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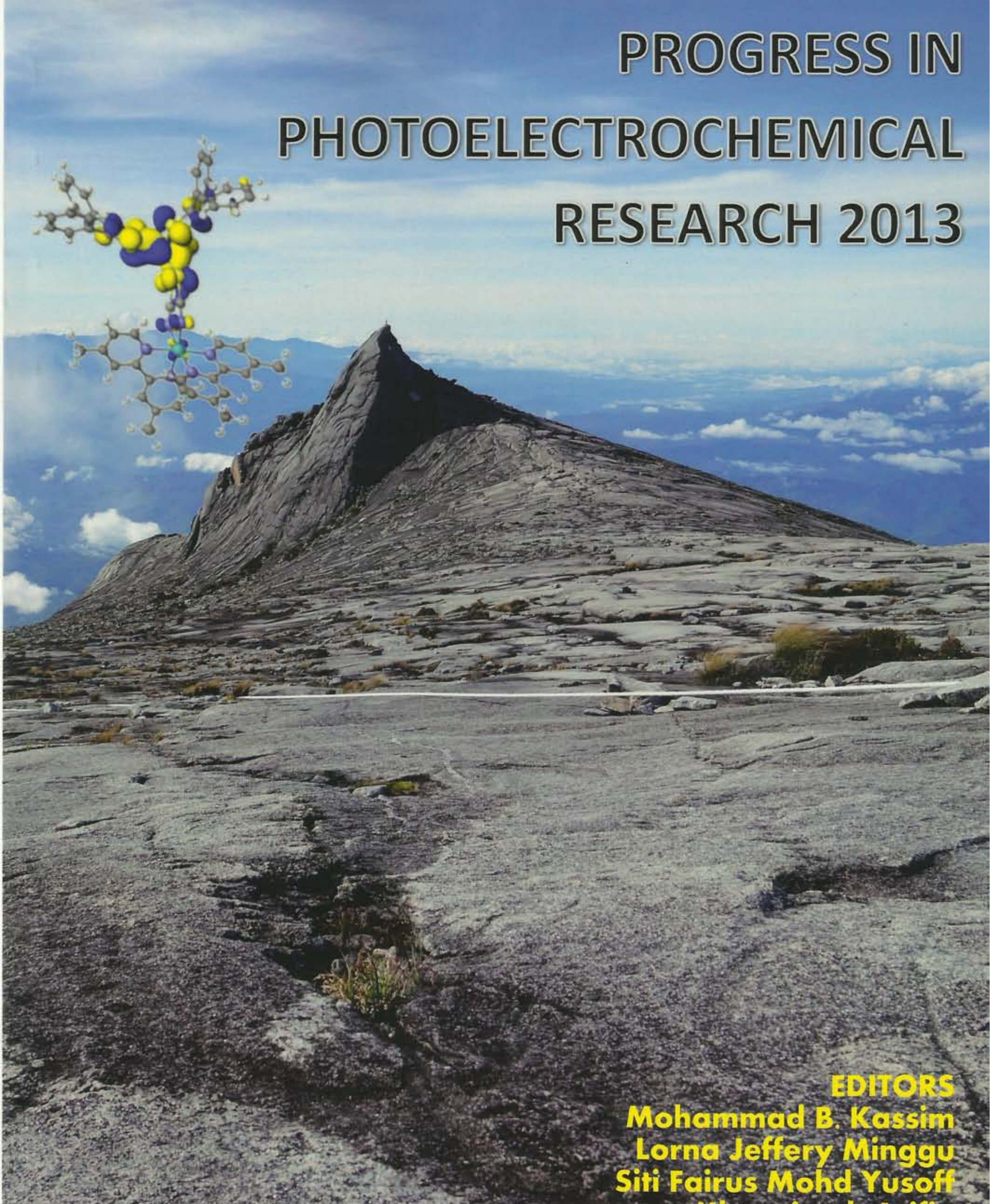

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A Brief Review of Dye Sensitized Solar Cell with Natural Dye Sensitizer

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Abstract

Dye sensitized solar cells (DSSCs) are a promising alternative for the development of a new generation of photovoltaic devices owing to their ease of manufacture, low cost and environmental advantage over conventional silicon-based crystalline solar cells. DSSC consists of four main components which are photosensitizer, photoanode, electrolyte and counter electrode. Organic DSSC which utilized nontoxic natural dyes as photosensitizer would enhance the environmental and economic benefits of DSSC for solar energy conversion.The cell performance is influenced by parameters such as the component of photosensitizer, the morphology of the photoanode, electrolyte conductivity andelectrocatalytic properties for the counter electrode. This review paper presents a brief review on the natural photosensitizers, semiconductor thin film, electrolyte and counter electrode of DSSCS.

