Effect of Zinc Oxide Nanowires Length On Efficiency Of Dye Solar Cells Sensitized

Mohammad Kazem Tabatabaei [1], Ahmad Afifi [2]

[1.] Department of Electrical Engineering, Amirkabir University of Technology, Hafez Ave, Tehran, Iran
[2.] MUT- Department of Electrical Engineering , Tehran, Iran
Smk_tabatabaee@yahoo.com

Abstract: Long and vertically aligned ZnO nanowire arrays were synthesized using fast-microwave-hydrothermal process and was used in dye sensitized solar cell. Effects of different lengths of ZnO nanowire arrays on efficiency changes of dye sensitized solar cell and also absorption of dye were studied. J–V curves of the fabricated ZnO nanowire-based mercurochrome-sensitized solar cells indicated that the short-circuit current density is increased with increasing the length of the nanowire array. Vertically aligned ZnO nanowire arrays were investigated by FESEM image.

[Tabtabaei M.K, Afifi A. **Effect of Zinc Oxide Nanowires Length On Efficiency Of Dye Solar Cells Sensitized.** *Life Sci J* 2026;23(2):30-35]. ISSN 1097-8135 (print); ISSN 2372-613X (online). http://www.lifesciencesite.com. 03. doi:10.7537/marslsj230226.03

Keywords: zinc oxide; solar cell; hydrothermal; nanowire

1. Introduction

All solar cells require a light absorbing material within their structure to absorb photons and generate electrons via the photovoltaic effect. Solar cells which were manufactured by silicon need a large thickness of silicon to improve the efficiency of solar cell. Because silicon is a poor material for absorption of light. So this type of solar cell is called solar cell based on wafer [1]. Another type of solar cell is thin-film solar cell that consists of several different materials'thin layers on substrate like a glass. Different technologies of thin layers causes to reduce cost production ratio compared to other solar cells and also efficiency of this type of solar cell is rather less than solar cells based on wafer. Several groups were used different material layers and several techniques of fabrication to improved efficiency of solar cells [2, 3].

Among different types of thin–film solar cells, because of their higher efficiency/production cost ratio compared to the other types of solar cells, dye-sensitized solar cells (DSSC) have been of great interest recently [4]. Most current researches in the field of dye-sensitized solar cells are on the light-absorbing of dye, improvement of stability of solar cell by replacing the electrolyte liquid cells with solid polymer ionic and electron transport in solar cell by high band gap semiconductor as alternative was concentrated. To obtain more efficiency of DSSC a suitable choice of semiconductor material and best structure, seeking to increase the surface to absorb the maximum amount of dye cells and improvement of electron transfer and reduction of electron recombination [5, 6, 7].

In recent years, due to their unique optical, chemical, electrical and piezoelectric properties, ZnO nanostructures have become very common in semiconductor devices [8], especially gas sensors [9] , light-emitting diodes [10] , field effect transistors [11], photo detectors[12], piezo-nano generators[13] and solar cells [14]. ZnO nanowires in a dye-sensitized solar cell create a direct electron pathway which leads to an increase in electron diffusion length and lifetime [14].

Several methods such as vapor–liquid–solid (VLS), metal–organic chemical vapor deposition (MOCVD) and thermal evaporation [5, 15] have been introduced in order to grow a high quality ZnO nanostructure array at high temperatures. To make the growth process of ZnO nanostructures more energy efficient and cost-effective, the temperature of the process should be reduced. Therefore, solution-based methods with the goal of low-cost ZnO nanostructure growth at low temperatures have been developed recently [5,16–18]. Solution-based methods include a process called hydrothermal [18]. The slow growth process in the hydrothermal method is the main problem, as in some cases reaching the appropriate length for the ZnO nanowires in order to create a large enough internal surface area for dye adsorption in dye-sensitized solar cells requires a time of about 20–150 h. Recently, a microwave-assisted hydrothermal method with the aim of rapid heating of the solution and thereby reducing the time needed for reaching the crystallization temperature in the growth environment has been tested and looks to be successful [17,18]. Using this method synthesized Zno nanowire on glass substrate for DSSC application is easily possible.

