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Eco-design for dye solar cells: From hazardous waste to profitable recovery

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ABSTRACT

Recycling is rarely considered in the field of dye solar cells. However, recycling should be a critical part of holistic eco-design, which considers the efficiency, lifetime, return of energy investment, safety, and availability of materials. The novelty and focus of this work is recycling, and this is the first contribution systematically analyzing how different material choices and their combinations affect the recycling of dye solar cells. By understanding the recycling processes and how the recycling of materials is interlinked in a multicomponent system, it is possible to eco-design systems and guide future research toward selecting materials that support sustainability and enable economically motivated recycling. Economic incentive is the biggest factor determining whether or not recycling will take place. With eco-design, it is possible to avoid future problems, such as trapping rare and expensive critical metals in waste from which they are difficult or even impossible to recover. In fact, the conventional dye solar cells create harmful waste with no economically profitable way of recycling. Interestingly, many of the alternative materials that enable recycling have not been originally designed for that purpose, and it is rarely obvious how the combination of different materials affects recycling. For instance, using thin flexible substrates, which have been developed for roll-to-roll manufacturing, supports the retrieval of Ag, and using high performance Co- or Cu-based electrolytes instead of iodine electrolyte eliminates toxic gas problems in pyrometallurgical recycling processes.

1. Introduction

As the number of solar cells will increase significantly in the following decades, many critical elements will be needed to convert sunlight into electricity. Solar cells are often only designed for a high performance, low cost, and long lifetime. However, they require critical materials to ensure those characteristics, and their suitability for recycling has been largely omitted in the discussions. For instance, around 10% of Earth's silver is expected to be utilized in photovoltaics by 2050 (Dias et al., 2016; Nevala et al., 2019), and solutions for its recovery, as well as that of other rare elements, are needed. Silicon solar cells struggle with the economic viability of recovering Ag – the average quantity being 630 g/ton in silicon solar cell waste (Dias et al., 2016) and the limit of economic viability being 700 g/ton (Nevala et al., 2019). Even large global use does not guarantee that the issues of recycling will be resolved. For instance, Lithium-ion batteries are not recycled in all western countries. When Li batteries are recycled, only foil materials (Cu and Al) and Co are recovered. While recovering Li is technically possible, it is not currently recovered at all since there is no return on investment (Fröhlich et al., 2017; Georgi-Maschler et al., 2012). The challenges for battery recycling are low volumes of the end-of-life devices compared to other waste streams as well as ultra-low quantities of the recovered metals. Emerging solar cells, such as dye solar cells (DSSCs), easily have similar challenges that could potentially be omitted if eco-design is considered while the development of materials is still ongoing.

When developing eco-design for photovoltaics, DSSCs are an interesting emerging technology since there are numerous alternative material combinations and preparation methods for all their components. DSSCs have a different structure and operation principle compared to conventional silicon solar cells. In fact, DSSCs are electrochemical devices, which consist of two electrodes and electrolyte (Fig. 1). For DSSCs, possible individual, eco-friendly materials, such as natural dyes (Golshan et al., 2020) and bio-based carbons (Tiihonen et al., 2021), and processing methods (Santos et al., 2019) have been recently suggested. However, a systematic eco-design perspective for the full DSSC system is

Abbreviations: DSSC, dye-sensitized solar cell; FTO, fluorine doped tin oxide; ITO, indium doped tin oxide; PEDOT, poly(3,4-ethylenedioxythiophene); PET, polyethylene terephthalate; TCO, transparent conducting oxide.

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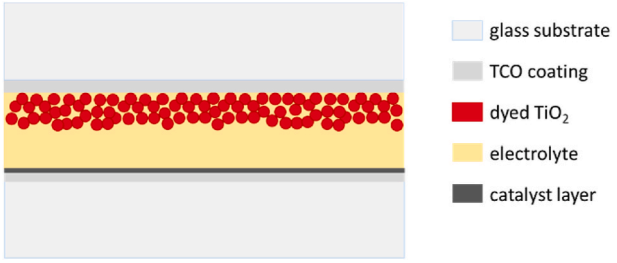

Fig. 1. Structure of a typical DSSC. Photoelectrode consists of a dyed TiO_2 layer on top of a glass substrate with TCO (transparent conductive oxide) coating. The counter electrode is another TCO-coated glass with a catalyst layer. The space between the electrodes is filled with liquid electrolyte. Not in scale.

lacking. Previously, it has only been pointed out that DSSCs are difficult to recycle due to the utilization of nanostructures (Reijnders, 2010). Eco-designs have mainly been prepared for simpler systems, like nanostructured cellulose sponges (Fiorati et al., 2020), where the material complexity is low. Another popular approach is to prepare an eco-design for full energy systems, like combined solar desalination plants (Monnot et al., 2018) or industrial water plants (Ahmadi et al., 2016), where eco-design is considered a life cycle assessment (LCA) analysis of the selected materials/components and their environmental impact to the final system. In this work, we want to demonstrate that, with the knowledge of individual recycling processes, it is possible to apply the eco-design approach to develop complex energy systems to have high recyclability.

It is also crucial to understand the drivers of recycling. In developed countries, materials are recycled if it is 1) economically profitable or 2) mandated by legislation. In developing countries, recycling usually takes place in the first case. Thus, the best guarantee for recycling is making products that are worth recycling in the economic sense – preferably with a significant profit. The utilization of the eco-design perspective before large-scale mass production aids in developing systems from which critical materials can be recovered, thus preventing the cost of critical metals, and consequently the device cost, from skyrocketing in the future. The metal price is bound to rise either if lower grade ores are needed or if the recovery from recycling is costly to fulfill the demand. Typically, what is worth recycling includes a) valuable materials (if they can be harvested efficiently to clean streams) and b) high volumes of pure material streams. Getting clean and/or large material streams from nanostructured devices is difficult, and in DSSCs, the nanomaterials are purposely intermixed (Fig. 1). The conventional recycling methods have exceptionally low selectivity to handle nanowaste, which has high diversity and complexity. Some new solutions for nanowaste recycling have been proposed. However, these solutions are focused on very valuable metals, such as Au, or high hazard nanomaterials, such as uranium rich nanocrystals (Chen et al., 2014; Pati et al., 2016). Even in the case of large global use, the material volumes coming from DSSCs would be small in comparison. Furthermore, the materials in DSSCs are not expensive or toxic enough to motivate the development of new recycling methods (unlike, e.g., nuclear waste). Thus, in this paper, we focus on how DSSCs could be recycled with existing recycling methods.

First, we discuss the primary approach of reusing DSSCs and their components. Second, we investigate recycling at the compound and elemental level with existing recycling processes. While many individual materials have existing recycling pathways (for instance, glass or Ag), they are often unsuitable when the material is a part of a complex system. Thus, using conventional recycling methods, it should be realized that not all materials can be recycled from such a complex system – so it is important to select which components and materials are critical to retrieve. Furthermore, it is crucial to select the other materials/components (cheap, abundant/renewable, environmentally friendly) so they can be lost and do not interfere with the capturing of critical materials.

