficiencies but requiring a higher amount of materials coupled to more elaborated production processes (**Figure 2**).

OPVs usually exhibit lower efficiency and shorter lifetime compared to silicon panels, but they always show lower cradle-to-gate life-cycle impacts [11]; OPV panels can save around one-sixth and one-fourth of the cradle-to-gate energy consumption compared to m-Si and a-Si (monocrystalline and amorphous silicon) panels, respectively [12].

Even if OPVs show higher environmental efficiency with respect to the more diffused silicon technologies, some failures have been determined.

PET, that is used both as a substrate and encapsulant, is a non-biodegradable polymer under environmental conditions. Even if it is not considered to be directly toxic, PET can be dangerous for the environment and can show ecotoxic issues when it is broken into small particles (diameter smaller than 5 mm) [13]. If so finely dispersed, it can reach organisms through the food chain. It has also been demonstrated that PET particles can sorb other persistent organic pollutants and, straightforwardly, these compounds can reach organisms more easily. Photo-degradation is another critical parameter considered in the literature [14]: the natural photo-degradation of PET leads to the formation of both monomer and dimer fragments. Thus, the employment of a stable substrate and enclosing system are essential to have a reasonable lifespan. Bio-plastics (such as PLA) have been considered to be adopted instead of PET, but even if they present a better LCA, their mechanic stability is not good enough. Straightforwardly, it is compulsory to design a configuration such as the persistent materials (not bio-degradable) can be easily recovered and then recycled [14]. In particular, PET recovery can be performed only through an efficient delamination process. In this context, it is necessary to identify the best encapsulant material that can be thermally or chemically separated from

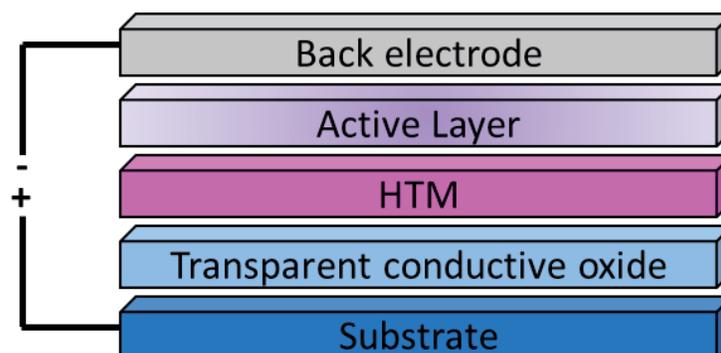


Figure 2.
General structure of an OPV device.

the substrate. It should have a different solubility or a melting point lower than the other device components. As far as we are aware, nowadays, researchers are focused on various features of an encapsulant such as chemical inertness, water vapour transmission rate (WVTR) and oxygen transmission rate (OTR), but recycling or recover perspective are not considered yet [15].

ITO, applied as conductive coating on the PET substrate, tends to etch by air and water becoming then a pneumo-toxic entity and a strong reactive oxygen species (ROS) producer when it is in its nanoparticulate form [16]. Further studies are still necessary to understand the fate aspects of ITO in the environment, but its behaviour should be more carefully investigated to highlight potential criticisms. The presence of indium, that is a CRM lead to focus the attention on the recovery of this material. Alternatively, efforts should be made on the research of similar but more environmental friendly, for example, FTO [14]. Nevertheless, FTO is defined as a hotspot in a cradle-to-grave OPV LCA too [11].

A meaningful focus on the active layers has been carried by different studies [14, 17, 18].

Zimmermann et al. [14] focused their attention on the degradation and the ecotoxicity of PCBM/P3HT active layer. The results show that P3HT is degraded by a radical building process. The formed compounds can be oxidised, and this reaction is found to be responsible for the degradation of the organic polymer layer. Although ecotoxicity data for P3HT are not available, they suggested to investigate the potential degradation in small pieces similarly to what happens with PET. The second component of the active layer is the fullerene derivative PCBM. Fullerenes' toxic effects have been thoroughly discussed in the literature [19, 20]: they exhibit acute toxicity and can sorb pollutants making them more bioavailable. These studies focused on fullerenes and not on their derivatives, such as PCBM. Therefore, further critical analyses on these compounds are essential to assess their fate and their ecotoxicity [14]. Very interestingly, Tsang et al. [11] reported a comparison between the OPV based on PCBM/P3HT and completely polymeric OPV (i.e. changing PCBM with an n-type polymer) showing that the latter is slightly better for some impact factors than the former one. In particular, an all-polymer-based device exhibits a water depletion factor lower (-12%) compared to the counterpart based on PCBM/P3HT. The substitution of the fullerene derivative with an n-type polymer has been suggested from the results of previous studies that identified PCBM as an important factor in the increase of the Cumulative Energy Demand (CED) component [17, 21–24]. CED is defined as an energetic indicator that quantifies the whole energy required during the life cycle of a product. It is obtained summing up both the direct energy (e.g. electricity) and the indirect energy (embodied energy of materials) contributions [25].

