Improved Performance in Dye-Sensitized Solar Cells Employing TiO\textsubscript{2} Photoelectrodes Coated with Metal Hydroxides

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The performance of dye-sensitized solar cells (DSCs) was compared before and after processing the TiO\textsubscript{2} electrodes by minute-order electrochemical reactions with metal nitrates, where the metals were Mg, Zn, Al, and La, in 2-propanol. An overcoating of metal hydroxide was formed without the need for a sintering process, and magnesium hydroxide was found to give the largest improvement in photovoltage, fill factor, and eventually overall conversion efficiency of the DSCs. To analyze the nature of the improvement, the diffusion coefficient (\(D\)) and electron lifetime (\(\tau\)) were determined. While little influence of overcoating on \(D\) was seen, a correlation between the increase in \(\tau\) and \(V_{oc}\) was observed for the metals examined here. The remarkable improvement in the electron lifetime of the DSCs suggests that an overcoating with magnesium hydroxide species function as the blocking layers at the fluorine-doped tin oxide and TiO\textsubscript{2} interfaces, thus contributing to the suppression of electron leakage, i.e., recombination processes between unidirectional transporting electrons and polyiodides such as tri-iodide in the processed TiO\textsubscript{2} photoelectrode systems. The increase in \(V_{oc}\) can be explained by the increased electron density caused by the increase in electron lifetime.

Introduction

Dye-sensitized solar cells (DSCs) based on the photosensitization of nanocrystalline TiO\textsubscript{2} electrodes, pioneered by O’Regan and Grätzel, are regarded as a potential cost-effective alternative to silicone-based solar cells.\textsuperscript{1} In DSCs, excited electrons in the sensitizing dye molecules under irradiation by light (1) are injected into the conduction band of the nanocrystalline TiO\textsubscript{2} electrode, (2) diffuse through the interconnecting network of TiO\textsubscript{2} particles, and (3) are collected at the transparent conducting oxide (TCO), as shown in Figure 1. (4) The resulting oxidized dye is reduced by the redox couple. The electron injected into the porous TiO\textsubscript{2} can be wasted by recombination with (5) the oxidized redox couple or (6) oxidized dye molecules. When sufficient dissolved I\textsuperscript{-} is present,\textsuperscript{2} dye cations are effectively reduced, and the main pathway of recombination of the injected electron is via (5) the oxidized redox couple. In the past decade, a considerable amount of research has focused on improving the performance of DSCs by suppressing recombination processes as leaking electrons, and improvements in photovoltage resulting from (5) suppressing recombination have also been actively studied.

The surface treatment of TiO\textsubscript{2} electrodes with organic molecules, such as pyridines\textsuperscript{3,4} and ammonia,\textsuperscript{5} has been shown to substantially improve the photovoltage of DSCs. Mesoporous TiO\textsubscript{2} electrodes consisting of nanocrystalline particles with a thin overcoat of different metal oxides with higher conduction band edges, e.g., ZnO, NbO\textsubscript{2}O\textsubscript{4}, Al\textsubscript{2}O\textsubscript{3}, SiO\textsubscript{2}, and ZrO\textsubscript{2}, have been shown to minimize interfacial recombination dynamics relative to unidirectional charge transport.\textsuperscript{6–11}

In a previous study, we prepared flexible DSCs fabricated by electrophoretic deposition (EPD) of TiO\textsubscript{2} photoelectrodes with Mg(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O, and the resulting product showed a relatively high photovoltage.\textsuperscript{12} The result might be due to a magnesium hydroxide coating on the TiO\textsubscript{2}. Magnesium hydroxide can be formed by electrochemical reactions at cathodes.

Figure 1. Schematic representation of electron-transfer processes in DSCs: (1) excitation of the dye under illumination, (2) injection of electrons from the dye into the conduction band of nanoporous TiO\textsubscript{2}, (3) diffusion of electrons through nanoporous TiO\textsubscript{2}, (4) regeneration of the dye by electron transfer from the redox couple, (5) recombination of injected electrons with the oxidized redox couple, (6) recombination of injected electrons with the oxidized dye.
Experimental Section

Mesoporous TiO2 film electrodes were prepared from a colloidal suspension of TiO2 nanoparticles (P-25, Nippon Aerogel, and Nanoxide-T, Solaronix) by casting on a fluorine-doped tin oxide (FTO, Asahi Glass, 8–10 Ω sq⁻¹) as a transparent conductive oxide glass using a doctor-blade technique. The films were annealed at 450 °C for 30 min in air. The thickness of the resulting TiO2 films was measured by means of a profiler (Sloan, Dektak3). Cathodic deposition (CD) reactions were carried out in electrolyte solutions composed of each metal nitrate salt. The solution for the CD of the Mg-(OH)2 coating used in this study was isopropyl alcohol (IPA, Sigma, 99.5%) containing 5 × 10⁻⁴ M Mg(NO3)2·6H2O (Kanto Chemical, 99.0%), with and without 5 vol % deionized water. For the deposition of Zn(OH)2, Al(OH)3, and La(OH)3, Zn(NO3)2·6H2O (Wako, 99.9%), Al(NO3)3·9H2O (Wako, 99.9%), and La(NO3)3·6H2O (Wako, 99.9%) were used as nitrate salts in the electrolyte solution for the CD. Stainess steel (SUS 304) was used as the anode during the CD process, and the distance between the anode and the TiO2 electrode was fixed at 1.5 cm. Cathodic deposition was performed for various deposition times at a fixed electric field of 20 V/cm.

