

CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Dye-Sensitized Solar Cells

The use of dye-sensitization in photovoltaics remained unsuccessful until professor Grätzel and his co-workers successfully developed a solar cell which the combination of nanostructured electrodes and efficient charge injection dyes, called the dye-sensitized nanostructured solar cell or the Grätzel cell after its inventor. The current DSSC are at 11% maximum energy conversion efficiency (Nazeeruddin *et al.*), compared to 7% of the first development by O'Regan & Grätzel.

In the dye-sensitized solar cell, the bulk of the semiconductor is used only for charge transport, while the photoelectrons are provided from a separate photosensitive dye. Charge separation occurs at the surfaces between the dye, semiconductor and electrolyte.

2.2 Operating principle of dye sensitized solar cell

Nanocrystalline TiO_2 is deposited on the conducting electrode (photoelectrode) to provide the large surface area to adsorb sensitizers (dye molecules). Upon absorption of photons, dye molecules (S^0) are excited from the highest occupied molecular orbitals (HOMO) to the lowest unoccupied molecular orbital (LUMO) states as shown schematically in Figure 2.1. This process is represented by **Equation 1**. Once an electron is injected into the conduction band (CB) of the wide bandgap semiconductor nanostructured TiO_2 film, the dye molecule (photosensitizer) becomes oxidized (S^+), (**Equation 2**). The injected electron is transported between the TiO_2 nanoparticles and then extracted to a load where the work done is delivered as an electrical energy, (**Equation 3**). Electrolyte containing I^-/I_3^- redox ions is used as an electron mediator between the TiO_2 photoelectrode and the carbon coated counter electrode (C.E.).

Therefore, the I_3^- substitutes the internally donated electron with that from the external load and reduced back to I^- ion, (Equation 4). The oxidized dye molecules (S^+) (photosensitizer) are regenerated by receiving electrons from the I^- ion redox mediator that get oxidized to I_3^- (Tri-iodide ions). This process is represented by Equation 5. The movement of electrons in the conduction band of the wide bandgap nanostructured semiconductor is accompanied by the diffusion of charge-compensating cations in the electrolyte layer close to the nanoparticle surface. Therefore, the generation of electric power in DSSC causes no permanent chemical change or transformation. (Grätzel *et al.*, 2005)

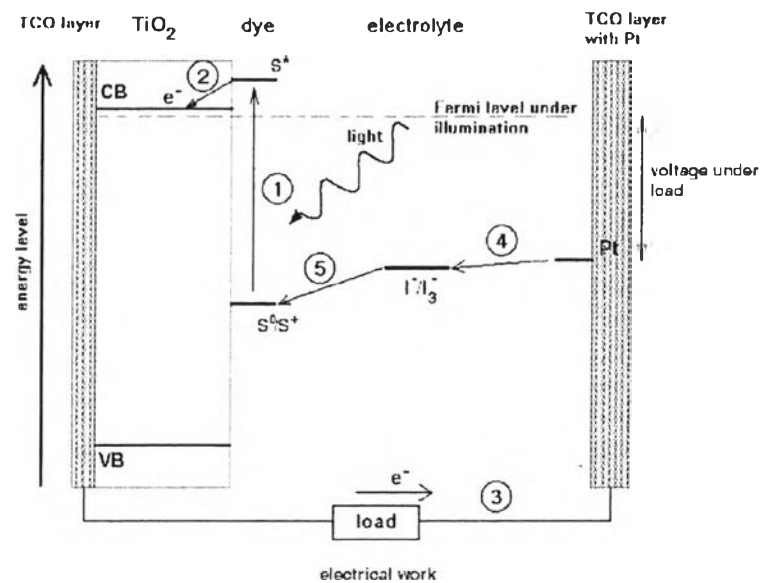


Figure 2.1 Principle of operation of dye-sensitized solar cell. (http://brojowesi.materialscience.blogspot.com/2010_03_01_archive.html)





2.3 Components of Dye-Sensitized Solar Cells

2.3.1 Photosensitizers

The ideal sensitizer for a single junction photovoltaic cell converting standard global AM 1.5 sunlight to electricity should absorb all light below a threshold wavelength of about 920 nm. In addition, it must also carry attachment groups such as carboxylate or phosphonate in order to be firmly grafted on the semiconductor oxide surface. Upon excitation, it should inject electrons into the solid with a quantum yield of unity. The energy level of the excited state should be well matched to the lower bound of the conduction band of the oxide to minimize energetic losses during the electron transfer reaction. Its redox potential should be sufficiently high that it can be regenerated via electron donation from the redox electrolyte or the hole conductor. Finally, it should be stable enough to sustain about 10⁸ turnover cycles corresponding to about 20 years of exposure to natural light. (Grätzel, 2003)

