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Short Communication

Effect of Multi Walled Carbon Nanotubes as Counter Electrode on Dye Sensitized Solar Cells

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The counter electrode is an important component in dye-sensitized solar cells (DSSC) where the mediator is reduced. It consists of fluorine-doped tin oxide (FTO) glass coated with platinum to afford more reversible electron transfer. In this research for increasing energy conversion efficiency of DSSC's, Multi-Walled carbon nanotubes (MWCNTs) were used in counter electrode. Three types of counter electrode (CE) were fabricated: (i) All platinum counter electrodes (Pt-CE) (ii) All Multi-Walled carbon nanotube counter electrodes (MWCNT-CE) and (iii) Mixed Platinum and Multi-Walled carbon nanotube counter electrodes (Pt-MWCNT-CE). All of counter electrodes prepared fabricated on FTO glasses and cells were assembled by these electrodes and its performance was measured by solar light simulator, their behavior were studied by cyclic voltammetry technique and their Structure were studied by SEM. Results revealed that enhanced efficiency was obtained by using the Pt-MWCNT-CE. Also by using this electrode, the energy conversion efficiency increased up to about 18% in comparison with standard DSSC's. Pt-MWCNT-CE displayed the highest catalytic activity for the reduction of tri-iodide ions and lowest transfer resistance in cyclic voltammetry tests which improves photovoltaic activity of cells.

Keywords: Carbon nanotube, dye sensitized solar cells, counter electrodes, Efficiency, platinum

1. INTRODUCTION

Dye-sensitized solar cells (DSSCs) based on dye-sensitized nanocrystalline titanium dioxide and [Ru(4,40-dicarboxylic acid 2,20-bipyridine)$_2$(NCS)$_2$] have been reported by Regan and Gratzel in 1991 [1]. DSSC has been attracting considerable attention for an alternative to conventional silicon solar cell because of its low cost, easy handling, relatively high photon-to-current conversion efficiency for low energy consumption and simple fabrication process [1–3]. Moreover, an increase in DSSC efficiency would provide enormous economical advantages. DSSC is composed of dye

molecules, nano crystalline titanium dioxide, and electrolytes containing a redox couple and counter electrode. The H_2PtCl_6-treated electrode is used as the counter electrode in DSSC because of its high electrochemical activity even though this electrode is expensive. A low cost electrode with high electrochemical activity is an important requirement to enhance the practical utility of DSSC's .

On the other hand, conversion efficiency of DSSC's is still lower than familiar silicon solar cells. Therefore, many studies have been conducted in order to obtain high efficiency DSSC's such as increasing porosity and crystallizing of TiO2 electrode [4], doping metal ions into TiO_2 electrode [5], using alternative electrolyte [6,7] or counter electrode [8]. Carbon nanotubes (CNTs) have recently attracted great attention because of their special properties such as very high mechanical strength, very good thermal stability, and excellent electronic properties [9–11].Also, electrical conductance of CNTs reveals their catalytic activity for the reduction of tri-iodide [12]. These useful properties make CNTs as good candidates in various application fields such as transistor, battery, field emission display, nano scale inter connects and solar cells[13].Sung Uk Lee et al. [14] used Single wall and multi wall carbon nanotubes (SWCNT and MWCNT) for the fabrication of efficient counter electrodes in dye-sensitized solar cells (DSSC).They fabricated the counter electrode of those cells by repeated deposition and drying of carbon nanotubes and Platinum over an FTO glass. Among two electrodes, the highest efficiency solar cells (4.36%) was achieved by using MWCNT and lower efficiency solar cells (4.03%) was fabricated by addition of SWCNT.

In this paper for increasing the efficiency of DSSCs, multi walled carbon nanotubes (MWCNT) were used in counter electrode and the effect of them on the efficiency of DSSC were investigated. Also their catalytic activity and there electrochemical behavior were studied and described.