The purpose of this work is to provide insight on how the different materials, and more importantly their combinations, affect the recycling of DSSCs to guide the materials' research. For instance, if we want to recycle Ag, we can affect that by selection of substrates (not by design of Ag current collector grids themselves). The novelty of this work is namely in the systematic investigation of recycling different material combinations in DSSCs. In eco-design, the ease of recycling needs to be considered against other key criteria, such as performance, lifetime, and return of energy investment. Many of these latter qualities have been reviewed many times in the literature even in recent years in terms of different components (e.g., natural dyes (Ghann et al., 2017), flexible substrates (P.D. Lund et al., 2018)) and large scale manufacturing in general (Gong et al., 2017). However, they need to be discussed here as well since we want to provide a balanced view and highlight that decisions cannot be made solely from a recycling perspective. Surprisingly, many materials that have been designed for higher efficiency or roll-to-roll manufacturing (not for recycling or environmental friendliness) can play a key role in recycling and thus in developing an eco-design for DSSCs. For instance, we show that the conventional glass-based DSSCs with iodine electrolyte have several issues that prevent recycling. At the same time, cobalt electrolyte-based DSSCs (motivated by reaching higher efficiencies) when used together with alternative substrates, such as flexible glass or bio/plastic substrates (motivated by roll-to-roll production), would allow the retrieval of all critical elements and avoid the development of hazardous gases in the recycling process.

2. Methods

In this work, we evaluate the recyclability of a full DSSC system and its components. Applying the principles of circular economy, we should always consider alternatives lighter than recycling down to the elemental level to use less energy and gain a higher value end product. Therefore, we will analyze the DCS system recyclability with the different levels of the recycling hierarchy, presented in Fig. 2.

When considering recycling, there are various levels of material recovery that require differing energy inputs, which are presented in Fig. 2. Examples of these levels in the case of DSSCs could be:

1) Reviving/restoring performance (e.g., adding electrolyte to the cell)
2) Reusing components (e.g., reutilizing counter electrodes or FTO glass)
3) Recycling materials (e.g., recycling dye molecules)
4) Recovering raw materials (e.g., extracting Ru from the dyes)

The left side of Fig. 2 shows the recycling hierarchy where each downward step requires more processing and, therefore, increased

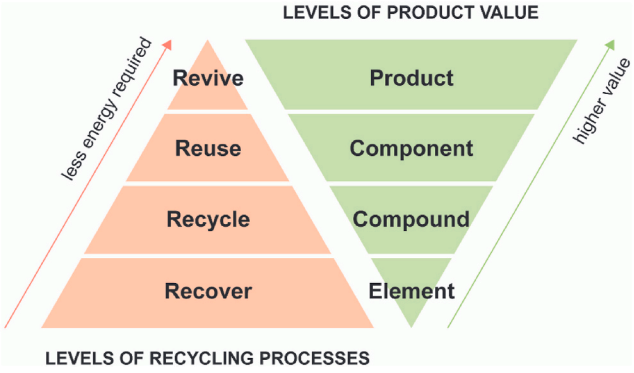

Fig. 2. The different recycling levels and their correspondence to product value levels.

energy input. The more specialized, complex, and multicomponent structures the device includes, the more steps are required for its recycling. At the same time, when requiring more energy to go from the product to element level, the value of the output product decreases (Fig. 2). In principle, the highest return on investment is achieved when reviving high value devices with modest effort and energy (Fig. 2 at the upper parts of the triangles), as opposed to utilizing a lot of energy to recover low value elements (Fig. 2 at the lower parts of the triangles). The key to an efficient recycling process is finding an optimal level at this triangle (Fig. 2). The less we need to process, the more likely it is that recycling makes economic sense. Going down to the element level is sometimes required if the reuse of components is prevented because they are too degraded or their cleaning takes too much labor-intensive processing.

We introduce an eco-design approach for the material selection to energy systems, as presented in Fig. 3. Many of the listed issues in Fig. 3 may seem rather obvious, but often when materials are designed, one or more of these listed characteristics are missing. In particular, recycling is often omitted from the material selection process most likely due to its complex nature. The novelty of this work comes from completing the eco-design decision approach by offering insight on how material combinations affect recycling.

As suggested by Fig. 3, the materials design should start from reaching sufficient efficiency and lifetime to merit further research. The next step is to investigate the return of energy investment (REI), which comes from the potential to produce energy (determined by efficiency and lifetime) compared to the energy embedded into the system during its production. Availability and safety of the materials should also be evaluated, as hazardous materials usually make recycling more challenging and, in the worst case, prevent it. In terms of recycling, the important aspect to consider is how to recycle the material system: choosing combinations and/or the weight portions of different materials to enable the retrieval of at least all the critical materials. In this work, we gather information related to the eco-design of DSSCs shown in Fig. 3 for different material combinations, and we particularly focus on developing insight related to recycling. Since DSSCs are not yet a fully commercial technology, it is still possible to propose new directions for the material's development. We will assess the hazard and recyclability of each material in DSSC and classify them by four different categories:

1) Recoverable – this material is possible to recover with current recycling processes.
2) Unrecoverable – this material is critical but is not possible to recover from this system with the current methods.
3) Unrecoverable but abundant – this material cannot be recovered with the current methods; however, the material itself is not critical and can be lost in the recycling process.
4) Hazardous – this material can cause a hazard during the recycling process, and its use should be avoided.

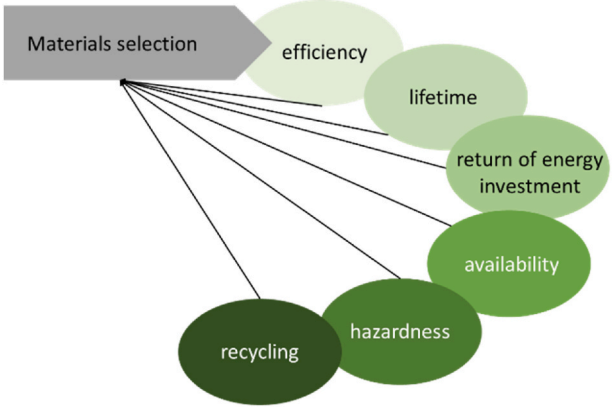

Fig. 3. Eco-design decision approach for the material selection to a DSSC system.

3. Results and discussion

3.1. Reviving DSSCs and the reuse of components

According to the recycling hierarchy (Fig. 2), we should first address the possibility of reviving the whole DSSC system. To do this analysis, it is critical to investigate the degradation processes. In the aging of DSSCs, the degradation of electrolyte often plays a key role (Asghar et al., 2010). In practice, charge carriers reacted and formed compounds that offered either no or extremely limited charge transfer. Thus, refilling DSSCs with fresh electrolyte would be an interesting option that has been suggested in the literature (Juhász Junger et al., 2018). However, the degradation is typically not limited to electrolyte. In a system with many sensitive components and variations in the cause of degradation, reviving devices may require too much manual case-by-case analysis, rendering the approach unfeasible.

If reviving complete DSSCs is too challenging, the next step is to consider reusing cell components (Fig. 2). When taking the cell apart, the first step is to separate the two electrodes (Fig. 4). The challenge in the reuse of separated electrodes is they may be too degraded, and they could degrade more during the recycling process (e.g., dye is typically sensitive to air and moisture). Another step down is to consider the recycling of conductive substrates. The glass substrates with a transparent conducting oxide (TCO, typically fluorine doped tin oxide (FTO)) layer are typically relatively robust parts of the device. Furthermore, the TCO glasses are the most expensive components of DSSCs, comprising up to 60% of the material's total costs (Hashmi et al., 2011), making their reuse lucrative. The viability of TCO glass reuse can be evaluated by comparing it with another technology. In the case of screens, it has been commercially profitable to dismantle them by hand and take their TCO plastic (ITO-PET, of a roughly similar or higher cost to FTO glass) (Hashmi et al., 2011) to make new products (Dang et al., 2015). However, the ITO-PET taken from screens is clean, whereas the TCO glass from DSSCs is topped with a multicomponent electrode and electrolyte residues. Therefore, an additional, labor-intensive step would be required, which increases the cost. In terms of the cleaning's feasibility, at the photoelectrode side, the porous TiO_2 layer is often relatively easy to scrape off. In the case of perovskite solar cells with relatively similar layers on TCO glass, the TCO glass was successfully reused in a new solar cell that reached practically the same device performance (Binek et al., 2016). Another hindrance is that the TCO layer on the substrates of solar cells is often cut into sections (in contrast to ITO-PET layers used in screens). Thus, while the reuse of TCO glass could be technically possible, its profitability as well as its geometrical suitability for reuse remain highly questionable.