Nowadays, dye or photosensitizer used in research can be divided to two main types: synthetic dyes and natural dyes. Commercially synthetic dyes such as N3, N719 or black dye derived from ruthenium–polypyridine complexes have been widely used as sensitizer for TiO₂- based DSSC. (Grätzel *et al.*, 1991, Nazeeruddin *et al.*, 2001, Wang *et al.*, 2004)

However, direct use of these dyes with ZnO is difficult because of the formation of the Zn²⁺/dye-complex layer on ZnO nanoparticle (Horiuchi *et al.*, 2003), resulting in poor dye adsorption and electron injection. The short immersion time and the optimal dye concentration can avoid the formation of Zn²⁺/dye complex. (Chou *et al.*, 2007)

Besides, at higher adsorption temperatures, the amount of dye adsorbed on ZnO was increased, and the dye aggregation was decreased. (Zhang *et al.*, 2008)

Due to the expensive of synthetic dyes and environmental concern, natural dyes have been applied to DSSC. The natural dyes that found in plant, fruits and other natural products such as red cabbage (Furakawa *et al.*, 2009), black rice (Hao *et al.*, 2006), rosella (Wongcharee *et al.*, 2007), mulberry (Thambidurai *et al.*, 2011) and spinach (Chang *et al.*, 2010) have been previously reported to be used in DSSC. However, low efficiency is obtained due to low interaction between natural dyes and oxide surface, which results in the low electron transfer from the dye molecules to the conduction band of oxide. (Narayan *et al.*, 2012) Nevertheless, the use of nontoxic natural pigments as sensitizers would definitely enhance the environmental and economic benefits of this alternative form of solar energy conversion.

2.3.2 photoanode or n-type semiconductor

Oxide semiconductors are preferential in photoelectrochemistry because of their exceptional stability against photo-corrosion on optical excitation in the band gap. (Kalyanasundaram *et al.*, 1998) Furthermore, the wide band gap (>3 eV) of the oxide semiconductors is needed in DSSC for the transparency of the semiconductor electrode in the major part of the solar spectrum. In addition to TiO₂ that has been the foundation semiconductor for dye-sensitized nanostructured electrodes for DSSC, semiconductors used in porous nanocrystalline electrodes in dye-sensitized solar cells include, for example, ZnO, CdSe, CdS, WO₃, Fe₂O₃, SnO₂, Nb₂O₅, and Ta₂O₅. (Hagfeldt *et al.*, 1995)

In present, the most successful DSSCs have been produced using porous TiO₂ nanocrystalline films combined with ruthenium polypyridine complex dyes. (O'Regan *et al.*, 1991, Nazeeruddin *et al.*, 1993) Among semiconducting materials, ZnO is one of the attractive semiconductor materials in solar energy conversion due to its stability against photocorrosion and photochemical properties similar to TiO₂, This material has a band gap similar to that of TiO₂ at 3.2 eV and a higher electron mobility 115- 155 cm²/V s² than that of TiO₂ (Chou *et al.*, 2007), that would be favorable for electron transport, with

reduced recombination loss. Moreover, ease of crystallization and anisotropic growth cause to wide variety of nanostructure. (Zhang *et al.*, 2009)

Dye-sensitized semiconducting single-crystal ZnO electrodes were studied early by Gerischer and Tributsch, 1969. In 1980, 2.5% energy conversion efficiency at 562 nm using sintered porous disks of ZnO was reported by Matsumura *et al.* In 1994, Redmond *et al.* achieved an incident photon-to-current conversion efficiency (IPCE) of 13% at 520 nm when using the Ru(dcbpyH₂)₂(NCS)₂ dye. The fabrication of ZnO and N719-sensitization led to a high short-circuit photocurrent density and energy conversion efficiency of 6.58% (AM 1.5, 100 mW/cm²) (Saito *et al.*, 2008). Using natural dyes extracted from *Ixora coccinea*, Mulberry and Beetroots to fabricate ZnO solar cells and reported the efficiency to lie in the range 0.28-0.41%. (Thambidurai *et al.*, 2011)

