

Natural Pigments as Photosensitizers for Dye-sensitized Solar Cells with TiO₂ Thin Films

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Abstract - Dye-sensitized solar cells (DSSCs) were fabricated using four natural dyes extracted from the leaves of lemon (*Citrus limon*) and morula (*Sclerocarya birrea*) and flowers of bougainvillea (*Bougainvillea glabra*). Optical characteristics of the dye extract solutions and photoelectrochemical performance of the cells were studied. DSSC from lemon showed the highest current density of 1.08 mA/cm² and highest solar energy conversion efficiency of 0.036 %. Natural pigments offer advantages of natural abundance, simplicity of preparation, low cost and environmental friendliness.

Keywords - Dye-sensitized solar cell; natural dye; conversion efficiency.

1. Introduction

The technology of converting solar energy to electrical energy for the future energy resources is an intensive research area worldwide. Unfortunately, there remain some challenges regarding the efficient harnessing and cost effectiveness of this abundant energy. The main concern has always been that the efficiency of conventional solid state-based solar cells, usually made of silicon is limited by recombination of charge carriers in the heterojunction of the semiconductor. Recombination of carriers decreases the quantum efficiency of the cells [1]. Considerable research has gone into finding alternative material with both good charge transportation and good light absorbing properties [1]. The second generation, thin film solar cells were conceptualized to lower the cost per unit watt to affordable levels. But the cost of the first and second generation solar cells still remains high. However, new materials and technologies are slowly emerging in this field and great promise is seen for the future.

Dye-sensitized solar cell (DSSC) has recently penetrated research and development lines of renewable energy, exploited as a promising concept and simple alternative power source. DSSC offers advantages of low fabrication cost, easy preparation methods, and minimal recombination losses as the role of the semiconductor in the DSSC device is merely to conduct the injected majority charge carriers [2] while the minority carriers are carried by the electrolyte [3,4]. Furthermore, the generation of electric power from sunlight is achieved without any permanent chemical transformation [5]. A DSSC is composed of a transparent conductive oxide substrate, a wide band gap semiconductor, photosensitizer (dye), a redox electrolyte (usually comprised of iodine/triiodine) or p-type semiconductor [6] and a counter electrode. Due to its attractive properties, titanium dioxide (TiO₂) is the most used semiconductor in the DSSC technology, although other materials such as zinc oxide (ZnO) [7-9], niobium pentoxide (Nb₂O₅) [10] have been investigated. The sensitizer plays an important role of capturing the photons and transforming solar energy to electric energy [11-12]. It has been the subject of more

recent studies as the efficiency of DSSC depends, mainly on its properties such as the absorption spectrum, lifetime, dye-to-TiO₂ charge transfer and the anchorage of the dye to the surface of TiO₂ [13-14].

1.2 Operating mechanism of the DSSC

DSSCs are normally based on the photo-excitation of sensitizer molecules, chemically adsorbed to the TiO₂ nanoparticles. Under illumination, an n-type semiconductor material is hit by visible light and photons of energy $h\nu$ excites the electrons in the dye (D) molecules (Eq.1), which are then injected into the conduction band of the semiconductor [1,2,5], oxidizing the dye to D⁺,



Where D* is the excited state of the dye.

The injected electron then flows through the semiconductor network to the back contact (anode) and finally through the load to the counter electrode (cathode). The oxidized mediator forms iodine or triiodide, which in turn obtains an injected electron at the counter electrode;



The electrons lost during the oxidation of the dye are quickly replaced by the iodine anion, regenerating the dye [1],



One process that limits the efficiency of the DSSC is the recapture of the injected electron by the oxidized mediator before the electron has been collected and passed through the load and the cathode electrode [15],



Another limiting reaction is the recombination of the injected electron with the oxidized sensitizer [1],



Currently, commercially available photosensitizers are polypyridyl complexes of ruthenium such as N719 and Ru535 (N3), which are preferred due to their intense charge-transfer absorption in the whole visible range [13-14]. However, the cost of fabrication, toxicity and scarcity of the metals associated with ruthenium complexes limit their application as alternative photosensitizers in DSSCs [13-14]. Recently, natural dyes have been receiving a considerable attention as alternative sensitizers to ruthenium complexes. Several natural dyes from leaves, flowers and fruits such as *Jathropa curcas* and *Citrus aurantium* leaves [13], *Petrocarpus erinaceus* (African rosewood) [16], pawpaw leaves [17], grapes [6] and many more natural pigments [14,18,19] have been synthesized and tested. The advantages of natural dyes include their availability, easy to prepare, environmental friendliness and low cost. However, the photoenergy conversion efficiencies of natural dye based

