2013 臺灣國際科學展覽會
優勝作品專輯

作品編號　**120006**

參展科別　**環境科學科**

作品名稱　**利用光合作用機制研發光電材料之研究**

得獎獎項　**四等獎**

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關 鍵 字　Photosynthesis、Photoelectric

作者簡介

我是田家瑋，很榮幸能夠參與跟科展有關之活動。從小就很喜歡科學，不論是電視上或是報章雜誌裡出現的科學新知，都能夠吸引我的目光。很高興我踏入了科展的世界!在這裡我能夠將我所想到的點子實際應用，不是只將春秋大夢寄託於書本裡。在研究的過程中，除了必須專注於眼前的實驗外，也要大量攝取國內或國外的文獻，自然而然習得了快速統整以及找重點的能力。

摘要

葉綠素為植物體內進行光合作用關鍵物質，在能源領域內也有不少的應用。葉綠素是光合作用的鑰匙，葉綠素能夠累積光的能量並放出激發態電子，利用激發態電子的能量進行一連串複雜的反應，本研究的理論就建立在光合作用上，利用葉綠素吸收光能轉為電能的特性開發新型光電池。光電池使用金屬或非金屬材料，照光後能產生電流之材料作為發電材料。電池的製作過程非常簡單，實驗發電材料葉綠素也很容易取得，完全沒有汙染環境的疑慮，是非常乾淨的綠色能源。另外也探討葉綠素濃度對於發電效能的影響。研究使用的裝置是由兩片玻璃與矽膠片組裝而成的電池，在電池中間加入葉綠素與電解液。藉由改變電解液與有無光照來探討葉綠素在該電池中的氧化還原作用是否有明顯的變化，並推出化學反應式。結果顯示在葉綠素與電解液的配合下能夠建立出一套循環產電系統[123]。

1 林鵬，黎上瑋，吳郁萱:〈新型葉綠素電池的研究與開發〉,《中華民國第 49 屆中小學科學展覽會》

2 周誌宸：「改善染料敏化太陽能電池二氧化鈦工作電極之研究」（國立東華大學/化學研究所碩士論文，2007）。

3 吳郁萱，黎上瑋：〈葉綠素電池特性研究〉,《2010 年臺灣國際科學展覽會》（2010）。

Abstract

Chlorophyll plays an important role during the Photosynthesis which takes place in plants. During the reaction, chlorophyll A absorbs photons and transfers the energy to release excited-state electrons to power the whole Photosynthesis. Our research and experiments are based on the Photosynthesis. Taking advantages of the chlorophyll's ability to convert light energy into electric energy, we came up with the idea to create the new Photoelectric Cells. Photoelectric Cells use matter (metals or non-metallic) to convert light energy into electric energy. The process to make the Cells is simple and environment-friendly, which our energy generating material chlorophyll is easy to access and friendly to environment. All of these made the new Photoelectric Cells a perfect access to produce green and clean energy. In our experiment, we discussed different influences to the Cells' efficiency by changing the condition of the electrolyte, light, and solution's concentration, and came up with a reasonable explanation of the Cells' chemical reaction mechanism. The results showed that combining chlorophyll and suitable electrolyte will lead the Cells to a circulation of chemical reaction, and generate energy continualously[123].

壹、Introduction

一、Motivation

Recent years, there were a lot of researches and references about or related to energy. Many of them were about using Chlorophylls as the dye in the dye-sensitized solar cell (DSSC) to improve its efficiency. What we found in these researches is that they all use chlorophylls only as a dye to widen the DSSC's range of the absorption of light's wavelength. But in nature, the chlorophylls work during a chain reaction called photosynthesis, as the chlorophylls absorb photons from the sun light and released exited-state electrons to produce the energy to power the whole reaction. And that has a lot more credits than just helping absorbing more light in the DSSC. Seems that DSSCs haven't let chlorophylls to reach its full potential in generating energy. So we brought out a series of experiments using chlorophylls not as a dye but rather than an energy generating material in our new photoelectric cells. Experiments and tests about the new photoelectric cells' characteristics and efficiency had also been done.

二、Purpose

（一）Using chlorophyll as an energy generating material in the new photoelectric cells, and infer the reaction formula.

（二）Measure and make up chlorophyll solutions of different concentrations by using the Beer–Lambert law, and study the concentrations influence to the cells' efficiency.

（三）Measure the changes of the fluorescent phenomenon in the new photoelectric cells to re-exam and verify our inference.

（四）Test and discuss the light influence to the new photoelectric cells.

（五）Compare the efficiency and the phenomenon of the cells' while respectively using artificial Chlorophyll (Chlorophyll Cu) and natural Chlorophyll (Chlorophyll Mg).

（六）Test and discuss the electrolyte influence to the new photoelectric cells.

（七）Test and discuss the cells' efficiency when using natural sunlight or halogen lamp light.

三、References Review

表 1. Chlorophyll Related References Review （Rewrite from《葉綠素電池的開發與研究》）

SN	year	Researcher	Service Unit	Research Project	Achievement & Results	Problems & Future
1	1882	恩格爾曼	美國科學家		以絲藻實驗證實光合作用所吸收的光，就是葉綠素所吸收的光。	
2	1991	Gratzel	瑞士科學家	A low-cost, high-efficiency solar cell bas ondye-sensitized colloidal TiO2 films	以多孔性奈米二氧化鈦做為半導體，並添加人工合成染料提高發電效能。	是目前效能最高的染料敏化電池，然人工合成染料昂貴且製程複雜。
3	1993	韓允雨、周瑞齡等	中國山東師範大學	盒式葉綠素電池光電化學性質的研究	將葉綠素作為染料敏化電池之染劑，塗於 SnO2 半導體上做為 P 型半導體，受光照與 N 型 SnO2 半導體發生光伏效應產生電能。	核心原理是染料依賴半導體支持發生光伏效應產生電能。其後將研究重點放於人工染料開發，與半導體的研究。

