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# Improved Performance in Dye-Sensitized Solar Cells Employing TiO<sub>2</sub> Photoelectrodes Coated with Metal Hydroxides

Jun-Ho Yum,<sup>†</sup> Shogo Nakade,<sup>‡</sup> Dong-Yu Kim,<sup>†</sup> and Shozo Yanagida<sup>\*,§</sup>

Department of Materials Science and Engineering, Gwangju Institute of Science and Technology, Gwangju 500-712, Republic of Korea, Material and Life Science, Graduate School of Engineering, Osaka University, Suita, Osaka 565-0871, Japan, and Center for Advanced Science and Innovation, Osaka University, Suita, Osaka 565-0871, Japan

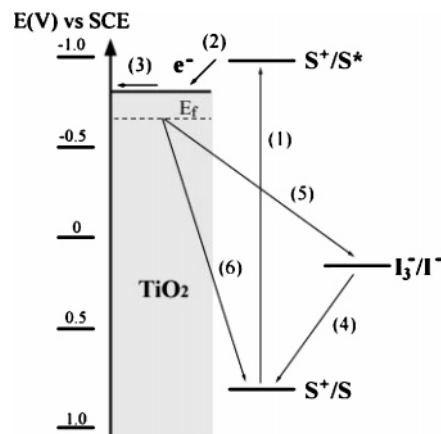
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The performance of dye-sensitized solar cells (DSCs) was compared before and after processing the TiO<sub>2</sub> electrodes by minute-order electrochemical reactions with metal nitrates, where the metals were Mg, Zn, Al, and La, in 2-propanol. An 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> electrodes, pioneered by O'Regan and Grätzel, are regarded as a potential cost-effective alternative to silicon-based solar cells.<sup>1</sup> In DSCs, excited electrons in the sensitizing dye molecules under irradiation by light (1) are injected into the conduction band of the nanocrystalline TiO<sub>2</sub> electrode, (2) diffuse through the interconnecting network of TiO<sub>2</sub> 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<sub>2</sub> can be wasted by recombination with (5) the oxidized redox couple or (6) oxidized dye molecules. When sufficient dissolved I<sup>−</sup> is present,<sup>2</sup> 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<sub>2</sub> electrodes with organic molecules, such as pyridines<sup>3,4</sup> and ammonia,<sup>5</sup> has been shown to substantially improve the photovoltage of DSCs. Mesoporous TiO<sub>2</sub> electrodes consisting of nanocrystalline particles with a thin overcoat of different metal oxides with higher conduction



**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<sub>2</sub>, (3) diffusion of electrons through nanoporous TiO<sub>2</sub>, (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.

band edges, e.g., ZnO, Nb<sub>2</sub>O<sub>5</sub>, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, and ZrO<sub>2</sub>, have been shown to minimize interfacial recombination dynamics relative to unidirectional charge transport.<sup>6–11</sup>

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

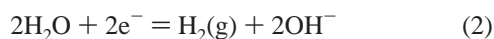
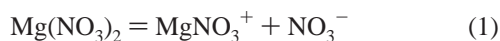
\* Author to whom correspondence should be addressed. Phone: +81-6-6879-7351. Fax: +81-6-6879-7351. E-mail: yanagida@mls.eng.osaka-u.ac.jp.

<sup>†</sup> Gwangju Institute of Science and Technology.

<sup>‡</sup> Material and Life Science, Osaka University.

<sup>§</sup> Center for Advanced Science and Innovation, Osaka University.

(1–3, especially 3)<sup>13,14</sup> as a subreaction during electrophoretic deposition.



The aim of this study was to systematically investigate the effects of a metal hydroxide coating on the performance of DSCs. To accomplish this, we prepared TiO<sub>2</sub> electrodes with an overcoating of Mg(OH)<sub>2</sub>, Zn(OH)<sub>2</sub>, Al(OH)<sub>3</sub>, and La(OH)<sub>3</sub>, and DSCs were prepared from the resulting electrodes. The *I*–*V* characteristics of the DSCs are discussed in terms of the measured values of the electron diffusion coefficients and electron lifetimes.