DSSCs (generally <1%) [11] remains the main challenge. Poor absorption in the visible region of the solar spectrum and instability of the dyes lead to their low efficiencies in DSSC technology [4]. This work is aimed at investigating the possibility of generating high quality but cheap dye sensitized solar cells by utilizing a cost effective preparative technique and photosensitizer extracted from leaves and flowers of natural plants, namely morula (*Sclerocarya birrea*), lemon (*Citrus limon*) and bougainvillea (*Bougainvillea glabra*). Optical characteristics of the dyes and photoelectrochemical performance of the solar cells were studied.

2. Materials and Methods

TiO₂ thin films were deposited on cleaned fluorine doped tin oxide (FTO) transparent conducting glass substrates (2 x 2 cm). A nanocrystalline suspension was prepared from 6 g of colloidal Degussa P25 TiO₂ powder, 0.2 ml of acetyl acetone and 1ml of deionized water. Additional 8 ml of deionized water was added in drops of 1ml to prevent re-aggregation of the particles while grinding until a porous, sponge-like mixture was formed. Adhesive tape was applied on the conductive side of the FTO substrates to mask a strip of about 5mm on each side, leaving an active area of 2.25 cm² (1.5 x 1.5 cm). The suspension was applied and spread uniformly onto the substrates using a glass rod and allowed to dry in room temperature. The deposited suspension was annealed at 400 °C for 10-15 minutes using a hotplate in a hood. The dye solutions for chlorophyll containing samples (lemon and morula leaves) and non-chlorophyll containing samples (red and orange bougainvillea flowers) were prepared by adding 10 g of chopped leaves and flowers, respectively to 100 ml of acetone and left over night in dark place. The coated substrates were soaked in different dye solutions for 24 hours to allow dye molecules to adsorb to the TiO₂ particles. The cathode electrode used is FTO coated with carbon. Carbon acted as the catalyst for the triiodide-to-iodide regeneration reaction [20]. The stained TiO₂ electrodes and the graphite coated counter electrode were assembled by placing the electrodes a little offset opposite to each other to expose the contact areas. Binder clips were used to press the electrodes together. To complete the cell a few drops of KI/iodine electrolyte were added to the edge of the plate and by capillary action it travelled between the two plates. The pictures of assembled DSSCs are shown in Fig.1.

A 500-ohm variable resistor was used to collect the open circuit photovoltage and short circuit photocurrent characteristics. To investigate the optical properties of the dye extracts, dye samples were prepared on glass substrates by soaking the glass slides in acetone and placing them in the sonicator for 10 minutes to clean them. The glass slides were then stained with the extracted dye solutions using a pipette and left to dry. The normal transmission and reflectance spectra of the four kinds of sensitizers were measured using a Cary 500 UV-VIS-NIR spectrophotometer in the spectral range of 200-1200 nm.



Fig. 1. Pictures of the prepared assembled solar cells of different dye extracts

3. Results and Discussions

3.1 Optical characteristics of the photosensitizers

Figure 2 and Figure 3 show the plots of optical spectra; transmittance and absorbance of different sensitizers extracted from natural plants prepared on glass substrates. A major observation from Fig.2 is that the orange bougainvillea sensitizer shows higher average transparency in the visible range (400-750 nm) of the optical spectrum, than red bougainvillea, morula and lemon. The average transmittance value of orange bougainvillea sensitizer in this range was 85% while that of lemon was 75%. Morula shows the lowest transparency throughout the spectrum.