The investigation of 15 different materials implemented as active materials in OPVs showed that fullerenes and their derivatives (used as electron-acceptors) have the highest CED in a cradle-to-gate LCA [17]. On the other hand, electron donor materials, such as polymers or small molecules, affect less sensibly the total cradle-to-gate CED. A deeper analysis on fullerenes showed that functionalized ones have a higher CED than the native counterparts, while the indene-C60 bis-adduct (ICBA) derivatives present a CED 40% lower than C60-PCBM and C70-PCBM. This behaviour can be explained by the fact that ICBA derivatives have a simpler reaction scheme that results in a lower number of synthetic step; in this way, the purification steps and the use of solvents are decreased. Fullerenes in any case have an embodied energy one or two orders of magnitude higher than the common semiconducting polymers [17]. The semiconducting P3HT is the polymer with the lowest CED because the number of steps for its synthesis is relatively lower; generally, the doubling of the number of steps lead to a 10-fold increase in the CED. Block

copolymers, such as PCDTB and PTB7, have a higher embodied energy but they show a lower CED with respect to fullerenes.

Interestingly, phthalocyanines and squaraines can be used in place of electron-donor polymers and have been thoroughly examined [17]; comparing these two classes of molecules, they show very similar CED except for the PdPc that has a higher embodied energy due to the Pd extraction. These small molecules compared to polymers showed a similar CED.

The embodied energy of polymer-based devices is mainly due to the intrinsic energy of materials while for the small molecule-based cells to the processing conditions (i.e. fabrication step). For this reason, multi-junction small molecule-based devices are energetically convenient compared to mono-junction. Indeed, for small molecule-based devices, the process to build a multi-junction device requires almost the same energy compared to a mono-junction, and the increase in the amount of required material does not sensibly affect the CED.

The hole transporting layer (HTL), usually made of a composite of PEDOT:PSS or MoO₃, contributes in a very minimal way to the overall CED. In particular, Anctil et al. [17] reported that, concerning PEDOT:PSS, the solvent used for the deposition is the main energy increasing factor. The interfacial layer can be also responsible for the device degradation. PEDOT:PSS is an hygroscopic material, and it is quite sensitive to oxidation reactions; this could cause an extremely fast degradation of the organic panels. PEDOT materials, in their particulate form, showed cytotoxicity, ROS production, apoptosis, and necrosis [26]. Such as for ITO, particular attention must be paid to a potential dispersion in water.

Finally, considerations about the use of silver must be done. Silver is one of the main responsible for resource depletion and freshwater eutrophication [14]. Espinosa et al. [27] carried out a cradle-to-grave (from the materials supply to the end-of-life) LCA of an organic solar park. They compared three different end-of-life scenarios: recycling, incineration and an average local mix. The results showed that the recycling scenario is favoured mainly because of PET and silver recovery.

Silver should be recovered or replaced by a non-metal electrode and bio-based electrode materials or production from waste should be considered. Alternative materials such as carbon, copper and aluminium have been studied, and the environmental impacts were proved to be the lowest for carbon-based modules [28]. The recovery of silver is of great importance also to avoid soil contamination. As a matter of fact, when a damaged panel is in contact with soil, the silver release is highly enhanced [18].

If the balance of system (BOS), consisting of mounting-structure, inverter and cables for electrical installation, is considered into the LCA of OPVs, the results showed that BOS is what affects more the apparatus impacts. On the other hand, the a-Si impacts depend more on the contribution from the panel itself. This shows that the eco-design should be more focused on the BOS improvement in OPV technologies. The contribution of BOS allowed to state that, generally, if the efficiency of the device decreases, the impact is higher; this relation depends on the increasing contribution of the background system [11, 27].

Organic photovoltaics show many advantages not only for their functionalities but also for an environmental point of view. They generally show better environmental performances than Si-PV and also lower Energy PayBack Time (EPBT) and Carbon PayBack Time (CPBT) compared to m-Si.

