LITERATURE REVIEW

1. Natural dyes as sensitizers for dye-sensitized solar cell using liquid electrolyte

Nerine J. Cherepy *et al.* (1997) reported that a photoelectrochemical cell utilizing flavonoid anthocyanin dyes extracted from blackberries was shown to convert sunlight to electrical power at an efficiency of 0.56% under full sun. Fluorescence quenching was observed for the excited state of the TiO_2-adsorbed anthocyanin dye, cyanin, and the photocurrent spectrum correlated well with the optical absorption of the cyanin-sensitized TiO_2 nanocrystalline film. The incident photon-to-current efficiency of 19% at the peak of the visible absorption band of the dye, the open-circuit voltages of 0.5-0.4 V, and short-circuit photocurrents of 1.5-2.2 mA/cm^2 were remarkable for such a simple system and suggest efficient charge carrier injection.

Alfredo Olea *et al.* (1999) investigated the functioning of black berry extract to sensitize TiO_2 for light absorption. TiO_2 thick films were screen-printed and sintered at 450°C in air. It was sensitized with a fruit extract, for example black berry extract that contained anthocyanin kind of organic dye. The black berry extract sensitized TiO_2 exhibited an increase in the photocurrent response indicating excess generation of photoelectrons due to light absorption by the extract. The photocurrent response in this case depended on parameters such as soaking time of TiO_2 in black berry juice, period of illumination, etc. The maximum current (I_{max}), the maximum voltage (V_{max}), and the overall energy efficiency (η) of dye-sensitized solar cell for a 4 cm^2 active area cell were estimated to be 4 mA, 300 mV, and 1%, respectively.The black berry extract was analyzed by optical absorption spectroscopy to characterize its absorption band. An absorption peak was observed at 517 nm, the intensity of which depends on the concentration of the black berry extract.

Christian Graziani Garcia *et al.* (2003) presented that fresh extracts of chaste tree fruit ("maria-preta", *Solanum americanum,* Mill.), mulberry ("amora", *Morus alba,* L.) and cabbage-palm fruit ("açaí", *Euterpe oleracea,* Mart) were employed as TiO_2 sensitizers in thin-layer sandwich-type photoelectrochemical solar cells. Conversion of visible light into electricity was accomplished with natural sensitizers resulting in I_{sc} and V_{oc} values similar to those obtained employing traditional synthesized dyes. The short-circuit current (I_{sc}) obtained from 0.5 cm^2 of dye-sensitized solar cells using the fresh extracts of chaste tree fruit, mulberry and cabbage-palm fruit as sensitizers were 1.06, 0.86 and 0.37 mA, respectively. And the open-circuit voltage (V_{oc}) obtained from 0.5 cm^2 of dye-sensitized solar cells using the fresh extracts of chaste tree fruit, mulberry and cabbage-palm fruit as sensitizers were 390, 422 and 442 mV, respectively. Fill-factor values from 0.40 to 0.61 were obtained with the fruit extracts.

Sancun Hao *et al.* (2006) reported that the dye-sensitized solar cells (DSSCs) were assembled by using natural dyes extracted from black rice, capsicum, erythrina variegata flower, rosa xanthina, and kelp as sensitizers. The short-circuit current (I_{SC}) from 1.142 mA to 0.225 mA, the open-circuit voltage (V_{OC}) from 0.551 V to 0.412 V, the fill factor from 0.52 to 0.63, and maximum power (P_{max}) from 58 μW to 327 μW were obtained from the DSSC sensitized with natural dye extracts using liquid electrolyte. In the extracts of natural fruit, leaves and flower chosen, the black rice extract performed the best photosensitized effect, which was due to the better interaction between the carbonyl and hydroxyl groups of anthocyanin molecule on black rice extract and the surface of TiO_2 porous film. The blue-shift of absorption wavelength of the black rice extract in ethanol solution on TiO_2 film and the blue-shift phenomenon from absorption spectrum to photoaction spectrum of DSSC sensitized with black rice extract were discussed in the paper. Because of the simple preparation technique, widely available and low cheap cost natural dye as an alternative sensitizer for dye-sensitized solar cell is promising.