2. EXPERIMENTAL

For fabrication of DSSC devices, TiO_2 paste (Dyesol company), N719 dye (Dyesol company), Iodine electrolyte (Dyesol company), H_2PtCl_6 (601450 Merck), multi walled carbon nanotubes (purity : >95%, diameter: 10-20 nm and length: 20 μm),TiCl4 (8.12382 Merck) and deionized water were used as raw materials. TiCl4 which used in this study was diluted at 0 °C by water to make 2 M stock solution; this solution was kept in a freezer and freshly diluted to 40 mM for each TiCl4 treatment. To prepare the DSSC working electrodes, FTO glasses (15Ω/Sq.m, Dyesol Company) were first cleaned in a detergent solution by using an ultrasonic bath for 15 min, and then rinsed with water and ethanol.

For applying paste, a layer of paste was coated on all of FTO glass plates by tape casting, kept in a clean box for 3 min in order to homogenize the paste and reduce the surface irregularity. After that, electrodes were dried at 130 °C for 6 minutes. For increasing thickness these steps were repeated five times. After drying, the electrodes coated with the TiO_2 pastes were gradually heated under air flow at 325°C, 380°C, 460°C, and finally 500°C. Total cycle was done at 40 minutes. After that, the TiO_2 electrodes were immersed into a 40 mM aqueous TiCl4 solution at 70 °C for 30min and washed with water and ethanol and heated under air flow at 500°C for 30 minutes. After cooling up to 80°C, TiO_2 electrodes was immersed into 0.5 mM N-719 dye solution and kept at room temperature for 20–24 h to assure complete sensitizer uptake.

To prepare the different counter electrodes, holes were drilled in the FTO glasses, the perforated glasses were washed with H_2O and 0.1 M HCl-ethanol solution and cleaned by ultrasound in an acetone bath for 10 min. After removing residual organic contaminants by heating in air for 15 min at 400 °C, for preparing platinum electrode ,the Pt catalyst were deposited on the FTO glasses by dipping in the 0.2 wt.% H_2PtCl_6 solution and heat treatment at 400 °C for 15 min. This counter electrode is called "platinum counter electrodes" (Pt-CE)."Multi-Walled carbon nanotube counter electrodes" (MWCNT-CE) and "Mixed Platinum and Multi-Walled carbon nanotube counter electrodes" (Pt-MWCNT-CE) was prepared by spraying of MWCNT solution or Pt-loaded MWCNT solution on FTO glasses and heat treatment of them at 400 °C. For preparing of MWCNT solution, 1 g of acid treated CNTs was added to 100 ml of distilled water and dispersed by ball milling for 24 h. After ball milling, 100 mg of carboxymethyl cellulose (CMC) was added to it as a condensation and dispersion agent. After further ball-milling, 400 ml of water was added to it and sonicated by ultrasonicator for 40 minutes. Pt-loaded MWCNT solution was prepared by direct mixing of acid treated CNT powders (0.2 wt. %) with 0.2 wt.% H_2PtCl_6 solution ,finally The dye-covered TiO_2 electrode and different counter electrode were assembled into a sandwich type cell, filled by electrolyte and sealed. Flow chart of the process and scheme of fabricated cells were shown in Figures 1 and 2. The microstructure and the thickness of the TiO_2 electrode and counter electrodes were measured by scanning electron microscopy (SEM) (cam scan MV2300). The catalytic properties of counter electrodes were measured by cyclic voltammetry (746 va trace analyzer and 747 vstand Methrohm).The performance of the dye-sensitized solar cell was examined by using a solar simulator (Model No.81172, Oriel Co.) at an intensity of 1000 w/cm^2.