3.2. Recycling of DSSCs and material recovery

Next, we provide an overview on recycling processes used for electronic and energy devices to recover pure material streams. A comprehensive review on these different processes is presented elsewhere (Velázquez-Martínez et al., 2019). Fig. 5 shows a schematic of recycling steps that can be applied for solar cells. The exact number of recycling steps depends on the material choices. The first step is the collection and transportation of aged devices to the recycling facility (Fig. 5). The importance of this step is easily forgotten, although arranging logistics can easily be a major bottleneck for recycling, especially as the volumes of solar cells are very small in comparison to other waste streams. Additionally, safety issues must be considered. For instance, DSSCs usually contain liquid electrolyte, thus the cells should be kept undamaged until they can be handled in proper safety conditions. The different recycling process steps and their applicability for DSSC recycling are discussed next.

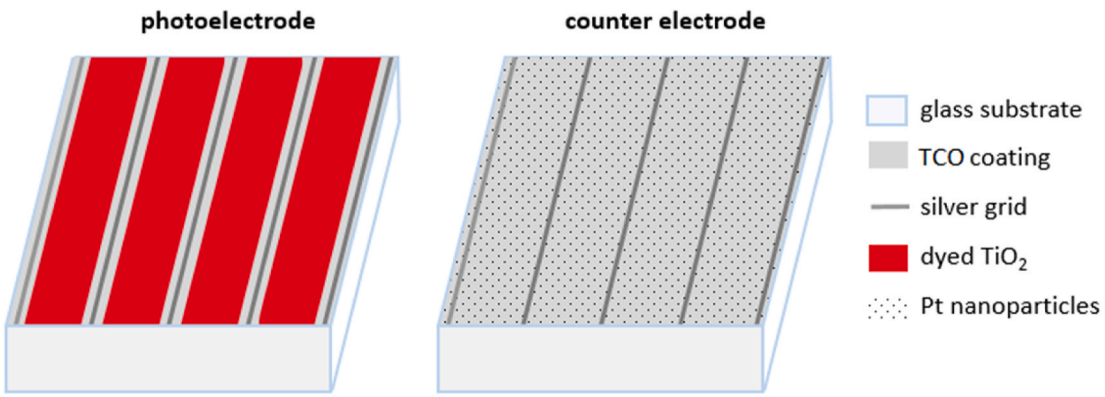

Fig. 4. The structure of the electrodes in conventional DSSCs. TCO stands for transparent conductive oxide.

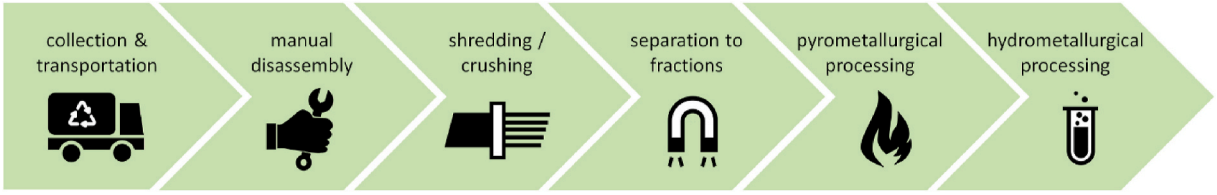

Fig. 5. Possible process steps for recycling DSSCs. These processes can be optimized by altering the number of steps, i.e., including only steps that are required and bring added value in the particular case.

3.2.1. *Mechanical processing*

The purpose of mechanical processing in recycling solid state waste is to liberate and separate different components into product streams that are as clean as possible. In reality, this is only performed in two different cases: 1) when it is economically feasible (e.g., a clean product stream can be obtained with high purity with economical value) or 2) when the device includes hazardous components or contaminants that could cause harm for the further processing or staff (Wills and Finch, 2016). In the case of valuable devices, there is a labor-intensive manual stage to separate clean parts or hazardous compounds. For example, in car recycling, the battery is removed and processed separately. In the case of DSSCs, if the devices are protected with a metallic frame and/or other casing, such a casing as well as external wiring should be taken apart at this stage (Fig. 5) and recycled as separate clean material streams.

After the manual dismantling, the comminution phase starts with liberating different materials from each other by crushing, shredding, or cutting them, depending on the material type (Fig. 5). For Si solar cells, crushing and shredding are used (Strachala et al., 2017). DSSCs would likely be processed in a similar manner unless they are directly imputed into pyrometallurgical processing.

In general, the next step in the mechanical process is the separation of materials into different fractions (Fig. 5) by exploiting differences in their physical properties to concentrate the materials of interest (Velázquez Martínez et al., 2019). Altogether, in these recycling processes, foil and sheet-type materials will remain at a larger size after shredding. They are also easy to separate from small particle size glass and any powders based on particle size and shape (Kaya, 2016). The mechanical separation steps can be based on visual appearance, relative density, surface properties, magnetic susceptibility, or electrical conductivity (Kaya, 2016; Wills and Finch, 2016). After these steps, the different fractions can be used in new products as they are or after further processing. To ensure efficient material separation, the comminution phase should be as efficient as possible. However, that is only obtained if each individual part contains one element. Note that the comminution phase depends on the physical properties of different materials, whereas nanomaterials might have completely different physical properties than their corresponding bulk materials.

There are two main challenges in this step for DSSCs: 1) nanomaterials are likely not separated from the substrates with shredding or crushing, and 2) the volume fraction of substrate in DSSCs is so large (typically around 99%) (Parisi et al., 2014) that it will dilute the waste and dominate the physical properties. Thus, the high-value nanomaterials cannot likely be separated in more concentrated fractions, and on the other side, the nanomaterials prevent the recovery of the glass as a pure high-volume stream. Assuming this part of the comminution phase is inefficient like we envision, it should be omitted if the recycling is continued directly with pyrometallurgical processing. Another aspect to consider is that if the volume fractions are unlikely to be increased, it is important to design the DSSCs in such a manner that the original concentrations of precious metals are high enough to motivate the recycling process.

3.2.2. *Pyrometallurgical processing*

When producing metals from ores, the metal is often an oxide or sulfide mineral that is reduced in a pyrometallurgical process (henceforth referred to as a pyro process) at a high temperature. The smelting process is optimized for one main metal (for instance, Cu) that will remain in liquid matte, and the remaining impurities separate into an oxide-based slag. It is possible to obtain certain other metals from the slag after further processing (Reuter, 2013). In recycling, mechanical treatment is often used to provide concentrated fractions as a feed to energy-intensive pyro processes (Fig. 5). In the case of batteries, there are processes in which they are directly inserted into the pyro process without any mechanical pretreatment. The advantage is that there is no need to invest in mechanical separation equipment, and if the feed batteries still possess some electrical charge, it will not damage the processing equipment (Ojanen et al., 2018). Therefore, pyro processing is a robust way to recycle complex energy devices in a safe way. The disadvantage of the direct feed of devices into the pyro process is that only one or possibly few metals are recovered (for instance, when combining Ag and Ti, only one of them can be recovered). Furthermore, there are some materials (unfortunately typical for DSSCs) that may cause problems in the pyro process. First, halogens, such as iodine and

fluorine, are volatile at high temperatures and can cause air pollutants. Secondly, glass is not incinerated in the pyro process, but it would significantly increase the volume of the slag and reduce the concentrations of the recovered metals in the slag. Nevertheless, some silicates are included in the pyro process to enhance the slag quality. The best-case scenario would be to add some glass-based solar cells that could reduce the need for process additives. However, this is a question for the overall process design in the future.

