Journal of Alloys and Compounds 504S (2010) S435–S438

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Fabrication of highly efficient flexible dye-sensitized solar cells

H. Chang[a,*], T.L. Chen[b], K.D. Huang[c], S.H. Chien[d], K.C. Hung[a]

[a] Department of Mechanical Engineering, National Taipei University of Technology, No.1 Sec.3, Chung Hsiao E. Rd., Taipei 10608, Taiwan
[b] Department of Industrial Design, National Taipei University of Technology, No.1 Sec.3, Chung Hsiao E. Rd., Taipei 10608, Taiwan
[c] Department of Vehicle Engineering, National Taipei University of Technology, No.1 Sec.3, Chung Hsiao E. Rd., Taipei 10608, Taiwan
[d] Institute of Chemistry, Academia Sinica, No. 128 Sec.2, Academia Rd., Nankang, Taipei 11529, Taiwan

ARTICLE INFO

Article history:
Received 25 June 2009
Received in revised form 15 January 2010
Accepted 10 February 2010
Available online 16 February 2010

Keywords:
DSSC
Flexible photoelectrode
Eletrophoresis deposition
TiO_2 nanoparticles

ABSTRACT

The paper studies the fabrication of a flexible dye-sensitized solar cell (DSSC). The photoelectrode substrates are flexible stainless steel sheet with thickness 0.07 mm and titanium (Ti) sheet with thickness 0.25 mm. For the photoelectrode fabrication process, eletrophoresis deposition (EPD) was employed for its merits of low-cost and fast fabrication. With an electric field of 40 V/cm, after undergoing EPD process twice, the TiO_2 nanofilm thickness could be controlled to around 13 μm thick. In addition, to achieve counter electrode, sputtering method was applied to deposit Pt on ITO-PET, resulting in thin films with four different thicknesses of 5, 8, 11 and 14 nm. The experimental results showed that the best colloid solution used in EPD process was a mixture of 100 ml isopropyl alcohol (IPA) and 0.4 g commercial TiO_2 nanoparticles, Degussa P25. The best flatness for a 13 μm thick film could be acquired under an electric field of 40 V/cm. Comparing the photoelectric conversion efficiency values of DSSC assembled by counter electrodes with different Pt thicknesses, the experimental results showed that the best Pt thickness was 11 nm, and the conversion efficiency could reach as high as 2.91%.

1. Introduction

At the beginning of the 21st century, different kinds of traditional petrochemical energy are getting dried up day by day, such as coal, fuel, natural gas, etc., creating serious pollution to environment. Therefore, different countries start to pay attention to the development of renewable energy. Solar cells are able to convert light directly into electricity by photovoltaic effect [1–3]. With solar cells, some energy loss caused by complicated procedures of energy conversion can be avoided. Nowadays, solar cells are divided into crystalline silicon solar cells, multicrystalline silicon solar cells, dye-sensitized nanostructured solar cells and organic solar cells. The first two kinds of solar cells have high efficiency, extensive application, and use silicon, which is very abundant; but their application is limited by their high price. The last two kinds of solar cells are still at the development stage. Although organic semiconductor thin film solar cells are flexible and controllable, their efficiency is still quite low. In 1990 Gratzel published a paper about DSSC. If low-cost and highly efficient dye-sensitized solar cells (DSSC) can be developed, it will become an important new direction for the development of solar cells. The term “dye-sensitized” indicates that a reaction is generated by the segregation of electron and whole pairs after stimulation by illumination and the segregated electron can just produce current. Nevertheless, the crucial technique is dye sensitization, and its unique formulation is still controlled by Gratzel’s patent on the dye, “ruthenium (Ru) complex”, making it extremely expensive.

DSSC is a third generation thin film solar cell. It has the merits of low material cost, easy fabrication process and simple fabrication equipment. The component structure of DSSC is comprised mainly of the glass substrate, transparent conductor (indium tin oxide, ITO), semiconductor material (titanium oxide), dye, electrolyte, and cathode (Pt). However, due to the fragility and inflexibility of the glass substrate, its application is limited. If a softer material could be used as the base material of DSSC, its flexible property could increase the potential development for DSSC. Flexible DSSC was initially proposed by Pichot et al. [4], though it was not until 2005 that the stainless steel was proposed as the substrate for flexible DSSC [5]. Although similar studies were presented subsequently, it was not until 2009 that the substitution of stainless steel sheet by titanium (Ti) sheet was proposed to achieve higher photoelectric conversion efficiency [6].

