

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

Kati Miettunen,^{1,*} Annukka Santasalo-Aarnio²

¹ Faculty of Science and Engineering, University of Turku, FI-20014 Turku, Finland

² Department of Mechanical Engineering, School of Engineering, Aalto University, P.O. Box
14400, FI-00076 Espoo, Finland.

* Corresponding author: Kati Miettunen, kati.miettunen@utu.fi

Abstract:

In their current state, conventional dye solar cells are harmful waste with no economically profitable way of recycling. However, by understanding the recycling processes and how the recycling of materials is interlinked in a multicomponent system, it is possible to eco-design the systems by selecting materials that enable economically motivated recycling and reach sustainability. Economic intensive is by far the best guarantee of recycling taking place at the end of life. With eco-design it is possible to avoid future problems, for instance having rare and expensive critical metals trapped in waste from which they are difficult or even impossible to recover. Recycling at the end of life is a perspective that is rarely considered in the field of dye solar cells research and this is the first contribution analyzing systematically how the conventional materials and their combination affect recycling and how alternative material choices change this equation. The purpose of this work is to describe the effect of multiple different material options that are still under development and to guide future research. Interestingly, many of the alternative materials that enable recycling have not originally designed for that purpose and it is often non-

obvious how the combination of different materials affects recycling. Our investigation reveals that the selection of substrate plays a major role in retrieval of other materials and the conventional thick glass substrates used in dye solar cells prevent the utilization of existing recycling methods for retrieving critical materials. Using plastic, paper, or wood substrates would allow retrieval of critical metals but those substrate types require further development in particular to reach sufficient stability. Another option is employing a very thin, flexible glass (motivated usually by enabling roll to roll mass production with high device efficiency and stability) to make the weight portion of silver in the system high enough for economically feasible recovery.

Keywords: Eco-design, Photovoltaics, Dye Sensitized Solar Cells, Material development, Recycling, Circular Economy

List of abbreviations

DSC	dye solar cell
FTO	fluorine doped tin oxide
ITO	indium doped tin oxide
PEDOT	poly(3,4-ethylenedioxythiophene)
PET	polyethylene terephthalate
TCO	transparent conducting oxide

1. Introduction

As the number of solar cells increases significantly in the following decades, a large amount of critical elements is needed to convert sunlight into electricity. However, when renewable energy devices such as solar cells are designed, they often aim only at high performance, low cost, or long lifetime. Additionally, they require critical materials to ensure those characteristics, but still their recyclability has not been given a priority. For instance around 10 % of earth's silver is expected to be in utilization in photovoltaics by 2050 (Dias et al., 2016; Nevala et al., 2019). Silicon solar cells, which have been on the market for some time, are now starting to face challenges of

recycling. In their case the recovery of materials such as Ag is currently struggling to be economically viable – the average quantity being 630 g/ton in silicon solar cell waste (Dias et al., 2016) and the limit of economic viability 700 g/ton (Dias et al., 2016; Strachala et al., 2017). The issues of recycling have not been resolved even in other energy applications which are already in large global use: for instance, Lithium-ion batteries are not recycled even in all western countries. When Li batteries are recycled only foil materials (Cu and Al) as well as Co are recovered, while for instance Li is not currently recovered at all – though there are technical methods to achieve this – since there is no return on the additional investment (Fröhlich et al., 2017; Georgi-Maschler et al., 2012). The challenges for their 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. In general, recycling is often looked quite late in the development, for instance when there is a ready product. However, implementing eco-design strategy when materials research is still very much ongoing ensures that research emphasis can be directed towards material combinations that allow economically feasible recycling.

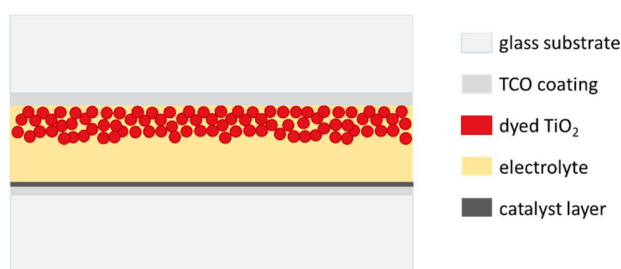


Figure 1. Structure of a typical DSC. Photoelectrode consists of a dyed TiO₂ layer on top of a glass substrate with TCO (transparent conductive oxide) coating. The counter electrode is another TCO coated glass with a catalyst layer. The space between the electrodes is filled with liquid electrolyte. Image is not in scale.

When developing eco-design for solar cells, dye solar cells (DSCs) are an interesting emerging technology since there are numerous alternative material combinations and preparation methods for all their components (Gong et al., 2017; Ye et al., 2015). DSCs have a different structure and operation principle compared to conventional silicon solar cells, in fact DSCs are electrochemical devices, which consist of two electrodes and electrolyte (Figure 1). While there is usually understanding on how materials choices of DSCs affect efficiency and some insight on stability, the information on how the material choices affect recycling is virtually non-existing. There is only one study that points out the complexity of the DSC recycling coming from the utilization of nanostructures (Reijnders, 2010).

For DSCs, possible individual eco-friendly materials or processing methods have been recently suggested (Dinesh et al., 2019; Golshan et al., 2020; Rezaei et al., 2019; Santos et al., 2019); but a systematic eco-design perspective for the full DSC system has not been proposed. Eco-designs have been prepared mainly for more simple systems as 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 as combined solar desalination plant (Monnot et al., 2018) or industrial water plant (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 knowledge of individual recycling processes, it is possible to apply eco-design approach also 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 takes place usually only 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. Another key advantage is utilization of eco-design perspective before large-scale mass production so that we can affect the recovery of critical materials that will prevent their cost, 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 very costly to fulfill the demand. The ease of recycling needs to be weight against other key criteria such as performance, lifetime, and cost. Thus, in addition to the information regarding recycling, we also shed light on the main challenges the different materials are facing in terms of commercialization to give a balanced view.

In this work, we first investigate the challenges that there are in the primary approach of reusing DSCs and their components. Secondly, we investigate recycling at the compound and elemental level. The focus of this work is to examine how DSCs would fit to existing recycling processes and what kind of tailored material solutions support recycling. It should be noted that while many of the individual materials have existing recycling pathways (for instance glass or Ag), some of them cannot be used when the material is a part of a complex device and there is no recycling

pathway that would deal with the combination of these materials. Typically, what is worth recycling are a) valuable materials (if they can be harvested efficiently to clean streams), and b) high volumes of pure materials streams. Getting clean and/or large material streams from nanostructured devices is hard in general, and in DSCs the nanomaterials are purposely intermixed, e.g. an atom layer of dye on TiO₂ nanoparticle layer penetrated with electrolyte. While it is excellent from cost and resource efficiency perspective to utilize nanostructures, the quantity of expensive materials is low, reducing the economic value at the end of life. The conventional recycling methods have very low selectivity to handle nanowaste which has high diversity and complexity. For this reason, the nanowaste would require unique, case specific recycling methods which development is costly, whereas the amounts of recovered metals are very low and do not provide the economic incentive for recovery. Some new solutions for particular nanowaste recycling have been proposed, however, they 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). Therefore, even though DSCs include rare and expensive elements that can be recycled such as Ag, Ru, and Pt, currently, in the conventional DSC the concentration of all precious metals remains below the limit of economically viable recovery as will be shown in detail in the following sections. Thus, the degraded conventional DSCs bare negative value and are considered hazardous waste since the devices contain hazardous material.

In this contribution we show that the situation can, however, be significantly improved, but setting realistic goals is important. Firstly, it should be realized that likely not all materials can be recycled in such a complex system – so it is important to think which components and materials are critical to retrieve. Secondly, having the other materials/components selected so that they do not need to be recycled (cheap, abundant/renewable, environmentally friendly) and that they do not interfere with the capturing of critical materials. Achieving these two points would already count as a great success for such a complex device. The purpose of this work is to bring insight on how the different materials, and more importantly their combinations, affect the recycling at the end of life to guide the materials research to find sustainable solutions. Surprisingly, many material approaches that have not been designed for better recycling or even for environmental friendliness (but for higher efficiency, better roll-to-roll manufacturing etc.) play a key role in developing eco-design for DSCs.

