Twin Pleasures of Plants' Leaves: UV Protection & Sensitizer of DSSC

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Abstract- Plants' leaves can prevent the UV attack although the ozone layer is still damaged by CFC emission due to the activities of human beings, and natural dyes extracted from leaves can be used in dye-sensitized solar cell (DSSC). In this work, the absorbance spectra and light harvesting efficiency (LHE%) of natural dye solutions extracted from the leaves of henna (*Lawsonia inermis*), ironwood (*Xyila xylocarpa*), sour sop (*Annona muricata*), mango (*Mongifera indica*), and marian (*Bouea macrophylla*) have been studied by UV-VIS spectroscopy to protect the effects of UV attack and to use as sensitizer for DSSC. There is 100% LHE between the wavelength of 190 nm and 400 nm for henna, sour sop, mango and marian. According to absorbance and light harvesting efficiency spectra, dye solutions can absorb all UV-C and most of UV-B. So, henna, sour sop, mango and marian leaves can be regarded as the best absorber of high energy photons in the UV region. The band-gap energy of all leaves is 1.8 eV. But the light harvesting efficiency of ironwood between the wavelength of 190 nm and 282 nm is 0%.

Index Terms- absorbance, CFC, DSSC, LHE%, ozone

1. INTRODUCTION

Serious environmental problem due to the large amount of chlorofluorocarbon (CFC) emission in the earth's atmosphere by the activities of human beings can cause the depletion of ozone layer. Ozone means "Smelling" in Greek. It has a very harsh odour. There is 90 percent of total ozone gas of the atmosphere in this layer. The thickness of layer (about 3 mm at STP) varies seasonally and geographically. It composes of three oxygen atoms, symbolized as O_3 and regarded as a shield for human beings to protect the dangers of UV radiation of cosmic rays.

The unit of the total amount of ozone in an overhead column of the atmosphere is Dobson Unit (DU). It is measured by how thick the ozone layer would be if it were compressed into one layer at STP. Every 0.01 mm thickness of the layer is equal to one DU. The average amount of ozone in this layer across the globe is about 300 DU or thickness of only 3 mm at STP. The term "ozone hole" should be applied to regions where the ozone depletion is so severe that levels fall below 200 DU[1][10].

Natural ozone layer exists in the second layer, stratosphere, in the height between 10 km and 50 km above the earth. The production of carbon-dioxide makes green-house effect and CFC emission causes the depletion of ozone layer. When the chemicals contain chlorine and bromine react with ozone layer, the fission of oxygen molecules (O_3) causes the ozone layer depletion. The substances that decrease the thickness of ozone layer are called Ozone Depleting Substances (ODS). They are Chlorofluoro carbon (CFC), Carbon Tetrachloride (CTC), Methyl Chloroform (MCF), Hydro Chlorofluoro Carbon (HCFC). Nowadays, the ozone layer is still being damaged by the activities of human beings.

In DSSC, the absorption of high energy photons in the UV and visible regions, and the broader absorption band are important facts for dye sensitizer. The energy levels of dye sensitizer need to match with the bottom edge of conduction band of semiconductor and the redox potential of electrolyte. It is necessary to make the good chemical bonding between the semiconductor and the dye for effective electron transfer[3-5].

UV radiation is divided into three groups: UV-A, UV-B and UV-C. UV-C has the strongest penetrating power of the three UV groups. Table 1.1

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shows the energy of the photon in the different wavelengths. Ozone layer cannot absolutely absorb UV-A, but it can absorb all of UV-C and most of UV-B. So, most UV-A and less UV-B can reach on the earth's surface. The decrease of thickness of ozone layer or its depletion can cause the problems for human beings and living things due to the falling of the intense unfiltered UV radiation. So, ozone layer is known as the natural cloth of the earth or precious gift for the earth given by Lord[11].