In the current experiment, stainless steel sheet and Ti sheet were taken as the photoelectrode substrates, and eletrophoresis deposition (EPD) method was adopted to deposite TiO_2 powder on photoelectrode substrates, completing the fabrication of the photoelectrode with TiO_2 thin film. For the counter electrode, Pt was plated on the indium tin oxide coated polyethylene terephthalate (ITO-PET) by sputtering. Then two electrodes were used

---

* Corresponding author. Tel.: +886 2 27712171x2063; fax: +886 2 27317191.
E-mail address: f10381@ntut.edu.tw (H. Chang).

0925-8388/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2010.02.044

for packaging in a sandwich structure and this assembly was tested.

2. Experimental procedures

2.1. Preparing photoelectrode thin film by the doctor-blade (DB) method

First, the TiO_2 colloidal paste required for the doctor-blade (DB) method was made by mixing 1 g commercial TiO_2 powder Degussa P25, 0.1 m ethyl acetone, 1 ml Triston-X 100 surfactants and 1.75 ml deionized water, all of which were poured into a bowl to be ground slowly [7]. Then, 3 M adhesive tape was stuck on the stainless steel sheet over an area of 2 cm × 2.5 cm, leaving an area 0.5 cm × 0.5 cm for applying paste. Paste was evenly applied on the stainless steel sheet to a thickness 0.07 mm by the DB method. When the stainless steel sheet was dried at room temperature for 30 min, the adhesive tape could be removed. After the thin film of paste had bee sintered in an oven at a constant sintering temperature of 400 °C (10 °C/min) for 30 min, a TiO_2 thin film was fabricated. These procedures were repeated to achieve two TiO_2 thin films with total thickness around 13 μm.

2.2. Using electrophoresis deposition (EPD) method to prepare photoelectrode thin film

The electrophoretic suspension, a mixed fluid of 100 ml isopropyl alcohol (IPA) and 0.4 g commercial TiO_2 powder, Degussa P25, was placed in an ultrasonic vibrator to be vibrated for around 3 h [8,9]. The anode (aluminum sheet) and cathode (stainless steel or Ti sheet) were placed in parallel into the electrophoretic suspension, leaving a distance of 1 cm between anode and cathode. The temperature of electrophoretic suspension was set at 14 °C, voltage at 40 V, electrophoretic time at 3 min for stainless steel and 2.5 min for Ti sheet to depose a single-layer TiO_2 thin film. The thin film underwent sintering at 400 °C for 50 min to increase its compactness. These procedures were repeated to acquire two layers of TiO_2 thin film for two kinds of photoelectrodes around 13 μm thickness.

2.3. Electrolyte blending and preparation of colloid electrolyte

The electrolyte was blended under the environment of inert gas or in a glove box full of nitrogen. 0.5 M LiI, 0.05 M I_2 and 0.5 M 4-tert-butylpyridine (4TBP) were mixed with acetonitrile solution, yielding the fabricated electrolyte. Furthermore, in order to solve the problems of leakage, insufficient electrolyte amount and electrolyte evaporation frequently encountered during DSSC packaging, this study additionally prepared a colloid electrolyte by adding a polymer material, polyvinylidenefluoride-co-hexafluoropro-pylene (PVDF-HFP), to two film-forming solvents, hexane and acetonitrile [10]. The 3 materials were mixed in a weight proportion of 1:2.5:7.5. After mixing, the mixture was heated for a short while and stirred until it became colloid solution. The transparent colloid solution was poured on a glass plate over an area of 5 cm × 5 cm. The glass was placed in an oven and heated at 5 °C/h to form a film. Finally, the oven temperature was raised to the boiling point of the film-forming solvents until the solvents were completely removed. After that, the newly made porous polymer thin film was soaked in liquid-state electrolyte fabricated previously, thus completing the fabrication of the colloid-state electrolyte.