### Experimental Section

Mesoporous TiO<sub>2</sub> film electrodes were prepared from a colloidal suspension of TiO<sub>2</sub> nanoparticles (P-25, Nippon Aerogel, and Nanoxide-T, Solaronix) by casting on a fluorine-doped stannic oxide (FTO, Asahi Glass, 8–10 Ω sq<sup>−1</sup>) 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 TiO<sub>2</sub> 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)<sub>2</sub> coating used in this study was isopropyl alcohol (IPA, Sigma, 99.5%) containing 5 × 10<sup>−4</sup> M Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Kanto Chemical, 99.0%), with and without 5 vol % deionized water. For the deposition of Zn(OH)<sub>2</sub>, Al(OH)<sub>3</sub>, and La(OH)<sub>3</sub>, Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Wako, 99.9%), Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (Wako, 99.9%), and La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (Wako, 99.9%) were used as nitrate salts in the electrolyte solution for the CD. Stainless steel (SUS 304) was used as the anode during the CD process, and the distance between the anode and the TiO<sub>2</sub> 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 TiO<sub>2</sub> film electrodes, after completion of the CD process, were immersed in an acetonitrile/*t*-BuOH (1:1) solution containing 0.3 mM Ru dye (*cis*-dithiocyanate-*N,N'*-bis(4-carboxylate-4-tetrabutylammonium-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 I<sub>2</sub>, 0.6 M 1,2-dimethyl-3-propylimidazolium iodide, and 0.5 M 4-*tert*-butylpyridine in methoxyacetonitrile and a Pt-sputtered TCO glass. The gap between the TiO<sub>2</sub> electrode and the counter electrode was sealed by means of a thermal adhesive film (Himilan, thickness = 30 μm, Mitsui-Dupont Polychemical). The amount of dye adsorbed on the electrodes was estimated by measuring the light absorption in dye solution after desorption using a 0.1 M NaOH aqueous solution.

The experimental setup for measuring electron diffusion coefficients (*D*) and electron lifetimes (*τ*) has been described in detail elsewhere.<sup>15</sup> 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 responding 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*/*τ*<sub>c</sub>), to the photocurrent transient and substituting the fitted time constant (*τ*<sub>c</sub>) into the following equation

$$D = w^2/(2.77\tau_c) \quad (4)$$

where *w* is the thickness of the electrode. The open-circuit electron lifetime was also obtained by fitting an exponential function to *V*<sub>oc</sub> 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.

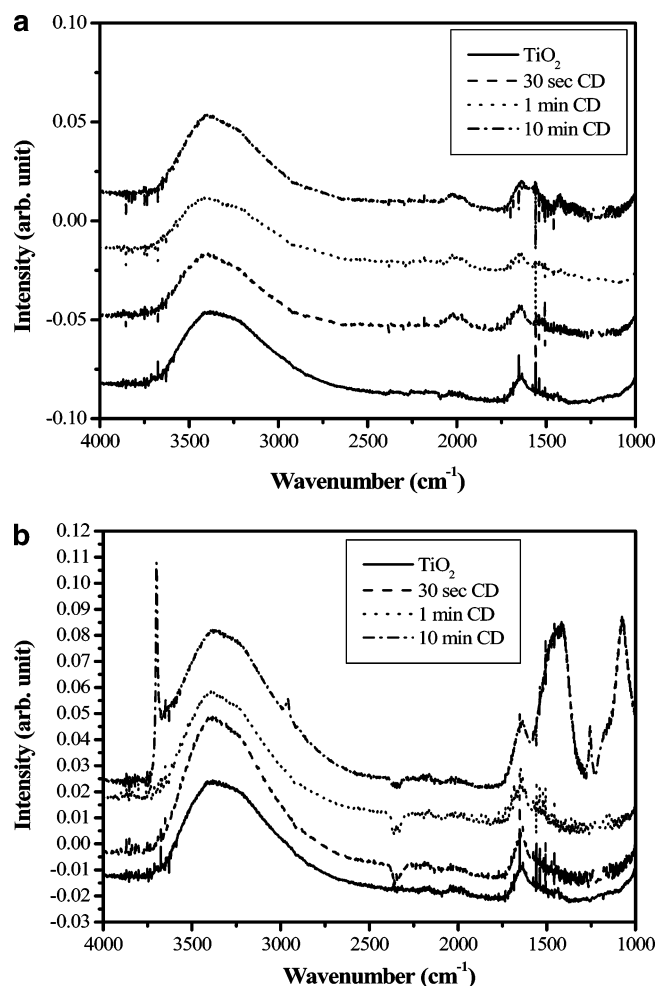
The photoelectrochemical properties of the DSCs were examined by recording the current–voltage (*I*–*V*) characteristics of the cell under illumination with AM1.5 (1 sun; 100 mW/cm<sup>2</sup>) using a solar simulator (Yamashita Denso, YSS-80). The materials on the TiO<sub>2</sub> after the CD process 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(NO<sub>3</sub>)<sub>2</sub> in IPA is dissociated to MgNO<sub>3</sub><sup>+</sup> as the result of reaction 1 rather than Mg<sup>2+</sup>, and the MgNO<sub>3</sub><sup>+</sup> and NO<sub>3</sub><sup>−</sup> species are the main charge carriers.<sup>13,16</sup> MgNO<sub>3</sub><sup>+</sup> ions contribute to the formation of hydroxides such as Mg(OH)<sub>2</sub>, as discussed above. With an increase in water concentration (> 5 vol %), hydroxide, Mg(OH)<sub>2</sub>, is readily formed at the cathode by reactions 2 and 3.

