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Recent progress and utilization of natural pigments in dye sensitized solar cells: A review

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ABSTRACT

Although efficiency of Dye Sensitized Solar Cell (DSSC) is still below the performance level of the market dominance silicon solar cells, in the last two decades DSSC has gathered sufficient interests because of the simplicity in device fabrication and low material cost, and therefore, DSSC is providing a possibility of solar cells production at a low entry cost. This review presents the research progress made in the implementation of natural pigments in DSSC. These pigments function as dye sensitizers and they play a major role in DSSC by absorbing light, and supplying electrons to the semiconductor matrixes in the cell. The common choices of dyes are the metal complexes, organic and/or natural dyes. A better efficiency with higher durability is observed for DSSC using metal complexes and organic dyes, however, the process of synthesizing these dyes is laborious, costly, and involves the use of toxic materials. As an alternative, natural pigments (dyes) found in plants such as anthocyanin, carotenoid, aurone, chlorophyll, tannin, betalain and many others are accepted as dyes in DSSCs. These natural pigments are easily obtained from fruits, flowers, leaves, seeds, barks and various parts of plants. Despite the limited performance of natural dyes, the prevailing advantages of natural dyes include high absorption coefficients, high light harvesting efficiency, low cost extraction and low toxicity. This review provides insight into the usage of the various natural pigments as sensitizers, the techniques to improve the pigments performance in DSSC, an outlook on the developmental work on the application of natural pigments in DSSC and their limitation. Additionally, the paper discusses the overall operation principle and the recent developments of each component of DSSC, as well as, comparing the material cost between natural dye and synthetic dye DSSC.

1. Introduction

The quest for sustainable living has triggered the development of alternative technologies which are capable of tapping into renewable resources and reducing pollutants [1–4]. One significant technology is solar photovoltaic (PV). The diffusion of solar PV technology varies across the global economic landscape often impeded by cost and availability of the technology. In general, the trend is the reducing installed cost of solar PV, for example in the USA the reduction of 6% in the residential sector between 2014 and 2016 has been observed [5]. Within the domain of solar PV there are over 2 dozen technologies or types of solar PV, where each of these technology has their own merits. The cost per unit energy (or power) is a determining factor on the diffusion level of solar PV technologies. In the residential sector, the average installed cost is around USD 3 per W, and this cost is down by 50% in the utility sector [6].

The capital cost for solar cell manufacturing is generally high, and for the case of crystalline silicon solar PV, the main contributing costs are the fabrication of wafer and the production of the poly-silicon [7]. In comparison, the emerging solar PV technologies like DSSC and Organic PV are cheaper at the material cost level because the materials used in DSSC or emerging solar PV are technically easier to synthesize or extracted from their natural sources [8]. These emerging solar PV are sometimes referred to as the 3rd and 4th generations PV technology. Dye sensitized solar cells (DSSC), hetero junction cells, quantum dot cells, polymer solar cells and hot carrier cells belong to the 3rd generation solar cells [9–12].

The motivation for this review is the low entry cost of DSSC fabrication. This means laboratories with the basic equipment and know-how could technically produce a laboratory level cell. Likewise, the manufacturing of DSSC does not require costly capex equipment

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like chemical vapour deposition (CVD), and involves costly trichlorosilane (TCS) Siemens process but mainly rely on widely available print technology.

DSSCs are structurally simple and the materials used are generally low cost. A typical DSSC consists of a transparent conducting oxide (TCO) glass substrate, a wide band-gap semiconductor (usually a nanocrystalline TiO_2 film which is deposited on the TCO glass substrate), a dye sensitizer anchored on to the surface of TiO_2 film, a redox mediator which is a volatile electrolyte, containing iodine/triiodide (I^-/I_3^-) redox couple, and a platinum-coated TCO glass substrate as a counter electrode [2–4,13–19].

DSSCs have unique features compared to the other solar cells, apart from being low in fabrication cost, it is can be made flexible, has various colors, made translucent, and has the ability to perform even under diffuse light condition [1,20]. DSSC have been integrated with other materials, especially those materials used in handbags and apparels. DSSC are also used indoors and as building-integrated photovoltaics, such as roll-able (flexible) devices for walls or windows [20,21].

Given the extensive use of DSSC there are still room for improving their cost and performance by targeting the cost, stability, durability, and performances of each individual components of the DSSC.

The dye sensitizer in DSSC has a major role in producing the primary charge separation through photo-excitation. The photo excited dye must possess the capability to inject electrons into the conduction band of TiO_2. The dye sensitizer is the most salient component which demands for further improvement in its photo-absorption efficiency and for this reason it has motivated many research efforts toward the improvement of dye, and the search for new families of dye sensitizers [22–25].