2.4. Simple package and testing of DSSC

So dye molecules could be adsorbed on the TiO_2 thin film, it was soaked in dye N719 for 24 h. After the photoelectrode had adsorbed the dye, its surface was cleaned by acetonitrile to remove any dye that had not adsorbed on the surface of TiO_2 nanoparticles. After it had remained still for air drying, the DSSC photoelectrode was obtained. In addition, after the redox electrolyte I^-/I_3^- was dropped onto the thin film of photoelectrode, it was covered by a counter electrode coated with platinum. To prevent bubbles, a binder clip was used for fixing; making a DSSC in sandwich structure was made. The power selected for testing the prepared DSSC was the light source of a 150-W xenon (Xe) lamp, which simulates the sunlight (AM 1.5) and was combined with Keithley 2400 to form an *I–V* curve analyzer. Before the test, the distance between the light source and the sample should be adjusted. The light source density was set to be 100 mW/cm^2. The measured results could form an *I–V* curve of DSSC. According to the *I–V* curve, the data of V_{oc} (V), J_{sc} (mA/cm^2), fill factor (*FF*) and η (%) could be obtained.

3. Results and discussion

First, stainless steel sheet was used as the photoelectrode substrate for discussion. In this experiment, photoelectrode thin films were prepared in 3 ways, namely the EPD process once, the EPD process twice and the DB method [11–16]. After these methods were used with a counter electrode (Pt), the photoelectric conversion efficiencies were acquired as 0.29%, 1.08% and 0.73% respectively. The thin films prepared by the DB method and the two EPD methods are shown in Figs. 1 and 2. As seen from Fig. 1, the prepared thin film that has undergone DB twice has more crevices. This is because when the colloid material was stirred, the evaporation of deionized water dried the paste, preventing the continuous stirring. Fig. 2(a) shows that there are still large crevices on the TiO_2 thin film after having undergone the EPD process once. In order to limit the creation of crevices, the EPD process was run a second time, with the results shown in Fig. 2(b). It can be seen that running the EPD process twice substantially decreased the surface crevices. In addition, EPD method could deposit TiO_2 on photoelectrode substrate rapidly, controlling the required thickness by deposition time and without needing to consider the temperature effect. These results show that a thin film prepared by DB has poor flatness due to the surface crevices, thus decreasing the amount of dye adsorbed and reducing the efficiency. With a single EPD process once, the thin film surface is flatter, but it is too thin, thus decreasing the amount of dye adsorbed. With the double EPD process, the film thickness reaches 13.4 μm, as shown in Fig. 2(c). As the figure also shows the crevices of the thin film are decreased, thus increasing the amount of dye adsorbed and further enhancing the photoelectric conversion efficiency.

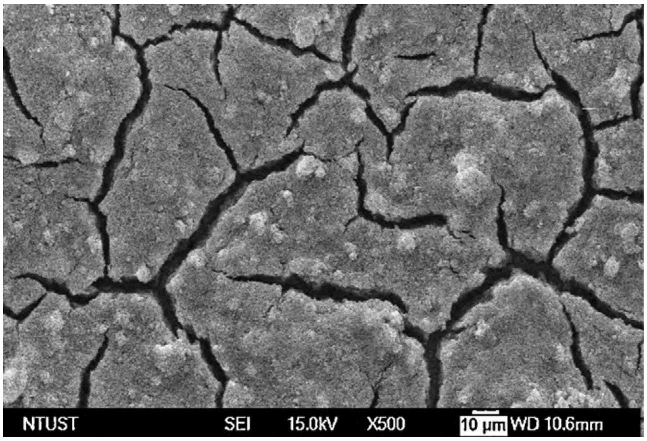

Fig. 1. SEM image of the surface of a photoelectrode thin film fabricated by the doctor-blade method.