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4	2004		來源: www.dev.nsta.org.	The CVC(chlorovoltaic cell) future.	1.提出以單向電子傳導特性之長鏈分子，作為葉綠素激發電子之受體的概念。2.提出以nanoprobe作為連結葉綠素分子之裝置。	僅為概念，尚未發表實驗成果。 (此概念為作為我們團隊開發第三代葉綠素電池之參考)
5	2005	王淨樺	國立台中女子高級中學	「金」枝「玉」葉—金奈米與葉綠素的交互作用(國際科展化學科)	金奈米粒子會和植物中的葉綠素分子產生鍵結作用力，並提升葉綠素激發電子的效率。	
6	2008	廖重賓等	國立虎尾科技大學	葉綠素有機電池(尚未發表，新聞資料)	仿水果電池原理，將葉綠素作為兩片不同電位之有機電極內的電解質發電。	資料不足，有機電極之材料需再了解。
7	2009	林鵬等人	麗山高中	葉綠素電池的開發與研究	第一代:利用葉綠素分子受光照將能量集於反應中心激發電子的機制，藉導電玻璃將激發出電子導至外電路使用。	已將光反應中心二內葉綠素激發電子的機制應用於電池發電，但離實用化仍需進一步改良。
					第二代:利用奈米金與葉綠素結合的特性增加葉綠素吸光表面積，並快速將激發的電子導至外部。	目前實驗發現，發電效果已較第一代佳。
8	2012	徐士庭等	國立羅東高中	黑暗中的光芒—林下植物葉綠體囊膜電 池	比較林下植物與向陽植物作為光敏電池的染料時的差異。	資料不足，葉綠體液的萃取有待深入探討。
9	2012	○○等人	○○高中	利用光合作用機制研發光電材料之研究 The Development of New Photoelectric Material Based On the Mechanism of Photosynthesis	完全不同於先前將葉綠素做為染料運用於DSSC等之研究，本研究運用葉綠素於光合作用中轉換光能成電能的機制進行研究。使用葉綠素為自行產電材料開發新型光電池。	

貳、Main Text

一、 Research Equipment

（一）Ultrasonic Bathing Machine

（二）Halogen lamp

（三）Spectrophotometer

（四）Fluorometer

（十）Silicone rubber sheet

（十一）Butterfly clips

（十二）Syringes and needles

（十三）KI

（五）Beaker

（六）Mortar

（七）Ammeter

（八）Measuring cylinder

（九）Volumetric flask

（十四）I_2

（十五）Artificial Chlorophyll Cu

（十六）Acetone

（十七）Spinach leaves

二、 Research Method and Experiment Process

（一）Introduction of Chlorophyll

There are different kinds of natural chlorophyll, such as Chlorophyll A, Chlorophyll B, Chlorophyll C1, Chlorophyll C2, Chlorophyll D, and Chlorophyll F. Most commonly seen is the Chlorophyll A, which exists in many kinds of plants. We use Chlorophyll A as our main natural chlorophyll in our experiments.

Artificial chlorophyll mostly has different central metal to the natural chlorophyll. Most commonly seen is Zinc and Copper. We use the Copper Chlorophyll as our artificial chlorophyll in our experiments.

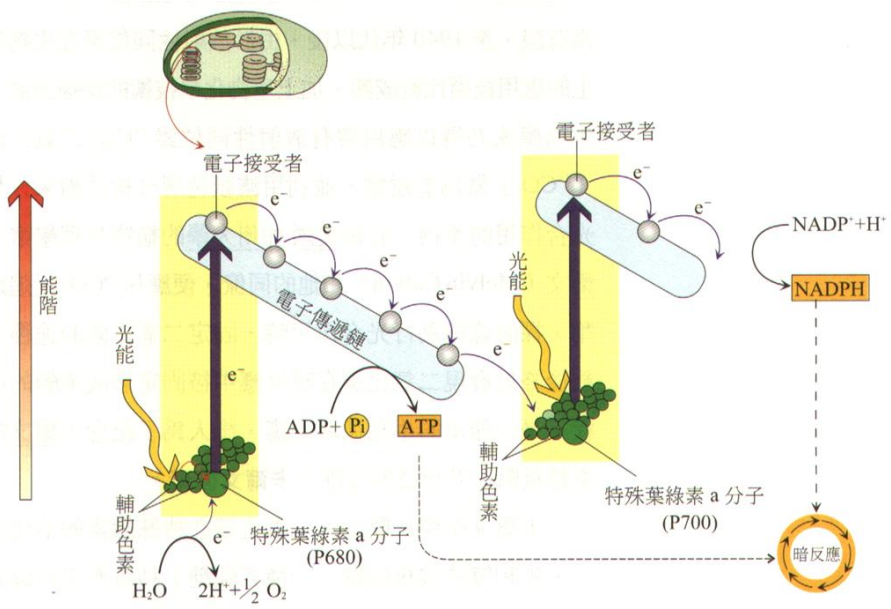

圖 1　Electrons transfer path

Photosynthesis can be divided into two different process, Photosystem Ⅱ (P680) and Photosystem Ⅰ (P700). The energy level of the excited-state electrons which released by Chlorophyll A is around 0.8V. If using Zinc (E^0=0.76V) as the conductor, it will be able to conduct the excited-state electrons out, and generate energy. This research is based on this inference to design the New Photoelectric cells, as the schematic diagram shown below.