The EPBT is expressed in years and quantifies the time that the system takes to generate the same amount of energy used in all production processes [9]. The CBPT is the ratio between the CO₂-equivalent emissions during the life-cycle of a PV panel and the CO₂-equivalent emissions of a conventional grid for the same kWh produced by the panel [11].

The factor that usually affects the impacts in a negative way is the too short lifetime of these devices. Thus, the increase in the lifetime of the panels is a feasible strategy to decrease their impact [11]. It is worth remembering that PET, PEDOT:PSS and P3HT are not fully biodegradable.

It could be interesting to re-think the OPV design in order to improve the recyclability and the biodegradability in environmental conditions of its components. The external apparatus should be resistant and durable during the use-phase and recyclable at its end of life; the internal materials that are often mixed or difficult to separate should be degradable when they reach the environment. Obviously, this is necessary if the risk of leaks is present, otherwise they can be collected and degraded in the suitable plants with adequate conditions.

The eco-design of a product is always a challenging perspective but it is what the paradigm that outlines the rules for a more sustainable economy dictates [29].

2.2 Dye-sensitised solar cells

Dye-sensitised solar cells (DSSCs) were invented by O'regan and Grätzel in 1991. A typical DSSC device consists of (**Figure 3**):

1. A transparent anode made of glass coated with a TCO (usually ITO or FTO)
2. A mesoporous TiO_2 layer
3. A monolayer of dye adsorbed onto TiO_2
4. An electrolyte
5. A glass cathode coated with a catalyst (usually Pt)

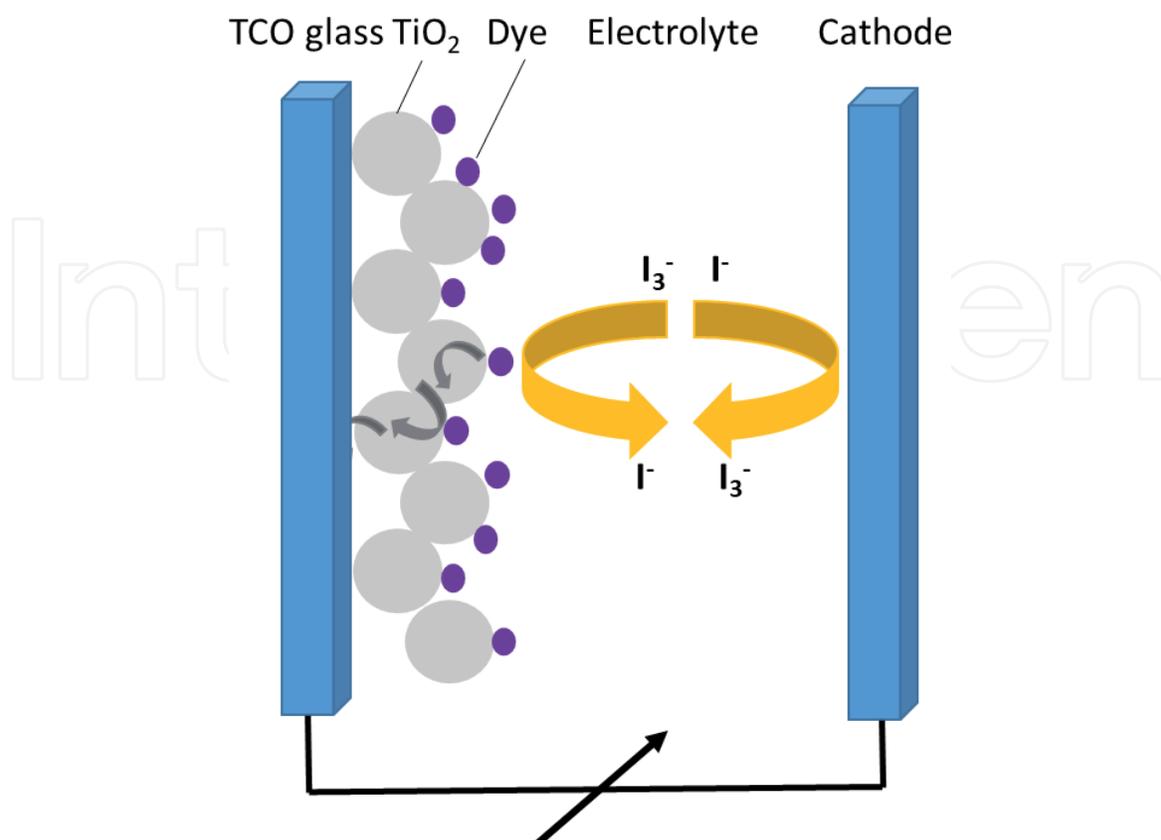


Figure 3.
Schematic diagram of the dye-sensitised solar cells.