After that, the best proportion of colloid concentration and photoelectric conversion efficiency of DSSC from the EPD method could be found. Fig. 3 shows the *I–V* curve of DSSC with a TiO_2 thin film for electrodes prepared by colloids under different concentrations. As Fig. 3 shows, the best proportion of colloid concentration is 0.4 g P25 mixed with 100 ml IPA. With this concentration, a thin film thickness of around 13.4 μm and the highest photoelectric conversion efficiency of 1.74% could be achieved after running the EPD process twice. Nevertheless, after the colloid solutions with other concentrations had undergone the EPD process twice under the parameters set by this experiment, it could be seen with the naked eye that surface crevices had appeared and the thin film was too thick. When the best concentration of colloid was achieved, the photoelectrodes with the two different substrates, stainless steel and Ti sheets, were compared under the same EPD parameters. The thickness (13.4 μm) and surface roughness (0.12 μm, R_a) of loaded TiO_2 thin film for two substrates are the same. The results show that the photoelectric conversion efficiency with a stainless steel sheet for the photoelectrode substrate is 1.74%, which is higher than the Ti sheet's efficiency of 1.43%. The lower efficiency from using Ti sheet as the substrate compared with stainless steel sheet was due to the resistance. This was because higher resistance hinders electronic transmission in a cell. When the Ti sheet was not sintered, its resistance was 36 Ω, which was higher than the stainless steel sheet's resistance of 27 Ω. After being sintered at 400 °C, stainless

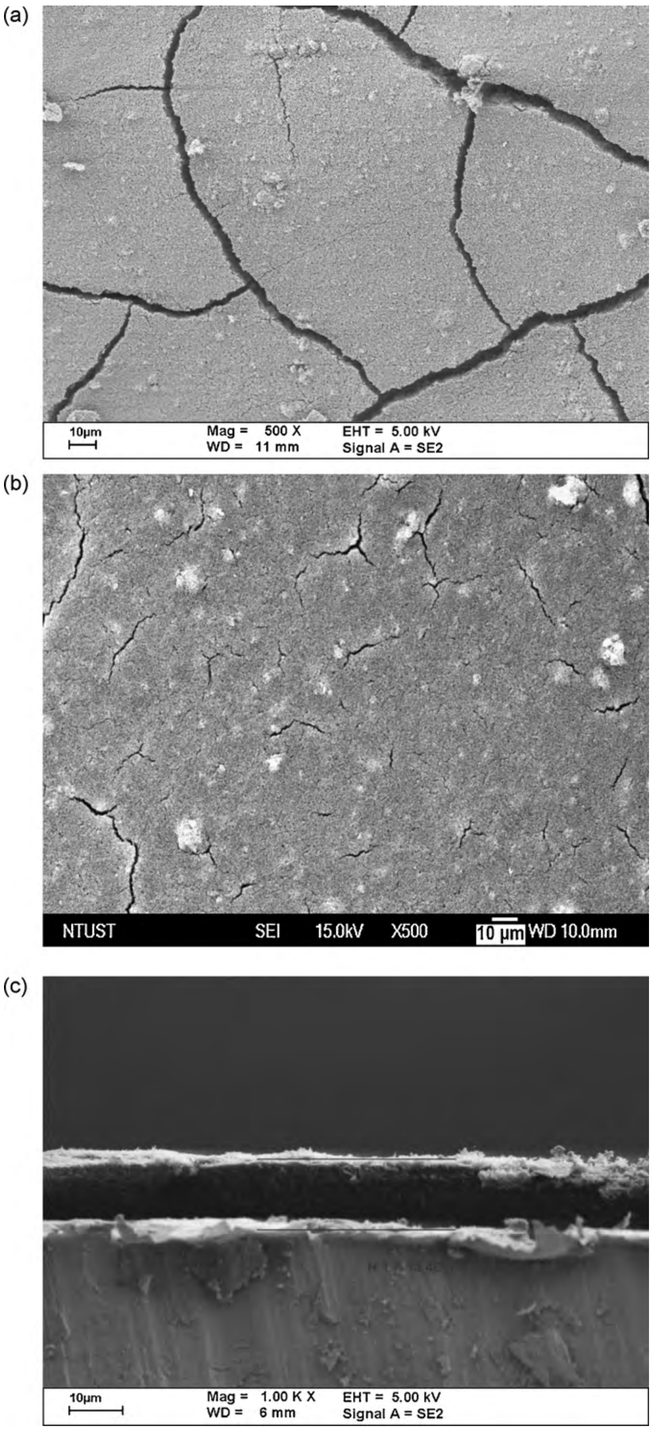

Fig. 2. SEM images of (a) single layer, (b) double layer, and (c) cross-section of double layer TiO_2 thin film by EPD.

steel sheet had a resistance 50 Ω, but Ti sheet had an resistance as high as 64 Ω.