For the sensitization study, the TiO2 film electrodes, after completion of the CD process, were immersed in an acetonitrile/cis-dithiocyanato-cis-bis(4-carboxylate-4-tetraethylammonium-carboxylate-2,2'-bipyridine) ruthenium(II) (known as N719, Solaronix) for 18 h at room temperature, and the films were then rinsed with acetonitrile. DSCs were prepared using an electrolyte consisting of 0.1 M LiI, 0.05 M I2, 0.6 M 1,2-dithiocyanate-t-bipyridine, and 0.5 M 4-tert-butylypyridine in methoxyacetonitrile and a Pt-sputtered TCO glass.

The gap between the TiO2 electrode and the counter electrode was sealed by means of a thermal adhesive film (Hisilicon, thickness = 30 μm, Mitsu-Dupont Polychemical). The amount of dye adsorbed on the electrodes was estimated by measuring the amount of dye adsorbed on the electrodes using a quartz cell with a 1 cm path length.

The experimental setup for measuring electron diffusion coefficients (D) and electron lifetimes (τ) was described in detail elsewhere. In short, the DSC was irradiated by a diode laser (Coherent, LabLaser, λ = 635 nm), and a small fraction of the laser intensity, e.g., less than 10% of the initial intensity, was stepped down, controlled by a function generator. Then, the values of D and τ were evaluated by measuring the corresponding current or voltage transients, through current and differential amplifiers on an oscilloscope, respectively. The value of D was derived by fitting an exponential function, exp(-t/τs), to the photocurrent transient and substituting the fitted time constant (τs) into the following equation

\[ D = w^2/(2.77\tau_s) \]

where w is the thickness of the electrode. The open-circuit electron lifetime was also obtained by fitting an exponential function to \( V_{oc} \) decay, and for this case, the fitted constant corresponds simply to the electron lifetime. The measurements were repeated under various laser intensities, controlled by a set of ND filters.

The photovoltaic properties of the DSCs were examined by recording the current vs voltage (I-V) characteristics of the cell under illumination with AM1.5 (1 sun; 100 mW/cm²) using a solar simulator (Yamashita Denso, YSS-80). The materials on the TiO2 after the CD process were examined by infrared absorption spectroscopy (Perkin-Elmer FT-IR spectrometer 2000). The morphologies of the electrodes were observed by scanning electron microscopy (SEM, S-4700, Hitachi).

Results

Analysis of Materials Derived from the Cathodic Deposition Reactions. Mg(NO3)2 in IPA is dissociated to Mg(NO3)2 as the result of reaction 1 rather than Mg2+ and NO3⁻ ions. The Mg2+ and NO3⁻ species are the main charge carriers. MgNO3 • 4H2O ions contribute to the formation of hydroxides such as Mg(OH)2, as discussed above. With an increase in water concentration (> 5 vol %), hydroxide, Mg(OH)2, is readily formed at the cathode by reactions 2 and 3.

IR spectra of materials on the TiO2 electrodes, produced by the CD in the presence of 5 vol % water, are shown in Figure 2a. The solid line indicates the IR spectrum of a TiO2 film without any treatment, and the dashed, dotted, and dash-dotted lines indicate IR spectra of the TiO2 film obtained by CD for 30 s, 1 min, and 10 min, respectively. When CD was carried out for a short time, such as 30 s and 1 min, the amount of deposited Mg(OH)2 was probably too small to be detected by IR measurement. At a longer deposition time such as 5 min (data not shown here because the spectrum is almost the same as that of 10 min) and 10 min, the OH stretching peak near 3700 cm⁻¹ became strong, and a peak at 1400 cm⁻¹ (OH bending) also appeared. These IR spectra show that a material including OH, as a form of Mg(OH)2, must have been deposited on TiO2 films during the CD. When CD was applied in the absence of water, the peaks near 3700 and 1400 cm⁻¹ did not appear, as shown in Figure 2b. These IR spectra indicate that the materials resulting from the CD changed depending on the vol % of water, as previously reported by Russ et al.13 When the water concentration in the deposition bath is high, hydroxide (Mg(OH)2) is smoothly deposited by reaction 3.