Keywords: Dye Sensitized Solar Cell, Natural Photosensitizer, Semiconductor Thin Film, Electrolyte, Counter Electrode

Introduction

Since O'Regan and Gratzel invented the dye sensitized solar cell in 1991, dye-sensitized solar cell have attracted tremendous attention (O'Regan and Gratzel 1991). This is due to theirease of manufacturing process and environmental advantages over commercial silicon based solar cell (Senthil et al. 2011). Typically, dye-sensitized solar cell have a sandwich structure which consists of a photoanode comprising TiO_2 nanoparticles sensitized by dye molecules deposited on fluorine doped tin oxide (FTO) glass, an electrolyte containing the iodine/triiodide (I^-/I_3^-) redox couple, and a counter electrode. Dye sensitized solar cell uttlized dye molecules adsorbed on the photoanode material such as titanium dioxide (TiO_2) to collect sunlight. The oxidized dye molecules are then regenerated by reduction of iodide ion in electrolyte (Grätzel 2001 & B. O'Regan et al. 1991).

Components of Dye Sensitized Solar Cell (DSSC)
Natural Photosensitizers

Among the natural dye sources, anthocyanin and betalain are two main sources for the dye sensitizers. Table 1 shows a list of dye sensitizers which were extracted from anthocyanin and betalain. Anthocyanin are natural compounds which occurs naturally in fruit, flowers and leaves. Among the anthocyanin dyes, red cabbage extract exhibited the best DSSC efficiency of 2.91%. This is due to red cabbage extract has strong anchoring groups to be attached to the semiconductor surface and also exhibit wide absorption spectrum which covers whole visible region and small part in near infrared region as reported by Liet al. (2013).Therefore, wide absorption ability and strong anchoring groups are two of the important requirements for a good dye sensitizer.

On the other hand, betalain raw pigments which can be simply extracted in acidic conditions for example wild Sicilian Prickly Pear gained solar energy conversion efficiency of 1.7% and short circuit current density (J_{sc}) 8.20 $mAcm^{-2}$ was effective in converting solar energy to electricity for more than 24 hours. However, the efficiency of the betalain based natural dye sensitizers have been improved by the Sandquist and McHale (2011) which achieved the maximum efficiency of 2.7% by using betanin pigment that extracted from the grown beets. It was found that betanin appears to be the best performing natural photosensitizers in DSSC by modifying the film with the blocking layer (Sandquist et al. 2011).

Table 1 Photoelectrochemical parameters of natural based DSSCs

Component	Source	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	η (%)	Reference
Anthocyanin	Red Cabbage	11.2	0.59	0.44	2.91	Liet al. (2013)
Anthocyanin	PunicaGranatum Peel	3.341	0.716	0.776	1.86	Hernandez-Martinez et al. (2012)
Anthocyanin	Hibiscus Sabdariffa	3.549	0.66	0.683	1.6	Hernandez-Martinez et al. (2012)
Betalain	Beets	13.91	0.36	0.56	2.71	Sandquist and Mchale (2011)
Betalain	Red Turnip	9.50	0.43	0.37	1.70	Calogeroet al. (2010)
Betalain	Wild Sicilian Prickly Pear	8.20	0.38	0.38	1.19	Calogeroet al. (2010)

Photoanode

Sabah, which has wide variety sources of flora is a good location to explore more natural dyes as dye sensitizers in dye sensitized solar cell. Hence, further research can be done on the locally sourced dye to evaluate their performance in dye sensitized solar cells. However, the efficiency and lifespan of the natural based DSSC is always a challenge to be improved. Therefore, further investigations are required to improve the efficiency and lifespan.

Photoanode which acts as the electron transporter and support for photosensitizer consisted of the photosensitizer attached on the layer of photoanode material such as TiO_2 (Kelly and Meyer 2001). TiO_2 nanoparticles had been extensively studied over other photoanode materials such as ZnO, SnO_2, and Nb_2O_5 due to its low cost, safety and closely energy band structure (Chen et al. 2012). However, the conversion efficiency of TiO_2 nanoparticles-based DSSC was limited by the slow transportation of electrons through the randomly arranged nanoparticles as well as the energy losses caused by the recombination (Huang et al. 2011 & Wang et al. 2011). Thus, various approaches such as surface treatment of TiO_2 to retard recombination and optimization the morphology of TiO_2 has been done to overcome the limitations.

