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參展科別 化學科

作品名稱 量子點敏化太陽能電池中光電極應用於水裂解之產氫

得獎獎項 二等獎

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關 鍵 字　量子點、光電極、水裂解產氫

作者簡介

我們是就讀於北一女中二年級數理資優班的學生，何芷寧及高廷瑋。

我們的興趣十分廣泛，對科學活動和創新思考都有著高度的熱忱。曾在高一暑假一起參加全國高中職智慧鐵人競賽，榮獲臺北區第一名並獲得晉級全國複賽的殊榮；此外，我們也分別積極參加各項校內外數理競賽與人才培育計畫，且表現優良，時有佳績。

在進行量子點太陽能電池專題研究的過程中，儘管我們遇到許多困難與挫折，但我們一路互相扶持、彼此信任，更能以同理心替對方著想，因此一次次地突破了種種瓶頸，並且對我們的研究擁有了更多的熱忱和展望！

摘要

本研究將探討所合成的金屬硫化物製備於量子點敏化太陽能電池之光電極，並應用於水裂解反應，使之產生氫氣作為新型替代能源。以硝酸鋅、硝酸鎘、氧化硒及硫化鈉作為起始物，利用化學浸泡法(Chemical Bath Deposition, CBD) 於氧化錫參雜氟之導電玻璃(fluorine-doped tin oxide, FTO)表面上，製備不同層數量子點硫化物之光電極。當 CBD 循環層數為 1、5 及 7 時，運用紫外光-可見光吸收光譜儀與掃描式電子顯微鏡分別可觀察到光譜變化，與球狀、團簇狀，以及緞帶狀奈米材料之結構。另外以線性掃瞄伏安法測量光電流，在一個太陽光強度(100 mW cm^{-2})照射下，當電壓為 1.3 V (vs. Hg/Hg_2Cl_2) 時， $TiO_2/(CdZnS)_4/(CdZnSe)_2/ZnS$ 光電極之光電流可達 79.24 mA，可證明經 CBD 循環製成之量子點電極具有高電催化活性。此外將沉積不同量子點的光電極與硫化鈷反電極結合後製成不同的太陽能電池，在一個太陽光強度照射下測量其光電轉化效率，當使用的光電極為 $TiO_2/(CdZnS)_4/(CdZnSe)_2/ZnS$ 時，可得最大轉化效率 η 為 2.40 %。更進一步，以此光電極在定電壓下進行水裂解反應，由自製的氫氣收集器收集氫氣，可得其與白金對電極產氫率為 0.98 mmol/hr，以此可確定最佳化的光電極。

Abstract

$Zn(NO_3)_2$, $Cd(NO_3)_2$, SeO_2, and Na_2S onto fluorine-doped tin oxide (FTO) glass substrates were deposited to function as photoelectrodes for polysulfide redox reactions in $(CdZnS)_4/(CdZnSe)_2/ZnS$ quantum dot–sensitized solar cells (QDSSCs). In scanning electron microscope images, the morphologies of spherical nanoparticles (NPs), aggregated NPs, and ribbon-shape NPs were observed, respectively. While increasing the layers through chemical bath deposition (CBD), UV-Vis absorption spectra indicated that the absorption band became broadened. Under illumination of one sun (100 mW cm^{-2}), the QDSSCs incorporating Pt counter electrodes provide the maximum current density of 79.24 mA/cm^2 at 1.3 V (vs. Hg/Hg_2Cl_2) in a linear sweeping voltagram. Measurements of fill factor and short-current density reveal that the electrocatalytic activities of photoelectrodes play important roles in determining the energy-conversion efficiency (η) of the QDSSCs. Under illumination of one sun, we use photoelectrodes incorporating Pt wire to conduct water splitting reaction, and the optimal yield of hydrogen is 0.98 mmol/hr.

一、前言

近日人類生活品質提升造成能源大量消耗，根據專家統計，目前全球的石油儲存量只剩四十年，天然氣只剩五十年，鈾礦只剩六十年，影響遍佈全球社會各階層，開發替代能源—氫能已成為目前最熱門議題之一。氫能不僅可減少傳統能源的倚賴，更可避免燃燒化石燃料所帶來的環境問題，更為一種潔淨自產能源。另外，太陽表面每秒能產生 $3.6x10^{20}$ 焦耳的能量，若換算為能量單位則約有 $1.7x10^{14}$ 千瓦，即使到達地球表面後仍剩 $1.2x10^{14}$ 千瓦，因此推算若將太陽照射地球一小時所有能量轉換成電能時則可供應全球一年所需電力。目前吸收太陽能之光電極材料仍以半導體矽為主，矽晶片必須在高溫、真空的環境中製作，製程繁雜，且成本高昂。另外，一般太陽能電池的反電極大多由貴金屬製成，所費不貲。故本研究嘗試以成本低廉且製程簡易的不同元素組合及層數的金屬硫化物奈米量子點材料製備光電極，以提高光電極上的觸媒活性與強化光能收集，並進行水裂解之應用，其所產生之光電流藉由外電路導入負極，於鉑金負極上裂解水，進行氫產量之效率探究，確定最佳化的光電極後，開發簡易製程之反電極，製備低成本、高效率的太陽能電池。

二、研究方法或過程

（一）製備 TiO_2 薄膜電極

1. 分別以肥皂水、二次水及酒精清洗 FTO 導電玻璃。
2. 於血清瓶中加入 6 克 P-25 TiO2、120 毫升 H2O 及 1 毫升濃 HNO3，維持 80 ℃加熱八小時後，減壓濃縮至乾燥。
3. 將 0.6 克 TiO2 粉末、0.18 克 PVP 和 0.06 克甲基纖維素及 3 mL 的水混合攪拌 8 小時後，除氣 30 分鐘。
4. 在導電玻璃上製備 TiO2 薄膜。