There are various ways in preparing ZnO electrodes such as doctor-blade (Saito *et al.*, 2008), electrophoretic deposition (EPD) (Yin *et al.*, 2010), screen printing (Hara *et al.*, 2000), and sol-gel technique, etc. (Redmond *et al.*, 1994) Doctor-blade method is one of the facile printing methods available for modern electronics. The synthetic ZnO powder was ground with acetylacetone, water and Triton X-100 (surfactant) to make the paste (Rensmo *et al.*, 1997). Then, the investigation of an amount of PEG as a binder affects to the performance of DSSC. (Saito *et al.*, 2009) Another one, electrophoretic deposition (EPD) is achieved via motion of charged particles in suspensions towards an electrode and deposit formation under an applied electric field. Cathodic or anodic deposits can be obtained depending on particle charge. (Li *et al.*, 2010) EPD is a useful method for the preparation of thick binder free particulate films on conductive substrates in a much shorter time, compared to the other coating techniques. It is especially attractive due to the low cost, simple equipment, formation of uniform layers of controlled thickness, and homogeneous microstructure. (Grinis *et al.*, 2008) In 2009, Jareenboon *et al.* observed that the film thickness correlated with increase of the deposition voltage and deposition time in the preparation of TiO₂ nanoparticles on FTO substrates (Jareenboon *et al.*, 2009). Nanostructured ZnO thin films were

electrophoretically deposited from ZnO colloidal suspensions and studied the influences of parameters such as applied voltage, deposition time, aging treatment and suspension concentration on the deposit weight, morphology and microstructure. (Miao *et al.*, 2010) This method (EPD) has been more frequently used to prepare film on plastic substrate for flexible DSSC since it does not require a high temperature during the deposition process. (Chen *et al.*, 2011)

2.3.3 Electrolytes and hole conductors

2.3.3.1 *Liquid electrolyte*

The first DSSC was reported in 1991 by M. Gratzel using organic liquid electrolyte containing LiI/I_2 , which obtained an overall light-to-electricity conversion efficiency of about 7.1% under irradiation of AM 1.5, 100 mW/cm^2 . Later, many kinds of liquid electrolytes containing iodide/triiodide redox couple and high dielectric constant organic solvents such as acetonitrile (AcN), propylenecarbonate (PC), 3-methoxypropionitrile (MePN), dimethylsulfoxide (DMSO), dioxane (DIO) and pyridine (PY) solutions were investigated. (Kebede *et al.*, 1999) Moreover, an additive in the electrolyte such as the 4-tertbutylpyridine (TBP) can decrease the recombination site on the ZnO/electrolyte interface and suppress the dark current, and finally increase the V_{OC} and FF. (Qin *et al.*, 2012)

Liquid electrolyte-based organic solvent usually has high ionic conductivity and excellent interfacial contact property, which are the factor for high photovoltaic performance of DSSC. Although a photoelectric conversion efficiency of 11% for the DSSC-containing liquid electrolyte has been achieved (Gratzel, 2005), the potential problems caused by liquid electrolytes, such as leakage and volatilization of organic solvents, are considered as some of the critical factors limiting the long-term performance and practical use of DSSC. Thus, solid-state and quasi-solid-state electrolytes with high long-term stability are attempted to replace liquid electrolytes.

2.3.3.2 *Solid-state electrolytes*

Hole transport materials (HTMs)

In 1998, an efficient solid-state DSSC based on organic HTM 2,2',7,7'-tetrakis(N,N-di-p-methoxyphenylamine) 9,9'-spirobifluorene (OMeTAD) was reported, although the overall light-to-electricity conversion efficiency of this DSSC only reached 0.74% under irradiation of 9.4 mW/cm^2 , it is a pioneer for fabricating DSSC with organic HTMs. (Bach *et al.*, 1998) However, the overall light-to-electricity conversion efficiencies of these DSSC are all much lower than that of the DSSC based on liquid electrolytes as a result of the low intrinsic conductivities of HTMs, the high frequencies of charge recombination from TiO_2 to HTMs, and the poor electronic contact between dye molecules and HTMs caused by incomplete penetration of solid HTMs into the pores of the mesoporous TiO_2 electrodes.

Quasi-solid-state electrolytes

The quasi-solid state, or gel state, is a particular state of matter. Generally, a quasi-solid-state electrolyte is defined as a system which consists of a polymer network (polymer host) swollen with liquid electrolytes. This electrolytes show better long-term stability than liquid electrolytes and have the merits of liquid electrolytes including high ionic conductivity and excellent interfacial contact property. Moreover, it is believed to be one kind of the most available electrolytes for fabricating high photoelectric performance of DSSC in practical applications. For example, a polyblend gel electrolyte was prepared by adding KI and I_2 to Poly(MMA-co-MAA)/PEG system. A light-to-electricity conversion efficiency of 4.85% for QS-DSSC was achieved under AM 1.5 simulated solar light illumination at 60°C . (Li *et al.*, 2007)

2.3.4 Counter-electrode

For sufficiently fast reaction kinetics for the triiodide reduction reaction at the FTO coated cathode, a catalyst coating is needed.

