ISSN: 0975-8585

Research Journal of Pharmaceutical, Biological and Chemical Sciences

Pigments for Generating Electric Power - An Overview.

Mary Rosana NT *.

Department of Chemical Engineering, Sathyabama University, Chennai-600119, Tamil Nadu, India.

ABSTRACT

Innovation of novel renewable energy technologies is of utmost importance in the present scenario. Among the several non conventional energy technologies available, harnessing the abundantly available solar energy remains challenging to the human society. Compared to the conventional silicon based diodes, dye sensitized solar cells (DSSC's) have gained considerable attention over the past two decades. This topic has attracted numerous research groups in recent days and constant focus is done on the various aspects of DSSC's such as molecular engineering of photosensitizing materials, better fabrication procedures, development of counter electrode materials etc. In this review paper, we have discussed the recent progress in this novel field of research in a broader sense and also emphasized the importance of natural photosensitizer's and their reported conversion efficiencies by various researchers. In addition, few recommendations are suggested for the better performance of the photovoltaic devices based on naturally extracted dyes.

Keywords: Renewable energy, Solar cells, conversion efficiency, natural photosensitizers

***Corresponding author**

INTRODUCTION

Clean energy is the utmost essential requirement of any sustainable society. The world's conventional energy resources such as coal, oil and natural gas are finite in nature and the extraordinary usage of these available resources has resulted in their rapid depletion. The repeated usage of these finite resources for energy supply has led to the emission of toxic gases into the atmosphere and has resulted in the global climatic changes. These changes caused are threatening the well being of human's presently. Therefore, in order to avoid the environmental catastrophe, and the future energy crisis, innovative and alternate renewable sources of energy has to be explored and it is of prime focus in recent days [1-4]. Among the available renewable energy technologies, solar energy has potential in generating electric power and the naturally available energy supply from the sun is enormous, about 10,000 times more than the current energy requirement. Highly skilled production process and expensive nature minimized the usage of conventional silicon based solar cells from various domestic and commercial applications [5, 6]. Dye sensitized solar cells(DSSC's) are of unique nature and have gained considerable attention and this technology is expanding at a rapid rate due to their high energy conversion efficiency, environmental friendly nature, light weight, recyclability, attractive appearance, ease of manufacture, low cost fabrication procedures [6-8].

DSSC was developed by Gratzel and his coworkers in the year 1991 at Swiss federal institute of technology, Lausanne, Switzerland [9]. It is a photo electrochemical device that directly converts visible light into electric current based on the photosensitization of a wide band gap semiconducting material [10].It lies between second and third generation solar cells [11].This novel technology lies between solid state photo voltaics and a regenerative photo electrochemical cell [12]. It is an upcoming research area in the area of nonconventional energy technologies with a lot of potential applications. This review mainly focuses on the role of photosensitizer's in the DSSC technology with much importance to naturally obtained dyes.

Basic Principle of a DSSC and Its Current Research Focus

DSSC is basically a photovoltaic device that converts the abundantly available sun's radiation into electrical energy. The components considered as essential for the operation of a DSSC are as follows. Transparent conductive oxide (TCO) layer used as a substrate, nano crystalline titanium dioxide layer (TiO_2) coated on to the transparent glass slide for electronic conduction, a monolayer of the photosensitizer or the charge transfer dye for the purpose of light absorption, an electrolyte for dye regeneration, gasket for sealing, platinum catalyst layer, and a TCO acting as a counter electrode [12, 13].

The absorption of sunlight by the dye molecule which acts a photosensitizer initiates the process of generating electric power. The photosensitizer adsorbed on to the nanocrystalline semiconducting layer absorbs the incident radiation and in turn the photosensitizer is excited from the ground state to the excited state .The electrons that are excited are injected into the conduction band of the electrode and hence the photosensitizer is said to be oxidized. The injected electrons in the TiO_2 conduction band travel through the TiO_2 nanoparticle to reach the counter electrode through the external load. The photosensitizer that is in oxidized state accepts the electrons from the redox electrolyte to return back to the ground state .Overall, the electric power is said to be produced without any permanent chemical transformation [14-16].

