Publications

Available Online

J. Sci. Res. **1** (3), 430-437 (2009)

JOURNAL OF SCIENTIFIC RESEARCH

www.banglajol.info/index.php/JSR

Effect of Single Walled Carbon Nanotube as Counter Electrode on Laser-deposited Fe_2O_3 and TiO_2 Films Solar Cells

B. Ahmmad, Y. Kusumoto*, M. Abdulla-Al-Mamun, A. Mihata, and H. Yang

Department of Chemistry and Bioscience, Graduate School of Science and Engineering, Kagoshima University, 1-21-35 Korimoto, Kagoshima 890-065, Japan

Received 9 June 2009, accepted in revised form 15 August 2009

Abstract

Laser-deposited Fe_2O_3 films or dye-fixed TiO_2 films were prepared for solar cells. For both the cells, a single walled carbon nanotube (SWNT) film or a Pt-loaded SWNT film, prepared by simply pasting over ITO glass, was used as a counter electrode. Stable current (I)-voltage (V) curves were found under UV-visible light irradiation using water containing KI and I_2 as an electrolyte. A comparison of I-V curves was made for Pt alone and SWNT alone films used as a counter electrode. Almost similar efficiency was found by using both types of counter electrodes. However, enhanced efficiency was obtained for the Pt-loaded SWNT-film counter electrode.

Keywords: TiO_2; Fe_2O_3 film; Solar cell; SWNT.

DOI: 10.3329/jsr.v1i3.2631 J. Sci. Res. 1 (3), 430-437 (2009)

1. Introduction

For the gratification of increasing world energy demand and the protection of the environment from pollution, renewable resources of energy are urgently needed. The search for such energy resources has led to an increasing interest in photoelectrochemical cells which take advantage of the fact that photons falling on a semiconductor can create electron-hole pairs, which may result in setting up of an electric potential difference across the interface at a junction between two different materials [1]. For the last twenty years much attention has been paid on the metal oxide-based thin film as a working electrode. Among the oxide semiconductors, TiO_2, ZnO, SnO_2, Nb_2O_5, $SrTiO_3$, In_2O_3 and WO_3 have been studied elaborately [1-3]. Semiconducting iron oxide (Fe_2O_3) is suitable to use as a photoelectrode because of its low cost as well as its small band gap energy of ~2.2 eV [4] which enables it to absorb the photons of the solar spectrum. Recently, in our laboratory a porous thin film of Fe_2O_3 was utilized in a new type of solar cell [5]. It was found that the bilayered Fe_2O_3 film prepared by the laser ablation and squeegee methods

---

* *Corresponding author*: kusumoto@sci.kagoshima-u.ac.jp

gives better physical stability and the stable photocurrent (*I*)-voltage (*V*) curve under visible light irradiation with Pt as a counter electrode. But the use of Pt is not economic way for mass production. Carbonaceous materials are quite attractive to replace Pt due to their high electric conductivity, corrosion resistance toward I_2, high reactivity for triiodide reduction and low cost [6]. Suzuki *et al.* [7] examined three kinds of nano-carbon materials for the search of an efficient counter electrode for dye-sensitized solar cells (DSC) i.e., SWNT, multi walled carbon nanotube (MWNT) and nanohorn. They prepared the carbon nanomaterial and the Pt film over an FTO glass by repeated deposition and drying processes. Among three electrodes the highest efficiency, 4.5%, was found for SWNT. MWNT and nanohorn showed low efficiencies of 0.2 and 0.04%, respectively. Moreover, they found that SWNT shows 85% efficiency of that in Pt electrode. However, they did not report the efficiency of the SWNT electrode in Fe_2O_3 film solar cells and also the effect of Pt loading over the SWNT electrode. In this paper we report the effect of Pt loading over SWNT films when used in the Fe_2O_3 film solar cells as well as dye-fixed TiO_2 films solar cells.

2. Experimental

1.2. *Materials*

The photocatalysts were Fe_2O_3 (Wako, 99.5%) and TiO_2 (Degussa, P25) with mainly anatage structure (ca. 80%). Other materials are as: EtOH (Wako, 99.5%), dicyclohexylcarbodiimide (DCC, Wako, 95%), γ-aminopropyltriethoxysilane (Alfa Aesar), tetrahydrofuran (THF, Wako, 99.5%), eosin Y (EY, Wako, 99%), single-walled carbon nanotubes (MTR Ltd, 50-70%) and Pt (Nilaco, 99.98%). All films were prepared on indium-tin-oxide (ITO, Aldrich) coated glasses which have a resistance of 8-12 ohms.

