Effective Sol-Gel Nanocoatings on ZnO Electrodes for Suppressing Recombination in Dye-Sensitized Solar Cells

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Attempts have been made to improve the performance of dye-sensitized solar cells by forming metal-oxide nanocoating layers on ZnO electrodes by a sol-gel transformation. SiO$_2$, Nb$_2$O$_5$, TiO$_2$, or ZrO$_2$ nanocoating layers could be formed by dipping ZnO films into metal alkoxide solutions of low concentrations and subsequent heat treatments. The performance of DSSCs using the coated ZnO electrodes depends strongly on the structure of coating layers such as the thickness and the surface coverage, which are significantly influenced by the coating conditions. In particular, SiO$_2$ and Nb$_2$O$_5$ coating layers are effective to suppress the recombination by constructing the energy barrier at the ZnO/electrolyte interface and enhance energy conversion efficiency. It is found that the coating layers also hinder the grain growth of ZnO, contributing to the enhanced cell performance as well.

1. Introduction

Conventional photovoltaic devices are based on light harvesting and charge separation at semiconductor p-n junctions. In contrast, dye-sensitized solar cells (DSSCs) utilize a combination of wide-gap semiconductors and organic or metal-organic complex dyes which play a fundamental role in light harvesting. DSSCs are expected as one of the promising candidates to partially replace conventional silicon-based solar cells because of their low manufacturing cost and higher conversion efficiency over 10% [1]. Furthermore, since DSSCs are also applicable to colorful, lightweight, and flexible devices, they can be installed in many kinds of places. Common DSSCs are composed of a conductive transparent glass substrate, a metal oxide layer, dye-sensitizers chemically bonded to metal oxides, a liquid electrolyte, and a counter electrode. In particular, an assembly of the conductive transparent glass substrate and the dye-sensitized n-type metal oxide semiconductor layer is called a photoanode, which is an essential part of DSSCs.

TiO$_2$ is recognized as the most common electrode material for DSSCs because the TiO$_2$-based cells generally have higher-energy conversion efficiencies. Many kinds of metal oxide semiconductors other than TiO$_2$ have also been applied to electrodes of DSSCs [5]. Among them, ZnO is the most promising alternative to TiO$_2$. Many researchers have tried to enhance the performance of ZnO-based DSSCs by modifying nanostructures of electrodes. For example, Law et al. reported the energy conversion efficiency ($\eta$) of 1.5% for a ZnO nanowire electrode [6]. Keis et al. reported porous ZnO electrodes fabricated by a doctor blading method showing $\eta = 5\%$ under lower irradiance at 0.1 sun [7]. Other structures have been reported later such as ZnO aggregate films comprising of closely packed nanocrystallites ($\eta = 5.4\%$, 1 sun), densely packed nanosheet ZnO films ($\eta = 5.41\%$, 1 sun), and ZnO nanoparticles-nanowire hybrid arrays ($\eta = 4.24\%$, 1 sun) [8–10]. A more complicated structure of hierarchical ZnO nanowire electrodes showed the $\eta$ of 2.63% [11]. We have also focused on ZnO as an electrode material in our series of studies on DSSCs [12–18]. Wurtzite-type ZnO is an n-type semiconductor with a wide band gap of 3.37 eV [19], which is similar to that of TiO$_2$ (3.2–3.3 eV) [20]. A conduction band edge energy ($E_{CB}$) of ZnO is located just above an $E_{CB}$ of TiO$_2$, and a difference in
The relationship between $V_{OC}$ based DSSCs are potentially comparable to TiO$_2$-based cells and the Nernst potential of an electrolyte \[1, 5\]. Therefore, ZnO-nanowires, and nanorod/nanoparticle composite, which are oxidized species in an electrolyte. In an I$^-$/I$_3^-$ conduction band of metal oxide semiconductor layers by nanocoating layers, which act as an energy barrier for the recombination at the ZnO/electrolyte interface. In ZnO electrodes, since the recombination sites correspond mainly to surface defects of ZnO particles, $V_{OC}$ values. Therefore, the recombination should be suppressed to improve the $V_{OC}$ values.