IR spectra of materials on the TiO<sub>2</sub> 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 TiO<sub>2</sub> film without any treatment, and the dashed, dotted, and dash-dotted lines indicate IR spectra of the TiO<sub>2</sub> 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)<sub>2</sub> 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<sup>−1</sup> became strong, and a peak at 1400 cm<sup>−1</sup> (OH bending) also appeared. These IR spectra show that a material including OH, as a form of Mg(OH)<sub>2</sub>, must have been deposited on TiO<sub>2</sub> films during the CD. When CD was applied in the absence of water, the peaks near 3700 and 1400 cm<sup>−1</sup> 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.<sup>13</sup> When the water concentration in the deposition bath is high, hydroxide (Mg(OH)<sub>2</sub>) is smoothly deposited by reaction 3.

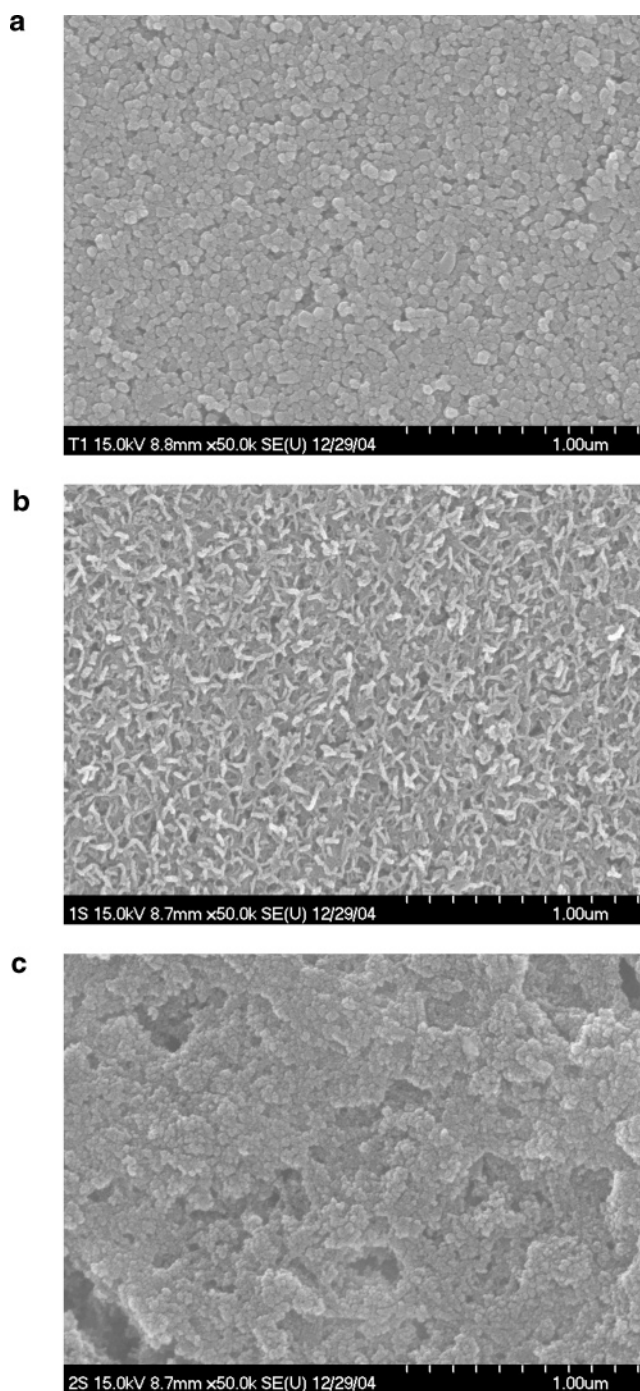
Scanning electron microscopy images of TiO<sub>2</sub> electrodes without CD treatment and with 1 and 5 min of CD treatment are shown in Figure 3. Newly deposited materials can be observed in the images when CD was applied. On the basis of the IR spectra, we assigned the material as Mg(OH)<sub>2</sub>. 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)<sub>2</sub> composed of smaller particles (below 10 nm) coagulated and the film became thicker, as shown in Figure 3c.