Subsequently, stainless steel and Ti sheets were used as the substrates. A colloid was made by mixing 0.4 g P25 with 100 ml IPA. Furthermore, counter electrodes with different Pt thicknesses were also used to compare the photoelectric conversion efficiency. Fig. 4 shows the *I–V* curve of the prepared DSSCs with different Pt thicknesses for counter electrodes using stainless steel sheet and Ti sheet as the photoelectrode substrates. In addition, Tables 1 and 2 show that when the Pt thicknesses of the counter electrode is 11 nm, the conversion efficiencies with stainless steel or Ti sheet as the substrate are highest, being 2.91% and 2.4% respectively. When Pt thickness was increased, its resistance would be reduced, thus enhancing the efficiency of DSSC. However, when Pt thickness was too thick, the ITO-PET transparency would be reduced, thus reducing the light transmission and further reducing the DSSC efficiency.

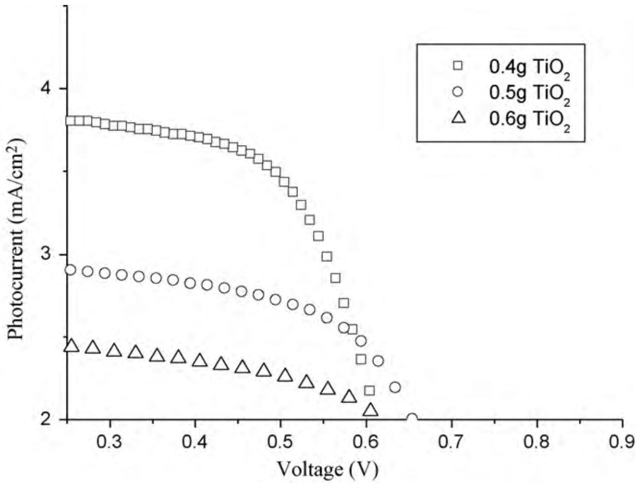

Fig. 3. *I–V* characteristics of DSSC prepared by EPD in IPA suspension with different TiO_2 concentrations: 0.4 g/100 ml, 0.5 g/100 ml and 0.6 g/100 ml.