To increase the phenomenon of electrical conductivity and light transmittance, either indium doped tin oxide (ITO) or fluorine doped tin oxide (FTO) coated glass is used as a substrate [6]. Titanium dioxide (TiO_2) semiconductor is widely preferred owing to its electrical properties. It generally occurs in three crystalline forms such as rutile, anatase and brookite [17].Titanium dioxide (TiO_2) is a an inexpensive, readily available, and a non toxic chemical commonly preferred owing to its good chemical stability under visible irradiation in solution and it is considered to be much stable in photo electrochemical systems even under extreme operating conditions. The exclusive properties of TiO_2 such as high dielectric constant and high refractive index makes it much suitable to be used as a semiconductor film electrode in dye sensitized solar cell technology. The porous structure and morphology of TiO_2 plays a crucial role in the operation of a DSSC.A thin film of the nanocrystalline titanium dioxide layer deposited onto the conducting glass substrate serves as the semiconductor electrode. The morphology of the TiO_2 film formed is of immense importance in DSSC performance since the electron recombination rate is influenced by it [12].Compared to TiO_2, ZnO semiconductor is reported for its high electronic mobility and similar energy level of the conduction band and serves as an alternate to the commonly used TiO_2 semiconductor [18].

The Electrolyte is an essential component in a DSSC which mediates the electrons between the photo electrode and the counter electrode. The electrolyte used influences the essential parameters such as short circuit current density (J_{SC}) and the open circuit voltage (V_{OC}). The commonly preferred electrolyte is iodide/ tri iodide (I^- /I^{3-}) redox couple dissolved in an organic solvent. A novel Disulfide/ thiolate redox couple was reported as the first alternate to rival the performance of iodide/ tri iodide (I^- /I^{3-}) redox couple. As an alternate to the iodide/ tri iodide (I^- /I^{3-}) redox couple, molecularly engineered cobalt complex was also reported as a redox mediator .A cobalt complex with tridendate ligands combined with cyclopenta-dithiophene bridged donor acceptor dye (Y123) was reported with a high open circuit voltage and a conversion efficiency exceeding 10%. Significant research is being conducted on the electrolytes used. Small addition of electric additives have also reported to enhance the performance of DSSC's. Solvent free Ionic liquids have been reported as electrolytes in DSSC's. Room temperature ionic liquids (RTIL's) possessing good chemical stability are incorporated into DSSC's for their long time operation. In order to overcome the sealing problems associated with using liquid electrolytes, solid state electrolytes and quasi solid state electrolytes have received considerable attention in DSSC research [19-21].

The Counter electrode plays an essential role in achieving a high photoconversion efficiency and hence it should possess high electro catalytic activity and it serves the purpose of transferring the electrons from the external circuit to the redox electrolyte. Platinum (Pt) has been the widely prefferred material for counter electrodes due to its excellent catalytic activity to reduce the tri iodide ions and various research groups have fabricated the cells with platinum counter electrodes to achieve the best conversion efficiencies. Carbon(C) has been reported as the material for the preparation of counter electrode. Carbon nano tubes(CNT's) have gained considerable importance due to its attractive features such as high conductivity, corrosion resistance, electro catalytic activity and its is reported to be suitable to replace platinum coated counter electrode . Single walled carbon nano tubes, double walled carbon nano tubes and multi walled carbon nano tubes have been investigated. CNT's with various diameters are reported as alternatives for counter electrodes in order to enhance the efficiency of the fabricated dye sensitized solar cell. Multi walled carbon nano tubes (MWCNT's) with larger diameter is reported to be used as a counter electrode. Recently, Tungsten carbide/Carbon(WC/C) composite nano fibers were prepared through electrospinning followed by a one step heat treatment and applied as low cost counter electrode for DSSC applications and compared to platinum ,the WC/C- nano fiber exhibited a consistent catalytic activity irrespective of the kind of electrolyte used. Graphene and their derivatives have gained huge attention in DSSC's due to their unique properties such as high electrical conduction, high optical transparency, mechanical flexibility etc. It is reported to perform various functions such as transparent anodes, non transparent anodes, transparent cathodes, catalytic counter electrodes, light harvesting material, electron transport layer etc [22-30].