Table 1.1 Energy of various spectra

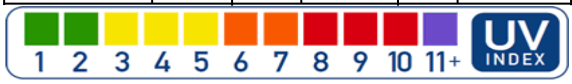
	Spectrum	Wavelength(nm)	Energy(eV)
	IR	1200~700	1~1.8
Visible	Red	700-620	1.8~2
	Orange	620-585	2~2.1
	Yellow	585-570	2.1~2.2
	Green	570-490	2.2~2.5
	Blue	490-440	2.5~2.8
	Indigo	440-420	2.8~2.9
	Violet	420-400	2.9~3
	UV-A	400-315	3~3.9
	UV-B	315-280	3.9~4.4
	UV-C	280~100	4.4~123

Although UV-A in the morning contains the health supports for human beings, the falling of UV-B from 9:00 am to 4:00 pm on the skin of human being thoroughly for 30 minutes can cause the burn of the skin, the skin cancer and the damage of cornea. UV-C with the shortest wavelength has high energy to penetrate into the skin. So, it can cause the immune system and even death, and then destroying the plants and vegetation and the death of aquatic animals. UV-A, falling on the earth, is about 95% and UV-B is about 5%. UV-B can cause the damage of the skin epidermis and the skin cancer. Between 10:00 am and 2:00 pm, 99% of UV-A and 1% of UV-B fall on the earth surface. 98.7% of all UV radiations falling on the earth is only UV-A.

UV-C with very shorter wavelength gives the dangerous conditions for human beings and living things. But it cannot reach on the earth by the filtering of ozone layer. If the ozone layer still exists without any problem, most of UV-A and less UV-B can only reach on the earth. If there is a problem on the ozone layer, all types of UV will fall on the earth, and the damage of all living things and non-living things will be caused by UV-B and UV-C. World Health Organization have developed the Global Solar UV index (UVI), which provides the public with an estimate of UV radiation on any given day, shown in Table 1.2. Everyone needs to avoid outdoor exposures from 10 am to 4 pm if UV index is 8 or higher.

Table 1.2 UV Index

UV Intensity	Minimal	Low	Moderate	High	Very High
International Colour Code	Green	Yellow	Orange	Red	Purple
Index	0~2	3~5	6~7	8~10	≥11



Ozone depletion substance such as CFC is used in refrigerator, air-conditioner, coding spray and foam. Material which contains bromain used in fire stop and Methyl Bromide used in insect killer in agricultural sector have more power than carbon-dioxide to create the depletion of ozone layer. Free chlorine reacts very rapidly with ozone. They also show that chlorine monoxide formed in that reaction undergoes further processes that regenerate the original chlorine, allowing the sequence to be repeated up to 100,000 times. Similar reactions also take place between bromine and ozone. The ozone destroying chain reaction is shown in the following equations.

$$Cl + O_3 \rightarrow ClO + O_2$$
$$ClO + O \rightarrow Cl + O_2$$

The solar system has been in existence over 4.6 billion years ago. The stratospheric ozone layer is not an original part of the earth's atmosphere. It is only a product of life on the earth. Living things could not inhabit on the surface of the earth first due to the intense unfiltered solar UV radiation after the earth. The protection against UV attack by ozone layer causes the existence of living things. But now the activities of human beings have caused the depletion of ozone layer. So there will be a question that which materials can be used to prevent the dangers of UV attack and how do we get UV protection due to the depletion of ozone layer. And then how do we solve the problem of energy crisis in the future, year after year. Planting many trees is a solution because leaves from trees can strongly absorb high energy UV photons in electromagnetic spectrum[1].

In this work, absorbance properties of dye solutions extracted from henna, ironwood, sour sop, mango and marian leaves have been analyzed by UV- VIS spectroscopy to protect UV attack due to the depletion of ozone layer and to use as sensitizer of DSSC. Fig 1.1 shows the electromagnetic spectrum for UV, visible and IR regions with different wavelengths.