2. Organic dyes as sensitizers for dye-sensitized solar cell

Qiao-Hong Yao *et al.* (2003) synthesized four hemicyanine derivatives, 2-[4-(*N*-ethyl-*N*-carboxyethyl)amino]phenylethenyl-1,3,3-trimethyl-3*H*-indolium iodide (BIDC1), 2-[4-(*N*,*N*-dicarboxyethyl)amino] phenylethenyl-1,3,3-trimethyl-3*H*-indolium iodide (BIDC2), 2-[4-(*N*-ethyl-*N*-carboxyethyl) amino]phenylethenyl-1,1,3-trimethyl-1*H*-benz[*e*]indolium iodide (BIDC3) and 2-[4-(*N*,*N*-dicarboxyethyl)amino]phenylethenyl-1,1,3-trimethyl-1*H*-benz[*e*] indolium iodide (BIDC4), the molecular structures of which are shown in Figure 8. It was found that the absorption spectra of BIDC3 and BIDC4 were broader than that of BIDC1 and BIDC2 because the former two had one more benzene ring on the electron acceptor side. Among the four hemicyanine dyes, BIDC4 generated the highest photoelectric conversion yield of 4.9%, with a short-circuit photocurrent of 21.4 mA cm^{-2}, an open-circuit voltage of 424 mV, and a fill factor of 0.49 under irradiation with 90.0 mW cm^{-2} white light from a Xe lamp.

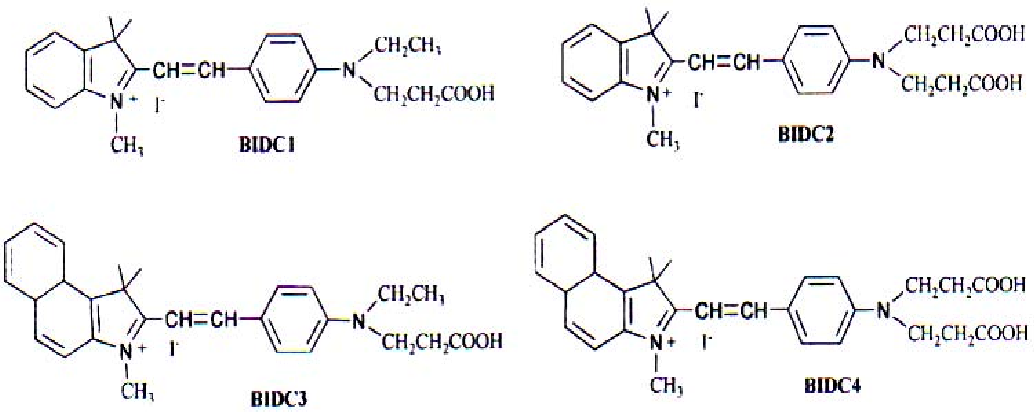


Figure 8 Molecular structures of (BIDC1), (BIDC2), (BIDC3) and (BIDC4)

Hideo Otaka *et al*. (2004) reported that multi-colored solar cells sensitized with organic dyes were developed by optimizing electrolytes and counter electrodes to enhance the transparence by reducing the concentration of iodine dissolved in the imidazolium-based electrolytes and by employing a platinum layer of 0.5 nm thickness. The solar cells were assembled by using nano-crystalline TiO_2 electrodes adsorbing sensitizing dyes, an electrolyte consisting of a mixture of iodine and 1-butyl-3-methylimidazolium iodide in a 0.2:10 molar ratio and the counter platinum electrode to give cells bearing red, purple, blue, green and black colors. The multi-colored solar cells were connected in series to exhibit a 2.1% conversion efficiency, 27.9 mA short-circuit current (I_{sc}) and 3.03 V open-circuit voltage (V_{oc}) under AM 1.5 (1 sun, 100mWcm^{-2}.) irradiation with a total semiconductor area of 25 cm^2.