A promising way to improve the efficiency of DSSC is increasing the life time and diffusion length of electron by use of high band gap semiconductor arrays[19,20]. In our investigation we fabricated long

and vertically aligned Zno nanowire arrays to use in DSSC. We show that long and vertically Zno nanowires caused the increment of absorption of dye and improvement in diffusion length and life time of electron. In this research we used nanoewire structures of ZnO to obtain direct electron transfer mechanism. This mechanism causes to reduce time of transfer electron to reach anode electrode In order to create a direct electron pathway which cause reduction of recombination of electrons.

2. Experimental

2.1 Fabrication Zno nanowire

Hydrothermal process consists of two parts. One is seeding a layer on a substrate and another growth of Zno nanowire, our proposed method, like in most of the other methods. Seed layer is the main part that affects the length and size of Zno nanowire. Hence the best choice of seeding layer method to obtain vertically and aligned Zno nanowire is problem . There are two main methods for seeding layer. One is drop-coating method and another is the spin-coating method [19]. In this research spin coating method was selected. Firstly, a 5 mM solution of zinc acetate dihydrate (Zn.CH3COO/2_2H2O) in acetone (CH3/2CO) was made at room temperature. The spin-coating method includes wetting the substrate surface with the zinc acetate solution and then spin-coating at a speed of 2000 rpm for 60 s. Seeding of the substrate surface using either of these methods was repeated five times to ensure the complete coverage of the substrate surface by the seed layer and afterwards the adhesive tapes were removed and then substrates were annealed in air at 350 ˚C for 20 min to decomposition of zinc acetate.

Figure 1 indicates the schematic of seeding layer on glass substrate by spin-coating method. Before seeding layer on substrate, it is essential to clean it by deionized water and acetone.

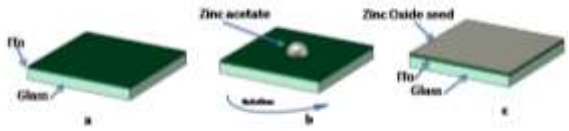


Figure 1. Schematic of seeding layer on ITO-glass substrate by spin-coating method.

The ZnO nanowires were grown in a solution containing 25 mM zinc nitrate hexahydrate (Zn.NO3/2_6H2O),12.5mM hexamethylenetetramine (.CH2/6N4, Merck), 5 mM polyethylenimine and 0.8 M ammonium hydroxide (NH4OH) in deionized water by dipping the substrates upside down into 200 ml of the solution. Afterwards, the whole system was heated in a common commercial microwave oven at different power levels for 4–80 min. At the end of the growth process, finally the substrates were removed from the growth solution, rinsed several times with deionized water and calcined in air at 350 ˚C for 30 min. Several length of Zno nanowire were fabricated and used in DSSC

2.2 Design of dye-sensitized solar cells

Firstly, we fabricated Zno nanowire on an ITO-coated glass substrate with several length by previous method which described in section 2.1. for improvement of dye absorption onto the array surface of Zno nanowire ,calcined of array at 450˚C for 1 h is useful [23].figure 2 indicate the schematic of dye sensitized solar cell manufacture process.

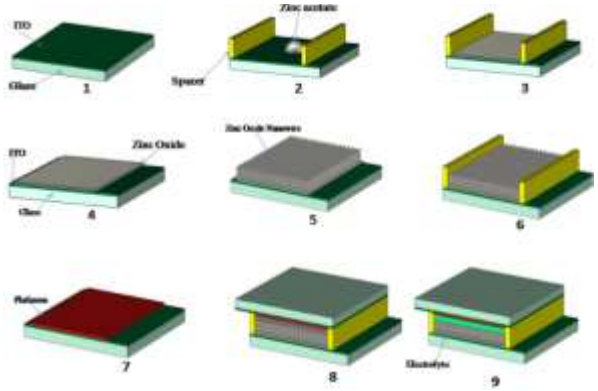
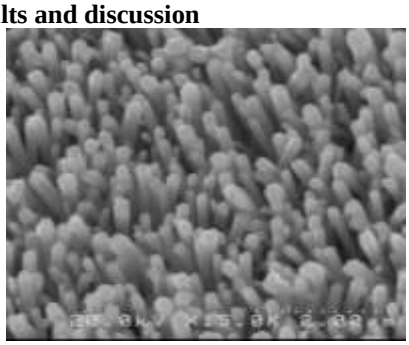


Figure 2. schematic of dye sensitized solar cell manufacture process.