3.2.3. Hydrometallurgical processing

After the pyro process or, in some cases, in streams directly from mechanical processing, the fraction can be upgraded with hydrometallurgical processes (henceforth referred to as hydro processes) where metals are recovered from aqueous solutions (Fig. 5). The key is that individual metals can be obtained in high quality by changing the process conditions, but these processes require a large amount of chemicals and/or thermal, pressure, or electrical input. The fraction entering the hydro process should be very fine to ensure good solubility and therefore high recovery. In a solution with various metals, their separation is dependent on the similarity of the conditions they precipitate: if the conditions closely resemble each other, it is very unlikely they can be recovered with high purity.

3.3. Eco-design of DSSCs

Next, we investigate the recycling options for each individual component of DSSCs and discuss how alternative material options affect the recycling when also considering the broader eco-design aspect (Fig. 3). Since substrates dominate the recycling process due to their weight portion being the highest, Fig. 6 summarizes the recyclability of different materials in the case of different substrate types. For instance, a typical DSSC prepared on thick glass substrates is not suited for commercially viable recycling, and it is hazardous in the recycling process. However, there are several pathways that allow the recovery of all critical elements and avoid the formation of hazardous gases (Fig. 6). In the following sections, materials shown in Fig. 6 are investigated component by component. In this elemental analysis, we omit investigation of low value, renewable (organic) materials that could be used in low quantities e.g. as binders or as dyes or parts of dye since they are neither interesting in terms of getting recycled nor preventing the recycling of other materials.

3.3.1. Conductive substrates

The substrate typically used for DSSCs is a thick glass with FTO coating, and the recycling of FTO glass as such is discussed in Section 3.1. Note that while glass as a pure material stream is recyclable, when it is connected with different metals, chemicals, and nanoparticles, it would most likely not be accepted for recycling but would be lost, as described in Section 3.2.1. To retrieve critical materials on top of the glass substrate, pyro or hydro processing would be used. For the recovery of Ag, one would use the Cu process, which allows the recycling of many other interesting metals, such as Pt and Co (Reuter, 2013). However, the thick glass that is normally used dilutes the proportion of other materials, in particular Ag (7.2 g/m^2, which is ~300 g/ton with 4 mm thick glasses) (Parisi et al., 2014), below the limit of economically viable retrieval (700 g/ton for Ag) (Nevala et al., 2019). Thus, to make DSSCs commercially interesting for recycling, it would be important to lower the total weight of the substrates to at least below 10,000 g/cm^2 (i.e., two 2 mm-thick glasses). Glass does not burn in the Cu pyro process, but it would go into slag. As mentioned in Section 3.2.2, it should be carefully considered how much glass can go to the slag without altering its composition too much. Using thinner glass sheets makes the device more fragile, and its suitability for recycling should not compromise the lifetime or safety of the device (Fig. 3). Another challenge with FTO glass is that FTO contains halogens, which may result in a toxic gas in the pyro process.

The typical alternative substrates are plastics, metals and, most recently, bio-based and bio-composite substrates (Miettunen et al., 2018). Plastic (as such with no conductive coatings) is a low value material like glass, thus only high-purity and high-volume plastic streams are economically interesting for recycling (e.g., plastic food containers and bottles). Neither of those criteria are fulfilled in DSSCs. Unlike normal glass, plastics are flexible, thin, and lightweight. Typical plastic substrates are 200 μm thick (P D Lund et al., 2018) with a resulting mass contribution of 200 g/m^2 per substrate. Therefore, using plastic substrates offers a large, over 20-fold reduction to the overall

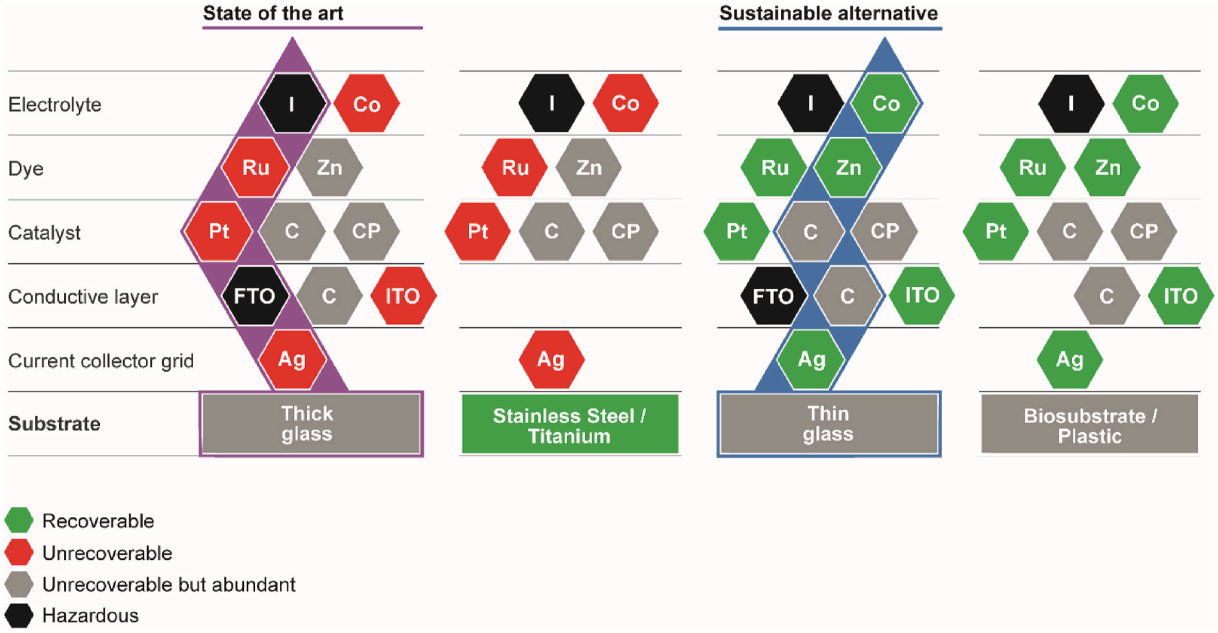

Fig. 6. Different material and element choices for DSSCs and their potential for recovery in current recycling processes. Hazardous refers to a hazard in the recycling, mainly the possible formation of toxic gases. CP stands for conducting polymer. The typical DSSC is noted as state of the art, and one of the possible sustainable alternative pathways is highlighted.

weight of the device compared to a conventional glass-based device. Consequently, the weight portion of Ag raises to around 15,000 g/ton – multiple times over the limit of economically viable retrieval. In the pyro process, plastics are incinerated to ash, reducing their weight by 99.8% (Sánchez et al., 2007). This would increase the weight portion of other materials even further (e.g., Ag would be in the order of 100,000 g/ton) – more than 100 times over the limit of an economically feasible recovery of Ag. The downsides of using plastics include that they are 1) based on fossil sources, 2) suited only for low-temperature treatments, and 3) permeable, causing stability issues (Miettunen et al., 2018). Bio-based substrates are renewable, but they have even more problems with permeability than plastics (Miettunen et al., 2018). Interestingly, as shown for other photovoltaic technologies, paper- (Fang et al., 2014) and wood-based (Li et al., 2019) substrates can provide superior optical properties compared to glass or plastic substrates due to high haze, which increases light absorption and, consequently, photocurrent. Plastic, paper, or other bio-based substrates that are easily incinerated could be inserted directly into Cu pyro processing where the recovery of Ag, Pt, Zn, Ru, Co, and In is technically possible (Fig. 6) (Sánchez et al., 2007).

