

Textile-Based Dye-Sensitized Solar Cells: Fabrication, Characterization, and Challenges



P. Salinas , D. Ganta , J. Figueroa , and M. Cabrera

1 Introduction

Dye-synthesized solar cells are solar cells that are made from plant dyes (Ananth et al. 2014; Calogero et al. 2014, 2010,2012; Chang and Lo 2010; Chien and Hsu 2014; Ganta et al. 2019, 2017; Hernandez-Martinez et al. 2011; Kumara et al. 2004, 2013a, b; Lai et al. 2008; Mathew et al. 2014; Noor et al. 2014; Shanmugam et al. 2013; Teoli et al. 2016; Wang et al. 2006; Yusoff et al. 2014; Zhou et al. 2011). A DSSC consists of three main components, the plant-based dye photoanode, an electrolyte with a redox couple, and a counterelectrode. Figure 1 shows the basic structure of a typical DSSC, consisting of a cathode, an anode, and a coating of TiO₂. Scientists and researchers alike are attempting to discover new ways to increase the conductivity and longevity of the solar cell. DSSCs first came to popularity in the late 2010s, with many studies focusing on DSSCs composed of two pieces of FTO glass slides. There are advantages of plant-based DSSCs over conventional DSSCs. Plant-based DSSCs are fabricated from natural plant-based dyes, unlike the toxic chemical dyes used in the case of chemical-based DSSCs. Plant-based DSSCs are inexpensive, simple to fabricate and easy to handle unlike the chemical-based DSSCs. DSSCs do boast excellent conversion efficiency and are somewhat portable but not flexible. Thus, this causes their usefulness to drop, especially as wearable energy devices. With a fully textile-based DSSC, it can be flexible, portable and can be placed in any number of configurations and is more practical for real-world usage.

Recently, there have been several papers published regarding FTO-fabric hybrid DSSCs (HDSSC) (Lam et al. 2017; Liu et al. 2019; Sahito et al. 2015, 2016; Xu et al. 2014). The textile was being integrated into a DSSC, and the research faces many

P. Salinas (✉) · D. Ganta · J. Figueroa · M. Cabrera
School of Engineering, Texas A&M International University, Laredo, TX 78041, USA
e-mail: petersalinas@dusty.tamui.edu

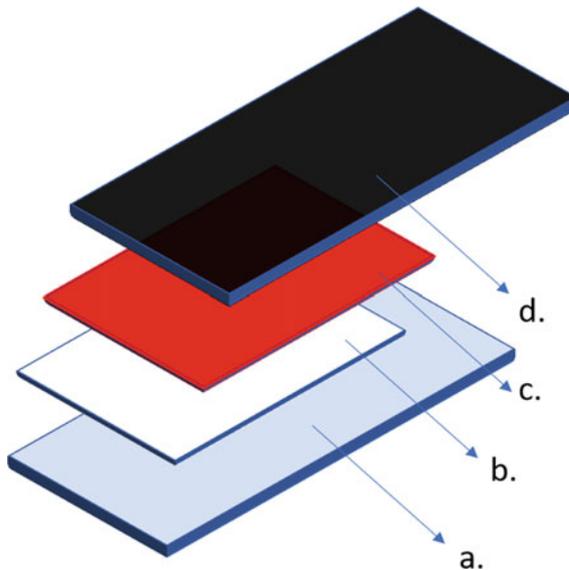


Fig. 1 Simple schematic of the components in a DSSC: **a** FTO glass anode, **b** FTO with TiO_2 nanomaterial paste, **c** addition of the plant dye to the FTO glass with TiO_2 nanomaterial paste, and **d** is the FTO cathode with a coating of a thin carbon film

challenges, the book chapter reviews some of the challenges faced in the fabrication of textile-based DSSC (TDSSC).

With large corporations such as Apple and Samsung—among others—popularizing products such as smartwatches, Bluetooth headphones, and virtual reality devices, the interest in and demand for wearable technology are at an all-time high. The research question posed to take DSSCs to the next level is to find a way to integrate a fully textile-based DSSC into a piece of clothing, enabling the clothing to store the charge for applications in a cell phone or similar small technologies. TDSSC is a DSSC composed solely of a textile fabric such as cotton. There is research attempting to fabricate a TDSSC that boasts good conductivity and a good enough efficiency to hold a charge. The goal for these is to implement them onto a piece of clothing such as a jacket or shirt to, for example, be able to charge a cellular or wearable device if a person is ever in need of a charge. In the medical field, a doctor requires that wearable medical devices have a continuous supply of energy to power them, helping save human life. A TDSSC is an environmentally friendly source of green energy, avoiding toxic waste recycled every year from the battery devices. TDSSCs can also see future applications in aerospace, military, outdoor equipment, and other flexible energy sources, so their applications are not just limited to clothing (Fu et al. 2018; Grancarić et al. 2018; Liang et al. 2018; Peng et al. 2018; Susrutha et al. 2015; Tsuboi et al. 2015). Figure 2 shows how a TDSSC would be composed, while Fig. 3 shows the composition of a conventional DSSC to serve as a comparison. The operation of a TDSSC includes the transport of electrons created by sunlight absorption via the

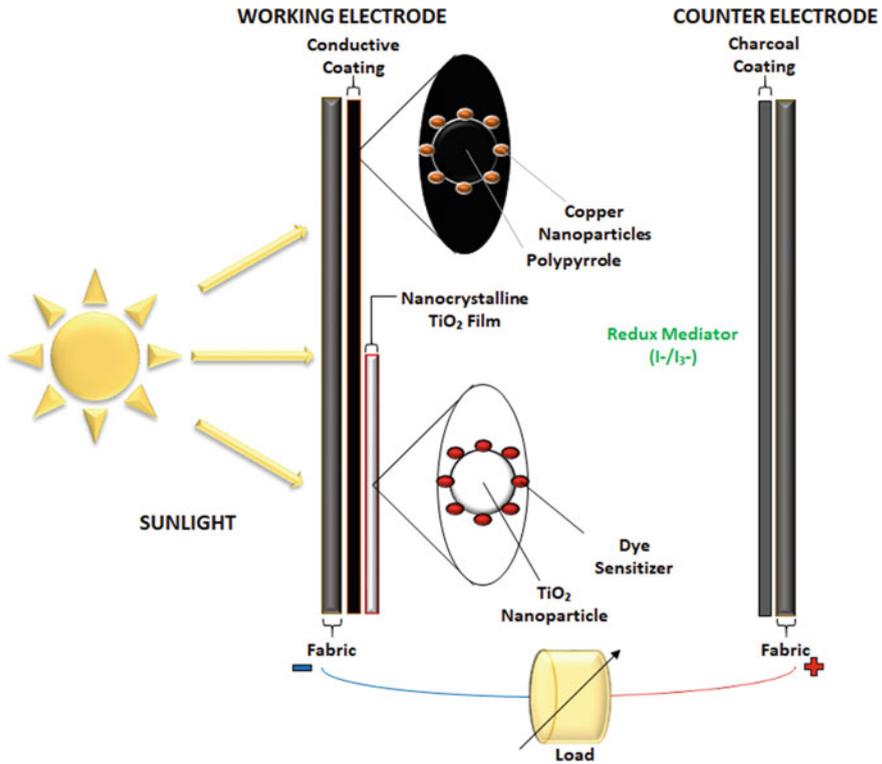


Fig. 2 Simple schematic of the operation of a TDSSC

plant dye. Electrons are generated because of the chemical reaction between the dye and sunlight.

The challenge with implementing a TDSSC into clothing is to find a proper method to make the material resistivity low enough to allow a charge to be held. In addition, a robust coating method that will evenly stay onto the chosen fabric has yet to be developed, and there is much to be discovered in terms of a TDSSC. The standard coating method used in most DSSCs is to add a TiO_2 paste onto the cathode of the cell, cure it using high heat, and then to add a dye that can absorb sunlight enough to create a sizable amount of voltage within the cell. Since this practice was introduced, scientists have implemented and tested new methods of coating a DSSC so that it can have a higher efficiency rating.