（二）沉積量子點

1. 先將 TiO_2 薄膜電極浸泡於 0.5 M Cd^{2+} 和 0.75 M Zn^{2+} 離子溶液五分鐘再將 TiO_2 薄膜電極浸泡 0.5 M Na_2S 五分鐘，此為一循環。
2. 改變不同循環數，沉積上一至四層的量子點 TiO_2 /$(CdZnS)_{1\sim4}$。
3. 將 TiO_2 / $(CdZnS)_{1\sim4}$ 分別泡入 0.5 M Cd^{2+}和 0.75 M Zn^{2+} 溶液中，浸泡五分鐘後，直接泡進 Se 溶液中，放進攝氏 50 ℃烘箱內一小時。重複上述步驟，形成 TiO_2 / $(CdZnS)_{1\sim4}$/$(CdZnSe)_2$。
4. 將 TiO_2 / $(CdZnS)_{1\sim4}$/$(CdZnSe)_2$洗淨後，泡入 0.5 M Zn^{2+}溶液中 5 分鐘，取出後略為輕洗吹乾，再泡入 0.5 M Na_2S 溶液中 5 分鐘形成 TiO_2/$(CdZnS)_{1\sim4}$/$(CdZnSe)_2$/ZnS。

（三）測量

1. 觀察各種量子點的 scanning electron microscope (SEM)及 energy dispersive spectrometer (EDS)分析。
2. 測量各種量子點的反射式吸收光譜圖。
3. 測量不同光電極的光電流。

（四）裂解

1. 將光電極照光後產生之光電流藉由外電路導入負極，在定電壓下於鉑金負上裂解水。
2. 氫離子在負極吸收電子產生氫氣。
3. 用自製的氫氣收集器收集氫氣。

（五）製作反電極

1. 取 0.116 g $Co(NO_3)_2$、10 mL H_2O、0.03 g thioacetamide、0.014 g PVP 和 2.4 mL 0.5 N NaOH 在 100 ℃下，油浴 1 小時。
2. 取上述材料 1 mL 和 0.5 mL 純酒精混合均勻後，以 12000 rpm 離心

10 分鐘後將上清液取出，再加 1 mL 酒精回溶再離心，取出上清液後，加入 1 mL 酒精回溶，並混合均勻。

3. 取上一步驟液體 0.02 mL 滴在 FTO 導電玻璃上，在 100 ℃的烘箱內烘乾。

（六）組成太陽能電池

1. 以不同光電極與反電極結合，組成太陽能電池。
2. 以光電流轉換效率測量儀測量不同太陽能電池組合效率。
3. 將光電流換效率與光電極的產氫率比較。

三、 研究結果與討論

（一）不同量子點光電極的外觀比較

1. .在圖 1 中，光電極由左行至右行依序沉積上 TiO_2、TiO_2/CdZnS、TiO_2/CdZnS/$(CdZnSe)_2$、TiO_2/CdZnS/$(CdZnSe)_2$/ZnS，其中每行由上到下，分別為鋪了一到四層的 CdZnS。
2. 相同種類的量子點隨著層數的遞增，色澤逐層加深。
3. 鋪上第二種量子點後，顏色由黃轉紅；鋪上第三種量子點後，顏色由紅轉棕。

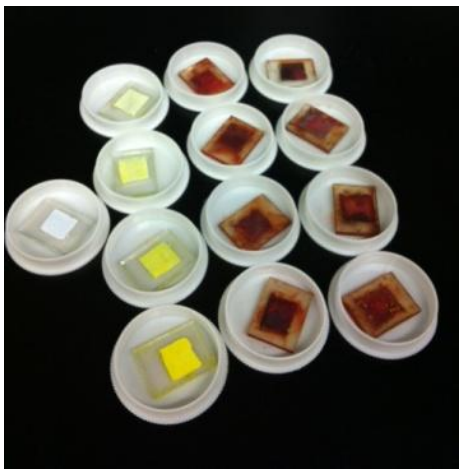


圖1 不同量子點光電極外觀

(二)不同量子點光電極的表面結構

1. 觀察圖 2 可知 TiO_2 之粒徑大約為 30~50 奈米之間，且之間有許多空隙。隨著鋪的量子點種類越多，量子點逐漸聚集，形成團簇狀。團簇狀量子點相較於原始的點狀量子點粒徑變大，且 TiO_2 間的孔隙漸被填滿。
2. 觀察圖 3 可知量子點會由結晶面形成量子堆與緞帶的奈米牆，而奈米牆也是由粒狀量子點構成。