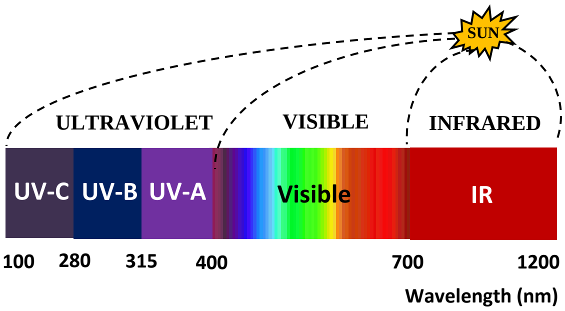


Fig 1.1 Electromagnetic spectrum

II. BACKGROUND THEORY

2.1. UV-VIS Spectroscopy

Ultraviolet visible (UV-VIS) spectroscopy is the measurement of attenuation of the beam of light after passing through the sample. Different molecules absorb radiation with different wavelengths. The absorption in the visible range directly affects the perceived colour of the chemical involved. Absorption of UV-VIS radiation causes electronic transitions from the ground state to the excited state in atoms or molecules. The minimum required energy for electronic transition from valence band to conduction band is known as band-gap energy[2].

The absorbance of a solution is directly proportional to the concentration of the absorbing species in the solution and the path length. So, UV-VIS spectroscopy is also called the absorption spectroscopy in UV-VIS spectral region. The following equation shows Beer-Lambert law for absorption spectroscopy.

$$A = \varepsilon \, c L = \log_{10} \frac{I_0}{I}$$

A = absorbance
ε = molar absorptivity or extinction coefficient
c = concentration of the absorbing species
L = path-length
I_0 = intensity of light before passing through the sample I = intensity of light after passing through the sample

The light harvesting efficiency (LHE%) of dye solutions can be calculated from the absorbance data by the following formula.

$$\%LHE = (1 - 10^{-A}) x 100\%$$

LHE = light harvesting efficiency
A = absorbance

In DSSC, the photon-to-current conversion efficiency (IPCE) is determined by LHE%.

$$IPCE = LHE \, \Phi_{inj} \, \eta_c$$

Φ_{inj} = the quantum yield of electron injection
η_c = the collection efficiency of the injected electrons at the back contact

If Φ_{inj} and η_c are close to 100%, IPCE is equal to LHE. Fig 2.1 shows the photograph of UV-VIS spectrophotometer.

Fig 2.1 UV-VIS spectrophotometer

III. EXPERIMENTAL DETAILS

3.1. Preparation of Dye Solutions

The leaves were cut into small pieces first and grounded using motor and pestle for 10 min. After that, the powder was mixed with deionized water for 24 h and the solution was filtered by the paper filter. Henna leaves and the colour of their dye is shown in Fig 3.1.

Fig 3.1 Henna leaves and their dye solution

As shown in Fig 3.2, the colour of ironwood dye is greenish-brown.

Fig 3.2 Ironwood leaf and its dye solution

Fig 3.3, Fig 3.4 and Fig 3.5 show the leaves and their dye colours for sour sop, mango and marian respectively[6][7][9].

Fig 3.3 Sour sop leaf and its dye solution

Figure 3.3 Mango leaf and its dye solution

Figure 3.2 Marian leaf and its dye solution

3.2. UV-VIS Spectroscopic Analysis

The point on the absorption spectrum of a solution which represents the minimum energy required for electronic transition from the valence band or HOMO level to the conduction band or LUMO level is the absorption edge of the solution. The wavelength at the absorption edge can be used to calculate the energy band-gap of the solution.

$$A = \varepsilon \, c L = \log_{10} \frac{I_0}{I} \quad \& \quad \%LHE = (1 - 10^{-A}) x 100\%$$

are the absorbance and the light harvesting efficiency formulae used in UV-VIS spectroscopy. By using the light intensity before passing through the sample I_0, and that after passing through the sample I, the absorbance of dye solutions extracted from leaves can be studied, and then LHE(%) can be calculated by absorbance data.