Some strategies have been conceived to suppress the recombination: (i) reducing the number of recombination sites, (ii) enhancing the electron transport inside electrodes, and (iii) constructing an energy barrier at an electrode/electrolyte interface. In ZnO electrodes, since the recombination sites correspond mainly to surface defects of ZnO particles, $V_{OC}$ is supposed to be improved by decreasing surface areas of ZnO electrodes. A better electron transport is expected for the structure free from grain boundaries such as nanorods, nanowires, and nanorod/nanoparticle composite, which are also effective for enhancing $V_{OC}$ \[6, 26\]. However, these ways (i) and (ii) are accompanied with a remarkable decrease in surface areas of electrodes, thereby resulting in a poor dye adsorption ability.

In the third way (iii), a formation of core-shell-type nanocoating layers, which act as an energy barrier for the recombination, on ZnO electrodes can reduce effectively the recombination kinetics constant $k_b$ \[27\]. A schematic energy diagram for the DSSC using an insulator-coated ZnO electrode is shown in Figure 1 with an illustration of an ideal coating layer structure. The difference in $E_{CB}$ between ZnO and proper coating materials can work as an energy barrier for the recombination at the ZnO/electrolyte interface. However, when $E_{CB}$ of the coating material lies above the excited state of dye ($S^*$), the coating layer also disturbs the electron injection from adsorbed dyes into the ZnO layer. Nonetheless, many works are found in the literature reporting that insulator-coated electrodes are utilized to enhance the cell performance by the suppression of the recombination \[28, 29\]. Some researchers explain that the electron injection through ultrathin coatings of insulator electrodes is achieved by a tunneling effect \[29, 30\]. In fact, the performance comparable to the TiO$_2$ electrodes was reported for SnO$_2$/ZnO electrodes \[31\].

In addition to the suppression of the recombination, metal-oxide coatings may be suitable for inhibiting aggregation of Zn$^{2+}$/Ru(II) dye complexes or improving a long-term durability. For metal oxide nanocoatings on porous ZnO electrodes, we employed a dip-coating method using various kinds of metal alkoxide solutions. The coating solutions penetrate inside porous, thick ZnO films as electrodes. Then thin metal-oxide coatings are formed on the surface of ZnO particles by a sol-gel transformation including hydrolysis and condensation of the metal alkoxides as follows \[32\]:

\[
M(OR)_m + nH_2O \rightarrow M(OR)_{m-n}(OH)_n + nROH \tag{2}
\]

M–OH + HO–M \rightarrow M–O–M + H$_2$O \tag{3}

In this paper, we review our works for enhancing the performance of DSSCs by the formation of SiO$_2$ and Nb$_2$O$_5$ nanocoating layers on ZnO electrodes \[2, 3\]. Additionally, we also report our recent works for the application of TiO$_2$ and ZrO$_2$ nanocoatings to the ZnO-based DSSCs.

2. Experimental

2.1. Fabrication of Porous ZnO Films. Porous, thick ZnO films used as a coating target were fabricated by a chemical bath deposition (CBD) method and subsequent pyrolytic transformation. Details of the fabrication process were reported previously \[14\]. Zinc acetate dihydrate ((CH$_3$COO)$_2$Zn·2H$_2$O; 99.0% purity, Wako Pure Chemical Industries Co., Ltd., Japan) was dissolved in dehydrated methanol at a concentration of 0.15 M. Fluorine-doped tin-oxide-coated glass substrates (FTO substrates; Nippon Sheet Glass Co., Ltd., Japan; sheet resistance of 10 ohm sq$^{-1}$) were immersed in the resultant solution, which was kept at 60°C for 30 h. Layered hydroxide zinc acetate (LHZA) films were formed on both sides of the FTO substrates. The unnecessary film on the bare glass side was completely removed by scratching. The film on the FTO substrate was heated at 450°C for 10 min in air to be converted to the porous, thick ZnO film (designated as the “uncoated” film).