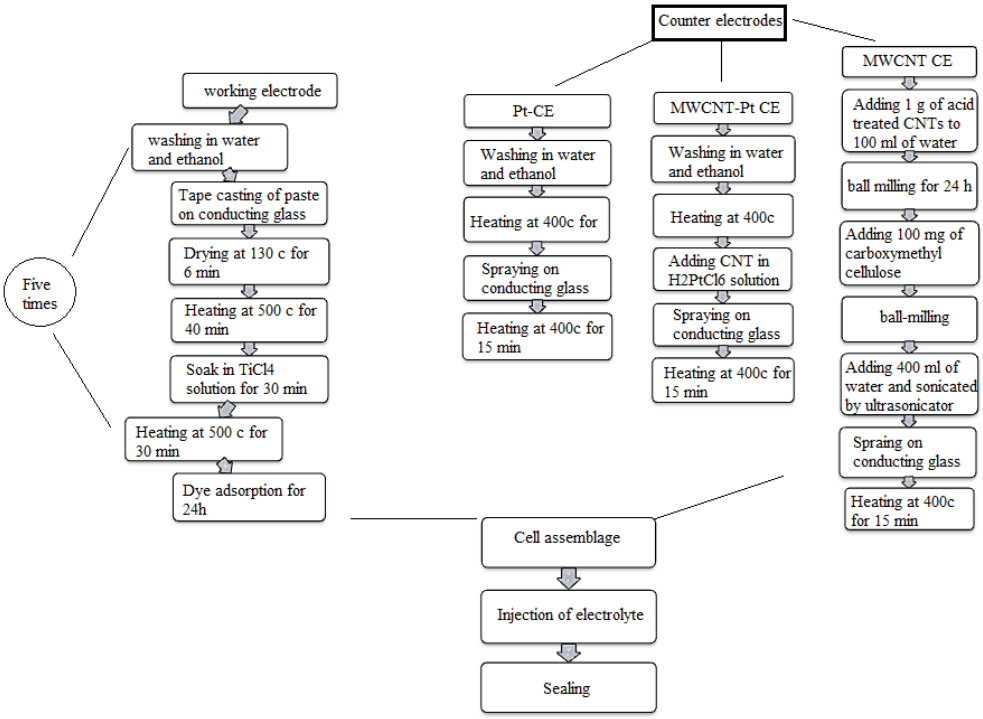


Figure 1. Flow chart for fabrication process

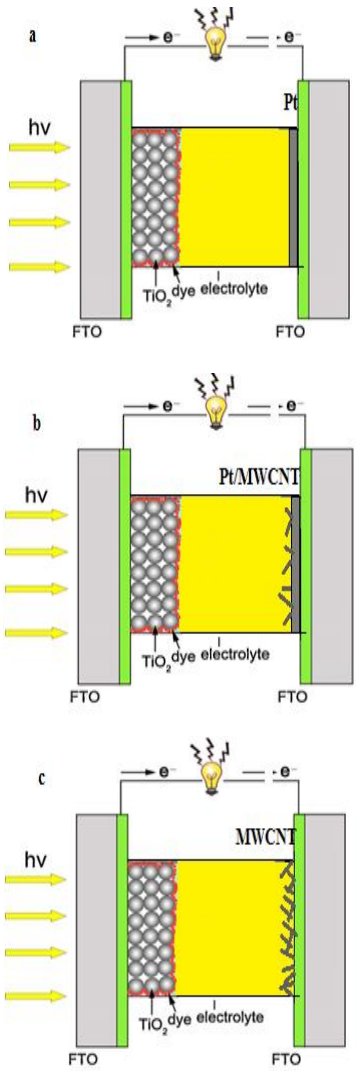


Figure 2. Schematic structures of the DSSCs , fabricated in this work(a)Pt-CE DSSC, (b)MWCNT-Pt CE DSSC ,and(c)MWCNT-CE DSSC.

The conversion efficiency of the cell was characterized by the short- circuit photocurrent density, the open-circuit voltage, the fill factor of the cell and the intensity of the incident light:[15]

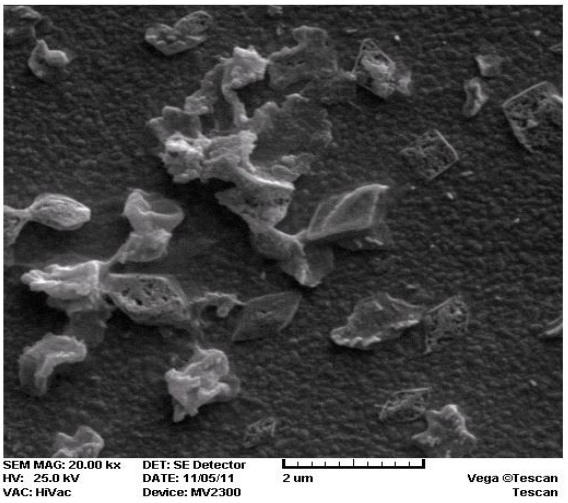
$$\eta = \frac{J_m V_m}{P_{in}} = \frac{FF\,(V_{oc} J_{sc})}{P_{in}} \quad (1)$$

