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Effects of Insulation Coating with Metal Salt on the Performance of Organic-Inorganic Hybrid Solar Cells

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This work reports on the preparation of modified TiO_2 *electrodes, which could be applied to the photoanodes in a dye-sensitized solar cells (DSSCs).* TiO_2 *layer was formed on a FTO (fluorine-doped tin oxide) coated glass via doctor-blade method and post heat treatment. Then, the various metal hydroxides and metal oxides were selectively deposited onto the* TiO_2 *layers via electrophoretic deposition and annealing process to give modified* TiO_2 *layer in DSSCs. When metal hydroxide-deposited electrodes were employed in DSSCs, photovoltaic efficiencies were improved by ca. 3–16% compared to those of the cells with bare* TiO_2 *electrodes. However, it was found that the efficiencies regressed when the metal hydroxides were converted to metal oxides via the annealing process.*

Keywords Dye-sensitized solar cells; electrophoretic deposition; metal hydroxide; metal oxide; TiO_2 electrode

Introduction

The dye-sensitized solar cells (DSSCs) have been regarded as a promising research field for next generation alternative energy sources due to their reasonable photovoltaic efficiency with low production costs and a quick brief fabrication process [1–6]. Many researchers have been intensively investigating DSSCs, especially since the outstanding breakthroughs made by the Grätzel group (Ecole Polytechnique Fédérale de Lausanne, EPFL) who developed DSSCs with conversion efficiencies close to 10% for the first time [7–11]. In the decade since, efficiencies over 10% have been obtained [1,3,12–16]. This rapid progress seems to have paralleled the meteoric development in nanotechnology over the past ten years since the preparation of core materials for DSSCs—such as the photoanode (semiconductor), the sensitizer (dye),

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Address correspondence to Yoon Soo Han, Division of Nano & Bio Technology, Daegu Gyeongbuk Institute of Science and Technology (DGIST) Hosan-dong, Dalseo-gu, Daegu 704-230, Korea (ROK). Tel.: (+82)53-430-8411; Fax: (+82)53-430-8422; E-mail: yshan@dgist.ac.kr and the electrolyte—has been intimately tied to nanotechnology development. Many investigators have made great efforts to enhance the performance of DSSCs by improving the constituents' properties. These efforts can largely be classified into four categories of development: sensitizers [17–21], anodic materials [22–28], electrolytes [29–31], and the modification of anodic materials, especially TiO_2 [32–34].

The electrons injected into the TiO_2 layer are sometimes able to return to the sensitizer or the electrolyte due to an electron recombination phenomenon. This back electron transfer causes a reduction in conversion efficiency; hence many researchers have investigated modifications to the TiO_2 layer. Two approaches are mainly used—coating the TiO_2 either with an insulator [35–37] or with another semiconductor [38–40].

In this study, we coated various metal hydroxides and metal oxides by using metal salts on TiO_2 layers via electrophoretic deposition process, and applied the resulting electrodes to the photoanode of DSSCs. The overall performance of each cell was measured and the effect of the electrodes on the performance was discussed.

Experimental

Materials

Commercial TiO_2 paste [T20/SP (20 nm), Ti-nanoxide 300 (400 nm); Solaronix] and metal salt (aluminum diacetate hydroxide, copper(II) acetate hydrate, lanthanium acetate hydrate, magnesium acetate tetrahydrate, sodium acetate, yttrium acetate hydrate and zinc acetate; Sigma-Aldrich) were selected as photoelectrode and insulation coating materials, respectively. Commercial N719[$RuL_2(NCS)_2(TBA)_2H_2 \bullet 4H_2O$, L = 2,2′-bipyridyl-4,4′-dicarboxylate, TBA = tetrabutylammonium; Solaronix] dye was employed as the sensitizer. Commercial electrolyte (AN-50; Solaronix) and Pt paste (PT1; Dyesol) were selected. All of the chemicals were used without any further purification in this study.

Preparation of DSSCs

To prepare working electrodes, FTO (fluorine-doped tin oxide, sheet resistance: $\sim 10\Omega/\square$) glasses were cleaned in a detergent solution with sonication for 20 min and rinsed with water and ethanol. After the treatment with a UV-O_3 for 20 min, FTO glasses were immersed into a 40 mM $TiCl_4$ solution at 70°C for 30 min and washed with water and ethanol to give a blocking layer. An active TiO_2 layer was formed on the FTO glass via a doctor-blade technique followed by firing at 500°C for 30 min. Then, a scattering TiO_2 layer was additionally deposited and calcined. Finally, the TiO_2 films were treated with 40 mM $TiCl_4$ solution again and sintered at 500°C for 30 min, thus TiO_2/FTO electrodes were finally prepared.

For electrophoretic deposition process, we used the TiO_2/FTO electrode as an anode and stainless steel as a cathode. Both electrodes were soaked in various metal hydroxide solutions and the distance between them was fixed at 1 cm. The two-electrode cell was biased with 30 V/cm for 10 sec to deposit metal hydroxides (MHs) onto the TiO_2/FTO surface to give MH/TiO_2/FTO (M means metal such as Al, Cu, La, Mg, Na, Y, and Zn, and H is abbreviation of hydroxide). We also calcined some of the MH/TiO_2/FTO electrode to obtain metal oxide (MO)-deposited TiO_2/FTO samples (MO/TiO_2/FTO).