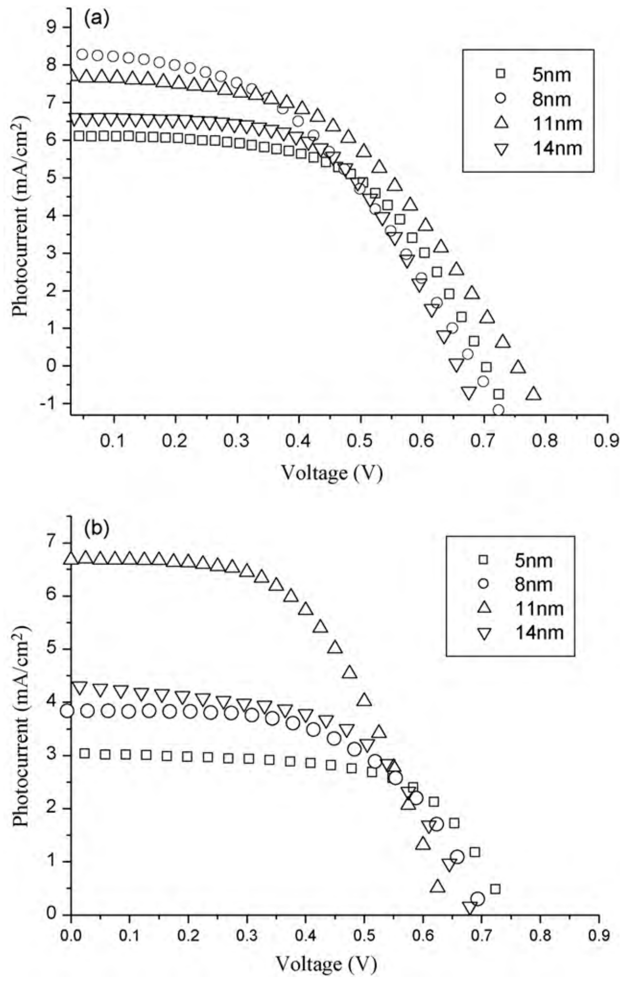

Fig. 4. *I–V* curve of the prepared DSSCs with different Pt thicknesses for counter electrode using (a) stainless steel sheet and (b) Ti sheet as the substrates of photoelectrode.

Table 1
Performance parameters of solar cells with photoelectrode on stainless steel substrates.

Pt thickness (nm)	V_{oc} (V)	J_{sc} (mA/cm^2)	η (%)	FF
5	0.705	6.09	2.46	0.57
8	0.69	8.29	2.59	0.45
11	0.755	7.7	2.91	0.50
14	0.66	6.59	2.53	0.58

Table 2
Performance parameters of solar cells with photoelectrode on Ti substrates.

Pt thickness (nm)	V_{oc} (V)	J_{sc} (mA/cm^2)	η (%)	FF
5	0.76	3.09	1.48	0.64
8	0.72	3.88	1.57	0.57
11	0.66	6.71	2.4	0.54
14	0.72	4.42	1.73	0.57

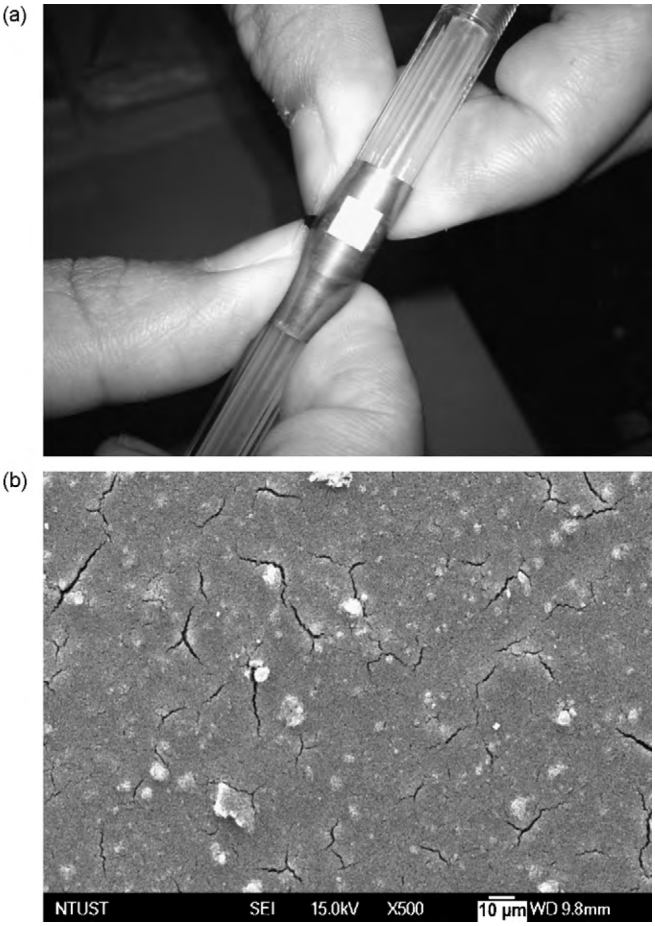

Fig. 5. (a) Photograph of a TiO_2 thin film after bending (curvature of 1/4) using stainless steel sheet as the photoelectrode substrate. (b) FE-SEM image of TiO_2 thin film after bending.

In order to test the flexibility of the prepared photoelectrode [17], the stainless steel photoelectrode sample was bent at a radius of 4 mm to the form shown in Fig. 5. Comparing Figs. 2(b) and 5(b), there is no obvious increase of surface crevices of the bent thin film, and the conversion efficiency is the same as the unbent sample.