2.2. Metal-Oxide Coating Method. Nanocoating layers were formed on the porous ZnO films through a dip-coating procedure. Four kinds of metal oxides were chosen as coating materials: SiO$_2$, Nb$_2$O$_5$, TiO$_2$, and ZrO$_2$. Metal alkoxide solutions were used for precursors. For the SiO$_2$ coating, a coating solution was prepared from 40 μL of tetraethylorthosilicate (TEOS; (C$_2$H$_5$O)$_4$Si; 95.0% purity, Wako), 500 μL of aqueous ammonia (28% mass/mass; Wako), and 20 mL.
of water [33]. For the Nb$_2$O$_5$ coating, 10–30 mM ethanolic solutions of niobium pentaethoxide ((C$_2$H$_5$O)$_5$Nb; 99.9% purity, Soekawa Chemicals Co., Ltd., Japan) were prepared as coating solutions. For the TiO$_2$ and the ZrO$_2$ coating, 10–30 mM ethanolic solutions of titanium tetraisopropoxide ([CH$_3$CO]$_4$Ti; 95.0% purity, Wako) and 10–50 mM 1-propanolic solutions of zirconium tetra-n-propoxide ((C$_3$H$_7$O)$_4$Zr; 23–28% free alcohol, Strem Chemicals, Inc., USA) were prepared as coating solutions, respectively. The ZnO films were immersed in the respective coating solutions and withdrawn at a speed of 0.1 mm/sec by using a Micro Speed Dip Coater (MS215, Asumi Giken Ltd., Japan). Then, the coated ZnO films were heated at 600 °C for 10 min in air. We also prepared a reference sample by heating the uncoated ZnO film at 600 °C for 10 min (the “uncoated/heated” film).

2.3. Characterization. The crystal structure was identified by X-ray diffraction (XRD) analysis (Bruker, AXS D8-02) using CuKα radiation. The Scherrer diameter of particles constituting the sample films was calculated with the Scherrer equation from the recorded XRD data. The morphology of the sample films was observed by field-emission scanning electron microscopy (FESEM; Hitachi, S-4700). The structure of the metal-oxide coating layers was examined by field-emission transmission electron microscopy (FETEM; FEI, Sirion or Tecnai Spirit) and X-ray photoelectron spectroscopy (XPS; JEOL, JPS 9000 MX).

2.4. Evaluation of Cell Performance. The uncoated and the coated ZnO films were dyed by immersion in a 0.3 mM ethanolic solution of RuL$_2$(NCS)$_2$:2TBA (L = 2,2’-bipyridyl-4,4’-dicarboxylic acid and TBA = tetrabutylammonium; N719, Solaronix SA, Switzerland) at 60 °C for 30 min. For J-V measurements, sandwich-type open cells were constructed with the ZnO/N719 photoanode, a 50 μm-thick spacer film, and a counter platinum electrode. The I$^-$/I$_3^-$ redox couple electrolyte, which was composed of 0.1 M LiI, 50 mM I$_2$, 0.6 M 1,2-dimethyl-3-propylimidazolium iodide, 1 M 4-tert-butylpyridine, and 3-methoxypropionitrile, was introduced between the electrodes. The characteristic values, $V_{OC}$, short-circuit photocurrent density (J$_{SC}$), fill factor (ff), and η, were determined from the J-V measurements. The active cell area was fixed at 25 mm$^2$ by a mask. A 500 W Xe lamp (Ushio, UXL-500SX) was used as the light source to produce the simulated AM 1.5 illumination at 100 mW/cm$^2$. An AM 1.5 filter, a water filter, and an infrared cut filter (Hoya, S76-HA50) were placed in the light path to regulate light in the wavelength range of 300–800 nm, reducing the mismatch of the simulated sunlight. J-V curves were measured under the simulated sunlight with a potentiostat (Hokuto Denko, HSV-100).

The amount of dyes adsorbed on the electrodes was estimated by removing them in a 0.5 M NaOH ethanol/water (v/v = 1) solution. The absorbance of the resultant dye solutions was measured by a spectrophotometer (Hitachi, U-3300 or Jasco, V-670) and calibrated with a standard solution of N719.