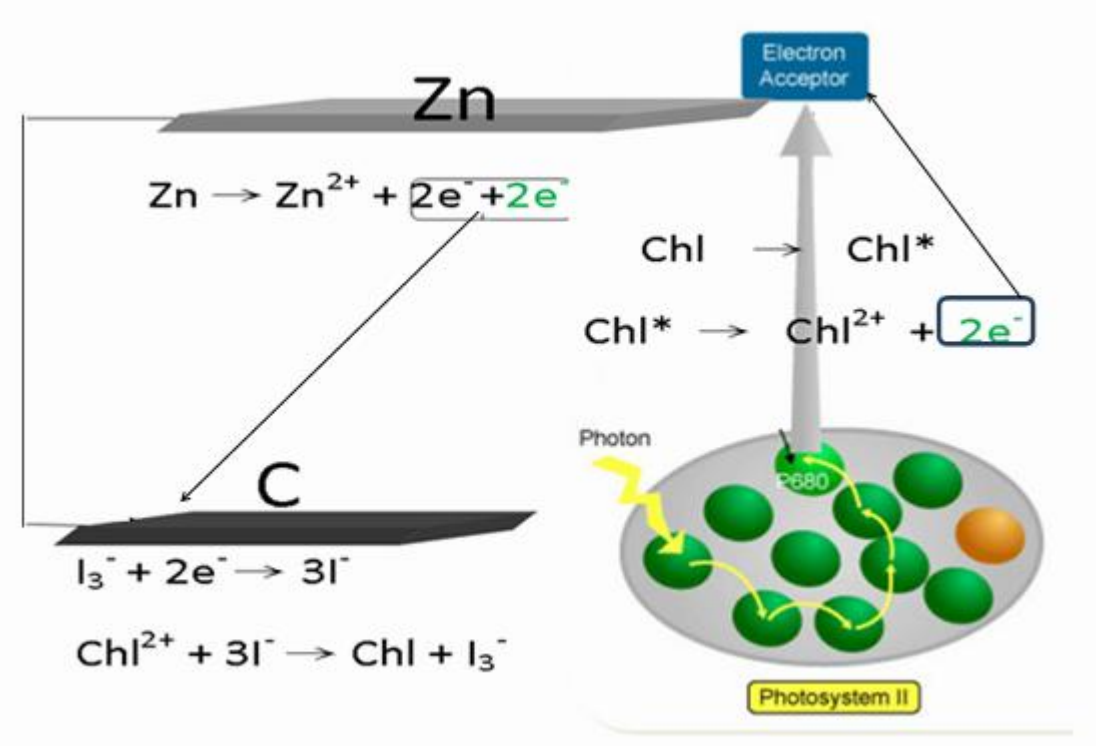

圖 2　New Photoelectric Cells working mechanism

三、 Pre-Experiment

（一）Experiment design ─ Extraction of Chlorophyll4：

1. Clean the spinach leaves with water than put the leaves into

[4] 張上鎮，王升楊：〈超音波快速萃取定量葉綠素〉（臺灣大學森林學研究所，1997 年）。

the oven to dry (60°C 1hr).

2. Use the grinding machine to grind the spinach leaves into small pieces.
3. Mix 20g spinach leaves with 200ml 80% Acetone.
4. Ultrasonic cleaning bath for 30 minutes.
5. Wait for the Acetone to evaporate and add 200ml water.

（二）Experiment design ─ Making artificial Chlorophyll Cu Solution.

1. Prepare 0.01M Chlorophyll solution.

四、 Experiment purpose 1. ─ New Photoelectric Cells

（一）New Photoelectric Cells' design

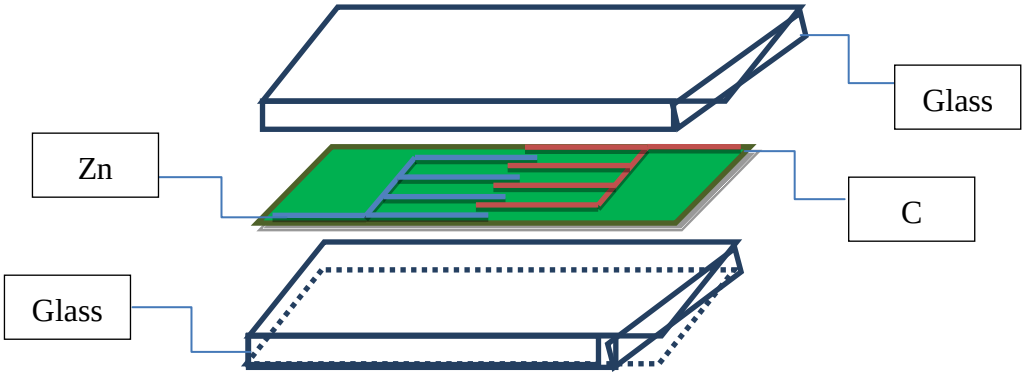

圖 3　New Photoelectric Cells

（二）Experiment Process[5]

1. Take two pieces of 9cm*9cm silicone rubber sheets and cut a

[5] 蘇建華：〈生物系統中的電子轉移反應〉，《中華技術學院學報》第 28 卷（2003/10），頁 1-12。

5cm*5cm square off from the center.

2. Put the electrodes between the two piece of silicon rubber sheets, and use two piece of glasses to clamp the silicon rubber sheets, like a sandwich. So there are around 6cm^3 of space in the cells.
3. Mix 0.5M $KI_{(aq)}$ with 0.05M $I_{2(aq)}$ as the electrolyte, and use needles to inject 1.5ml into the cells.
4. Use needles to inject 4.5ml of Chlorophyll solution into the cells.

五、 Experiment purpose 2.－Concentrations influence to the cells' efficiency

（一）Experiment Process

1. Make five different concentrations artificial chlorophyll solutions.
2. Use spectrophotometer to measure the five solutions' absorbance, and draw a graph of the Beer's law calibration curve.
3. Make three different concentrations natural chlorophyll solutions.
4. Use spectrophotometer to measure the three solutions' absorbance, and compare with the artificial chlorophyll's Beer's law calibration curve to calculate the natural chlorophyll solutions' concentrations.
5. Inject 4.5ml natural chlorophyll solution and 1.5ml KI-$I_{2(aq)}$

into the photoelectric cells and test its efficiency.

6. Discuss and come out with an explanation from data.

六、 Experiment purpose 3. ─ The relation between voltage and the fluorescence

（一）Experiment Process

1. Using the most suitable concentration of chlorophyll solution, which had most stable and lasting voltage in “Experiment purpose two”, to be the experiment solution.
2. **Experimental group:** Open circuit. **Control group:** Broken circuit.
3. Put both groups under the same luminance of Halogen lamp.
4. Measure and record both groups’ voltage changes and fluorescence intensity changes.