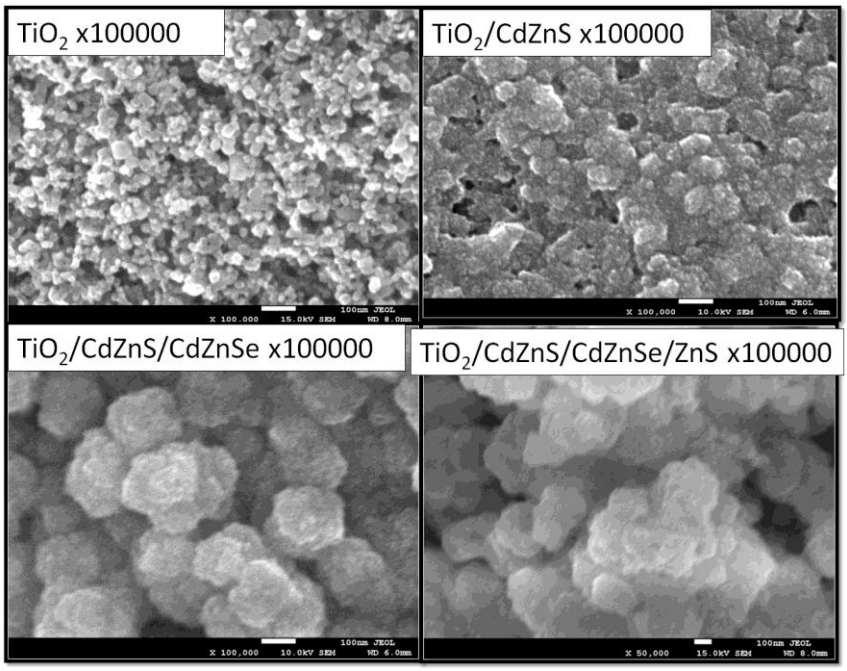


圖2 不同量子點在 SEM 下的團狀結構

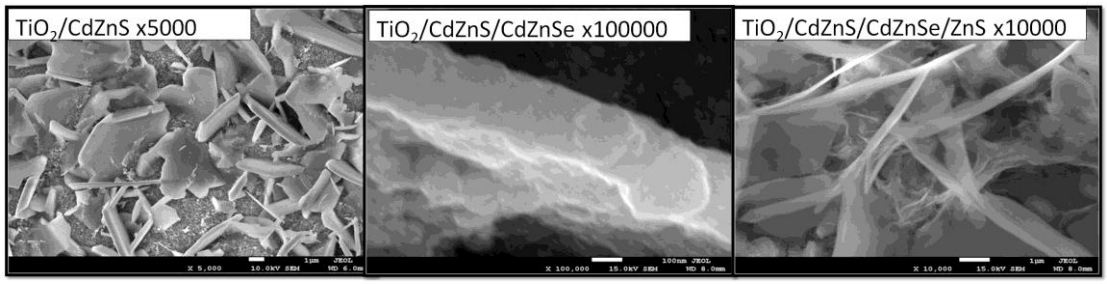
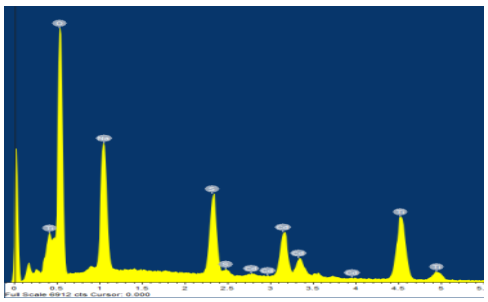


圖3 不同量子點在 SEM 下的緞帶狀結構

(三)不同量子點光電極的元素分析

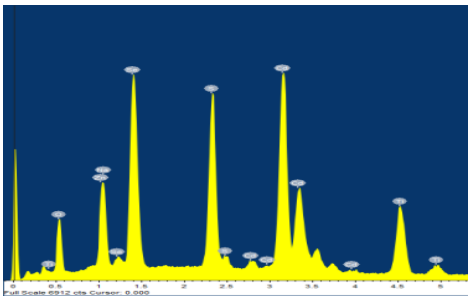
由EDS分析數據可得知，我們所浸泡的量子點元素確實有沉積

上光電極。比如由圖5 可知，新鋪上的量子點 $(CdZnSe)_2$ 具有其他量子點所沒有的Se元素，在EDS分析中，則確實多了Se元素的存在。



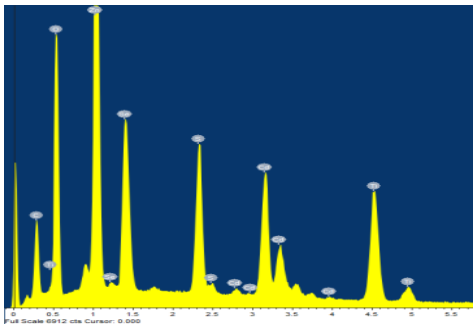
Element	Weight%	Atomic%
O K	41.49	67.55
Na K	7.27	8.24
S K	7.66	6.22
Ti K	25.30	13.76
Cd L	18.28	4.24
Totals	100.00	

圖4 $TiO_2/(CdZnS)_4$ 之EDS分析



Element	Weight%	Atomic%
O K	14.75	40.75
Na K	3.90	7.49
S K	10.30	14.20
Ti K	10.13	9.35
Zn L	4.78	3.23
Se L	17.51	9.80
Cd L	38.62	15.19
Totals	100.00	

圖5 $TiO_2/(CdZnS)_4/(CdZnSe)_2$ EDS分析



Element	Weight%	Atomic%
C K	12.38	27.99
O K	27.43	46.55
S K	4.98	4.22
Ti K	8.83	5.00
Zn L	23.28	9.67
Se L	9.73	3.34
Cd L	13.36	3.23
Totals	100.00	

圖6 $TiO_2/(CdZnS)_4/(CdZnSe)_2/ZnS$ EDS分析

（四）同量子點光電極的吸收光譜圖(UV-Vis)

1. 由圖 7 可知，當光電極上沉積 $TiO_2/(CdZnS)_{1\sim4}$ 時，吸收波長範圍為 300~500 奈米，且隨層數越多，光電極吸收能量越強；由圖 8 可知，當光電極上沉積 $TiO_2/(CdZnS)_{1\sim4}/(CdZnSe)_2$ 時，吸收波長範圍為

300~600 奈米，且可看出曲線中出現兩個波峰；由圖 9 可知，當光電極上沉積 $TiO_2/(CdZnS)_{1\sim4}/(CdZnSe)_2/ZnS$ 時，吸收波長範圍為 300~700 奈米，且頂部為一平滑曲線。

2. 由 UV-Vis 曲線頂部可知，沉積上越多的量子點，其頂部曲線越平滑，可分析出鋪上越多的量子點，吸收度也會越穩定。

3. 不同量子點材料具有不同的吸收波長範圍，本實驗設計希望能有效運用每一種量子點材料吸收的波長。由圖 7、圖 8、圖 9 可推測，不同量子點材料的吸收範圍確實有疊加效果，使之吸收範圍逐漸增大，強度也越趨穩定。