Every electrode (TiO_2/FTO, MH/TiO_2/FTO, and MO/TiO_2/FTO) was immersed into a 0.5 mM of N719 dye solution (mixture of acetonitrile and tert-butyl alcohol, volume ratio = 1:1) and kept for 24 h to assure complete sensitizer uptake. To prepare counter electrode, two holes were formed in the FTO glass by drill, and cleaned as the method described previously. After cleaning, the Pt paste was deposited onto the FTO glass by doctor-blade technique, followed by firing at 400°C for 30 min. Each TiO_2-based electrode and the counter electrode were assembled into a sandwich type and sealed with a hot-melt sealing materials (SX1170-60PF; Solaronix).

Measurements

Photocurrent-voltage measurement was performed with a Keithley model 2400 Source Meter and a Newport 91192 solar simulator system (equipped with a 1 kW xenon arc lamp, Oriel). Light intensity was adjusted to AM 1.5 and 1 sun (100 mW cm^{-2}) with a Radiant Power Energy Meter (model 70260, Oriel).

Results and Discussion

Metal Hydroxide Treatment

We first prepared homogeneous metal salt solutions for TiO_2 surface treatment via an electrophoretic deposition process. Various metal salts were individually dissolved in isopropyl alcohol, and small amount of deionized water was additionally injected for its hydrolysis. As mentioned in the Experimental section, as a cathode and an anode we used TiO_2/FTO and stainless steel, respectively. The electrochemical reactions, which could possibly occur at each electrode when aluminum diacetate hydroxide was adopted, were presented below.

$$\begin{aligned}\text{Anode: } & 2H_2O \rightarrow 4H^+ + O_2(g) + 4e^- \\ & CH_3COO^- + H^+ \leftrightarrows CH_3COOH \\ \text{Cathode: } & 2H_2O + 2e^- \rightarrow 2OH^- + H_2(g) \\ & Al^{3+} + 3OH^- \rightarrow Al(OH)_3\end{aligned}$$

Aluminum diacetate hydroxide is dissociated to a trivalent Al(III), an acetate ion and hydroxide ion in isopropyl alcohol/water. The Al(III) is attracted to the anode, TiO_2/FTO, due to its electrochemical interaction, and then Al(III) is reacted with a hydroxyl group originated from hydrolysis of water. Thus aluminum hydroxide [$Al(OH)_3$] is deposited onto the surface of the TiO_2/FTO electrode (AlH/TiO_2/FTO). Besides, we individually attached the other metal hydroxides to the electrodes by means of the same method (MH/TiO_2/FTO, M=Cu, La, Mg, Na, Y, Zn) and employed each modified electrode as the photoanode in a DSSC.

According to the overall performances of the DSSCs, the cells recorded improved photovoltaic efficiencies by 3–16% depeding on the MH chosen as shown in Table 1. Figure 1 shows current-voltage characteristics of DSSCs with pristine and MH-coated TiO_2 layer. When the AlH/TiO_2/FTO photoanode was selected, the cell efficiency was enhanced due to the noticeable increment of Jsc (Fig. 1). We expected

Table 1. Photovoltaic properties of DSSCs with pristine and MH-coated TiO_2 layer

Metal hydroxide	Voc (V)	Jsc (mA/cm^2)	FF (%)	Efficiency (%)
No treatment	0.55	20.45	56.09	6.3
$Al(OH)_3$	0.55	23.31	56.28	7.3
$Cu(OH)_2$	0.68	16.61	60.45	6.9
$La(OH)_3$	0.66	16.89	65.88	7.3
$Mg(OH)_2$	0.65	16.71	64.23	7.0
NaOH	0.68	16.01	59.92	6.5
$Y(OH)_3$	0.66	17.08	60.03	6.8
$Zn(OH)_2$	0.68	14.56	65.55	6.5

that $Al(OH)_3$ played a role in increasing the dye adsorption sites on the TiO_2 surface and this led to the improvement of Jsc and the efficiency.

Meanwhile, photovoltaic efficiencies were advanced due to the rise in Voc and fill factor (FF) when $MH/TiO_2/FTO$ (M=Cu, La, Mg, Na, Y, Zn) photoanodes were adopted instead of $AlH/TiO_2/FTO$ (Table 1). In this case, the Voc values of the photoanodes were found to increase as high as 680 mV. The increases of Voc possibly indicate that the conduction band edges of the photoanodes have moved to the directions of more negative energy potentials since Voc is dominated by the energy difference between the Fermi-level of TiO_2 and the electrochemical potential of electrolyte [36,41–42]. We expect that the values of FF should also increase because the injected electrons from excited dye could have been well transferred into the photoanodes due to their sequential edges of conduction bands. In other words, the MH layers functioned as energy barriers, which are able to repress back electron transfer [43–44], thus the FF values could have increased. Consequently, we considered that these metal hydroxides have offered new energy bands to the cells resulting in the generation of various heterojuctions with TiO_2 layers, which brought us the remarkable increase of both Voc and FF.

