

Modification of TiO₂ Photoanode and Its Improvement in Efficiency for Dye-sensitized Solar cells

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ABSTRACT

In this study, Sol-Gel TiO₂ were used as the working electrode (photo-anode) of the dye-sensitized solar cells(DSSC). The key process parameters in fabricating high efficiency of DSSC including the deposition of wide band gap semiconductor thin films, the sensitized dye(chromophore), the mediator(redox couples, electrolyte), cell assembly, etc. It has been investigated by the preliminary tests for further detailed study later. The porous TiO₂ thin films were indeed formed by the sintered Sol-Gel TiO₂, which resulting in being essential to deposited porous TiO₂ thin film with controlled morphology both with large surface area as well as optimal porosity. Unfortunately, due to these two factors of contradiction each other: if the porosity becomes too large, the surface area of the films will decrease.; on the other hand, if the pore size of the porous films becomes smaller, the overall surface of TiO₂ films will increase rapidly while the smaller the pore radius will hinder the diffusion of redox couple which can in turn decrease the photocurrent from the TiO₂ photoanode. As for the most optimal cell performance, it is laborious to find the suitable parameters in DSSC fabrication.

In this study, the process parameters in fabricating high efficient TiO₂ working electrodes for the photo-injected electron transport had been investigated.

Finely ground Sol-Gel TiO₂ was evenly deposited on ITO by spin coating. Different ratio additives, such as PEG were tested. The as-deposited films were further annealed at different temperature with different thickness of the TiO₂ films. Two Iodide/Iodine electrolytes was used to compare the influence of redox mediator in regenerative photo-electrochemical reaction in this system. The addition of PEG was capable of manipulating the pore size of porous photo-anode by which the ions transferring rate at the counter-electrode interface was improved. Under higher annealing temperature, the sintering of TiO₂ microstructures were more prominent while the crystalline phase might have transformed to the thermodynamically stable phase. The photocurrent conversion efficiency was closely related to the sintering crystalline phase of TiO₂.

The result of the preliminary results in this study shows that the best cell performance was under these given conditions: $V_{OC}=0.7$ V , $J_{SC}=10$ mA/cm² , $FF=63\%$, $\eta=4.05\%$. In addition to the process parameters, the choice of chromophore is still another vital factor for high efficient DSSC. Owing to the unstable character and relatively low spectrum response, the sensitized dye used here suffered from low photocurrent and FF which need endeavor to recognize more efficient ones.

Keywords : Dye-sensitized solar cells、Sol-Gel、TiO₂、SnO₂

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REFERENCES

- [1] <http://www.funddj.com/KMDJ/Report/ReportViewer.aspx?a=98890fd3-76f9-4afa-9893-efea2ba1a06a>(DJ財經知識庫)[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.Gr?tzel, " Powering the planet " *Nature*,403,363(2000)[4]B. O ' Regan , M.Gr?tzel, " A low-cost,high-efficiency solar cell based on dye-sensitized colloidal TiO₂ films " *Nature*,353,737(1991)[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]南台科技大學機械工程研究所碩士論文, " 應用於染料敏化太陽能電池之二氧化鈦薄膜與粉末製程及其特性研究 ", 郭正鏞, P7, 2004.
- [7]R. Woodyard and G.A. Camdoes, *Solar Cells*, 31(1991),297.
- [8]N.Chu and D.Honemam, *Solar Cells*, 31 (1991) 197.
- [9]Ramanathan, K., et al., Properties of 19.2% efficiency ZnO/CdS/CuInGaSe₂ Thin-film solar cell. *Prog. photovolt: Res. Appl.*,2003. 11: p. 225-230.
- [10]V. Y. Merritt. and H. J. Hovel, " Organic solar cell of hydroxy squarylium " , *Appl. phys. Lett.*, 29, 414, 1976.
- [11]C. W. Tang, " Two-layer organic photovoltaic cell " , *Appl. phys.Lett.* 48, 183, 1986.
- [12]P. Peumans, V. Bulovic, and S. R. Forrest, " Efficient photon harvesting at high optical intensities in ultrathin organic double-heterostructure photovoltaic diodes " , *Appl. phys. Lett.* 76, 2650, 2000.
- [13]P. Peumans, and S. R. Forrest, " Very-high-efficiency double-heterostructure copper phthalocyanine/C60 photovoltaic cells " , *Appl. phys. Lett.*, 79, 126, 2001.
- [14]J. Xue, S. Uchida, B. P. Rand, and S. R. Forrest, " 4.2% efficient organic photovoltaic cells with low series resistances " , *Appl. phys. Lett.*, 84, 3013, 2004.
- [15]F. Padinger, R. S. Rittberger, and N. S. Sariciftci, *Adv. Funct. Mater.* 13, 85, 2003.
- [16]M. K. Nazeeruddin, A. Kay, I. Rodicio, R. HumpHry-Baker, E. Muller, P. Lijsa, N.Vlachopoulos, M. Gr?tzel, " Conversion of Light to Electricity by cis-X₂Bis(2,2 -bipyridyl-4,4 -dicarboxylate)ruthenium (Charge-Transfer Sensitizers (X=Cl-,Br-,I-,CN-,and SCN-) on Nanocrystalline TiO₂ Electrodes " , *J. Am. Chem. Soc*, 115, 6382, 1993.
- [17]J.Ferber,M.Hilgendorff,A.P.Yartsev,V.Sundstrom,J.p.Hys.Chem. B2001,105,4895-4903.
- [18]東華大學 羅幼旭, TiO₂ 奈米多孔性薄膜於染料敏化太陽能電池(dye-sensitized solar cell, DSSC) 之應用, http://tns.ndhu.edu.tw/~nano/labtext/DSSC_lab.pdf[19]工業材料, 奈米光電池, 劉茂煌, 203期, 91-97[20]C.J Barbe, F.Areddse,P. Comte,M. Jirousek, F Lenzmann, V Shklover, M. Gr?tzel, " Nanocrystalline Titanium Oxide Electrode for pHotovoltaic Application, " *J.Am. Cream. Soc.*80,3157(1997).
- [21]A.Kay,M. Gr?tzel, " Artificial photosynthesis.1. photosensitization of TiO₂ solar Cells With Chlorophyll Derivatives and Related Natural Porphyrins, " *J.phys. Chem.* 1993,97,6272-6277.
- [22]T.Ma*,K. Inoue,H. Noma,K.Yao,E.Abe, " Effect of functional group on photochemical properties and photosensitization of TiO₂ electrode sensitized by porpHyryn derivatives, " *J. of photochemistry and photobiology a:chemistry* 152(2002).
- [23]S.Chерian,C. Wamser, " AdsorPtion and photoactivity of Terta(4-carboxypHenyl)porphyrin(TCPP) on Nanoparticulate TiO₂ " *J. phys. Chem.B* 2000,104,3624-3629.
- [24]Suman Cherian and Carl C. Wamser " AdsorPtion and photoactivity of Tetra(4-carboxyphenyl)porphyrin (TCPP) on Nanoparticulate TiO₂ " , *J. phys. Chem. B* 2000, 104, 3624-3629[25]Y. Tachibana, S.A. Haque,I.P.Durrant D.R. Klug, " Electron Injection and Recombination in Dye Sensitized Nanocrystalline Titanium Dioxide Films:A comparison of Ruthenium Bipyridyl sensitized Dyes, " *J. phys. Chem.B* 2000,104,1198-1205.
- [26]朱奕融, 奈米TiO₂ 粒子應用於染料敏化太陽能電池之研究, 南台科技大學電機工程研究所碩士論文, 2004[27]Y. Tachibana, J.E. Moser, M. Gr?tzel, D.R. Klug and J.R. Durrant, " Subpicosencond Interfacial Charges Separation in Dye-Sensitized Nanocrystalline Titanium Dioxide Films, " *J. phys. Chem.* 100,20056(1996).
- [28]T. Hannapple, B. Burfeindt,W. Storck and Willig, " Measurement of Ultrafast photoinduced Electron Transfer From Chemically anchored Ru-dye Molecules into EmPty Electronic States in a Colloidal Anatase TiO₂ Films, " *J. phys. Chem.B*,101,6799(1997).