$$FF = \frac{J_m V_m}{J_{sc} V_{oc}} \quad (2)$$

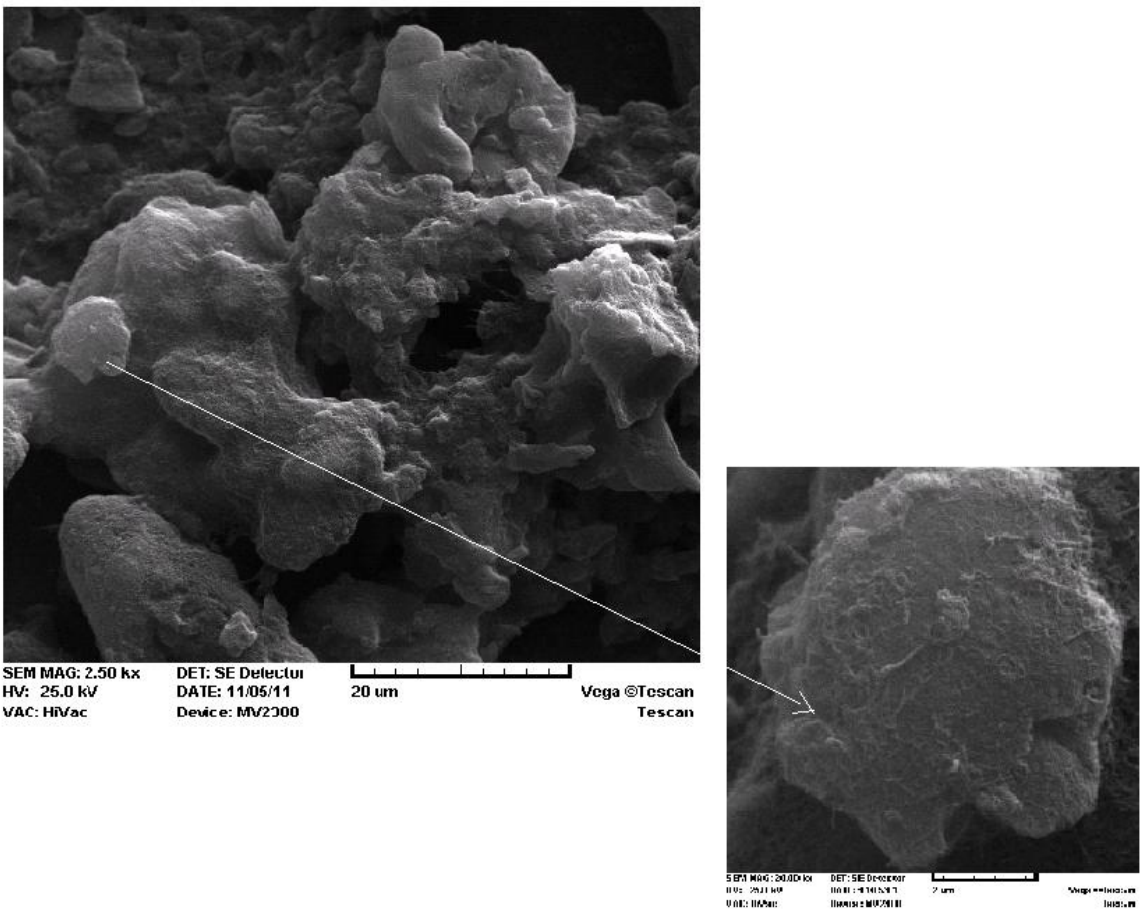
In Eq. (1), η is the the conversion efficiency of the cell, J_m is the maximum current density, V_m is the maximum voltage , P_{in} the intensity of the incident light, and in Eq. (2), FF is the fill factor , V_{oc} is the open-circuit voltage and J_{sc} is the short- circuit photocurrent density.