Additionally, the dye used in all DSSCs is an essential component since its efficiency, along with that of the TiO_2 paste, will be the deciding factors on whether the produced cell will be functional or unusable. To thoroughly test a dye's potential, and analysis using a spectrophotometer may be done. The spectrophotometer measures the amount of light absorbed by the dye as it passes through a selected range in nanometers. If too much light goes through the solution, then that dye

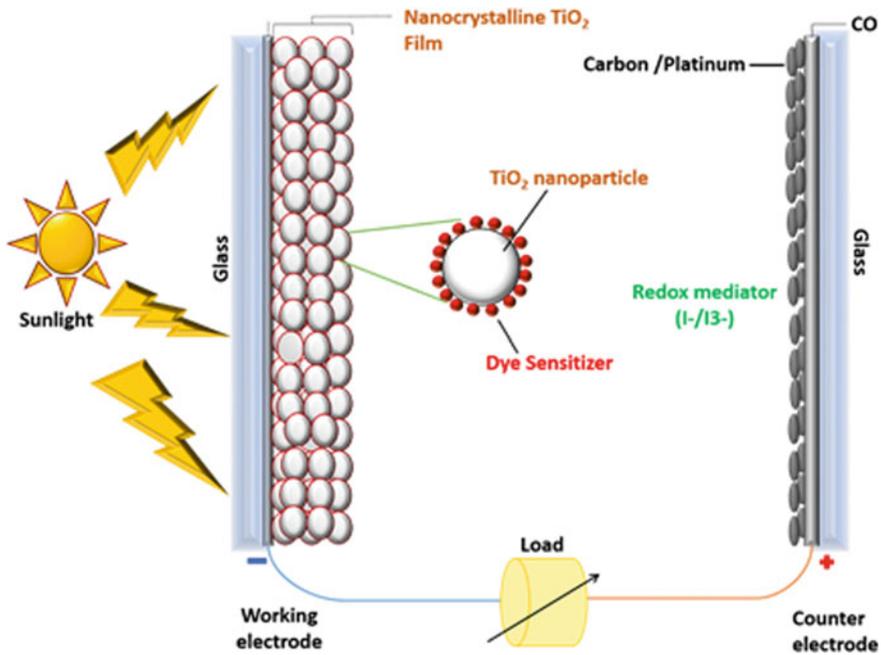


Fig. 3 Schematic of the operation of a typical DSSC. The image is reproduced with permission from Ganta et al. (2019) © 2012, Springer (Ganta et al. , 2019)

may not be suitable for use in the fabrication of DSSCs. Figure 4 demonstrates an example of a blackberry dye's UV–Vis Absorption Spectra using a UV 2450 UV–Vis Spectrophotometer.

As illustrated in Fig. 4, the optical absorption characteristics of the blackberry dye were measured on a range of 400–650 nm. The absorbance peaked at an approximate wavelength of 526 nm. This value matches the data values reported in the literature (DeSilva et al. 2017; Olea et al. 1999).

Once either type of cell is assembled, it is placed under natural or simulated sunlight and connected to a source measure unit with access to KickStart software in order to measure the relationship between the current and voltage. This relationship is characterized as an I–V curve shown through a current vs. voltage graph. The higher the current and voltage being produced by the cell, the better the potential of the cell will be. We reviewed some of the results published in the literature. As illustrated in Fig. 5, is the comparison of four differently prepared DSSCs, with a pair of a single-walled carbon nanotube (SWCNT) and Ag-PEDOT (poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate)) cells left in light, and a pair of SWCNT and AG-PEDOT left in the dark (Kye et al. 2018; Zhang et al. 2017). The cells, when left in light, will absorb more light as can be expected and exhibit the right voltage and current readings.

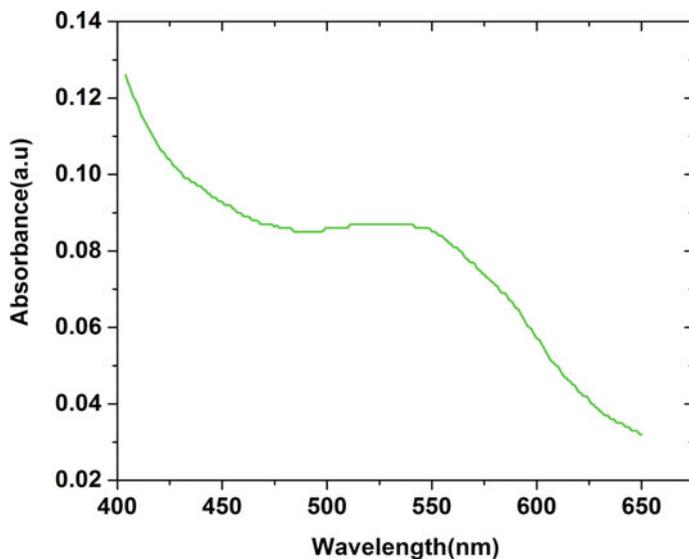


Fig. 4 UV-Vis Absorption Spectra of a blackberry-based dye

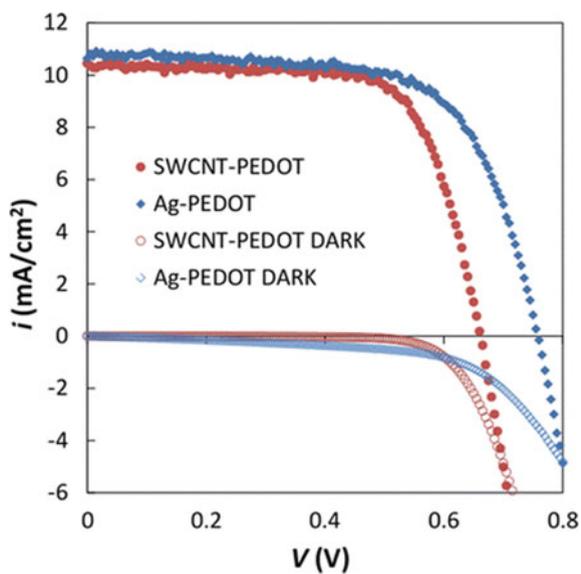


Fig. 5 I-V curves of the DSSC with different material counterelectrodes and their dark current curves. The image is reproduced with permission from Aitola et al. (2015) © 2012, Springer (Aitola et al. 2015)

2 Methods

2.1 Integration of Plant Dyes in Solar Cells

Natural plant dyes have been used to fabricate dye solar cells. A dye-sensitized solar cell's main component is the dye that is used. Differing dyes allow for different types of properties and different reactions to occur within the cell; therefore, the electrical output of the cell will be different depending on the type of dye being used on the cell. Issues when working with dye-sensitized solar cells primarily involve the foldability and stretchability of the fabric that the cell is being integrated on, as well as the ability for the coatings to stay with the material as the material gets washed. A paper cites Lam et al. (2017) in which they create a perovskite solar cell using PEDOT: PSS coating as an anode for the cell while using another PEDOT: PSS coating (low-conductive) on top of the anode layer and using a PCBM (phenyl-C61-butyric acid methyl ester) as the electron layer for the solar cell (Lam et al. 2017). This solar cell gained efficiencies of 5.72%.

Grassmann et al. (2019) used organic plant-based dyes in the creation of TDSSCs (Grassmann et al. 2019). The article primarily discusses different types of solar cells, including plant-based, dye-sensitized based, and organic-based. Each cell has its type of coating that makes it differ from the other cells due to each of the different coatings having its different type of property that affects the way that each cell acts. Two different types of DSSCs were assembled for electrical testing, ones that implement the use of counter electrodes, where the molten electrolyte was dripped on the dye and put together with conductively coated fabric, and ones that implemented the use of working electrodes, where the gelatin electrolyte was poured onto the graphite coated glass counter electrode (Grassmann et al. 2019). Before the cell was gelled, both electrodes were added together. Initial testing of the two types of DSSCs was done using two multimeters that measured short-circuit currents and open-circuit voltages that were under an 800 W halogen lamp.