Role of a Photosensitizer

The photosensitizer plays an essential role in determining the overall conversion efficiency of a DSSC. Some of the requirements of the dye molecule to serve as a photosensitizer are as follows. Strong absorption in the visible region and near infrared region, it must carry carboxylate or phosphonate attachment groups to bind strongly with the semiconductor surface, capable of injecting the electrons upon excitation , it should be more stable in order to withstand many oxidation and reduction cycles without undergoing any degradation and it should be cost effective in nature [12,15,31].

Synthetic Photosensitizers

Since last two decades, Constant focus is being done on developing new sensitizers suitable for this purpose by studying more on their electrical and optical properties. Ruthenium complex dyes are well known for their suitability as sensitizers for DSSC Applications. The widely investigated charge transfer sensitizers in DSSC are bis(tetrabutylammonium)cis-di(thiocyanato)-bis(4,4'–dicarboxy-2,2'–bipyridine)ruthenium (II)- N719 dye and trithiocyanato–(4,4',4''- tricarboxy-2,2':6',2'' – terpyridine)ruthenium(II)-black dye exhibiting a overall conversion efficiency greater than 11% under AM 1.5 irradiation. Various complexes of ruthenium have been synthesized and reported with considerable conversion efficiencies by various researchers [32].

Two Hydrophobic Ruthenium (II) sensitizers SY-04 and SY-05 with molar extinction coefficient were synthesized through highly efficient synthetic routes and the SY-04 based DSSC exhibited a conversion efficiency of 7.70% and was reported to be 27% higher than the N3 based DSSC under the same cell fabrication conditions [33].The dyes SY-04 and SY-05 synthesized through highly efficient synthetic routes were compared with Z907 dye. The dyes exhibited better molar extinction coefficients and displayed better metal ligand charge transfer (MLCT) absorption bands. The SY-04 sensitizer is reported with an overall conversion efficiency of 8% in quasi solid state dye sensitized solar cells using a supramolecular oligomer based electrolyte [34].Although ruthenium (II) polypyridyl complexes are reported with high efficiencies, there are various drawbacks associated on practical application of these dyes such as the rare availability of the metal, its expensive nature, skilled synthesis and purification procedures [32].

Other than the ruthenium based dyes, porphyrin based dyes also find application in DSSC.A solar cell sensitized with the porphyrin compound, using cobalt(II / III) based redox electrolyte exceeded 12% efficiency under simulated 1.5 AM sunlight [35].

The metal free organic dyes have gained considerable focus recently due to the low cost of production. Metal free organic dyes can be synthesized in a cost effective manner by the well established design protocols and still remains a challenge to be explored. Through various molecular design strategies the absorption, fluorescence, emission and the electrochemical properties could be fine tuned. Due to their high molar (II) extinction coefficient values, they increase the conversion efficiency of the fabricated DSC. The efficiencies of the metal free organic sensitizers are said to be on par with the Ruthenium based dyes [32,36]. Organic dyes have attracted research focus due to the advantages such as high molar absorption coeffecients than Ruthenium complexes, involves low cost preparation and purification procedures, possess different structures with the variety of substituents added onto the chromophores and metal free in nature [37]

In this discussion, squaraine dyes are highly stable organic compounds and well suitable for a variety of applications due to their high extinction coefficient, photoconductive nature and intense fluorescence. Squaric acid based dyes exhibit sharp absorption band in the near infrared region and hence it has gained attraction as a sensitizer in Photovoltaic applications [38,39].A novel direct aromatic ring carboxy functionalized based on pyrroloquinoline unsymmetrical squaraine dye which is far red sensitive is reported with a power conversion efficiency of 3.33% under simulated solar conditions of 100Mw/cm^2 at AM 1.5 condition [40].A far red sensitive unsymmetrical squaraine dye containing a direct cyanoacrylate functionalized indole ring has been synthesized and used for photosensitization in DSSC and reported with a photoconversion efficiency of 5.03% under the simulated solar irradiation at AM 1.5 conditions [41].