The properties of counter electrode are a high electrical conductivity, porous and a good catalyst. The materials used as the counter electrode is platinum metal (Pt). Because platinum is expensive, carbon is a favourable alternative as counter electrode material. Various carbon materials such as carbon nanotubes (CNT) (Lee *et al.*, 2009), activated carbon (Imoto *et al.*, 2003) and carbon nanofibers (Joshi *et al.*, 2010) have

been investigated as counter electrodes for DSSC applications, based on their high electrochemical activity, high specific surface area, chemical inertness and high electrical conductivity.

2.4 Solar cell efficiency factors

The testing of efficiency with sunlight directly is concerned about direction and intensity of sunlight that result to calculation of solar cell efficiency. Therefore, it is tested at reference conditions (Standard Testing Conditions, STC, AM = 1.5 corresponds to an angle of incidence of 37° , an incident power density = 1000 w/m^2 and a temperature of 25°C) by solar simulation. AM 1.5 solar emission was simulated by passing the output of the high-pressure 450-W xenon lamp through a 3-mm-thick Schott I13 interference filter. (Nazeeruddin, 1993)

The operating regime of the solar cell is the range of bias, from 0 to V_{oc} , in which the cell delivers power. The cell power density is given by:

$$P = JV$$

P reaches a maximum at the cell's operating point or maximum power point (P_{max}). This occurs at some voltage V_m with a corresponding current density J_m , shown in Figure 2.2

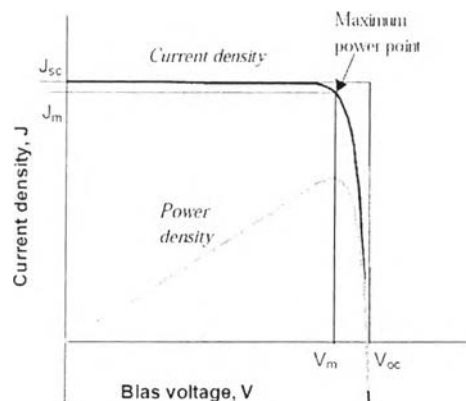


Figure 2.2 The current voltage (black) and power-voltage (grey) characteristics of an ideal cell.

Power density reaches a maximum at a bias V_m , close to V_{oc} . The maximum power density $J_m \times V_m$ is given by the area of the inner rectangle. The outer rectangle has area $J_{sc} \times V_{oc}$. If the fill factor were equal to 1, the current voltage curve would follow the outer rectangle. (Nelson, 2004)

The fill factor can assume values between 0 and less than 1 and is defined by the ratio of the maximum power (P_{max}) of the solar cell per unit area divided by the V_{oc} and J_{sc} according to:

$$FF = P_{max} / (J_{sc} V_{oc})$$

$$FF = \frac{J_m V_m}{J_{sc} V_{oc}}$$

The overall solar-to- electrical energy conversion efficiency, η , for a solar cell is given by the photocurrent density measured at short-circuit (J_{sc}), the open-circuit photovoltage (V_{oc}), the fill factor of the cell (FF), and the intensity of the incident light (P_{in}).

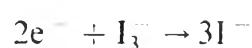
$$\eta = P_{max} / P_{in}$$

$$\eta = \frac{J_{sc} V_{oc} FF}{P_{in}}$$

These four quantities: J_{sc} , V_{oc} , FF and η are the key performance characteristics of solar cell. All of these should be defined for particular illumination conditions (Standard Test Condition, STC)

2.5 Dark current or recombination reaction

Dark current arises in the dye cell from the recombination of charge carriers by reduction of I_3^- at the dye-free sites at the TiO_2 particle surfaces. (**Figure 2.3**)



In principle, this charge recombination can occur at surfaces other than that of TiO_2 . Due to the porous nature of the TiO_2 film, it can also occur at the back conducting glass (ITO) electrode. In reality, the reaction occurs at the TiO_2 particle / redox electrolyte interface due to the relatively large surface area of the nanocrystalline film. (Kalyanasundaram *et al.*, 1998)

In order to reduce the dark current, an oxide underlayer is deposited. The formation of ZnO thin layers on nanoporous TiO_2 in DSSCs by a layer-by-layer method (Mane *et al.*, 2005). The ZnO layers on TiO_2 effectively form an energy barrier reducing the recombination reaction.