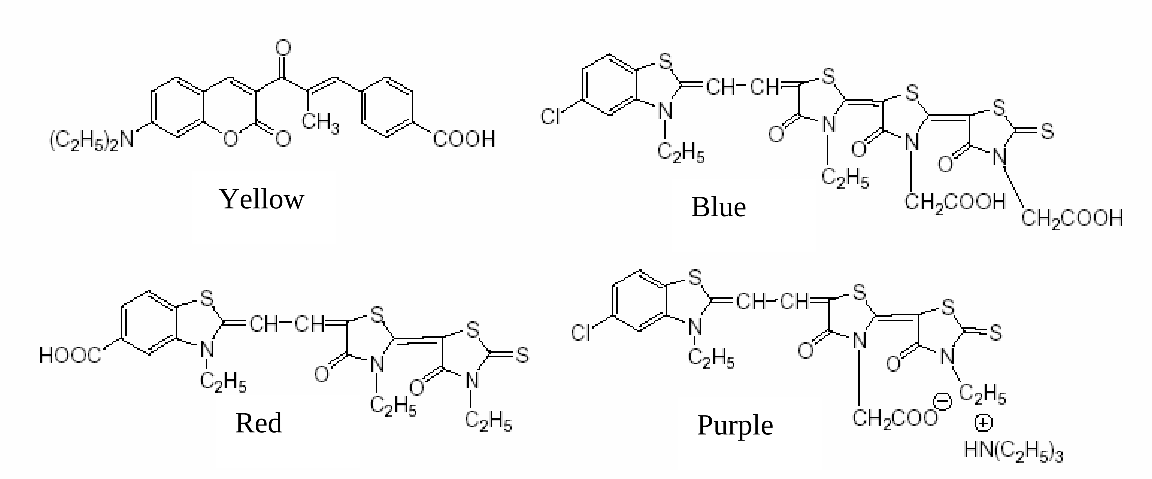


Figure 9 Molecular structures of sensitizing dyes in Hideo Otaka *et al.*'s report

Ravi Mosurkal *et al.* (2004) studied various commercially available organic dyes with catechol groups, triphenylmethyne dye, anthraquinone dye and xanthene dye, as sensitizers for dye-sensitized solar cells. The absorption maxima of these dyes ranges from 470 to 570 nm with cut off wavelengths at around 700 nm which, makes them potential candidates for light harvesting in dye-sensitized solar cells. All dyes showed quasi-reversible wave with oxidation potentials ranging from +0.6 to 0.9 V versus SCE. From the results, a xanthene dye, 9-phenyl-2, 3, 7-trihydroxy-6-fluorone, as shown in Figure 10, was found to be efficient sensitizer in dye-cells sensitized solar compared to other dyes when a liquid electrolyte was used. The short-circuit photocurrent density (I_{SC}), the open-circuit photovoltage (V_{OC}), the fill factor (FF) and the overall energy efficiency (η) were estimated to be 3 mAcm.$^{-2}$, 443 mV, 33% and 0.74%, respectively.

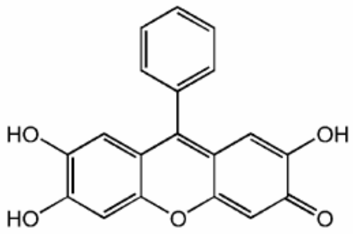


Figure 10 Molecular structure of 9-phenyl-2,3,7-trihydroxy-6-fluorone

T. Matsubara *et al.* (2004) tested xylenol orange (3,3’-bis[N,N-di(carboxymethyl)aminomethyl]-o-cresolsulfonephthalein), which was a water-soluble dye of the triphenylmethane group for a dye-sensitized solar cells. The observed short-circuit current (2.2 mAcm^{-2}) was compared with the theoretical value (3.8 mAcm^{-2}) which was estimated from the radiation spectrum of light source and the absorption spectrum of adsorbed dye on TiO_2. The overall energy efficiency was 1.3%. The addition of 05 M water in the electrolyte did not show a bad effect. A molecule of xylenol orange occupied 1.48 nm^2 of the TiO_2 surface. The roughness factor of the utilized TiO_2 electrode was 630.

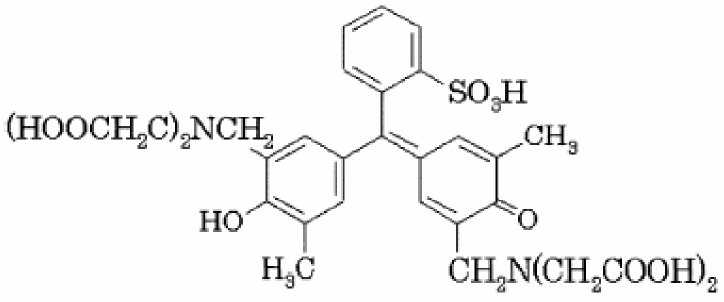
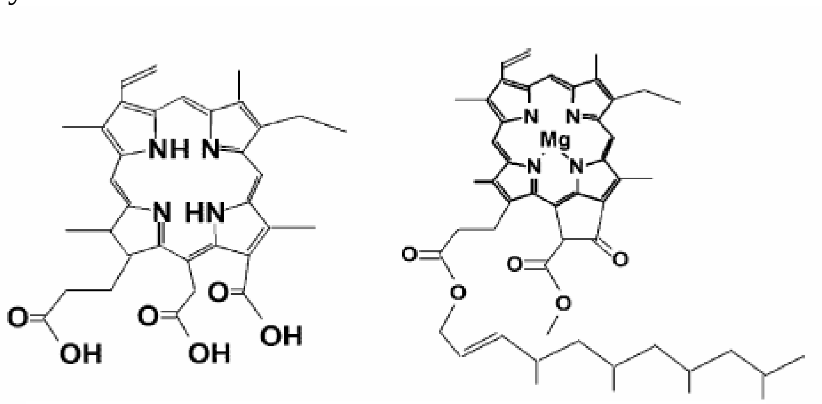