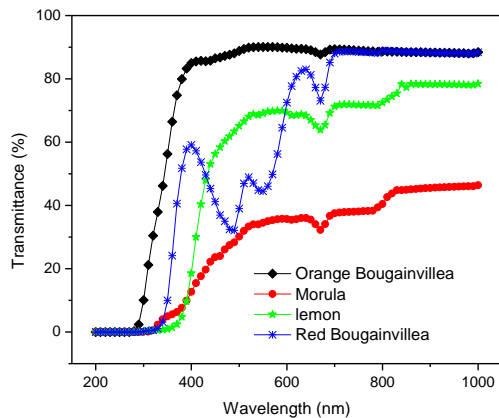


Fig. 2. Transmittance spectra of four natural dyes prepared on glass substrates

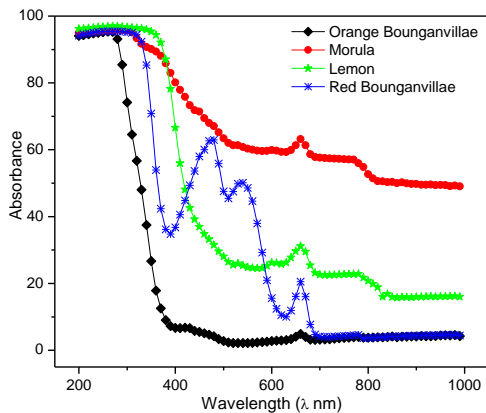
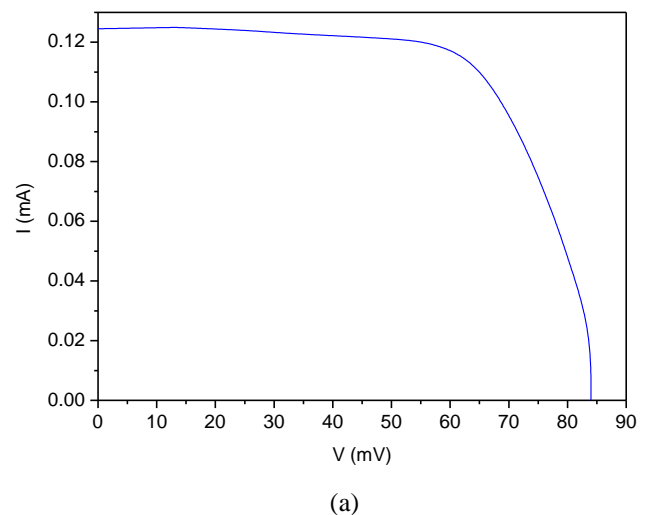


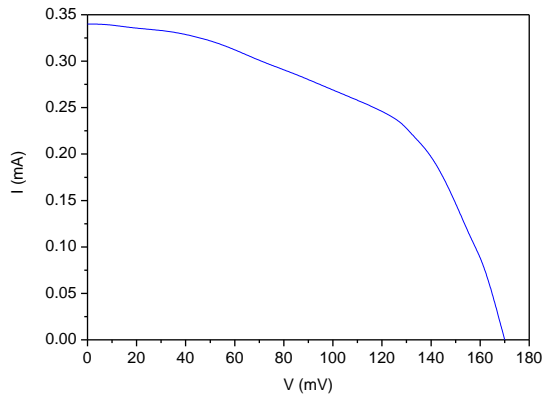
Fig. 3. Absorbance spectra of four natural dyes prepared on glass substrates

The absorption characteristic is a very important property in DSSC as it directly reflects the optical transition probability [11]. Absorption spectral characteristics of all dyes are shown in Fig.3. It can be seen that all dyes show absorption in the visible region, 400-750 nm. Chlorophyll absorbs light and transfer that light energy by resonance energy transfer to a specific chlorophyll pair in the reaction center of the photosystems. Chlorophyll absorbs strongly in the blue and red regions of the absorption spectrum while reflecting green [14]. From Fig.3, it can be seen that both morula and lemon leaves have only one and same absorbent peak in the red region at the wavelengths of about 675nm. No blue peaks were observed in this study. Comparatively, Moustafa *et al.* [14] reported both blue and absorption peaks, at 475 and 675 nm, respectively for lemon leaves, wherein blue shift (from 475 nm to 390 nm) was attributed to the linkage between the hydrocarbon ester groups in chlorophyll and TiO₂ surface [21].The absorption peaks for lemon and morula corresponds to absorption values of around 30 and 70 respectively. Orange bougainvillea shows little absorbance variation, similar to the absorption spectrum reported by Lai *et al* [11] for *Bougainvillea brasiliensis* Rausch. Red bougainvillea dye shows absorption peaks at 475, 550 and 675 nm. The difference in absorption spectra of both chlorophyll and non-chlorophyll is already explained by other researchers [11,14,21]. Different chlorophyll and non-chlorophyll pigments associated with the photosystems have different spectra properties because of the modified pigments by protein structures surrounding them [11].