Alternatively, soaking the dye-coated electrode to a solution of a pyridine derivative (donor) such as 4-*t*-butylpyridine was found to improve dramatically the fill factor (ff) and the open-circuit voltage (V_{oc}) of the device without affecting the short-circuit photocurrent (i_{sc}) in a significant fashion. (Nazeeruddin *et al.*, 1993).

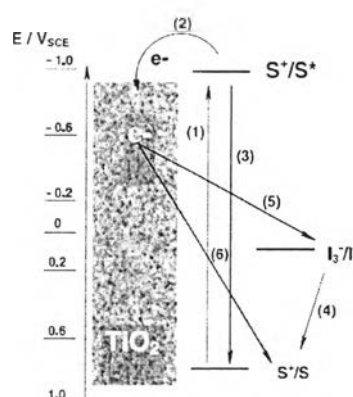


Figure 2.3 (5) conduction band electron capture by redox mediator giving rise to dark current. (Lagref *et al.*, 2008)

2.6 Natural sensitizers

Since environment concern is an important issue, many researchers have tried to develop DSSC sensitized with natural dyes, which still provide low efficiency due to low light absorption in the whole visible region range, weak binding energy with TiO_2

film (Chang *et al.*, 2010), high electron recombination, and low stability. The weak binding energy stems from the lack of anchoring groups such as dyes in chlorophyll and carotenoid groups. Besides, strong steric hindrance of the bulky structure or very long alkyl chain could prevent dye arraying on TiO₂ surface efficiently (Hao *et al.*, 2006 and Wongcharee *et al.*, 2007). The interaction between natural dyes and TiO₂ surface is exhibited by the broadening and the red shift of the absorption band of dye adsorbed on TiO₂ surface. As a result, the absorption band shifts to lower energy, owing to the electronic coupling between the adsorbed dyes and TiO₂ (Wongcharee *et al.*, 2007).

Nevertheless, the high recombination and low electron injection efficiency due to quenching of the excited state of natural dyes is attributed to a dye aggregation (Lee and Yang, 2011). Lee and Yang mentioned that this phenomenon could be observed in ruthenium based-dyes with a large number of carboxyl groups, which have tended to form intermolecular aggregation from hydrogen bonding between carboxyl groups. Also, the dye aggregation is the main drawback of the organic dyes as Liu *et al.*, (1997) reported. In case of natural dye, this could be seen from broadening shape of visible absorption spectrum of natural dye adsorbed on TiO₂ (Kay, 1994 and Vougioukalakisa *et al.*, 2011). To solve this, use of coadsorbates, such as organic acids with carboxyl group was the way (Calogero *et al.*, 2010 and Kay, 1994). However, acid results in lowering the V_{oc} due to positive shift of TiO₂ fermi level (Calogero *et al.*, 2010).

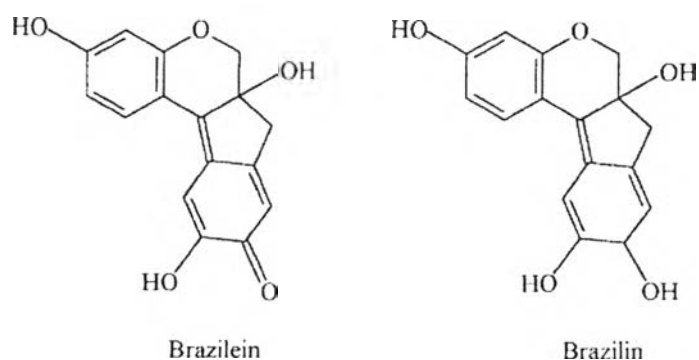


Figure 2.4 Chemical structures of Brazilin and Brazilein. (Oliveira *et al.*, 2002)

Caesalpinia sappan, named sappan wood, is native to south India and Asia. The structural formulae of Brazilin and Brazilein are depicted in figure 2.4. It is interesting to note that brazilin is the major component in the crude dye, and brazilein can be isolated in large quantities when the organic extract is exposed to air and light, resulting in the oxidation of the hydroxyl of brazilin to carbonyl group.