Figure 11 Molecular structure of xylenol orange

Yutaka Amao *et al.* (2004) used chlorophyll-a derivative, chlorine-e_6 (Chl-e_6) immobilized TiO_2 film electrode as working electrode for a dye-sensitized solar cell. The short-circuit photocurrent density (I_{SC}), the open-circuit photovoltage (V_{OC}), and the fill factor (FF) of solar cell consisting of Chl-e_6 immobilized on TiO_2 film electrode and platinum-coated substrate electrode using liquid electrolyte were estimated to be 1.47mAcm.$^{-2}$, 425mV, and 57.0%, respectively. The monochromatic incident photo-to-electron conversion efficiency (IPCE) at 400, 541 and 661 nm were 11.0, 4.7 and 7.9%, respectively.



Chlorine-e_6 (Chl-e_6) **Chlorophyll-a**

Figure 12 Molecular structure of chlorine-e_6 (Chl-e_6) and chlorophyll-a

Masaki Matsui *et al.* (2005) synthesized and examined novel near-infrared absorbing heptamethine cyanine dyes derived from indole, benzoxazole, benzothiazole and quinoline as sensitizers for a zinc oxide solar cell. A 2-carboxyphenylthio-substituted indolium heptamethine cyanine dye showed incident photon-to-current efficiency (IPCE) of 4.17% at 804 nm. The short-circuit photocurrent density (I_{SC}), the open-circuit photovoltage (V_{OC}), the fill factor (FF) and the overall energy efficiency (η) were estimated to be 0.73 mAcm^{-2}., 370 mV, 55% and 0.16%, respectively

Xiuying Chen *et al.* (2005) synthesized two novel cyanine dyes (Sqb and Cyb3 the molecular structures of which are shown in Figure 8.) with carboxylbenzyl group and different methine chains as solar cell sensitizers and investigated the photoelectrochemical behaviors of the TiO_2 nanocrystalline electrode sensitized by them. The results showed that the short-circuit current, I_{sc} (2.76 mA/cm^2), the open-circuit voltage, V_{oc} (455 mV/cm^2) monochromatic incident photon-to-current conversion efficiency, *IPCE* (46%) and the $_o$ overall energy efficiency, η (1.7%) of TiO_2 nanocrystalline solar cell sensitized by Sqb were higher than that of TiO_2 nanocrystalline solar cell sensitized by Cyb3 when TiO_2 nanostructured porous film was 6.5 μm thick and was sensitized for 6 h and 4 h, respectively.

