Electrode Properties of Dye-Sensitized Solar Cell using Ruthenium Complex/Titania Nano Crystal

著者	HORIKAWA Hajime, OGIHARA Takashi, OGATA Nobuo, ASAHARA Masahiro, WU Xing-Zheng
journal or publication title	Key Engineering Materials
volume	320
page range	231-234
year	2006
URL	http://hdl.handle.net/10098/1876

doi: 10.4028/0-87849-411-1.231

Electrode Properties of Dye-Sensitized Solar Cell using Ruthenium Complex/Titania Nano Crystal

Hazime Horikawa, Takasi Ogihara, Nobuo Ogata, Masahiro Asahara and Xing-Zheng Wu
The Graduate School of Fiber Amenity Engineering Course, Faculty of Engineering, the University of Fukui

Keywords: Dye-Sensitized Solar Cell, Titania, Nanocrystal, Thin film, Dip coating

ABSTRACT

Titania nanocrystals were prepared by hydrolysis of titanium alkoxide in ethanol solution. The preparation of titania / alumina thin film was performed on ITO coated glass substrate by dip coating method using ethanol of titania nanocrystal and boemite sol. The crystal structures, microstructure and thickness of titania / alumina thin film were examined by XRD and SEM. The adsorption of dye was influenced by the surface structure of thin film. The adsorption of dye on the films was improved by the immersion of acid as HNO_3 . Ruthenium polypyridyl complex and triarylmethyl cation salt were used as dye. Electrode using titania / alumina thin film for dye-sensitized solar cell was constructed.

1. INTRODUCTION

It is well-known that dye-sensitized solar cell is an alternative photovoltaic device for electricity generation with high conversion efficiency and low cost compared to silicon-based solar cells. Unlike silicon-based solar cells, dye-sensitized solar cells contain liquid electrolyte. Ruthenium polypyridyl complexes have been used as an efficient photosensitizer. Dye-sensitized solar cell is consisted of dye, electrolyte solution and two electrodes. The dye-sensitized solar cell developed by Gratzel et al is well known and the optimized system is reported have practically viable energy efficiencies [1,2]. It has generally been difficult to achieve practical use of cells due to leakage and vaporization of the liquid electrolyte. Energy conversion efficiency of dye-sensitized solar cell is 1/2 or less of silicon-based solar cell [3]. To improve energy conversion efficiency of dye-sensitized solar cell, it is necessary to increase adsorption of dye on the surface of titania film [4]. Boemite sol was used to the adsorption of dye. In this paper, the attempts were made for improving the photovoltaic performance of dye-sensitized solid-state cells by developing nanoporous films with high surface roughness. In addition, triarylmethyl cation salts refined from α -mangostin was used as an another dye. Triarylmethyl cation salts refined from α -mangostin was very low cost and abundant resource. We constructed dye-sensitized solar cell using triarylmethyl cation salts as a dye.

2. EXPERIMENTAL

Titania nanocrystals were prepared by the hydrolysis of 0.1M titanium tetrabutoxide in an ethanol solution.

As-prepared particles were separated by centrifuge from ethanol and heated at 500°C for

2h. TiO_2 nanocrystals were ultrasonically dispersed in

ethanol. TiO_2 nanocrystals were ultrasonically mixed with boemite sol (Kawaken fine chemicals, Alumina Sol 10), polyethylene glycol (PEG Mw.2000), silane coupling agent (ShinEstu, 3-glycidoxypopylmethyldiethoxysilane KBM-403) with the weight ratio of 50 : 1.6 : 0.5 in an ethanol. TiO_2 thin film was produced by dip coating on ITO substrate. Using mixture solution, TiO_2 thin film was coated on ITO glass (1×1 cm, Kuramoto Seisakusyo Co.). 0.3mmol/l Ruthenium polypyridyl complex (Kojima Chemical Reagents, N3) was adsorbed TiO_2 thin film for 12 h. Triarylmethyl cation salts (Fig.1) refined from α -mangostin was used as another dye. Titania nanocrystals and thin film were characterized by SEM (Hitachi S-2300), TEM (JEOL FX-2000) and XRD (Shimadzu, XRD-6100). This sample was used as an anode for dye-sensitized solar cell. ITO glass which gold was coated by sputtering was used as a cathode. LiI/I_2 solution in 2-methyl-2-oxazolidinone was prepared and this solution was added dropwise on anode. Dye-sensitized solar cell was constructed by these anode and cathode. The solar cell was set up in front of Xe-Lamp and the filter to shut out the light of 450nm or less was done between the lamp and the solar cell. After the solar cell was linked

Fig. 1 The molecular formula : (a) Ruthenium complex (N3) , (b)

Fig. 2 XRD patterns for TiO_2 nanocrystals

Fig. 3 TEM photographs (a) and particle size distributions (b) of TiO_2 nanocrystals

to digital multi meter (Advantest TR6847) and recorder (Sekonic Co. SS-250F), light was irradiated from the lamp and short-circuit current density (J_{sc}) and open circuit Voltage (V_{oc}) of this sample was measured by digital multi meter and recorder.