3. Results and Discussion

3.1. Structure of SiO$_2$- and Nb$_2$O$_5$-Coated ZnO Films. The film obtained by the CBD method was identified as LHZA with the chemical formula of Zn$_5$(OH)$_8$(CH$_3$COO)$_2$·2H$_2$O. They had a unique flower-like morphology. The LHZA film could be converted into ZnO completely by pyrolysis at 450 °C for 10 min. An FESEM image of the resultant ZnO film is shown in Figure 2(a), where the flower-like morphology originated from the LHZA film is maintained well. There exist micrometer-sized spaces inside as well as between the flower-like ZnO units, which can facilitate the penetration of the coating solutions in the coating process, the dye loading during the immersion in the dye solution, and the diffusion of the electrolyte in the solar-cell operation.
Figures 2(b) and 2(c) show FESEM images of the films that were coated with the TEOS solution and the 10 mM \((\text{C}_2\text{H}_5\text{O})_5\text{Nb}\) solution, respectively, and subsequently heated at 600°C for 10 min (denoted as the “SiO\(_2\)-coated” and the “Nb\(_2\)O\(_5\) (10 mM)-coated” film, resp.). The flower-like morphology of the ZnO film does not change after the SiO\(_2\) and the Nb\(_2\)O\(_5\) coating. The thickness of the coated films (approximately 30 μm) was also the same as that of the ZnO film. Therefore, it is not necessary to consider influences of dissolution or morphological change in discussing the structure and properties of the coated ZnO films.

The presence of the coating materials was confirmed by XPS. Figure 3(a) compares XPS spectra in the Si 2p region for the uncoated and the SiO\(_2\)-coated ZnO film. While no peak is detected for the uncoated ZnO film in this region, a peak due to the Si 2p electrons is clearly observed at 102.0 eV for the SiO\(_2\)-coated ZnO film, supporting the presence of SiO\(_2\) in the coated film. We also tried to observe directly the SiO\(_2\) coating layers by FETEM. Figure 4 shows an FETEM image of the SiO\(_2\)-coated ZnO particles found in the film. The core-shell-type SiO\(_2\) coating layers with a thickness of 1–3 nm are formed on the surface of the ZnO particles. We have reported previously that the structure of the silica layers, such as the thickness and the surface coverage, depends on the TEOS concentration and the coating time [4]. Basically, in the presence of the diluted ammonia catalyst, the formation of an amorphous SiO\(_2\) layer proceeds as the following hydrolysis and condensation reactions [32]:

\[
\text{Si}((\text{C}_2\text{H}_5\text{O})_4 + n\text{OH}^- \rightarrow \text{Si}((\text{C}_2\text{H}_5\text{O})_4 - n\cdot(\text{O}^-)_n + n\text{C}_2\text{H}_5\text{OH}
\]

(4)

\[
=\text{Si}-\text{OH} + \text{O}^- -\text{Si} \equiv \equiv =\text{Si} - \text{O} - \text{Si} \equiv + \text{OH}^-
\]

(5)

Because of the lower stability of TEOS in the aqueous system, the reactions might proceed rapidly. Then the core-shell structure is formed by the reaction between the surface OH groups of the ZnO particles and the hydrolyzed TEOS. Actually, the thin SiO\(_2\) nanocoating layers were successfully formed by using the low TEOS concentration of approximately 9 mM and the relatively short coating time (the ZnO film was immersed in the coating solution only for a few minutes). It should be noted that the thin shell layers could cover partially the surface of the ZnO particles in such the condition.

The SiO\(_2\) coating layers were in the amorphous state regardless of the subsequent heat treatments. In contrast, for the crystalline metal oxide coatings, it is important to know crystalline phases formed in the sol-gel transformation under the given experimental conditions. Since niobium is a multivalent metal element, there are various stoichiometries found in niobium oxides, Nb\(_x\)O\(_y\). Moreover, as far as Nb\(_2\)O\(_5\)
is concerned, at least 12 types of crystal structures are known [34]. In our case [3], the Nb$_2$O$_5$ coating layer derived from the (C$_2$H$_5$O)$_5$Nb solution was supposed to be the TT phase which could be classified as the quasi-hexagonal crystal system. Figure 3(b) compares XPS spectra in the Nb 3d region for the uncoated and the Nb$_2$O$_5$-coated ZnO films. No peak is seen for the uncoated ZnO film, whereas the Nb 3d$^{3/2}$ and 3d$^{5/2}$ peaks appear at 209.5 and 207.0 eV, respectively, for all the Nb$_2$O$_5$-coated ZnO films. The presence of niobium in the films is, thus, confirmed and the formation of the Nb$_2$O$_5$ coating layer is supported. Unfortunately, the Nb$_2$O$_5$ coating layers could not be observed directly by FETEM because the ZnO particles were decomposed by an electron beam accelerated at high voltage. In turn, an additional effect of the coatings was found in the TEM observation. Figure 5(a) shows a TEM image of the ZnO particles of the uncoated film which was used as the coating target. ZnO nanoparticles around 20 nm in size are clearly observed. When the uncoated ZnO film is heated at 600°C for 10 min, the growth of the ZnO particles was promoted and the particle size was increased up to more than 50 nm (Figure 5(b)). On the other hand, the growth of both the SiO$_2$ and the Nb$_2$O$_5$-coated ZnO particles is hindered even after heating at 600°C, and the particle size is kept around 20 nm (Figures 5(c)–5(f)). These results imply that the nanocoating layers actually exist on the surface of the ZnO particles and disturb the mass transport related to the grain growth or sintering during heating. Accordingly, the SiO$_2$ and the Nb$_2$O$_5$ nanocoatings are successfully formed on the ZnO electrodes. In the XRD analysis, diffraction peaks due to ZnO did not show any shift after the SiO$_2$ and Nb$_2$O$_5$ coating process, indicating that the lattice strain due to doping or stress was negligible for discussing the coating effect.

