CRUDE DYES EXTRACTED FROM PLANTS AND *MONASCUS* RICE CULTURES AS SENSITIZERS IN SOLID-STATE DYE-SENSITIZED SOLAR CELLS

INTRODUCTION

Traditional fossil fuel energy sources are finite and release waste products into the atmosphere, such as NO_2 and CO_2, that are detrimental to the earth' s global environment. As a result, alternative energy sources are receiving increasing attention. Examples include wind, hydroelectric and solar power. In particular, solar power is attractive because the sun is the biggest energy source of the world. In 1991, O' Regan and Grätzel discovered a new type of solar cell which is called "dye–sensitized solar cell (DSSC)". DSSCs have attracted a great deal of interest as they offer high energy conversion efficiencies at low cost. Dye-sensitized solar cell based on electrochemistry at the interface between a dye adsorbed onto a porous network of nanometer-sized titanium dioxide particles and electrolyte. The components of dye-sensitized solar cell is shown in Figure 1.

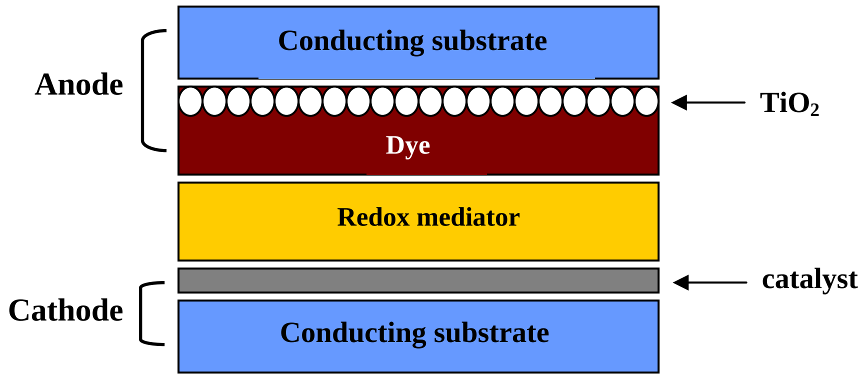


Figure 1 The components of dye-sensitized solar cell

The dye-sensitized solar cell consists of anode (working electrode), cathode (counter electrode) and redox mediator. Anode consists of a dye adsorbed onto a porous of nanometer-sized titanium dioxide (TiO_2) particles which is deposited onto a transparent conducting substrate. The dye molecule which is adsorbed onto a porous of TiO_2 is called sensitizer. Cathode consists of a catalyst such as platinum (Pt), carbon (C) coated onto a conducting substrate. And redox mediator is an electrolyte solution which is filled between anode and cathode. Normally, redox mediator consists of iodide (I^-) and triiodide (I_3^-).