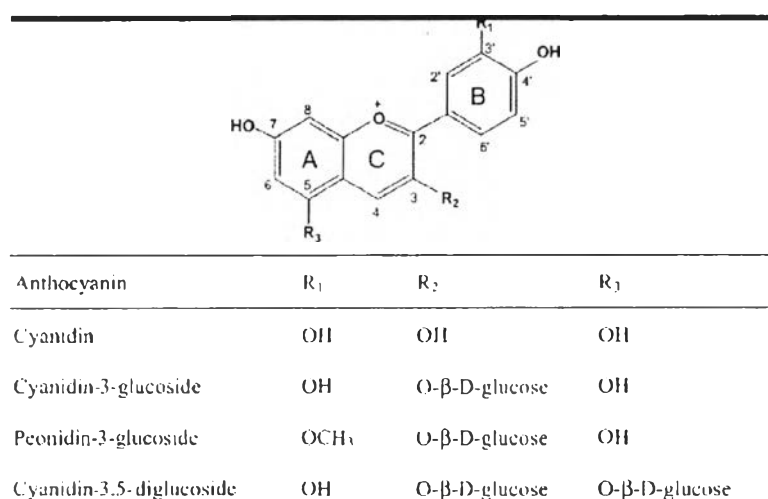


Figure 2.5 Chemical structures of anthocyanins (black rice). (Hiemori *et al.*, 2009)

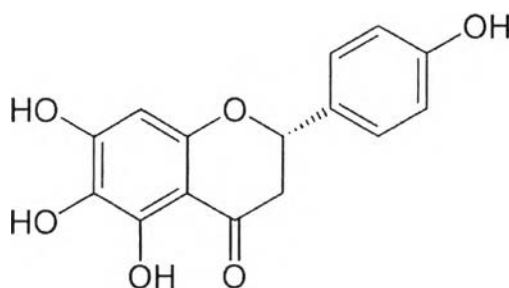


Figure 2.6 Chemical structure of carthamidin (safflower petals). (Machewad *et al.*, 2012)

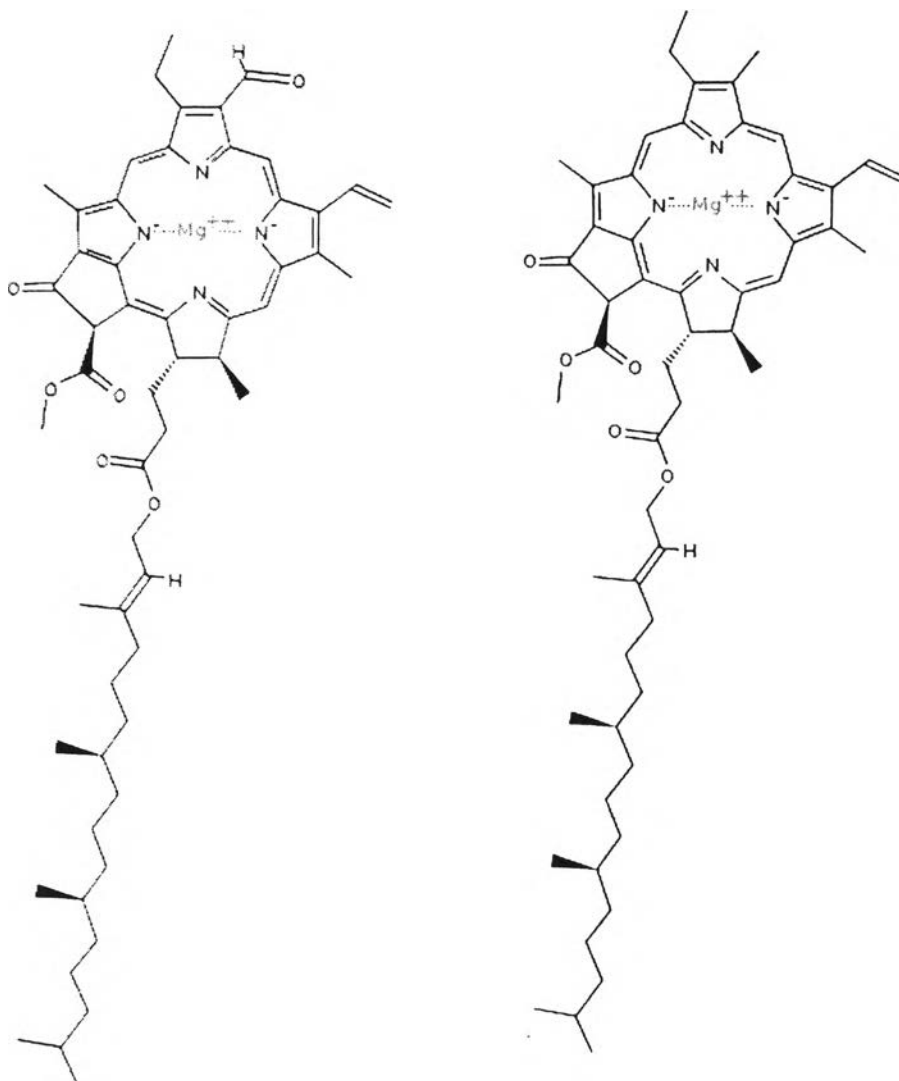


Figure 2.7 Chemical structure of chlorophyll (noni leaves). (Wang *et al.*, 2002)