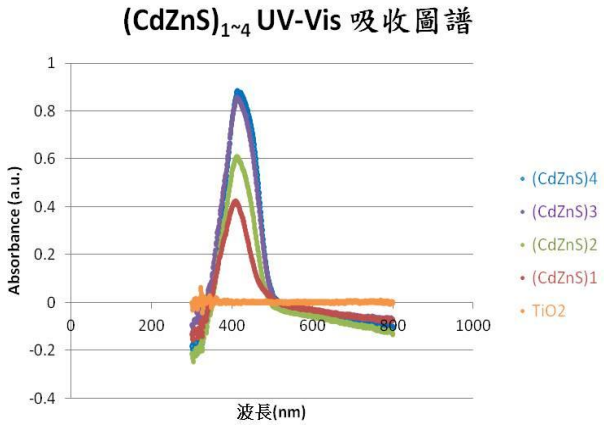


圖7 $TiO_2/(CdZnS)_{1\sim4}$ UV-Vis吸收圖譜

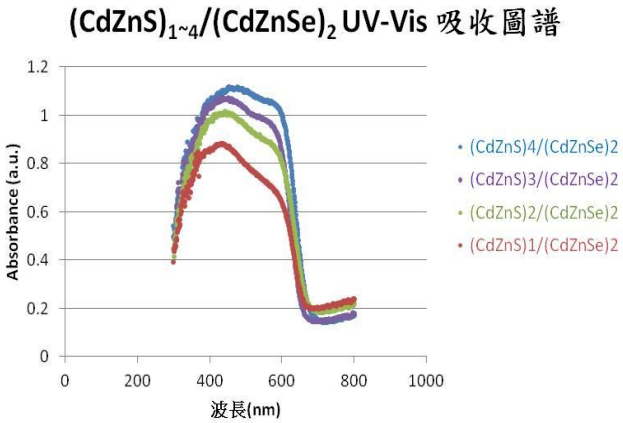


圖8 $TiO_2/(CdZnS)_{1\sim4}/(CdZnSe)_2$ UV-Vis吸收圖譜

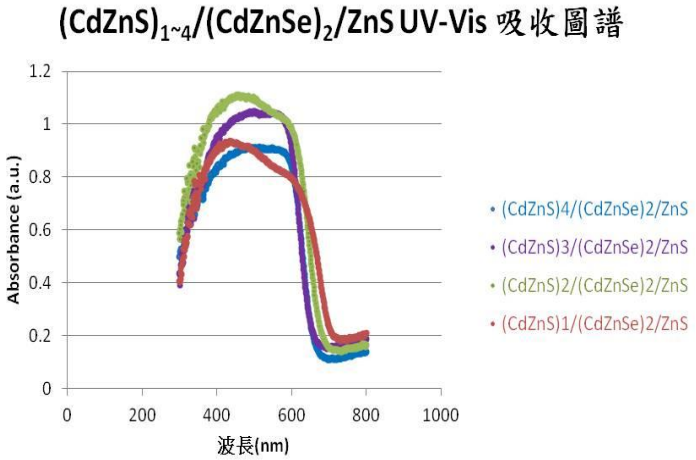


圖9 $TiO_2/(CdZnS)_{1\sim4}/(CdZnSe)_2/ZnS$ UV-Vis吸收圖譜

（五）不同量子點光電極的光電流比較

1. 由圖可知在相同電壓下，鋪越多層數及種類的量子點具有越大的電流，表示此電極對於電解液有較大的電催化活性。
2. 2.在 1.3 V 下，TiO2/(CdZnS)4 具有最大電流約 0.052 A；TiO2/(CdZnS)4 /(CdZnSe)2 具有最大電流約 0.075 A；TiO2/(CdZnS)4/(CdZnSe)2 /ZnS 具有最大電流約 0.08 A 。

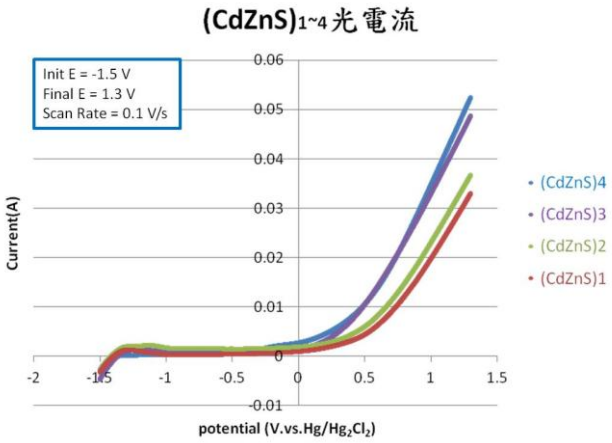


圖10 $TiO_2/(CdZnS)_{1\sim4}$ 電壓電流圖

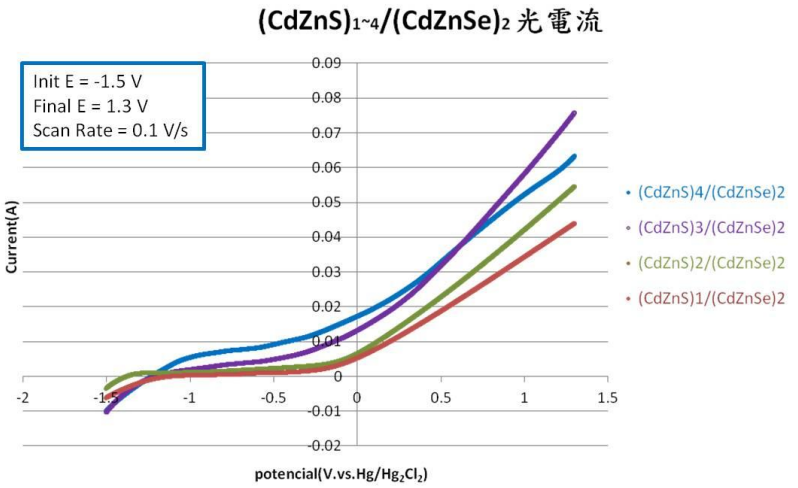


圖11 $TiO_2/(CdZnS)_{1\sim4}/(CdZnSe)_2$ 電壓電流圖

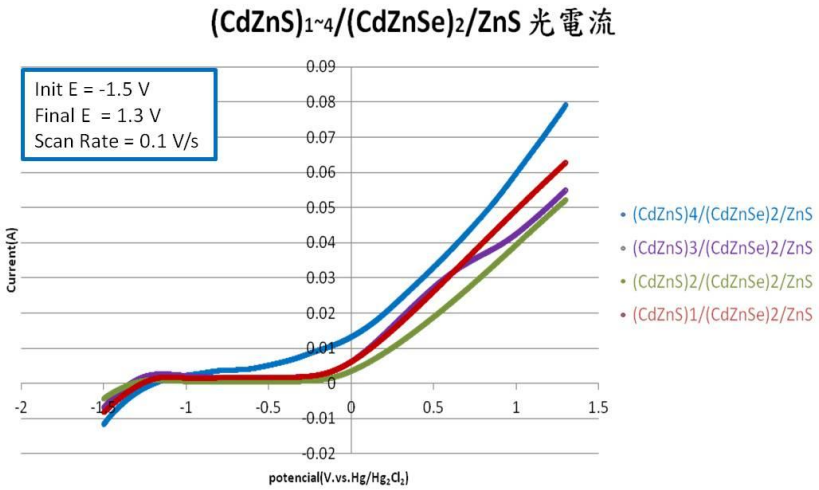


圖12 $TiO_2/(CdZnS)_{1\sim4}/(CdZnSe)_2/ZnS$ 電壓電流圖

(六)不同量子點光電極的產氫率

由表1可知，在定電壓下，隨著量子點種類的增加，光電流及產氫率也隨之增加，且在觀測時間內，每單位時間內所產生的氫氣量及光電流皆為穩定的。

表1 不同量子點光電極產氫率

光電極	定電壓(V)	光電流(mA)	產氫率(mmol/hr)
(CdZnS)4	0.8	49.7	0.73
(CdZnS)4/(CdZnSe)2	0.8	51.6	0.76
(CdZnS)4/(CdZnSe)2/ZnS	0.8	66.3	0.98