Finally, the test results for DSSC efficiency of the colloid-state electrolyte showed that its photoelectric conversion efficiency was 2.24%. Moreover, an AC-impedance analyzer was adopted to measure the ionic conductivity of the colloid-state electrolyte reaching 4×10^{-3} S/cm and liquid-state electrolyte achieving 4.13×10^{-2} S/cm. Although the ionic conductivity of the colloid-state polymer thin film was lower and the efficiency of DSSC was rather low, this process could effectively decrease the use of liquid-state electrolyte, thus increasing the feasibility of a flexible DSSC.

4. Conclusion

According to the above experimental results and related discussion, the following conclusions can be drawn:

1. The best Pt thin film thickness for the counter electrode was 11 nm. When the Pt film was thicker, the resistance from counter resistance could be reduced.
   Compared to the use of Ti sheet, the DSSC prepared by using stainless steel sheet as the substrate could achieve the highest photoelectric conversion efficiency of 2.91%.
2. After the photoelectrode of the prepared flexible TiO_2 thin film underwent flexibility test, its conversion efficiency was not decreased.
   The use of a colloid electrolyte not only can effectively improve the problems of leakage, insufficient electrolyte amount and electrolyte evaporation, but also can solve the electrolyte leakage problem commonly encountered when a flexible DSSC is bent.

Acknowledgements

This study was supported by the National Science Council of Taiwan, Republic of China under grant NSC 97-2221-E-027-046. In addition, the authors would like to thank the Research and Development Center of the Vehicular Ultra-Low-Carbon Energy and System, Taiwan, Republic of China for financially supporting this research.

References

[1] B. O'Regan, M. Grätzel, Nature 353 (1991) 737–740.
[2] M. Grätzel, Nature 414 (2001) 338–344.
[3] A. Hagfeldt, M. Grätzel, Chem. Rev. 95 (1995) 49–68.
[4] F. Pichot, J.R. Pitts, B.A. Gregg, Langmuir 16 (2000) 5626–5630.
[5] M.G. Kang, N.-G. Park, K.S. Ryu, S.H. Chang, K.-J. Kim, Sol. Energy Mater. Sol. Cells 90 (2006) 574–581.
[6] W. Tan, X. Yin, X. Zhou, J. Zhang, X. Xiao, Y. Lin, Electrochim. Acta 54 (2009) 4467–4472.
[7] Z.-S. Wang, H. Kawauchi, T. Kashima, H. Arakawa, Coord. Chem. Rev. 248 (2004) 1381–1389.
[8] G.R.A. Kumara, A. Konno, K. Shiratsuchi, J. Tsukahara, K. Tennakone, Chem. Mater. 14 (2002) 954–955.
[9] G.S. Kim, H.K. Seo, V.P. Godble, Y.S. Kim, O.B. Yang, H.S. Shin, Electrochem. Commun. 8 (2006) 961–966.
[10] M.G. Kang, K.M. Kim, K.S. Ryu, S.H. Chang, N.G. Park, J.S. Hong, K.J. Kim, Electrochem. Soc. 151 (2004) E257–E260.
[11] K. Onoda, S. Ngamsinlapasathian, T. Fujieda, S. Yoshikawa, Sol. Energy Mater. Sol. Cells 91 (2007) 1176–1181.
[12] S. Nakade, M. Matsuda, S. Kambe, Y. Saito, T. Kitamura, T. Sakata, Y. Wada, H. Mori, S. Yanagida, J. Phys. Chem. B 106 (2002) 10004–10010.
[13] M. Toivola, F. Ahlskog, P. Lund, Sol. Energy Mater. Sol. Cells 90 (2006) 2881–2893.
[14] Y. Jun, M.G. Kang, Electrochem. Soc. 154 (2007) B68–B71.
[15] Y. Jun, J. Kim, M.G. Kang, Sol. Energy Mater. Sol. Cells 91 (2007) 779–784.
[16] X. Fang, T. Ma, M. Akiyama, G. Guan, S. Tsunematsu, E. Abe, Thin Solid Films 472 (2005) 242–245.
[17] T. Miyasaka, Y. Kijitori, T.N. Murakami, N. Kawashima, Proc. SPIE 5215 (2004) 219–225.