Novel Photoanode Structures and Its Application in Dye-sensitized Solar Cells

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ABSTRACT

In this study, sol-gel TiO2 were used as the photo-anodes of the dye-sensitized solar cells(DSSC). The pristine nanocrystalline TiO2 , owing to the lack of internal built-in electric filed to swift off charge carriers and suppressing the recombination of photo-generated charge carriers, suffers from extremely low charge carrier density.Therefore, the key role to improve the activity of these photo-anodes is to retard (slow) the recombination of photo-generated charge carriers. Therefore, it is our goal to adapt concept by using a second semiconductor to sensitize the first one to overcome this problem. An efficient charge separation can be obtained by coupling two semiconductors particles. As the result of vectorial transfer of electrons, or inter-particles electron transfer (IPET), keeping the carriers of opposite sign reside on corresponding semiconductors, the recombination of photo-generated charge carriers were thus efficiently suppressed.In this study, the process parameters in fabricating working electrodes had been investigated. Firstly, the finely grinded TiO2 paste was spin-coated on ITO glass w thvarious layers at different speed. The as-deposited films were further annealed at different temperature. Finally, mesoporous TiO2 films with different thickness were obtained. The study found: Nanotechnology porosity by sintering of TiO2 compact structure easy to form thin film electrode, by adding different proportions of the polymers, an increase in the overall surface area, increased the amount of dye adsorption, absorption of visible light help to stimulate electronics, improved effectiveness of the overall conversion. The purpose of this study to look at a variety of different thickness and annealing temperature of TiO2 films produced by the working electrode, the photoelectric conversion efficiency of the impact. The photoanode with 1.55?慆 in thickness seems to be the best choice of process parameters. Nevertheless, as the thickness of the photoanode is lower than 1.55?慆 ,the overall surface area as well as the amount of dye adsorption reduced. In addition iiasthe film thickness was over 1.68?慆, the as-deposited films is vulnerable to cracking during the drying which will deteriorate the film quality and the overall cell performance. In a preliminary study, annealing at 450oC resulted in the best cell performance and was chose for further studies.Novel photoanode structures had been evaluated under simulated standard AM1.5 light source. In the two-tier structure (TCO / TiO2-SnO2 / TiO2 / Dye)decreased slightly at JSC in addition to 0.23 mA/cm2, VOC, FF, ? are rising. In the three-tier structure (TCO / SnO2 / TiO2-SnO2 / TiO2 / Dye), and single-layer structure (TCO / TiO2 / Dye) compared to the working electrode, photoelectric conversion efficiency of no significant impact.In summary, the optimal process parameters seems to be that: TiO2 film thickness 1.55?慆. Photoelectric conversion efficiency of the largest structure of its single-layer(TCO/ TiO2(1.55?慆)/ Dye) ； VOC=0.69V, JSC=10 mA/cm2, FF=0.56,?鉖3.9%. Two-tier structure(TCO/ TiO2-SnO2/ TiO2(1.55?慆)/ Dye) ；VOC=0.71V,JSC=9.77 mA/cm2, FF=0.64, ?鉖4.53%. Three-tier structure(TCO/ SnO2/ TiO2-SnO2 /TiO2(1.55?慆)/ Dye)；VOC=0.68V, JSC=10.1 mA/cm2, FF=0.57, ?鉖4%.

Keywords : Dye-Sensitized Solar Cells, sol-gel, TiO2, Novel Photoanode Structures

Table of Contents

授權書.. iii 中文摘要 .... iv ABSTRACT.. vi 誌謝... viii 目錄... ix 圖目錄.. xii 表目錄.. xiv 第一章 緒論 .... 1 1.1 前言 .... 1 1.2 太陽能電池種類 .... 2 1.2.1 無機太陽能電池 .... 3 1.2.2 有機太陽能電池 .... 5 1.3 研究背景與目的 .... 7 1.4 本文架構 .... 7 第二章 文獻回顧與理論原理 .... 8 2.1 DSSC .... 8 2.2 TiO2 工作電極 .... 10 2.3 染料 .... 12 2.4 對電極 .... 14 - x - 2.5 染料敏化太陽能電池之等效電路 .... 15 2.6 染料敏化太陽能電池之光電轉換特性 .... 16 2.6.1 短路電流(ISC，short circuit current) .... 16 2.6.2 開路電壓(VOC，open circuit voltage) .... 17 2.6.3 填充因子(FF，fill factor) .... 17 2.6.4 能量轉換效率(η，power conversion efficiency) .... 18 第三章 實驗設備與方法 .... 20 3.1 實驗設備 .... 20 3.2 藥品耗材 .... 21 3.3 實驗方法 .... 22 3.3.1 實驗流程 .... 22 3.3.2 ITO 玻璃基板之清洗 .... 23 3.3.3 製備工作電極 .... 24 3.3.4 能隙阻障光電極製備 .... 29 3.3.4.1 新穎工作電極雙層結構 .... 29 3.3.4.2 新穎工作電極三層結構 .... 29 3.3.5 Pt 對電極製備 .... 30 3.3.6 染料配製

