

## CHAPTER II

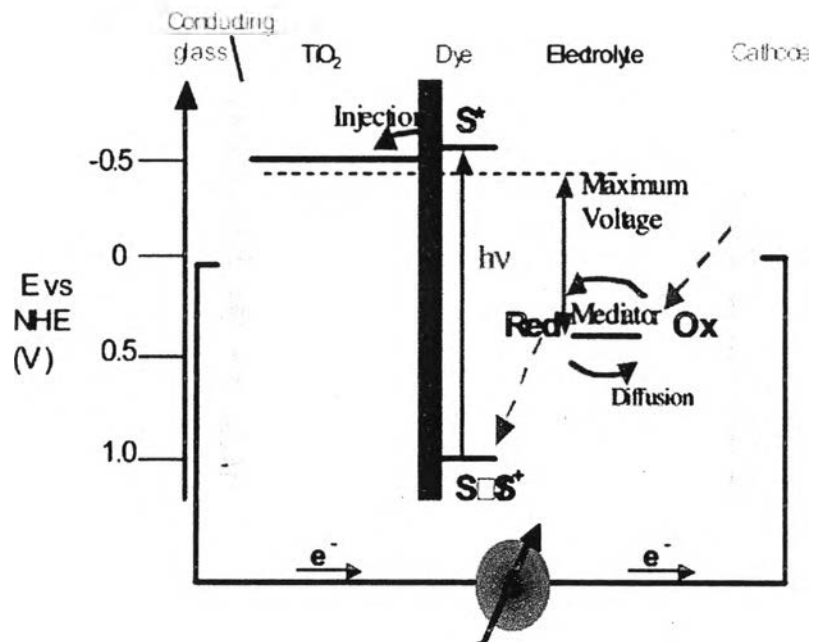
### THEORETICAL BACKGROUND AND LITERATURE REVIEW

#### 2.1 Dye-Sensitized Solar Cells

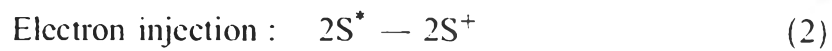
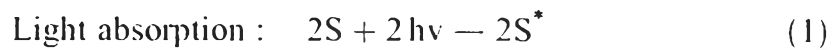
Dye-sensitized solar cells (DSSCs) are the photovoltaic device which is used for the conversion of sunlight into electricity based on wide band gap semiconductor. The history of DSSC was developed with chlorophyll sensitized zinc oxide (ZnO) in 1972 (Tributsch *et al.*, 1969). But DSSC has become truly attractive photovoltaic devices when Grätzel and co-workers succeeded in developing a new type of DSSC which combined with titanium dioxide (TiO<sub>2</sub>) and novel ruthenium (Ru) bipyridyl complex as a sensitizer (Grätzel, 2005).

#### 2.2 Operating Principle of Dye Sensitized Solar Cell

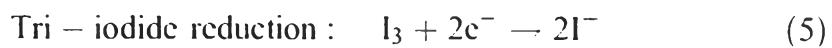
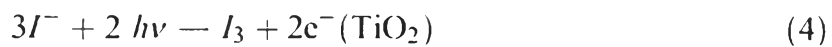
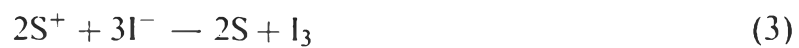
A schematic presentation of the operating principle of DSSC is given in figure 2.1 The heart of DSSC is nanocrystalline semiconductor which is placed to contact both dye and redox couple electrolyte. The well-known material of nanocrystalline semiconductor is titanium dioxide (TiO<sub>2</sub>) with anatase structure. Nowadays, the alternative semiconductor which is used and has band gap similar to the alternative TiO<sub>2</sub> is zinc oxide (ZnO). The absorption of sunlight in DSSC occurs in the dye molecule as light sensitizer. When they absorb the sunlight, they will generate the electron-hole pair which is called photon and then the electron is transported through the band gap of semiconductor. The dye is regenerated by electron donation from the electrolyte, usually an organic solvent containing a redox couple, such as iodide/triiodide couple. The iodide is regenerated by reduction of triiodide at the counter electrode.



