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Natural Dye Based-Dye Sensitized Solar Cells: A Review

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Abstract: Dye sensitized solar cells (DSSCs) is a third generation of solar cells which possess low cost of materials and fabrication process compared to silicon based solar cells added with reasonable efficiency (η). Ruthenium (Ru)-based dye DSSC shows constant high photovoltaic performance until now, but the resource of noble metal Ru is scarce, hence their costly production. Natural dyes are interesting candidates to be applied in DSSC as an alternative dyes. Natural dyes can be produced by extraction of pigments using simple procedures from flowers, leaves, and fruits. This resource not only abundance but also easy to be attained. This paper give an overview on recent researches of the application of natural dyes in DSSC.

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INTRODUCTION

Dye sensitized solar cells (DSSCs) is a third generation of solar cell that use dye to absorb light and generate electricity. Compared to silicon based solar cells, DSSC possess low cost of materials and fabrication process added with reasonable efficiency (η) (Green, 2001). Nanoporous metal oxide of titanium dioxide (TiO_2) was introduced in DSSCs by M. Gratzel and made the breakthrough in η of DSSCs with the value of 10% at AM 1.5 solar radiation. The Gratzel's cell was composed of nanocrystalline colloidal TiO_2 films sensitized by polypyridyl complexes of Ruthenium (Ru) known as the N3 dye and I^-/I^{-3} solution in volatile organic solvent as an electrolyte (O'Regan and Grätzel, 1991). Basically, DSSC architecture is built by nanocrystalline semiconductor oxide film electrode, dye sensitizers, electrolytes, counter electrode and transparent conducting substrate. Dye acts as an absorber of photon from sunlight and transform it into electricity. Until now, Ru complexes have proved to be the most effective constantly. However the resource of noble metal Ru is scarce, hence their costly production Senthil et al., 2011). Due to this problem, researcher searched other ways to substitute the Ru-based dye and lead to the findings in application of organic dyes and natural dyes into DSSC. Organic dyes are economically and the highest η reported by using this kind of sensitizers as high as 9.8% (Zhang et al., 2009). Unfortunately, organic dyes also have the drawbacks, such as cumbersome synthetic routes and low yields. In other hand, natural dyes can be produced by extraction of pigments using simple procedures from flowers, leaves, and fruits. This resource not only abundance but also easy to be attained. Even though the performance of DSSC based on natural dyes are lower than organic based one, the efforts to improve it still continues motivated by its cost efficiency, non-toxicity, and complete biodegradation (Sirimanne et al., 2006).

CONCEPTUAL OF MECHANISM IN DSSC

Basically, DSSC is like a photochemical cells that its principal of working is based solely on chemical reactions. Three basics steps involve in DSSC are absorption, separation and collection of charge carriers. All of this three steps are studied, attuned and optimized intensively in numerous researches to attain better efficiency. By referring to Figure 1, Right after light illumination upon DSSC, molecules in dye became photo excited (Eq. 1) and within few femto seconds, the electron injection is prompted from excited dye S* to the CB of semiconductor (Eq.2) within the sub pico second time scale (at this moment, they are rapidly thermalized by lattice collisions and phonon emissions within less than 10 fs. In other hand, the occurrence of intermolecular relaxation of dye excited states might complicate the injection process and change the timescale). In a right condition, the relaxation of the excited dye S* (within nanosecond) (Eq. 3) is rather slow compared to injection, ensuring the injection efficiency to be unity. After that, within microseconds the HOMO of dye is regenerated by I^- (Eq. 4) effectively annihilating S* and intercepting the recombination of electrons in semiconductor with S^+ that happens in the millisecond domain. Then, the two most important processes which are electron percolation across the semiconductor layer and the redox capture of the electron by the oxidized relay (back reaction, Eq.

5), I^{3-} , within milliseconds or even prolonged into seconds (Matthews et al., 1996).

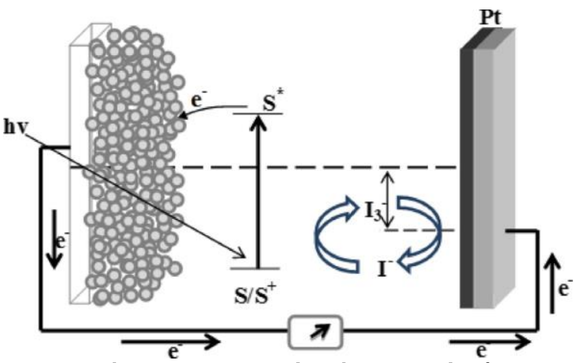


Figure 1: Schematic structure and working principle of DSSC (Monishka, 2012).