When exposed to the sunlight, dye electrons are excited, and they are injected into the mesoporous material (titanium dioxide). Electrons move from the mesoporous layer to the anode and then into the circuit reaching the cathode. At this point, electrons are used to close the cycle: the electrolyte is reduced by the electrons coming from the circuit and in turn it re-reduces the dye that can be excited again [30].

The traditional electrolyte used in DSSCs is an organic solvent-based liquid electrolyte, usually iodide/triiodide (I^-/I_3^-) redox couple. It has been observed that this redox couple, usually dissolved in acetonitrile, is one of the main factors that affects the device lifetime [31]. In particular, the leakage of the solvent, evaporation of volatile iodine ions and corrosion are the dominant causes of damaging. In view of this fact, alternative redox couples [32–34] and different phases for the electrolytes have been investigated.

Among the alternative redox shuttles, the best performances have been obtained with cobalt complexes [31]. Cobalt is defined as a CRM in Europe: it is principally mined in the Democratic Republic of Congo that is a politically sensitive region. In 2017, the Financial Times reported the necessity to investigate the ethical issues regarding cobalt mining [35]; the establishment of the Cobalt Institute “promoting the sustainable and responsible use of cobalt in all forms” says a lot about the urgency to regulate the supply and use of this element. It should be clear, that this element, nowadays is mainly used in rechargeable batteries, is not a good candidate for a sustainable photovoltaic device.

Liquid-state electrolyte drawbacks can also be overcome through the implementation of quasi-solid (gel) and solid-state electrolytes [36]. Quasi-solid electrolytes are obtained by the entrapment of the liquid electrolyte into polymeric or inorganic networks. They present the best trade-off between efficiency and durability [37]. On the other hand, solid electrolytes exhibit a lower efficiency but the advantages of solid phase materials. Generally, solid materials are safer because they prevent leakage and evaporation; therefore, emissions and inhalation are avoided. Solid-state electrolytes also guarantee a better mechanical stability and simplified fabrication processes. In order to obtain such a geometry, the liquid electrolyte is replaced with an inorganic p-type semiconductor [38] or an organic hole transporting material [37].

Keeping the phase unchanged (i.e. liquid electrolytes), it is worth to mention both room temperature ionic liquids [39] and aqueous DSSCs [36]. Room temperature ionic liquids have been suggested mostly as a solution for the high volatility of organic solvents in liquid electrolytes. These molten salts are chemically and thermally stable, and they do not present inhalation and emission issues, due to the low vapour pressure (low volatility) and flammability hazards. Anyway, ionic liquids are controversial materials from a green chemistry point of view: on the one hand, they are really stable and safe, and on the other hand, they are not completely sustainable from a synthetic point of view and for their recovery [40, 41]. Very recently, deep eutectic solvents (DESs) have exploited as a valid and completely green alternative to ILs [42, 43].

Aqueous DSSCs have also been studied in order both to avoid all the negative effects of the organic solvents and to build a solar cell that is inherently thought to work in the presence of water moisture [36]. In fact, some studies [44–46] showed that water is a detrimental factor for DSSCs. Instead of performing laborious processes to avoid water penetration, researchers tried to build partially or fully aqueous solar cells [47, 48]. Water is considered to be the greenest solvent as it is safe, not-flammable and non-toxic but attention must be paid to a couple of aspects when water is considered. The first one is that fresh water is a limited resource

[49, 50]; as reported by Shiklomanov [49] and USGS [51], fresh water resources are just 2.5% of total water amount present in the world and only a small part is really available. This means that available water is less than the aforementioned 2.5%. The second significant point to stress is that any impurities or contaminants released in aqueous waste streams will, by their nature, readily find their way into aquifers, enhancing the risk of human exposure. Water is inherently a safe substance, but its precious value should be recognised. The transition from an organic solvent to water, especially when organic molecules are involved, has its own barriers. Initially, chemists have put their efforts either in the optimization of aqueous DSSCs using traditional electrolytes and dyes or in the investigation of not-fully aqueous (mixture of water and organic solvents) electrolytes [52]. Nowadays, the major trend is to re-think completely the chemistry aiming to completely aqueous DSSCs, using, for instance, surfactants [53]. It is still worth highlighting that water displays many attractive features as a solvent, but it is not without its own set of problems though.