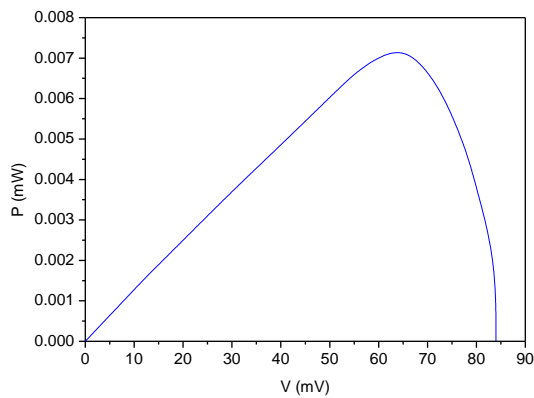
3.2 Photoelectrochemical performance of the DSSCs

The assembled DSSCs were tested and analyzed for photoelectrochemical performance. Measurements were done under standard AM 1.5 sunlight with intensity of 80 mW/cm². A polycarbonate cover was used to minimize over-exposure to UV light. Fig.4 shows sampled photocurrent-voltage (I-V) and P-V characteristics of the DSSCs.

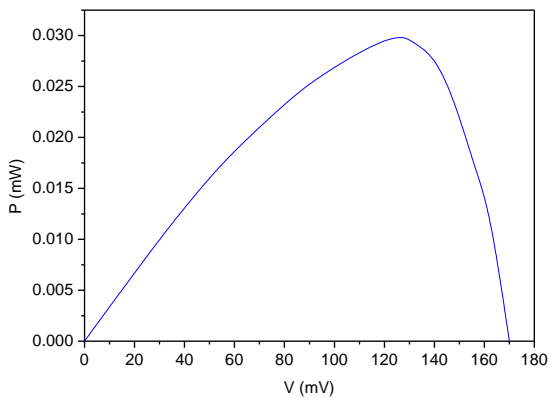




(b)



(c)



(d)

Fig. 4(a-b): I-V curves of the solar cells sensitized with (a) orange bougainvillea, (b) red bougainvillea, 4(c-d): P-V curves of cells sensitized with (c) orange bougainvillea, (d) red bougainvillea

The I-V curve of a solar cell yields important photovoltaic properties [11], these include the short-circuit photocurrent density J_{sc} , the open-circuit potential V_{oc} , and the maximum power point, P_{max} . The fill factor, FF and conversion efficiency, η are the other factors used to characterize a solar cell. The short-circuit current, I_{sc} is the current due to generation

and collection of light generated carriers. The open-circuit voltage of a solar cell corresponds to amount of forward bias of the solar cell junction due to the light generated current. FF , the ratio of the maximum output power from the solar cell to the theoretical maximum power is calculated as [11];

$$FF = I_m V_m / (V_{oc} I_{sc}) \quad (7)$$

where I_m and V_m are solar cell photocurrent and voltage at maximum power point, respectively. The fill factor reflects the electrical and electrochemical losses occurring during the operation of the DSSC [1]. The conversion efficiency of the solar cell reflects the performance of the solar cell itself. It is defined as the ratio of energy output from the solar cell to input energy from the sun. The efficiency depends on the spectrum and intensity of the incident sunlight and can be calculated as [16],

$$\eta = FF \cdot V_{oc} \cdot I_{sc} / I \quad (8)$$

where I is the solar radiation intensity, W/m^2 .

From Table 1, it can be seen that DSSC sensitized with lemon exhibit the highest measured open-circuit photovoltage of 0.592 V. The V_{oc} value is quite close to the one reported by Moustafa *et al.* [14] for lemon leaves, 0.537 V. However, the I-V curves did not converge to the same value of V_{oc} when the cells were subjected to a load. The highest current density was obtained for lemon (1.08 mA/cm^2). The value is close to that reported for ruthenium complex N3 by Moustafa *et al.* [14]. The bougainvillea flowers gave close current densities, (0.335 and 0.320 mA/cm^2) while morula exhibit the lowest value. The difference in the current densities of the cells may be attributed to the difference in the structure of the dyes, and how fast the charge is injected into the conduction band of the TiO_2 film [14]. The photoenergy conversion efficiency of lemon, red bougainvillea, orange bougainvillea and morula are 0.036%, 0.023%, 0.005% and 0.008% respectively. The red bougainvillea extract proved to be a better dye than their orange counterpart. Morula extract gave the lowest efficiency, despite the highest absorbance value.

Table 1. Summary of photoelectrochemical parameters of the DSSCs sensitized with different natural dyes.