3. RESULTS AND DISCUSSION

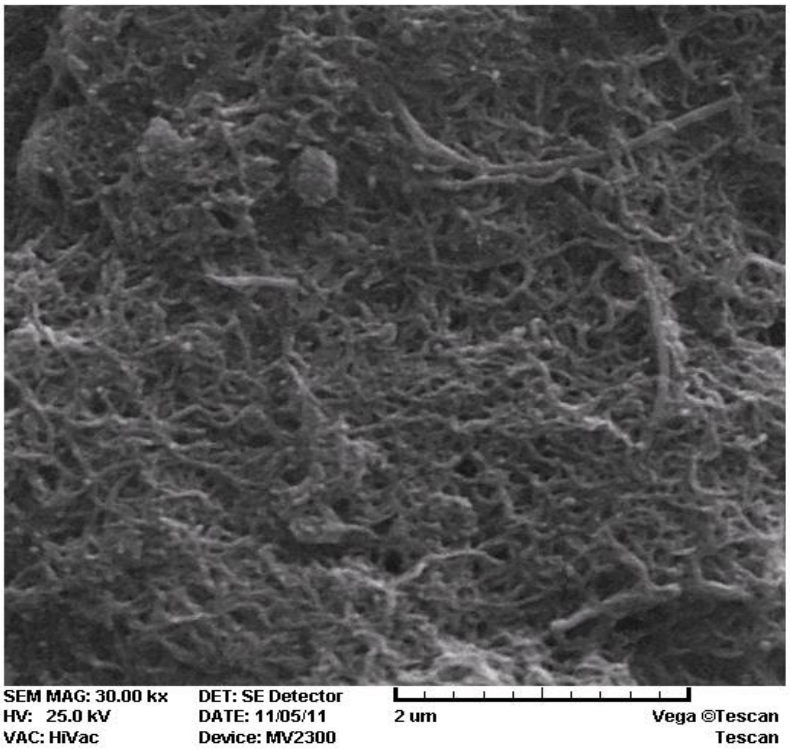
The SEM images of different counter electrodes are shown in Fig.3. From these images it can be found that, the Platinum film is not compact and some part of FTO glass is not covered by Pt particles, then large pore were seen on Pt film that may decrease its catalytic properties (Fig3.a).



(a)



(b)

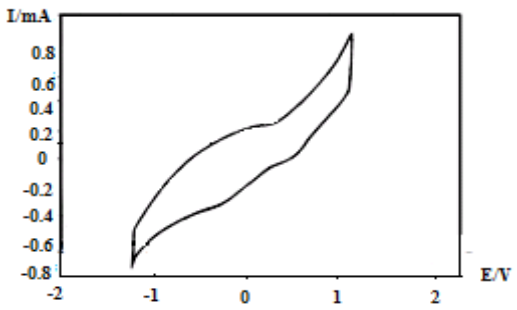


(c)

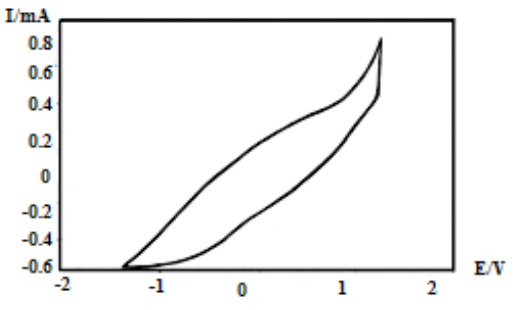
Figure 3. The SEM images of counter electrodes (a) Pt-CE (b) Pt-MWCNT-CE (c) MWCNT-CE

Based on Fig. 3.b, by addition of carbon nanotubes in Pt film, these particles were deposited on the surface or inside the porosity of Platinum films and this will be lead to increasing surface area of the Platinum films. Fig.3.c shows the microstructure of CNT electrode, it reveals that the film has uniform structure and less pores were generated in the structure.