.... 31 3.3.6.1 染料用於不同溶劑製備 .... 31 3.3.6.2 測試工作電極表面吸附染料量 .... 32 3.3.7 電解液調製 .... 33 3.3.8 元件組裝 .... 33 3.4 量測設備 .... 35 3.4.1 紫外光-可見光光譜儀(UV-Vis)分析 .... 35 3.4.2 太陽能電池效率量測系統 .... 35 3.4.3 場發射電子顯微鏡 .... 37 3.4.4 XRD 繞射分析 .... 38 第四章 結果與討論 .... 40 4.1 工作電極之分析 .... 40 4.1.1 TiO2 膜層厚度分析 .... 40 4.1.2 新穎工作電極之分析 .... 44 4.1.3 熱處理的溫度 .... 51 4.1.4 UV-Vis 吸收光譜分析圖 .... 55 4.1.5 D719 染料於D.I Water 溶劑分析...................... 59 4.2 PEG 於TiO2 工作電極之影響 .... 61 第五章 結論 .... 63 5.1 結論 .... 63 5.2 建議 .... 64 參考文獻 .... 65 圖目錄 圖1-1 太陽能電池的種類 .... 3 圖2-1 DSSC 之基本結構 .... 9 圖2-2 DSSC 之工作原理 .... 10 圖2-3 各種氧化物半導體的能階示意圖 .... 12 圖2-4 染料敏化太陽能電池之等效電路 .... 16 圖2-5 染料敏化太陽能電池未受光之I-V 特性曲線圖 .... 19 圖2-6 染料敏化太陽能電池受光之I-V 特性曲線圖 .... 19 圖3-1 DSSC 製作流程圖 .... 22 圖3-2 新穎工作電極製作流程圖 .... 23 圖3-3 TiO2 製備流程示意圖 .... 25 圖3-4 濃縮系統 .... 26 圖3-5 Sol-gel SnO2.. 27 圖3-6 雙層結構 .... 29 圖3-7 能隙阻障結構 .... 30 圖3-8 三層結構 .... 30 圖3-9 DSSC 結構示意圖 .... 34 圖3-10 UV-Vis 儀器 .... 36 圖3-11 太陽能電池效率量測系統 .... 36 圖3-12 場發射電子顯微鏡 .... 37 圖4-1 TiO2 各塗層之SEM 的膜厚圖.......................... 42 圖4-2 工作電極不同膜厚之IV curve .... 43 圖4-3 單層工作電極之IV curve .... 45 圖4-4 雙層工作電極之IV curve .... 46 圖4-5 三層工作電極之IV curve .... 47 圖4-6 TiO2 表面形態 .... 48 圖4-7 TiO2-SnO2 表面形態 .... 48 圖4-8 SnO2 表面形態 .... 49 圖4-9 TiO2-SnO2/TiO2 表面形態 .... 49 圖4-10 SnO2/TiO2 表面形態 .... 50 圖4-11 SnO2/TiO2-SnO2/TiO2 表面形態 .... 50 圖4-12 TiO2 退火300°C到450°CXRD .... 51 圖4-13 TiO2 一層退火300°C到450°C .... 52 圖4-14 TiO2 二層退火300°C到450°C .... 53 圖4-15 TiO2 三層退火300°C到450°C .... 54 圖4-16 未吸收染料之TiO2 工作電極之吸收光譜 .... 56 圖4-17 未吸附和已吸附染料之TiO2 工作電極之吸收光譜 .... 56 圖4-18 已吸附染料之新穎工作電極單層之吸收光譜 .... 57 圖4-19 已吸附染料之新穎工作電極雙層之吸收光譜 .... 57 圖4-20 已吸附染料之新穎工作電極三層之吸收光譜 .... 58 圖4-21 不同D719 濃度於去離子水中 .... 59 圖4-22 不同染料濃度於水溶劑之310nm 對照吸收峰............ 60 圖4-23 不同TiO2 層數之吸附染料反萃取於水溶劑之吸收光譜.... 60 圖4-24 不同PEG 添加量於TiO2 溶液中 .... 62 表目錄 表1-1 無機太陽能電池的種類與能量轉換效率................. 4 表1-2 世界各國DSSC 研究近況 .... 6 表3-1 實驗設備 .... 20 表3-2 藥品名稱 .... 21 表3-3 配製不同濃度染料溶液樣品 (溶劑：D.I. Water) .... 32 表3-4 TiO2 rutile 與anatase 相之XRD peaks 相關位置 .... 39 表4-1 工作電極不同膜厚之IV 表現 .... 43 表4-2 單層工作電極之IV curve .... 45 表4-3 雙層工作電極之IV curve .... 46 表4-4 三層工作電極之IV curve .... 47 表4-5 TiO2 一層退火300°C到450°C .... 52 表4-6 TiO2 二層退火300°C到450°C .... 53 表4-7 TiO2 三層退火300°C到450°C .... 54 表4-8 不同TiO2 層數之吸附染料反萃取於水溶劑 .... 61 表4-9 不同PEG 添加量 62

REFERENCES

[1] M.Gratzel, ” pHotoelectrochemical cells, ” Nature , 414,338-334(2001) [2] 莊嘉琛 ” 太陽能工程-太陽能電池篇 ” , 全華，台北市，第一章、第二章、第四章，民86.