The other typical alternative substrates are metals. Besides giving sufficient conductivity without additional conductive layers, metals also endure high-temperature treatments, which are important in reaching top efficiencies. The main challenge in using metals in DSSCs is their corrosion in the liquid electrolyte. When using iodine-based electrolyte, Ti has been the only stable metal that can be used without protective coatings (Miettunen et al., 2018). Ti foils are expensive (90 $/m^2, 5–10 times the cost of FTO glass substrates) (Hashmi et al., 2011), causing a major increase to the overall device cost. When using less-corrosive Co complex electrolyte, cheaper metals, such as stainless steels (Miettunen et al., 2012) or even ferritic steels (Miettunen et al., 2014), remain stable. Stainless steels could be up to 80% cheaper than conventional FTO glass substrates (Hashmi et al., 2011), so they are interesting from a commercial perspective and conform to metal recycling. However, the pyro processes of Fe (used for stainless steel) and Ti prevent the recovery of Pt, Ag, Co, or Ru, as shown in Fig. 6 (Sánchez et al., 2007).

Another, very unusual approach for flexible solar cells is to utilize extra thin flexible glass (0.1–0.2 mm) (Sheehan et al., 2015). While conventional glass is brittle as a thin layer, willow glass is flexible and more costly. The flexible glass provides a series of advantages because it is a good barrier, is inert toward corrosion, enables high-temperature treatments (up to 550 °C) (Sheehan et al., 2015), and conforms to roll-to-roll processing, which lowers the manufacturing costs. By utilizing thin flexible glass substrates, the total weight of the substrate reduces to 500-1000 g/m^2, making the proportion of Ag 3000–6000 g/ton. This is high enough to motivate the recycling of Ag from a commercial perspective (at best, almost 10 times above the limit of economic viability).

While utilizing substrates other than glass supports recycling, an alternative conductive coating should be found to replace FTO. All except metal foils require a separate conductive layer. The typical alternatives for FTO are indium doped tin oxide (ITO), thinly printed metal grids, conductive polymers, and carbon nanotubes. Replacing FTO with ITO resolves the toxic gas problems, and In can be recycled in some cases (Fig. 6). However, In is a very rare metal, and its global reserves are insufficient for the large-scale manufacturing of photovoltaics (Grandell and Höök, 2015). Another option for a transparent conductive layer is thin metal grids made from Ag or Ni, but they both corrode in the conventional electrolyte (Fang et al., 2005). Conductive polymers and carbons can also be used for conductive layers, but they are often catalytic and therefore cannot be used at the photoelectrode. These materials are discussed in detail in Section 3.3.2. Developing low-cost, transparent conductive layers from abundant materials is still a major issue before considering the recycling problems related to FTO.

3.3.2. Catalyst layer at the counter electrode

The conventional catalyst, Pt, used at the counter electrode is a rare and expensive metal, with likely availability issues in the large-scale manufacturing of solar cells (Hinsch et al., 2014). This is true even though the evaluated amount of Pt in DSSCs is small since only a very thin layer is needed and the amount varies between 0.02 and 0.1 g/m^2 (0.8–4 g/ton) (Hinsch et al., 2014; Veltkamp, 2007). A 1 nm-thick layer of Pt relates to the portion of Pt to be 1 g/ton in the conventional glass-based device. The limit of the economically viable recovery of Pt is 1–7g/ton from the ore depending on what other minerals there are or how difficult the deposit is to excavate (Lewins et al., 2008). Utilizing thin flexible glass, plastic, or bio-based substrates, the proportional amount of Pt is raised to 10–50 g/ton depending on the substrate, and Pt retrieval can be made viable (Fig. 6). Note that the pyro recycling processes of stainless steel and Ti do not allow the recovery of Pt (Fig. 6) (Sánchez et al., 2007).

More abundant alternatives to Pt should be preferred, and the most common abundant alternatives are carbons and conducting polymers, which in best-case scenarios can serve as both a catalyst and a conductive layer at the counter electrode. These materials can reach efficiencies roughly similar to Pt in DSSCs with iodine-based electrolytes (Thomas et al., 2014). Furthermore, in DSSCs with Co complex electrolyte, alternative materials can even outperform Pt, and record efficiencies have been reached with carbon catalysts (13%) (Mathew et al., 2014). From a stability perspective, carbon catalysts are usually stable. They have been utilized, for instance, in the longest reported outdoor stability test of DSSCs (Kato et al., 2009). In contrast, conductive polymers are known to degrade, for instance, under UV light (Thomas et al., 2014). Carbon and conducting polymers cannot be retrieved from degraded solar cells, but they would be burned in pyro processing. Acknowledging that these alternative materials would be lost further highlights the importance of selecting options that are as sustainable and preferably renewable as possible. Recently, renewable options for carbons have been suggested, such as bio-carbons that can be prepared from bio-waste streams using waste from food production (e.g., fish waste (Ma et al., 2018), pumpkin stems (Madhu et al., 2014), mangosteen peels (Maiaugree et al., 2015), eggshells (Wang et al., 2015), and brewery residues (Tiihonen et al., 2021)), forestry waste (Xu et al., 2018), or marine biomass (Wang et al., 2014).

3.3.3. Electrolytes

The operation of DSSC requires that electrolyte penetrates both electrodes well. Consequently, electrolyte residues will be present at both electrodes, which can prevent the recycling of all materials in DSSCs in the worst case. As mentioned earlier in Section 3.1, electrolyte is often among the first components to degrade, and its reuse as such is unlikely. The availability of iodine for conventional DSSC electrolytes is questionable when considering large-scale manufacturing (Hinsch et al., 2014). Iodine is also harmful for aqueous life and must be disposed as harmful waste. Another reason to avoid using Iodine is that in pyro processes (used, for instance, to recover Ag), it can cause harmful HI that will be released as part of flue gases.

There are several alternative redox couples. Most of them, such as pseudohalogen redox couples, disulfide/thiolate redox couples, and ferrocene/ferrocenium, reach only low efficiencies and suffer from poor stability (Wu et al., 2015), currently rendering them uninteresting for large-scale manufacturing. In contrast, Co (Mathew et al., 2014) and Cu (Cao et al., 2017) complex-based electrolytes have resulted in record-breaking efficiencies, and their main challenge has been stability (Hinsch et al., 2014). Modifications to the electrolyte composition has improved the stability of DSSCs with Co complex electrolyte resulting in results such as Jiang et al. have reporting 2000 h stability (Jiang et al., 2014) and recently the effects of both electrolyte and counter electrode catalysts on lifetime were shown (Kamppinen et al., 2020). Co complexes are toxic materials, and their leakage to soil needs to be prevented (critical concentration in soil is approximately 0.1 g kg^{-1}) (Hinsch et al.,

2014). In a metal recovery process, Co would not be released as a gas but would end up in the oxide slag. From there, Co and a series of other precious metals (e.g., Ag and Pt), can be recovered (Fig. 5) with Cu pyro processing (Reuter, 2013). Co complexes have virtually no limitations in availability (Hinsch et al., 2014). However, if there is enough Ag to motivate pyro processing, then even low quantities of Co can be economically captured since the energy intensive part (the expensive part) of the process is already done.