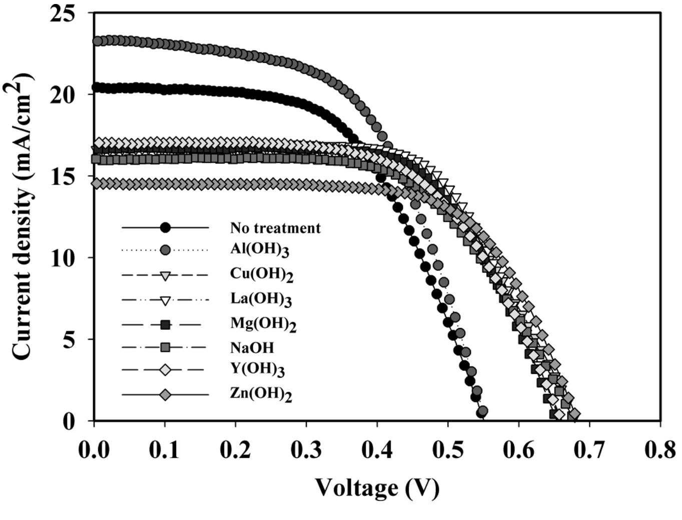

Figure 1. Current-voltage characteristics of DSSCs with pristine and MH-coated TiO_2 layer.

Table 2. Photovoltaic properties of DSSCs with pristine and MO-coated TiO_2 layer

Metal oxide	Voc (V)	Jsc (mA/cm^2)	FF (%)	Efficiency (%)
No treatment	0.55	20.45	56.09	6.3
Al_2O_3	0.66	10.83	41.66	3.0
CuO	0.66	10.84	54.05	3.9
La_2O_3	0.65	11.96	26.75	2.1
MgO	0.61	10.01	49.11	3.0
Na_2O	0.64	10.73	42.92	3.0
Y_2O_3	0.65	10.73	55.42	3.9
ZnO	0.65	11.65	55.99	4.0

Metal Oxide Treatment

As stated in the Experimental section, metal oxide layers were formed on TiO_2 films by annealing the MH/TiO_2/FTO electrodes, thus metal oxide-coated electrodes (MO/TiO_2/FTO, M=Al, Cu, La, Mg, Na, Y, Zn) were obtained. DSSCs were fabricated with these electrodes. In this case, however, the photovoltaic efficiencies decreased in the wake of Jsc regression as shown in Table 2 and Figure 2.

We considered that the metal oxides should obstruct electron transfer since they can possibly work as insulators in the photoanodes. The decreased FF values of MO/TiO_2/FTO also proved this since FF is closely involved in the resistance of photovoltaics [35,45]. In addition to interruption of electron transfer, the decreased dye absorption is also responsible for declining the Jsc from 20.45 to about 11 mA/cm^2. The thermal annealing in high temperature (over 500°C) to convert MHs to MOs could drop surface area of TiO_2 by aggregation. Thus, the absorption content of dye (N719) could be lowered. This leads to the immediate decrease of photocurrent and cell efficiency.

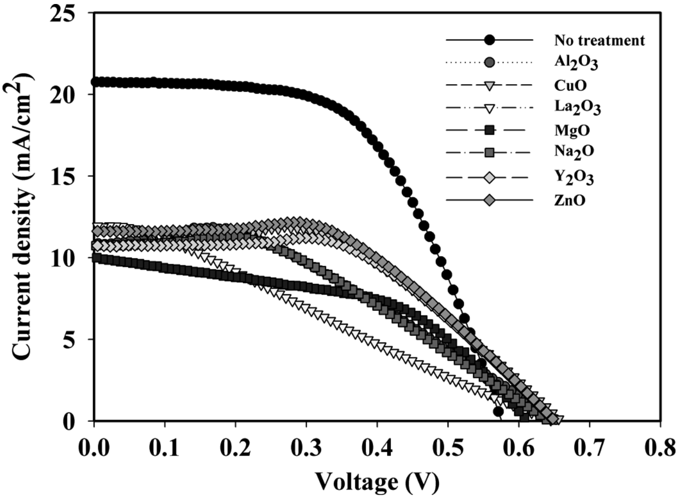

Figure 2. Current-voltage characteristics of DSSCs with pristine and MO-coated TiO_2 layer.

Conclusions

In the present study, we coated various metal hydroxides (MH) and metal oxides (MO) on the surface of TiO_2/FTO electrodes via electrophoretic deposition and annealing process. We applied these electrodes to the photoanode of a DSSC, and observed its effect on the cell performance. When the MH/TiO_2/FTO electrodes were adopted, photovoltaic efficiencies were improved by 3–16% compared to those of reference cells (having TiO_2/FTO photoanodes) due to the increment of Jsc, Voc and FF. Meanwhile, the efficiency drop was confirmed when MH/TiO_2/FTO was replaced with MO/TiO_2/FTO.

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