[3] M.Gratzel, ” Powering the planet ” Nature , 403,363(2000) [4] wikipedia http://en.wikipedia.org/wiki/Solar_power_satellite [5] 大葉大學電機工程研究所碩士論文, “ CuPc-C60有機光電元件之製作與特性研究 ” , 沈師宇2006.

[6] 林明獻,太陽電池技術入門.P1-7.

[7] http://www.eettaiwan.com/ART_8800403155_480202_NT_f6a216a0.HTM [8] J. Xue, S. Uchida, B. P. Rand, and S. R. Forrest, “ 4.2% efficientorganic photovoltaic cells with low series resistances ” , Appl.phys. Lett, 84, 3013.(2004).

[9] F. Padinger, R. S. Rittberger, and N. S. Sariciftci, Adv. Funct.Mater. 13, 85.(2003).

[10] H. Tsubomura；M. Matsumura；Y. Nomura and T. Amamiya , Nature,261,402.(1976).

[11] Graetzel, M. et al., Nature, 335, p737.(1991).

[12] Graetzel, M., Inorg. Chem., 44(20),P6841.(2005).

[13]李元智,染料敏化太陽電池與模組,工業材料雜誌255期,P102.

[14]荒川裕則,色素增感太陽電池最新技術, P214,日本.

[15] D. Matthews, P. Infelta, M. Gratzel, “ Calculation of the photocurrent-potential characteristic for regenerative, sensitized semiconductor electrodes ” , Sol. Energy Mater. Sol. Cells, 44,119.(1996).

[16] K. Kalyanasundaram , M. Gratzel, " Applications of functionalized transition metal complexes in photonic and optoelectronic devices ", Coordination Chemistry Reviews, 77, 347~414.(1998).
[17] M. Gratzel, " Photoelectrochemical cells. " Nature, Vol. 414,338-344, Nov 15.(2001).
[18] 劉茂煌,奈米光電池,工業材料雜誌203期,P93.
[19] K. Kalyanasundaram and M. Gratzel, " Applications of functionalized transition metal complexes in photonic andoptoelectronic devices, " Coordin. Chem. Rev., 77, 347.(1998).
[20] K. Hara, Y. Tachibana, Y. Ohga, A. Shinpo, S. Suga, K. Sayama,H. Sugihara, H. Arakawa, " Dye-sensitized nanocrystalline TiO2 solar cells based on novel coumarin dyes ", Sol. Energy Mater.Sol. Cells, 77, 89.(2003).
[21] T. Horiuchi, H. Miura, S. Uchida, " Highly-efficient metal-free organic dyes for dye-sensitized solar cells ", Chem. Commun.,3036. (2003).
[22]童永樑,釕金屬染料在染料敏化太陽電池的演進,工業材料雜誌255期,P110.
[23] A. Kay, M. Gratzel, " Low cost photovoltaic modules based on dye sensitized nanocrystalline titanium dioxide and carbon powder ", Sol. Energy Mater. Sol. Cells,44, 99(1996).
[24] J.photochem.,and photobio.A:Chemistry,164(2004)179-182.
[25] J.Am.Chem.SOC.,115(1993)6382-6390.
[26] J.photochem.,and photobio.A:Chemistry,145(2001)107-112.
[27] Electrochimica Actr.,51(2006)3814-3819.
[28] Synthetic Metal.,77(1996)47-49182.
[29]國立交通大學電子物理系博士論文, " GaNAs材料磊晶成長與AlAs濕氧化膜之研究 ", 2001.
[30] Holger Spanggaard, Frederik C. Krebs, " A brief history of the development of organic and polymeric photovoltaics ", Solar Energy Materials & Solar Cells 83 (2004) 125-146.
[31] Jin-Kook Lee A Bo-Hwa Jeong A Sung-Il Jang A Yun-Seon Yeo A Sung-Hae Park A Ji-Un Kim A Young-Guen Kim A Yong-Wook Jang A Mi-Ra Kim; J Mater Sci: Mater Electron .
[32] Zhaoyue Liua,b, Kai Pana, Min Liua, Meijia Wanga, Qiang L··ua,Jinghong Lib,Yubai Baia, Tiejin Lia; Electrochimica Acta 50 (2005) 2583 – 2589.
[33] Andrew Stanley ;Dennis Matthews; Aust. J. Chem,1995,48,1293-1300.
[34] Christophe J. Barbe ', Francine Arendse, Pascal Comte, Marie Jirousek, Frank Lenzmann, Michael Gratzel " Nanocrystalline Titanium Oxide Electrodes for Photovoltaic Applications " J.Am. Ceram. Soc.,80,3157-7171.(1997).