3. RESULT AND DISCUSSION

3.1 Preparation of titania nanocrystal

XRD patterns of as-prepared titania nanocrystals and heated at 500°C for 2 h are shown in Fig.2. Crystallinity of as-prepared particles was very low, but became higher by heating at 500°C and anatase phase was observed.

Fig. 4 SEM photographs of TiO_2 films (a) fracture surface and (b)

Figure 3 (a) shows TEM photograph of titania nanocrystals heated at 500°C for 2 h. Figure 3 (b) shows the particle size distribution of titania nanocrystals. Average particle size of titania nanocrystals was about 14nm. Particle size distribution of titania nanocrystals was 8 to 23 nm and geometrical standard distribution was 1.20. Figure 4 shows SEM photographs of titania thin film on ITO glass substrate obtained by dip coating. The titania content in the coating solution was 0.08wt%. SEM showed that the film thickness was about 1.5 μm and had an uneven surface. The crack was observed here and there on the surface when coating time was over three because of the intense evaporation of organic species such as alkoxyl group, polyethylene glycol and silane coupling agent under an air atmosphere. Figure 5 shows the relation between film thickness and coating time. Film thickness increased with increasing coating times. ITO glass coated by titania thin film was

Fig.5 Relation between thickness of TiO_2 film and coating time

Fig. 6 Transmittance of TiO_2 film immersed by HNO_3 solution

Fig.7 Transmittance of TiO_2 film with TiO_2 content of coating solution

Table 1. Jsc and Voc of Dye-sensitized solar cell

Dye	Jsc ($\mu\text{A}/\text{cm}^{-2}$)	Voc (mV)
Ruthenium complex (N3)	216	530
Triarylmethylium salts	3.2	96

immersed into the dye solution for 12 h. However the adsorption of dye was poor on the film when the film surface was flat and uniform. To obtain roughness and pore on the film surface, the thin film was immersed with 1 mol% HNO_3 aqueous solution for 1 h. Figure 6 and 7 show the transmittance of film adsorbed by N3. The transmittance of film treated with HNO_3 is less than that without treatment. This finding that the adsorption of dye was improved by HNO_3 treatment. In addition, the adsorption of dye increased with increasing titania content.

3.2 Dye-Sensitized Solar Cell

Table 1 shows Jsc and Voc of dye-sensitized solar cell constructed by titania/N3 electrode and titania/triarylmethylium salts. Jsc and Voc of dye-sensitized solar cell constructed by titania/N3 were $216 \mu\text{A}/\text{cm}^{-2}$ and 530mV, respectively. On the other hand, Jsc and Voc of dye-sensitized solar cell constructed by titania/triarylmethylium salts were $3.2 \mu\text{A}/\text{cm}^{-2}$ and 96mV. This result suggested that the low Jsc and Voc were resulted in very poor dye adsorption on the titania film.

CONCLUSION

Titania nanocrystals were prepared by hydrolysis of titanium alkoxide in ethanol solution. As-prepared particles have an average size of 14nm with narrow size distribution. Anatase nanocrystals with high crystallinity were obtained by the calcination at 500°C . Titania thin film with $1.5\mu\text{m}$ thickness was prepared on ITO glass substrate by dip coating using titania nanocrystals. Dye-sensitized solar cell was constructed by using N3 and triarylmethylium salts as a dye. When N3 was used, Jsc and Voc of dye-sensitized solar cell were $216 \mu\text{A}/\text{cm}^{-2}$ and 530mV, respectively. When triarylmethylium salt was used, Jsc and Voc of that were $3.2 \mu\text{A}/\text{cm}^{-2}$ and 96mV, respectively. This lower electrode property was resulted in poor adsorption of dye on the film surface.

REFERENCES

- [1] B. O'Regan and M. Gratzel, *Nature.*, 353 (1991), p. 737.
- [2] M. K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Muller, P. Liska, N. Vlachopoulos, and M. Gratzel, *J. Am. Chem. Soc.*, 115 (1993), p. 6382.
- [3] M. Gratzel, *J. Photochem. Photobiol. C: Photochem. Rev.*, 4 (2003), p. 145.
- [4] S.G. Chen, S. Chappel, Y. Diamant, A. Zaban, *Chem. Mater.*, 13 (2001), p. 4629.

e-mail: ogihara@matse.fukui-u.ac.jp

Fax: 0776-27-8624