2.2. *Preparation of dye-fixed TiO_2 film*

In the first step, the TiO_2 film was prepared by the pulse laser ablation method as shown schematically in Fig. 1(a). TiO_2 targets were prepared by mixing 5.5 g of TiO_2 with 0.55 g of paraffin (10%) to prevent cracking. The mixed powder was pressed at 20 MPa for 1 hour and calcined at 400 °C for 6 hours to form a TiO_2 pellet. The pellet was introduced into a vacuum chamber (O_2 atmosphere), where the laser pulse enters through a window and impinges on the target materials to be deposited. A laser power of 2.8 J / (pulse cm^2) was used throughout the experiment. The wavelength of the laser was 532 nm (Nd-YAG laser). The substrate temperature and time of laser irradiation were 600 °C and 24 min., respectively. Irradiation of the target with a laser beam melted the target to form a plume. The plume was accumulated on the ITO coated glass to form the TiO_2 thin film.

In the second step, the TiO_2 film was fixed with EY using a silane-coupling reagent as described by Ryo *et al.* [8]. The silane-coupling reagent was stirred in aqueous EtOH solution for 1 hour at room temperature. After the stirring, the TiO_2 film was dipped into the solution under stirring for 1 hour using a magnetic stirrer. The film was dried by heating at 100 °C for 15 min. The propylamine modified TiO_2 film was dipped into a solution containing 100 ml of THF, EY and DCC and the mixture was stirred for 6 hours. The film was then air-dried and stirred twice in aqueous EtOH (pH=12, adjusted by NaOH) for 24 hours and also twice in distilled water for 12 hours to remove excess dyes which were physically adsorbed or bound with the ester bond on the TiO_2 surface.

2.3. *Preparation of Fe_2O_3 film*

The bilayered Fe_2O_3 film was prepared by the laser ablation and squeegee methods. Initially, a compact thin film of Fe_2O_3 was deposited on the ITO coated glass with the same method as for TiO_2 film preparation. The substrate temperature in the chamber was set at room temperature. The compact thin film was further coated with porous Fe_2O_3 by the squeegee method. The preparation method of the Fe_2O_3 paste is as follows: Fe_2O_3 powder (2 mg) was mixed with nitric acid (0.1 ml) and water (2 ml). After well mixing, 2 ml of Triton X-100 were mixed to get a paste. The paste was then used to prepare the film by the squeegee method. Finally the film was heated at 450 °C for 1hour under air environment. The total thickness of the film was about 10 μm.

2.4. *Preparation of counter electrode films*

The film of SWNT was prepared by the doctor-blade technique. First, 5 mg of SWNT were smashed softly for 2 min. 1 ml of a surfactant (Triton X-100) was added and mixed to get a paste. The paste was spread over an ITO glass to get a thin film (a) which was then heated at 450 °C for 1h under oxygen atmosphere (1 atm). Another SWNT film (b) was heated comparatively at lower temperature (250 °C) for 30 min. under N_2 gas atmosphere (1 atm). Hereafter, the films (a) and (b) are indicated as O-SWNT and N-SWNT, respectively. Another type of Pt-loaded SWNT film was prepared by the following method: 5 mg of SWNT and 0.4 ml of ethanol were put into a mortar and mixed well to get a paste-like suspension. The paste was spread almost homogeneously over the ITO glass and dried at room temperature for two days. Then a layer of Pt was made over the SWNT film by the sputtering method. The overall thickness of the Pt- loaded SWNT film was about 15 μm. Hereafter, the film (c) is indicated as SWNTPt.

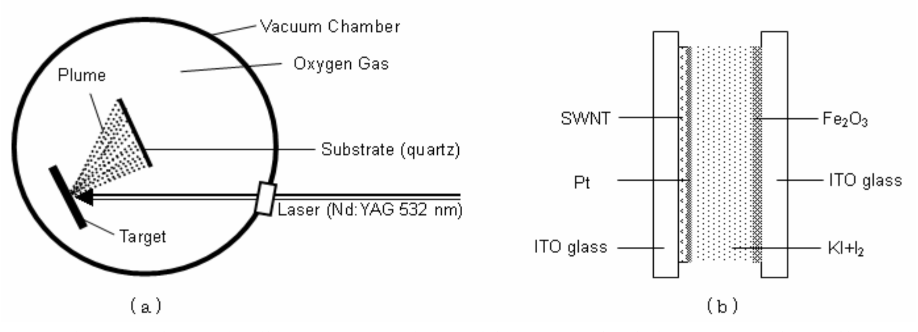

Fig. 1. Schematic diagram of (a) laser ablation method (b) Fe_2O_3 solar cell.