IV. RESULTS AND DISCUSSION

4.1 Optical Properties of henna, iron-wood, sour sop, mango and marian leaves' dyes

The photon absorption of dye solution in the UV, visible and IR regions of solar spectrum is important for the protection against UV attack and the sensitizer of DSSC. The broader absorption gives the high performance for UV protection and DSSC sensitization, and the difference between HOMO level and LUMO level of the dyes needs to match with the energy of incident photons to absorb high energy UV photons. In this work, all absorbance data are grouped into three regions such as UV region, visible region and IR region to study.

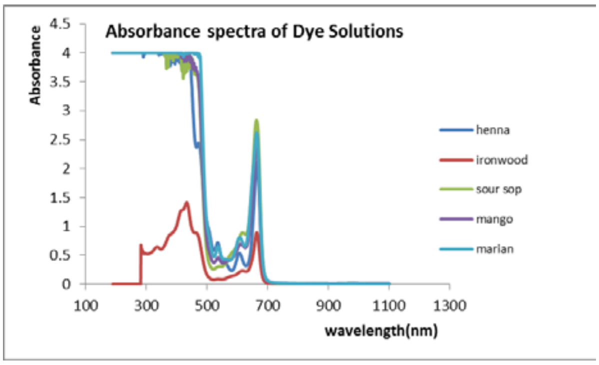


Fig 4.1 Absorbance spectra of dye solutions

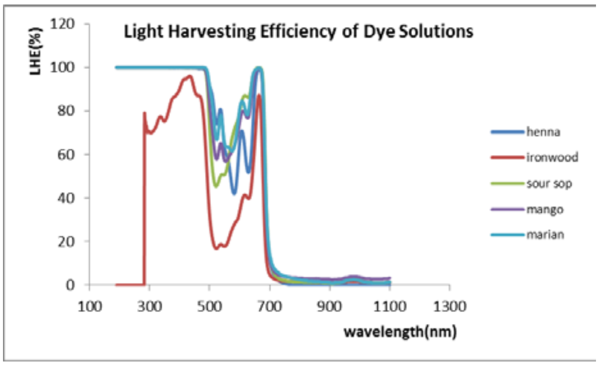


Fig 4.2 Light harvesting efficiencies of dye solutions

Fig 4.1 shows the absorbance spectra of henna, ironwood, sour sop, mango and marian dyes extracted from leaves in Sittway township, Rakhine state, Myanmar. And then light harvesting efficiency of all dyes is shown in Fig 4.2.

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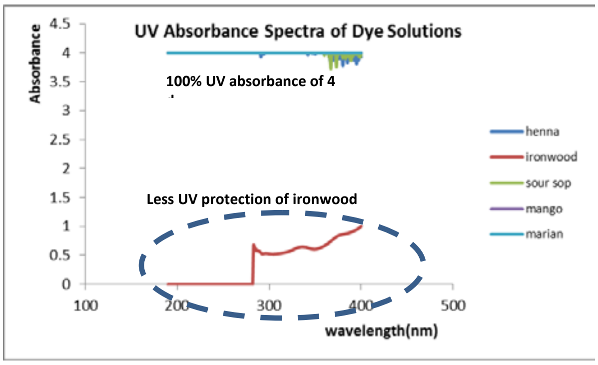


Fig 4.3 UV Absorbance spectra of dyes

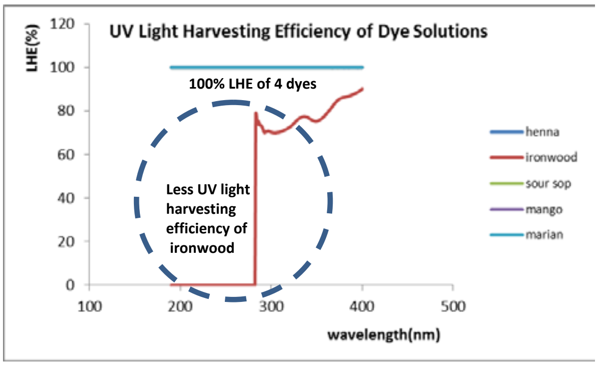


Fig 4.4 UV Light harvesting efficiencies of dyes

According to the absorbance and LHE spectra of UV region, ironwood between the wavelength of 190 nm and 282 nm has 0 absorbance and 0% LHE, shown in Fig 4.3 and Fig 4.4 respectively. So ironwood leaves cannot protect UV attack and should not be used as sensitizer of DSSC.