Regarding differing types of DSSCs, the ones that contain a TiO₂ layer are more effective because of the high conversion efficiency potential, the chemical stability, and intense charge-transfer absorption in the entire visible light spectrum (Al-Alwani et al. 2017). Natural dyes are primarily used to their low cost, the efficiency of the dyes themselves, and the different types that can be studied. Different types of plant-based dyes show differing properties and energy-to-electric conversion efficiencies. This is all dependent on the type of dye that is being used for the solar cell, as the reason for each dye having a different efficiency is dependent on the properties of the dye, such as light absorption. Various researchers, including Al-Alwani et al. (2017) and Calogero et al. (2010, 2012), have shown that chlorophyll can absorb red, blue, and violet wavelengths and reflect green light, giving it its pigment (Calogero et al. 2010, 2012, 2014). *Pandanus Amaryllifolius* (*P. Amaryllifolius*), was ground up and used as a natural dye due to the high source of natural green extracts, theoretically allowing for a high amount of light absorption and green light reflection. TiO₂ was mixed with 3.0 ml of polyethylene glycol (PEG, MW 20,000). When mixed with

PEG, cracking on the surface of the cell was minimized, which usually occurs during high-temperature testing with solar cells. Triton X-100 was added to TiO_2 particles to adhere better. Results showed that the chlorophyll was suitable for being used as a photosensitizer in the visible-light region (Al-Alwani et al. 2017).

Researchers Gu et al. (2018) used different types of vegetables, natural plants, for the plant-based dyes; the vegetables extracted include purple cabbage, purple grape skin, mulberry, carrot, and potato (Gu et al. 2018). The amount of absorption and the overall efficiency of the dye is dependent on the pigment of the dye itself; purple cabbage showed absorption peaks of 336 and 531 nm. This is based on the different overall compositions of the vegetable itself, as shown with the carrot dye in which the much different composition led to 453 and 484 nm of absorption. Carrot, mulberry, and purple cabbage have a higher absorption rate when compared to potato and grape due to their better overall absorption of light; absorption density is proportional to the dye's concentration. Purple cabbage, however, showed the overall better optimal performance with the DSSC and the power conversion efficiency.

A disadvantage to natural dye sensitizers is that it typically contributes to poor cell stability. The natural plant-based dyes used in this conducted research primarily come from Indian plants due to unspecified limitations. Warmer colors, the color spectrum range of red, yellow, and orange, absorb a range between 470 and 550 nm that is not usually absorbed by chlorophyll, these are known as carotenoids. Carotenoids consist of eight different isoprenoid units. Carotenoids are widely produced in nature; 108 tons/year. Carotenoids typically have a higher absorption coefficient, but they generally give a reduced efficiency in a DSSC due to their poor dye regeneration. Chlorophyll is what gives plants the green color pigmentation, and it is usually unstable regarding being used with an acid or base, one of the disadvantages of it being used in a solar cell. For whatever dye is being used, it must follow the criteria that it should have an excellent anchoring to it, as well as good stability regarding being used with an acid or a base and of course, excellent electrical efficiency when converting the light into energy.

While organic dyes are used in DSSC fabrication, in the case of Mathew et al. (2014), he and his fellow researchers looked at how the implementation of a molecularly engineered porphyrin dye, SM315, performs as part of a DSSC. Previous DSSCs had only reached a peak PCE efficiency of 12.3% (Mathew et al. (2014)). A previously molecularly engineered green dye used by the researchers, SM371, yielded an efficiency of 12%. Porphyrin-based dyes absorb sunlight very well in the Soret and Q bands but much else. The new engineered SM315 improved upon the previously used SM371 and made the already excellent absorption in the Soret and Q bands greater. The DSSCs prepared by the authors are made with TiO_2 paste, and no counterelectrode is mentioned. What the researchers were able to find through testing was that the SM315 posted a new efficiency high of 13%, 0.8 larger than the previously recorded high and 1% larger than SM371. The V_{oc} readings taken for SM315 were 0.96 V and the J_{sc} was 15.9 mA/cm^2 , which is decent when compared to past results. The use of these two dyes is a steppingstone in improving the efficiency of dyes to possibly 1% or even 20% efficiency.

2.2 Fabrication and Coating

The necessity of having a good coating method when producing a solar cell is a primary indicator if the cell will be good or not. Many researchers solely study the effects that different coating methods can have on a solar cell's performance. In an article written by Azizi et al. (2016) looks at two different ways to prepare a DSSC; electrophoretic deposition process (EPD) and doctor blade technique (DB) (Azizi et al. 2016). For the EPD technique, 21 nm TiO_2 nanoparticles and phase composition of 80% anatase and 20% rutile were used. This technique is electrochemical based, in that they apply an electric field to two electrodes and charged particles, and then the particles accumulate to create a film. This film was used on one of the DSSCs with aluminum as the CE, and 60 V of power was applied to the FTO glass slide. For the doctor blade technique, 5 g of nanocrystalline titanium dioxide was mixed with 3 ml of diluted acetic acid and then ground for half an hour until it was in paste form. Both techniques used anthocyanin obtained from Karkade flowers as the dye. In total, six DSSCs were tested. What the authors looked at to compare the two techniques were the cracks that formed in the films. These cracks decreased the conversion efficiency in the DSSCs, so the numbers are not what they should be.

Like TDSSCs, fiber-shaped dye-sensitized solar cells (FDSSCs) with a Triboelectric Nanogenerator (TENG) integrated are the focus of an article written by Pu et al. (2016). FDSSCs are an attractive DSSC application due to their low cost and decent energy production, and the capability to be sewn into fabrics adds to the attractiveness. TENG was chosen due to their ability to use human motion, such as the arms swinging or legs moving to create mechanical energy. This combined with an FDDSC that absorbs sunlight to use as energy, can be sewn into an article of clothing such as a shirt that opens doors for creating a textile that can power a small device like a cell phone. The TENG used is polyester cotton that had intricate patterns etched into the fabric by way of laser-scribing. It was then coated with Ni using a technique called electroless deposition (ELD). The FDSSCs used were fabricated by having two Ti wires coated in TiO_2 , which are then sintered at 450 °C for 30 min. They are then left to soak in ethanol for 24 h. The counterelectrode for the cells is a Pt wire that is put into a transparent and flexible plastic tube filled with liquid electrolyte. The tube was filled with an electrolyte, acetonitrile, dimethyl imidazolium iodide, I_2 , LiClO_4 , 4-tert-butylpyridine, and guanidine thiocyanate solution that is then sealed with glue. Overall, the efficiency for the TDSSC-TENG combo was 6% with short circuit density, J_{sc} , of 10.6 mA/cm^2 and an average open-circuit voltage V_{oc} , of 0.6 V.

Research has been conducted and tested regarding perovskite solar cells (PVSCs) and the various ways in which they could be improved while using differing structure types, known as n-i-p and p-i-n. Different materials were tested and compared with one another to observe which material would work best with the different environmental effects that would be applied to it when being used in a perovskite solar cell along with different chemicals. Chemicals included would be with a formula of ABX_3 (Lam et al. 2017). These chemicals include CH_3 , NH_3 , and PBI_3 . The data

recorded and examined primarily came from various charts according to measurement as well as multiple J-V curves. The PVSCs were set in a series connection to test if it can light up a diode on the same textile as the PVSC. This would allow for different ways of testing how much power and energy are being transferred within the cell. The cell was tested within the water by immersing the device in water with no variables affecting it. After a non-specified period, the textile was taken out of the water, showing no conflicts or issues after coming from the water. With this, it is shown that the cell that the researchers have created is able to work after being washed. Although not specified, considering the way that solar cells act over differing actions over an interval of time, there could be a chance that after repeated washings of the textile, there could be a chance that the effectiveness of the cell could significantly decrease before washing.