Anode:
S + hv → S* photon absorption (1)
S* → S^+ + (TiO_2) electron injection (2)
$2S^+ + 3I^-$ → $2S + I^-_3$ regeneration (3)
Cathode:
$I^-_3 + 2e^-$(Pt) → $3I^-$ redox process (4)
Cell:
e^-(Pt) + hv → $3I^-$ (5)

DSSC FABRICATION

DSSC is composed of photoanode (conductive substrate, semiconductor and dye), electrolyte and counter electrode.

Photoanode

Photoanode consist of conductive substrate typically either indium tin oxide (ITO) substrate or flurinated tin oxide (FTO) substrate, semiconductor (metal oxide: TiO_2, ZnO, ZnS and Nb_2O_5) and dye (Ru-based, organic and natural). This paper only focus on the comparison between natural dyes that have been reported for achieving better efficiency.

Electrolyte

Two main characteristic acquired in electrolyte medium; electrically conductive and also generates dye. Based on their physical state, the electrolytes can be classified into 3 groups; liquid electrolyte, quasi-solid electrolyte and solid electrolyte (Jinchu et al., 2014).

Counter electrode

Counter electrode is the last part in DSSC architecture. In typical DSSC counter electrode consist of metal casted on conductive substrate. The counter electrode must have ohmic contact with the material and also inert, which do not chemically react with the materials but able to diffuse on the surface and into the interior of the material of even at room temperature (Qiao, 2006).

PHOTOVOLTAIC PARAMETERS

In DSSC, the photovoltaic performances (*I-V* measurement) are mainly characterize by the following parameters; open-circuit voltage (*Voc*), short-circuit photocurrent density (*Jsc*), fill factor (*FF*), efficiency (η). All of these parameters mostly be measured under light radiation with intensity of 1000 W/m^2 at AM 1.5.*Voc* is the maximum voltage the solar cells can generate under the incident of light. *Voc* is produced when the solar cell is connected to a load with infinite resistance (*I* = 0). *Voc* is corresponded to gap between the quasi-Fermi level of the semiconductor and the redox potential of the electrolyte while *Jsc* is the photocurrent generated per unit area of under short circuit current condition. It is depended on the optical properties of the dye and also to different dynamic processes in the cell. In J-V curve (Figure 2), the intersection in y- axis is regarded as *Jsc* while in x-axis is *Voc*. *FF* is the product of maximum power (J_{max} x V_{max}) per the product of multiplication of *Voc* and *Jsc*. Finally η can be determined by ratio of maximum power of output to the power of incident light.

$FF = (J_{MP}V_{MP} / J_{SC}V_{OC}) = P_{max} / J_{SC}V_{OC}$ (6)
$\eta = (P_{max} / P_{in})$ x 100 %
$= [FFJ_{SC}V_{OC} / P_{in}]$ x 100% (7)

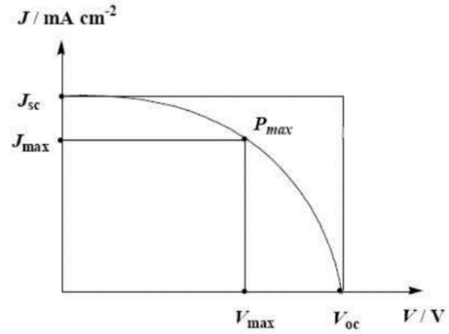


Figure 2: J-V curve of photovoltaic (Jinchu et al., 2014).

NATURAL DYES APPLICATION IN DSSC

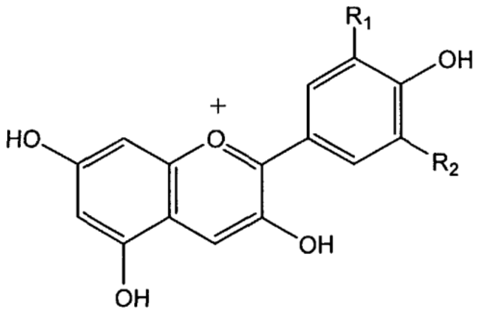
The color of flowers, fruits and leaves all depend on their second metabolites also known as pigments. The colorful of flowers and fruits is a way of plant to attract the pollinators together with another factors including fragrance, floral shape and nectar reward. Pigmentation of plant occurs due to the interaction between electronic structures of pigment and sunlight which alter the wavelengths that are either transmitted or reflected by the plant tissue. There are two ways to describe pigments;