3.2. Structure of TiO$_2$- and ZrO$_2$-Coated ZnO Films. To know crystal phases of TiO$_2$ and ZrO$_2$ coating layers, we characterized first as-prepared and heat-treated gels which were
obtained by forced hydrolysis of [(CH₃)₂CHO]₄Ti in ethanol and (C₃H₇O)₄Zr in 1-propanol by adding water. XRD patterns of the as-prepared and the heated titanium oxide gels are shown in Figure 6(a). The as-prepared titanium oxide gel is amorphous, whereas the gel heated at 600°C is a mixture of anatase and brookite phases of TiO₂. The as-prepared zirconium oxide gel is also amorphous, and a crystalline phase is observed for the gel heated at 600°C (Figure 6(b)) with XRD peaks originating from tetragonal or cubic ZrO₂. The heated gel was further analyzed by Fourier transform infrared (FT-IR) spectroscopy (data not shown). The result showed that a band related to the tetragonal ZrO₂ was detected at 575 cm⁻¹ [35]. Therefore, the TiO₂ and the ZrO₂ coating layers, as described below, are regarded as the mixture of anatase- and brookite-type TiO₂ and the tetragonal ZrO₂, respectively.

For the TiO₂- and the ZrO₂ coated ZnO films, the morphology and the thickness did not change after the coating procedures including subsequent heating. The coated films were examined by XPS to confirm the presence of the TiO₂ and the ZrO₂ coating layers. Figure 7(a) compares XPS spectra of the uncoated and the TiO₂-coated ZnO films. For the TiO₂ (20 mM)-coated and the TiO₂ (30 mM)-coated ZnO film, a Ti 2p₁/₂ peak can be observed at 458.6 eV. Figure 7(b) compares XPS spectra of the uncoated and the ZrO₂-coated ZnO films. While no peak is seen for the uncoated ZnO film, two peaks appear in all the spectra for the coated films at approximately 184.4 eV and 182.0 eV, corresponding to the binding energy of Zr 3d₃/₂ and 3d₅/₂ electrons, respectively. The XPS results suggest that the ZrO₂-coating layers are formed on the ZnO particles regardless of the (C₃H₇O)₄Zr concentration, whereas the TiO₂ coating layers are formed at least in the TiO₂ (20 mM)-coated and the TiO₂ (30 mM)-coated film.

The formation of the TiO₂ and the ZrO₂ coating layers could not be observed by FETEM, for the same reason as mentioned above. Then we tried to see the hindrance of the grain growth. Low magnification TEM images of the TiO₂- and the ZrO₂-coated ZnO films is shown in Figure 8. Compared to the uncoated/heated ZnO particles shown in Figure 5(b), the size of the TiO₂- and the ZrO₂-coated ZnO particles are smaller, indicative of the hindrance effect. The TiO₂ and the ZrO₂ coating layers are then suggested to be formed on the ZnO particles, as in the case of the SiO₂ and the Nb₂O₅ coating.