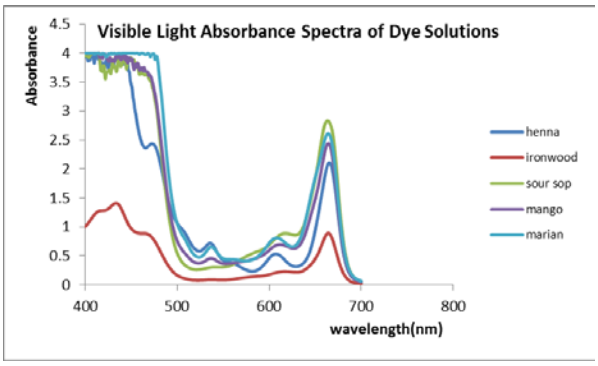


Fig 4.5 Visible light absorbance spectra of dyes

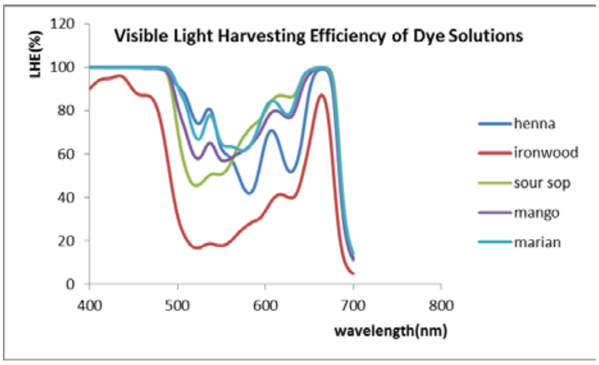


Fig 4.6 Visible light harvesting efficiencies of dyes

As shown in Fig 4.5, sour sop dye has more absorbance than others in visible region and the minimum value of LHE of sour sop at the wavelength of 521 nm is 45% and the maximum is about 100%, in Fig 4.6.

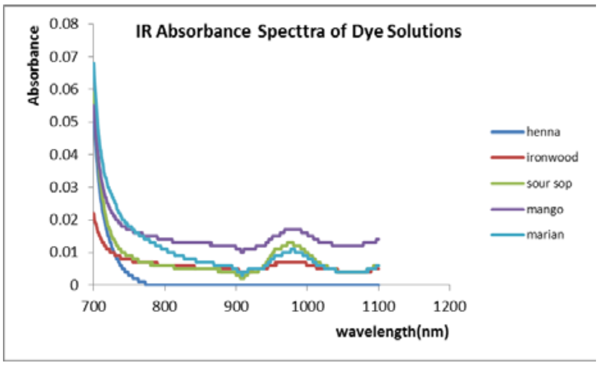


Fig 4.7 IR absorbance spectra of dyes

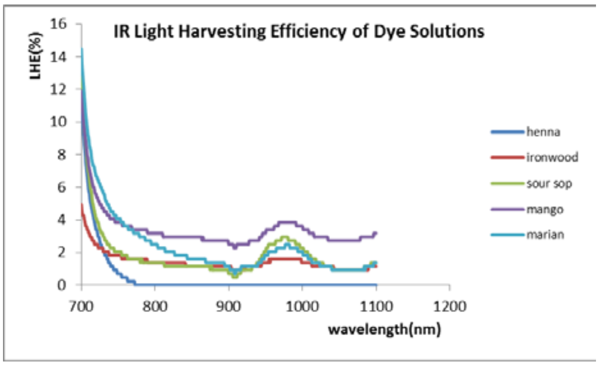


Fig 4.8 IR light harvesting efficiencies of dyes

IR absorbance spectra of all dye solutions are shown in Fig 4.7. LHE of henna is 0% from the wavelength 773 nm to 1100 nm. Since the strong cut-off point of all dyes is the wavelength of about 700 nm, the band-gap energy is about 1.8 eV[8].