（七）不同太陽能電池光電轉化效率

1. 組合太陽能電池後，以 IPCE 測量其光電轉換效率，可知隨著量子點種類的增加，其短路電流密度(Jsc)及光電轉換效率也提高。
2. 在一個太陽光強度照射下測量其光電轉化效率，當使用的光電極為 $TiO_2/(CdZnS)_4/(CdZnSe)_2/ZnS$ 時，可得最大轉化效率 η 為 2.40 % 。

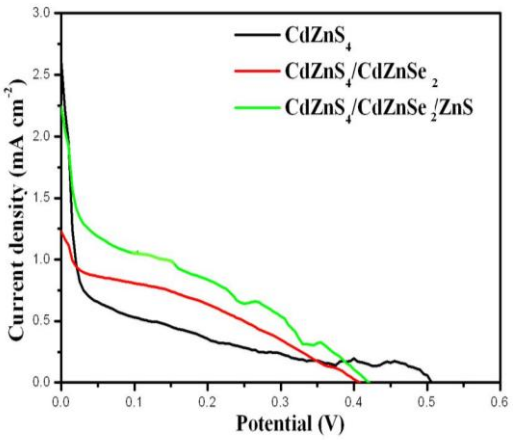


圖13 不同太陽能電池 J-V 圖

四、結論與應用

實驗中發現，經過不同 CBD 循環數製備流程，可在導電玻璃上有效地製成不同形狀的量子點奈米材料，又因量子點奈米材料結構的差異性，導致其電催化活性、吸收光譜及光電流也隨之改變，並影響產氫率及光電轉換效率。所產生的氫能可用於累積太陽能電池的能量，

增加太陽能電池的使用範圍，因此在光電材料上極具潛力。

五、參考文獻

1. 陳家瑩，**2011 年六月**，*金屬硫化物於量子點敏化太陽能電池與超級電容之應用*，國立台灣大學理學院化學研究所碩士論文。
2. Zusing Yang, Chia-Ying Chen, Chi-Wei Liu, and Huan-Tsung Chang, **2010**, *Electrocatalytic Sulfur Electrodes for CdS/CdSe Quantum Dot–Sensitized Solar Cells.*

評語

1. 研究題目相當先進且已有不錯的成果。
2. 宜再加強數據的解釋，例如Z_n所扮演的角色及其原理。

Quantum Dot-Sensitized Solar Cells for Hydrogen Generation by Photocatalytic Water Splitting

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ABSTRACT

Energy harvested directly from sunlight offers a desirable approach, with minimal environmental impact, fulfilling the need for clean energy. Solar cells producing hydrogen is a significant strategy for storing solar energy only with the utilization of water. In this research, we tried to fabricate higher efficiency photoelectrodes by using different quantum dots (QDs) to pursuit the optimum yield of hydrogen. In our research, TiO_2 were coated onto fluorine-doped tin oxide (FTO) glass substrates as photoelectrodes. So as to broaden the absorption bands from ultraviolet light to visible light, CdS, CdSe, and ZnS were deposited via chemical bath deposition (CBD). For fabricating the most efficient solar cells, we investigated the optimum photoelectrodes through varying the layers and types of metal sulfide QDs. We finally obtained different structures of QDs while varying the number of CBD cycles, which play important roles in determining the hydrogen generation and the energy-conversion efficiency of the solar cells.

OBJECTIVES

1. The search for high efficiency of photoelectrodes by varying the types and layers of metal sulfide QDs.
2. Generation of environmental friendly hydrogen energy using the optimum photoelectrodes.

DESIGN OF QUANTUM DOT-SENSITIZED SOLAR CELLS

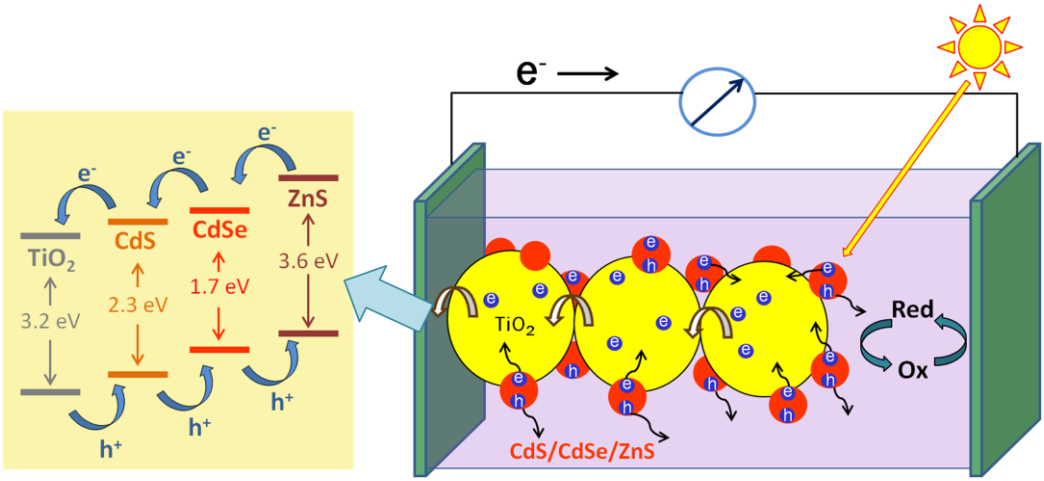


Fig. 1 Theory of QDSSCs

$$Q + h\upsilon \rightarrow Q^*$$
$$Q^* \rightarrow Q^+ + e^- (TiO_2)$$
$$nQ^+ + Redox \rightarrow nQ + Ox$$
$$Ox + ne^- (Pt) \rightarrow Redox$$

1. CdS and CdSe QDs were added on TiO_2 film to enhance the absorption bands.
2. The higher energy gap of ZnS QDs was used to protect the photoelectrodes.