七、 Experiment purpose 4. ─ Light influence to the cells

（一）Experiment Process

1. Put the cells under the Halogen lamp and black box respectively.

八、 Experiment purpose 5. ─ Natural chlorophyll and artificial chlorophyll

（一）Experiment Process

1. Prepare 0.05M natural chlorophyll solution and 0.05M artificial chlorophyll solution.

2. Inject these two solutions into two different cells respectively.
3. Measure and record the two different cells' voltage data.

九、 Experiment purpose 6.－The electrolyte influence to the cells' efficiency

（一）Experiment Process

1. Prepare two new photoelectric cells, one add electrolyte in it, another don't.
2. Measure and record the two different cells' data.

十、 Experiment purpose 7.－Natural sunlight and Halogen lamp light

（一）Experiment Process

1. Prepare two cells, one put under the sunlight, another put under the Halogen lamp light.
2. Measure and record the to cells' voltage data.

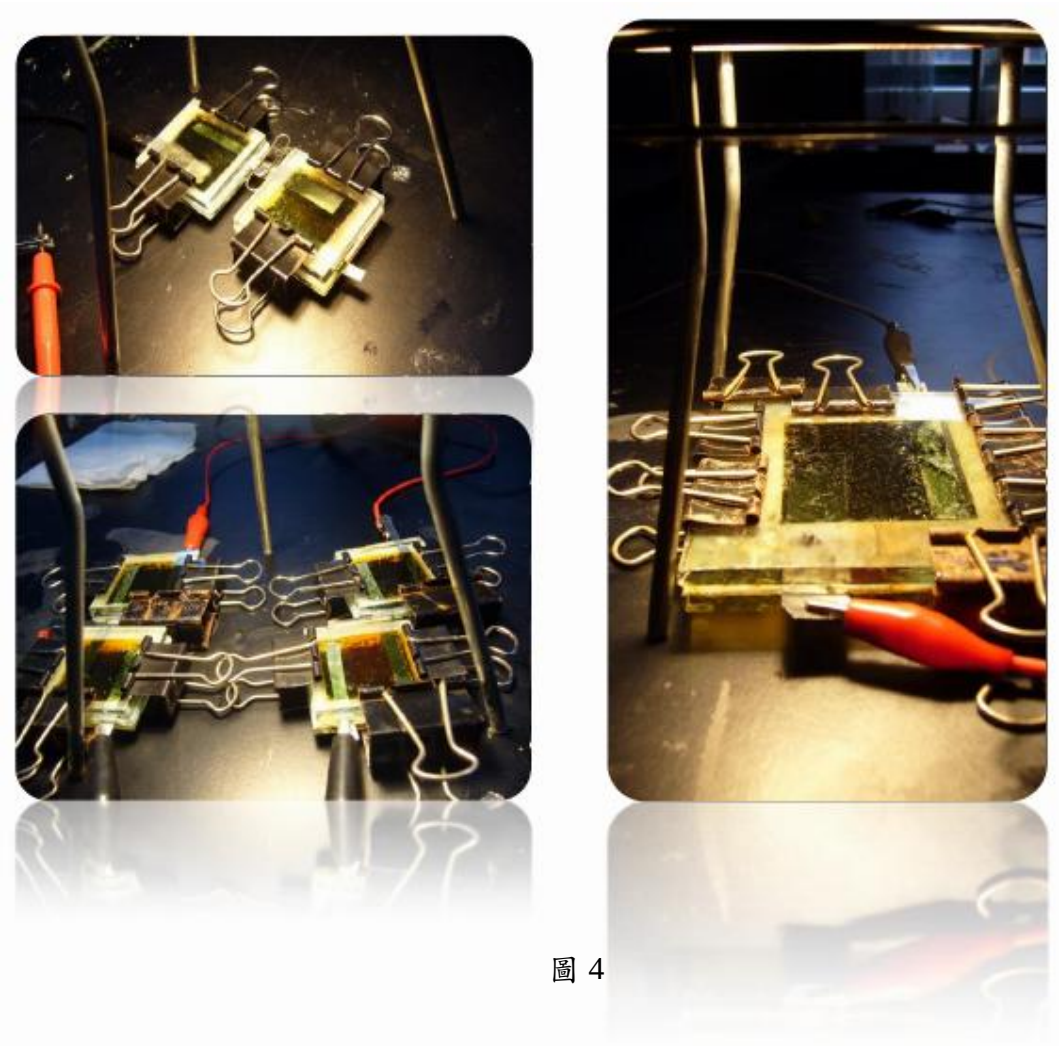

圖 4

十一、 Results

（一）Experiment Purpose 2.

1. Artificial chlorophyll’s graph of Beer’s law calibration curve.

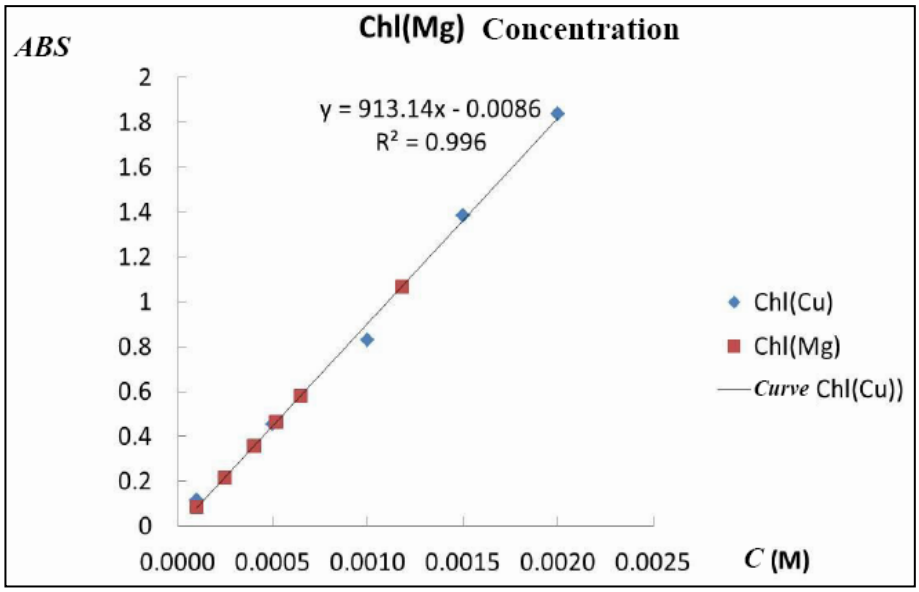

圖 5　Artificial chlorophyll's graph of Beer's law calibration curve.