Another alternate coating method that researchers investigated developing is a spray that would act as the dye for the solar cell. Other types of coating methods for fabrics primarily include screen printing, inkjet printing, and dispenser printing (Li et al. 2019). The advantages of using the spray coating as opposed to a standard dye coating include the spray coating being incredibly lightweight and minimizes the impact on the feel of the fabric (Li et al. 2019). The primary goal of using a spray coating for a textile solar cell would be to keep the cell as durable as possible while being able to maintain a relatively high-power output. Optimization is tested through various types of cells, including PV2000 and Pt-4, with Pt-4 having better optimization results due to better thickness in the cell. After multiple cycles of the device, the efficiency continued to drop with each cycle. After a certain number of cycles, the researchers recorded efficiency of 0.05% and after more cycles afterward, it eventually decreased to 0.03%, showing that the device usually deteriorates after multiple washing cycles.

Due to rapid growth in the application of photovoltaic electric power generation, there has been an increasing demand for lightweight and flexible solar cells. Most of the research done in past years revolved around flexible plastics. However, the transparent conductive oxide (TCO) films used are brittle and can be easily fractured. Therefore, attention has been placed upon textiles due to their lightweight, flexibility, and mechanical properties (Yun et al. 2014). Wu et al. (2017) researched creating more lightweight solar textiles onto fabrics to advance better the quality of textile-based solar cells. A primary issue with creating one is that it is difficult and complicated in order to intricately weave a fiber-based solar cells into different textiles and fabrics. The solar cell constructed during this research primarily includes two electrodes, and two different layers: a light-harvesting active layer and a blocking or transport layer (Wu et al. 2017). After a certain amount of time or number of folds/actions taken, the efficiency and effectiveness of the solar cell will significantly decrease. When creating an ultra-lightweight wearable solar cell, it is essential to take the washability, stretchability, and foldability factors into consideration. The demand for lightweight power sources has increased within recent years, conducting research based on these types of solar cells much desired.

Since DSSCs have a low production cost and relatively high efficiency, they are of high interest. An advantage DSSCs have is their ability to separate their photoanode and counter electrode via a liquid electrolyte insertion. By sewing textile-structured electrodes onto fabrics like cotton, a highly flexible and efficient DSSC can be developed (Yun et al. 2014). The textile-based cell is made by weaving each electrode by the loom and depositing TiO_2 , heat treating, sewing to form the core-integrated DSSC device, and dye loading. Both, the photoanode and counter electrode, consist of a 3:1 woven structure of stainless-steel ribbon and Ti wire and a woven structure of glass fiber yarns and more Ti wire. The counterelectrodes were prepared and deposited onto the designated textile and then by the deposition of a paste before being heat treated. The textile-structured electrodes were then attached using a sewing machine. Overall, even though it had a high current density, the efficiency was approximately 4.3%, of which 5.3% corresponded to the maximum efficiency. At bending conditions, the photovoltaic performance was maintained at 80% of its original value with a curvature radius of 10 cm and 30% with a curvature radius of 4 mm. After 1000 bending cycles over the curvature of 1 cm, the performance remained at 70% of its original value. It was determined that the pattern of the weave and the material of the textile could influence the performance of the DSSC.

In a study by Yang et al. (2014), a new and general method of production for a stretchable, wearable photovoltaic textile based on elastic, electrically conducting fibers were developed (Yang et al. 2014). To prepare the fiber electrodes, first, an aligned multi-walled carbon nanotube (MWCNT) sheet was wound onto rubber fibers. Then, a Ti wire was twisted onto the MWCNT fiber and was coated in a photoactive material to make a wire-shaped DSSC. These DSSCs were then woven onto a textile. The DSSC had a conversion efficiency rate of 7.13% and was well maintained under tension. The conducting fibers were found to be highly stretchable and flexible, retained their structure, and their electrical resistance was nearly unchanged when stretched. The resistance of the fibers was further tested at various helical angles. Due to a deformation rate of 50%, the resistance values did not recover to their original value (Yang et al. 2014). These fibers can be used to create stretchable electronics. This design allows for the flexibility of the DSSC. These can be woven into various textiles and maintain a high rate of elasticity and an efficient photovoltaic performance. The MWCNT arrays are made from a chemical vapor deposition of $\text{Fe}/\text{Al}_2\text{O}_3$ on a silicon substrate at 740 °C (Yang et al. 2014). The carbon source was ethylene, and the thickness of the arrays used was of 250 μm .

Zhang et al. (2017) reported DSSC textiles fabricated using polybutylene terephthalate (PBT) polymer yarns woven into different fabrics (Zhang et al. 2017). This achieved a power conversion efficiency (PCE) of 1.3% per fiber, the highest reported at the time. Unfortunately, due to the bending limitations, the fibers tend to break and loose performance as they degrade. Furthermore, when woven into textiles, they tend to lose PCE due to partial shading. Additionally, since they are liquid-based DSSCs, they suffer from leakage, corrosion, or stability issues. This, however, could be avoided by using a solid electrolyte with a PCE of 2.7% for Ag and 2.8% for AgNW. By using the architecture of a solid-state (ss) DSSC on FTO glass and spin

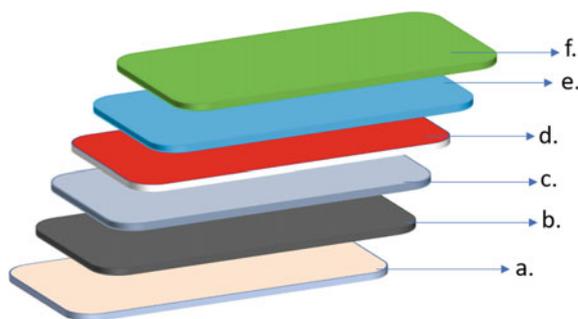


Fig. 6 Composition of the textile-based ssDSSC anode. **a** Textile/FTO, **b** polyimide, **c** silver, **d** TiO₂ with dye, **e** PEDOT: PSS, and **f** AgNWs

coating with a solid electrolyte, the PCE was 3.7% (Liu et al. 2019). An investigation was held regarding the implementation of a DSSC on Kapton, which yielded an efficiency of 7.03%. However, FTO glass was used as the electrolyte which made it inflexible. Additionally, it was determined that using a liquid electrolyte may not be suitable in fabricating TDSSCs because the fabric is porous, which causes the electrolyte to soak through and evaporate. TiO₂ was similarly investigated leading to an efficiency of 7.41%. However, it was found that the TiO₂ layer requires a minimum temperature of 450 °C to sinter the film and achieve the recorded efficiency. Consequently, the fabrication of a 2-D ssDSSC woven into high-temperature glass fiber textile substrates is presented in this article Liu et al. (2019). The fabrication consists of five steps: first, the roughness of the fabric must be reduced via a flexible polyimide layer. The use of liquid polyimide differs from the use of polyurethane. Then, the silver bottom electrode must be screen printed onto the dried polyimide. Then, there is a decomposition of the TiO₂ (Liu et al. 2019). Then, a TiO₂ film is applied during spraying. Finally, it is spray-coated with PEDOT: PSS and then AgNW over it. This structure can be seen as illustrated in Fig. 6.

The ssDSSC on FTO glass had an efficiency of 2.8% with a V_{OC} of 0.44 V and a current density, J_{SC} , of 18.5 mA/cm². The surface roughness was then further reduced, allowing for a smoother surface, effectively reducing the resistance. This led to a maximum PCE of 0.4% with a V_{OC} of 0.31 V and a J_{SC} of 5.2 mA/cm² (Liu et al. 2019). The J/V curve for the two different ssDSSCs fabricated by the researchers can be found in Fig. 7. The fabric ssDSSC indicates there is resistance to charge movement between the functional layers due to the excessive and uneven film thicknesses (Liu et al. 2019). This set of J/V curves is good because both ssDSSCs reach 1 V of power generated which for a non-conventional solar cell is difficult to reach at the current state of affairs.