2. Methods

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

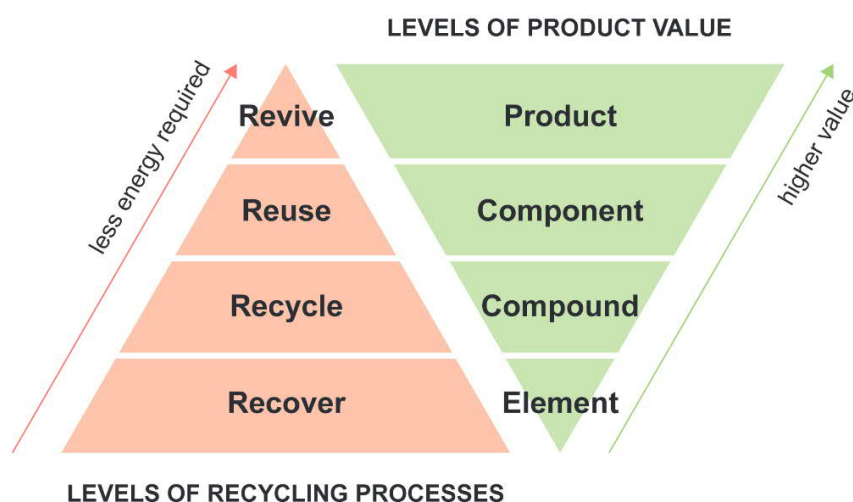


Figure 2. The different recycling levels and their correspondence to product value levels.

When considering recycling, there are various levels of material recovery that require differing energy input which are presented in Figure 2 and examples of these levels in the case of DSCs could be:

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

The left-hand-side of Figure 2 shows the recycling hierarchy where each step downwards requires more processing and therefore increased energy input. The more specialized, complex multicomponent structures the device includes, the more steps are required for their recycling. At the same time, when requiring more energy to go from product to element level, the value of the output product decreases (Figure 2). In principle the highest return on investment is achieved when

reviving high value devices with modest effort and energy (Figure 2 at the upper parts of the triangles), as opposed to utilizing a lot of energy to recover low value elements (Figure 2 at the lower parts of the triangles). The key to efficient recycling process is finding an optimal level at this triangle (Figure 2): the less we need to process, the more likely it is that recycling makes economic sense. Going down to element level is sometimes required if the reuse of components is prevented by them being too degraded or their cleaning takes too much labor-intensive processing.

Furthermore, we consider that eco-design approach should be used in materials development of new energy systems to increase the recyclability rate and to avoid unintended consequences such as degraded devices causing environmental problems. Since DSCs are not yet a fully commercial technology, it is still possible to propose new directions for the material development. We introduce a new eco-design approach for materials selection to energy systems that is presented in Figure 3.

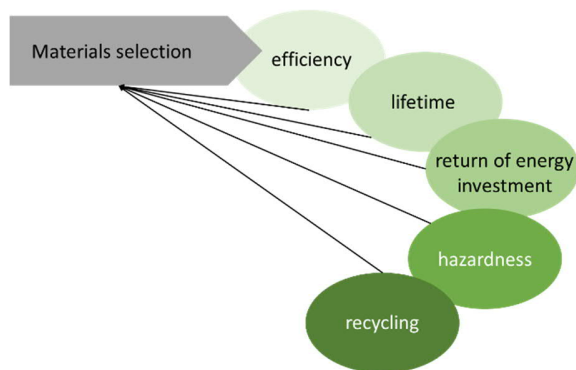


Figure 3. Eco-design decision approach for the material selection to a DSC system.

As is presented in Figure 3, the materials design should start from reaching sufficient efficiency and lifetime to merit further research. The next step is to look into return of energy investment (REI) which comes from potential to produce energy (determined by efficiency and lifetime) compared to energy embedded into the system during its production. It is important that solar cells produce a lot of energy and their replacement time is long. The REI values are unknown for many of the materials used in DSCs and such values are basically known only for the most typical conventional DSC materials (Parisi et al., 2014; Veltkamp, 2007). Eventually, all solar cells degrade and having suitable means for their recycling is critical to retrieve in particular rare

materials back to use. The first step in the recycling is to evaluate the safety of the components – hazardous materials usually make recycling more challenging and in worst case prevents it. Then, it is good to investigate if there is recycling pathways for the individual materials – this was not the main challenge here but should be kept in mind when considering new alternative materials. In terms of recycling the important aspect to consider is the how to recycle the material system: choosing combinations and/or the weight portions of different materials to enable recycling. In this work, we gather information related to the eco-design of DSCs shown in Figure 3 for different material combinations, and particularly focus on developing insight related to recycling. Some material options are incompatible with each other and only compatible ones are considered in this work. We will assess the hazardness and recyclability of each component separately and after that as a full system and classify them by 4 different categories:

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

Each of the different parts of DSCs and their materials choices are discussed in detail in the following sections taking into account the large variety of different material choices and their combinations for the full recyclability of this energy system. After that we have prepared a recyclability analysis for each mix-component DSC system and found alternative routes that will provide high recyclability.

3. Results and Discussion

Reviving DSCs and reuse of components

According to the recycling hierarchy (Figure 2), we should first address the possibility to revive the whole DSC system. For that analysis it is pivotal to investigate the degradation processes. In

the aging of DSCs, the degradation of electrolyte often plays a key role (Asghar et al., 2010; Ye et al., 2015). For instance, in our studies both in accelerated aging tests and in outdoor conditions, the loss of charge carriers in electrolyte was the main reason for degradation (Lepikko et al., 2018; Mastroianni et al., 2014; Miettunen et al., 2016; Poskela et al., 2018; Tiihonen et al., 2015). In practice, charge carriers reacted and formed compounds that offered either no or very limited charge transfer. If the electrolyte was the only degraded component and if there were effective methods for flushing aged electrolyte out the device without damage to other components, then refilling DSCs with new electrolyte could be the cheapest option for reviving them in an economical manner. Those two requirements are not, however, easy to fulfill. If the cells degrade due to leakage, it is likely that the incoming impurities would degrade the entire device, and managing the leakage and refilling is unlikely to suffice. In a system with many sensitive components and variation in the cause of degradation, reviving devices may require too much manual case-by-case analysis rendering the approach unfeasible.

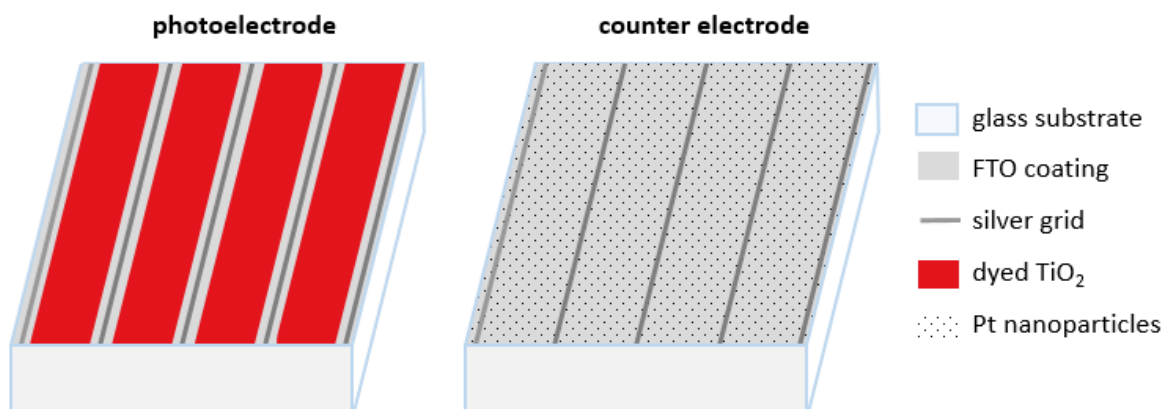


Figure 4. The structure of the electrodes in conventional DSCs.