Put the solution's absorption photometric into the equation to calculate the concentration.

2. Test of different concentration of natural chlorophyll solutions.

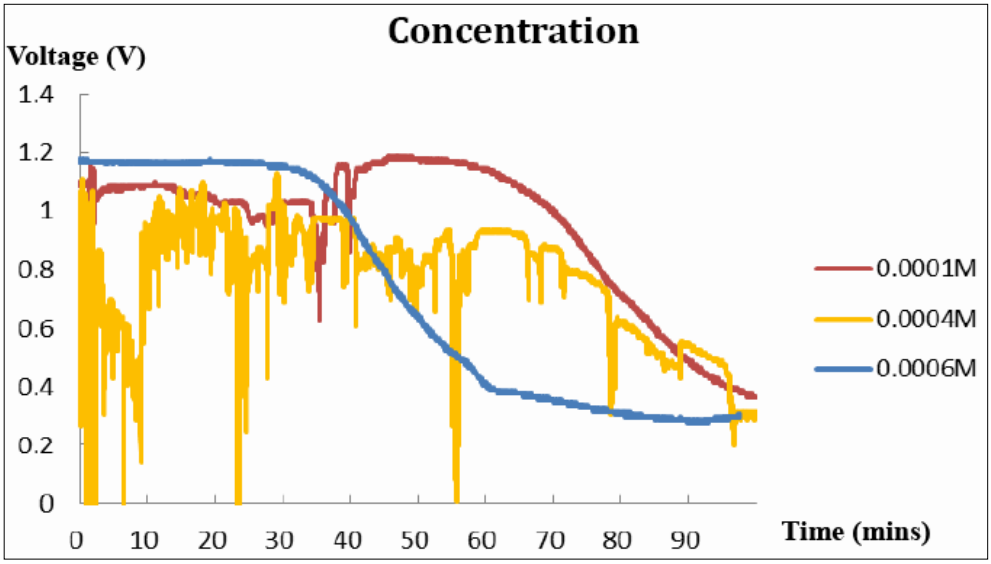

圖 6　Different concentration of natural chlorophyll solutions and voltage

（二）Experiment Purpose 3.

1. Comparison of experimental group's and control group's fluorescence intensity changes.

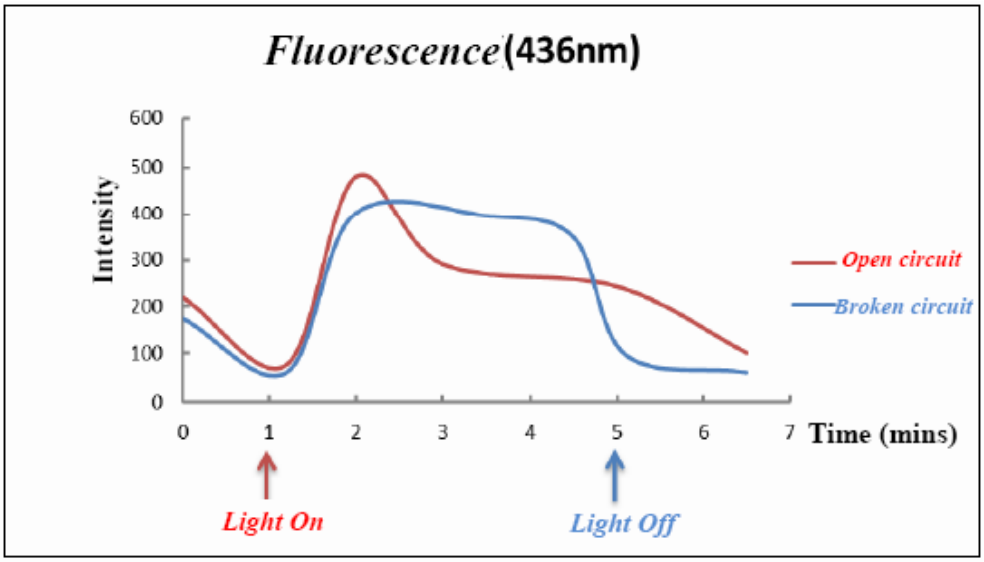

圖 7 Experimental group's and control group's fluorescence intensity changes.

Experimental group's (Open circuit) fluorescence intensity started to decrease apparently after one minute of illumination.