A DSSC is incomplete without the addition of a CE, due to it causing the electrical reaction that produces the voltage required to power devices. In an article written by Xin et al. (2011), they implemented a copper–zinc tin sulfide counterelectrode. The research implements the copper–zinc tin CE by way of a solution-based synthesis approach (Xin et al. 2011). They first started by dissolving the CZSC in oleylamine

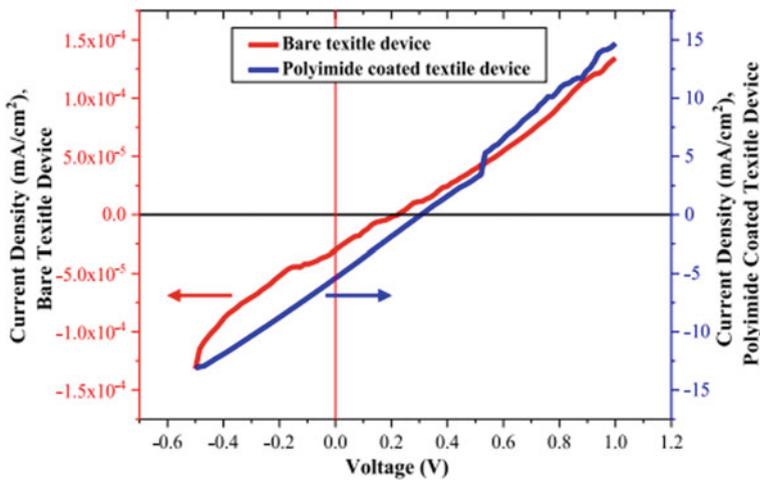


Fig. 7 The J/V curves of ssDSSCs fabricated on bare glass textiles and polyimide-coated glass (Liu et al. 2019)

and purifying them at 130 °C. They then injected a sulfur solution and stirred it at 225 °C for an hour. The solution was then centrifuged to yield nanoparticles of CZSC. At this point, the solution is ready to be placed onto DSSC glass slides as a CE. The DSSC created by the authors that yielded the best results was the spin-coated post-treated DSSC, with a V_{OC} of 0.80 V, J_{SC} of 17.7 mA/cm², and a PCE of 7.37%. The testing of various DSSCs helped the authors determine that the optimum thickness of a CZSC layer is 1–2 μm. The authors concluded that CZSC is much more cost-efficient, easy to produce than other alternatives such as platinum, and the potential for eliminating expensive CEs for DSSCs is on the horizon.

A paper by Sahito et al. (2015) details using graphene and carbon nanotubes to coat the counterelectrode used in a DSSC (Sahito et al. 2015). Graphene oxide was created from graphene that was synthesized by way of the Hummers method (Sahito et al. 2015, 2016; Song et al. 2011; Berendjchi et al. 2016). This was then combined with sulfuric acid in an ice bath and stirred for 30 min. A reaction occurred after 4 h of continuous stirring, which was then quenched by dropping the temperature to 10 °C. Afterward, hydrogen peroxide was stirred for 30 min. Afterward, water was added, and the solution was sonicated for 30 min. The fabric used, cotton, was then soaked into a slightly diluted and sonicated graphene oxide solution. After drying for 20 min at 80 °C, the fabrics were treated with hydroiodic acid fumes for 20 min. The fabric was then rinsed with DI water until a neutral pH was achieved and dried at 100 °C for 30 min. The results showed that the CE created has a resistance of 55 ohms/sq., which is like that of a standard FTO glass slide. Though the cell created showed an efficiency reading of 2.52% with a J_{SC} of 9.08 mA/cm², it is still commendable and can be improved upon by implementing other methods. Figure 8 demonstrates the graphite-coated fabric (GCF) CE when compared to more expensive platinum, Pt, coated CE. The platinum-coated is far superior, but the cost-effectiveness and

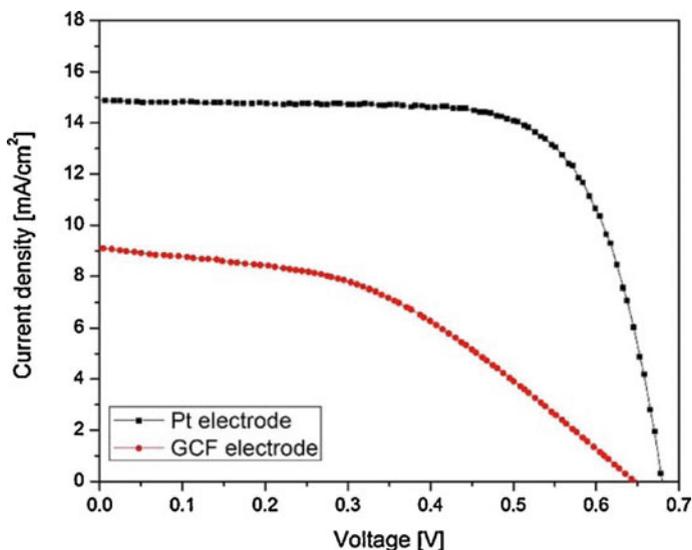


Fig. 8 Graph of voltage versus current density with two different types of electrodes used on a DSSC. The image is reproduced with permission from Sahito et al. (2015) © 2015, Elsevier

improvability of the graphene-coated CE make it more attractive to use in further experimentation.

Polypyrrole is used as the chemical in the creation of a DSSC in an article by Xu et al. (2016). A Ni, nickel plating, on the chosen fabric, cotton, used. The pyrrole was synthesized using polymerization (Xu et al. 2014, 2016; Zhang et al. 2017; Calvo et al. 2002; Bu et al. 2013; Nagai and Segawa 2004). Cotton, platinum (Pt) foil, and KCl saturated calomel electrode was used as the working, counter, and reference electrodes, respectively. The pyrrole was polymerized for 1, 1.5, and 2.5 h. The surface resistance readings for the polypyrrole coated cotton read 7.01 ohms/cm², 7.16 ohms/cm², and 7.42 ohms/cm², respectively. The efficiency of each polymerized pyrrole showed readings of 3.41%, 3.83%, 3.73% and the J_{SC} of each read 7.39 mA/cm², 7.85 mA/cm², and 7.90 mA/cm². The V_{OC} values read 720 mV, 740 mV, and 720 mV, respectively. It can be concluded that the 1.5-h polymerized polypyrrole is the most viable coating to be used in the creation of DSSCs.

Table 1 summarizes the produced open-circuit voltages (V_{OC}), photovoltaic energy conversion efficiencies (η), and current densities (J_{SC}) of several hybrid DSSCs—composed of an FTO anode and a textile cathode—and TDSSCs reported from the literature. They were compared to their corresponding conventional DSSC counterparts.

Table 1 Comparison of the performance of TDSSCs, HDSSCs, and DSSCs

Type of solar cell	Substrate material for anode/cathode	V_{oc} (V)	η (%)	J_{sc} (mA/cm ²)	Ref
DSSC	FTO	0.56	1.50	10.6	37
HDSSC	FTO/cotton	0.52	1.00	8.06	37
TDSSC	Cotton	0.50	0.40	3.44	37
DSSC	FTO	0.44	2.83	18.6	22
TDSSC	Glass fiber	0.31	0.40	5.20	22
DSSC	FTO	0.66	7.20	14.9	23
HDSSC	FTO/cotton	0.64	2.52	9.08	23
DSSC	FTO	0.67	8.44	15.9	24
HDSSC	FTO/cotton	0.66	6.93	14.8	24
DSSC	FTO	0.70	6.16	15.1	25
HDSSC	FTO/cotton	0.65	3.30	9.60	25

3 Challenges and Perspectives

In recent years, multiple advancements have been made regarding TDSSC research. Li et al. (2019) and his group were able to optimize a coating method in the fabrication of a TDSSC that utilizes a spray to coat the textiles. This coating possesses a power conversion of 0.4% and allows for improved durability and life expectancy (Li et al. 2019). Furthermore, Grassmann et al. (2019) put forth the idea of using a gelled electrolyte and developed one using gelatin that produced some impressive results (Grassmann et al. 2019). Most interestingly, Liu and his group investigated a novel fabrication method that screen prints a solid-state DSSC directly onto a woven glass fiber textile, allowing for a prolonged avoidance of oxidation and obtaining an efficiency of 0.4% (Liu et al. (2019).