Dye	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	η (%)
Lemon	0.592	1.08	0.1	0.036
Red Bougainvillea	0.492	0.335	0.25	0.023
Orange Bougainvillea	0.465	0.32	0.06	0.005
Morula	0.472	0.059	0.05	0.0008

This may be understood by a thorough analysis of the chemical properties of the dye and electron reactions between the dye and TiO_2 which is not well understood now. The obtained efficiencies are lower than those usually reported [2,13,14,22-35] for organic dye based DSSCs using ruthenium

complexes. Low efficiencies may be attributed to poor adsorption of dye molecules onto the TiO₂ particle. Nanostructures of TiO₂ provide paths for the electrons while maintaining high surface area for dye absorption. Therefore, non-availability of bonds between the dye and TiO₂ molecules through which electrons can transport from the excited dye molecules to the TiO₂ film has been reported to result in low efficiencies [13].

Despite the low efficiencies, the DSSCs exhibit promising photoelectrochemical conversion potential. The merits of natural extracts DSSCs stem from reduced cost/Watt and environmental friendliness as compared to the ruthenium complexes based solar cells. The data recorded from parallel and series combinations of solar cells agrees with expectations derived from theory. When two lemon DSSCs were placed in parallel, the current generated from this circuit was 1.06mA, double the amount of current from one lemon DSSC alone. Similarly, the total voltage of four DSSCs placed in series was comparable to the sum of each individual cell's voltage for a total of 1.86V. A combination of four solar cells in series was able to generate enough energy to power an LED light bulb and a small alarm clock. It should be noted that the

power of a solar cell is proportional to the surface area. DSSC are quite promising for use in low power micro-mechanical systems (MMS).

4. Conclusion

Four natural dyes extracted from plant leaves and flowers, namely morula (*Sclerocarya birrea*), lemon (*Citrus limon*) and bougainvillea (*Bougainvillea glabra*) (orange and red flowers), were used to make dye-sensitized solar cells. The dyes were attached to TiO₂ thin films and they showed absorption in the visible region, 400 - 750 nm. DSSCs studied in this work exhibit promising solar energy conversion potential, with lemon being a more suitable source of natural dye for DSSC fabrications. The highest current density was obtained for lemon leaves (1.08 mA/cm²) while the lowest was for morula leaves (0.059 mA/cm²). Lemon dye cell has the highest conversion efficiency, 0.036 %, then red bougainvillea and orange bougainvillea, 0.023 and 0.005 % respectively, and the lowest value was obtained for morula as 0.0008 %. Although the efficiencies of natural dyes are relatively lower than for those of commercial photosensitizers, they provide cheap and environmental friendly alternative to commercial synthetic dyes.

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References

[1] Md. K. Nazeeruddin, E. Baranoff, and M. Grätzel, "Dye-sensitized solar cells: A brief overview", *Solar Energy*, vol. 85, pp. 1172-1178, 2011.