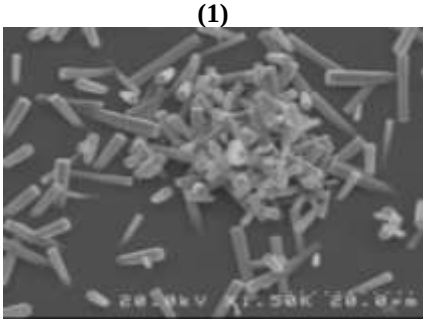
fabrication DSSCs process consist of seeding layer of zinc oxide on selective space of glass substrate which indicated on figure 2-1, figure 2-2 and figure 2-4 then growth of Zno nanowire depicted on figure 2-5 and figure 2-6. The counter electrode was prepared by spreading a few drops of a 10 mM solution of hexachloroplatinic acid hexahydrate (H2PtCl6.6H2O) in ethanol on the conductive side of another ITO substrate which is shown in figure 2-7. The substrate was then annealed at 450˚C for 30 min. A 50 µm thick hot melted double-layer parafilm with two sides left open was sandwiched between the sensitized electrode and the platinized counter electrode. The electrolyte solution consisting of 0.3 M lithium iodide (LiI, Merck) and 0.03 M iodine (I2, Merck) in acetonitrile was injected into the cell from an opening of the sealing frame using a syringe and then the openings were immediately sealed with silicone which is shown on

figure 2-9. Figure 2 shows all the process that is needed to fabricate solar cell by ZnO nanowire.
Finally, The morphology of ZnO nanowire was investigated by FESEM (Hitachi, S-4160) and for realization of the performance of solar cell j-v (Metrohm, Auto lab PGSTAT302N) curve was measured. And also because the main goal of this paper is studying the effect of length of Zno nanowire on efficiency of solar cells, some cells by different length of ZnO nanowires were fabricated and characterized.

3. Results and discussion



(1)



(2)

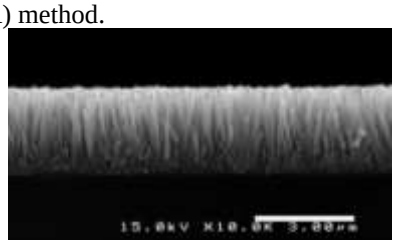
Figure 3. SEM image of Zno nanowire arrays grown using substrate seeding method : (1) spin coating method (2) twice-performed spin coating method.

Figure 3-2 indicates SEM image of Zno nanowire on glass substrate with a seed layer which seeding layer done by spin coating method. In most of the methods based on the hydrothermal process, seeding of the substrate surface before the growth of the nanowires is essential. Figure 3-1 shows Zno nanowire grown on glass substrate that were seeded a layer twice by repeating spin coating method. By comparing figure 3-1 and 3-2 repeating spin coating method cause uniform and narrow diameter distribution of Zno nanowires. As shown in the figure, in addition to a narrow diameter distribution, nanowires are well aligned because of the increased seed layer thickness. Therefore, seeding the substrate twice using the spin-coating method seems to be the optimum approach for hydrothermal process.

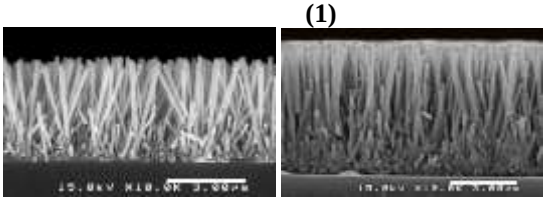
Figure 4 shows the SEM images of the longest possible ZnO nanowire arrays grown using the fast method at different microwave power levels without any growth solution refreshment. The increase of the growth rate and the aspect ratio enhancement of the ZnO nanowires by increasing the microwave power level are clearly visible in the figure. Cross-sectional SEM images revealed that the power level is proportional to the growth rate of the nanowires, which means increasing the power lengthens the nanowire arrays and reduces the growth process time.