**Figure 2.1** Principle of operation of dye-sensitized solar cell (Grätzel, 2005).



Dye reduction and iodide oxidation :



**Figure 2.2** All reactions of DSSC (Tripathi *et al.*, 2012).

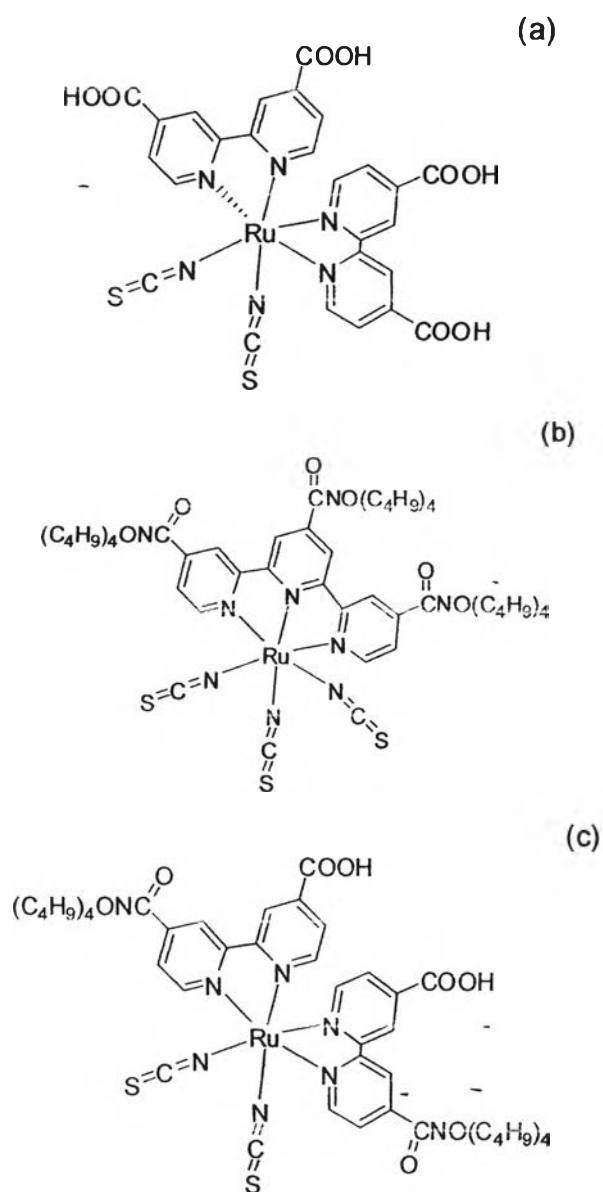
## 2.3 Components of Dye-sensitized Solar Cells

### 2.3.1 Photosensitizers

Dye or photosensitizer plays an important role in absorption and conversion of sunlight to electricity. Many researches have focused on molecule engineering of several organic metal complexes especially ruthenium complexes (Ru). These complexes are one of the most effective sensitizers because of their high efficiency, good chemical stability, and intense charge transfer absorption in the wide visible range (Hao *et al.*, 2006). Moreover, Ru sensitizers show intense absorption range in visible to the near-infrared region (Monari *et al.*, 2011). An efficient sensitizer must have certain requirements such as; an intense absorption in the visible region, strong adsorption onto the semiconductor surface, effective electron injection to the conduction band of the semiconductor, and it should have several carbonyl (C=O) or hydroxyl (-OH) groups to chelate with semiconductor surface (Smestad, 1998).

Nowadays, dye can be divided into two main types which are synthetic dyes and natural dyes. Grätzel and co-worker developed many Ru complexes. The outstanding synthetic dyes are cis-bis(isothiocyanato)bis(4,4'-dicarboxylic acid-2,2'-bipyridine)Ru(II) complex coded as N3 or red dye; tris(isothiocyanato)-2,2',2''-terpyridyl-4,40,4''-tricarboxylate)Ru(II) complex coded as N749 or black dye and di(tetrabutylammonium)cis-bis(isothiocyanato)bis(4-carboxylic acid-4'-carboxylate-2,2'-bipyridine)Ru(II) complex coded as N719 (Figure 2.3). For natural dyes, organic dyes and metal complexes such as porphyrins and phthalocyanine were usually used as sensitizers. However, they cannot compete with Ru sensitizer because of their low near infrared absorption. Furthermore, the LUMO level of them is very low for electron transfer to conduction band of semiconductor (Grätzel, 2003). In Ru complexes, this transfer is much faster rate than back reaction which the electron recombines with oxidized dye more than general flowing and working (Ryan, 2009). However, Ru complexes contain a heavy metal which is dangerous to the environment and expensive cost of production. So that using natural dyes are the alternative sensitizers. Their advantages over synthetic