It should be noted that the size of the TiO₂- and the ZrO₂-coated ZnO particles appears to be slightly larger than that of the SiO₂- and the Nb₂O₅-coated particles.
Figure 6: XRD patterns of (a) the as-prepared and the heated titanium oxide gel and (b) the as-prepared and the heated zirconium oxide gel.

Figure 7: XPS spectra (a) in the Ti 2p region for the uncoated and the TiO$_2$-coated electrodes and (b) in the Zr 3d region for the uncoated and the ZrO$_2$-coated electrodes.
Scherrer diameter of the uncoated and all the coated ZnO films was evaluated quantitatively from the XRD data by using the following Scherrer equation [36]:

\[ D = \frac{0.9\lambda}{\beta \cos \theta}, \]  

where \( \lambda \) is the wavelength of the X-ray irradiation (CuK\( \alpha = 1.5418 \) Å), \( \beta \) is the full width of half maximum (FWHM) of the peak, and \( \theta \) is the diffraction angle. Figure 9 compares the Scherrer diameters calculated for the (100), (002), and (101) peaks of ZnO. In Figure 9(a), the Scherrer diameters of the SiO\( _2 \)- and the Nb\( _2 \)O\( _5 \)-coated ZnO particles are approximately the same as that of the uncoated ZnO (around 21 nm). In contrast, for the uncoated/heated ZnO, the Scherrer diameter increases up to 35 nm due to the grain growth by heating. The TiO\( _2 \)- and the ZrO\( _2 \)-coated ZnO particles show the larger diameters than that of the uncoated ZnO particles (Figure 9(b)), indicating that the hindrance of the grain growth is less effective for the TiO\( _2 \) and the ZrO\( _2 \) coating. There are two possible reasons for such the difference between the coating materials. Firstly, the ability to suppress the grain growth of ZnO may be peculiar for a certain kind of metal oxides. Secondly, the surface coverage of the coating layers formed by the sol-gel transformation is different among the respective metal oxides. The hindrance of the ZnO grain growth arises from disturbing the mass transportation by the coating layers, which means that the latter reason is more probable. That is, the coating layers on the ZnO particles with the lower surface coverage allow the grain growth to occur more rapidly by heating. Actually, the Scherrer diameter of the TiO\( _2 \)- and the ZrO\( _2 \)-coated ZnO decreases with the concentration of the metal alkoxides in the coating solutions (Figure 9(b)). This fact is consistent with the basics of the dip-coating method; the thickness and the surface coverage of the coating layers depend directly on the concentration of the metal source. The XPS results also suggested the lower surface coverage for the films coated with the lower concentration of the coating solutions. Hence, we tentatively conclude that the increase in the Scherrer diameter for the TiO\( _2 \)- and the ZrO\( _2 \)-coated ZnO particles is attributed to the lower surface coverage of the coating layers, which might be influenced by the kinetics of the sol-gel transformation. Additionally, the lattice strain of ZnO due to doping or stress was not found by the coating process as in the case for the SiO\( _2 \) and Nb\( _2 \)O\( _5 \) coating.

### 3.3. Performance of DSSCs using the Coated Electrodes

The cell performance of DSSCs using the uncoated and the coated ZnO electrodes was evaluated from the \( J-V \) measurements. The characteristic values, \( V_{OC} \), \( J_{SC} \), \( ff \), and \( \eta \), together with the amount of the adsorbed dye, are summarized in Table 1. \( J-V \) curves of the uncoated, the uncoated/heated, and the
SiO$_2$-coated ZnO electrodes are shown in Figure 10(a). Firstly, the cell performance of the DSSCs using the uncoated and the uncoated/heated electrodes is discussed. The cell using the uncoated ZnO electrode shows $V_{OC}$ of 0.683 V, $J_{SC}$ of 11.59 mA/cm$^2$, and conversion efficiency of 4.57%. In the cell using the uncoated/heated electrode, $V_{OC}$ increases to 0.718 V while $J_{SC}$ decreases to 7.11 mA/cm$^2$. These changes can be explained with the progress of the grain growth during heating [37]. The size of the ZnO particles heated at 600°C for 10 min increases up to more than 50 nm, leading to the significant decrease in the net surface area of the electrodes. Simultaneously, the recombination sites located at the surface of the ZnO particles are diminished by the high-temperature heating. Dark current-voltage curves shown in Figure 10(b) reveal that the dark current of the uncoated/heated electrode is much smaller than that of the uncoated electrode at the same bias. This fact also suggests that the recombination is strongly suppressed in
the uncoated/heated electrode. Hence, according to (1), the relatively high $V_{OC}$ is obtained for the cell using the uncoated/heated electrode. On the other hand, the amount of the adsorbed dye decreases by half with the decrease in the surface area of the electrode, resulting in the significantly lowered $J_{SC}$. As a result, the energy conversion efficiency of the cells using the uncoated ZnO electrodes decreases from 4.57% to 2.73% by heating.