For obtaining large internal surface area of the ZnO nanostructure in a highly effective agent to improve the separation of electrical charges in semiconductor devices [21], we should reduce diameters and increment length of Zno nanowire. In conventional hydrothermal method we cannot achieve such structure. Recently some researchers introduced ammonium hydroxide and polyethylenimine (PEI) to be added to the growth solution in order to reduce the homogeneous nucleation rate and thus wasting less precursor material which this process is called preferential growth [21].

In this paper our proposed method and preferential growth method were investigated and for more realization, results of these methods compared to fast hydrothermal methods introduced by Unalan et al [22], which are called rapid micro wave assisted (rapid MWA) method.



(1)



(2) **(3)**

Figure 4. SEM images of the longest possible ZnO nanowire arrays grown using the proposed method at different microwave power levels: (1) 180W 80 min (2) 450 W 50 min (3) 850 W 30 min, without any growth solution refreshment.

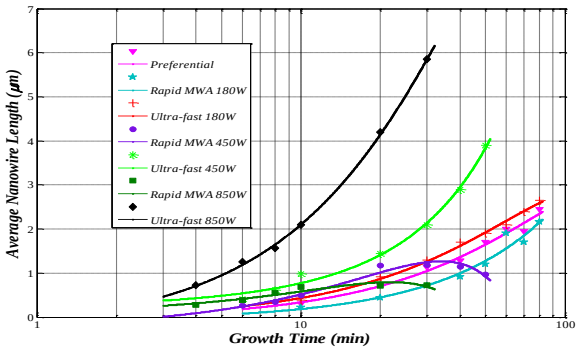


Figure 5. Average length of nanowires grown using different hydrothermal methods without refreshing the growth solution: preferential [21], rapid microwave-assisted [22] methods and proposed method.

Figure 5 shows the average longitudinal growth of ZnO nanowires versus growth process time for t rapid MWA, preferential growth method and our proposed ultra-fast method at different microwave power levels. At growth times more than 10 min, for low microwave power levels, the longitudinal growth of ZnO nanowires continued its rising trend by increasing the process time. However, when higher powers were applied to the system, despite the observation of higher growth rates by increasing the microwave power at short process times, the axial growth of the nanowires stopped at longer growth times so, in other words, the growth reached a saturation condition.

In addition, as the applied power increased, the saturation occurred sooner and the resultant nanowires were shorter. As a result, in our system, it was impossible to grow nanowires with lengths more than 1.2 μm at 450 W power level or nanowires longer than 700 nm at 850 W applied power without refreshing the growth solution.

Results of our proposed method clearly demonstrates the advantage of the proposed method over the preferential and rapid microwave assisted methods. As is obvious from the figure, the proposed method has a higher growth rate in comparison with the other fast methods, even at low power levels.

We used mercurochrome for sensitization of ZnO nanowires, because it is much cheaper than the Ru-based dyes and also proved to have better performance than the Ru-based N3 dye for ZnO nanowire-based DSSCs [23]. Table 1 show the summary of results for short-circuits current density (JSC), open-circuit voltage (VOC), fill factor (FF) and power conversion efficiency (η).

Table 1. Summary of the performance results for fabricated ZnO nanowire DSSCs.