**Figure 2.** Attenuated total reflectance infrared spectra of  $\text{TiO}_2$  films without CD (solid line) and with CD for 30 s (dashed line), 1 min (dotted line), and 10 min (dash-dotted line) in a deposition bath with (a) 5 vol % water and (b) no added water.

***I*–*V* Characteristics of DSCs Using CD-Treated  $\text{TiO}_2$  Electrodes.** The *I*–*V* characteristics of DSCs employing the CD-treated  $\text{TiO}_2$  electrodes are shown in Figure 4.  $\text{TiO}_2$  electrodes with a thickness of around  $5\ \mu\text{m}$  were prepared using a doctor-blade technique, and CD was then carried out in the presence of 5 vol % water. DSCs employing  $\text{TiO}_2$  electrodes without a CD treatment yielded an open-circuit voltage ( $V_{\text{oc}}$ ) of 0.704 V and a short-circuit current density ( $J_{\text{sc}}$ ) of  $8.20\ \text{mA}/\text{cm}^2$  under 1 sun irradiation, and the corresponding fill factor (ff) and efficiency were 0.729 and 4.2%, respectively. When the  $\text{TiO}_2$  film was overcoated with  $\text{Mg}(\text{OH})_2$ , the  $V_{\text{oc}}$  and short-circuit current ( $J_{\text{sc}}$ ) of the DSC increased. It is noteworthy that  $V_{\text{oc}}$  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  $\text{Mg}(\text{OH})_2$  became thicker with the formation of the small particles, as seen in Figure 3c, the  $J_{\text{sc}}$  of the DSC was reduced to  $5.22\ \text{mA}/\text{cm}^2$  following a decrease in overall efficiency to 2.9%.

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

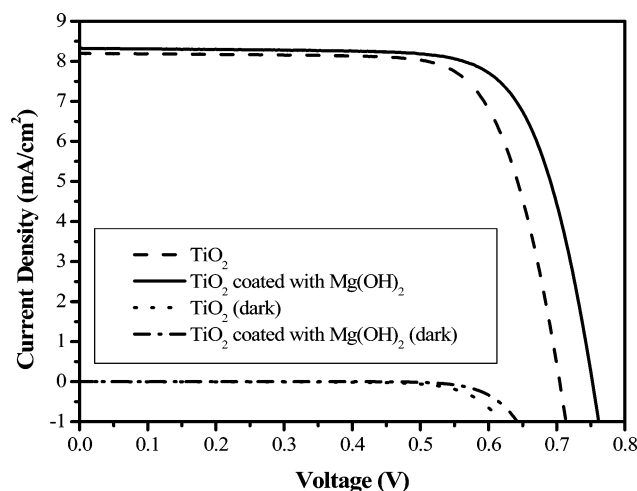


**Figure 3.** Scanning electron microscopy images of the surface of (a) a  $\text{TiO}_2$  film, (b) a  $\text{TiO}_2$  film treated by CD for 1 min, and (c) a  $\text{TiO}_2$  film treated by CD for 5 min.