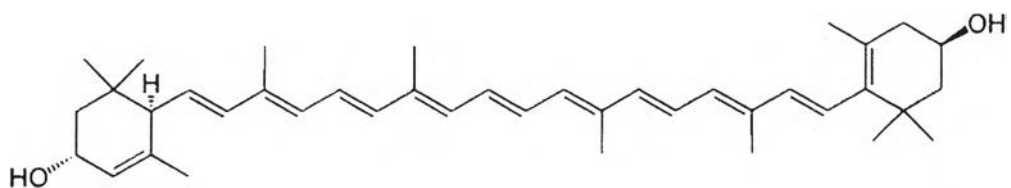


Figure 2.8 Chemical structure of lutein (sunflower). (Chethan *et al.*, 2010)

2.7 Electrophoretic deposition

Electrophoretic deposition (EPD) is one of the colloidal processes in ceramic production and has advantages of short formation time, needs simple apparatus, little restriction of the shape of substrate, no requirement for binder burnout as the green coating contains few or no organics. Compared to other advanced shaping techniques, the EPD process is very versatile since it can be modified easily for a specific application. For example, deposition can be made on flat, cylindrical or any other shaped substrate with only minor change in electrode design and positioning. In particular, despite being a wet process, EPD offers easy control of the thickness and morphology of a deposited film through simple adjustment of the deposition time and applied potential. In EPD, charged powder particles, dispersed or suspended in a liquid medium are attracted and deposited onto a conductive substrate of opposite charge on application of a DC electric field. The term 'electrodeposition' is often used somewhat ambiguously to refer to either electroplating or electrophoretic deposition, although it more usually refers to the former.

The basic difference between an electrophoretic deposition process (EPD) and an electrolytic deposition process (ELD) is that the former is based on the suspension of particles in a solvent whereas the later is based on solution of salts, i.e., ionic species [3]. There can be two types of electrophoretic deposition depending on which electrode the deposition occurs. When the particles are positively charged, the deposition happens on the cathode and the process is called cathodic electrophoretic deposition. The deposition of negatively charged particles on positive electrode (anode) is termed as anodic electrophoretic deposition. By suitable modification of the surface charge on the particles, any of the two mode of deposition is possible.

In DSSC application, the electrophoretic deposition technique is one technique which does not need a lot of organic additives (Miyasaka et al., 2002), which are burned out at high temperature since only charges and solvent mediate facilitate the film

formation while screen printing and doctor blading techniques need surfactant and polymer to adjust wet ability and viscosity of the paste.

Solvent used in EPD should be inert with respect to the particles and also originates charges on the colloid particles. The organic solvents such alcohols are the most suitable choice since they behave as proton donors and are important for particle charging (Zhitomirsky, 2002). Except from the proton donor role of solvents, Zhitomirsky reported that non-aqueous solvent or mixture solvent with low dielectric constant could result in reducing of double layer thickness of colloid particles, which led to particle coagulation while it help to reduce the solubility of deposits. As a result, optimization for system is needed.

Other parameters control both quantity and quality of deposited film. For example, to obtain thicker film, higher concentration of suspension, higher electric field, and longer deposition time are used. However, these are usually limited by film quality. Grinis *et al.*, (2008) found that low P25 concentration gave the best DSSC efficiency since high P25 content made more agglomeration and led to poor packing density. Meanwhile, Chen *et al.*, (2011) explained that the morphology of the film surface could be controlled by the potential different between two electrodes because higher electric field provided less order structure and packing density, which led to non-smooth film. Besides, the deposition temperature influences directly to the electronic property of the film. Tirosh *et al.*, (2006) found that low temperature of EPD induced the preferential orientation of TiO₂ nanocrystals. This led to increase in electron transport in porous TiO₂ which reached the optimum value at 0 °C of EPD, but not influence to the recombination rate of injected electron and electrolyte.