Scanning electron microscopy images of TiO2 electrodes without CD treatment and with 1 and 5 min of CD treatment are shown in Figure 3. Newly deposited materials can be observed in the images when CD was applied. On the basis of the IR spectra, we assigned the material as Mg(OH)2. SEM images also showed that the morphology changed with the deposition time. While no particle was seen before 1 min of deposition, after 5 min of deposition, Mg(OH)2 composed of smaller particles (below 10 nm) coagulated and the film became thicker, as shown in Figure 3c.
Characteristics of DSCs Using CD-Treated TiO$_2$ Electrodes. The $I$–$V$ characteristics of DSCs employing the CD-treated TiO$_2$ electrodes are shown in Figure 4. TiO$_2$ electrodes with a thickness of around 5 $\mu$m were prepared using a doctor-blade technique, and CD was then carried out in the presence of 5 vol % water. DSCs employing TiO$_2$ electrodes without a CD treatment yielded an open-circuit voltage ($V_{oc}$) of 0.704 V and a short-circuit current density ($J_{sc}$) of 8.20 mA/cm$^2$ under 1 sun irradiation, and the corresponding fill factor ($ff$) and efficiency were 0.729 and 4.2%, respectively. When the TiO$_2$ film was overcoated with Mg(OH)$_2$, the $V_{oc}$ and short-circuit current ($J_{sc}$) of the DSC increased. It is noteworthy that $V_{oc}$ dramatically increased to 0.752 V and the fill factor also increased to 0.743. In addition, the resulting overall conversion efficiency increased to 4.7% from 4.2%. When the layer of Mg(OH)$_2$ became thicker with the formation of the small particles, as seen in Figure 3c, the $J_{sc}$ of the DSC was reduced to 5.22 mA/cm$^2$ following a decrease in overall efficiency to 2.9%.

Concerning the $I$–$V$ characteristics of the DSCs employing photoelectrodes, the TiO$_2$ electrodes that had been overcoated with other metal hydroxides, Zn(OH)$_2$, Al(OH)$_3$, and La(OH)$_3$, are summarized in Table 1. All metal hydroxide species were deposited on TiO$_2$ electrodes by CD for 30 s. For all of the metal hydroxides examined here, the $V_{oc}$ values were improved without any loss in $J_{sc}$, as shown in Table 1. Among these results, Mg(OH)$_2$ gave the best performance.

To confirm the effect of the Mg(OH)$_2$ coating, TiO$_2$ electrodes were prepared from different TiO$_2$ samples (Nanoxide-T, Solaronix). TiO$_2$ films having a thickness of around 2.0 $\mu$m were prepared using a doctor-blade technique, and the resulting TiO$_2$ electrodes were subjected to the CD reactions used above. The results, shown in Table 2, confirm the improvement in performance.

Effects on Electron Diffusion Coefficients and Electron Lifetimes in CD-Pretreated DSCs. Figure 5 shows the values for the electron diffusion coefficient ($D$) in DSCs having various metal hydroxide coatings, under different laser intensities. The CD treatment had little influence on the values of $D$. It has been interpreted that intraband charge traps give rise to the
diffusion coefficient dependent on the light intensity. On the basis of the interpretation, the results in Figure 5 suggest that the CD treatment did not form any electron trap sites. Figure 6 shows a plot for the change in electron lifetime ($\tau$) for the above-discussed DSCs. Electron lifetimes in CD-pretreated DSCs were longer than those for the reference DSC without posttreatment. The increase was in the order of TiO$_2$ < TiO$_2$/Al(OH)$_3$ < TiO$_2$/La(OH)$_3$ < TiO$_2$/Zn(OH)$_2$ < TiO$_2$/Mg(OH)$_2$. This order is consistent with the increase in the $V_{oc}$ of the DSCs.

Discussion

It has been reported that an overcoating of a thin insulating layer results in a suppression of recombination. The results shown in Figure 6 suggest that a Me(OH)$_n$ layer, which is deposited onto the TiO$_2$ film as well as on the exposed FTO surface among TiO$_2$ particles at the FTO/TiO$_2$/electrolyte interfaces, also acts as an insulating layer, resulting in the retardation of recombination. The formation of Mg(OH)$_2$ to be deposited on TiO$_2$ films during the CD was investigated by using IR spectra as mentioned above. To ensure the deposition of hydroxides but not oxides, the sintering above 450 °C, known

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an effect of morphology of TiO₂ film, we used Solaronix-T thickness and Nanoxide-T with a 2 nm thickness. To investigate the improvement of electron density and porosity of the electrodes, we obtained the same effect of an increase in Voc, Jsc, and fill factor together.

Conclusions

The adsorption of metal hydroxide was introduced to improve the performance of DSCs. The electrochemical but second-order adsorption of species represented by Me(OH)₃, especially Mg(OH)₂, at the TiO₂/FTO and TiO₂/electrolyte interfaces without a thermal treatment resulted in increases in both the photovoltage and the fill factor without any loss of photocurrent, leading to an increase in the overall conversion efficiency. An increase in electron lifetime was observed with DSCs containing a thin layer of Me(OH)₃, showing that the layer acts as an insulating layer, suppressing recombination between injected electrons and I₃⁻ in the electrolyte. A good correlation was observed between the increases in the Voc and the electron density of the DSCs, suggesting that the suppression of recombination is the main reason for the improvement. The highest improvement in Voc for Mg(OH)₂ is probably due to the similarity in ionic radii between Ti and Mg, which would result in a more uniform insulating film.

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References and Notes