If reviving complete DSCs proves to be too challenging, the next step would be to consider reusing cell components (Figure 2). When taking the cell apart, the first step is to split the cell into two by separating the two electrodes (Figure 4). Firstly, reusing electrodes as such (after rinsing electrolyte residues) should be considered. The challenges in electrode reuse are that the electrode materials may be too degraded, and they could degrade more during the recycling process (e.g. dyes at the photoelectrode are typically sensitive to air and moisture). Another step down is to consider recycling the conductive substrates. Glass substrates with the transparent conducting

oxide layer (TCO, typically fluorine doped tin oxide (FTO)) are typically a relatively robust part of the device. Furthermore, the TCO glasses are the most expensive components of DSCs comprising up to 60% of the total materials costs (Hashmi et al., 2011; Kalowekamo and Baker, 2009; Kroon et al., 2007), and thus their reuse is lucrative. The viability of TCO glass reuse can be evaluated with comparing with another technology: In the case of screens, it has been commercially profitable to dismantle screens by hand and take their TCO plastic (ITO-PET, of roughly similar or higher cost to FTO glass) (Hashmi et al., 2011a) to make new products (Dang et al., 2015). However, the ITO-PET taken from screens is clean whereas the TCO glass from DSCs is topped with a multicomponent electrode and electrolyte residues – so an additional labor-intensive step would be required which increases the cost. In terms of feasibility of the cleaning, 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 to 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 to sections (in contrast ITO-PET layers used in screens). Thus, while the reuse of TCO glass could be technically possible, its profitability as well as geometrical suitability for reuse remain highly questionable.

Recycling of DSCs and material recovery

The purpose of the next sections is to provide a holistic overview on the recycling processes used for electronic and energy devices to recover pure material streams. Comprehensive review on these different processes to recycle energy devices is presented elsewhere (Velázquez-Martínez et al., 2019). Figure 5 shows a schematic of different possible recycling steps that can be applied for solar cells and the recycling path is selected to optimize the recovery (i.e. which exact steps are needed). The first step of the recycling process is the collection and transportation of the aged devices to the recycling facility (Figure 5). For DSCs, arranging logistics can be a significant challenge since large enough volumes are needed to motivate it. Additionally, safety issues must be considered: for instance, DSCs contain typically liquid electrolyte and therefore it is important to keep the cells undamaged until they can be handled in proper safety conditions. The different recycling process steps and their applicability for DSC recycling are discussed next.

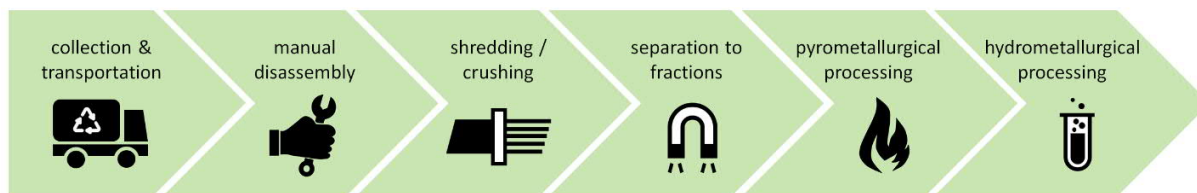


Figure 5. Possible process steps for recycling DSCs. These processes can be optimized by altering the number of steps i.e. including only steps that necessarily required and bring added value in a particular case.

Mechanical processing

The purpose of mechanical processing in recycling solid state waste is to liberate and separate different components to as clean product streams as possible. In reality, this is only performed in two different cases: 1) it is economically feasible (e.g. a clean product stream can be obtained with high purity with economical value), often at higher levels of recycling processes (Figure 2) or 2) 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 before the actual mechanical recycling, there is a labor-intensive manual stage to separate clean parts or hazardous compounds, for example in car recycling, the battery needs to be removed and processed separately. In the case of DSCs, if the cells are protected with a metallic frame and/or other casing, such casing as well as external wiring should be taken apart at this stage (Figure 5) and recycled separately since in this way pure material stream can be obtained.

After the manual dismantling stage, the comminution phase will start to liberate different materials from each other by crushing or shredding to as clean stream as possible (Figure 5). In DSCs, the layers are nanometers or micrometers thick and they are purposely intermixed, for instance the electrolyte penetrating the electrodes. Furthermore, the electrode materials in DSCs are deposited/printed on glass substrates unlike in silicon solar cells where wafers are protected by glass that can be detached. The material liberating is ensured by utilization of different shredders, crushers, or cutters depending on the material type; for Si solar cells crushing and shredding are used (Strachala et al., 2017) and most likely DSCs would be mechanically recycled in a similar manner unless they are directly inputted into pyrometallurgical processing.

In general, the next step in the mechanical processing is the separation of materials into different fractions (Figure 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 of materials will remain at larger size after shredding and are easy to separate from small particle size glass and any powders based on particle size and shape (Kaya, 2016). Thus, to ensure liberation, powder materials need to be detached from surfaces where they were originally attached to and this is challenging for nanomaterial powders in DSCs. One of the first process steps is often magnetic separation that will collect material streams that possess magnetic properties. The following mechanical separation steps (Figure 5) can include properties as 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 such 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 only one element. It is also good to keep in mind 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, for instance Co metal is not magnetic whereas some Co nanoparticles are strongly magnetic. Another challenge with nanowaste is that it can easily be diluted in the waste stream, and therefore some nanoparticles cannot be separated by a magnet even if they are magnetic.

Since the volume fraction of substrate in DSCs is so dominant (typically around 99 %) (Parisi et al., 2014) because the active materials are at most micrometer level thick, the substrate will dominate the physical properties preventing separation of the active components with all the above mentioned methods. Since the nanolayers/nanoparticles are attached to the substrates, those will not be separated by shredding or crushing. Thus, the high value nanomaterials cannot be separated in a high value stream with the conventional methods, and on the other side the nanomaterials prevent the recovery of the glass as a pure high-volume stream.

Pyrometallurgical processing

When producing metals from ores, the metal is often as an oxide or sulfide mineral that is reduced in a pyrometallurgical process (referred here on as pyro process) at high temperature. The smelting process is optimized for one main metal (for instance Cu) that will remain in liquid matte and the

rest of impurities separate to an oxide based slag and there are possibilities 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 (Figure 5). In the case of batteries, there are processes where batteries are directly inserted to the pyro process without any mechanical pretreatment. The advantage in this approach is that there is no need to invest into mechanical separation equipment and if the feed batteries still include some electrical charge, it will not damage the processing equipment (Ojanen et al., 2018). Therefore, pyrometallurgical processing is a robust way to recycle complex energy devices in a safe way. The disadvantage of the direct feed of devices into pyro process is that only one or possibly few metals are recovered while the rest of the materials are utilized only as energy (incinerated at high temperature). Furthermore, there are some materials (unfortunately typical for DSCs) that are not wanted in the pyro process: firstly halogens, such as iodine and fluorine, are volatile at the high temperatures and can cause air pollutants. Secondly, a large amount of glass will not be incinerated but would significantly increase the volume of the slag and reduce the concentrations of the recovered metals in the slag. Nevertheless, some silicates are included to the pyrometallurgical processing to enhance the slag quality. The best-case scenario is that adding some glass-based solar cells could even reduce the need for process additives. However, this is a question of overall process design in the future.

Hydrometallurgical processing

After the pyro process or, in some cases, streams directly from mechanical processing, the fraction can be upgraded with hydrometallurgical processes (referred here on as hydro processes) where metals are recovered from aqueous solutions (Figure 5). The key is that individual metals can be obtained in quite 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 to hydro process should be very fine to ensure good solubility and therefore high recovery. In solution with various metals, their separation is dependent on how similar conditions they precipitate: if the conditions are close to each other it is very unlikely that they can be recovered with high purity.

These basic principles from the recycling process are to provide a view on how difficult it is to recycle complex multimaterial devices. The reality is that if recycling is omitted at the design

stage, most likely it is possible to recover just few elements and all economic incentive is lacking. This increases the probability that the devices have a significant risk to end to a landfill. It is quite unlikely that all the materials can be recycled from such a complex system. Therefore, it is important to establish which materials are most crucial to recover and how this process can be made economically motivated for instance by selecting other materials so that they do not prevent the recovery process and the lost materials are preferably abundant and renewable.

Eco-Design of DSCs

Next, we investigate the possible recycling options for each individual component of DSCs and discuss how the alternative material options and eco-design methodology affect the recycling. Figure 6 illustrates how material choices in DSC design will affect the recyclability of the entire system and we go through each case in the following sections. Since substrates dominate the recycling process due to their highest weight portion, Figure 6 summarizes how the substrate selection affects the recycling of materials in DSCs. For instance, a typical DSC prepared on thick glass substrates is not suited for commercially viable recycling and furthermore it is hazardous in the recycling process. However, there are several pathways which allow recovery of all critical elements and do not lead to formation of hazardous gases in the recycling process (Figure 6). In the following sections, all materials shown in Figure 6 are investigated component by component.