Natural photosensitizers

Natural dyes are considered as a viable alternative to the synthetic ones owing their advantages such as easy preparation, inexpensive nature, ecofriendly nature, biodegradable nature and wide availability. Different parts of a plant have been used as photosensitizers over last two decades. Some of the pigments responsible for producing colour in plants are classified as chlorophylls, carotenoids, flavonoids, and betalains .Table 1 represents some of the major pigments present in plants, their common type, occurrence and colour produced in their presence [12, 42]. Some of the conversion efficiencies reported by researchers on natural dyes as photosensitizers are given in Table 2

Table 1: Major pigments found in plants [12, 42]

Pigment	Type	Localization	Colour produced
Chlorophyll	Chlorophyll a, b	All photosynthetic plants	Green
Carotenoids	Carotenes Xanthophylls	Photosynthetic plants, bacteria, and some crustaceans	Yellow, orange, red
Flavonoids	Anthocyanins Chalcones Flavonols Aurones proanthocyanidins	Gymnosperms, angiosperms, ferns and bryophytes	Cream, pale yellow, pink, red, blue, black
Betalains	Betacyanins Betaxanthins	Caryophyllales, cactus and some fungi	Yellow, red

Table 2: Performance of DSSCs based on naturally extracted dyes [43-48]

Natural Dye	J_{sc}(mA/cm^2)	V_{oc} (V)	FF	η (%)	Ref
Wormwood	1.96	0.585	0.47	0.538	43
Purple cabbage	2.08	0.66	0.53	0.75	43
Cocktail dye (Wormwood+Purplecabbage,1:1)	3.16	0.66	0.62	1.29	43
Rosella	1.63	0.404	0.57	0.37	44
Blue Pea	0.37	0.372	0.33	0.05	44
Mixed dye (Rosella+Blue Pea)	0.82	0.382	0.47	0.15	44
Ivy gourd fruits	0.24	0.644	0.49	0.076	45
Red frangipani flowers	0.94	0.495	0.65	0.301	45
Begonia	0.63	0.537	0.722	0.24	46
Mangosteen pericarp	2.69	0.686	0.633	1.17	46
Perilla	1.36	0.522	0.696	0.50	46
Rhododendron	1.61	0.585	0.609	0.57	46
Pomegranate leaves	2.05	0.560	0.52	0.597	47
Mulberry fruit	1.89	0.555	0.49	0.548	47
Cocktail dye (Pomegranate leaves + Mulberry fruit)	2.80	0.53	0.49	0.722	47
Fruit of Calafate	6.20	0.47	0.36	-	48
Skin of Jaboticaba	7.20	0.59	0.54	-	48

Chlorophyll

Chlorophyll is a widespread plant pigment found in leaves and other parts of the plant. Chlorophyll pigments play a crucial role in the process of photosynthesis. The common types of chlorophyll are chlorophyll a present in all photosynthetic plants and chlorophyll b found widely in higher plants and algae. It possess a common basic structure, a porphyrin structure consisting of four pyrrole rings. Presence of magnesium ion in the center is the unique feature of the chlorophyll structure and it plays an important role in the absorption of light energy [42]. Chlorophylls in their raw form are not efficient sensitizers for DSSC applications. Hence different approaches have been adopted to improve the performance of the cells [49].

One of the stratergy adopted to enhance the efficiency of the cell is by mixing the chlorophyll dye with other pigment containing dyes. Chlorophyll dye from pomegranate leaves and anthocyanin dye from mulberry fruit were extracted and reported that the chlorophyll – anthocyanin dye mixture yielded a higher conversion efficiency of 0.722% [47]. Chlorophyll dye was extracted from wormwood and anthocyanin dye was extracted from purple cabbage and both were mixed in 5 different ratios to form a cocktail dye and a 1:1 combination of the dyes exhibited a photoelectric conversion efficiency of 1.29% [43].