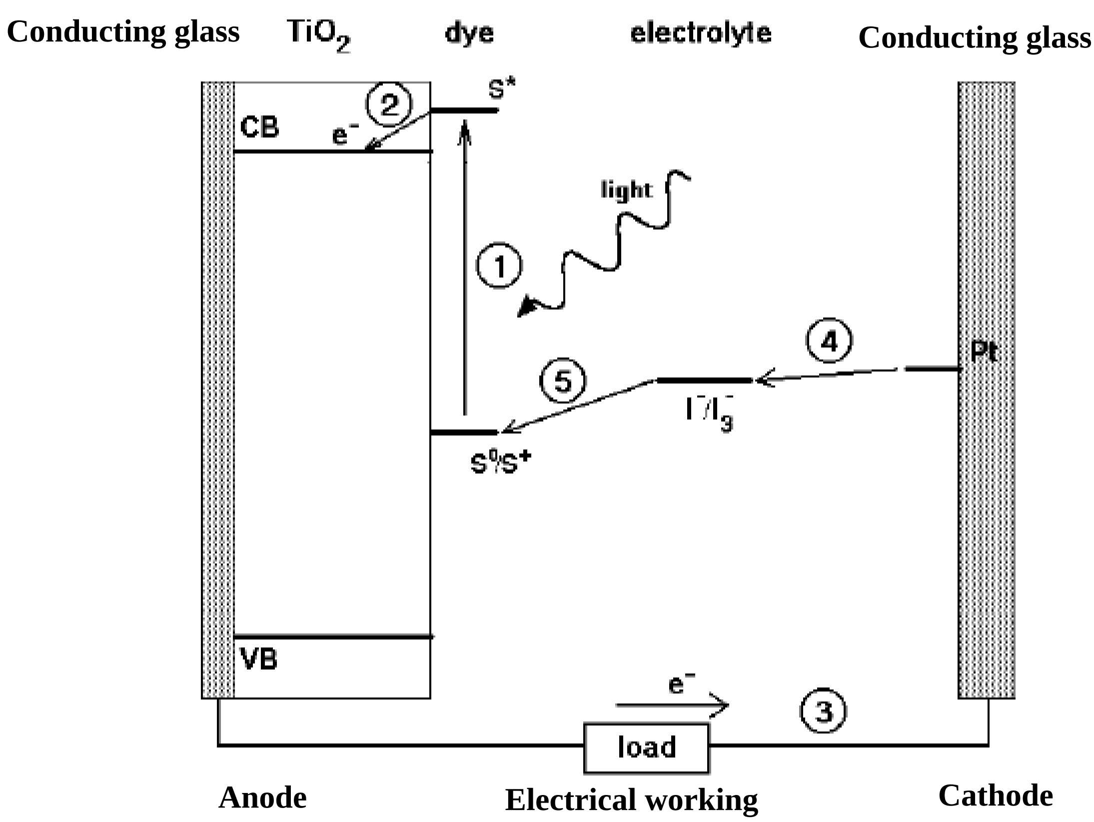


Figure 2 The working principle of the dye-sensitized solar cell.

The regenerative working cycle of the dye-sensitized solar cell is depicted in Figure 2. The incoming photon is absorbed by the dye molecule adsorbed on the surface on the nanocrystalline TiO_2 particle and an electron from a molecular ground state S^0 is exited to a higher lying excited state S* (1). The exited electron is injected to the conduction band (CB) of the TiO_2 particle leaving the dye molecule to an oxidized state S^+ (2). The injected electron percolates through the porous nanocrystalline structure to the transparent conducting layer of the glass substrate (negative electrode, anode) and finally through an external load to the counter-electrode (positive electrode, cathode) (3). At the counter-electrode the electron is transferred to triiodide in the electrolyte to yield iodide (4), and the cycle is closed by reduction of the oxidized dye by the iodide in the electrolyte (5). From this cycle, the cell can generate electric current.

The operating cycle can be summarized in chemical reaction terminology as

Anode : $S + h\nu \longrightarrow S^*$ Absorption (1)

$S^* \longrightarrow S^+ + e^- (TiO_2)$ Electron injection (2)

$2S^+ + 3I^- \longrightarrow 2S + I_3^-$ Regeneration (3)

Cathode : $I_3^- + 2e^- (Pt) \longrightarrow 3I^-$ (4)

Cell : $2e^- (Pt) + h\nu \longrightarrow 2e^- (TiO_2)$ (5)

The solar cell performance is determined by its overall energy conversion efficiency (η). When an external load is connected to the illuminated solar cell, the highest total current value (short-circuit current, I_{sc}) is obtained under short-circuit condition (voltage = o) and the maximum voltage value (open-circuit voltage, V_{oc}) is obtained under open-circuit condition (no current can flow) as seen from the current-voltage (I-V) curve under illumination in Figure 3. The maximum power, P_{max}, which can be delivered, $P_{max} = I_{mp} \times V_{mp}$, is indicated by the area of the rectangle in Figure 3. From the maximum power point, the fill factor (FF) can be calculated, which is a quantitative measurement of the device quality defined by the squareness of the I-V curve. The fill factor (FF) is defined as

$$FF = \frac{I_{mp} V_{mp}}{I_{sc} V_{oc}} \tag{6}$$

The overall energy conversion efficiency (η) of a solar cell is defined as the power produced by the cell (P_{mp}) divided by the power incident on the representative area of the cell (P_{light}):

$$\eta = \frac{P_{mp}}{P_{light}} = \frac{I_{mp}V_{mp}}{P_{light}} = \frac{I_{sc}V_{oc}FF}{P_{light}} \tag{7}$$

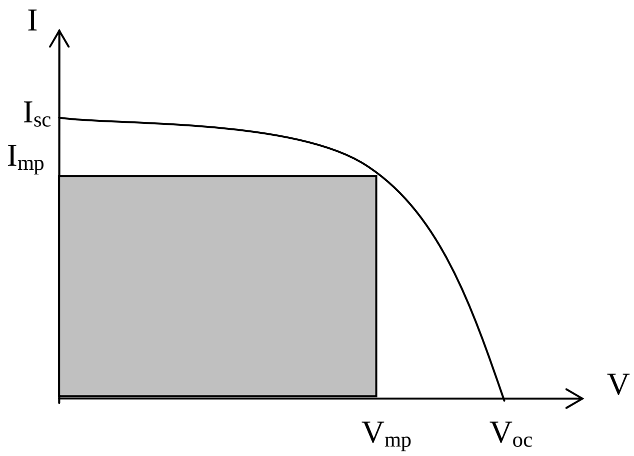


Figure 3 I-V curve of a solar cell under illumination

To achieve a high energy conversion efficiency in the dye-sensitized solar cell, the properties of the nanocrystalline TiO_2 film, the dye molecule (sensitizer) as attached to the TiO_2 particle surface and the electrolyte are essential. In this thesis, the properties of the dye molecule (sensitizer) are focused. The desirable properties of dye molecule (sensitizer) can be summarized as:

1. *Absorption***:** The dye molecule should absorb all wavelength below a threshold wavelength of about 920 nanometers.

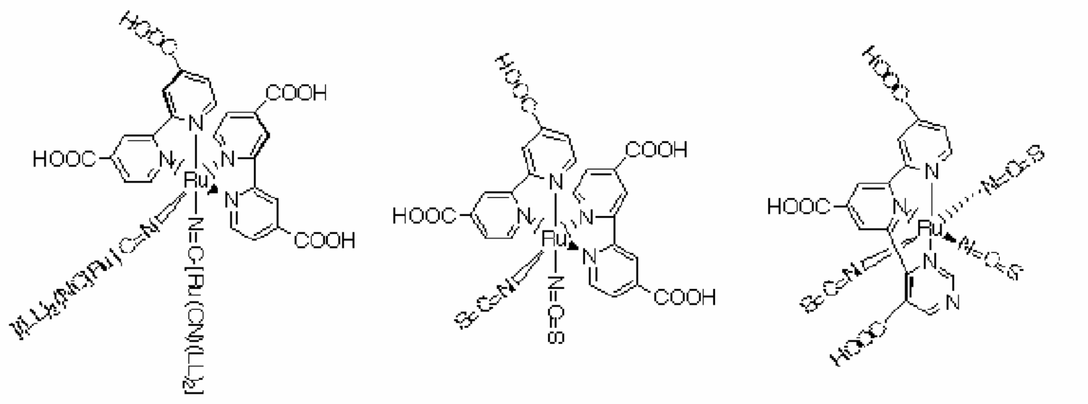
2. *Energetics:* The energy level of the excited state should be well matched to the lower bound of the conduction band of the oxide to minimize energetic losses during the electron transfer reaction.

3. *Interfacial properties:* The dye molecule must also carry attachment groups such as carboxylate or phosphonate to firmly graft it to the semiconductor oxide surface.

4. *Stability:* The adsorbed dye molecule should be stable enough in the working environment (at the semiconductor-electrolyte interface) to sustain about 20 years of operation at exposure to natural daylight.

5. *Practical properties:* e.g. high solubility to the solvent used in the dye impregnation.

Ruthenium (Ru) complex dyes, the molecular structures of which are as shown in Figure 4, have been mainly used as sensitizer in dye-sensitized solar cells. They have good photoelectric properties, but have some drawbacks such as high cost, scanty resources of Ru and biological toxicity. Therefore organic dyes, for example chlorophyll, coumarin, polyene, merocyanine, indoline and anthocyanins, have been tested as sensitizer.



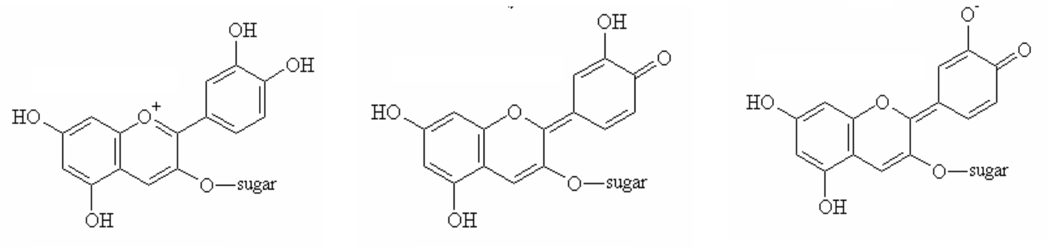
[Ru(dc-bpyH$_2$)$_2${(CN)$_2$Ru(LL)$_2$}$_2$] [Ru(dc-bpyH$_2$)$_2$(NCS)$_2$] [Ru(tc-terpyH$_3$)(NCS)$_3$]

Figure 4 Molecular structures of three ruthenium (Ru) complex dyes. From left: a trinuclear Ru dye, the N3 dye, and the black dye.