- [2] B. O'Regan and M. Grätzel, "A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO₂films", *Nature*, vol.353, pp. 737-740, 1991.
- [3] G.E. Tulloch, "Light and energy-dye solar cells for the 21st century", *Journal of Photochemistry and Photobiology A: Chemistry*, vol. 164, pp.209-219, 2004.
- [4] O. Shevialeevskiy, "The future of solar photovoltaics: A new challenge for chemical physics", *Pure Appl. Chem.*, vol. 80, pp. 2079-2089, 2008.
- [5] M. Grätzel, "Conversion of sunlight to electric power by nanocrystalline dye-sensitized solar cells", *Journal of Photochemistry and Photobiology A: Chemistry*, vol. 164, pp. 3-14, 2004.
- [6] G.G.G.M.N. Hemamali and G.R.A. Kumara, "Dye-sensitized solid state solar cells sensitized with natural pigment extracted from the grapes", *International Journal of Scientific and Research Publications*, vol. 3, pp. 1-3, 2013.
- [7] S. Rani, P. Suri, P.K. Shishodia, and R.M. Mehra, "Synthesis of nanocrystalline ZnO powder via sol-gel route for dye-sensitized solar cells", *Solar Energy Materials & Solar Cells*, vol. 92, pp. 1639-1645, 2008.
- [8] D.-I. Suh, S.-Y. Lee, T.-H. Kim, J.-M. Chun, E.-K. Suh, O.-B. Yang and S.-K. Lee, "The fabrication and characterization of dye-sensitized solar cells with a branched structure of ZnO nanowires", *Chemical Physics Letters*, vol. 442, pp. 348-353, 2007.
- [9] K. Keis, E. Magnusson, H. Lindström, S.-E. Lindquist, and A. Hagfeldt, "A 5% efficient photoelectrochemical solar cell based on nanostructured ZnO electrodes", *Solar Energy Materials & Solar Cells*, vol. 73, pp. 51-58, 2002.
- [10] A. Le Viet, R. Jose, M.V. Reddy, B.V.R. Chowdari, and S. Ramakrishna, "Nb₂O₅ photoelectrodes for dye-sensitized solar cells: Choice of the polymorph", *J. Phys. Chem. C*, vol.114, pp. 21795-21800, 2010.
- [11] W.H. Lai, Y.H. Sub, L.G. Teoh, and M.H. Hon, "Commercial and natural dyes as photosensitizers for a water-based dye-sensitized solar cell loaded with gold nanoparticles", *Journal of Photochemistry and Photobiology A: Chemistry*, vol. 195, pp. 307-313, 2008.
- [12] M. Grätzel, "Dye-sensitized solar cells", *Review Journal of Photochemistry and Photobiology C: Photochemistry Reviews*, vol. 4, pp. 145-153, 2003.
- [13] A.C. Nwanya, P.E. Ugwuoke, P.M. Ejikeme, O.U. Oparaku, and F.I. Ezema, "Jathropa curcas and citrus aurantium leaves dye extract for use in dye sensitized solar cell with TiO₂films", *Int. J. Electrochem. Sci.*, vol. 7, pp. 11219-11235, 2012.
- [14] K.F. Moustafa, M. Rekaby, E.T. El Shenawy, and N.M. Khattab, "Green dyes as photosensitizers for dye-sensitized solar cells", *Journal of Applied Sciences Research*, vol. 8, pp. 4393-4404, 2012.