V. CONCLUSION

The absorbance properties of 5 dye solutions have been studied by UV-VIS spectroscopy. The dye with broader absorption band gives the high absorbance in UV and visible region. As shown in absorbance spectra of dyes, henna, sour sop, mango and marian leaves strongly absorb the high energy photons in UV region. On the other hand, there is 100% UV light harvesting efficiency between the wavelength of 190 nm and 400 nm. In Fig 4.3 and Fig 4.4, ironwood absorbance is zero and LHE(%) is 0% between 190 nm and 282 nm. Ozone layer depletion strongly effects on human and animal health, terrestrial plants, aquatic ecosystems, bio-geo-chemical cycles, air quality, materials, climate change and ground level UV radiation on the earth. So planting many trees is one of the protections against UV attack for human beings and living things, and plants' leaves can be used as dye-sensitizer of DSSC.

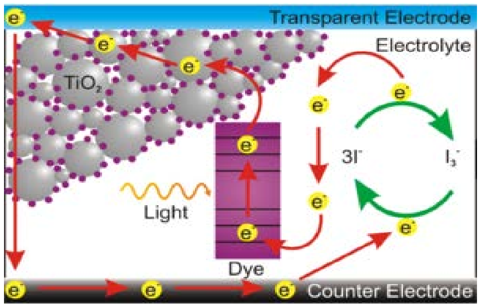
But ozone layer can be automatically created in the stratosphere when UV radiation from the sun strikes molecules of oxygen (O_2) and causes two oxygen atoms to split apart. If a free atom bumps into another O_2, it joins up, forming ozone (O_3). This process is photolysis.

$$O_2 \xrightarrow{UV\ radiation} O + O$$
$$+$$
$$O_2 \rightarrow O_3$$

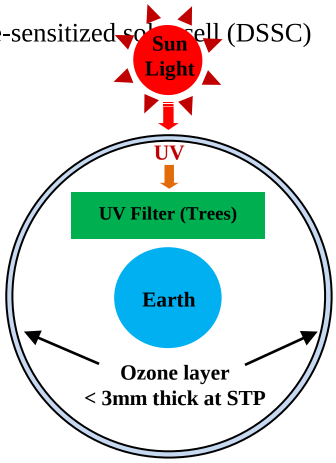
So, everybody needs to obey *Montreal Protocol* to become the original condition of ozone layer, our precious gift given by Lord, because only 3 are ozone when 2 million are normal oxygen in 10 million air molecules.

This research work can give the solution about the problem: (i) how to protect UV attack because of the damage of ozone layer? (ii) which materials used to prevent the dangers of intense unfiltered UV radiation? (iii) how to solve the problem of energy crisis in the future, year after year? To get electronic transition from valence to conduction band in DSSC, high energy UV photons must be absorbed. High energy photon absorption makes the protection against UV attack. So, plants' leaves give twin pleasures: **UV Protection** and **Sensitizer of DSSC**. Although ozone layer is still damaged by the activities of human beings, we can protect UV attack by planting many trees and we can solve the problem of energy crisis in the future by using NDSSCs. So, we must avoid the destroying the plants. To increase the number of plants, we should use other wood-replaced materials. And then it is necessary to reduce the use of ODS all over the world. Scientists predict that ozone layer will become the original condition only when we all act to obey the laws of International Convention. If not so, two-third of the ozone layer will disappear in the earth's atmosphere in about 2065.

APPENDIX



Dye-sensitized solar cell (DSSC)



UV protection by trees

Henna Tree

Ironwood Tree

Sour sop Tree

Mango Tree

Marian Tree

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