2.5. *Methods*

Both films of Fe_2O_3 and EY-fixed TiO_2 were used as a working electrode and SWNT and or Pt-based films were used as a counter electrode. The two electrodes were sandwiched and a mixture of KI (0.8 M) and I_2 (0.2 M) in water solvent was used as an electrolyte that was filled into a space between the two electrodes.

The structure of the Fe_2O_3 solar cell is schematically shown in Fig. 1(b). A xenon lamp (Inotex 300-W LX-300F) with an IR cut- off filter was used as a light source (power 1 sun). For the measurement of the performance of solar cell, an *I-V* meter (Keithly 2400) was used. The *I-V* meter was connected to a computer with a Peccell *I-V* curve analyzer (PECK2400-N). The mixture of KI (0.8 M) and I_2 (0.2 M) in water solvent was used as an electrolyte. The thin films were characterized by a scanning electron microscope (SEM, Hitachi S-4100), X-ray diffraction (XRD) using an X-ray diffractometer (Rigaku) with Cu $K\alpha$ radiation and absorption spectroscopy (Shimadzu, MPS-2000 spectrophotometer).

3. Results and Discussion

3.1. *Characteristics of the films*

The UV-visible spectra for the Fe_2O_3 and dye-fixed TiO_2 films are shown in Fig. 2. We can see that both films have the absorption edges in the visible range at around 580 nm. However, both films show the strong absorption also in the UV range. Figs. 3(a) and (b) show the SEM images of Fe_2O_3 and TiO_2 films, respectively, prepared by the laser ablation method. The particle sizes of TiO_2 on the film are almost homogenous, although some aggregated particles are found. In case of the Fe_2O_3 film, porous particles are found with particle sizes ranging from 90 to 120 nm. Fig. 3(c) shows the SEM image of N-SWNT film heated in low temperature (250 °C) under N_2 gas atmosphere. It is seen that the porous film is composed of a considerable amount of amorphous carbon along with carbon nanotubes. It was found from the SEM images of very thin SWNT films that poorly formed carbon nanotubes were burned out by heating at higher temperature (>400 °C) under oxygen atmosphere (data not shown).

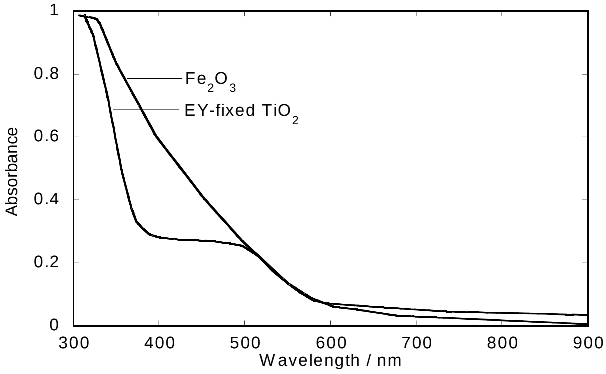

Fig. 2. UV-visible spectra of Fe_2O_3 and EY-fixed TiO_2 thin films

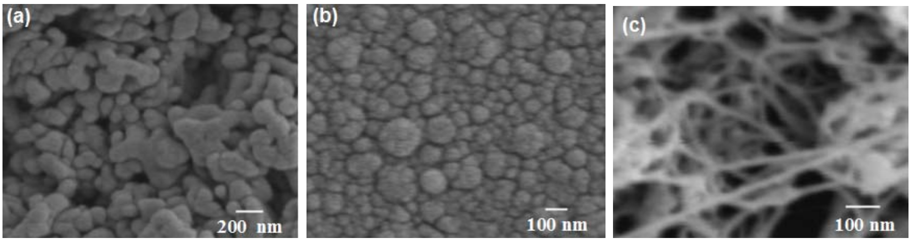

Fig. 3. SEM images of (a) Fe_2O_3, (b) TiO_2 and (c) N-SWNT films

The crystal structure of the Fe_2O_3 and TiO_2 films were studied by XRD spectroscopy and the results are shown in Figs. 4(I) and 4(II), respectively. From the XRD patterns of the Fe_2O_3 powder and the Fe_2O_3 film on the ITO coated glass, it is seen that the crystal structure of α-Fe_2O_3 is not destroyed by the laser ablation under the experimental conditions used. But it was found that the phase transition occurs during the film preparation by the laser ablation method from TiO_2 (P25) powder because of high temperature of the substrate [9] and the crystal structure of TiO_2 on the ITO glass is composed of about 40% anatase and 60% rutile forms.