We conducted preliminary experiments for the fabrication of TDSSCs and the challenges faced involved: increasing the conductivity of the textile, sufficient adherence of solution to fabric, a proper curing process, proper dilution and application of chemicals, limited plant-dye shelf life, the hindrance with the flexibility of cells, and liquid electrolyte application. A significant issue was encountered in the very first step of producing a TDSSC: making the resistance of the desired fabric low enough so that a sufficient charge could be produced. The resistance of an FTO glass slide is, on average, between 30 and 60 ohms. Various methods exist to lower the resistivity of the fabric in order to replicate such resistivity measurements. One such method is to coat both sides of the cell. There are two ways to go about this method. The first is to create a conductive polypyrrole paste and coat one side of the fabric. The difficulty in this is making sure the fabric can adequately absorb the paste. After each coating, it is advised to rinse the fabric with DI water then apply another coating. The second is to create an aqueous solution of polypyrrole and leave the fabric soaking in it for any specified amount of time, between 1 and 24 h. The issue with both methods is that



Fig. 9 Different fabrics coated with a polypyrrole paste: **a** nylon, **b** chamois, **c** leather, and **d** canvas

after a certain amount of coatings, the resistance in the fabric does not go down any further. Therefore, choosing a proper coating method can be quite limiting. Shown in Fig. 9 are various fabrics coated with polypyrrole paste previously discussed. In the image, the coating is smooth, but after a day or so, the coating starts to crack. Unfortunately, if this occurs, the fabric must be cleaned to apply a new coating, rendering previous results, essentially, useless. The fabrics shown in the image are nylon, chamois, leather, and canvas.

When coating material such as nylon, it is difficult to use the aqueous solution due to the fabric's hydrophobic qualities. If left in the solution, it will absorb it but will not give favorable resistance readings. Figure 10 shows how the coating will look after a day of drying.

Curing the polypyrrole paste onto the fabrics on a hot plate at 50 °C for anywhere between five to ten minutes—depending on the specific fabric and amount of coatings—has proven to help reduce the cracking of the coating. However, by introducing high heat to the fabrics, the risk of burning the material is significantly increased. Consequently, this added risk also negatively affects the paste, rendering the entire anode useless if such a case were to occur. This consequence is shown in Fig. 11.

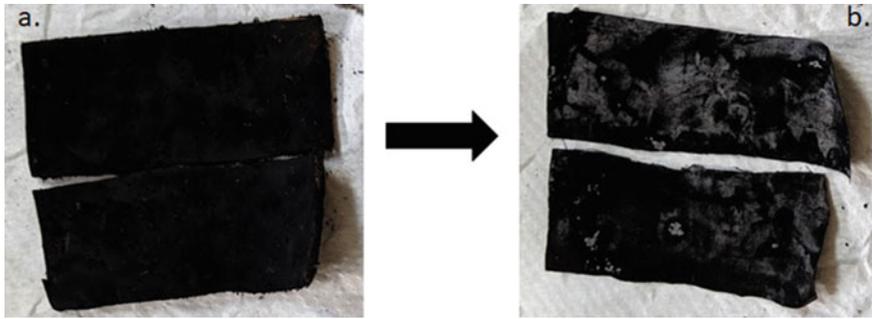


Fig. 10 Coating of polypyrrole on the textile over time: **a** prior, **b** after a day has passed, showing mild to severe cracking on the surface

Fig. 11 Result of a nylon anode due to the over-curing



Therefore, it can be inferred that by using lower heat at an extended period in the curing process, the burning issue could be mitigated.

Similarly, when applying the necessary layer of TiO_2 paste onto the anode, curing must take place in order for it to adhere to the fabric. The same issues that plague the curing process of the polypyrrole substance onto the fabric are the leading challenges here as well. If not careful, the fabric will burn, consequently rendering the conductive paste and the TiO_2 on it, useless. This is shown in Fig. 12.

A most recent issue encountered is the improper dilution of nitric acid when preparing the TiO_2 paste. This caused an intense chemical reaction that created smoke when applied onto the anode components of the cell. Shortly after, said component began to melt through the conductive coating, then proceeded to burn and contort or

Fig. 12 Fragmented, cured TiO_2 paste peeling off from the coated canvas fabric



melt away its fabric, depending on the material. The result of the chemical reactions can be seen in Figs. 13 and 14.

Additionally, the plant-based dyes also have a short shelf life and must be used within that lifespan to maintain its efficiency. Due to the dyes being made of organic plant leaves or fruit, it begins to spoil around the month mark of its conception if refrigerated or approximately a week if left at room temperature. This process is aided by the dye's contact with oxygen and sunlight, as well as its separation from the ethanol within its vial due to the differing densities. Shown in Fig. 15 is an example of a decomposing dye.



Fig. 13 Nylon anode melted away after improper TiO_2 paste coating

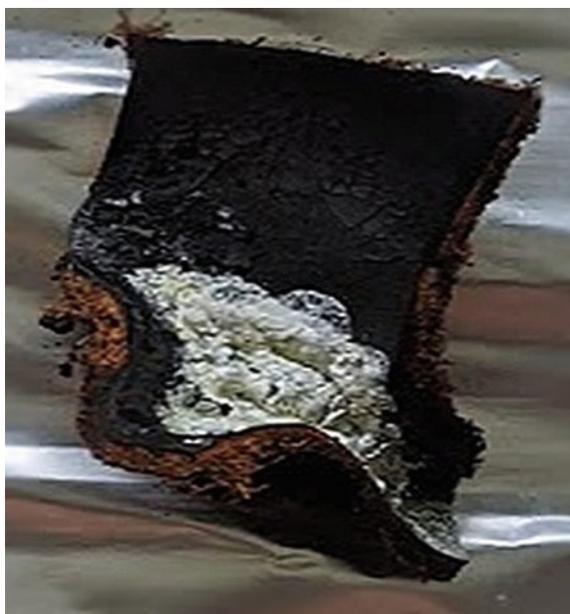


Fig. 14 Leather anode burnt and contorted after improper TiO_2 paste coating

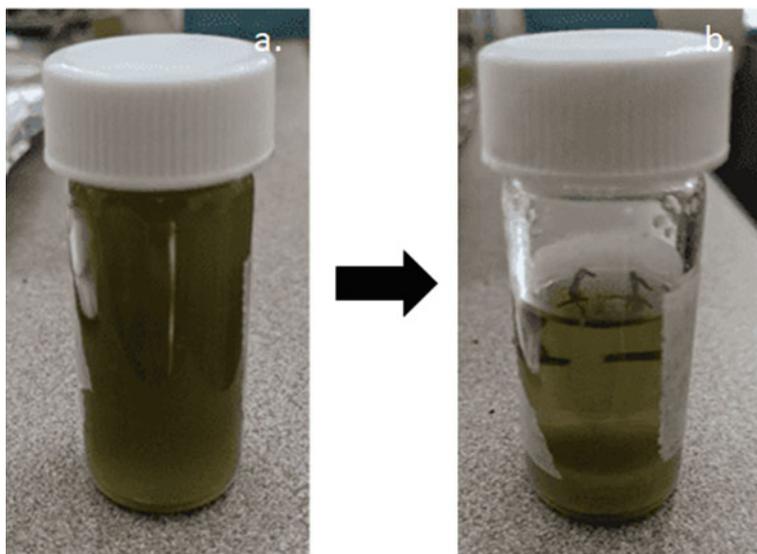


Fig. 15 **a** Fresh spinach-based dye, **b** spinach-based dye in state of decomposition



Fig. 16 Assembled TDSSC cell held together by binder clips before the application of the electrolyte

Due to the fabrics' flexibility, it is challenging to keep the anode and cathode in tight contact, as would be a conventional FTO glass DSSC. To mitigate this problem, 2–3 binder clips were used per cell, as seen in Fig. 16, in preparation for the addition of the electrolyte. However, this did not yield the best results since the cells were not entirely held together, but rather only partially.