- [15] G.P. Smestad, "Education and solar conversion: Demonstrating electron transfer", *Solar Energy Materials and Solar Cells*, vol. 55, pp. 157-178, 1998.
- [16] K.A. Aduloju and F. Ezema, "Effect of natural dye extracting temperature on the performances of dye-sensitized solar cells using *petrocarpus erinaceus*", *Archives of Physics Research*, vol. 2, pp. 191-196, 2011.
- [17] J.O. Ozuomba, A.J. Ekpunobi, and P.I. Ekwo, "The viability of a natural dye extracted from pawpaw leaves as photosensitizer for dye-sensitized solar cells", *International Science Research Journal*, vol. 3, pp. 3-5, 2011.
- [18] N. Li, N. Pan, D. Li, and S. Lin, "Natural dye-sensitized solar cells based on highly ordered TiO₂ nanotube arrays", *International Journal of Photoenergy*, vol. 2013, pp. 1-5, 2013.
- [19] L.U. Okoli, J.O. Ozuomba, and A.J. Ekpunobi, "Influence of local dye on the optical band-gap of titanium dioxide and its performance as a DSSC material", *Research Journal of Physical Sciences*, vol. 1, pp. 6-10, 2013.
- [20] G.P. Smestad and M. Grätzel, "Demonstrating electron transfer and nanotechnology: A natural dye-sensitized nanocrystalline energy converter", *Journal of Chemical Education*, vol. 75, pp. 752-756, 1998.
- [21] B.-Q. Liu, X.-P. Zhao, and W. Luo, "The synergistic effect of two photosynthetic pigments in dye-sensitized mesoporous TiO₂ solar cells", *Dyes and Pigments*, vol. 76, pp. 327-331, 2008.
- [22] M.K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Müller, P. Liska, N. Vlachopoulos, and M. Grätzel, "Conversion of light to electricity by *cis*-X₂Bis(2,2'-bipyridyl-4,4'-dicarboxylate) ruthenium (II) charge transfer sensitizers (X = Cl⁻, Br⁻, I⁻, CN⁻, SCN⁻) on nanocrystalline TiO₂ electrodes", *J. Am. Chem. Soc.*, vol. 115, pp. 6382-6390, 1993.
- [23] M.K. Nazeeruddin, P. Péchy, T. Renouard, S.M. Zakeeruddin, R. Humphry-Baker, P. Comte, P. Liska, L. Cevey, E. Costa, V. Shklover, L. Spiccia, G.B. Deacon, C.A. Bignozzi, and M. Grätzel, "Engineering of efficient panchromatic sensitizers for nanocrystalline TiO₂-based solar cells", *J. Am. Chem. Soc.*, vol. 123, pp. 1613-1624, 2001.
- [24] M.K. Nazeeruddin, R. Humphry-Baker, P. Liska, and M. Grätzel, "Investigation of sensitizer adsorption and the influence of protons on current and voltage of a dye-sensitized nanocrystalline TiO₂ solar cell", *J. Phys. Chem. B*, vol. 107, pp. 8981-8987, 2003.
- [25] P. Wang, S.M. Zakeeruddin, J.-E. Moser, M.K. Nazeeruddin, T. Sekiguchi, and M. Grätzel, "A stable quasi-solid-state dye-sensitized solar cell with an amphiphilic ruthenium sensitizer and polymer gel electrolyte", *Nature Materials*, vol. 2, pp. 402-407, 2003.
- [26] Z.-S. Wang, T. Yamaguchi, H. Sugihara, and H. Arakawa, "Significant efficiency improvement of the black dye-sensitized solar cell through protonation of TiO₂ films", *Langmuir*, vol. 21, pp. 4272-4276, 2005.
- [27] M.K. Nazeeruddin, F. De Angelis, S. Fantacci, A. Selloni, G. Viscardi, P. Liska, S. Ito, B. Takeru, and M. Grätzel, "Combined experimental and DFT-TDDFT computational study of photoelectrochemical cell ruthenium sensitizers", *J. Am. Chem. Soc.*, vol. 127, pp. 16835-16847, 2005.
- [28] Y. Chiba, A. Islam, Y. Watanabe, R. Komiya, N. Koide, and L. Han, "Dye-sensitized solar cells with conversion efficiency of 11.1%", *Japanese J. Appl. Phys.*, vol. 45, pp. 24-28, 2006.
- [29] D. Kuang, S. Ito, B. Wenger, C. Klein, J.-E. Moser, R. Humphry-Baker, S.M. Zakeeruddin, and M. Grätzel, "High molar extinction coefficient heteroleptic ruthenium complexes for thin film dye-sensitized solar cells", *J. Am. Chem. Soc.*, vol. 128, pp. 4146-4154, 2006.
- [30] F. Gao, Y. Wang, J. Zhang, D. Shi, M. Wang, R. Humphry-Baker, P. Wang, S.M. Zakeeruddin, and M. Grätzel, "A new heteroleptic ruthenium sensitizer enhances the absorptivity of mesoporous titania film for a high efficiency dye-sensitized solar cell", *Chem. Comm.*, Number 23, pp. 2635-2637, 2008.
- [31] F. Gao, Y. Wang, D. Shi, J. Zhang, M. Wang, X. Jing, R. Humphry-Baker, P. Wang, S.M. Zakeeruddin, and M. Grätzel, "Enhance the optical absorptivity of nanocrystalline TiO₂ film with high molar extinction coefficient ruthenium sensitizers for high performance dye-sensitized solar cells", *J. Am. Chem. Soc.*, vol. 130, pp. 10720-10728, 2008.
- [32] S. Ito, T.N. Murakami, P. Comte, P. Liska, C. Grätzel, M.K. Nazeeruddin, and M. Grätzel, "Fabrication of thin film dye sensitized solar cells with solar to electric power conversion efficiency over 10%", *Thin Solid Films*, vol. 516, pp. 4613-4619, 2008.
- [33] S.-Q. Fan, C. Kim, B. Fang, K.-X. Liao, G.-J. Yang, C.-J. Li, J.-J. Kim, and J. Ko, "Improved efficiency of over 10% in dye-sensitized solar cells with a ruthenium complex and an organic dye heterogeneously positioning on a single TiO₂ electrode", *J. Phys. Chem. C*, vol. 115, pp. 7747-7754, 2011.
- [34] T. Funaki, H. Funakoshi, O. Kitao, N. Onozawa-Komatsuzaki, K. Kusaga, K. Sayama, and H. Sugihara, "Cyclometalated ruthenium (II) complexes as near-IR sensitizers for high efficiency dye-sensitized solar cells", *Angew. Chem. Int. Ed.*, vol. 51, pp. 7528-7531, 2012.
- [35] Y. Qin, and Q. Peng, "Ruthenium sensitizers and their applications in dye-sensitized solar cells", *International J. Photoenergy*, doi: 10.1155/2012/291579, 2012