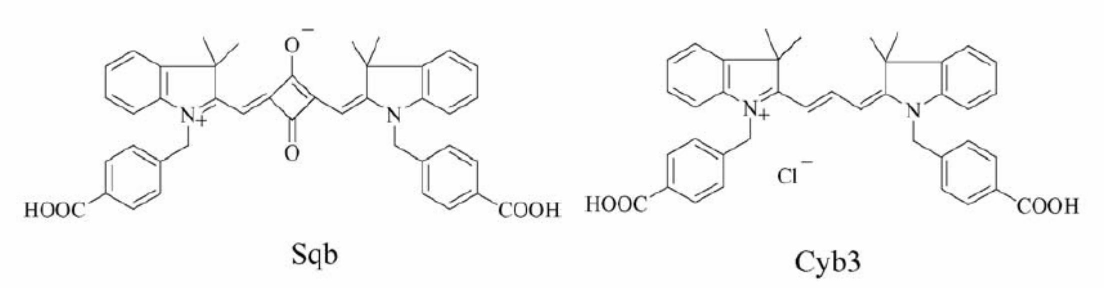


Figure 13 Molecular structure of Sqb and Cyb3

3. Inorganic dyes as photosensitizers for dye-sensitized solar cell

M.K. Nazeeruddin *et al.* (1993) prepared cis–X_2Bis(2,2'-bipyridyl-4,4'-dicarboxylate)ruthenium(II) complexes (X = Cl^-, Bl^-, CN^-, and SCN^-). They act as efficient charge-transfer sensitizers for nanocrystalline TiO_2 films (thickness 8-12 μm) of very high internal surface area (roughness factor ca. 1000), prepared by sintering 15-30 nm colloidal titania particles on a conducting glass support. Short-circuit currents exceeding 17 $mAcm^{-2}$ were obtained in simulated AM 1.5 sunlight using lithium iodide/triiodide in acetonitrile or acetonitrile/3-methyl-2-oxazolidinone mixtures as redox electrolyte. The open-circuit voltage was 0.38 V and increased to 0.72 V by treating the dye-covered film with 4-tert butylpyridine. An energy conversion efficiency of 10% was attained with this system.

P. M. Jayaweera *et al.* (2001) had found that when di(aqua)bis(oxalato) iron(II) moiety ($[Fe(II)(H_2O)_2(C_2O_4)_1]^{2-}$) was complexed with bromopyrogallol ligand and used as the sensitizing dye material, the photovoltaic properties was enhanced on comparing with the photovotaic cells coated by bromopyrogallol ligand only. Complexation of bromopyrogallol ligand with di(aqua)bis (oxalato)iron(II) moiety ($[Fe(II)(H_2O)_2(C_2O_4)_1]^{2-}$) has increased the cell efficiency from 0.2 to 0.3%, the short-circuit current (I_{sc}) from 0.83 to 1.23 $mAcm^{-2}$ and the open-circuit current (V_{oc}) from 411 to 423 $mVcm^{-2}$. Electrochemical and absorption spectroscopic data suggested the nature of the lowest electronic transition of iron(II) complex as a $\pi^*_{(bpr)} \leftarrow d\pi_{(Fe)}$, metal to ligand charge transfer transition. Photovoltaic cells coated with bromopyrogallol ligand complexed with iron(II) showed higher stability for photodegradation with a UV radiation blocking filter and better incident photocurrent conversion efficiency.

S. Anandan *et al.* (2005) reported that dye-sensitized TiO_2 solar cells were fabricated using tridentate ligand ruthenium(II) complexes, [Ru(dcbpy) (tptz)X]X (where dcbpy = 4,40-dicarboxy-2,20-bipyridine, tptz = 2,4,6-Tris(2-pyridyl)-s-triazine and X = Cl^-, SC N^-, CN^-) attached to sol–gel processed TiO_2 electrodes. The ligand tptz functions as spectator ligand and dcbpy functions as the anchoring ligand with sufficient visible light absorption. The synthesized complexes were characterized by spectroscopy and electrochemical techniques before assembling as solar cells. The short-circuit current, I_{sc} from 23 to 255 μA, the open-circuit voltage, V_{oc} from 210-325 mV, monochromatic incident photon-to-current conversion efficiency, *IPCE* from 4.59 to 49.72% and the overall energy efficiency, η from 0.28 to 6.15% were obtained from dye-sensitized solar cells using these complexes as sensitizers with 1.2 $mWcm^{-2}$ illuminator.

4. Solid-state dye-sensitized solar cell

Dong-Won Kim *et al.* (2005) prepared a gel polymer electrolyte by soaking a porous membrane in an organic electrolyte solution containing the I_3^- /I^- redox couple. The ionic conductivity of the gel polymer electrolyte is 2.7 x 10^{-3} Scm^{-1} at room temperature, and encapsulates the electrolyte solution well without solvent leakage. A dye-sensitized solar cell (DSSC) employing the gel polymer electrolyte and using *cis*-bis(isothiocyanato) bis(2,2'-bipyridyl-4,4'-dicarboxylato)-ruthenium(II) as photosensitizer gives an open-circuit voltage of 0.72 V and a short-circuit current of 6.27 $mAcm^{-2}$ at an incident light intensity of 100 $mWcm^{-2}$. This yields a conversion efficiency of 2.4%. The DSSC employing the gel polymer electrolyte shows a more stable photovoltaic performance than a DSSC assembled with liquid electrolyte.