LCA studies on dye-sensitised solar cells assessed that the main contributor to energy and environmental impacts is the coated glass [9, 54, 55] due to the high consumption of energy during the production and its preponderant presence with respect to the total mass.

Comparing three different dyes, Parisi et al. [9] found out that N719, a ruthenium-based dye is one of the main contributors to many cradle-to-gate impacts such as metal depletion, marine and freshwater ecotoxicity. The other two investigated sensitizers are D5, an organic metal-free dye and YD2-o-C8, which is a zinc-based porphyrin. The latter two dyes show lower impacts in all impact categories except for the ozone depletion parameter, mainly due to the massive use of solvents throughout their synthesis. As a further focus on these dyes, CEDs was carried out: N719 owns the lowest CED value compared with the others. This factor can be explained by the fact that the Ru-based dye (and straightforwardly its synthetic pathways) is the most optimised one. Anyway, for any dye, the total CED is mainly attributed to the embodied energy of raw materials and, to a minor extent, for the energy needed for the synthesis. Optimisation of synthetic processes for other kind of molecules can lead to better LCA results.

Even if ruthenium-based dyes require less energy and show lower impacts, attention on the scarce material ruthenium must be paid. In 2017, the European Commission defined ruthenium as a CRM as its supply is concentrated in South Africa and it presents low substitution and low recycling rates [37]: this statement strengthens the necessity of fully organic dyes to avoid the use of rare elements. The CEDs obtained from the LCA show that considering different configurations, the main component that affect the total energy is the embodied energy of raw materials and not the energy consumed during the production process of the device. This result lead to think that is more important to choose less energy demanding materials than improve the manufacturing process.

DSSCs (14.3%) [56] have not reached the efficiency of silicon-based photovoltaics yet. Anyway, their use in smart windows or their indoor application [57] gives the opportunity to this technology to enter the market, in particular in the building-integrated photovoltaics [58]. The added value of DSSCs is that they are not only functional but they also have a pleasant aesthetics.

Finally, it is worth highlighting that DSSCs can achieve further improvements in terms of sustainability through the implementation of nature-based dyes [48, 59], the use of alternative substrates [60], such as paper [61, 62] and the re-design of the devices in order to make them adequate for dye refurbishment. Obviously, these improvements should be coupled to give enough high photoconversion efficiency.

2.3 Perovskite solar cells

The name perovskite was firstly used for the calcium titanium oxide (CaTiO_3) mineral in 1839, named after the Russian mineralogist Lev Perovski. In 1957, Christian Møller discovered that caesium lead halides (CsPbX_3 , $X = \text{Cl, Br or I}$) owned the same structure of CaTiO_3 [63] and found out that they were photoconductive behaving as semiconductors.

An important step towards the development of photovoltaics based on perovskites was made when Weber replaced caesium with methylammonium cations and obtaining in this way an organic-inorganic hybrid perovskites [64]. In particular, methylammonium lead iodide (general formula: $\text{CH}_3\text{NH}_3\text{PbI}_3$) is one of the most implemented materials in PSCs. It is a semiconducting pigment that can absorb light over the whole visible solar emission spectrum. Excitons produced in $\text{CH}_3\text{NH}_3\text{PbI}_3$ dissociates very rapidly into excitons (i.e. free carriers of different sign) and exhibits high carrier mobilities for electrons and holes and also long carrier-diffusion lengths when coupled with efficient Electron Transport Layer (ETL) and Hole Transport Material (HTM), respectively. These properties are responsible for the great potential of hybrid perovskites in photovoltaics. The choice of the different ETL and HTM should be thoughtfully made, because they should be inert towards the Perovskite layer but, on the other hand, they should assure a good electronic matching (**Figure 4**).

The first studies on perovskite solar cells (PSCs) were carried out only in 2009 [65] and since then different types of PSCs were developed as they are promising for their relatively low cost and high power conversion efficiency. These advantages could be eclipsed by the potential toxicity of lead even if many studies revealed that the main environmental impacts are due to the presence of gold (as back contact) and the use of organic solvents throughout the fabrication process [66–68]. For a better understanding of these impacts, a description of PSC modules and an overview of their hotspots will be given.