EXPERIMENTAL PROCEDURES

I. Fabrication of Photoelectrodes

A. Preparation of $TiO_2/(CdZnS)_{1\sim4}$

1. Fabricate TiO_2 film onto fluorine-doped tin oxide (FTO) glass with stirring rods.
2. TiO_2-based photoelectrodes were immersed into a solution of 0.5 M $Cd(NO_3)_2$ and 0.75 M $Zn(NO_3)_2$ for 5 min, rinsed with DI water, and dried with an air gun. They were then dipped for 5 min into 0.5 M aqueous Na_2S, rinsed with DI water, and dried with an air gun. These processes were a cycle of CBD.
3. Through 1~4 CBD cycles, $TiO_2/(CdZnS)_{1\sim4}$ electrodes were obtained.

B. Preparation of $TiO_2/(CdZnS)_{1\sim4}/(CdZnSe)_2$

1. Prepare $TiO_2/(CdZnS)_{1\sim4}$ electrodes with the process mentioned in A.
2. Immerse $TiO_2/(CdZnS)_{1\sim4}$ electrodes into a solution of 0.5 M $Cd(NO_3)_2$ and 0.75 M $Zn(NO_3)_2$ for 5 min. Then directly dip them into 0.08 M aqueous Na_2SeSO_3 for 1 h at 50 °C, followed by rinsing with DI water and drying with an air gun. Repeat the process up to 2 times, and $TiO_2/(CdZnS)_{1\sim4}/(CdZnSe)_2$ electrodes were obtained.

C. Preparation of $TiO_2/(CdZnS)_{1\sim4}/(CdZnSe)_2/ZnS$

1. Prepare $TiO_2/(CdZnS)_{1\sim4}/(CdZnSe)_2$ electrodes with the process mentioned in B.
2. The $TiO_2/(CdZnS)_{1\sim4}/(CdZnSe)_2$ electrodes were immersed into a solution of 0.5 M $Zn(NO_3)_2$ for 5 min, rinsed with DI Water, and dried with air gun. They were then dipped for 5 min into 0.5 M aqueous Na_2S, followed by rinsing with DI Water and drying with an air gun, and $TiO_2/(CdZnS)_{1\sim4}/(CdZnSe)_2/ZnS$ electrodes were obtained.

D. Preparation of $TiO_2/(CdS)_4/(CdSe)_2/ZnS$

1. TiO_2-based photoelectrodes were immersed into a solution of 0.5 M $Cd(NO_3)_2$ for 5 min, rinsed with DI Water, and dried with an air gun. They were then dipped for 5 min into 0.5 M aqueous Na_2S, rinsed with DI Water, and dried with an air gun. The process was repeated up to four cycles, and $TiO_2/(CdS)_4$ electrodes were obtained.
2. The electrodes were dipped into a solution of 0.5 M $Cd(NO_3)_2$ for 5 min at room temperature and then immersed into 0.08 M aqueous Na_2SeSO_3 for 1 h at 50 °C, followed by rinsing with DI Water and drying with an air gun. The process was repeated up to two cycles, and $TiO_2/(CdS)_4/(CdSe)_2$ electrodes were obtained.
3. Repeat the process mentioned in C, and $TiO_2/(CdS)_4/(CdSe)_2/ZnS$ electrodes were obtained.

II. Measurements of Photoelectrodes

1. Energy dispersive X-ray spectroscopy (EDXS) was used to analyze the elements deposited on photoelectrodes.
2. Scanning electron microscope (SEM) was used to monitor the morphology evolution of QDs.
3. UV-Vis absorption spectrometer was used to measure the absorption properties of different QDs.
4. Electrochemical analyzer was used to measure the photocurrent density of photoelectrodes.

III. Energy Conversion Efficiency of Solar Cells

A. Fabrication of solar cells

1. Deposit CoS/carbon nanotube (CNT) onto FTO glass substrates, and CoS/CNT counter electrodes were obtained.
2. The devices of quantum dot-sensitized solar cells (QDSSCs) were obtained after assembling one of the photoelectrodes with a counter electrode by using thermoplastic films.
3. The electrolyte was a polysulfide solution: 2.0 M Na_2S and 0.5 M Na_2SO_3.

B. Energy conversion efficiency

1. Place the solar cell devices under illumination of one sun (100 mW/cm^2).
2. The energy conversion efficiency of QDSSCs was studied by digital source meter.

IV. Hydrogen Generation by Water Splitting

1. Under illumination of one sun, incorporate one of the photoelectrodes with Pt counter electrodes to produce hydrogen by water splitting.
2. Collect hydrogen by water displacement.

RESULTS AND DISCUSSION

I. Photoelectrodes Studied

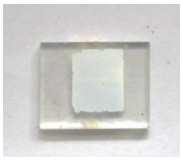
Table 1 Four types of photoelectrodes

Photoelectrode			
Type 1	**Type 2**	**Type 3**	**Type 4**
$(CdZnS)_1$	$(CdZnS)_1/(CdZnSe)_2$	$(CdZnS)_1/(CdZnSe)_2/ZnS$	$(CdS)_1/(CdSe)_2/ZnS$
$(CdZnS)_2$	$(CdZnS)_2/(CdZnSe)_2$	$(CdZnS)_2/(CdZnSe)_2/ZnS$	
$(CdZnS)_3$	$(CdZnS)_3/(CdZnSe)_2$	$(CdZnS)_3/(CdZnSe)_2/ZnS$	
$(CdZnS)_4$	$(CdZnS)_4/(CdZnSe)_2$	$(CdZnS)_4/(CdZnSe)_2/ZnS$	

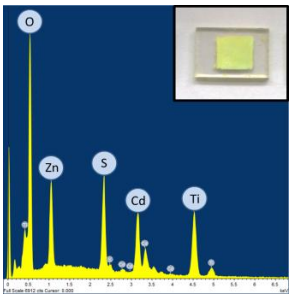
1. Photoelectrodes were fabricated with only one type of QDs by depositing different layers of CdZnS onto TiO_2 film (Type 1).
2. Electrodes were also fabricated with the combination of CdZnS and CdZnSe (Type 2).
3. In order to avoid the electric leakage, ZnS QDs were added as protective film of the electrodes (Type 3).
4. For the comparison, $(CdS)_4/(CdSe)_2/ZnS$ photoelectrodes (Type 4) were fabricated without the protection of inner layers of ZnS.