E. Chatzivasiloglou *et al*. (2005) synthesized, characterized and used the complex $[Ru(II)(dcbpyH_2)(Cl_2)]\cdot 2H_2O$ (where $dcbpyH_2$ = 4,4'-dicarboxy-2,2'-bipyridine as shown in Figure 14) as the dye to sensitize nanocrystalline TiO_2 film electrodes. A composite polymer solid-state electrolyte was developed and incorporated into the corresponding dye-sensitized solar cells. The cells under direct sunlight illumination, produced a photocurrent as high as 0.84 $mAcm^{-2}$ and a photovoltage of 618 mV, yielding an overall energy conversion efficiency of 0.27%.

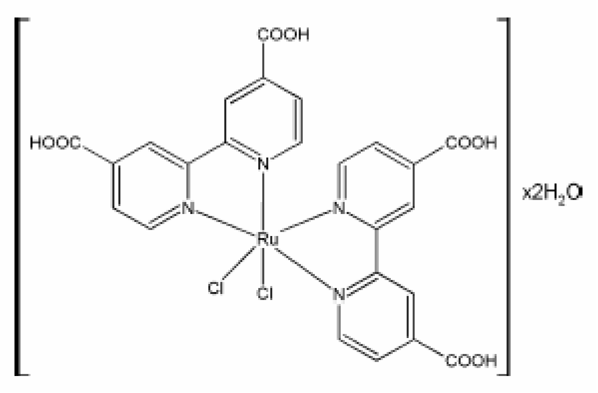


Figure 14 Molecular structure of $[Ru(II)(dcbpyH_2)(Cl_2)]\cdot 2H_2O$ (where $dcbpyH_2$ = 4,4'-dicarboxy-2,2'-bipyridine)

V.P.S. Perera *et al.* (2005) described construction of a semiconductor-dye heterostructure of the configuration n-TiO_2/D1/*p-CuSCN*/D2/*p-CuSCN*/D3/ p-CuSCN as shown in Figure 15. (n-TiO_2 is the nanocrystalline TiO_2 film deposited on conducting glass, *p-CuSCN* = ultra-thin (~2 nm) layers of Cu(I) thiocyanate, p-CuSCN = thick layer of p-CuSCN , D1=Fast Green, D2=Rhodamine 6G and D3= Acridine Yellow). It is found that this heterojunction generates photovoltaic response to light absorption by all the three dyes. The mechanism involved is suggested to be transfer of electrons to n-TiO_2 and holes to p-CuSCN via tunneling. This technique could be a strategy to broaden the spectral response and enhance the efficiency of dye-sensitized solar cells. The short-circuit photocurrent (I_{SC}), the open-circuit photovoltage (V_{OC}) and the overall energy efficiency (η) of the configuration n-TiO_2/D1/*p-CuSCN*/D2/*p-CuSCN*/ D3/p-CuSCN were estimated to be 4.5 mAcm.$^{-2}$, 650 mV and 1.5%, respectively.