2.8 Polythiophene

Whiffen *et al.* (1979) proposed a two-step mechanism for the polymerization of thiophene monomer. Polymerization starts with the formation of a cation radical that is formed by a loss of an electron from the monomer, as shown in Figure 2.9. Thiophene

radical can give either a substitution or combination reaction. The oxidation of thiophene is irreversible and the cation radical can be formed in the first step. Thiophene is extremely reactive.

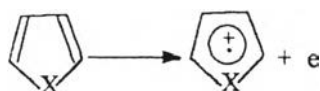


Figure 2.9 Oxidation of thiophene monomer (X= S).

Polythiophene can be synthesized either electrochemically or chemically by using simple oxidation.

2.8.1 Electrochemical polymerization

The mechanism of polymerization involves the formation of radical cations that react with each other or with starting monomer to develop the polymeric structure. (Figure 2.10)

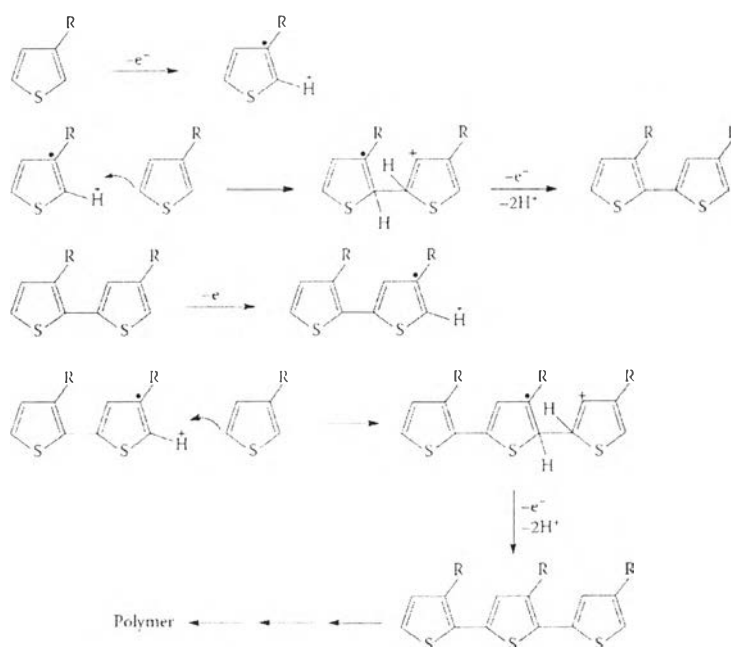


Figure 2.10 Polymerization of thiophene (R = H or substituent).

Polythiophene (PTh) and its derivatives are conductive polymer. They are intensively studied due to their easy synthesis, high conductivity, photochemically and thermally stable under photoirradiation. Among the various properties of thiophene-based conjugated polymers, the outstanding characteristics are the high absorption coefficient and wide absorption wavelength in the visible part of the spectrum, which allow a thinner nanocrystalline film to harvest the incident light efficiently in dye-sensitized solar cells. Considering the good performance in polymer solar cells and the efficient light harvesting properties, thiophene-based conjugated polymers are promising light sensitizers for application in dye-sensitized solar cells. (Chen *et al.*, 2009)

In fact, polythiophene can serve as both photosensitizers and solid electrolytes in DSSC, because they not only can absorb visible light, but also possess hole-transfer properties. (Tan *et al.*, 2005)

The polythiophene-sensitized DSSC with an overall conversion efficiency (η) of ~2.4% by introducing carboxylic acid into the polymers and ionic liquids into electrolytes; this is the best result for DSSC based on thiophene sensitizers so far. (Yanagida *et al.*, 2004) Introduction of electrochemically polymerized polythiophene layer on Ru-dyes in DSSC has been found to be beneficial. In situ polymerization enables the formation of uniform polythiophene layers on Ru-complex/TiO₂. The dark currents reduced in the presence of polythiophene protecting layers indicating the reduction of recombination reaction. The power conversion efficiency of DSSC with polythiophene layers on Ru photosensitizer was 6.01%, which is higher when compared to one without polythiophene layers. (Lee *et al.*, 2009)

Investigation of photovoltaic devices based on electrochemically deposited monolayer of neat polythiophene (PT) films onto fluorinedoped tin oxide (FTO)/glass substrates and the thickness being controlled by time deposition. (Valaski *et al.*, 2007) Also, this method is a feasible way of preparing layer of insoluble polythiophene coated TiO₂ composite nanoparticles. (Pfleger *et al.*, 2004)