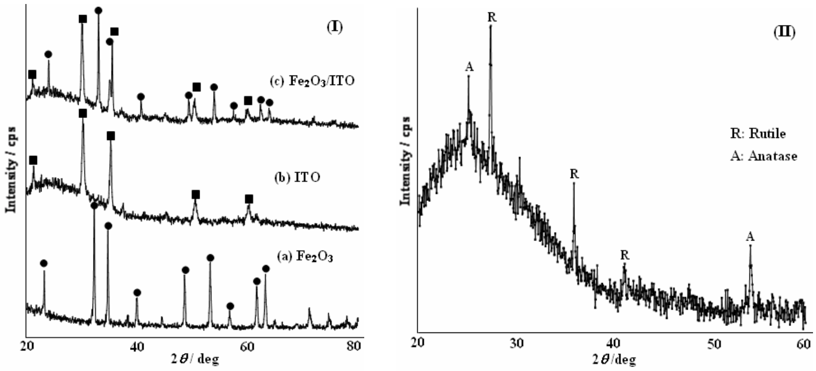

Fig. 4. (I) XRD patterns of (a) α-Fe_2O_3 powder (b) an ITO glass (c) the Fe_2O_3 film prepared by the laser ablation method on the ITO glass. The peaks of α-Fe_2O_3 are marked by the closed circle and those of ITO are marked by the closed square. (II) XRD pattern of the TiO_2 film prepared by the laser ablation method on the ITO glass

3.2. *Current-voltage characteristics*

The characteristics of I-V curves of Fe_2O_3-film and EY-fixed TiO_2-film solar cells using different counter electrodes are shown in Figs. 5(a) and (b), respectively. It is seen that the open circuit voltage is higher for the EY-fixed TiO_2-based solar cell but the closed circuit current is higher in case of the Fe_2O_3-film solar cell. These differences arise from the different band positions, light absorption ability of the dye and semiconductor materials [10]. Also, it was found that the solar cells composed of SWNT films (especially, N-

SWNT film) as counter electrodes had comparable conversion efficiency with the Pt electrode. This comparable efficiency of SWNT electrodes immerges from its metallic nature [11] with the extraordinary high electrical conductivity [12] and the large surface area [13]. Thus, it can be concluded that the SWNT-based counter electrode is feasible to use also in the Fe_2O_3-film solar cells.

It was reported by Suzuki *et al.* [7] that the electrochemical activity of carbon materials depends on the size, the surface area and the resistance of the films. The sheet resistance of an electrode has an effect on the internal resistance of a solar cell and consequently, influences the fill factor of the cell and its conversion efficiency. The impurities (amorphous carbon, fullerene and other graphitic materials) present in the SWNT may induce increased resistance and cause decrease in the efficiency of the solar cell. Previously, we have shown that the impurity has negligible effect on the efficiency of TiO_2- and Fe_2O_3-based solar cells [14].

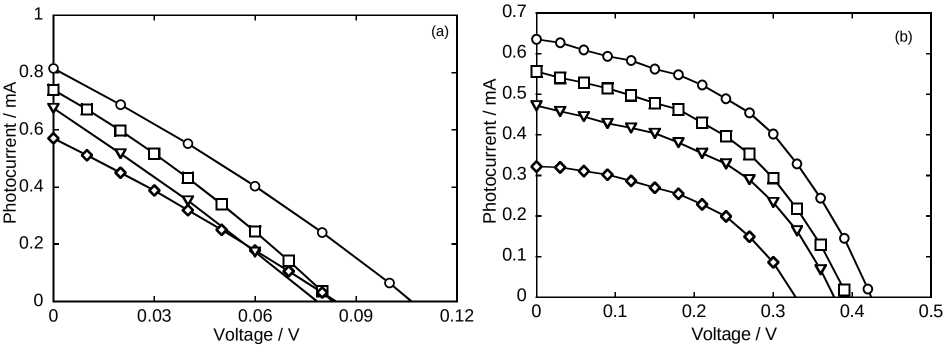

Fig. 5. *I-V* curves for solar cells with (a) Fe_2O_3 film and (b) EY-fixed TiO_2 film using counter electrodes:○; SWNTPt, □; Pt, ∇; N-SWNT, ◊; O-SWNT.

Applying high temperature during the preparation process of SWNT films, it was seen by the SEM image that part of the nanotubes as well as amorphous carbon were burnt out. To protect the burning of SWNT, lower temperature and N_2 gas atmosphere was used for other SWNT films. As seen from Figs. 5(a) and (b), these films gave the comparatively higher efficiency.