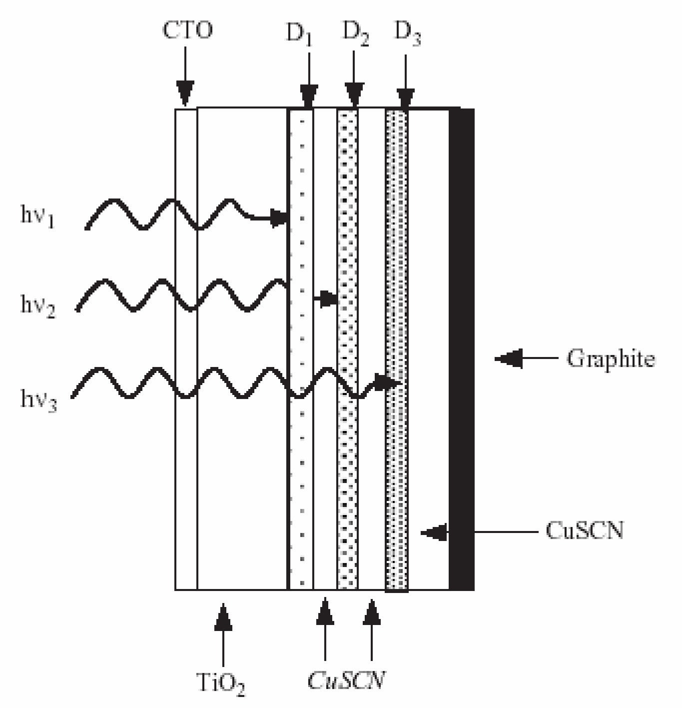


Figure 15 A schematic diagram showing the construction of the 3-dye cell

Weiying Li *et al.* (2005) investigated the characteristics of electrolytes containing novel polymer quarternary ammonium iodide, polysiloxane with quarternary ammonium side groups (PSQAS). PSQAS exhibits a single-anionic conductivity and has special advantages over usually used iodides in dye-sensitized solar cells. Electrolytes based on PSQAS exhibited the maximum ambient conductivity (25 °C) of 4.96 x 10^{-3} Scm^{-1}. The polymer gel electrolyte based on PAN and PSQAS has been employed to fabricate quasi-solid-state dye-sensitized solar cell using *cis*-di(thiocyanato)-*N*,*N*_-bis(2,2'-bipyridyl-4,4'-dicarboxylic acid) ruthenium(II) complex ($[RuL_2(NCS)_2]$) as sensitizer with an overall conversion efficiency of 2.67% at irradiation of 100 $mWcm^{-2}$.

G.R.A. Kumara *et al.* (2006) reported that a dye-sensitized solar cell was made by coating pigments in an extract from shiso leaves on a nanocrystalline film of TiO_2. Leaves of this plant contain two anthocyanin pigments referred to as shisonin and malonylshisonin (structure as shown in Figure 16) as well as chlorophyll and other photosynthetic pigments. It was found that a solid-state solar cell made with a nanocrystalline film of TiO_2 sensitized with an extract of shiso leaves and p-CuI as a hole collector, gave an efficiency as high as 1.3%, a short-circuit photocurrent of 4.8 mA/cm^2 and an open-circuit voltage of 534 mV. Both shisonin and chlorophyll contribute to light energy harvesting as seen from the photocurrent action spectrum of the cell. This is the first successful example of synergistic sensitization by dye cocktail extracted from a single natural resource.

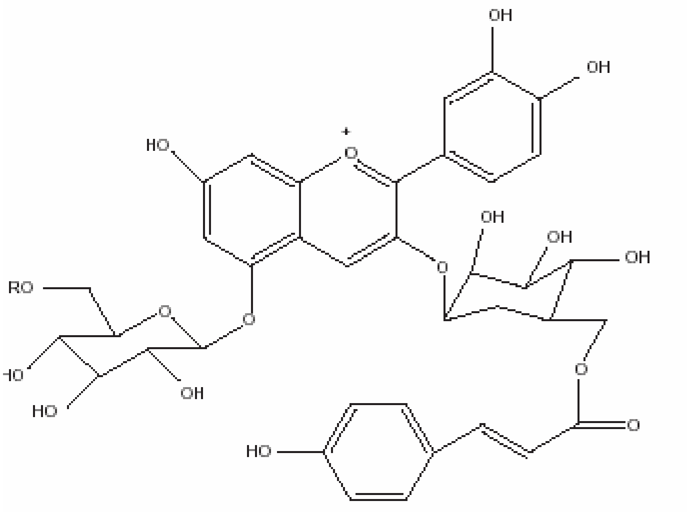


Figure 16 Molecular structure of Shisonin: R = H and Malonylshisonin: R = Malonic acid

5. Voltametric study of dyes

M. Valnice B. *et al.* (1995) reported direct current and differential pulse polarographic and cyclic voltammetric studies of Procion blue MX-R (PB) and Cibacron blue 3GA (CB) and methods for the determination of PB and CB. For both dyes reduction peaks were observed for the two-electron reversible reduction of the anthraquinone moiety, followed by one (CB) and two (PB) reduction processes associated with the reduction of the mono- and dichlorotriazine groups, respectively.

Claudia C.I. Guaratini *et al.* (2001) reported that the electrochemical reduction of two reactive dyes: Procion Red HE-3B 9 (RR120) and Procion Green HE-4BD (RG19) was investigated using cyclic voltammetry, differential pulse and DC_t polarography, chronoamperometry and controlled potential electrolysis at mercury electrodes.

Fatima Esteves *et al.* (2005) investigated the voltammetric behavior of two reactive dyes, C.I.Reactive Orange 16 and C.I.Reactive Blue 19. Cyclic voltammetry technique (CV) on a glassy carbon electrode was used in order to identify the electrochemical activity of the chromophore group in each case, under the experimental conditions.