Carotenoids

Carotenids are generally considered as terpenes or derivatives of terpenes widely found in photosynthetic bacteria, algae, fungi and higher plants. These pigments provide red, orange and yellow colors to the naturally available flowers and fruits. They are categorized into orange red carotenes and yellow orange oxycarotenoids or xanthophylls which is an oxygenated derivative of carotene. β carotene and lycopene are the common carotenoids offering colour to carrots and tomatoes. Carotenoids absorb light of 400-500nm wavelength [42]. Recently natural dyes were extracted from the fruits of ivygourd which are identified to be rich in β carotene and red frangipani flowers that are rich in anthocyanins with a reported effeciencies of 0.076% and 0.301% [45].

Anthocyanins

Anthocyanins are the largest group of pigments belonging to the flavonid group which absorb light at the longest wavelength and offers red, blue or violet colour to the various parts of the plants. The variety of colours offered by anthocyanins is due to the oxidation of the central chromophore,anthocyanidin and other modifications to the main structure. In acidic medium anthocyanins appear red and in basic medium they appear blue. Few anthocyanidins and their respective colours identified are pelargonidin – orange red, cyanidin – purplish red, delphinidin - blue, malvidin – purple violet, peonidin – rose and petunidin – purple violet. Many types of anthocyanins have been observed in plants and all possess 2-phenylbenzopyrylium(flavylium) ion basic core structure [12,42,49]. Anthocyanin dyes were extracted from Rosella and blue pea flowers and repoted with an efficiency of 0.37% and 0.05 %, additionally these extracts were mixed together to observe the effect on the conversion efficiency of the cell and gave an efficiency of 0.15% [44].In another study, anthocyanin pigments were extracted from rhododendron arboretum zeylanicum, sesbania grandiflora scarlet, hibiscus rosasinensis, hibiscus surattensis, nerium oleander, and ixora macrothyrsa and the pigment obtained from hibiscus surattensis exhibited the best photovoltaic performance of 1.14% [50]. Anthocyanins contain (-OH) functional group to attach itself firmly to the titanium dioxide nanoparticles [45].

Future Direction

Although numerous natural dyes have been extracted, purified and tested in the modern DSSC research, the conversion efficiencies reported are considerably less and cannot compete with the performance of the synthetic photosensitizers such as ruthenium and other synthetic based dyes. As far as our knowledge, the overall performance of the cell may be improved by further purification using advanced instrumentation and sophisticated techniques, so as to remove other plant material and obtain a dye that is enriched with only the desired pigments for photosensitization effect. A large number of raw materials rich in pigments are yet to be explored and to be tested as photosensitizers in this novel field of research.

CONCLUSION

This review clearly discussed on the novel dye sensitized solar cell technology and the recent progress in this field of research. In addition, different photosensitizers used for photosensitization were discussed briefly. Special emphasis was made on the natural dyes and their potential as a photosensitizer was understood. However, the performances of the naturally extracted dyes were reported to be low and hence cannot match with the traditionally used silicon based photovoltaic devices. Hence it requires further purification and additional studies. Naturally extracted plant material contains oils, xanthophylls, steroids, fatty material, saponins, alkaloids and other constituents of plant origin. Qualitative and quantitative studies has to be carried out on the crude extracts, which may pave a way for the better photovoltaic performances. To make the natural based dyes more effective as a photosensitizer, it is pertinent to carry out the purification of the crude extracts. Additionally, quantification of the pigments can also be done. Development of renewable energy technologies is of prime importance in the present scenario and especially focusing on solar based technologies receives more of government support and guidance especially in India. These efforts taken may pave a way in the near future to meet the energy demands of the growing Indian population and also to march towards a greener,sustainable and a eco-friendly environment.