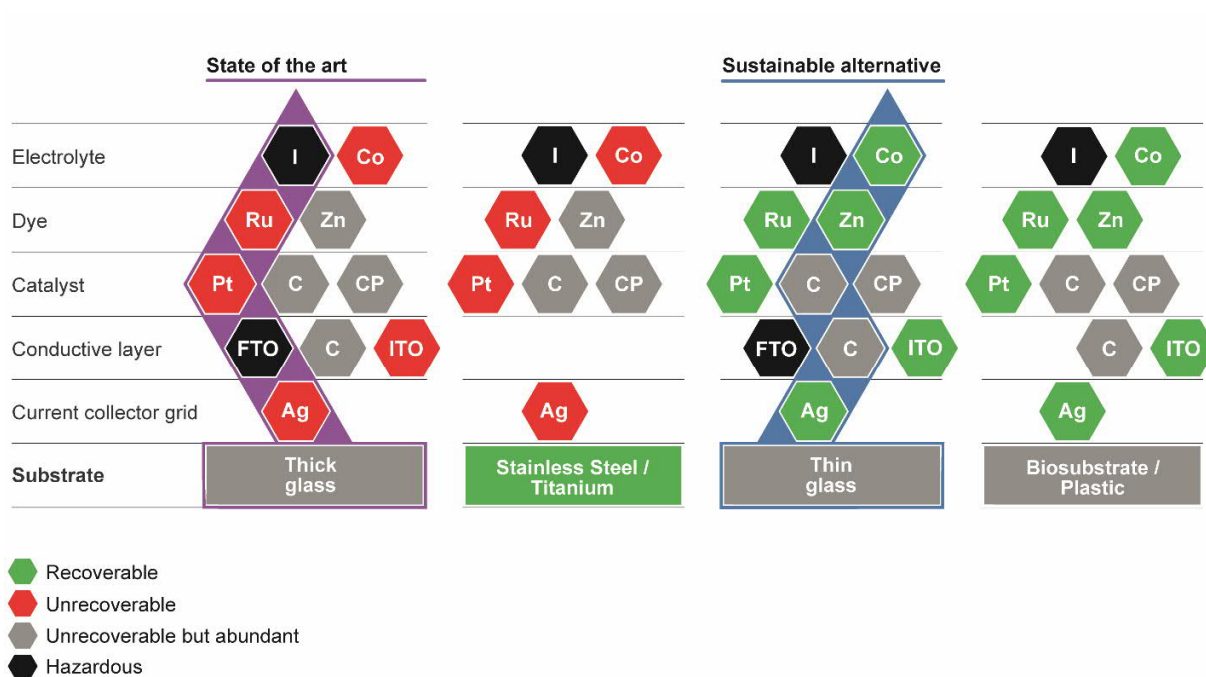


Figure 6. Different material and elements choices for DSCs and their potential for recovery in current recycling processes. Hazardous refers to hazard in the recycling, mainly formation of toxic gases. CP stands for conducting polymer. The typical DSC is noted as state of the art and one of the possible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

Substrates

The typically used substrate for DSCs is a thick glass with the FTO coating. As mentioned earlier, recycling of the FTO glass as a complete component would be excellent if it could be done in an economically viable manner. For that limitations arise from how well the degraded topping electrodes can be removed and how much energy and manual labor that requires. If the FTO glass cannot be recycled as a component, it is crushed together with other components for pyro or hydrometallurgical processing. A major challenge in the pyro or hydro processing is that the normally used thick glass dilutes the proportion of other materials, in particular Ag, (7.2 g/m^2 which is $\sim 300 \text{ g/ton}$ with 4 mm thick glasses) (Parisi et al., 2014) below the limit of economically viable retrieval (700 g/ton for Ag) (Dias et al., 2016; Strachala et al., 2017). Thus, to make DSCs commercially interesting for recycling, it would be important to lower the total weight of the substrates at least below $10,000 \text{ g/cm}^2$ (i.e. two 2 mm thick glasses) but preferably even more so that the device at the end of life would have significant value to motivate recycling. Typically, thick glass sheets are used to make the device less fragile so it should be carefully weight how thin

the glass layer can be without major compromises on safety or stability of the device. 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 as well (Reuter, 2013). As discussed earlier, as a pure material stream glass is recyclable, however, with the connection of different metals, chemicals, and nanoparticles, most likely it would not be accepted for glass recycling. Furthermore, thick glass substrates would not be accepted for direct pyro processing to recover the other materials as the vast weight portion of glass in the solar cell would increase the slag amount and its composition. Therefore, all compounds and elements in the DSCs (except perhaps the external casing) would be lost as illustrated in Figure 6.

The typical alternative substrates are plastics, metal foils, and most recently bio-based and bio-composite substrates (Miettunen et al., 2018). Typically the motivation to use of these alternative substrate is that they enable roll-to-roll manufacturing, which has been seen critical in keeping the manufacturing costs down, as well as in some cases getting also direct reductions in materials costs since the FTO glasses are the single most expensive components in DSCs (Hashmi et al., 2011; Kalowekamo and Baker, 2009; Kroon et al., 2007). Notably, the value of the FTO coating on top of the glass is not separated in these calculations but it plays a major role. Like FTO glass, if these alternative conductive substrates can be reused that would be a priority, but they are facing the same issues as the FTO glass discussed earlier. Here, we discuss how these supporting materials affect recycling; separate conductive layers (e.g. FTO) are discussed separately later.

Plastic (as such with no conductive coatings) is a low value material like glass and thus only high purity and high-volume plastic streams are economically interesting for recycling (e.g. plastic food containers such as bottles). Neither of those criteria is fulfilled when used in DSCs. The benefit of using plastics instead of glass in DSCs is that they are flexible but also thin and lightweight; typical plastic substrates are 200 μm thick (Lund et al., 2018) so their mass contribution would be only around 200 g/m^2 per substrate. Therefore, if plastic is used on both electrodes, it offers a massive over 20-fold reduction to the overall device weight compared to a conventional glass-based device. The utilization of plastic substrates would thus increase the weight portion of silver to around 15,000 g/ton making it multiple times over the limit of economically viable retrieval. Furthermore, since the reuse of plastics from DSCs would not be interesting, they can even be burned in the

retrieval of metals, the amount of remaining ash is estimated to be around 0.2 % for the plastic (Sánchez et al., 2007), which would increase the weight portion of other materials even further (e.g. Ag would be in the order of 100,000 g/ton) – over 100 times over the limit of economically feasible recovery of Ag and in such case the degraded solar devices would have a significant value at the end of life. It should be noted that utilization of plastic substrates results in losses in the overall device performance since high temperature treatments in the manufacturing cannot be employed (which is particularly problematic when considering the use of cobalt complex electrolyte) and additionally the plastic substrate are permeable which results in stability issues (Lund et al., 2018; Miettunen et al., 2018). The other downside with plastics is that they are not renewable and recently bio-based alternatives and composite structures have been investigated (Miettunen et al., 2018). Burning bio-based materials at the end of life would be even less of a concern. However, the bio-based substrates have at the moment even more challenges with permeability compared to plastic substrates that limit the cell lifetime (Miettunen et al., 2018). But quite interestingly paper and wood based substrates can provide superior optical properties – allowing light reflection inside the device due to high haze – resulting in higher photocurrent compared to glass or plastic substrates as has been demonstrated in other photovoltaic technologies (Chen et al., 2018; Fang et al., 2014; Hu et al., 2013; Li et al., 2018, 2016; Ma et al., 2019). In DSCs, the studies of bio-based approaches have been limited to opaque substrates (Hashmi et al., 2014). 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 (Figure 6) (Sánchez et al., 2007).