To confirm the effect of the  $\text{Mg}(\text{OH})_2$  coating,  $\text{TiO}_2$  electrodes were prepared from different  $\text{TiO}_2$  samples (Nanoxide-T, Solaronix).  $\text{TiO}_2$  films having a thickness of around  $2.0\ \mu\text{m}$  were prepared using a doctor-blade technique, and the resulting  $\text{TiO}_2$  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





**Figure 4.** Current–voltage characteristics of a DSC composed of TiO<sub>2</sub> films under 1 sun (dashed line) (dark current, dotted line) and a TiO<sub>2</sub> film overcoated with Mg(OH)<sub>2</sub> (solid line) (dark current, dash dotted line).

**TABLE 1: Current–Voltage Characteristics of DSCs Composed of TiO<sub>2</sub> (P-25) and TiO<sub>2</sub> Overcoated with a Metal Hydroxide**

	$I_{sc}$ (mA/cm <sup>2</sup> )	$V_{oc}$ (V)	ff	$\eta$	thickness <sup>c</sup> ( $\mu$ m)
without	8.20	0.704	0.729	4.2	5.2
Mg(OH) <sub>2</sub> <sup>a</sup>	8.32	0.752	0.743	4.7	5.2
Mg(OH) <sub>2</sub> <sup>b</sup>	5.22	0.754	0.734	2.9	5.3
Zn(OH) <sub>2</sub>	8.47	0.731	0.736	4.6	5.4
Al(OH) <sub>3</sub>	8.24	0.724	0.734	4.4	5.0
La(OH) <sub>3</sub>	8.54	0.723	0.729	4.5	5.5

<sup>a</sup> CD for 30 s. <sup>b</sup> CD for 5 min. <sup>c</sup> Thickness of TiO<sub>2</sub> film on FTO glass.

**TABLE 2: Current–Voltage Characteristics of DSCs Composed of TiO<sub>2</sub> (Nanoxide-T) and TiO<sub>2</sub> Overcoated with Magnesium Hydroxide**

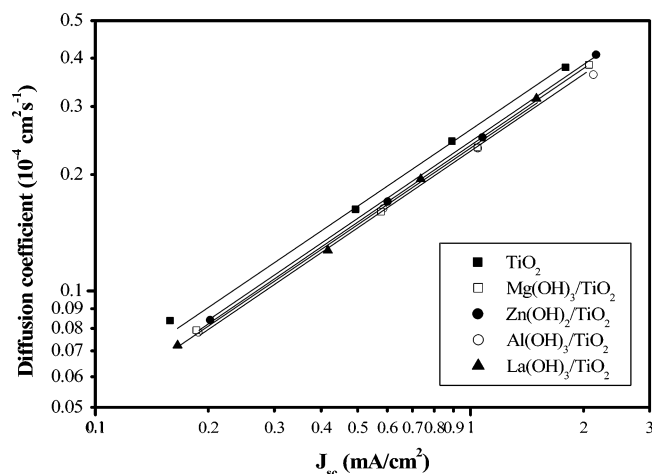
	$I_{sc}$ (mA/cm <sup>2</sup> )	$V_{oc}$ (V)	ff	$\eta$	thickness ( $\mu$ m)
without	6.43	0.696	0.736	3.3	2.1
Mg(OH) <sub>2</sub>	6.61	0.758	0.740	3.7	2.1

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.