REFERENCES

[1] Sambandam Anandan, Solar Energy Materials & Solar Cells, 2007, 91, 843-846.
[2] Rajan Jose,Velmurugan Thavasi, Seeram Ramakrishna, J.Am .Ceram.Soc, 2009,92(2),289-301.
[3] Jude O.Ozuomba,Laeticia U.Okoli, Azubuike J.Ekpunobi, Advances in applied science research, 2013,4(2), 60-69.
[4] Renewables 2014, global status report.
[5] Luis Moreira Goncalves, Veronics de Zea Bermudez, Helena Aguilar Ribeiro, Adelio Magalhaes Mendes, Energy and environmental science, 2008,1,655-667.
[6] Jiawei Gong, Jing Liang, K. Sumathy, Renewable and sustainable energy reviews, 2012, 16, 5848-5860.
[7] Aduloju K.A, Fatigun A.T, Ewumi T.O, European journal of applied engineering and scientific research,2013, 2, 44-47.
[8] Brian E.Hardin, Henry J Snaith, Michael D.Mcgehee, Nature photonics, 2012, 6, 162- 169.
[9] Brian O Regan and Michael Gratzel, Letters to nature, 1991, 737-739.
[10] Michael Gratzel,Journal of photochemistry and photobiology C: photochemistry reviews, 2003,4,145-153.
[11] Anders Hagfeldt, Gerrit Boschloo, Licheng sun, Lars Kloo, Henrik pettersson, Chem rev, 2010, 110,