A perovskite solar cell is usually composed of (**Figure 4**):

1. A glass substrate
2. An ITO or FTO layer
3. A compact layer made of TiO_2 (SnO_2 and ZnO)
4. A mesoporous or compact TiO_2 layer as electron transporting layer (ETL) on the previous layer.
5. Perovskite ($\text{CH}_3\text{NH}_3\text{PbI}_3$) layer
6. A hole transport material (HTM) layer
7. A gold or silver cathode

The most implemented technologies are the mesoporous and the planar structures: the former involves the use as electron transporting material of a compact and a mesoporous layer of TiO_2 , while the latter is composed only of a compact layer (**Figure 4**) of TiO_2 , SnO_2 or other semiconducting metal oxides.

The main point to consider regarding the environmental impact of PSCs is that ITO or FTO glass represents about the 97% of the total mass of the modules; for this reason, the substrate is the main contributor to the energy consumption due to the embedded energy of materials.

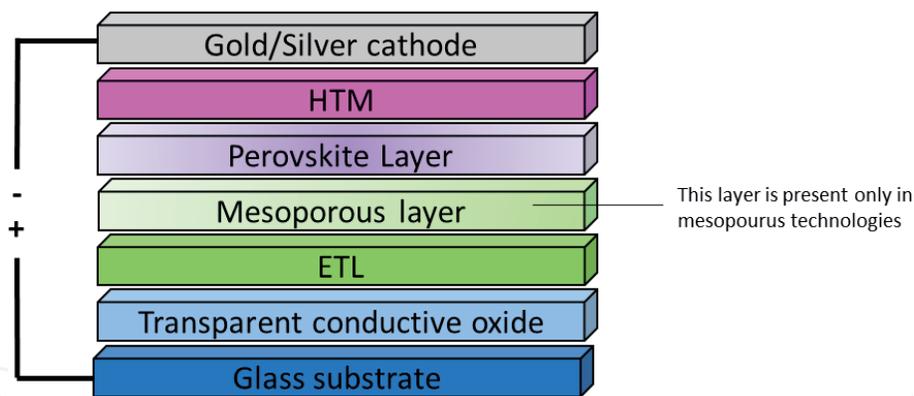


Figure 4.
General structure of a perovskite solar cell.

When gold is used as cathode, the energy consumption is mainly equally distributed between the substrate [ITO (FTO)-glass] and gold. The substitution of gold with silver can decrease not only the energy demand but also the environmental impact: gold is also mainly responsible for eutrophication, fresh water aquatic ecotoxicity, fresh water sediment ecotoxicity, human toxicity, land use, marine aquatic ecotoxicity, marine sediment ecotoxicity, depletion of abiotic resources, stratospheric ozone depletion, and terrestrial ecotoxicity [68]. Deposition of gold is also an important factor affecting the energy demand: its deposition and evaporation under vacuum is an intensive-energy process. Anyway, we have to consider all the issues belonging to silver already cited in the OPV section.

As we already said for the other technologies, ITO glass should be replaced with the FTO substrate since avoiding the use of precious metal (In) improves the environmental impacts of the modules.

Among the TCO/glass and the gold cathode, solvents used to rinse the ITO (FTO) glass and to prepare the perovskite layer play an important role in the environmental impacts. Even if they could be partially recycled, solvents show negative impacts due to the electricity needed in the recycling process; in particular, the solvent recycling exhibits the worst environmental performances for the ozone depletion potential and for the global warming potential [66]. Straightforwardly, the use of solvents should be directly downgraded or greener solvents should be preferred [69, 70].

Since the lead toxicity is of really high concern [71], many studies focused their attention on this element: the impacts of lead derivatives and disposal scenarios have been analysed in detail. Lead can cause irritability, difficulty in concentrating, headache, and anaemia and in higher concentrations (over 100 $\mu\text{g}/\text{dL}$) gives rise to seizures, delirium and even coma [72]. Lead toxicity is well documented, so regulation promoting the gradual phasing out of this substance has been promulgated by EU [73]. The Restriction of Hazardous Substances Directive (RoHS) [73] affirms that the maximum permitted concentrations are 0.1% or 1000 ppm by weight. The restrictions are on each homogeneous material in the product and understanding. If lead halide perovskites are considered homogeneous materials or not is a matter of study. If perovskites were considered homogeneous materials, they would not meet the regulatory restrictions. The regulation is not applied to PVs intended for a defined location (e.g. solar parks) but put limits on portable devices. In this case, where the regulation must be followed, PSCs would not match the 0.1% limit as lead is present in higher concentrations.