Once the cells are assembled and prepared for testing, the analysis must be done as soon as possible after the liquid electrolyte is incorporated for the best possible results. This is due to the fast evaporation rate of the electrolyte and drying of the conductive paste. Unlike an FTO glass-based DSSC, since there is a lack of pressure to keep the electrolyte from escaping the internal workings of the cell, the TDSSC will decay and cease to function within several hours. Similarly, the moisture within the conductive paste of the cell will begin to escape, causing the paste to dry and crack, leading it to fall or peel off the fabric, rendering what was once a functional TDSSC into a non-functional material.

4 Conclusions

In summary, various TDSSC fabrication and coating methods which use natural plant-based or laboratory-manufactured dyes as sensitizers were reviewed. DSSCs and, more specifically, TDSSCs are a fundamental step towards making green energy extensively available by way of portable energy conversion. The environment will benefit significantly from making plant-based solar energy more popular in the industry and something as compact as a textile solar cell can go a long way in helping maintain a healthier environment.

The future of DSSCs and their implementation onto fabrics seem to be on the right path, and, soon, the proper scientific development methods will be further advanced.

The current conversion efficiencies for textile-based DSSCs are still lower than traditional DSSCs, but the challenges are being addressed in future work. Additionally, implementation into fabric will become much more streamlined once researchers have figured out the proper way to address the fabrication problems. Humans will be able to use this technology to improve both the quality of life and well-being. The majority of the people including doctors will have access to this inexpensive and sustainable green energy technology.

While different coating techniques were reported to coat each component of the TDSSC, the method that yields the best efficiency, and that is most cost-effective has yet to be identified. The copious amounts of plant-based and laboratory-manufactured dyes available for use in the TDSSC fabrication make it challenging to pinpoint the exact dye that should be used in any configuration. Therefore, it is unlikely that there will ever be one specific dye that will be universally used. The discovery of new materials is still in the works in order to improve the energy transport across the materials in the TDSSCs.

The challenges currently holding back advancement in the successful creation of TDSSCs, especially in the coating and fabrication methods, were numerous, but are not impossible to hurdle over. It is only a matter of time until researchers find a way past these hurdles and begin to manufacture textiles that can turn sunlight into electrical charge. These textiles can never truly replace commercial electricity, but having the ability to produce energy to power an electronic device on the go, such as a cell phone, will improve the quality of life of everyday activities.

References

- Aitola K, Zhang J, Vlachopoulos N, Halme J, Kaskela A, Nasibulin AG, Kauppinen EI, Boschloo G, Hagfeldt A (2015) Carbon nanotube film replacing silver in high-efficiency solid-state dye solar cells employing polymer hole conductor. *J Solid State Electrochem* 19:3139–3144
- Al-Alwani MA, Mohamad AB, Kadhum AAH, Ludin NA, Safie N, Razali M, Ismail M, Sopian K (2017) Natural dye extracted from *Pandanus amaryllifolius* leaves as sensitizer in fabrication of dye-sensitized solar cells. *Int J Electrochem Sci* 12:747–761
- Ananth S, Vivek P, Arumanayagam T, Murugakoothan P (2014) Natural dye extract of lawsonia inermis seed as photo sensitizer for titanium dioxide based dye sensitized solar cells. *Spectrochim Acta Part a Mol Biomol Spectrosc* 128:420–426
- Azizi T, Touihri A, Karoui MB, Gharbi R (2016) Comparative study between dye-synthesized solar cells prepared by electrophoretic and doctor blade techniques. *Optik* 127:4400–4404
- Berendjchi A, Khajavi R, Yousefi AA, Yazdanshenas ME (2016) Improved continuity of reduced graphene oxide on polyester fabric by use of polypyrrole to achieve a highly electro-conductive and flexible substrate. *Appl Surf Sci* 363:264–272
- Bu C, Tai Q, Liu Y, Guo S, Zhao X (2013) A transparent and stable polypyrrole counter electrode for dye-sensitized solar cell. *J Power Sources* 221:78–83
- Calogero G, Di Marco G, Cazzanti S, Caramori S, Argazzi R, Di Carlo A, Bignozzi CA (2010) Efficient dye-sensitized solar cells using red turnip and purple wild sicilian prickly pear fruits. *Int J Mol Sci* 11:254–267

- Calogero G, Yum J-H, Sinopoli A, Di Marco G, Grätzel M, Nazeeruddin MK (2012) Anthocyanins and betalains as light-harvesting pigments for dye-sensitized solar cells. *Sol Energy* 86:1563–1575
- Calogero G, Citro I, Di Marco G, Minicante SA, Morabito M, Genovese G (2014) Brown seaweed pigment as a dye source for photoelectrochemical solar cells. *Spectrochim Acta Part a Mol Biomol Spectrosc* 117:702–706
- Calvo P, Rodriguez J, Grande H, Mecerreyes D, Pomposo J (2002) Chemical oxidative polymerization of pyrrole in the presence of m-hydroxybenzoic acid-and m-hydroxycinnamic acid-related compounds. *Synth Met* 126:111–116
- Chang H, Lo Y-J (2010) Pomegranate leaves and mulberry fruit as natural sensitizers for dye-sensitized solar cells. *Sol Energy* 84:1833–1837
- Chien C-Y, Hsu B-D (2014) Performance enhancement of dye-sensitized solar cells based on anthocyanin by carbohydrates. *Sol Energy* 108:403–411
- DeSilva LA, Pitigala P, Gaquere-Parker A, Landry R, Hasbun J, Martin V, Bandara T, Perera A (2017) Broad absorption natural dye (Mondo-Grass berry) for dye sensitized solar cell. *J Mater Sci: Mater Electron* 28:7724–7729
- Fu X, Xu L, Li J, Sun X, Peng H (2018) Flexible solar cells based on carbon nanomaterials. *Carbon* 139:1063–1073
- Ganta D, Jara J, Villanueva R (2017) Dye-sensitized solar cells using Aloe Vera and Cladode of Cactus extracts as natural sensitizers. *Chem Phys Lett* 679:97–101
- Ganta D, Combrink K, Villanueva R (2019) Natural dye-sensitized solar cells: fabrication, characterization, and challenges. In: Tyagi H, Agarwal AK, Chakraborty PR, Powar S (eds) *Advances in solar energy research*. Springer Singapore, Singapore, pp 129–155
- Grancarić AM, Jerković I, Koncar V, Cochrane C, Kelly FM, Soulat D, Legrand X (2018) Conductive polymers for smart textile applications. *J Ind Text* 48:612–642
- Grassmann C, Grethe T, Krause A, Großberhede C, Störck JL, Ehrmann A, Van Langenhove L, Schwarz-Pfeiffer A (2019) Textile based dye-sensitized solar cells with natural dyes. In: AUTEK2019, Autex
- Gu P, Yang D, Zhu X, Sun H, Li J (2018) Fabrication and characterization of dye-sensitized solar cells based on natural plants. *Chem Phys Lett* 693:16–22
- Hernandez-Martinez AR, Estevez M, Vargas S, Quintanilla F, Rodriguez R (2011) New dye-sensitized solar cells obtained from extracted bracts of *Bougainvillea glabra* and *spectabilis* betalain pigments by different purification processes. *Int J Mol Sci* 12:5565–5576
- Kumara N, Ekanayake P, Lim A, Iskandar M, Ming LC (2013a) Study of the enhancement of cell performance of dye sensitized solar cells sensitized with *Nephelium lappaceum* (F: Sapindaceae). *J SolEnergy Eng* 135:031014
- Kumara G, Okuya M, Murakami K, Kaneko S, Jayaweera V, Tennakone K (2004) Dye-sensitized solid-state solar cells made from magnesiumoxide-coated nanocrystalline titanium dioxide films: enhancement of the efficiency. *J Photochem Photobiol A: Chem* 164:183–185
- Kumara N, Ekanayake P, Lim A, Liew LYC, Iskandar M, Ming LC, Senadeera G (2013b) Layered co-sensitization for enhancement of conversion efficiency of natural dye sensitized solar cells. *J Alloy Compd* 581:186–191
- Kye MJ, Cho J, Yu JC, Chang Y-W, Han J, Lee E, Lim HS, Lim JA (2018) “Drop-on-textile” patternable aqueous PEDOT composite ink providing highly stretchable and wash-resistant electrodes for electronic textiles. *Dyes Pigm* 155:150–158
- Lai WH, Su YH, Teoh LG, Hon MH (2008) Commercial and natural dyes as photosensitizers for a water-based dye-sensitized solar cell loaded with gold nanoparticles. *J Photochem Photobiol A: Chem* 195:307–313
- Lam J-Y, Chen J-Y, Tsai P-C, Hsieh Y-T, Chueh C-C, Tung S-H, Chen W-C (2017) A stable, efficient textile-based flexible perovskite solar cell with improved washable and deployable capabilities for wearable device applications. *RSC Adv* 7:54361–54368
- Liang X, Long G, Fu C, Pang M, Xi Y, Li J, Han W, Wei G, Ji Y (2018) High performance all-solid-state flexible supercapacitor for wearable storage device application. *Chem Eng J* 345:186–195