2. Relation between voltage changes and fluorescence intensity changes.

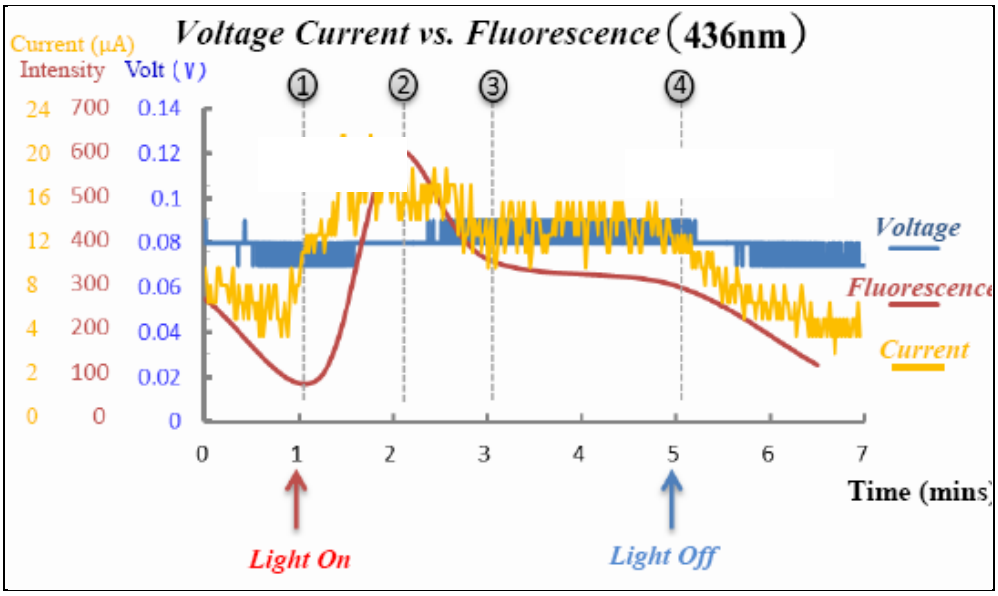

圖 8 Relation between voltage changes and fluorescence intensity changes

① ~ ②	Light on. The number of the excited-state electrons had increased, so the fluorescence intensity increased.
② ~ ③	Excited-state electrons were conducted out by the electrode, so the voltage increased and the fluorescence intensity decreased.
③ ~ ④	The number of the conducted electrons and the not-conducted electrons reached a balance, so the voltage and the fluorescence intensity remained unchanged.
④ ~	Light off. The number of the excited-state electrons started to decrease, so the voltage and the fluorescence intensity had also started to decrease.

（三）Experiment Purpose 4.

1. Light influence to the cells' voltage.

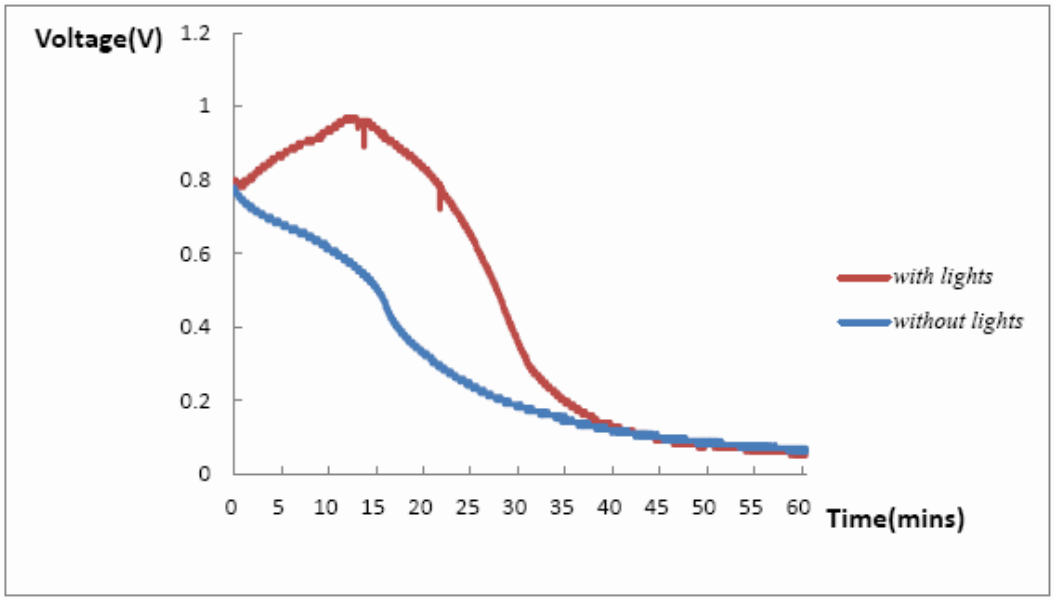

圖 9　Light influence to the cells' voltage

（四）Experiment Purpose 5.

1. Comparison between artificial chlorophyll and natural chlorophyll.

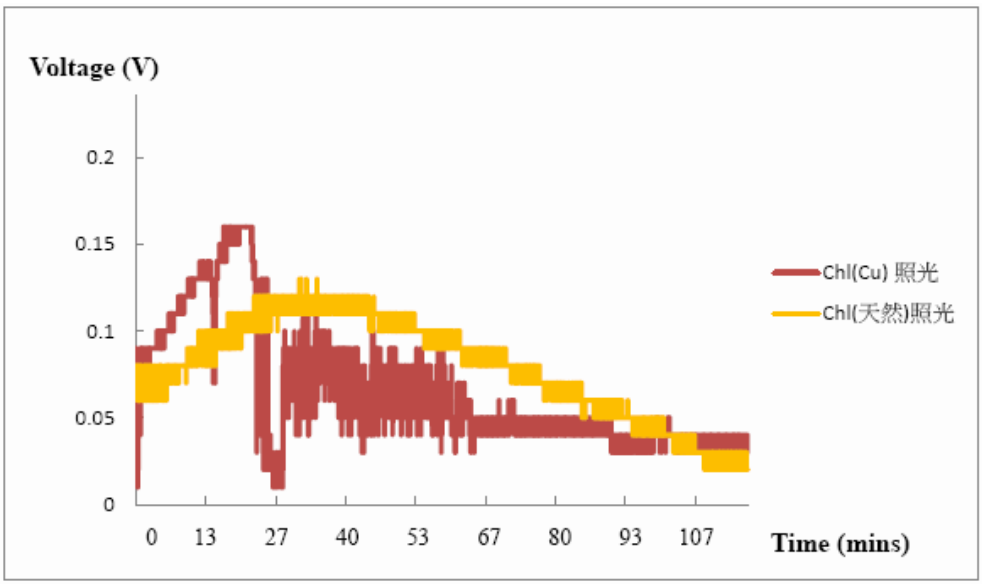

圖 10　Artificial chlorophyll's and natural chlorophyll's voltage

（五）Experiment Purpose 6.