II. Photo Images and Elemental Analyses

(A) Control: TiO_2

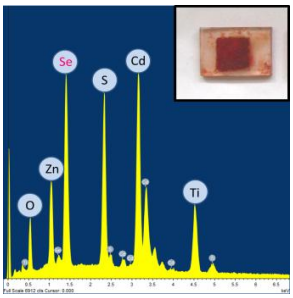


(B) Type 1: TiO_2/CdZnS



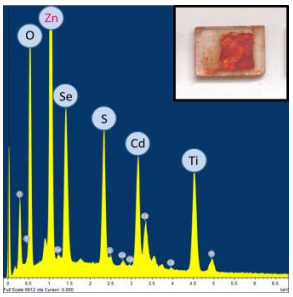
Element	Atomic%
O K	67.55
S K	6.22
Ti K	13.76
Cd L	4.24
Zn L	8.24

(C) Type 2: TiO_2/CdZnS/CdZnSe



Element	Atomic%
O K	40.75
Na K	7.49
S K	14.20
Ti K	9.35
Zn L	3.23
Se L	9.80
Cd L	15.19

(D) Type 3: TiO_2/CdZnS/CdZnSe/ZnS



Element	Atomic%
C K	27.99
O K	46.55
S K	4.22
Ti K	5.00
Zn L	9.67
Se L	3.34
Cd L	3.23

Fig. 2 Photographs of photoelectrodes and EDXS spectra of QDs

EDXS data show that QDs were successfully deposited onto FTO glass substrates.

III. Morphologies of QDs

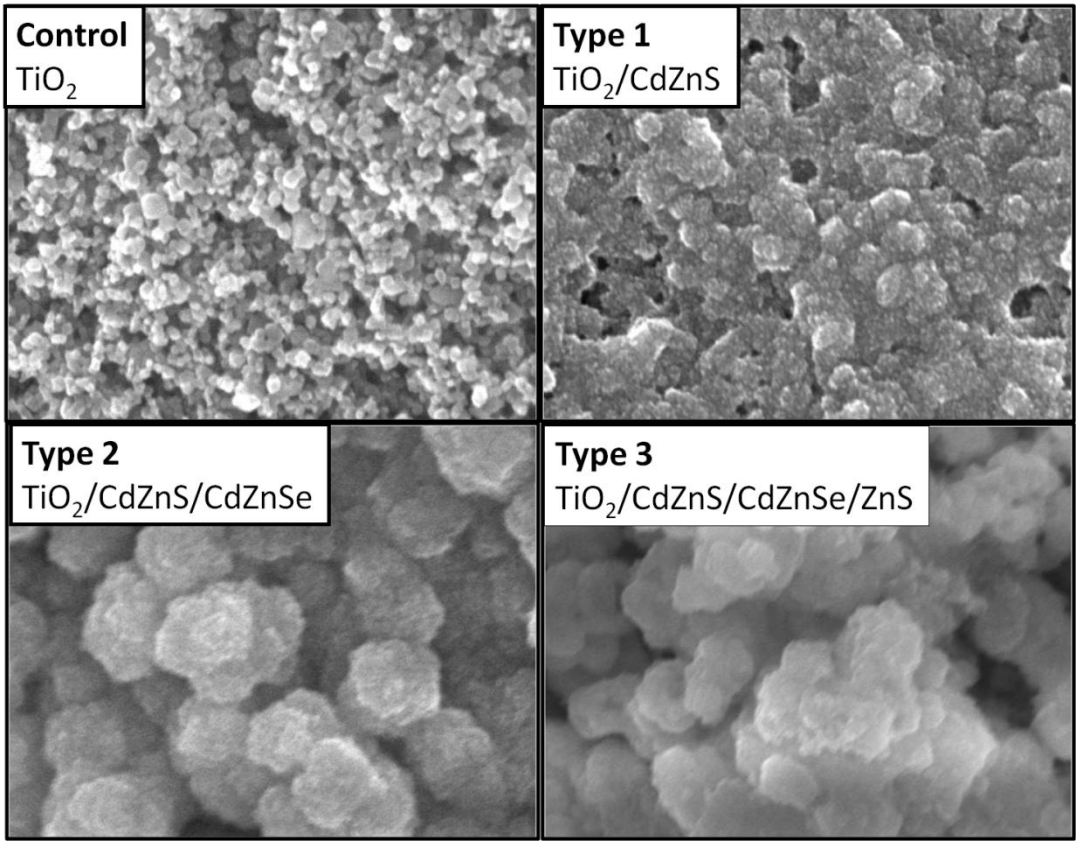
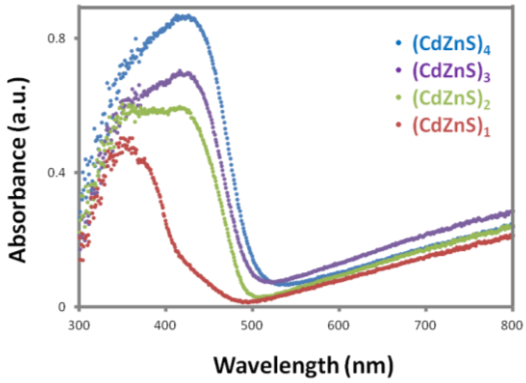


Fig. 3 Morphology evolution of QDs

1. The TiO_2 particles were 30~50 nm in diameter. There was still substantial space available between TiO_2 particles.
2. The degree of aggregation was considerably increased when the QDs were deposited on top, and the space between TiO_2 is gradually filled.