3.3.4. Photoelectrode

The photoelectrode is composed of a dyed TiO_2 layer. TiO_2 is a cheap and abundant material that is used by many industries as a filler. The dye layer covering the nanoparticle TiO_2 layer is known to be the valuable material, but its proportion is extremely small since its thickness is only one atom layer. Conventional, stable, high-performance dyes in DSSCs are Ru complexes. Ru is known for being expensive and scarce to the extent that its availability is insufficient for the large-scale manufacturing of DSSCs (Hinsch et al., 2014). The dye is a sensitive component, which is among the most likely to degrade (Asghar et al., 2010), making its direct reuse unlikely. Recovering Ru as a metal from (crushed) DSSCs is problematic since the amounts of dye are so negligible, 0.1 g/m^2 (Hinsch et al., 2014). In conventional, glass-based DSSCs, the amount of Ru is only 0.5 g/ton. Ru can be recovered in a process similar to Pt (Fig. 6), and it is economically motivated only as a part of other recovery processes (Fröhlich et al., 2017).

With natural dyes, the use of precious metals and energy intensive synthetization is omitted (Ludin et al., 2014). However, natural dyes have major limitations in stability (Ludin et al., 2014) and performance (the highest efficiency is only 2.67%) (Maiaugree et al., 2015). Thus, they are unviable alternatives commercially and even environmentally when considering aspects such as the return of energy investment (Fig. 3).

There are other alternatives, such as organic synthesized dyes or dyes with a non-rare metal center. Some of them require even more energy to prepare than the conventional Ru-based dyes. For instance, the preparation of 5,15-bis(2,6-dioctoxyphenyl)-10-(bis(4-hexylphenyl)amino-20-4-carboxyphenyl ethynyl)porphyrinato]Zinc (II) (known as YD2-o-CB) takes three times more energy than Di-tetrabutylammonium cis-bis(isothiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylato)ruthenium(II) (known as N719) (Parisi et al., 2014). However, since dyes are used in such a negligible weight percentage, even tripling the energy required for the manufacturing of the dye itself had only a marginal effect on the overall embedded energy of the device. Interestingly, the highest performances in DSSCs have been reached with organic dyes (Cao et al., 2017) and porphyrin dyes with Zn as the central metal (Yella et al., 2011). Zn is abundant, but it could also be recycled (Fig. 6).

4. Conclusions

The main scope of this contribution is to initiate a discussion on the consequences of different material selections for the recyclability of DSSCs and provide eco-design strategies for the development of devices. As this work concludes, components or elements that can generally be recycled may be unrecoverable when used as a part of DSSCs. Thus, when considering recycling, it is imperative to widen the view from individual materials to the entire system. The combination and proportions of materials defines which materials, if any, can be retrieved. Taking an eco-design approach already at a material research phase (i.e., prior to commercialization) supports the development of a holistically sustainable device design from which all critical materials are recovered. If it is economically meaningful to collect degraded DSSCs because, for instance, their Ag concentration is high enough, we not only enable recycling but also prevent harmful chemicals in DSSCs from ending up untreated in the soil.

Reviving complete devices or reusing components should be preferred, but it is questionable whether they can be obtained in a good enough condition and what type of labor-intensive steps are required for reuse. Furthermore, having large enough quantities of aged DSSCs to warrant economic profitability for such tailored recycling processes is an issue. Among the different DSSC components, conductive substrates are the parts most likely to reach economically profitable reuse, but even they have major challenges primarily related to the amount and cost of work required to separate and clean them.

When considering the retrieval of elements from degraded DSSCs, existing recycling pathways could be utilized, which relaxes the need for large quantities of degraded devices. The challenge in utilizing existing recycling methods is complicated since DSSCs consist of multiple materials, many of which are nanostructured and appear in small quantities. In fact, the conventional DSSCs with thick glass substrates do not conform to economically viable recycling, and they include toxic materials. There are, however, several material combinations that enable the retrieval of critical materials. For instance, changing from thick glass substrates to thin flexible substrates is enough to change the weight percentage of Ag current collector grids so their recovery is economically motivated (in the best case, more than100 times above the limit of commercial viability for recycling). Flexible plastic and bio-based substrates still need development mainly in stability, and these results give further motivation for that research. The utilization of a thin flexible glass (i.e., using a similar type of base material but in smaller quantities) would suffice to motivate the recycling of Ag without sacrificing the advantages that glass substrate gives in terms of performance and stability. Interestingly, DSSCs based on Co or Cu complex electrolytes, which are known for their high performance, are also better suited for the recycling process compared to iodine-based electrolytes, and they work better with other, more sustainable materials, such as carbon catalysts and organic dyes.

CRediT authorship contribution statement

Kati Miettunen: Conceptualization, Investigation, Writing – original draft, Visualization. **Annukka Santasalo-Aarnio:** Methodology, Investigation, Writing – original draft.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

Ahmadi, A., Tiruta-Barna, L., Benetto, E., Capitanescu, F., Marvuglia, A., 2016. On the importance of integrating alternative renewable energy resources and their life cycle networks in the eco-design of conventional drinking water plants. J. Clean. Prod. 135, 872–883. https://doi.org/10.1016/j.jclepro.2016.06.201.

Asghar, M.I., Miettunen, K., Halme, J., Vahermaa, P., Toivola, M., Aitola, K., Lund, P., 2010. Review of stability for advanced dye solar cells. Energy Environ. Sci. 3, 418. https://doi.org/10.1039/b922801b.

Binek, A., Petrus, M.L., Huber, N., Bristow, H., Hu, Y., Bein, T., Docampo, P., 2016. Recycling perovskite solar cells to avoid lead waste. ACS Appl. Mater. Interfaces 8, 12881–12886. https://doi.org/10.1021/acsami.6b03767.

Cao, Y., Saygili, Y., Ummadisingu, A., Teuscher, J., Luo, J., Pellet, N., Giordano, F., Zakeeruddin, S.M., Moser, J.-E., Freitag, M., Hagfeldt, A., Grätzel, M., 2017. 11% efficiency solid-state dye-sensitized solar cells with copper(II/I) hole transport materials. Nat. Commun. 8, 15390. https://doi.org/10.1038/ncomms15390.

Chen, Z., Zhuang, Z., Cao, Q., Pan, X., Guan, X., Lin, Z., 2014. Adsorption-induced crystallization of U-rich nanocrystals on nano-Mg(OH) 2 and the aqueous uranyl enrichment. ACS Appl. Mater. Interfaces 6, 1301–1305. https://doi.org/10.1021/am405306j.

Dang, M.T., Lefebvre, J., Wuest, J.D., 2015. Recycling indium tin oxide (ITO) electrodes used in thin-film devices with adjacent hole-transport layers of metal oxides. ACS Sustain. Chem. Eng. 3, 3373–3381. https://doi.org/10.1021/acssuschemeng.5b01080.

Dias, P., Javimczik, S., Benevit, M., Veit, H., Bernardes, A.M., 2016. Recycling WEEE: extraction and concentration of silver from waste crystalline silicon photovoltaic modules. Waste Manag. 57, 220–225. https://doi.org/10.1016/j.wasman.2016.03.016.