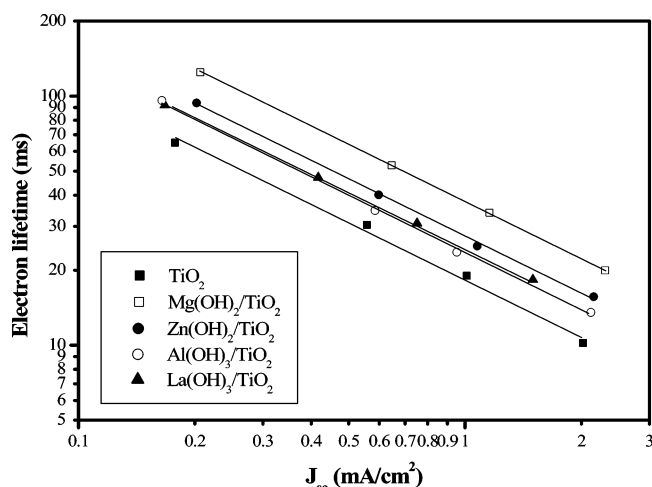
Figure 6 shows a plot for the change in electron lifetime ( $\tau$ ) for the above-discussed DSCs. Electron lifetimes in CD-pretreated DSCs were longer than those for the reference DSC without posttreatment. The increase was in the order of TiO<sub>2</sub> < TiO<sub>2</sub>/Al(OH)<sub>3</sub>  $\approx$  TiO<sub>2</sub>/La(OH)<sub>3</sub> < TiO<sub>2</sub>/Zn(OH)<sub>2</sub> < TiO<sub>2</sub>/Mg(OH)<sub>2</sub>. 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)<sub>n</sub> layer, which is deposited onto the TiO<sub>2</sub> film as well as on the exposed FTO surface among TiO<sub>2</sub> particles at the FTO/TiO<sub>2</sub>/electrolyte interfaces, also acts as an insulating layer, resulting in the retardation of recombination. The formation of Mg(OH)<sub>2</sub> to be deposited on TiO<sub>2</sub> 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



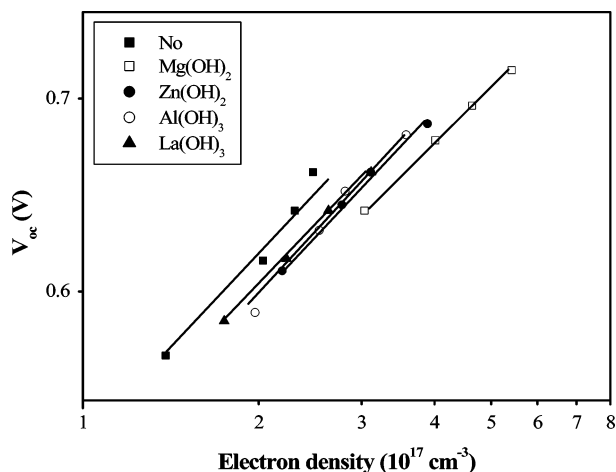
**Figure 5.** Electron diffusion coefficients in DSCs employing only TiO<sub>2</sub> films (■), TiO<sub>2</sub> films overcoated with Mg(OH)<sub>2</sub> (□), Zn(OH)<sub>2</sub> (●), Al(OH)<sub>3</sub> (○), and La(OH)<sub>3</sub> (▲).



**Figure 6.** Electron lifetimes in DSCs employing only TiO<sub>2</sub> films (■), TiO<sub>2</sub> films overcoated with Mg(OH)<sub>2</sub> (□), Zn(OH)<sub>2</sub> (●), Al(OH)<sub>3</sub> (○), and La(OH)<sub>3</sub> (▲). The bottom axis shows the  $J_{sc}$  under the laser intensity used to measure the electron lifetime at open-circuit conditions.

as the process to convert hydroxides to oxides, was applied to our photoelectrode. The same effect that is an increase in photovoltage did not appear, and this result also ensured that the materials were hydroxides in this work (data is not shown here). In view of the thickness of the insulating layer, as it becomes thicker, the photocurrent is expected to be significantly decreased due to disturbed electron transfer from the dye to the nanocrystalline semiconductor.<sup>9</sup> The phenomenon was observed in our work; i.e., a large amount of Mg(OH)<sub>2</sub> induced a drop in the photocurrent as shown in Table 1. A similar tendency was found when other Me(OH)<sub>x</sub> were applied. A large amount of insulating metal hydroxide can reduce not only the efficient charge injection from dye to TiO<sub>2</sub> films but also the amount of the dye from being adsorbed to TiO<sub>2</sub>, reducing the short-circuit current. The decrease of the dye adsorption was confirmed by investigating the amount of dye desorbed from TiO<sub>2</sub> and the TiO<sub>2</sub>/Me(OH)<sub>x</sub> electrode. The amount of dye adsorbed to the TiO<sub>2</sub> film treated by CD for 5 min was  $3.70 \times 10^{-9}$  mol/cm<sup>2</sup>, about 70% in comparison with the amount of dye on a typical TiO<sub>2</sub> film without any treatment or with CD for a shorter time (below 1 min),  $5.21 \times 10^{-9}$  mol/cm<sup>2</sup>.