1) The wavelength of maximum absorbance (λ_{max}),

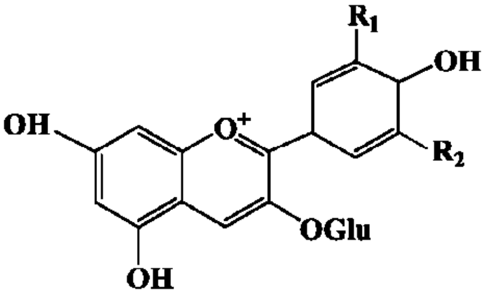
2) The color perceived by human's eye (Monishka, 2012).

Some common pigments are betalains (betacyanins and betaxanthins), carotenoids (carotenes and xanthophylls), chlorophyll and flavonoids (anthocyanins, aurones, chalcones, flavonols and proanthocyanidins). Most popular natural dyes in DSSC are shown in Figure 3.

(a)



(b)



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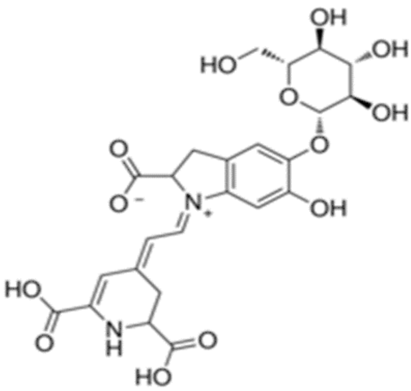

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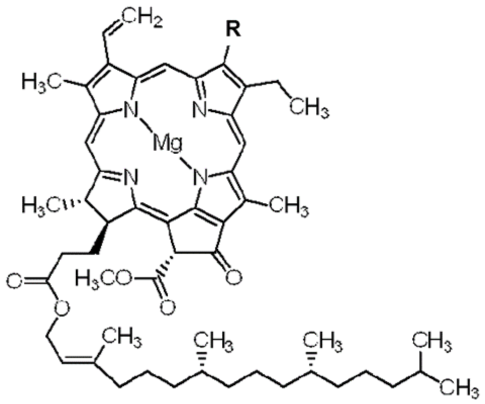

Figure 3: Molecule structures of some most common pigments used as a dye a) anthocyanidin, b) anthocyanin. c) betanins and d) chlorophyll.

The photovoltaic parameters of DSSC based on various natural dyes were summarized in Table 1. The "*" symbol indicates the high efficiency in terms of natural dye based DSSC in the meantime. From Table 1 we can speculate that DSSC with anthocyanin dye have relatively higher η among the natural based dye DSSC. Eventhough, it supposed the chlorophyll dye based DSSC has higher η because chlorophyll absorb red light which is the most intense in visible region of electromagnetic, the anthocyanin in flavylium state is a cation which its net electric charge is unstable hence has more tendency to mobilize electron. Smestad and Grätzel, 1998 was concluded that the interaction between anthocyanin and TiO_2 is high. Anthocyanin has –OH groups and capable in chelating to the Ti^{IV} sites on TiO_2 surface as shown in Figure 4

Natural dye suffer from low V_{oc}. It is speculated that recombination pathways of electron/dye cation are inefficient and acidic environment of dye absorption. In acidic environment, H^+ is absorbed by TiO^2 (H^+ are the potential determining ions for TiO^2) and caused a positive shift on the Fermi level of the TiO^2, thus deterred the maximum photovoltage that could be delivered by DSSC. The charge transfer resistance in the TiO_2/dye/electrolyte interface caused the decreasing in J_{sc} and to overcome this problem, the natural dye must have several =O or –OH functional groups in their molecule structure (Calogero et al., 2010, Smestad and Grätzel, 1998). In our work, we use anthocyanin dye extracted from red frangipani flowers as a sensitizer and hydrothermally grown ZnO nanorods as metal oxide semiconductor in photoanode of our DSSC. We post anneal our ZnO nanorods at various temperature and then sensitize it in red frangipani dye for varied duration. Red frangipani dye is suitable to be applied as sensitizer because of its low unoccupied molecular orbital (LUMO) is higher than the conduction band of ZnO which is one of pre requirements for DSSC material choices.