The other typical alternative substrates are metals. The benefit with metals is that they allow using high temperature treatments and reaching higher efficiencies in flexible solar cells is easier compared to plastic substrates alone (Lee et al., 2013; Li et al., 2019; Liang et al., 2015). The main challenge in using metals in DSCs is their corrosion in the liquid electrolyte – the particular problem is that the charge carriers in the liquid electrolyte corrode the metal and whilst doing so the reacted charge carriers are rendered useless from the operational perspective of the solar cells (Miettunen et al., 2015). In other words, the metal is typically only marginally affected by the corrosion but the loss of corrosive agents, the charge carriers, degrades the cell performance (Miettunen et al., 2015). Thus, the corrosion prevention needs to be at a considerably higher level

than what is needed to prevent harmful degradation of the metal itself, and there are very few metals that can reach such stability in the iodine based electrolyte (Miettunen et al., 2015). When using iodine based electrolyte, Ti has been the only stable metal that can be used without additional coatings (Miettunen et al., 2018). Ti foils are expensive (90 \$/m², 5-10 times the cost of FTO glass substrates)(Hashmi et al., 2011) causing a significant increase to the overall device cost making large scale manufacturing questionable. When using Co complex electrolyte which is less corrosive, cheaper metals, such as stainless steels (Miettunen et al., 2012) or even ferritic steels (Miettunen et al., 2014), can be utilized. Stainless steels could be up to 80 % cheaper than conventional FTO glass substrates (Hashmi et al., 2011) so they are interesting from commercial perspective, and conformable for metal recycling. However, the pyrometallurgical recycling processes of both Fe (used for stainless steel) and Ti do not allow the recovery of Pt, Ag, Co, or Ru as shown in Figure 6 (Sánchez et al., 2007). Metal substrates offer a simpler structure compared to glass or plastics since no additional current collectors are needed on that side and therefore both TCO and Ag grids can be omitted. This is because metals even with poor conductivity have more than 1000 times higher conductivity compared to TCO layers such as FTO (Ma et al., 2004). Metal foils are opaque so only one electrode, typically the counter electrode, can be made on it and a separate catalyst layer is still needed (Miettunen et al., 2013). In the case of metal electrode, it would be important to separate the two electrodes so that for instance Ag current collector grid on the window electrode could be recycled. It is also possible to make a monolithic solar cell on a metal foil and omit other substrate completely (Fu et al., 2013). The monolithic cell design is more difficult to prepare – making all layers work together (e.g. without peeling off) and avoiding pinholes that could lead to short circuiting is challenging. In the case of a metal based monolithic cell, the metal substrate would be the only part that could be recovered. Another option to avoid using TCO altogether is preparing DSCs on metal meshes (Yang et al., 2020).

Another, very unusual approach for flexible solar cells is to utilize extra thin flexible glass layers (0.1-0.2 mm) (Sheehan et al., 2015). Whilst the conventional soda glass is very brittle as a thin layer, the willow glass is flexible. There are benefits of utilization of extra thin flexible glass when considering device performance and lifetime: it is a good barrier (unlike plastics), it is inert towards corrosion (unlike many metals), and it enables high temperature treatments (up to 550 °C) (Sheehan et al., 2015) which is essential for the preparation of the highest quality photoelectrodes

to reach top performance. Utilization of flexible willow glass is likely more expensive compared to normal soda glass sheets, but its flexibility would enable roll to roll manufacturing which in turn lowers the manufacturing costs. By utilizing super thin flexible glass substrates instead of typical thick ones, the total weight of the substrate reduces to 500-1,000 g/m², which increases the percentage of silver in the whole device to 3,000-6,000 g/ton which is high enough to motivate recycling of Ag from commercial perspective (at best almost 10-times above the limit of economic viability). Glass cannot be reduced in volume/mass further by burning unlike plastics or bio-substrate, but it is inert and not harming recovery of other materials. For thin glass, similar recycling approach as for the alternative substrates could be utilized: if DSCs with thin glass substrate would be possible to insert directly into Cu pyro process, the recovery of valuable metals is possible (Sánchez et al., 2007). Thin glass would not burn but it would go into slag, however due to its smaller volume, it might not alter the slag volume or composition too much. This is a research field that would require further investigation. Utilization of super thin glass is a prime example of how change in one component could tip the balance so that it would make the recycling of another component (Ag current collector grids) in the device economically profitable.

Conductive layers

As mentioned, the FTO coating on the conventional glass substrate is hindering recycling of other components since in the pyro process it results in toxic gas. The typical alternatives are indium doped tin oxide (ITO), thinly printed metal grids, conductive polymers, and carbon nanotubes (Ellmer, 2012). These different materials can be applied on variety of substrates and the only approach which does not work for all substrates is FTO. Since FTO requires high temperature manufacturing, it cannot be applied on plastics or bio-based substrates, and the common low temperature alternative has been ITO. Replacing FTO with ITO resolves the toxic gas problems related to fluorine during recovery of metals, but causes another critical recycling problem: indium is a very rare metal and its amounts are insufficient for large scale global manufacturing of photovoltaics (Grandell and Höök, 2015). Thus, utilization of other alternatives is highly recommended even if In could be recycled in some cases (Figure 6).

One option for the preparation of transparent conductive layers is to utilize thin metal grids, e.g. from Ag. Although Ag is in limited supply if it is used anyway to make the current collectors and the cell design is commercially viable for the recycling of Ag, having more of the same metal on

the same substrate would make this additional coating directly economically feasible for recycling. In general, having fewer different materials is typically easier from recycling perspective. The transparent Ag grids cannot, however, be utilized in all DSC types since Ag corrodes very easily in iodine based electrolytes (Miettunen et al., 2015), and they cannot be protected like the larger scale current collector grids. Thin Ni grids have been demonstrated in DSCs (Okada et al., 2004), but later on also Ni was shown to corrode in the iodine based electrolyte (Fang et al., 2005).

Conductive polymers such as poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT-PSS) are another option to make a transparent conductive layer. Such polymers are uninteresting for commercially viable recycling from DSCs, but they are abundant and do not hinder recycling of other more critical materials. It should be noted that some of conducting polymers are also catalytic: at the counter electrode, the conducting polymers could replace even both the conductive and the catalyst layer which is discussed more in the following section. PEDOT based materials are actually one of the highest performing catalysts for Co complex electrolyte (Park et al., 2014; Tsao et al., 2011). In contrast at the photoelectrode, conductive polymers are highly problematic since even a poor catalyst can cause massive back reaction resulting in major losses in efficiency. Another issue is sufficient stability for the conducting polymers – it should be kept in mind that photovoltaic devices are subjected to very harsh environmental stress, e.g. UV light, that may degrade the polymers.

Another option are carbons structures which are generally rather robust. Although stability needs to be validated case by case, carbon structures have been used in many cases to reach long term stability for DSCs (Kato et al., 2009). Thick carbon layers can be also utilized as a catalyst layer like some conductive polymers discussed above. Interestingly, whilst carbon nanotubes have some catalytic features, they can be utilized also at the photoelectrode: for instance they have even been mixed into the porous dyed TiO₂ to improve the charge transfer at the photoelectrode (Yen et al., 2008). Thus, the transparent carbon nanotube layers could potentially be utilized at both electrodes. Carbons, also for carbon nanotubes, can be sourced from fossil sources or from renewable biomass. In particular in the latter case, they could offer an environmentally sustainable option that supports the recovery of critical materials in DSCs.

Counter electrode

As mentioned earlier, the conventional catalyst Pt is problematic – it is rare and expensive metal, with likely availability issues in large scale manufacturing of solar cells (Hinsch et al., 2014). This is even though the evaluated amount of Pt in DSCs is very small since only a very thin layer is needed and the amount varies between 0.02-0.1 g/m² (0.8-4 g/ton) (Hinsch et al., 2014; Veltkamp, 2007). 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 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 so the suggested amounts of Pt are on the borderline (Lewins et al., 2008). Utilizing thin 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 (Figure 6). Note that in the case of stainless steel and Ti substrates, the pyrometallurgical recycling process of neither stainless steel nor Ti allows the recovery of Pt (Figure 6) (Sánchez et al., 2007).

Although Pt could be in some cases recovered, more abundant alternatives should be preferred. In previous section, we already discussed some alternatives: carbons and conducting polymers. These materials can reach roughly similar efficiencies than Pt in DSCs with iodine based electrolytes (Thomas et al., 2014). Furthermore in DSCs with Co complex electrolyte, alternative materials can even outperform Pt, and record efficiencies have been reached with carbon catalyst (13 %) (Mathew et al., 2014). From stability perspective, carbon catalysts are usually stable and they have been utilized for instance in the longest reported outdoor stability test of DSCs (Kato et al., 2009). In conclusion, the utilization of carbon-based catalyst does not compromise performance, lifetime, or cost compared to Pt – in fact carbon could even surpass Pt. For conductive polymers, there are some concerns about their stability (Thomas et al., 2014). Carbon and conductive polymer catalysts are normally used in much larger amounts compared to Pt (carbons typically around 10-60 µm thickness). Whilst the layers are thicker, these materials are abundant and lower value compared to Pt. They cannot be sourced back from degraded solar cells, but instead carbon and conducting polymers would be burned in the retrieval of precious metals. Depending on how the carbon and polymers have been sourced, the issue of not retrieving them varies. In the most environmentally sound end, there are for instance bio-carbons that are prepared from bio-waste streams using waste from food production (Ma et al., 2018; Madhu et al., 2014; Maiaugree et al.,

2015; Wang et al., 2015), forestry waste (Jiang et al., 2010; Xu, 2017; Xu et al., 2018), or marine biomass (Wang et al., 2014). Carbon catalyst layers are often composite layers containing materials such as ZnO, ZrO₂, and TiO₂ (Hashmi et al., 2014; Ogata et al., 2019; Wu et al., 2011). Since such composite materials are cheap, abundant, and safe, not recycling them is not an issue.