1. Compare the cells' (with electrolyte) efficiency when puts under light or in dark.

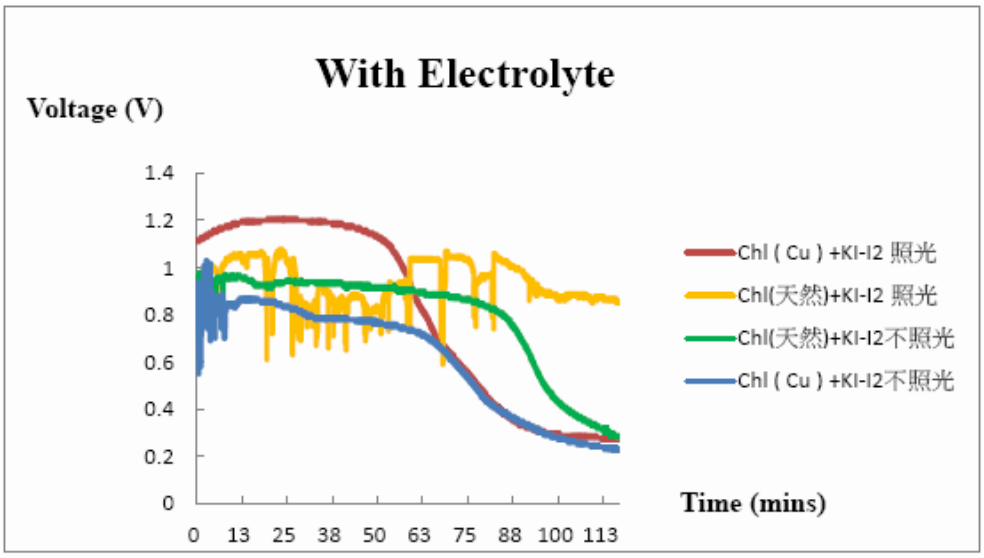

圖 11　Light influence to cells with electrolyte.

Light has a big influence to the new photoelectric cells. When natural chlorophyll receives energy from light, the Hydrolase will decompose H_2O into H^+ and OH^-. Since H^+ will help the reaction

generate more energy, this result in a more stable and lasting voltage.

2. Compare the cells' (without electrolyte) efficiency when put under light or in dark.

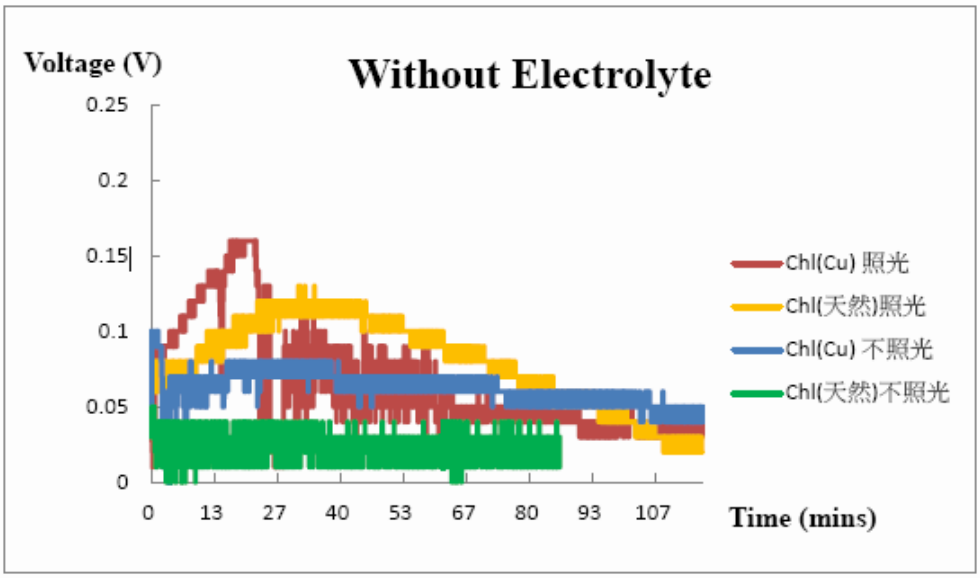

圖 11. Light influence to cells without electrolyte

The cells had lower voltage without the supports from the electrolyte, but meanwhile, natural chlorophyll still had a higher voltage than artificial chlorophyll.

（六）Experiment Purpose 7.

1. Using natural sunlight or Halogen lamp light as the light resource of the cells.

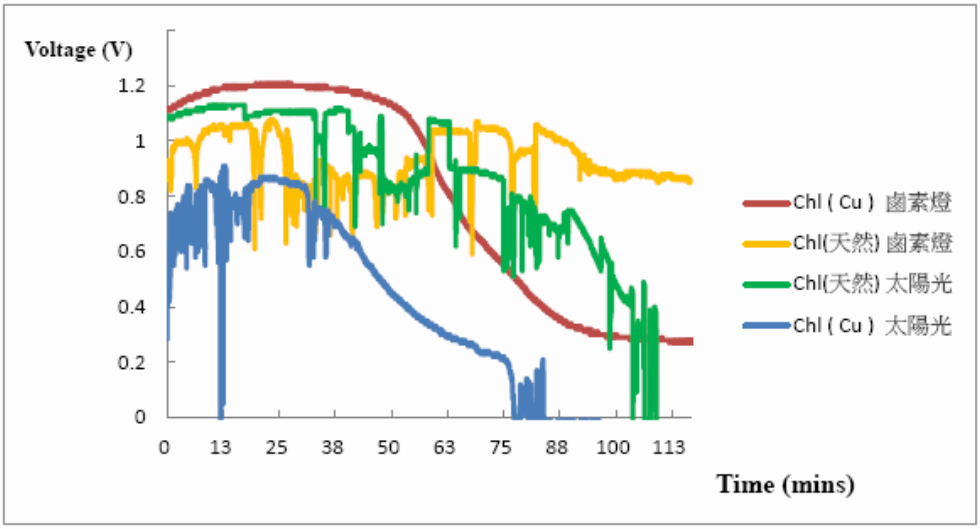

圖 12. Natural sunlight and Halogen lamp light

十二、 Discussions

（一）Experiment purpose 1. ─ Using Chlorophyll as the energy generating material in the new photoelectric cells.