- Liu J, Li Y, Yong S, Arumugam S, Beeby S (2019) Flexible printed monolithic-structured solid-state dye sensitized solar cells on woven glass fibre textile for wearable energy harvesting applications. *Sci Rep* 9 (1362)
- Li Y, Arumugam S, Krishnan C, Charlton MD, Beeby SP (2019) Encapsulated textile organic solar cells fabricated by spray coating. *ChemistrySelect* 4:407–412
- Mathew S, Yella A, Gao P, Humphry-Baker R, Curchod BF, Ashari-Astani N, Tavernelli I, Rothlisberger U, Nazeeruddin MK, Grätzel M (2014) Dye-sensitized solar cells with 13% efficiency achieved through the molecular engineering of porphyrin sensitizers. *Nat Chem* 6:242
- Nagai H, Segawa H (2004) Energy-storable dye-sensitized solar cell with a polypyrrole electrode. *Chemical communications* 974–975
- Noor M, Buraidah M, Careem M, Majid S, Arof A (2014) An optimized poly (vinylidene fluoride-hexafluoropropylene)–NaI gel polymer electrolyte and its application in natural dye sensitized solar cells. *Electrochim Acta* 121:159–167
- Olea A, Ponce G, Sebastian P (1999) Electron transfer via organic dyes for solar conversion. *Sol Energy Mater Sol Cells* 59:137–143
- Peng M, Dong B, Zou D (2018) Three dimensional photovoltaic fibers for wearable energy harvesting and conversion. *J Energy Chem* 27:611–621
- Pu X, Song W, Liu M, Sun C, Du C, Jiang C, Huang X, Zou D, Hu W, Wang ZL (2016) Wearable power-textiles by integrating fabric triboelectric nanogenerators and fiber-shaped dye-sensitized solar cells. *Adv Energy Mater* 6:1601048
- Sahito IA, Sun KC, Arbab AA, Qadir MB, Jeong SH (2015) Graphene coated cotton fabric as textile structured counter electrode for DSSC. *Electrochim Acta* 173:164–171
- Sahito IA, Sun KC, Arbab AA, Qadir MB, Choi YS, Jeong SH (2016) Flexible and conductive cotton fabric counter electrode coated with graphene nanosheets for high efficiency dye sensitized solar cell. *J Power Sources* 319:90–98
- Shanmugam V, Manoharan S, Anandan S, Murugan R (2013) Performance of dye-sensitized solar cells fabricated with extracts from fruits of ivy gourd and flowers of red frangipani as sensitizers. *Spectrochim Acta Part A Mol Biomol Spectrosc* 104:35–40
- Song J, Yin Z, Yang Z, Amaladass P, Wu S, Ye J, Zhao Y, Deng WQ, Zhang H, Liu XW (2011) Enhancement of photogenerated electron transport in dye-sensitized solar cells with introduction of a reduced graphene oxide–TiO₂ junction. *Chem–A Eur J* 17:10832–10837
- Susrutha B, Giribabu L, Singh SP (2015) Recent advances in flexible perovskite solar cells. *Chem Commun* 51:14696–14707
- Teoli F, Lucioli S, Nota P, Frattarelli A, Matteocci F, Di Carlo A, Caboni E, Forni C (2016) Role of pH and pigment concentration for natural dye-sensitized solar cells treated with anthocyanin extracts of common fruits. *J Photochem Photobiol A: Chem* 316:24–30
- Tsuboi K, Matsumoto H, Fukawa T, Tanioka A, Sugino K, Ikeda Y, Yonezawa S, Gennaka S, Kimura M (2015) Simulation study on optical absorption property of fiber-and fabric-shaped organic thin-film solar cells with resin sealing layer. *Sen-I Gakkaishi* 71:121–126
- Wang X-F, Matsuda A, Koyama Y, Nagae H, Sasaki S-I, Tamiaki H, Wada Y (2006) Effects of plant carotenoid spacers on the performance of a dye-sensitized solar cell using a chlorophyll derivative: enhancement of photocurrent determined by one electron-oxidation potential of each carotenoid. *Chem Phys Lett* 423:470–475
- Wu C, Kim TW, Guo T, Li F (2017) Wearable ultra-lightweight solar textiles based on transparent electronic fabrics. *Nano Energy* 32:367–373
- Xin X, He M, Han W, Jung J, Lin Z (2011) Low-cost copper zinc tin sulfide counter electrodes for high-efficiency dye-sensitized solar cells. *Angew Chem Int Ed* 50:11739–11742
- Xu J, Li M, Wu L, Sun Y, Zhu L, Gu S, Liu L, Bai Z, Fang D, Xu W (2014) A flexible polypyrrole-coated fabric counter electrode for dye-sensitized solar cells. *J Power Sources* 257:230–236
- Xu Q, Li M, Yan P, Wei C, Fang L, Wei W, Bao H, Xu J, Xu W (2016) Polypyrrole-coated cotton fabrics prepared by electrochemical polymerization as textile counter electrode for dye-sensitized solar cells. *Org Electron* 29:107–113

- Yang Z, Deng J, Sun X, Li H, Peng H (2014) Stretchable, wearable dye-sensitized solar cells. *Adv Mater* 26:2643–2647
- Yun MJ, Cha SI, Seo SH, Lee DY (2014) Highly flexible dye-sensitized solar cells produced by sewing textile electrodes on cloth. *Scient Rep* 4:5322
- Yusoff A, Kumara N, Lim A, Ekanayake P, Tennakoon KU (2014) Impacts of temperature on the stability of tropical plant pigments as sensitizers for dye sensitized solar cells. *J Biophys* 2014 (2014)
- Zhang X, Zhang B, Ouyang X, Chen L, Wu H (2017) Polymer solar cells employing water-soluble polypyrrole nanoparticles as dopants of PEDOT: PSS with enhanced efficiency and stability. *J Phys Chem C* 121:18378–18384
- Zhou H, Wu L, Gao Y, Ma T (2011) Dye-sensitized solar cells using 20 natural dyes as sensitizers. *J Photochem Photobiol A: Chem* 219:188–194