Electrolytes

The selection of electrolyte plays a critical role: the good operation of DSC requires that the electrolyte penetrates well both electrodes, which consequently means that its residues will be present at both electrodes in the recycling. As mentioned earlier, electrolyte is often among the first components to degrade and its reuse is not possible. The sufficient availability of iodine for very large scale use in DSCs has also been questioned (Hinsch et al., 2014). However, iodine should be collected from degraded devices since it is harmful for aqueous life and requires to be disposed as harmful waste. Iodine in the conventional pyrometallurgical metal recovery process (i.e. those used for recovery of Ag) can cause harmful HI that will be released as part of flue gases and should therefore be avoided. Since the electrolyte is present on all the active components of DSCs, it can in the worst case prevent the recycling of all other components.

There are, however, alternative redox couples. Most of them, such as pseudohalogen redox couples, such as SeCN⁻/(SeCN)₃⁻ (Wang et al., 2004), disulfide/thiolate redox couples (Wang et al., 2010), or ferrocene/ferrocenium (Daeneke et al., 2011) result in lower efficiencies compared to iodine based electrolytes and many suffer from poor stability in the final device rendering them uninteresting for large scale manufacturing at the moment (Wu et al., 2015). The exception among alternative electrolytes are the Co complex based electrolytes, which have been used to exceed the efficiencies of the conventional iodine based electrolytes (Mathew et al., 2014), and more recently also Cu based electrolytes (Cao et al., 2017). The Co complex electrolytes have suffered from stability issues (Hinsch et al., 2014), but modifications to the electrolyte composition has improved the situation (Jiang et al., 2014; Kamppinen et al., 2020; Wu et al., 2015). It has been evaluated that unlike iodine based electrolytes, those based on Co complexes based have virtually no limitations of availability (Hinsch et al., 2014). It should be remembered that like iodine also Co complexes as such are not environmentally friendly materials, and the leakage of Co to soil needs to be prevented (critical concentration in soils 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

and from there it, as well as series of other precious metals (e.g. Ag, Pt), can be recovered (Figure 6) if Cu pyro processing is used (Reuter, 2013). Note that if there is a sufficient amount of Ag to economically motivate recycling – the other metals such as Pt or Co can be retrieved economically from the slag even if they were present in much lower quantities than needed for their economical viable recovery as an individual element. This is because the energy intensive part (expensive part) of the processing is already done.

Photoelectrode

The photoelectrode is composed of a dyed TiO₂ layer. TiO₂ is a cheap and abundant material that is also used by industry as a filler. It is significantly more valuable, approximately 100 times, as a nanostructured screen printing paste ready to be utilized in DSCs (Hashmi et al., 2011a). It cannot be retrieved in the form of paste and thus recycling it is not motivated. Luckily the TiO₂ particles do not interfere with the recycling of other materials. The dye layer on top of the nanoparticle TiO₂ layer is the valuable material, but its proportion is extremely small since it is only one atom layer thick. Conventional high performance and stability dyes in DSCs with iodine electrolyte are typically Ru complexes (Asghar et al., 2010; Harikisun and Desilvestro, 2011). Ru is an expensive and scarce to extent that its availability may hinder very large scale manufacturing of DSCs (Hinsch et al., 2014). Therefore, it should not be wasted and preferably it should be replaced. Alongside the electrolyte, the dye is one of the components that are most likely subjected to degradation (Asghar et al., 2010). Thus, whilst the dye layer can be detached, for instance with water/ethanol mixture containing tetrabutylammonium hydroxide which is used in the analysis of the degradation of dye (Rendon et al., 2015), it is highly unlikely that the dye could harvested in a good condition without impurities ready to be used again. The degradation products of the dye vary based on the composition of the electrolyte, impurities in the device, and on the weathering conditions (Rendon et al., 2015; Tiihonen et al., 2015; Tuyet Nguyen et al., 2010, 2009). In other words, the dye does not end up in one single degraded state, which would be easier to manage in the revival and reuse of the degraded dye. Recovering Ru as a metal from a degraded (crushed) solar cell, is even more problematic since the amounts of dye are so negligible, 0.1 g/m² (Hinsch et al., 2014). In conventional glass-based DSCs, the amount of Ru is only 0.5 g/ton. Ru can be recovered in a similar process as Pt (Figure 6) and is economically motivated only as a part of other recovery processes (Fröhlich et al., 2017).

When considering alternative dyes, natural dyes, such as Chlorophyll, have been suggested since their utilization would remove not only the need for precious metals in dyes but also the costly and energy intensive synthesis process of dyes (Ludin et al., 2014). However, natural dyes have major limitations in terms of both performance (highest efficiency only 2.67 % with mangosteen peels) (Maiaugree et al., 2015) and poor stability (Escobar and Jaramillo, 2015; Ludin et al., 2014). Thus, they are not currently able to provide a commercially or even environmentally sound alternative, when considering aspects such as return of energy investment of the entire device.

There are other alternatives such as organic synthesized dyes or dyes with non-rare metal center. Some of them are even more energy intensive to prepare than the conventional Ru based dyes, such as 5,15-bis(2,6-dioctoxyphenyl)-10-(bis(4-hexylphenyl)amino)-20-4-carboxyphenyl ethynylporphyrinato]Zinc (II) (known as YD2-o-CB) is three times more energy intensive to prepare compared to Di-tetrabutylammonium cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium(II) (known as N719) (Parisi and Basosi, 2015). However, since dyes are used in such a negligible weight percentage, even tripling the energy required for manufacturing of the dye itself does not add significantly to the overall embedded energy at the device level. Interestingly, the conventional Ru based dyes do not result in the highest performances in DSCs with alternative electrolyte, but top performances are reached with a porphyrin dye with Zn as the central metal such as the above mentioned YD2-o-CB (Yella et al., 2011) or an organic dye 3-{6-[4-[bis(2',4'-dihexyloxybiphenyl-4-yl)amino-]phenyl]-4,4-dihexyl-cyclopenta-[2,1-b:3,4-b']dithiophene-2-yl}-2-cyanoacrylic acid (Y123) (Cao et al., 2017). Having Zn instead of Ru relaxes the need to recover the dye due to utilizing a less scarce metal. Zn is abundant so if cannot be recycled if used for instance with stainless steel substrates (Figure 6), it is not significant loss. However, Zn could be recycled when used together with thin glass, plastic or bio-based substrate (Figure 6).

4. Conclusions

The main scope of this contribution is to initiate discussion on the consequences of different material selections for the recyclability of DSCs and provide eco-design strategies for development of devices. In the future, all produced energy production devices having metallic or harmful components need to be recycled. But unfortunately, such recycling processes are highly non-trivial

for advanced nanostructured devices like DSCs, and it is questionable if they can become economically viable. As this work concludes, components or elements, that in general can be recycled, may not be possible to recover as a part of a DSC system. It is not just the individual components but the entire system that needs to be considered – the combination and proportions of materials defines which materials, if any, can be retrieved. Proper eco-design prior to commercialization, preferably already during material development, ensures that any critical materials needed for the high performance is recovered.

Reviving complete devices or reusing components should be preferred in the recycling process, but it is questionable if they can be obtained in good enough condition and what type of labor-intensive steps are required. Building such tailored recycling processes requires that very large quantities of aged solar cells are put through it. Among the different DSC components, conductive substrates are the most likely parts to reach economically profitable reuse, but even they have major challenges. Primarily the work required to separate and clean them may be too costly.