dyes are easy obtainable, large abundance source, using without purification, environmental friendly and lower production cost.



**Figure 2.3** Chemical structures of (a) N3, (b) N749 and (c) N719.

### 2.3.2 Electrolytes

The first DSSC employed lithium iodide/iodine as an organic liquid electrolyte (Grätzel, 1991). From this device, conversion efficiency was obtained about 7.1% under irradiation of AM 1.5, 100 mW/cm<sup>2</sup>. In addition, many types of liquid electrolytes containing iodide/triiodide redox couple and high dielectric constant organic solvents such as acetonitrile (AcN), propylene carbonate (PC), 3-methoxypropionitrile (MePN), dimethylsulfoxide (DMSO), dioxane (DIO) and pyridine (PY) solutions were investigated (Kebede *et al.*, 1999).

Liquid electrolyte based on organic solvent usually has high ionic conductivity and excellent interfacial contact with electrodes, which are the main factors contributing to the high photovoltaic performance of DSSC. The conversion efficiency reached 11% for the DSSC-containing liquid electrolyte (Grätzel, 2005). However, leakage and volatilization of organic solvents affect to the decreased conversion efficiency and the long term stability of DSSC. Among all of the problems, the solid state electrolyte and polymeric electrolyte are used as alternative electrolyte.

### 2.3.3 Counter-electrode

The requirement of material which were used as counter electrode in DSSC is that it should has a low charge transfer resistance (Anandan, 2007). The counter electrode deals to transfer electrons from the external circuit back to the redox couple electrolyte. Until now, Platinum (Pt) has been the aspired material for using as the counter electrode since it is a good catalyst for I<sub>3</sub><sup>-</sup> reduction (Luque *et al.*, 2003).

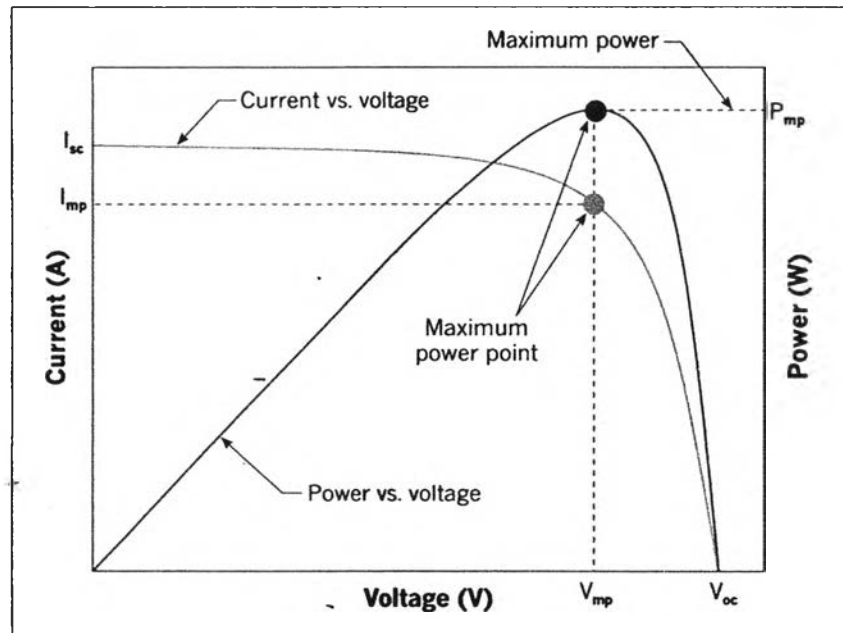
An interesting low cost for counter electrode is carbon (C) because of their good catalyst for I<sub>3</sub><sup>-</sup> reduction. Moreover, it is combined sufficient conductivity, corrosion resistance and heat resistance as well (Kay *et al.*, 1996). Porous carbon electrode was prepared from graphite powder. The Pt/carbon black counter electrode achieved 6.72% of conversion efficiency under one sun illumination (Li *et al.*, 2009).

