Semiconductor MgTiO_3 , MgTi_2O_5 and Mg_2TiO_4 double-oxide electrodes for dye-sensitized solar cells

Natsumi Ishii^a, Yuji Okamoto, Yoshikazu Suzuki^b

Graduate School of Pure and Applied Sciences, University of Tsukuba, Ibaraki 305-8573, Japan

^{a,b}E-mail address: s-natsumi@ims.tsukuba.ac.jp, suzuki@ims.tsukuba.ac.jp

ABSTRACT

MgTiO_3 , MgTi_2O_5 and Mg_2TiO_4 were examined as DSC electrodes to improve photoelectric conversion efficiency. MgCO_3 (basic) and TiO_2 powders (nominally, Mg:Ti = 1:1, 1:2 and 2:1 in mole fraction) were wet-ball milled in ethanol for 24 h. The mixed powders were calcined in air at 1100 °C for 2 h to obtain the MgTiO_3 and MgTi_2O_5 powders, and at 1300 °C for 2 h to obtain the Mg_2TiO_4 powder. Single-phase MgTiO_3 , MgTi_2O_5 and Mg_2TiO_4 powders were successfully synthesized. Although the DSC performance was not as high as expected, all samples were functioned as DSC.

Keywords: MgTiO_3 ; MgTi_2O_5 ; Mg_2TiO_4 ; Dye-sensitized solar cell (DSC); pseudobrookite-type structure; TiO_2

1. INTRODUCTION

Dye-sensitized solar cell (DSC) is easy to fabricate, and thus, the production cost of DSC is lower than that of silicon solar cell. In addition, the appearance of DSC is suitable for the interior. However, the conversion efficiency of DSC is about 10%, whereas that of silicon solar cell is about 20%.

Therefore, DSC is widely studied on the improvement of conversion efficiency [1]. Band gap (E_g) is an important factor to decide the conversion efficiency. TiO_2 anatase (E_g of 3.2 eV) is usually used as a porous electrode. Recently, our group reported DSC using perovskite-type double oxide electrodes with wider band gaps than TiO_2 [2].

In the MgO- TiO_2 binary system, three types of stable double oxides exist, viz., MgTiO_3 , MgTi_2O_5 and Mg_2TiO_4 . The band gap of MgTiO_3 , MgTi_2O_5 and Mg_2TiO_4 are 3.7 eV, 3.4 eV, and 3.7 eV, respectively [3,4].

So, in this study, we examined the feasibility of MgTiO_3 , MgTi_2O_5 and Mg_2TiO_4 as DSC electrodes to improve conversion efficiency.

2. EXPERIMENTAL

Similarly to our previous works [5-8], commercially available MgCO_3 (basic) powder (99.9% purity, Kojundo Chemical Laboratory Co. Ltd., Saitama, Japan) and TiO_2 anatase

powder (99.9% purity, Kojundo Chemical Laboratory Co. Ltd.) were used as the starting materials. Since the MgCO_3 (basic) powder contains plenty of OH groups and H_2O molecules, quantitative analysis of the starting powder was performed by thermogravimetry and differential thermal analysis (TG-DTA). Based on the compositional calibration using TG-DTA data, MgCO_3 (basic) and TiO_2 powders (nominally, $\text{Mg}:\text{Ti} = 1:1, 1:2$ and $2:1$ in mole fraction) were wet-ball milled in ethanol for 24h. The mixed slurry was vacuum dried, and the dried powder was put into the oven at $80\text{ }^\circ\text{C}$ for 1 night. The mixed powder was then sieved through a 150-mesh screen. The mixed powders were calcined in air at $1100\text{ }^\circ\text{C}$ for 2 h to obtain the MgTiO_3 and MgTi_2O_5 powders, and at 1300°C for 2 h to obtain the Mg_2TiO_4 powder [8]. The crystal structure of obtained powders was analyzed by X-ray diffraction method (XRD, Rigaku, Multiflex, $\text{Cu-K}\alpha$, 40 kV and 40 mA). The microstructure of synthesized powders was observed by scanning electron microscopy (SEM, TM3000 Tablemicroscope, Hitachi, Tokyo, Japan).

The obtained MgTiO_3 , MgTi_2O_5 and Mg_2TiO_4 powders were mixed with polyethylene glycol (molecular weight: 20,000, Wako Pure Chemical Industries Ltd.), 2:1 mass fraction, in an agate mortar. To prepare the pastes, some distilled water and acetylacetone (dispersant, 99%, Wako Pure Chemical Industries Ltd., Osaka, Japan) were added into the mixed powders. Each mixture was pestled for 20 min. The MgTiO_3 , MgTi_2O_5 and Mg_2TiO_4 pastes were coated on ITO conducting glass (Type 0052, $10\text{ }\Omega/\text{sq.}$, Geomatec Co. Ltd., Yokohama, Japan) using the squeegee technique with the electrode area of 1 cm^2 . Porous film electrode was prepared by sintering at $450\text{ }^\circ\text{C}$ for 30 min in air.