The increase in  $V_{oc}$  as a result of the CD treatment could be due to the increased electron density in the DSCs at open-circuit conditions and/or a negative shift in the TiO<sub>2</sub> band edge



**Figure 7.** Relationship of open-circuit voltage with electron density in DSCs employing only TiO<sub>2</sub> films (■), TiO<sub>2</sub> films overcoated with Mg(OH)<sub>2</sub> (□), Zn(OH)<sub>2</sub> (●), Al(OH)<sub>3</sub> (○), and La(OH)<sub>3</sub> (▲). Electron density was estimated by multiplying  $J_{sc}$  by the electron lifetime, divided by the thickness of the electrode.

potential. The negative shift could take place because negatively charged species, such as Al(OH)<sub>4</sub><sup>−</sup>, La(OH)<sub>4</sub><sup>−</sup>, Mg(OH)<sub>3</sub><sup>−</sup> or Zn(OH)<sub>3</sub><sup>−</sup> would be formed through reaction 5, and this could shift the band edge of the TiO<sub>2</sub> electrodes.



Me = Mg, Zn, Al, or La

To analyze the improvement in  $V_{oc}$  in a more quantitative manner, we plotted  $V_{oc}$  versus electron density in the DSCs, as shown in Figure 7. The electron density was estimated by multiplying the electron lifetime by  $J_{sc}$  and then dividing the result by the TiO<sub>2</sub> thickness and the electron charge. Note that the porosity of the electrodes was not taken into account. A strong correlation between the electron density and  $V_{oc}$  was observed, showing that the increase of  $V_{oc}$  was mainly due to the increase of the electron density in the DSCs as the result of the retardation of charge recombination. The higher  $V_{oc}$  from the DSC without CD was probably due to the higher porosity of the electrode. The highest improvement observed for Mg(OH)<sub>2</sub> suggests that a specific interaction of Mg(OH)<sub>2</sub> at the interfaces with nanocrystalline TiO<sub>2</sub> occurs due to the similarity of their ionic radii, i.e., Ti<sup>4+</sup> = 0.0605 nm and Mg<sup>2+</sup> = 0.066 nm,<sup>17</sup> thus creating a better insulating layer on the top of the TiO<sub>2</sub> surface. This suggests that ionic radius is an important factor for the formation of the insulating layer for DSCs, in addition to the band gap and basicity of the insulating materials.

The efficiency in this work was not high because we employed rather thin TiO<sub>2</sub> layers using P-25 with a 5 μm thickness and Nanoxide-T with a 2 μm thickness. To investigate an effect of morphology of TiO<sub>2</sub> film, we used Solaronix-T which has smaller crystalline particles (13 nm) than P-25. After investigation of the films, we obtained the same effect of an increase in  $V_{oc}$  and electron lifetime as mentioned above. We understand that the optimized cell could be obtained by

improvement of  $J_{sc}$ , e.g., surface treatments with aqueous TiCl<sub>4</sub>, usage of multiple TiO<sub>2</sub> layers with high thicknesses and large porosities using various sizes of freshly prepared nanocrystallites, and the introduction of a diffraction layer and antireflectance films. We are now carefully studying how to maximize our method when we employ the thicker and modified TiO<sub>2</sub> cells to maximize  $V_{oc}$ ,  $J_{sc}$ , 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)<sub>x</sub>, especially Mg(OH)<sub>2</sub>, at the TiO<sub>2</sub>/FTO and TiO<sub>2</sub>/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)<sub>x</sub>, showing that the layer acts as an insulating layer, suppressing recombination between injected electrons and I<sub>3</sub><sup>−</sup> in the electrolyte. A good correlation was observed between the increases in the  $V_{oc}$  and the electron density of the DSCs, suggesting that the suppression of recombination is the main reason for the improvement. The highest improvement in  $V_{oc}$  for Mg(OH)<sub>2</sub> 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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