Fang, X., Ma, T., Akiyama, M., Guan, G., Tsunematsu, S., Abe, E., 2005. Flexible counter electrodes based on metal sheet and polymer film for dye-sensitized solar cells. Thin Solid Films 472, 242–245. https://doi.org/10.1016/j.tsf.2004.07.083.

Fang, Z., Zhu, H., Yuan, Y., Ha, D., Zhu, S., Preston, C., Chen, Q., Li, Y., Han, X., Lee, S., Chen, G., Li, T., Munday, J., Huang, J., Hu, L., 2014. Novel nanostructured paper with ultrahigh transparency and ultrahigh haze for solar cells. Nano Lett. 14, 765–773. https://doi.org/10.1021/nl404101p.

Fiorati, A., Grassi, G., Graziano, A., Liberatori, G., Pastori, N., Melone, L., Bonciani, L., Pontorno, L., Punta, C., Corsi, I., 2020. Eco-design of nanostructured cellulose sponges for sea-water decontamination from heavy metal ions. J. Clean. Prod. 246, 119009. https://doi.org/10.1016/j.jclepro.2019.119009.

Fröhlich, P., Lorenz, T., Martin, G., Brett, B., Bertau, M., 2017. Valuable metals-recovery processes, current trends, and recycling strategies. Angew. Chem. Int. Ed. 56, 2544–2580. https://doi.org/10.1002/anie.201605417.

Georgi-Maschler, T., Friedrich, B., Weyhe, R., Heegn, H., Rutz, M., 2012. Development of a recycling process for Li-ion batteries. J. Power Sources 207, 173–182. https://doi.org/10.1016/j.jpowsour.2012.01.152.

Ghann, W., Kang, H., Sheikh, T., Yadav, S., Chavez-Gil, T., Nesbitt, F., Uddin, J., 2017. Fabrication, optimization and characterization of natural dye sensitized solar cell. Sci. Rep. 7, 41470. https://doi.org/10.1038/srep41470.

Golshan, M., Osfouri, S., Azin, R., Jalali, T., 2020. Fabrication of optimized eco-friendly dye-sensitized solar cells by extracting pigments from low-cost native wild plants. J. Photochem. Photobiol. Chem. 388, 112191. https://doi.org/10.1016/j.jphotochem.2019.112191.

Gong, J., Sumathy, K., Qiao, Q., Zhou, Z., 2017. Review on dye-sensitized solar cells (DSSCs): advanced techniques and research trends. Renew. Sustain. Energy Rev. 68 (1), 234–246. https://doi.org/10.1016/j.rser.2016.09.097.

Grandell, L., Höök, M., 2015. Assessing rare metal availability challenges for solar energy technologies. Sustain. Times 7, 11818–11837. https://doi.org/10.3390/su70911818.

Hashmi, G., Miettunen, K., Peltola, T., Halme, J., Asghar, I., Aitola, K., Toivola, M., Lund, P., 2011. Review of materials and manufacturing options for large area flexible dye solar cells. Renew. Sustain. Energy Rev. 15, 3717–3732. https://doi.org/10.1016/j.rser.2011.06.004.

Hinsch, A., Veurman, W., Brandt, H., Flarup Jensen, K., Mastroianni, S., 2014. Status of dye solar cell technology as a guideline for further research. ChemPhysChem 15, 1076–1087. https://doi.org/10.1002/cphc.201301083.

Jiang, R., Anderson, A., Barnes, P.R.F., Xiaoe, L., Law, C., O'Regan, B.C., 2014. 2000 hours photostability testing of dye sensitised solar cells using a cobalt bipyridine electrolyte. J. Mater. Chem. 2, 4751–4757. https://doi.org/10.1039/C4TA00402G.

Juhász Junger, I., Tellioglu, A., Ehrmann, A., 2018. Refilling DSSCs as a method to ensure longevity. Optik 160, 255–258. https://doi.org/10.1016/j.ijleo.2018.01.123.

Kamppinen, A., Aitola, K., Poskela, A., Miettunen, K., Lund, P.D., 2020. Stability of cobalt complex based dye solar cells with PEDOT and Pt catalysts and different electrolyte concentrations. Electrochim. Acta 335, 135652. https://doi.org/10.1016/j.electacta.2020.135652.

Kato, N., Takeda, Y., Higuchi, K., Takeichi, A., Sudo, E., Tanaka, H., Motohiro, T., Sano, T., Toyoda, T., 2009. Degradation analysis of dye-sensitized solar cell module after long-term stability test under outdoor working condition. Sol. Energy Mater. Sol. Cells 93, 893–897. https://doi.org/10.1016/j.solmat.2008.10.022.

Kaya, M., 2016. Recovery of metals and nonmetals from electronic waste by physical and chemical recycling processes. Waste Manag. 57, 64–90. https://doi.org/10.1016/j.wasman.2016.08.004.

Lewins, J.D., Hunns, S., Badenhorst, J., 2008. The Kalahari Platinum project 355–366.

Li, Y., Cheng, M., Jungstedt, E., Xu, B., Sun, L., Berglund, L., 2019. Optically transparent wood substrate for perovskite solar cells. ACS Sustain. Chem. Eng. 7, 6061–6067. https://doi.org/10.1021/acssuschemeng.8b06248.

Ludin, N.A., Al-Alwani Mahmoud, A.M., Bakar Mohamad, A., Kadhum, A.A.H., Sopian, K., Abdul Karim, N.S., 2014. Review on the development of natural dye photosensitizer for dye-sensitized solar cells. Renew. Sustain. Energy Rev. 31, 386–396. https://doi.org/10.1016/j.rser.2013.12.001.

Lund, P.D., Halme, J., Hashmi, G., Asghar, I., Miettunen, K., 2018. Application of dye-sensitized and perovskite solar cells on flexible substrates. Flex. Print. Electron. 3 https://doi.org/10.1088/2058-8585/aaabc9.

Lund, P.D., Halme, J., Hashmi, G., Asghar, I., Miettunen, K., 2018. Application of dye-sensitized and perovskite solar cells on flexible substrates. Flex. Print. Electron. 3, 013002 https://doi.org/10.1088/2058-8585/aaabc9.

Ma, P., Lu, W., Yan, X., Li, W., Li, L., Fang, Y., Yin, X., Liu, Z., Lin, Y., 2018. Heteroatom tri-doped porous carbon derived from waste biomass as Pt-free counter electrode in dye-sensitized solar cells. RSC Adv. 8, 18427–18433. https://doi.org/10.1039/C8RA02575D.

Madhu, R., Veeramani, V., Chen, S.-M., Palanisamy, J., Ezhil Vilian, A.T., 2014. Pumpkin stem-derived activated carbons as counter electrodes for dye-sensitized solar cells. RSC Adv. 4, 63917–63921. https://doi.org/10.1039/C4RA12585A.

Maiaugree, W., Lowpa, S., Towannang, M., Rutphonsan, P., Tangtrakarn, A., Pimanpang, S., Maiaugree, P., Ratchapolthavisin, N., Sang-aroon, W., Jarernboon, W., Amornkitbamrung, V., 2015. A dye sensitized solar cell using natural counter electrode and natural dye derived from mangosteen peel waste. Sci. Rep. 5, 15230. https://doi.org/10.1038/srep15230.

Mathew, S., Yella, A., Gao, P., Humphry-Baker, R., Curchod, B.F.E., Ashari-Astani, N., Tavernelli, I., Rothlisberger, U., Nazeeruddin, M.K., Grätzel, M., 2014. Dye-sensitized solar cells with 13% efficiency achieved through the molecular engineering of porphyrin sensitizers. Nat. Chem. 6, 242–247. https://doi.org/10.1038/nchem.1861.