When considering the retrieval of elements from degraded DSCs, existing recycling pathways could be utilized which relaxes the need for very large quantities of degraded devices. The challenge in utilization of existing recycling methods is complicated since DSCs consist of multiple materials, many of which are nanostructured and appear in such small quantities that their recovery may not be economically feasible. For instance, the conventional of DSCs with thick glass substrates do not conform to economically viable recycling for rare metals and in addition it includes toxic materials. There are, however, several material combinations that lead to sustainable options in regard to recycling. For instance, changing from thick glass substrates to thin flexible substrates is enough to change the weight percent of Ag current collector grids so that their recovery is economically motivated. The utilization of a super thin flexible glass (i.e. using same type of base material but in smaller quantities) would suffice to motivate recycling without sacrificing the advantages that glass substrate gives in terms of performance and stability. Some of the substrates, such as plastic or cellulose based foils, could even be burned off, raising the proportion of Ag over 100 times above the limit of commercial viability for recycling, meaning that DSC waste would have significant value. However, these substrates still face other challenges, in particular in stability, before they can be utilized in commercial devices, but these results give

further motivation for their research. Interestingly, DSCs based on cobalt or copper complex electrolytes, which are known for their high performance, suit also better for the recycling process compared to iodine-based electrolytes. Furthermore, Co or Cu based devices show highest performance with abundant alternative materials such as carbon catalysts and organic dyes or dyes based on Zn. If it is economically meaningful to collect degraded DSCs because for instance their Ag concentration is high enough, the benefit is that the cells will go to the recycling process and other harmful chemicals that the cells contain do not end up untreated in the soil.

Acknowledgements

We thank Glen Forde from Aalto Energy Platform for his help in the preparation of this work, particularly the design work for Figure 2 and Figure 6. Kati Miettunen thanks Academy of Finland (project BioEST, 318557). We are grateful for the support by the FinnCERES Materials Bioeconomy Ecosystem.

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, S., Song, Y., Xu, F., 2018. Highly Transparent and Hazy Cellulose Nanopaper

- Simultaneously with a Self-Cleaning Superhydrophobic Surface. *ACS Sustain. Chem. Eng.* 6, 5173–5181. <https://doi.org/10.1021/acssuschemeng.7b04814>
- 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>
- Daeneke, T., Kwon, T.-H., Holmes, A.B., Duffy, N.W., Bach, U., Spiccia, L., 2011. High-efficiency dye-sensitized solar cells with ferrocene-based electrolytes. *Nat. Chem.* 3, 211–215. <https://doi.org/10.1038/nchem.966>
- 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>
- Dinesh, V.P., Sriram kumar, R., Sukhananazerin, A., Mary Sneha, J., Manoj Kumar, P., Biji, P., 2019. Novel stainless steel based, eco-friendly dye-sensitized solar cells using electrospun porous ZnO nanofibers. *Nano-Structures & Nano-Objects* 19, 100311. <https://doi.org/10.1016/j.nanoso.2019.100311>
- Ellmer, K., 2012. Past achievements and future challenges in the development of optically transparent electrodes. *Nat. Photonics* 6, 809–817. <https://doi.org/10.1038/nphoton.2012.282>
- Escobar, M.A.M., Jaramillo, F., 2015. Natural Dyes Extraction, Stability and Application to Dye-Sensitized Solar Cells. *J. Renew. Mater.* 3, 281–291. <https://doi.org/10.7569/JRM.2014.634142>
- 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. Chemie Int. Ed.* 56, 2544–2580. <https://doi.org/10.1002/anie.201605417>
- Fu, D., Lay, P., Bach, U., 2013. TCO-free flexible monolithic back-contact dye-sensitized solar cells. *Energy Environ. Sci.* 6, 824. <https://doi.org/10.1039/c3ee24338a>
- 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>
- 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. A 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, 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.* 7, 11818–11837. <https://doi.org/10.3390/su70911818>
- Harikisun, R., Desilvestro, H., 2011. Long-term stability of dye solar cells. *Sol. Energy* 85, 1179–1188. <https://doi.org/10.1016/j.solener.2010.10.016>
- 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>
- Hashmi, S.G., Ozkan, M., Halme, J., Paltakari, J., Lund, P.D., 2014. Highly conductive, non-permeable, fiber based substrate for counter electrode application in dye-sensitized solar cells. *Nano Energy* 9, 212–220. <https://doi.org/10.1016/j.nanoen.2014.07.013>
- 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>
- Hu, L., Zheng, G., Yao, J., Liu, N., Weil, B., Eskilsson, M., Karabulut, E., Ruan, Z., Fan, S.,

- Bloking, J.T., McGehee, M.D., Wågberg, L., Cui, Y., 2013. Transparent and conductive paper from nanocellulose fibers. *Energy Environ. Sci.* 6, 513–518. <https://doi.org/10.1039/C2EE23635D>
- Jiang, Q.W., Li, G.R., Wang, F., Gao, X.P., 2010. Highly ordered mesoporous carbon arrays from natural wood materials as counter electrode for dye-sensitized solar cells. *Electrochem. commun.* 12, 924–927. <https://doi.org/10.1016/j.elecom.2010.04.022>
- 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. A* 2, 4751–4757. <https://doi.org/10.1039/C4TA00402G>
- Kalowekamo, J., Baker, E., 2009. Estimating the manufacturing cost of purely organic solar cells. *Sol. Energy* 83, 1224–1231. <https://doi.org/10.1016/j.solener.2009.02.003>
- 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>
- Kroon, J.M., Bakker, N.J., Smit, H.J.P., Liska, P., Thampi, K.R., Wang, P., Zakeeruddin, S.M., Grätzel, M., Hinsch, A., Hore, S., Würfel, U., Sastrawan, R., Durrant, J.R., Palomares, E., Pettersson, H., Gruszecki, T., Walter, J., Skupien, K., Tulloch, G.E., 2007. Nanocrystalline dye-sensitized solar cells having maximum performance. *Prog. Photovoltaics Res. Appl.* 15, 1–18. <https://doi.org/10.1002/pip.707>
- Lee, K.-M., Chen, C.-Y., Tsai, Y.-T., Lin, L.-C., Wu, C.-G., 2013. Efficient and stable back-illuminated sub-module dye-sensitized solar cells by decorating SiO₂ porous layer with TiO₂ electrode. *RSC Adv.* 3, 9994. <https://doi.org/10.1039/c3ra41687a>
- Lepikko, S., Miettunen, K., Poskela, A., Tiihonen, A., Lund, P.D., 2018. Testing dye-sensitized

- solar cells in harsh northern outdoor conditions. *Energy Sci. Eng.* 6, 187–200. <https://doi.org/10.1002/ese3.195>
- Lewins, J.D., Hunns, S., Badenhorst, J., 2008. The Kalahari Platinum project 355–366.
- Li, G., Sheng, L., Li, T., Hu, J., Li, P., Wang, K., 2019. Engineering flexible dye-sensitized solar cells for portable electronics. *Sol. Energy* 177, 80–98. <https://doi.org/10.1016/j.solener.2018.11.017>
- Li, Y., Fu, Q., Yu, S., Yan, M., Berglund, L., 2016. Optically Transparent Wood from a Nanoporous Cellulosic Template: Combining Functional and Structural Performance. *Biomacromolecules* 17, 1358–1364. <https://doi.org/10.1021/acs.biomac.6b00145>
- Li, Y., Vasileva, E., Sychugov, I., Popov, S., Berglund, L., 2018. Optically Transparent Wood: Recent Progress, Opportunities, and Challenges. *Adv. Opt. Mater.* 6, 1800059. <https://doi.org/10.1002/adom.201800059>
- Liang, J., Zhang, G., Sun, W., Dong, P., 2015. High efficiency flexible fiber-type dye-sensitized solar cells with multi-working electrodes. *Nano Energy* 12, 501–509. <https://doi.org/10.1016/j.nanoen.2015.01.023>
- 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, 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>
- Ma, T., Fang, X., Akiyama, M., Inoue, K., Noma, H., Abe, E., 2004. Properties of several types of novel counter electrodes for dye-sensitized solar cells. *J. Electroanal. Chem.* 574, 77–83. <https://doi.org/10.1016/j.jelechem.2004.08.002>
- Ma, X., Deng, Q., Wang, L., Zheng, X., Wang, S., Wang, Q., Chen, L., Huang, L., Ouyang, X., Cao, S., 2019. Cellulose transparent conductive film and its feasible use in perovskite solar cells. *RSC Adv.* 9, 9348–9353. <https://doi.org/10.1039/C9RA01301F>