Moreover, lead presence could affect consumers' choices as the public opinion owns a solid awareness of lead toxicity raised through historical facts such as Romans poisoning caused by lead present in drinking-water, Goya's and Van Gogh's mental disorder probably due to lead contained in their colours and Kabwe inhabitants poisoned by mining activities.

In contrast to the high concern for lead toxicity, the results reported by Alberola-Borràs et al. [74], Billen et al. [75] and Zhang et al. [66] deserve particular attention. They have demonstrated that the content of Pb in the perovskite contributes to the human toxicity cancer impact category 1–2 orders of magnitude less than the rest of the module components [Glass/ITO (FTO), ETM, HTM and back contact] [74]. Furthermore, the energy used for the manufacturing of panels is the dominant contributor to lead emissions [75]. Zhang et al. highlighted that lead contributes less than 1% to the Human Toxicity Potential (HTP) and Ecotoxicity Potential (ETP). It is possible to conclude that lead is not the factor of main concern for these parameters although the widespread belief.

Commercialization of PSCs is still far to be achieved. This technology presents short life-time, substantial stability issues and lacks scale-up processes and waste disposal strategies. In order to overcome these limits, researchers foresaw and analysed different emissions and disposal scenarios. Alberola-Borràs et al. [74] studied three disposal scenarios for both planar and mesoporous structures. The three considered disposal routes were: (i) inertization and residual landfill, (ii) re-use and residual landfill and (iii) reuse and recycling. For re-use, they mean regenerative cycles suggested from Kim et al. and Huang et al. [76, 77]. As largely expected, reuse strategies reduced the values of all impact category. Additionally, they found that the device with a mesoporous TiO₂ substrate is the one with the largest improvement in all impact categories. This highlights that the mesoporous TiO₂ reuse is of great importance to reduce the environmental impacts, while Pb derivatives recovery does not affect the performances in a significant way.

Billen et al. [75] considered potential lead emissions during the use phase and two different end-of-life scenarios. They proved that the lead emissions are dominated from those produced from the energy production for the manufacturing of the panel itself and of the BoS; indeed, the components that do not include the panel (BoS) are the main contributors. This study analysed a disposal scenario in which no lead release was supposed, and a second case in which lead is completely released in groundwater. They demonstrated that even in the worst case, the toxicity potential is smaller than that one calculated for an offset grid [75].

Although lead toxicity potential concern is minimised by different researches, aforementioned studies highlight the necessity to avoid incidental release, adopting proper encapsulating materials and maintenance measures, as well adequate disposal strategies. Encapsulant should be resistant and stable under environmental conditions but easily removable through solvent dissolution or by thermal decomposition without the production of toxic substances [78]. The recovery of TiO₂ and lead derivatives from the perovskite layer is necessary for an environmental benefit but it is not economically attracting for their relatively small contribution on the cost; specifically, TiO₂ can be substituted with SnO₂ and ZnO; Gong et al. [68] reported that the use of ZnO decreases almost every impact. These studies are performed on data obtained for cells and considered scalable to a module.

On the other hand, the recycling of the TCO/glass is convenient for both an economic and an environmental perspective [79]. Another important aspect to consider is that even if the lead emissions during the use-phase are unlikely (if a proper encapsulating strategy is adopted), the occupational exposure and the chronic exposure to lead must be considered [80].

In light of an industrial development of the modules, electrodes made of noble metals will be not feasible [81]: carbon-based electrodes could be the best available solution. Furthermore, the slot-die coating will be preferred to the spin-coating as a perovskite deposition method as the slot-die coating allows material savings. The deposition methods are not analysed in this chapter because the attention has been focused on the materials to comply the extension of this chapter. In a recent study

about PSC specifically tailored for a commercial purpose, Celik et al. [81] pointed out the fact the most commonly used organic HTM are very expensive and they do not exhibit a good stability. They suggested a copper-based semiconductor CuSCN as inorganic HTM suitable in an industrial outlook.

The results obtained through many LCA analyses [66, 81] also suggest the importance of increasing the energy efficiency, (especially during the thermal deposition methods), of the PSCs manufacturing process as well the need of decrease the quantity of solvents used.