Table 2 Performance of photoanode in DSSC using TiO_2photoanode material

Photoanode Materials (Source)	Modification	Dye	Jsc ($mAcm^{-2}$)	V_{OC} (V)	FF	η (%)	Reference
TiO_2 (P25)	Unmodified	Red cabbage	11.2	0.59	0.44	2.91	Li et al. (2013)
TiO_2 (P25)	Unmodified	Grown beets	10.55	0.35	0.57	2.04	Sandquist and Mchale (2011)
TiO_2 (P25)	$TiCl_4$	Grown beets	9.34	0.44	0.57	2.27	Sandquist and Mchale (2011)
TiO_2 (P25)	BL	Grown beets	13.91	0.36	0.56	2.71	Sandquist and Mchale (2011)
TiO_2 (Sol gel synthesized)	BL and $TiCl_4$	Wild Sicilian Prickly pear	8.20	0.38	0.38	1.19	Calogeroet al. (2010)
TiO_2(Sol gel synthesized)	SL, BL and $TiCl_4$	Wild Sicilian Prickly pear	9.4	0.35	0.38	1.26	Calogeroet al. (2010)

*$TiCl_4$= $TiCl_4$treatment, BL = Blocking Layer, SL = Scattering Layer

Table 2 shows the photovoltaic performance of photoanode in DSSC using TiO_2 photoanode materials with various modifications sensitized by natural dyes. The efficiency of DSSC fabricated varies from 1.19 to 2.91%. It can be seen that $TiCl_4$ treatment on TiO_2 layer greatly improved the cell performance. The $TiCl_4$ can increase the interconnectivity of TiO_2 nanoparticles which increase the contacting surface for dye adsorption. The blocking layer which is usually done by immersing the FTO glass into $TiCl_4$ solution before application of TiO_2 paste act as an insulating layer to prevent direct contact of electrolyte with FTO glass. Besides, the application of light scattering layer also increases the path length of incident light which increases the DSSC performance. Thus, from the discussions above, we can conclude that photoanode with modified TiO_2 can effectively enhanced the performance of DSSC.

Electrolyte

Generally the electrolyte that applied in DSSC can be categorized into three categories which are liquid electrolyte (LE), solid electrolyte (SE) and quasi-solid electrolyte (QSE). To be a good electrolyte, it needs to be electrochemically stable, thermally stableand high ionic conductivity. As shown in Table 3, DSSC based on LE gave higher energy conversion efficiency (η). However, problem such as leakage, solvent evaporation, desorption and photodegradation of the attached dyes limiting the long term performance of the DSSC. SE based DSSC has been introduced and it gave a better lifespan. However, poor interface contact and lower conductivity of DSSC that used SE leads to lower η as shown in Table 3. In order to improve both the η and lifespan of the DSSC, QSE has been applied in DSSC. QSE based DSSC gave a better lifespan than LE based DSSC. Its η was comparable to the LE based DSSC as showed in table 3.

Table 3 Performance of DSSC based on different categories of electrolyte

Category	Jsc(mAcm^{-2})	V_{OC}(V)	FF	η (%)	Lifespan	Reference
LE	13.5	0.704	0.67	6.39	-	Lee at al. (2008)
QSE	14.48	0.736	0.57	6.04	-	
LE	15.82	0.678	0.65	7.01	η drop 21% (1000hr)	Huo et al. (2007)
QSE	15.24	0.686	0.69	7.18	η drop 10% (1000hr)	
SE	6.62	0.646	0.62	2.66	-	Xiang et al. (2009)
SE	6.05	0.620	0.61	2.3	-	Kanga et al. (2006)