Length of Zno nanowire arrays (μm)	J_{SC} (mA/cm^2)	V_{OC} (V)	FF	η (%)
9	3.15	0.40	0.34	0.43
11	4.59	0.44	0.37	0.75
13	4.96	0.43	0.37	0.79
16	3.98	0.46	0.34	0.62

As is obvious from the obtained performance results, the efficiency of the DSSCs gradually increases with increasing length of the nanowire arrays, increment of length of Zno nanowire cause increase absorption dye on surface Zno nanowire [24]. A maximum efficiency of 0.79% was achieved in a DSSC prepared by a 13μm long nanowire array, with short-circuit current density of 4.96 mA/ cm2, open-circuit voltage of 0.43 V and fill factor of 0.37. The enhancement in the power conversion efficiency of the cells seems to be mainly attributed to the increased short-circuit current density because, as we compare the cells with minimum and maximum efficiency, the improvement in short-circuit current density (~120%) is much larger than the open-circuit voltage (~16%). In our opinion, the increased internal surface area in the lengthened nanowire array, which leads to the improved dye loading, is the main reason for the short-circuit current density increase and, as a result, the power conversion efficiency enhancement.

We see efficiency of cell by 16 μm long nanowire arrays are less than 13μm long nanowire arrays. The reduction in the short-circuit current density of the cell with 16 μm long nanowire arrays could be attributed to the decreased internal surface area for dye adsorption. This could happen because, according to the SEM image of the array, at this level of growth the nanowires were mostly fused together as a result of their excessive lateral growth.

It should be noted that the efficiency of N719-sensitized TiO2 nanoparticle DSSCs is still much higher than that of our mercurochrome-sensitized ZnO nanowire DSSCs. The reason could be the wider absorbance spectrum of the N719 dye than that of the mercurochrome and larger internal surface area for dye adsorption and to more efficiency of DSSC [25].

4. Conclusion

In this research, we fabricated vertically aligned Zno nanowire arrays by microwave hydrothermal process which were used for manufacturing dye sensitized solar cells. We grew several length of Zno nanowire by proposed which has a higher growth rate in comparison with the other fast method and low power level. Finally, performance of DSSCs was investigated and results clearly show that the efficiency of the DSSCs gradually increases with

increasing length of the nanowire arrays, increment of length of Zno nanowire cause increase in the absorption of dye on surface the of Zno nanowire. it should be noted that in this research, variation of efficiency is important because of mercurochrome dye was used as dye at DSSC which has wider narrow absorbance spectrum.

Corresponding Author:
M.K Tabatabaei
Electrical Engineering Department, Amirkabir University of Technology, Tehran, Iran
E-mail: mk.tabatabaei@aut.ac.ir