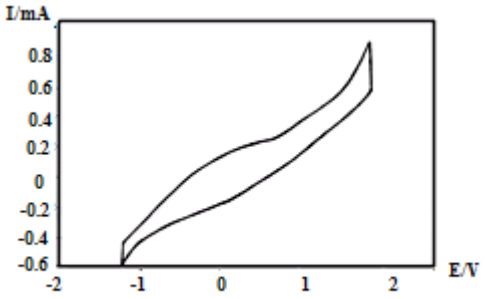
The cyclic voltammograms of all counter electrodes in iodide electrolyte were shown in Fig. 4. Based on this figure, the electrochemical properties of Pt-MWCNT-CE were found to be better than the Pt-CE for using as DSSC counter electrodes. This counter electrode showed a highest current density at the reduction reaction peak (0.25 V) than Pt-CE and MWCNT-CE. This indicates that the redox reaction rate of the Pt-MWCNT-CE is higher than that of Pt-CE and MWCNT-CEs.



(a)



(b)



(c)

Figure 4. CV curve for DSSC with different counter electrodes (a)- Pt-MWCNT-CE , (b)- Pt-CE , (c) - MWCNT-CE

Moreover, This suggests that an increase in the effective area of catalysis enhances current density because the specific surface area of CNT-Pt counter electrodes is much larger than that of the Pt and CNT counter electrodes [15,16]. These advantages due to enough regeneration of iodide ions help to achieve a high conversion efficiency of DSSC.

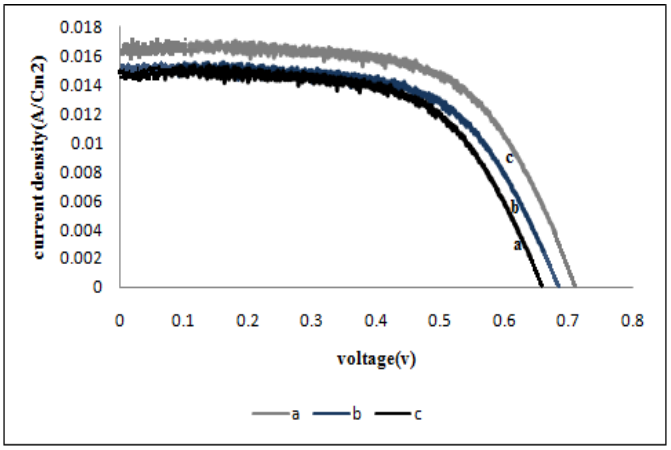


Figure 5. I–V curve for DSSC with different counter electrodes ,C(Pt-loaded CNT) B(Pt electrode) A(CNT electrode)

Table I. J–V parameters of cells with different counter electrode

Number	Counter electrode	Short circuit Current (*Jsc*) (mA/cm2)	Open circuit voltage (*Voc*) (V)	Fill factor	conversion efficiency (Ƞ) (%)
1	Pt	15.3	0.670	0.70	7.2
2	Pt-MWCNT	17.2	0.690	0.71	8.6
3	MWCNT	15.1	0.655	0.68	6.7

The I-V curve characteristics and calculated efficiency of solar cells which were fabricated by these counter electrodes are shown in Fig. 5 and table 1. It is seen that the solar cells with MWCNT-CE had more conversion efficiency than other cells. Other studies postulated that efficiency of MWCNT electrodes immerges from its metallic nature [17] or their extraordinary high electrical conductivity [18] or large surface area of electrodes [19].If all of these finding are true, efficiency of cells which was fabricated by MWCNT-CE must better than others but results shows opposite results, then may be combination of platinum and MWCNT generate new structure and improve efficiency of cells. This structure is seen in case of the cells with Pt-MWCNT-CE. As seen from Fig. 3, the Pt film is not compact and the large pore is present on it. Therefore, during the CNT spraying, the particle of CNT can be deposited on the surface of Pt and also into the porous space and thus the surface area of the Pt is increased. Moreover, Pt itself acts as a light reflector at the same time and thus can remarkably improve the light absorption by the semiconductor surface [20]. These dual facts may be the main reason for the increased efficiency of the solar cell when the Pt-loaded MWCNT film is used as a counter electrode. These findings are similar to B. Ahmmad et al. [21] and Jing-Zhi Chen et al. [22] results. They investigated effect of SWCNT counter electrodes on efficiency of dye sensitized solar cells and showed that DSSCs were made of Pt alone and SWNT alone films had similar efficiency but the best efficiency was obtained for the Pt-loaded SWNT-film counter electrodes[21].