Counter Electrode

Table 4 Type of Counter Electrode for non- natural based DSSCs

Counter electrode		Electrolyte	J_{sc}, mA/cm[2]	V_{oc}, mV	Electron transfer resisitance, R_{ct}	FF, %	ŋ, %	Reference (s)
CM	Substrate							
PEDOT + 15 % CB	MM/ PEN	I^-/I^-_3	12.60	739	-	58.00	5.50	Huang et al.(2012)
PEDOT + 15 % CB	ITO/PEN	I^-/I^-_3	13.30	756	-	60.00	6.00	Huang et al.(2012)
Pt	FTO	I^-/I^-_3	16.08	810	4.86Ω.cm[2]	65.00	8.49	Zhang et al.(2011)
DWCNTs	FTO	I^-/I^-_3	15.43	800	3.13 Ω.cm[2]	65.20	8.03	Zhang et al. (2011)
SWCNTs	FTO	I^-/I^-_3	14.94	800	6.72 Ω.cm[2]	64.00	7.61	Zhang et al. (2011)
MWCNTs	FTO	I^-/I^-_3	15.25	800	10 Ω.cm[2]	56.40	7.06	Zhang et al. (2011)
G	FTO	I^-/I^-_3	16.99	750	-	53.60	6.82	Zhang et al. (2011)
Gt-CB	FTO	I^-/I^-_3	11.34	830	-	71.20	6.67	Zhang et al. (2011)
Gt	Copper	MPN-100	2.10	360	-	70.00	5.29	Bazarganet al. (2010)
Gt	ITO	MPN-100	1.40	345	-	70.00	3.38	Bazarganet al. (2010)
CoS	FTO	I^-/I^-_3	14.17	730	1.45 Ω.cm[2]	63.00	6.01	Lin et al. (2010)
Wurtzite CZTS	FTO	I^-/I^-_3	13.41	750		68.70	6.89	Kong et al. (2013)
CNP + Ni gel	Ti foil	I^-/I^-_3	13.3	710		70.00	6.60	Zheng et al. (2013)
CTSe	FTO	I^-/I^-_3	14.69	710	5.34 Ω.cm[2]	72.95	7.75	Zhu et al. (2013)

Fluorine-doped tin oxide glass (FTO); Indium doped Tin Oxide (ITO); Platinum (Pt); Graphenes (G); Carbon black (CB); Poly (3,4ethylenedioxythiophen) (PEDOT); Metal mesh (MM); Polyethylene naphthalate (PEN); Single-wall carbon nanotubes (SWCNT); Double-wall carbon nanotubes (DWCNT); Multiple-wall carbon nanotubes (MWCNT); Cobalt sulfide (CoS);Graphite (Gt);Cu_2ZnSnS_4(CZTS);Carbon nanoparticle (CNP) and Cu_2SnSe_3(CTSe).

Most of the natural photosensitizers based DSSCs were using platinum (Pt) as the catalyst material (CM) and fluorine-doped tin oxide glass (FTO)/indium doped tin oxide (ITO) as the substrate (Polo and Murakami 2006 & Giuseppe and Gaetano 2008). The high popularity of Pt may be due to its superior electrocatalytic activity forI-/I^-_3 redox couple, however, Pt is expensive.

Most of the researches of CE were on non-natural photosensitizers based DSSCs. According to Table 4, a lot of effort has been made to find alternative metal-free materials such as carbon materials in order to replace Pt (Suzuki et al. 2003). The highest cell efficiency (ŋ) was 8.49% which used Pt as catalytic material due to the betterelectrocatalytic activity of Pt to I^-/I^-_3 redox couple (Zhang et al. 2011).

According to Table 4, the second highest cell efficiency was 8.03% which used double-wall carbon nanotubes (DWCNT) as the catalytic material. Zhang et al. (2011) reported that it may be due to the large inner surface area and the 3D structures with suitable poresprovided by DWCNT. Compared to the Pt based cell, the carbon nanotubes (CNTs) based cells have lower cell efficiency. Lee et al. (2009) attributed the effect to the Pt CE that consists of activated platinum nanoclusters, which can reflect portion of the unabsorbed incident light back to the TiO_2 electrode. Besides, other problem associated with CE was the detachment of the catalyst material layer from the substrate layer.

Conclusions

Overall, DSSC has been known as a potential solar energy conversion device. It has received a great attention during the last decade. It was mainly due to its potential for low cost and high efficiency. The optimization of semiconductor film is needed to overcome the competition between generation and recombination of the photoexcited electrons. Furthermore, the CE will also affect the whole DSSC system. One of the main problems of CE was the detachment of catalyst material layer from the substrate layer. It decreases the cell efficiency. Hence, more research needs to be done in order to solve this problem. In conclusion, natural dyes as sensitizers of DSSCs are promising because of their environmental friendliness and low-cost production.

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