References

[1] M.A Green, "Thin-film solar cells: review of materials, technologies and commercial status, *" J Mater Sci: Mater Electron.* **18**15-19 (2007).
[2] N.O. Plank, I. Howard, A. Rao, M.B. Wilson, M.E. Welland and et.al, "Efficient ZnO Nanowire Solid-State Dye-Sensitized Solar Cells Using Organic Dyes and Core-shell Nanostructures," *J. Phys. Chem. C.* **113**18515–22 (2009).
[3] J.A. Anta, E. Guillen and R. Tena-Zaera, "ZnO-Based Dye-Sensitized Solar Cells*" J. Phys. Chem. C.* **116** 11413–25 (2012).
[4] B. O'regan and M. Gratzel, "A low-cost, high-efficiency solar cell based on dye-sensitized colloidal Ti02 films," *Nature*. **353** 737–40 (1991)
[5] M. Law, L. E. Greene, J. C. Johnson, R. Saykally, and P. Yang, "Nanowire dye-sensitized solar cells," *Nat Mater*. **4** 455-59 (2005).
[6] H. Horiuchi et al., "Electron Injection Efficiency from Excited N3 into NanocrystallineZnO Films: Effect of (N3−Zn2+) Aggregate Formation," *J. Phys. Chem. B.* **107** 2570-74 (2003).
[7] J.J Wu, G.R Chen, H.H Yang, C.H Ku, and J.Y Lai, "Effects of dye adsorption on the electron transport properties in ZnO-nanowire dye-sensitized solar cells," *Applied Physics Letters*. **90** 213109 (2007).
[8] S.K. Arya, S. Saha, J.E. Ramirez Vick, V.Gupta, S.Bhansali, S.P. Singh, "Recent advances in ZnO nanostructures and thin films for biosensor applications " *AnalyticaChimicaActa.* **737** 1– 21 (2012).
[9] Wang J X, Sun X W, Yang Y, Huang H, Lee Y C, Tan O K and Vayssieres L, "Hydrothermally grown oriented ZnO nanorod arrays for gas sensing applications " *Nanotechnology.* **17** 4995–8 (2006)
[10] Konenkamp R, Word R C and Schlegel C, "Vertical nanowire light-emitting diode" *Appl. Phys. Lett.* **85** 6004–6 (2004).
[11] Goldberger J, Sirbuly D J, Law M and Yang P , "ZnO Nanowire Transistors" *J. Phys. Chem. B.* **109** 9–14 (2005)
[12] Suehiro J, Nakagawa N, Hidaka S I, Ueda M, Imasaka K, Higashihata M, Okada T and Hara M, "Dielectrophoretic fabrication and characterization of a ZnO nanowire-based UV photosensor " *Nanotechnology.* **17** 2567–73 (2006)
[13] Wang Z L and Song J H, "Piezoelectric Nanogenerators Based on Zinc Oxide Nanowire Arrays" *Science*. **312** 242–6 (2006)
[14] Law M, Greene L E, Johnson J C, Saykally R and Yang P, "Nanowire dye-sensitized solar cells" *Nature Mater.* **4** 455–9 (2005)
[15] E. Stathatos, P. Lianos, S. Zakeeruddin, P. Liska, and M. Grätzel, "A quasi-solid-state dye-sensitized solar cell based on a sol-gel nanocomposite electrolyte containing ionic liquid," *Chemistry of materials.* **15** 1825–29 (2003).
[16] L. E. Greene et al., "Low-Temperature Wafer-Scale Production of ZnO Nanowire Arrays," *AngewandteChemie International Edition*. **42** 3031-34 (2003).
[17] L. E. Greene et al., "General Route to Vertical ZnO Nanowire Arrays Using Textured ZnO Seeds," *Nano Lett.* **5** 1231-36 (2005).
[18] H. E. Unalan, P. Hiralal, N. Rupesinghe, S. Dalal, W. I. Milne, and G. A. J. Amaratunga, "Rapid synthesis of aligned zinc oxide nanowires," *Nanotechnology*. **19** 255608 (2008).
[19] K. D. Benkstein, N. Kopidakis, J. van de Lagemaat, and A. J. Frank, "Influence of the Percolation Network Geometry on Electron Transport in Dye-Sensitized Titanium Dioxide Solar Cells," *J. Phys. Chem. B.* **107** 7759-67 (2003).
[20] P. Yang et al., "Controlled Growth of ZnO Nanowires and Their Optical Properties," *Advanced Functional Materials.* **12** 323-31 (2002).
[21] Y. Zhou, W. Wu, G. Hu , H. Wu, S. Cui, "Hydrothermal synthesis of ZnOnanorod arrays with the addition of polyethyleneimine," *Materials Research Bulletin*. **43** 2113–18 (2008).
[22] C. Xu, P. Shin, L. Cao, and D. Gao, "Preferential Growth of Long ZnO Nanowire Array and Its Application in Dye-Sensitized Solar Cells," *J. Phys. Chem. C*, vol. 114, no. 1, pp. 125-129, 2009.
[23] Wu J-J, Chen G-R, Yang H-H, Ku C-H and Lai J-Y 2 "Effects of dye adsorption on the electron transport properties in ZnO-nanowire dye-sensitized solar cells "*Appl. Phys. Lett.* **90** 213109 (2007)
[24] C.Y Lin ,Y.H Lai, H.W Chen, J.G Chen, C. Wei Kung , R. Vittal and K.C Ho, "Highly efficient dye-sensitized solar cell with a ZnO nanosheet-based photoanode, " *Energy Environ. Sci.* **4** 3448-55 (2011).
[25] E. Guill, F. Casanueva, J.A Anta, A. Vega-Poot, G. Oskam, R. Alcantara, C. Fernandez-Lorenzo and J. Martın-Calleja, "Photovoltaic performance of nanostructured zinc oxide sensitised with xanthene dyes" *J. Photochem. Photobiol. A.* **200** 364–70 (2008).