To be considered as an efficient dye for DSSC application, a dye should fulfil several essential requirements including:

1) The ability to bind strongly with TiO_2 through an anchoring group, e.g.: the anchoring group is either a carboxylic or a hydroxyl group, so that electrons can be efficiently injected into the TiO_2 conduction band (CB),
2) A high molar absorption coefficients, which implies the capability to absorb solar radiation from the visible to the near- IR region,
3) A faster electron transfer rate from the dye sensitizer to the TiO_2 than the decay rate of the dye, and
4) Has sufficiently higher energy level of lowest unoccupied molecular orbital (LUMO) than the CB level of TiO_2. This is to allow for efficient charge injection into the TiO_2, and at the same time having a sufficiently low energy level of highest occupied molecular orbital (HOMO) compared to the redox couple so as to achieve an efficient regeneration of the oxidized dye [20,26,27].

Among the dye sensitizers discovered, Ru(II) and Os(II) polypyridine complexes are the most efficient sensitizers for DSSC. However, these are expensive metal complexes dyes. The synthesis process is a multistep complex procedure and expensive metal catalyses are required. In addition, the synthesis process releases harmful chemicals as by-products, and consumes rare metals. This makes the overall production of DSSC to be highly dependent on rare resources, and it is non-sustainable and uneconomical for large scale production of DSSC. Thus, the metal complexes sensitizers are not recommended. This major constraint largely influenced researchers to look for new sensitizers as replacements for Ru(II) metal complexes dye sensitizers [1,20].

The introduction of the metal-free organic dyes to DSSC was one such effort to replace the expensive metal complexes dye sensitizers. Organic dyes have a number of advantages over metal complexes dyes such as, simple design, attractive colors, reduction of noble metal complexes, and higher molar extinction coefficients compared to Ru(II) complexes. On the other hand, the organic dyes have several disadvantages, and one of which is their non-sustainability. The metal-free organic dyes are unstable, which means the dyes have a tendency to degrade with time, and their manufacturing tend to be a tedious process. The dyes themselves could be toxic, or the by-products from the manufacturing process might be environmental pollutants [2,15,16,19,26].

In the 25 years of DSSC research a preference toward the use of natural dyes is observed. Natural dyes have a number of beneficial features such as, simple preparation technique, low cost of production, complete biodegradation, easy access, high availability, purity grade, environmental friendliness, and most importantly, high reduction of noble metals usage [21,28–33].

In taking advantage of the beneficial features of natural dyes, many research groups have focused on the sensitization of nano-crystalline TiO_2 with natural pigments. Natural pigments are grouped into three main families which are chlorophylls, betalains and anthocyanins. The motivation of related research is to achieve low cost and efficient photovoltaic devices. The research have branched into the sub-groups of flavonoid such as carotenoid, cyanine, etc. as well [2,15,16,19,21,30,33–36].

Although these natural dyes are suitable for the DSSCs, a major constraint associated with their chemical structure limits the research to some extent. This is because the natural pigments are developed through natural evolution, their structural arrangement is difficult to change in vitro [20]. To overcome this limitation, certain alternatives are identified to maximize the function of those dyes in DSSC, such as concentration or pH changes, modification of extraction techniques, co-pigmentation from different sources, application of different sensitization methods (e.g.: co-sensitization), optimizing the size of TiO_2 nanoparticles or the thickness of TiO_2 film, optimizing soaking time of TiO_2 electrode in pigments solution and adjusting the electrolyte composition, etc. [37–45]. Researchers are now able to identify the ideal natural source for the isolation of a particular sensitizer, and explore the best operating conditions for DSSCs with the current continued interest in the evaluation of the pigments [38,41].

This review has three major objectives:

1) To provide the knowledge on; the various types of natural pigments that are already being used, the techniques to improve the pigment performances, the direction for future research and the limitations of natural pigments in DSSCs,
2) To give a basic understanding of the overall operation principle and recent developments of each component of DSSC, and
3) To provide a general idea of cost estimation of each of the required material for the fabrication of DSSCs.

1.1. A brief history of DSSC

Over the last three decades, much attention has been paid to the development of low cost PV devices, paving the way to the development of 3rd generation of solar cells [10,11,46]. DSSC forms part of this group of PV devices, and much interests have been shown in the ways and means of increasing the efficiency of DSSC with different interventions [1,13,47,48].

The idea of DSSC was first proposed by Vogel et al. in 1870. Vogel demonstrated that silver halide alone could not show any activity towards visible light, however, silver halide in gelatin medium is reactive to visible light [49–51]. Thereafter, that phenomenon was further proved by James Moser in 1887. The voltage developed from those initial DSSC was around 0.04 V, which is too low to be of use as a PV device [51,52]. After nearly one century, in 1965–1968, Hishiki and Gerischer improved Moser's DSSC by introducing ZnO and dyes such as rose bengal and cyanine [53,54]. In later years, Rhodamine B was introduced as a new dye on to the ZnO system by Daltrozzo and Tributsch [55]. In 1977, ZnO was replaced with TiO_2 by Spitler and Calvin, and they were able to elucidate an important result showing