6595-6663.
[12] Monishka Rita Narayan, Renewable and sustainable energy reviews, 2012, 16,208-215.
[13] Kuppuswamy Kalyanasundaram, Michael Gratzel, Material Matters, 2009.
[14] Kohjoro Hara and Hironori Arakawa,Dye sensitized solar cells, Handbook of photovoltaic science and engineering, 2003, 663- 696.
[15] Michael Gratzel, Journal of photochemistry and photobiology A:Chemistry, 2004,164,3-14.
[16] Fan-Tai Kong, Song- Yuan Dai, Kong-Jia Wang, Advances in Optoelectronics, 2007, 1-13.
[17] Robert G.Breckenridge,William R.Hosler, Physical Review, 1953,91, 793-802.
[18] Masaru Saito, Shinobu Fujihara, Energy & Environmental science, 2008,1, 280-283.
[19] Jun Ho Yum,Etienne Baranoff, Florian Kessler, Thomas Moehl, Shahzada Ahmad, Takeru Bessho, Arianna Marchioro, Elham Ghadiri, Jacques-E Moser, Chenyi Yi, Md.K.Nazerruddin, Michael Gratzel, Nature communications, 2012,1-8.
[20] Shaik M. Zakeeruddin, Michael Gratzel, Advanced functional materials, 2009, 19, 2187-2202.
[21] Jihuai Wu, Zhang Lan, Sanchun Hao, Pingjiang Li, Jianming Lin, Miaoliang Huang, Leqing Fang, Yunfang Huang, Pure appl. Chem,2008,80, 2241-2258.
[22] Jung Gyu Nam, Young Jun Park, Bum Sung Kim, Jai Sung Lee, Scripta Materialia, 2010, 62, 148-150.
[23] S.Hwang, J.Moon, S.Lee, D.H.Kim, D.Lee, W.Choi, M.Jeon, Electronics Letters, 2007, 43.
[24] Dingwen Zhang, Xiadong Li,Si Chen, Zhuo Sen, Xi Jiang Yin, Sumei Huang, Microchim Acta, 2011, 174, 73-79.
[25] Jing – Zhi Chen, Yin- Cheng Yan, Kuan –Jiuh Lin, Journal of the Chinese chemical society, 2010,57, 1180-1184.
[26] Chandra Sekharan Nair Omana Amma Sreekala, Jinchu Indiramma, Kandala Bala Subramanya Pavan Kumar, Karyaveettil Savithriamma Sreelatha, Mahesh Saran Roy, Journal of nanostructure in chemistry, 2013,3:19.
[27] Inyoung Jeong, Jaehyuk Lee, K.L.Vincent Joseph, Hyung lk Lee, Jin Kon Kim, Jinwoo Lee, Nano Energy, 2014, 9, 392-400.
[28] Zongyou Yin, Jixin Zhu, Qiyuan He, Xiehong cao, Chaoliang Tan, Hongyu Chen, Qingyu Yan, Hua Zhang, Adv.Energy.Mater, 2014, 4, 1-19.
[29] Joseph D.Roy – Mayhew, Ilhan A.Aksay, Chemical Reviews, 2014,114, 6323-6348.
[30] Chih- Hung Hsu, Jia-Ren Wu, Lung-Chien Chen, Po-Shun Chan, Cheng-Chiang Chen, Advances in material science and engineering,2014, 1-4.
[31] Michal Skolsky, Julius Cirak, Acta Electrotechnica et informatica,2010,10,78-81.
[32] Ravi Kumar Kanaparthi, Jaipal Kandhadi, Lingamallu Giribabu, Tetrahedron, 2012, 68,8383-8393.
[33] A.Anthonysamy, Y.Lee, B.Karunagaran, V.Ganapathy, S.W.Rhee, S.Karthikeyan, K.S.Kim, M.J.Ko, N.G.Park, M.J.Ju, J.K.Kim, Journal of material chemistry, 2011, 21, 12389-12397.
[34] K.L.Vincent Joseph, Anthonysamy.A, P.Sudhagar, Woohyung cho, Young soo kwon, Taiho Park, Jin Kon Kim, Journal of material chemistry A, 2014, 2, 13338- 13344.
[35] Aswani Yella, Hsuan-Wei Lee, Hoi Nok Tsao, Chenyi Yi, Aravind Kumar Chandiran, Md.Khaja Nazeeruddin, Eric Wei –Guang Diau, Chen-Yu Yeh, Shaik M Zakeeruddin, Michael Gratzel,Science,2011,334, 629-633.
[36] Amaresh Mishra, Markus K.R.Fischer, Peter Bauerle, Angewandte Chemie, 2009, 48, 2472-2499.
[37] Yousuke Ooyama, Yutaka Harima, Chemphyschem, 2012, 13, 4032-4080.
[38] Patrick Marks, Mindy Levine, Journal of Chemical Education, 2012, 89, 1186-1189.
[39] Zhengquan Yan, Shanyi Guang, Xinyan Su, Hongyao Xu, Journal of Physical Chemistry, 2012,116, 8894-8900.
[40] Shyam S.Pandey, Naotaka Fujikawa, Rie Watanabe, Yuhei Ogomi, Yoshihiro Yamaguchi, Shuzi Hayase, Japanese journal of applied physics, 2012,51.
[41] Gururaj M.Shivashimpi, Shyam S.Pandey, Rie Watanabe, Naotaka Fujikawa, Yuhei Ogomi, Yoshihiro Yamaguchi, Shuzi Hayase, Tetrahedron Letters, 2012,53, 5437-5440.
[42] Ewa Mlodzinska, Acta Biologica Cracoviensia, 2009, 51, 7-16.
[43] Ho Chang, Mu Jung Kao, Tien-Li Chen, Chih- Hao Chen, Kun-Ching Cho, Xuan Rong Lai, International journal of Photoenergy, 2013,1-8.
[44] Khwanchit Wongcharee, Vissanu Meeyoo, Sumaeth Chavadej, Solar energy materials & Solar cells,2007,91, 566-571.
[45] Vinoth Shanmugam, Subbaiah Manoharan, Sambandam Anandan, Ramaswamy Murugan, Spectrochimica Acta part A : Molecular and Biomolecular Spectroscopy, 2013,104, 35-40.
[46] Huizhi Zhou, Liqiong Wu, Yurong Gao, Tingli Ma, Journal of photochemistry and photobiology

A:Chemistry, 2011,219, 188-194.
[47] Ho Chang, Yu Jen Lo, Solar Energy, 2010, 84, 1833-1837.
[48] Andre Sarto Polo, Neyde Yukie Murakami Iha, Solar energy materials & Solar cells, 2006, 90, 1936.
[49] Giuseppe Calogero, Jun-Ho Yum, Alessandro Sinopoli, Gaetano Di Marco, Michael Gratzel, Mohammad Khaja Nazerruddin, Solar energy, 2012, 86,1563- 1575.
[50] J.M.R.C.Fernando, G.K.R.Senadeera, Current science, 2008, 95, 663-666.