Substitution of lead with less toxic materials is one of the main challenging purposes for different reasons: (i) the elimination of a cause of concern due to the toxic metal, (ii) the facilitation of the market entry of this new technology also due to the consumer scepticism towards devices containing lead and (iii) the removal of administrative barriers built by the European Union (EU) regarding hazardous materials.

In this way, tin has been suggested as a solution. Nevertheless, it does not seem to be a promising solution. It exhibits ecotoxicity and global warming potential factors higher than lead impacts [53] and, additionally, it is a metal with a low substitution potential. Additionally, its low distribution in the world (Peru, Indonesia, China), which could lead to supply disruption, is dramatically remarkable. Tin is also more expensive than lead, so it could result in a less sustainable PV technology from an economic point of view. Moreover, this evidence is coupled with sensible lower photoconversion efficiency assured by tin-based PSC [64].

Lead is considered an issue for its intrinsic toxicity, but many studies have demonstrated that lead present in PSCs is not the main contributor both for lead emission potential and toxicity potential. Once that the risk and the intensity (lead emission potential) of lead are proved to be admissible, R&D should invest in improve stability, energy efficiency in manufacturing and waste management strategies.

3. Conclusion and perspectives

Organic photovoltaics (OPVs), dye-sensitised solar cells (DSSCs) and perovskites solar cells (PSCs) show promising results regarding costs and environmental performances compared to silicon-based PVs. OPVs and DSSCs still present low efficiencies while PSCs show efficiency values comparable to silicon-based devices.

All the technologies described in this chapter exhibit stability issues and short life-times—the resolution of these drawbacks can only further improve the environmental performances. Pursuing the target of more sustainable emerging photovoltaics, we focused our attention on those that are identified as the hotspots of the studied LCAs. These are: (i) the coated glass, (ii) the precious metals used in the cathode and (iii) the significant use of solvents.

Suggestions to achieve a reduction of the impacts are (i) the use of alternative substrates (e.g. plastic substrates), (ii) the implementation of electrodes not based on precious metals and (iii) the application of the green chemistry principles. Considering the substitution of the coated glass, plastic substrates have been tested and they generally show lower impacts. Yet, is the use of plastic a good idea for the substitution of glass? This question must be asked considering the lower mechanical properties of plastics with respect to glass and the problem of plastic pollution. Regarding the electrodes, carbon-based and inorganic electrodes have been tested and they can be a suitable solution for the industrial fabrication of these emerging technologies.

Solvents are often the most problematic factor in the evaluation of how a process is green. They are used both as the reaction medium and for the purification steps; the huge amount of solvents sensibly affects the green metrics as they produce significant amount of waste. The use of solvents and, in general, the synthesis of new materials, can be regulated through the 12 principles of Green Chemistry [82], with particular attention on the 5th principle as a guideline for solvents.

The use of auxiliary substances (e.g. solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used.

When the minimization of solvents amount is not feasible, the choice of greener ones is the most sustainable practice. Nowadays, charts to choose the greenest solvent are available as those suggested by Prat et al. [83] and Byrne et al. [84]. Also pharmaceutical companies published papers and tables for their selection showing the importance of this topic in the industrial application too [85, 86].

The research cannot pursue only an efficient technology but also a sustainable one, and this is even more important when dealing with alternative energy sources; the energy transition should not be only towards renewable but renewable and sustainable energy. This goal can be achieved only through a responsible research, a production regulated by eco-norms and a properly and thoughtfully designed waste management.

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Conflict of interest

The authors declare no conflict of interest.

Abbreviations

a-Si	amorphous silicon
BOS	balance of system
CED	cumulative energy demand
CPBT	carbon payback time
CRM	critical raw material
DSSC	dye sensitised solar cell
EPBT	energy payback time
ETL	electron transport layer
ETP	ecotoxicity potential
FTO	fluorine doped tin oxide
HTM	hole transport material
HTP	human toxicity potential
ICBA	indene-C60 bis-adduct
ITO	indium tin oxide
LCA	life cycle assessment
m-Si	monocrystalline silicon
OPV	organic photovoltaic
P3HT	poly-3-hexyl-tiophene

PCBM	[6,6]-phenyl-C61-butyric acid methyl ester
PEDOT:PSS	poly(3,4-ethylenedioxythiophene) polystyrene sulfonate
PET	polyethylene terephthalate
PSC	perovskite solar cell
PV	photovoltaic
ROS	reacting oxygen species
TCO	transparent conducting film

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