DENSITY FUNCTIONAL THEORY IN DSSC

Density functional theory (DFT) is quantum chemistry approach to matter to investigate the electronic structure. Mostly it is applied for calculating, e.g., binding energy of molecules in chemistry and the band structure of solids in physics (Capelle, 2006). In DSSC, DFT is used to investigate the electronic structure of dyes. Most reported literatures used GAUSSIAN 09W software (Frisch et al., 2010) software package to run the characterization of DFT and time dependent density functional theory (TD-DFT) (Kumara et al., 2013, Capelle, 2006). DFT method is capable to give insight in electron movement and mechanisms that took place in DSSC. Most studies use DFT as a screening method to find the right material combinations to be used in future or as a tool to investigate any possible errors occurred in an unsatisfied results from experiments. Kumara et al., 2013 reported the theoretical studies of black tea waste extract as a potential sensitizer and four theaflavin analogues which are responsible for the dark color of black tea were studied using DFT and TD-DFT. It was reported that theaflavin and theaflavin digallate were the most probable sensitizers (Figure 5).

Table 1: Summary of natural dye based DSSCs photovoltaic performance.

Natural dye	J_{sc} **(mA/cm^2)**	V_{oc} **(V)**	***FF***	η **(%)**	**References**
Rosella	1.63	0.40	0.57	0.37	Wongcharee et al., 2007
Blue pea	0.37	0.37	0.33	0.05	
Mixed rosella blue pea	0.82	0.38	0.47	0.15	
Bixin	1.10	0.57	0.59	0.37	Gòmez-Ortíz et al., 2009
Annatto	0.53	0.56	0.66	0.19	
Norbixin	0.38	0.53	0.64	0.13	
Fruit of Calafate	6.20	0.47	0.36		Polo and Iha, 2006
Syrup of Calafate	1.50	0.38	0.20		
Skin of Jaboticaba	7.20	0.59	0.54		
Dragon fruit	0.20	0.22	0.30	0.22	Ali and Nayan, 2010
Pomegranate juice	0.20	0.40	0.45	1.50*	Bazargan, 2009
Begonia	0.63	0.537	0.72	0.24	Zhou et al., 2011
Tangerine peel	0.74	0.592	0.63	0.28	
Marigold	0.51	0.542	0.83	0.23	
Perilla	1.36	0.522	0.69	0.50	
Rhododendron	1.61	0.585	0.61	0.57	
Fructus lycii	0.53	0.689	0.46	0.17	
Herba artemisiae scopariae	1.03	0.484	0.68	0.34	
Chinaloropetal	0.84	0.518	0.62	0.27	
Petunia	0.85	0.616	0.60	0.32	
Bauhinia tree	0.96	0.572	0.66	0.36	
Yellow rose	0.74	0.609	0.57	0.26	
Flowery knotweed	0.60	0.554	0.62	0.21	
Lithospermum	0.14	0.337	0.58	0.03	
Violet	1.02	0.498	0.64	0.33	
Chinese rose	0.90	0.483	0.62	0.27	
Broadleaf holly leaf	1.19	0.607	0.65	0.47	
Rose	0.97	0.595	0.66	0.38	
Cofee	0.85	0.559	0.68	0.33	
Lily	0.51	0.498	0.67	0.17	
Mangosteen pericap	2.69	0.686	0.63	1.17*	
Black rice	1.14	0.55	0.52		Hao et al., 2006
Capsicum	0.23	0.41	0.63		
Rosa xanthina	0.64	0.49	0.52		
Kelp	0.43	0.44	0.62		
Erythrina variegate	0.78	0.48	0.55		
Crocetin	2.84	0.43	0.46	0.56	Yamazaki et al., 2007
Crocin	0.45	0.58	0.60	0.16	
Red Sicilian orange	3.84	0.34	0.50		Calogero and Marco, 2008
Purple eggplant extract	3.40	0.35	0.40		
Red turnip	9.50	0.43	0.37	1.70*	Calogero et al., 2010
Wild Sicilian prickly pear	8.20	0.38	0.38	1.19*	
Sicilian Indian	2.70	0.38	0.54	0.50	
Bougainvillea	2.10	0.30	0.57	0.36	
Hibiscus surattensis	5.45	0.39	0.54	1.14*	Hernández-Martínez et al., 2010
Hibiscus rosasinesis	4.04	0.40	0.63	1.02*	
Sesbania grandiflora	4.40	0.41	0.57	1.02*	
Ixora macrothyrsa	1.31	0.40	0.57	0.30	
Rhododendron arboretum zeylanium	1.15	0.40	0.64	0.29	
Ipomoea	0.91	0.54	0.56	0.28	Lai et al., 2008
Curcumin	3.039	0.51	0.44	1.42*	Jinchu et al., 2014
Shisonin	3.56	0.55	0.51	1.01	Kumara et al., 2006
Chlorophyll	3.52	0.43	0.39	0.59	
Shisonin and chlorophyll	4.80	0.53	0.51	1.31*	
Red Bougainvillea glabra	2.34	0.26	0.74	0.45	Chang et al., 2010
Red Bougainvillea spectabilis	2.29	0.28	0.76	0.48	
Violet Bougainvillea glabra	1.86	0.23	0.71	0.31	
Violet Bougainvillea spectabilis	1.88	0.25	0.73	0.35	
Bongainvillea brasiliensis	5.00	0.25	0.36	0.45	Lai et al., 2008 (water based DSSC)
Garcinia suubelliptica	6.48	0.32	0.33	0.69	
Ficus reusa	7.85	0.52	0.29	1.18*	
Rhoeo spathacea	10.9	0.50	0.27	1.49*	
Black tea waste	4.21	0. 268	0.41	0.46	Kumara et al., 2013
Syzygium guineense	2.03	0.506	50.0	0.51	Tadesse et al., 2012
Delonix regia	1.33	0.30	0.39	0.317	Senthil et al., 2011
Eugenia Jambolana	1.49	0.35	0.48	0.505	
Eriglossum rubiginosum	0.035	0.240	0.708	5.948*	Hambali et al., 2015
Syzygium cumini	0.1	0.063	0.317	2.00*	
Husk of purple corn	3.57	0.46	0.64	1.06*	
Cob of purple corn	3.42	0.48	0.62	1.01*	
Silk of purple corn	3.25	0.48	0.62	0.96	Phinjaturus et al., 2016