During the experiment, we also tested the cells while the electrolyte was not added, and there were still voltages generated by the chlorophyll. While the cells was not added an electrolyte, the chlorophyll in the cells also played a role as an electrolyte, but a weak one. So adding an electrolyte ($KI\text{-}I_2$) will help increasing the voltages by improving the solution's ability of passing electrons, and reduce the chlorophyll, as the chemical formula shown below：

$$\text{Anode：}\ 2\ \text{Chl}^* \rightarrow 2\ \text{Chl}^+ + 2\ e^-$$
$$2\ \text{Chl}^+ + 3\ I^- \rightarrow 2\ \text{Chl} + I_3^-$$

$$\text{Cathode：}\ I_3^- + 2\ e^- \rightarrow 3\ I^-$$

（二）Experiment purpose 2. ─ The chlorophyll solution's concentration

influence.

While using a lower concentration will shows a more significant ability of chlorophyll to released excited-state electrons, which makes the cells has a more lasting voltage. While using a higher concentration will has a higher initial voltage but not lasting.

（三）Experiment purpose 3. ─ The relation between the changes of voltages and fluorescence intensity.

The experimental group which the cells was open-circuit, its fluorescence intensity increased after illuminated, but started to decrease after the electrode conducted the excited-state electrons out, rather than letting the excited-state electrons to release fluorescence and back to ground-state electrons, the fluorescence intensity started to decrease. Since the electrode had conducted the excited-state electrons out, so the voltage started to increase.

（四）Experiment purpose 4. ─ Light influence to the new photoelectric cells.

The cells' voltage started to increase while putted under light, and it shown that light has a big influence to the cells' voltage.

（五）Experiment purpose 5. ─ Artificial chlorophyll and natural chlorophyll.

The artificial chlorophyll made a higher initial voltage but remained shorter time, while the natural chlorophyll made a more stable and lasting voltage. We speculate that the center metal is the reason that

caused this result. Since the artificial chlorophyll's center metal is Cu, it is easily to have oxidation-reduction reaction with the electrode (Zn), and that made the artificial chlorophyll unstable. So the initial voltage was higher but the voltage didn't stay long.

（六）Experiment purpose 6. ─ Electrolyte influence to the new photoelectric cells.

From the discussion in the "experiment purpose 1", the electrolyte can reduce the chlorophyll after it release an excited-state electron, and this help the reaction keep running on.

（七）Experiment purpose 7. ─ Natural sunlight and Halogen lamp light influence to the new photoelectric cells.

Artificial chlorophyll made a higher voltage while was given Halogen lamp light than natural sunlight, since the artificial chlorophyll's absorption spectrum is more similar to the Halogen lamp light's spectrum. Natural chlorophyll's absorption spectrum has more and wider ranges than the artificial chlorophylls', so natural chlorophyll give a higher voltage when it is put under natural sunlight.

參、Conclusion

一、 Using Chlorophyll as an Energy Generating Material

（一）Using natural chlorophyll will have a more lasting voltage than using artificial chlorophyll. Since the natural chlorophyll solution contain Hydrolase and pigments, the former helps the energy

generating process to produce more energy transferred and the latter lower the chance of chlorophyll to decompose.

（二） Adding electrolyte will increase the efficiency of the chlorophyll to release excited-state electrons, through a smoother electrons transferring, the voltage will be higher, more lasting and stable.

二、 The Influence of the Chlorophyll Solution's Concentration to the Cells' Efficiency

（一）While the chlorophyll solution's concentration is below 6×10-4 M, chlorophyll's "capacitance effects" could be seen, which made the voltage last longer.

（二）The solution's concentration did effect the cell's voltage. Lower concentration had more lasting voltage but relatively less stable voltage. Higher concentration had a higher and more stable initial voltage, but relatively lasted shorter.

三、 The Relation Between the Changes of Voltages and Fluorescence Intensity

（一）The number of the excited-state electrons would directly affect chlorophyll's fluorescence intensity. Therefore, we could know from the decrease of the fluorescence intensity and the increase of the voltage happened at the same time that the increasing voltage was due to the energy transferred from the excited-state electrons.

四、 The Influence of the Light to the New Photoelectric

Cells

（一）Chlorophyll would release excited-state electrons more efficiently after receiving energy from light. Result in that light influence the cells' voltage greatly.

五、 Artificial Chlorophyll and Natural Chlorophyll

（一）Artificial chlorophyll's center metal is copper. Since copper would easily have an oxidation-reduction reaction with the electrode (Zn), the artificial chlorophyll would give a higher initial voltage. But due to the unstable of the chlorophyll, the voltage could not last long and started to decrease.

（二）Natural chlorophyll's center metal is magnesium, magnesium is relatively stable and would not react with the electrode (Zn), the cells' voltage would last longer.

（三） The chlorophyll's center metal would affect its stability.

六、 The Influence of the Electrolyte to the New Photoelectric Cells

（一）Either using natural chlorophyll or artificial chlorophyll, adding electrolyte ($KI\text{-}I_2$) would help transferring electrons more efficiently so the voltage would increase greatly.

七、 Natural Sunlight and Halogen Lamp Light Influence to the New Photoelectric Cells

（一）The more the light's spectrum is similar to the chlorophyll's absorption spectrum, the higher voltage will the cell's generate.

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評語

本作品利用葉綠素 A，探討其吸收光能轉為電能的特性，以開發新型光電池。研究內容包括電磁之製作過程、葉綠素濃度、電解液之影響與光照度之氧化還原作用變化等，雖為常見之葉綠素電池研發，但研究過程仍具實用參考價值。