In previous report, fresh extracts of fruits, including chaste tree fruit (maria-preta, *Solanum americanum*, Mill.), mulberry (amora, *Morus alba*, L.), California blackberry (*Rubus ursinus*) and cabbage palm fruit (açai, *Euterpe oleracea*, Mart), were used as natural sensitizers in dye-sensitized photoelectrochemical solar cell. In this work other natural dyes from roselle (*Hibiscus sabdariffa*, L.) and turmeric (*Curcuma longa*, L.) disseminated around in Thailand and *Monascus* pigments obtained from cultivation of *Monascus* mold on rice solid culture are studied for alternative natural sensitizers in dye–sensitized solar cells.

Roselle

Roselle (*Hibiscus sabdariffa*, L.) is a crop widely cultivated in Thailand and tropical countries. The flowers of roselle are used to produce a red, pleasant flavored extract for use as a food and beverage in a number of tropical countries. The roselle flowers contain high content of anthocyanin pigments, the molecular structures of which are as shown in Figure 5.

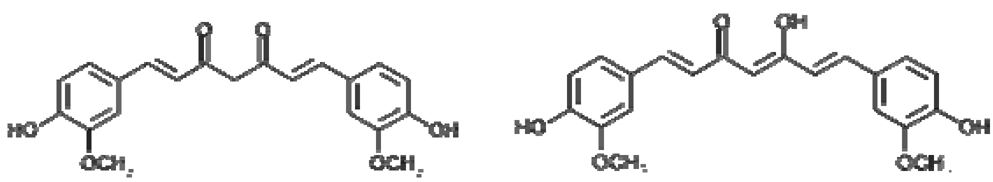


Red at pH = 3 Violet at pH = 7-8 Blue at pH > 11

Figure 5 Molecular structures of anthocyanin at various pH

Turmeric

Turmeric (*Curcuma longa*, L.) is used to give a yellow color to some prepared mustards, canned chicken broth, and other foods. Its active ingredient is curcumin. It is a significant ingredient in most commercial curry powders. The active substance of turmeric is the polyphenol curcumin, also known as C.I. 75300, or Natural Yellow 3. Systematic chemical name is (1*E*,6*E*)-1,7-bis(4-hydroxy-3-methoxyphenyl)-1,6-heptadiene-3,5-dione, the molecular structures of which are as shown in Figure 6. It can exist at least in two tautomeric forms, keto and enol. The keto form is preferred in solid phase and the enol form in solution.



Curcumin Keto form **Curcumin Enol form**

Figure 6 Molecular structures of Curcumin

***Monascus* pigment**

Red yeast rice, also known as “Red Koji” or “Ang-kak”, obtained as a culture of fungal species of the genus *Monascus* on rice has long been used in East Asia as a natural food colorant, e.g. for red rice wine, red soy bean cheese, meat products and fish. *Monascus* pigments are secondary metabolites possessing an azaphilone skeleton examples are: orange pigments, e.g. monascorubrin and rubropunctatin, which possess the oxo-lactone ring; red pigments, e.g. monascorubramine and rubropunctamine, the nitrogen analogues of the orange pigment; and yellow pigments such as monascin and ankaflavin. The molecular structures of pigments isolated from *Monascus* pigment are shown in Figure 7.

	R
Yellow	
Monascin	n-C_5H_{11}
Ankaflavin	n-C_7H_{15}
Orange	
Rubropunctatin	n-C_5H_{11}
Monascorubin	n-C_7H_{15}
Red	
Rubropunctamine	n-C_5H_{11}
Monascorubramine	n-C_7H_{15}

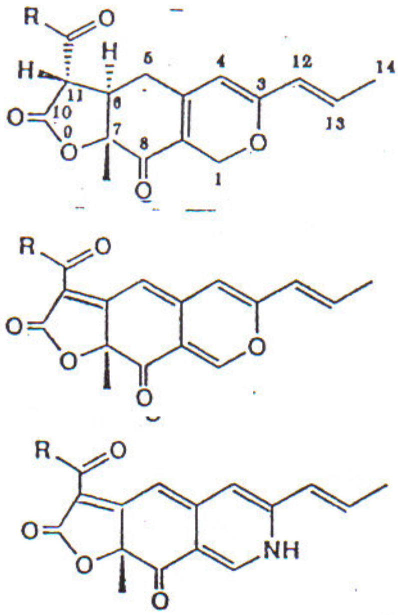


Figure 7 Molecular structures of pigment isolated from *Monascus* pigment

The objective of this work is to study optimum condition of crude dyes extracted from roselle, turmeric and *Monascus* rice cultures which are used as sensitizers in dye-sensitized solar cells and to study efficiency and durability of dye-sensitized solar cells when these dyes are used as sensitizers.