The most noticeable result is seen in case of the Pt-loaded SWNT electrode. It has comparatively higher efficiency than any other electrodes used in this experiment. As seen from Fig. 3(c), the SWNT film is not compact and the large pore is present on it. Therefore, during the Pt sputtering, the particle of Pt can be deposited on the surface of SWNT 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 [15]. These dual facts may be the main reason for the increased efficiency of the solar cell when the Pt-loaded SWNT film is used as a counter electrode. However, as no surfactant was used in case of SWNTPt film, SWNT was weakly attached over the ITO glass. Therefore, the prolong usage of this type of film was not possible. For the stability of the film the following two alternative processes are under investigation; (i) usage of a conductive surfactant for SWNT film preparation and (ii) growth of SWNT directly on a conducting substance followed by coating with Pt. We are coming with these reports in our next papers.

4. Conclusion

We have shown the simple preparation method of TiO_2, Fe_2O_3 and SWNT films and the effect of Pt loading to SWNT on the *I-V* characteristics of solar cells. Although the efficiency of these solar cells was poor due to the low photon-to-current conversion efficiency of Fe_2O_3 and dye-fixed TiO_2 films for practical uses, it was found that the Pt-loaded SWNT film gives comparatively better efficiency than that of Pt film only. Further studies for enhancing the efficiency of the working electrode as well as the SWNT based counter electrode are under investigation in our laboratory.

Acknowledgements

The present work was partly supported by Grant-in-Aid for Scientific Research (19360367 and 20·08081) from Japan Society for the Promotion of Science (JSPS). The authors wish to thank Prof. Yuji Horie for kindly permitting us to use the laser equipment facility and valuable advices. The authors are also thankful to Prof. Junichi Kurawaki for his instructions and suggestions.

References

1. M. Grätzel, Nature **414**, 338 (2001). doi:10.1038/35104607
2. K. Ramamoorthya, K. Kumara, R. Chandramohan, and K. Sankaranarayanan, Mater. Sci. Eng. B. **126**, 1 (2006). doi:10.1016/j.mseb.2005.08.117
3. C. Santato, M. Ulmann, and J. Augustynski, J. Phys. Chem. B **105**, 936 (2001). doi:10.1021/jp990066k
4. S. U. M. Khan and J. Akikusa, J. Phys. Chem. B **103**, 7184 (1999). doi:10.1021/jp990066k
5. S. Somekawa, Y. Kusumoto, S. Miyamae, T. Kamiwaki, and Y. Horie, A Novel Type of Solar Cell Based on Visible-light Responsive Photocatalyst Films, *Proc. ISES Solar World Congress 2007*, ed. D. Y. Goswami, Y. Zhao (Tsinghua University Press, Beijing, 2007) vol. **3**, pp. 1329-1333.
6. Z. Huang, X. Liu, K. Li, D. Li, Y. Luo, H. Li, W. Song, L. Chen, and Q. Meng, Electrochem. Commun. **9**, 596 (2007). doi:10.1016/j.elecom.2006.10.028
7. K. Suzuki, M. Yamaguchi, M. Kumagai, and S. Yanagiday, Chem. Lett. **32**, 28 (2003). doi:10.1246/cl.2003.28
8. R. Abe, K. Hara, K. Sayama, K. Domen, and H. Arakawa, J. Photochem. Photobiol. A: Chem. **137**, 63 (2000). doi:10.1016/S1010-6030(00)00351-8
9. S. Somekawa, Y. Kusumoto, M. Ikeda, B. Ahmmad, and Y. Horie, Catal. Commun. **9**, 437 (2008). doi:10.1016/j.catcom.2007.07.035
10. M. Grätzel, Energy Resources Through Photochemistry and Catalysis, (eds.) (Academic Press, New York, 1983).
11. P. M. Ajayan, Chem. Rev. **99**, 1787 (1999). doi:10.1021/cr970102g
12. A. Thess, R. Lee, P. Nikolaev, H. Dai, and P. Petit *et al.* Science **273**, 483 (1996). doi:10.1126/science.273.5274.483

13. P. Serp, M. Corrias, and P. Kalck, Appl. Catal. A: Gen. **253**, 337 (2003). doi:10.1016/S0926-860X(03)00549-0
14. B. Ahmmad and Y. Kusumoto, A new approach to alternative counter electrode for a novel type of solar cell – *Proc. ISES Solar World Congress 2007*, (ed. D. Y. Goswami and Y. Zhao Tsinghua University Press, Beijing, China, 2007) vol. **3**, pp. 1352-1356.
15. M. K. Nazeeruddin, A. Kay, I. Rodicio, R. H. Baker, E. Müller, P. Liska, N. Vlachopoulos, and M. Grätzel, J. Am. Chem. Soc. **115**, 6382 (1993). doi:10.1021/ja00067a063