- 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>
- Mastroianni, S., Asghar, I., Miettunen, K., Halme, J., Lanuti, A., Brown, T.M., Lund, P., 2014. Effect of electrolyte bleaching on the stability and performance of dye solar cells. *Phys. Chem. Chem. Phys.* 16, 6092. <https://doi.org/10.1039/c3cp55342f>
- 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., Etula, J., Saukkonen, T., Jouttijärvi, S., Halme, J., Romu, J., Lund, P., 2015. Insights into corrosion in dye solar cells. *Prog. Photovoltaics Res. Appl.* 23, 1045–1056. <https://doi.org/10.1002/pip.2534>
- Miettunen, K., Halme, J., Lund, P., 2013. Metallic and plastic dye solar cells. *Wiley Interdiscip. Rev. Energy Environ.* 2, 104–120. <https://doi.org/10.1002/wene.46>
- 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., Poskela, A., Tiihonen, A., Rendon, S., Axenov, K., Kronberg, L., Leino, R., Lund, P.D., 2016. From identification of electrolyte degradation rates to lifetime estimations in dye solar cells with iodine and cobalt redox couples. *Nano Energy Syst.* <https://doi.org/10.24274/nes.2016.a7>
- 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>
- Ogata, Y., Iguchi, K., Oya, T., 2019. “Paper Dye-Sensitized Solar Cell” Based on Carbon-Nanotube-Composite Papers. *Energies* 13, 57. <https://doi.org/10.3390/en13010057>
- 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>
- Okada, K., Matsui, H., Kawashima, T., Ezure, T., Tanabe, N., 2004. 100 mm × 100 mm large-sized dye sensitized solar cells. *J. Photochem. Photobiol. A Chem.* 164, 193–198. <https://doi.org/10.1016/j.jphotochem.2004.01.028>
- Parisi, M.L., Basosi, R., 2015. Environmental Life Cycle Analysis of Nonconventional Thin-Film Photovoltaics: The Case of Dye-Sensitized Solar Devices, in: *Energy Security and Development*. Springer India, New Delhi, pp. 195–210. https://doi.org/10.1007/978-81-322-2065-7_12
- 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>
- Park, B., Pazoki, M., Aitola, K., Jeong, S., Johansson, E.M.J., Hagfeldt, A., Boschloo, G., 2014. Understanding Interfacial Charge Transfer between Metallic PEDOT Counter Electrodes and a Cobalt Redox Shuttle in Dye-Sensitized Solar Cells. *ACS Appl. Mater. Interfaces* 6, 2074–2079. <https://doi.org/10.1021/am405108d>
- 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>

- Poskela, A., Miettunen, K., Tiihonen, A., Lund, P.D., 2018. The state of external circuit affects the stability of dye-sensitized solar cells. *Electrochim. Acta* 275, 59–66. <https://doi.org/10.1016/j.electacta.2018.04.117>
- Reijnders, L., 2010. Design issues for improved environmental performance of dye-sensitized and organic nanoparticulate solar cells. *J. Clean. Prod.* 18, 307–312. <https://doi.org/10.1016/j.jclepro.2009.10.021>
- Rendon, S.M.K., Mavrynsky, D., Meierjohann, A., Tiihonen, A., Miettunen, K., Asghar, I., Halme, J., Kronberg, L., Leino, R., 2015. Analysis of dye degradation products and assessment of the dye purity in dye-sensitized solar cells. *Rapid Commun. Mass Spectrom.* 29, 2245–2251. <https://doi.org/10.1002/rcm.7384>
- Reuter, M., 2013. *Metal Recycling Opportunities*.
- Rezaei, B., Irannejad, N., Ensafi, A.A., Kazemifard, N., 2019. The impressive effect of eco-friendly carbon dots on improving the performance of dye-sensitized solar cells. *Sol. Energy* 182, 412–419. <https://doi.org/10.1016/j.solener.2019.02.072>
- 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., Fafílek, 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. A* 2, 4474–4490. <https://doi.org/10.1039/C3TA13374E>
- Tiihonen, A., Miettunen, K., Rendon, S., Mavrynsky, D., Halme, J., Leino, R., Lund, P., 2015.

- The Effect of Electrolyte Purification on the Performance and Long-Term Stability of Dye-Sensitized Solar Cells. *J. Electrochem. Soc.* 162, H661–H670. <https://doi.org/10.1149/2.0671509jes>
- Tsao, H.N., Burschka, J., Yi, C., Kessler, F., Nazeeruddin, M.K., Grätzel, M., 2011. Influence of the interfacial charge-transfer resistance at the counter electrode in dye-sensitized solar cells employing cobalt redox shuttles. *Energy Environ. Sci.* 4, 4921. <https://doi.org/10.1039/c1ee02389f>
- Tuyet Nguyen, P., Degn, R., Thai Nguyen, H., Lund, T., 2009. Thiocyanate ligand substitution kinetics of the solar cell dye Z-907 by 3-methoxypropionitrile and 4-tert-butylpyridine at elevated temperatures. *Sol. Energy Mater. Sol. Cells* 93, 1939–1945. <https://doi.org/10.1016/j.solmat.2009.07.008>
- Tuyet Nguyen, P., Rand Andersen, A., Morten Skou, E., Lund, T., 2010. Dye stability and performances of dye-sensitized solar cells with different nitrogen additives at elevated temperatures—Can sterically hindered pyridines prevent dye degradation? *Sol. Energy Mater. Sol. Cells* 94, 1582–1590. <https://doi.org/10.1016/j.solmat.2010.04.076>
- Velázquez-Martínez, Valio, Santasalo-Aarnio, Reuter, Serna-Guerrero, 2019. 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., 2019. 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>
- Wang, M., Chamberland, N., Breau, L., Moser, J.-E., Humphry-Baker, R., Marsan, B.,

- Zakeeruddin, S.M., Grätzel, M., 2010. An organic redox electrolyte to rival triiodide/iodide in dye-sensitized solar cells. *Nat. Chem.* 2, 385–389. <https://doi.org/10.1038/nchem.610>
- Wang, P., Zakeeruddin, S.M., Moser, J.-E., Humphry-Baker, R., Grätzel, M., 2004. A Solvent-Free, SeCN⁻/(SeCN)³⁻-Based Ionic Liquid Electrolyte for High-Efficiency Dye-Sensitized Nanocrystalline Solar Cells. *J. Am. Chem. Soc.* 126, 7164–7165. <https://doi.org/10.1021/ja048472r>
- 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>
- Wu, M., Lin, X., Wang, T., Qiu, J., Ma, T., 2011. Low-cost dye-sensitized solar cell based on nine kinds of carbon counter electrodes. *Energy Environ. Sci.* 4, 2308. <https://doi.org/10.1039/c1ee01059j>
- Xu, S., 2017. One-step fabrication of carbon fiber derived from waste paper and its application for catalyzing tri-iodide reduction. *IOP Conf. Ser. Earth Environ. Sci.* 52, 012014. <https://doi.org/10.1088/1742-6596/52/1/012014>
- 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>
- Yang, S., Sha, S., Lu, H., Wu, J., Ma, J., Wang, D., Sheng, Z., 2020. Electrodeposition of hierarchical zinc oxide nanostructures on metal meshes as photoanodes for flexible dye-sensitized solar cells. *Colloids Surfaces A Physicochem. Eng. Asp.* 594, 124665. <https://doi.org/10.1016/j.colsurfa.2020.124665>
- Ye, M., Wen, X., Wang, M., Iocozzia, J., Zhang, N., Lin, C., Lin, Z., 2015. Recent advances in dye-sensitized solar cells: from photoanodes, sensitizers and electrolytes to counter electrodes. *Mater. Today* 18, 155–162. <https://doi.org/10.1016/j.mattod.2014.09.001>
- Yella, A., Lee, H.-W., Tsao, H.N., Yi, C., Chandiran, A.K., Nazeeruddin, M.K., Diao, 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* (80-.). 334, 629–634. <https://doi.org/10.1126/science.1209688>
- Yen, C.-Y., Lin, Y.-F., Liao, S.-H., Weng, C.-C., Huang, C.-C., Hsiao, Y.-H., Ma, C.-C.M., Chang,

M.-C., Shao, H., Tsai, M.-C., Hsieh, C.-K., Tsai, C.-H., Weng, F.-B., 2008. Preparation and properties of a carbon nanotube-based nanocomposite photoanode for dye-sensitized solar cells. *Nanotechnology* 19, 375305. <https://doi.org/10.1088/0957-4484/19/37/375305>