## 2.4 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 ambient conditions (Standard Testing Conditions, STC, AM = 1.5 corresponds to an angle of incidence of  $37^\circ$ , an incident power density =  $1000 \text{ w/m}^2$  and a temperature of  $25^\circ\text{C}$ ) 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 113 interference filter (Nazeeruddin *et al.*, 2003).

The performance of DSSC has been estimated by open circuit voltage ( $V_{oc}$ ), short current ( $I_{sc}$ ), fill factor ( $FF$ ) and conversion efficiency ( $\eta$ ). Open circuit voltage occurs when there is not any load connected to the cell and current is not flowing. Maximum power voltage is the amount of voltage produced by the cell which corresponds to the maximum amount of power for cell. The yellow line on Figure 2.3 below, the current versus voltage curve shows that the open circuit voltage ( $V_{oc}$ ) occurs at the bottom right side of the curve. At this point, the voltage is maximal value and the current flow is zero. On the same graph, the blue line shows that the power versus voltage. The maximum power voltage ( $V_{mp}$ ) is directly below the curvature of blue line.  $V_{oc}$  is always greater than  $V_{mp}$  for DSSC.

The straight line which is drawn down from the curvature of the power versus voltage curve intersects with the current versus voltage then the maximum power current ( $I_{mp}$ ) will appear. The product of those two values ( $V_{mp} \times I_{mp}$ ) results in the maximum power value in watts if the fill factor is equal to one (Nelson *et al.*, 2004).



**Figure 2.4** The current versus voltage curve and power versus voltage curve (<http://ecmweb.com/green-building/highs-and-lows-photovoltaic-system-calculations>).

The fill factor ( $FF$ ) of DSSC is scale of resistance and junction quality of the cell. The fill factor can assume values between zero and less than one which is defined by the ratio of the maximum power ( $P_{max}$ ) of the solar cell per unit area divided by the  $V_{oc}$  and  $I_{sc}$  following the equation 6 or 7 (Ludin *et al.*, 2014).

$$FF = \frac{P_{max}}{I_{sc}V_{oc}} \quad (6)$$

$$FF = \frac{I_{mp}V_{mp}}{I_{sc}V_{oc}} \quad (7)$$

Where,  $I_{sc}$  and  $V_{oc}$  are the short circuit currents and the open circuit voltage, respectively.

From the entire variable above, the overall conversion efficiency ( $\eta$ ) of DSSC can be defined following the equation below.

$$\eta = \frac{P_{max}}{P_{in}} \quad (8)$$

$$\eta = \frac{I_{sc}V_{oc}FF}{P_{in}} \quad (9)$$

Where,  $P_{max}$  is the maximum output power and  $P_{in}$  is the input power or incident light which is measured in  $\text{mWcm}^{-2}$