- [29]R. J. Ellingson, J. B. Asbury, S Ferrere, H. N. Ghosh, J. R. Sprague, T. Lian and A. J. Nozik, " Dynamics of Electron Injection in Nanocrystalline Titanium Dioxide Films Sensitized with [Ru(4,4'-dicarboxy-2,2'-bipyridine)₂(NCS)₂] by Infrared Transient Absorption," J. phys. Chem.B,102,6455(1998).
- [30]A. Hagfeldt and M. Grätzel, " Molecular photovoltaics," Acc. Res.,33,269(2000).
- [31]G. Schlichthorl, S. Y. Huang, J. Sprague and A. J. Frank, " Band Edge Movement and Recombination Kinetics in Dye-Sensitized Nano crystalline TiO₂ Solar Cells: A study by Intensity Modulated photovoltage Spectroscopy," J. phys. Chem.B,101,8141(1997).
- [32]K. Schwarzburg and F. J. Willig, " Origin of photo voltage and photocurrent in the Nanoporous Dye-Sensitized Electrochemical Solar Cell " J. phys. Chem.B,103,5743(1999).
- [33]S. Y. Huang, G. Schlichthorl, A. J. Nozik, M. Grätzel, and A. J. Frank, " Charge Recombination in Dye-Sensitized Nanocrystalline TiO₂ Solar Cells," J. phys. Chem. B,101, 2576 (1997).
- [34]D. Cahen, G. Hodes, M. Grätzel, J. F. Guillemoles and I. Riess, " Nature of photovoltaic Action in Dye-sensitized Solar Cells," J. phys. Chem. B,104, 2053 (2000).
- [35]J. photochem., and photobio. A: Chemistry, 164(2004)179-182 [36] J. Am. Chem. Soc., 115(1993)6382-6390 [37] J. photochem., and photobio. A: Chemistry, 145(2001)107-112 [38] Electrochimica Acta., 51(2006)3814-3819 [39] Synthetic Metal., 77(1996)47-49 [40] J. Electrochem. Soc., 144(1997)876 [41] <http://yctrade.netfirms.com/page1.htm> [42] 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.
- [43] Christophe J. Barbe, Francine Arendse, Pascal Comte, Marie Jirousek, Frank Lenzmann, Valery Shklover, and Michael Grätzel " Nanocrystalline Titanium Oxide Electrodes for Photovoltaic Applications " J. Am. Ceram. Soc., 80, 3157 – 71. (1997) [44] Advanced Materials Research Center, Materials and Energy Research Center, Karaj, Iran " SnO₂/ZnO double-layer thin films: A novel economical preparation and investigation of sensitivity and stability of double-layer gas sensors " Materials Chemistry and Physics 110 (2008) 89 – 94