Miettunen, K., Jouttijarvi, S., Jiang, R., Saukkonen, T., Romu, J., Halme, J., Lund, P., 2014. Low cost ferritic stainless steel in dye sensitized solar cells with cobalt complex electrolyte. J. Electrochem. Soc. 161, H138–H143. https://doi.org/10.1149/2.054403jes.

Miettunen, K., Saukkonen, T., Li, X., Law, C., Sheng, Y.K., Halme, J., Tiihonen, A., Barnes, P.R.F., Ghaddar, T., Asghar, I., Lund, P., O'Regan, B.C., 2012. Do counter electrodes on metal substrates work with cobalt complex based electrolyte in dye sensitized solar cells? J. Electrochem. Soc. 160, H132–H137. https://doi.org/10.1149/2.074302jes.

Miettunen, K., Vapaavuori, J., Poskela, A., Tiihonen, A., Lund, P.D., 2018. Recent progress in flexible dye solar cells. Wiley Interdiscip. Rev. Energy Environ. 7, e302 https://doi.org/10.1002/wene.302.

Monnot, M., Carvajal, G.D.M., Laborie, S., Cabassud, C., Lebrun, R., 2018. Integrated approach in eco-design strategy for small RO desalination plants powered by photovoltaic energy. Desalination 435, 246–258. https://doi.org/10.1016/j.desal.2017.05.015.

Nevala, S.-M., Hamuyuni, J., Junnila, T., Sirviö, T., Eisert, S., Wilson, B.P., Serna-Guerrero, R., Lundström, M., 2019. Electro-hydraulic fragmentation vs conventional crushing of photovoltaic panels – impact on recycling. Waste Manag. 87, 43–50. https://doi.org/10.1016/j.wasman.2019.01.039.

Ojanen, S., Lundström, M., Santasalo-Aarnio, A., Serna-Guerrero, R., 2018. Challenging the concept of electrochemical discharge using salt solutions for lithium-ion batteries recycling. Waste Manag. 76, 242–249. https://doi.org/10.1016/j.wasman.2018.03.045.

Parisi, M.L., Maranghi, S., Basosi, R., 2014. The evolution of the dye sensitized solar cells from Grätzel prototype to up-scaled solar applications: a life cycle assessment approach. Renew. Sustain. Energy Rev. 39, 124–138. https://doi.org/10.1016/j.rser.2014.07.079.

Pati, P., McGinnis, S., Vikesland, P.J., 2016. Waste not want not: life cycle implications of gold recovery and recycling from nanowaste. Environ. Sci. Nano 3, 1133–1143. https://doi.org/10.1039/C6EN00181E.

Reijnders, L, 2010. Design issues for improved environmental performance of dye-sensitized and organic nanoparticulate solar cells. J. Clean. Prod. 18 (4), 307–312. https://doi.org/10.1016/j.jclepro.2009.10.021.

Reuter, M., 2013. Metal Recycling Opportunities.

Sánchez, M.E., Morán, A., Escapa, A., Calvo, L.F., Martínez, O., 2007. Simultaneous thermogravimetric and mass spectrometric analysis of the pyrolysis of municipal solid wastes and polyethylene terephthalate. J. Therm. Anal. Calorim. 90, 209–215. https://doi.org/10.1007/s10973-006-7670-7.

Santos, F., Hora, C., Bernardo, G., Ivanou, D., Mendes, A., 2019. Efficient monolithic dye sensitized solar cells with eco-friendly silica-titania spacer layers. Sol. Energy 183, 419–424. https://doi.org/10.1016/j.solener.2019.03.056.

Sheehan, S., Surolia, P.K., Byrne, O., Garner, S., Cimo, P., Li, X., Dowling, D.P., Thampi, K.R., 2015. Flexible glass substrate based dye sensitized solar cells. Sol. Energy Mater. Sol. Cells 132, 237–244. https://doi.org/10.1016/j.solmat.2014.09.001.

Strachala, D., Hylský, J., Vaněk, J., Fafilek, G., Jandová, K., 2017. Methods for recycling photovoltaic modules and their impact on environment and raw material extraction. Acta Montan. Slovaca 22, 257–269. https://doi.org/10.2478/cdem-2013-0008.

Thomas, S., Deepak, T.G., Anjusree, G.S., Arun, T.A., Nair, S.V., Nair, A.S., 2014. A review on counter electrode materials in dye-sensitized solar cells. J. Mater. Chem. 2, 4474–4490. https://doi.org/10.1039/C3TA13374E.

Tiihonen, A., Siipola, V., Lahtinen, K., Pajari, H., Widsten, P., Tamminen, T., Kallio, T., Miettunen, K., 2021. Biocarbon from brewery residues as a counter electrode catalyst in dye solar cells. Electrochim. Acta 368, 137583. https://doi.org/10.1016/j.electacta.2020.137583.

Velázquez-Martínez, Valio, Santasalo-Aarnio, Reuter, Serna-Guerrero, 2019a. A critical review of lithium-ion battery recycling processes from a circular economy perspective. Batteries 5, 68. https://doi.org/10.3390/batteries5040068.

Velázquez Martínez, O., Van Den Boogaart, K.G., Lundström, M., Santasalo-Aarnio, A., Reuter, M., Serna-Guerrero, R., 2019b. Statistical entropy analysis as tool for circular economy: proof of concept by optimizing a lithium-ion battery waste sieving system. J. Clean. Prod. 212, 1568–1579. https://doi.org/10.1016/j.jclepro.2018.12.137.

Veltkamp, A.C., 2007. Environmental life cycle analysis of large area dye sensitized solar modules; status and outlook. Present. 22nd Eur. Photovolt. Sol. Energy Conf. Exhib. 3, 3–7.

Wang, C.-L., Liao, J.-Y., Chung, S.-H., Manthiram, A., 2015. Carbonized eggshell membranes as a natural and abundant counter electrode for efficient dye-sensitized solar cells. Adv. Energy Mater. 5, 1401524. https://doi.org/10.1002/aenm.201401524.

Wang, Liang, Shi, Y., Bai, X., Xing, Y., Zhang, H., Wang, Lin, Guo, W., Wang, N., Ma, T., Grätzel, M., 2014. From marine plants to photovoltaic devices. Energy Environ. Sci. 7, 343–346. https://doi.org/10.1039/C3EE42767F.

Wills, B.A., Finch, J.A., 2016. Introduction. In: Wills' Mineral Processing Technology. Elsevier, pp. 1–27. https://doi.org/10.1016/B978-0-08-097053-0.00001-7.

Wu, J., Lan, Z., Lin, J., Huang, M., Huang, Y., Fan, L., Luo, G., 2015. Electrolytes in dye-sensitized solar cells. Chem. Rev. 115, 2136–2173. https://doi.org/10.1021/cr400675m.

Xu, S., Liu, C., Wiezorek, J., 2018. 20 renewable biowastes derived carbon materials as green counter electrodes for dye-sensitized solar cells. Mater. Chem. Phys. 204, 294–304. https://doi.org/10.1016/j.matchemphys.2017.10.056.

Yella, A., Lee, H.-W., Tsao, H.N., Yi, C., Chandiran, A.K., Nazeeruddin, M.K., Diau, E.W.-G., Yeh, C.-Y., Zakeeruddin, S.M., Gratzel, M., 2011. Porphyrin-Sensitized solar cells with cobalt (II/III)-Based redox electrolyte exceed 12 percent efficiency. Science 84 334, 629–634. https://doi.org/10.1126/science.1209688.