## 2.5 Natural Dye for Sensitizer

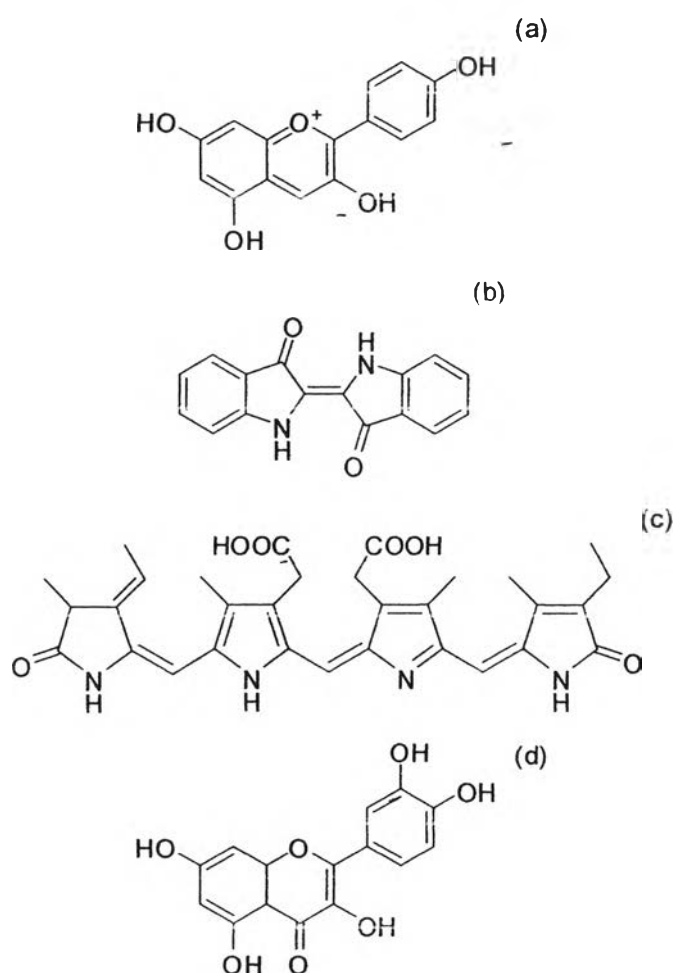
In nature, some flowers, leaves, fruits perhaps animals or minerals show various colors which consist of several pigments that can be readily extracted and used for DSSC (Chang *et al.*, 2010). Natural pigments have been considered as alternative sensitizers for DSSC because of their simple preparation, low cost, complete biodegradation, available all around, environmental friendly and unpurified grade. The electronic structure of pigments reacting the sunlight can be described by maximum absorption wavelength ( $\lambda_{max}$ ) (Davies, 2004). There are numerous natural dyes which is used as sensitizers in DSSC such as chlorophyll, carotenoid, anthocyanin, flavonoid, cyanine and tannin (Ludin *et al.*, 2014). Almost natural dyes have a hydroxyl group in their structure and exhibit water solubility (Wongcharee *et al.*, 2007). However, the natural DSSC still provide low efficiency due to low light absorption in visible region, weak binding energy with semiconductor, high electron recombination and low stability (Chang *et al.*, 2012). The weak binding energy is obtained by the reason of lacking anchored groups. Moreover, steric hindrance of the bulky structure or very long alkyl chain prevent dye to hold on  $\text{TiO}_2$  surface (Hao *et al.*, 2006). The interaction between natural dyes and  $\text{TiO}_2$  surface is exhibited by the broadening and the red shift of the absorption band of dyes on  $\text{TiO}_2$  (Wongcharee *et al.*, 2007).

Furthermore, the high recombination due to quenching of the excited state of natural dyes is attributed to a dye aggregation. In case of DSSC with ruthenium dyes, a large number of carbonyl groups in structure will form intermolecular



aggregation by hydrogen bond between carbonyl groups (Lee *et al.*, 2008). Also, the dye aggregation is the main drawback of the DSSC.

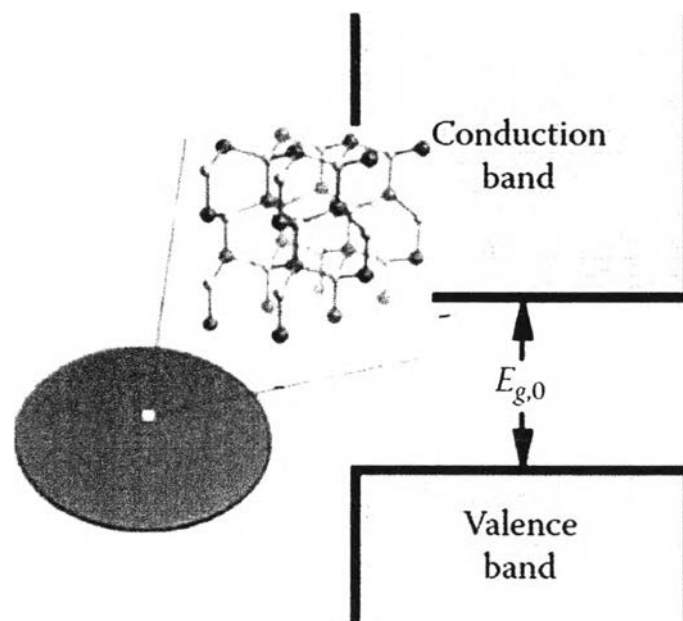
New four natural dyes with ZnO semiconductor which are red orchid, spirulina, indigo and yellow cotton flower were used as sensitizers. The structure formula of each dye is depicted in Figure 2.4