The sintered porous electrodes (thickness of $30\text{--}40\text{ }\mu\text{m}$) were immersed in a 0.3 mM ethanol solution of a ruthenium dye (N719, Sigma-Aldrich Co. LLC) at $40\text{ }^\circ\text{C}$ for 24 h. The redox electrolyte was composed of 0.5 M LiI (97%, Wako Pure Chemical) and 0.05 M I_2 (99.9%, Wako Pure Chemical) in acetonitrile. Pt-coated ITO was used as a counter electrode. A spacer film with the thickness of $100\text{ }\mu\text{m}$ (T284, Nitoms, Inc., Tokyo, Japan) was used to prepare open-type cells. Solar energy conversion efficiency was measured under simulated solar light, i.e., AM 1.5, $100\text{ mW}/\text{cm}^2$ using a solar simulator (XES-40S1, San-Ei Electric, Osaka, Japan). The light intensity of the illumination source was calibrated by using a standard silicon photodiode (BS520, Bunkoh-Keiki Co. Ltd., Tokyo, Japan). The photocurrent–voltage curves were measured by using a source meter (6241A, ADCMT, Tokyo, Japan).

3. RESULTS AND DISCUSSION

Figure 1 shows XRD patterns of MgTiO_3 , MgTi_2O_5 and Mg_2TiO_4 powders. These patterns indicate that the obtained powders were successfully synthesized as single phase compounds. Figure 2 demonstrates SEM images of MgTiO_3 , MgTi_2O_5 and Mg_2TiO_4 powders. Due to the different calcination temperature, the particle size of MgTiO_3 and MgTi_2O_5 were relatively small (calcined at $1100\text{ }^\circ\text{C}$) but that of Mg_2TiO_4 was relatively large (calcined at $1300\text{ }^\circ\text{C}$). Note that the particle sizes of these three powders were larger than that of commercial TiO_2 P-25 powder, which is widely used for the DSC researches.

Figure 1. XRD patterns of MgTiO_3 , MgTi_2O_5 and Mg_2TiO_4 powders.

MgTiO_3

Figure 2. SEM images of MgTiO_3 , MgTi_2O_5 and Mg_2TiO_4 powders.

Figure 3 and Table 1 show the photovoltaic properties of DSC samples. For Table 1, data of TiO_2 P-25 is also given as a comparison. In this preliminary work, we found that MgTiO_3 , MgTi_2O_5 and Mg_2TiO_4 acted as DSC semiconductor electrodes despite much lower efficiencies than TiO_2 . With the thicker film formation, MgTi_2O_5 had somewhat larger J_{sc} (0.060 mA/cm^2) value among the three MgO- TiO_2 samples.

Figure 3. J-V and P-V curves of DSC samples using MgTiO_3 , MgTi_2O_5 and Mg_2TiO_4 .

Table 1. Results of J-V measurements.

	MgTiO_3	MgTi_2O_5	Mg_2TiO_4	TiO_2
Thickness (μm)	28.8	42	30.8	29
J_{sc} (mA/cm^2)	0.052	0.060	0.033	9.892
V_{oc} (V)	0.515	0.465	0.586	0.677
FF	0.317	0.248	0.293	0.533
Efficiency(%)	7.86×10^{-3}	6.93×10^{-3}	5.60×10^{-3}	3.568

Data of TiO_2 P-25 is also given as a comparison.

$$FF = \frac{V_{\text{max}} \times J_{\text{max}}}{V_{\text{oc}} \times J_{\text{sc}}}$$

Figure 4. Appearance of prepared DSC samples. Electrode area was 1 cm².

Figure 4 demonstrates the appearance of prepared DSC samples. Since TiO₂ P-25 powder has much larger surface area (~ 50 m²/g) than MgTiO₃, MgTi₂O₅ and Mg₂TiO₄ powders, DSC with TiO₂ was deeply dyed compared with other samples. It is expected that MgTiO₃, MgTi₂O₅ and Mg₂TiO₄ powders with larger surface area must improve the dye absorption. In this preliminary study, the obtained V_{OC} values were not as large as those expected by considering the band gaps. Optimization of dye molecules based on band engineering is necessary for future study.

4. CONCLUSIONS

In this study, three types of MgO-TiO₂ binary double oxides were synthesized for DSC electrodes. Single-phase MgTiO₃, MgTi₂O₅ and Mg₂TiO₄ powders were successfully prepared. Although the DSC performance was not as high as expected, all samples were functioned as DSC. Future optimization of the powder size as well as the type of dye molecules based on band engineering is required.

Acknowledgements

This work was supported by Grant-in-Aid for Science Research No. 23350111 for Basic Research: Category B. We thank Dr. Tohru S. Suzuki at NIMS for his help on SEM observation.

References

- [1] B. O'Regan, M. Grätzel, *Nature* 353 (1991) 737- 740.
- [2] Y. Okamoto and Y. Suzuki, *J. Ceram. Soc. Jpn.* 122 (2014) 728-731.
- [3] Y. Qu, *Chem. Comm.* 49 (2013) 8510-8512.
- [4] Y. -D. Ho, C. -H. Su and C. -L. Huang, *J. Am. Ceram. Soc.*, 97 (2014) 358-360.
- [5] Y. Suzuki, M. Morimoto, *J. Ceram. Soc. Jpn.* 118 (2010) 819-822.
- [6] Y. Suzuki, M. Morimoto, *J. Ceram. Soc. Jpn.* 118 (2010) 1212-1216.
- [7] Y. Suzuki, T. S. Suzuki, Y. Shinoda, K. Yozhida, *Adv. Eng. Mater.* 14 (2012) 1134-1138.
- [8] T. Kozawa, H. Hattori, S. Ogo, Y. Ide and Y. Suzuki, *J. Mater. Sci.* 48 (2013) 7969-7973.

(Received 30 December 2014; accepted 15 January 2015)