(a)

(b)

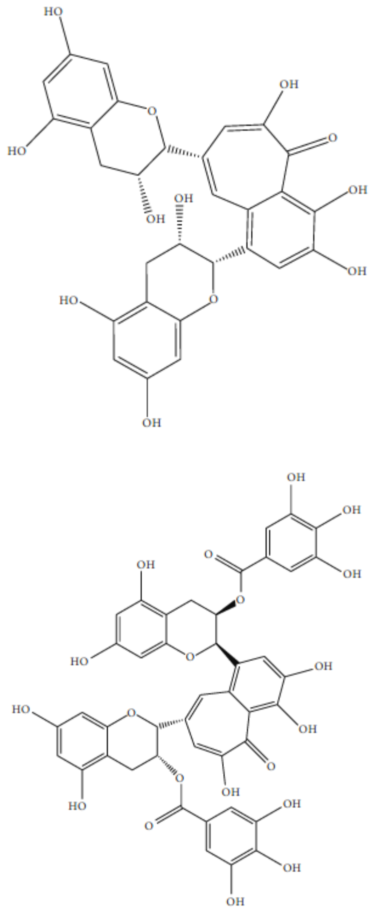

Figure 5: Molecular structure of (a) theaflavin and (b) theaflavin digallate (Kumara et al., 2013).

Ekanayake et al., 2013 investigated the molecular geometries, electronic structures, optical absorption spectra and proton affinity of cyanidin, pelargonidin and maritimein from constituents of Canarium odontophyllum with DFT/TDDFT. It was reported photovoltaic performance of cyanidin-DSSC is the best compared with the other two and cyanidin was presented with the smallest band gap.

CONCLUSION

Despite of Ru-based dye DSSC exhibit a constant high photovoltaic performance, their synthesis is tedious and expensive. In other hand natural dye is inexpensive, abundance, easy to be prepared and biodegradation completely. Currently, natural dyes based DSSC performed rather low η. In natural dye based DSSC realm, the DSSC that contain anthocyanin one possess the highest η. The molecular structure of anthocyanin itself assist the efficient electron mobility from anthocyanin to metal oxide semiconductor (TiO_2 mostly) compared to other kind of natural dye. However, modification on molecular structure and architecture of DSSC need to be considered in order to optimize its photovoltaic performance. In our work, we use red frangipani dye and ZnO nanorods as active materials in photoanode for DSSC and currently is in progress.

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