IV. UV-Vis Absorption Spectra

(A) Type 1: $(CdZnS)_{1\sim4}$



(B) Type 2: $(CdZnS)_{1\sim4}/(CdZnSe)_2$

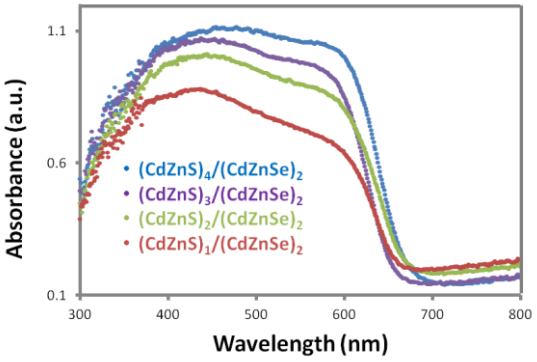
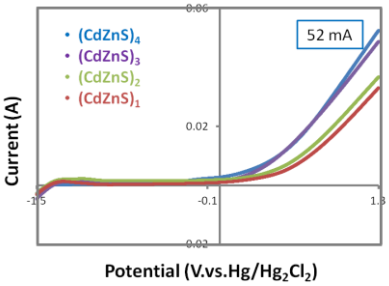


Fig. 4 Absorption spectra of three types of QDs

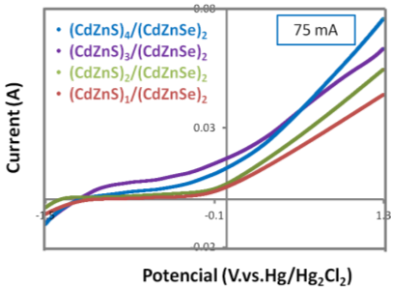
1. The more layers of QDs, the higher the absorbance.
2. The addition of QDs with narrow energy gap (CdSe) changed the absorption bands from 300~500 nm to 300~650 nm.
3. With more layers and more types of QDs, the photocatalytic efficiency was expected to increase.

V. Photocurrent Density

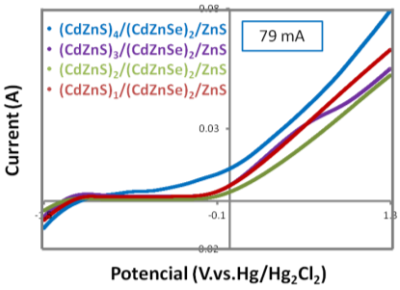
(A) Type 1: $(CdZnS)_{1\sim4}$



(B) Type 2: $(CdZnS)_{1\sim4}/(CdZnSe)_2$



(C) Type 3: $(CdZnS)_{1\sim4}/(CdZnSe)_2/ZnS$



(D) Type 4: $(CdS)_{1\sim4}/(CdSe)_2/ZnS$

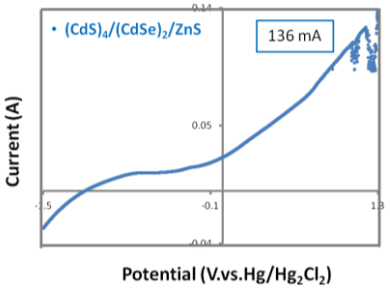


Fig. 5 Photocurrent densities of different types of QDs

1. Photoelectrodes with multilayers (Fig. A) and more types (Fig. B) of QDs provided higher photocatalytic efficiency (photocurrent density).
2. When ZnS QDs were deposited as a protective film, the difference between Fig. C and D (electric leakage was observed) indicated that the inner layers of ZnS were critical for the stability of photoelectrodes.

VI. Energy Conversion Efficiency

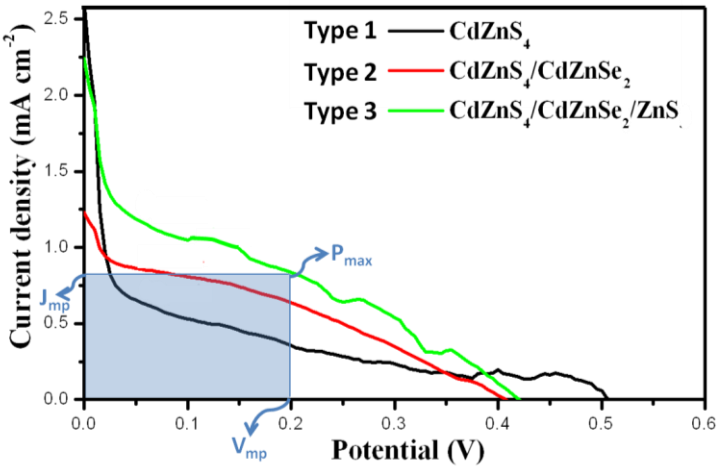


Fig. 6 J-V curves of different sets of solar cells

1. The energy conversion efficiency ($V_{mp} \times J_{mp} / P_{in}$) increased with more types of QDs. (V_{mp} is the maximum power voltage; J_{mp} is the maximum power photocurrent density; P_{in} is the intensity of the incident light.)
2. The $TiO_2/(CdZnS)_4/(CdZnSe)_2/ZnS$ photoeletrodes provided the maximum energy conversion efficiency of 2.4 % (using CoS/CNT counter electrode).

VII. Hydrogen Generation

Table 2 Hydrogen generation of photoelectrodes (n=6)

	Photoelectrodes	Yield of hydrogen (mmol/g · hr)
Type 1	$(CdZnS)_4$	105.43
Type 2	$(CdZnS)_4/(CdZnSe)_2$	123.00
Type 3	$(CdZnS)_4/(CdZnSe)_2/ZnS$	133.25

The yield of hydrogen increased with more types of QDs.

※We need to emphasize that because the voltage produced by photoelectrodes (0.4 V) was not high enough for water splitting (1.2 V), 0.8 V was applied in hydrogen generation.

Conclusions

1. According to UV-Vis absorption spectra, the more layers of QDs, the higher the absorbance.
2. The combination of CdS with CdSe QDs broadened the absorption bands from 300~500 nm to 300~650 nm.
3. Because of the higher energy gap, ZnS QDs, especially the inner layers, avoided the electric leakage of photoelectrodes.
4. Photoelectrodes with multilayers and more types of QDs provided higher photocurrent density and higher energy conversion efficiency.
5. $(CdZnS)_4/(CdZnSe)_2/ZnS$ was found to be the best photoelectrodes for the hydrogen generation.

References

1. Ranjitha, N. Muthukumarasamy, M. Thambidurai, Dhayalan Velauthapillai, R. Balasundaraprabhu, and S. Agilan. CdS quantum dot sensitized nanocrystalline Gd-doped TiO_2 thin films for photoelectrochemical solar cells. *J. Mater. Sci.: Mater Electron*, **2013**, DOI: 10.1007/s10854-013-1205-3.
2. Nguyen, V. H. and Nguyen, B. H. Visible light responsive titania-based nanostructures for photocatalytic, photovoltaic and photoelectrochemical applications. *IOP Science*, **2012**, DOI: 10.1088/2043- 6262/3/2/023001.