**Figure 2.5** Chemical structure of (a) pelargonidin (red orchid) , (b) indigo (indigo), (c) *c*-phycocyanin (spirulina) and (d) quercetin (yellow cotton).

All of the chosen dyes contain hydroxyl group which results in water solubility. Furthermore, both indigo dye and spirulina dye also contain carbonyl group that other two dyes have not.

## 2.6 Quantum Dot Sensitizer (QD)



**Figure 2.6** Valence energy bands separated with energy gap,  $E_{g,0}$  (Klimov, 2010).

### 2.6.1 Preparation of QD

Semiconductor QDs have been prepared by a variety of “physical” and “chemical” methods. Some example of physical processes, molecular-beam-epitaxy (MBE) and metalorganic-chemical-vapor-deposition (MOCVD) approaches to QDs (Serpone *et al.*, 1994) and vapor-liquid-solid (VLS) approaches to quantum wires (Osterloh, 2008). For chemical process, colloidal chemical synthesis is used to produce nanocrystal quantum dots. Chemical bath deposition (CBD) is widely used in situ methods for preparation of QD on nanostructured wide bandgap semiconductors. CBD has been used to deposit QD film onto semiconductor. Direct growth is done by immersing the semiconductor into the solution which contains the cationic and anionic precursors of aspiring QD (Gorer *et al.*, 1995).

### 2.6.2 Electrolyte-mediated Charge Transport

From flow pathways, a proposed mechanism was the electrolyte-mediated charge transport from outer QDs to the QDs which were next to the conductive glass. To confirm this mechanism, two new electrolyte solutions were tested (Calzaferri *et al.*, 1995). They are the aqueous solution of NaI, NaOH and the aqueous solution of tetrabutylammonium iodide (TBAI), tetrabutylammonium hydroxide (TBAOH). In case of the NaI and NaOH electrolyte solution, the overall efficiency was affected that was lower value than the standard electrolyte solution which was Na<sub>2</sub>S and NaOH. However, when the electrolyte solution consisting of TBAI and TBAOH was used, no overall efficiency was observed. Calzaferri and co-worker explicated that aggregation of salts (represent QD) in the zeolite (represent semiconductor) is necessary to photovoltaic performance. Moreover, photovoltaic performance was disappeared when TBAI and TBAOH were used as electrolyte solution; this is indicated that huge structure of electrolyte acted as barrier to block electron transfer. Therefore, the mechanism was proved.

### 2.6.3 CdS OD

CdS is the most active research one due to their advantages such as narrow bandgap of 2.42 eV, promoting the carrier transfer and enhancing the visible light absorption capability. These properties can be enhanced more when combine CdS with ZnO (Zou *et al.*, 2013).

### 2.6.4 ZnS OD

ZnS is also a kind of important semiconductor. It has the largest bandgap among II-VI compounds. Moreover, it is well-known luminescent material which widely used in many applications such as flat-panel displays, electroluminescent devices, sensors, lasers and photocatalysts. Therefore, ZnS have been studied (Rani *et al.*, 2013).

### 2.6.5 Ag<sub>2</sub>S OD

Ag<sub>2</sub>S is nontoxic, inert to oxidation and possesses a narrow bandgap (1.0 eV) (Pathan *et al.*, 2001). Moreover, energy level configuration can induce vectorial transfer of photo generated charges and avoid reverse injection of photo induced electrons that usually occurred in CdS (Ji *et al.*, 2013). While the problems of commercial ZnO such as fast recombination rate of the photoexcited electron-hole pairs are concerned. Therefore, commercial ZnO can be enhanced the efficiency using Ag<sub>2</sub>S (Subash *et al.*, 2013).