4. CONCLUSION

The effect of carbon nanotubes on the performance of DSSC showed that the DSSC fabricated with Pt-MWCNT-CE had current density of 17.2 mA/cm2 and voltage of 0.690V and conversion efficiency of %8.6.this cell showed highest photovoltaic performances. These results attributes to the increasing the surface area of counter electrode. Furthermore, CNTs behaved as catalysts in the iodide/tri-iodide redox reaction, and Improved catalytic activity .moreover Pt itself acts as a light reflector at the same time and thus may remarkably improve the light absorption by the semiconductor surface.

References

1. B.O'Regan ,M. Gratzel, *Nature* 353 (1991) 737–740.
2. M. K. Nazeeruddin , R. Humphry-Baker ,P. Liska, M. Gratzel,*J.Phys.Chem*.B107 (2003) 8981–8987.
3. S. Nakade, M. Matsuda ,S. Kambe , Y. Satio , T. Kitamura ,T. Sakata ,Y. Wada, H. Mori ,S. Yanagida ,*J. Phys. Chem*.B106 (2002) 10004–10010.
4. S. Kambe ,S. Nakade ,Y. Wada ,T. Kitamura ,S. Yanagida , *J.MaterChem*.12 (2002) 723–728.
5. K.H. Ko, Y.C. Lee, Y.J. Jung, *J. Colloid Inter. Sci*. 283 (2005) 482–487.
6. M.A. De Paoli, A.F. Nogueira, D.A. Machado, C. Longo, *Electro- chim. Acta* 46 (2001) 4243–4249.
7. M. Berginc, U. Opara Kraˇsovec , M. Jankovec, M. Topic, *Sol. Energy Mater. Sol. Cells* 91 (2007) 821–828.
8. Y. Satio, T. Kitamura, Y. Wada, S. Yanagida, *Chem. Lett.* 31 (2002) 1060–1061.

9. S.Fan,M.G.Chapline,N.R.Franklin,T.W.Tombler,A.M.Cassell,H.Dai,*Science* 283 (1999) 512–514.
10. P.G.Collins, A.Zettl ,*J.Phys.Rev*.B55 (1997) 9391–9399.
11. J.M.Bonard ,F.Maier , T.St ¨ ockli, A. Chˆatelain, W.A. deHeer ,J.P. Salvetat , L. Forro´ , *Ultra microscopy* 73 (1998) 7–15.
12. H.S. Wroblowa,A. Saunders, *Chem.*42 (1973) 329–346.
13. W.J. Jong, S.H. Lai, K. H. Hong, H. N. Lin, H. C. Shih, *Diam. Relat. Mater*. 11 (2002) 1019–1025.
14. Sung Uk Lee, Won Seok Choi, Byungyou Hong, *Solar Energy Materials & Solar Cells* 94 (2010) 680–685.
15. Chuen-Shii Chou , Che-I Huang, et al. *Advanced Powder Technology* (2010)
16. O. Topon, et al. Proc. Symposium on Photovoltaic for the 21st Century 5 in the 216th ECS Meeting, Vienna, Austria, (Oct. 4-9, 2009), to be published.
17. P. M. Ajayan, *Chem. Rev*. 99 (1999) 1787.
18. A. Thess, R. Lee, P. Nikolaev, H. Dai, and P. Petit et al. *Science* 273 (1996) 483.
19. P. Serp, M. Corrias, and P. Kalck, *Appl. Catal. A: Gen*. 253 (2003) 337.
20. M. K. Nazeeruddin, A. Kay, I. Rodicio, R. H. Baker, E. Müller, P. Liska, N. Vlachopoulos, and M. Grätzel, *J. Am. Chem. Soc*. 115 (1993) 6382.
21. B. Ahmmad ,*J. Sci. Res*. 1 (3) (2009) 430-437.
22. Jing-Zhi Chen ,*Journal of the Chinese Chemical Society* 57 (2010) 1180-1184.