In the cell using the SiO$_2$-coated electrode, $V_{OC}$ and $J_{SC}$ increase to 0.724 V and 12.05 mA/cm$^2$, respectively, even after heating at 600$^\circ$C [2]. The particle size does not change by heating due to the hindrance of the grain growth by the formation of the SiO$_2$ nanocoating layer on the ZnO particles. Therefore, the enhancement of the cell performance is attributed not to the decrease in the net surface area of the electrode but to the suppression of the recombination by constructing the energy barrier at the ZnO/electrolyte interface. The presence of the energy barrier is also suggested strongly by the smaller dark current of the SiO$_2$-coated electrode compared to that of the uncoated electrode at the same bias (Figure 10(b)). $E_{CB}$ of SiO$_2$ is located at $-0.20$ eV versus $E_{VAC}$, which is approximately 4.0 eV above $E_{CB}$ of ZnO, and this energy difference works as the barrier for the recombination [38]. Additionally, as the decrease in the surface area of the electrode can be avoided by the hindrance of the grain growth, the amount of the adsorbed dye for the SiO$_2$-coated electrode is comparable to that for the uncoated electrode. Both the suppression of the recombination and the hindrance of the grain growth by the SiO$_2$ coating layer contribute to the enhancement in $J_{SC}$. Due to the increase in $V_{OC}$ and $J_{SC}$, the SiO$_2$-coated ZnO electrode exhibits higher-energy conversion efficiency of 4.80%. This result demonstrates that even the insulator coatings are effective to improve the cell performance including $J_{SC}$. Since $E_{CB}$ of SiO$_2$ is located at higher energy level than the $S^*$ state of N719 (approximately 3.65 eV above) [39], the electron injection may be retarded considerably. In the present case, the electron injection to the SiO$_2$-coated ZnO might be possible from the dye adsorbed on the “bare” ZnO surface rather than the tunneling effect because the thickness of the SiO$_2$ coating layer (1–3 nm) is too large.

Contrary to SiO$_2$, $E_{CB}$ of Nb$_2$O$_5$ is located approximately 0.2 eV above $E_{CB}$ of ZnO and 0.3 eV below the $S^*$ state of N719 [39, 40]. Therefore, the Nb$_2$O$_5$-coating would not disturb the electron injection when they act as the energy barrier for the recombination [27]. $J$-$V$ curves and dark current-voltage curves of the uncoated and the Nb$_2$O$_5$-coated ZnO electrodes are shown in Figure 11. As mentioned above, the hindrance effect of the grain growth is found in all the Nb$_2$O$_5$-coated electrodes. Higher $V_{OC}$ for the Nb$_2$O$_5$-coated electrodes is then ascribed to the suppression of the recombination by the Nb$_2$O$_5$ coating layers. In addition, as can be seen in Figure 11(a) and Table 1, $V_{OC}$ of the cells using the Nb$_2$O$_5$-coated ZnO electrodes increases from 0.712 to 0.755 V when the (C$_2$H$_5$O)$_5$Nb concentration increases from 10 to 30 mM. This tendency of the $V_{OC}$ increase may be due to the increase in the surface coverage of the Nb$_2$O$_5$ coating layers which work as the energy barrier for the recombination. In fact, as found in Figure 11(b), the dark current of the Nb$_2$O$_5$-coated electrodes decreases with the (C$_2$H$_5$O)$_5$Nb concentration. Especially for the Nb$_2$O$_5$ (30 mM)-coated electrode, the dark current is as small as that.
Figure 11: (a) J-V curves and (b) dark current-voltage curves of the cells using the uncoated, the uncoated/heated, and the Nb2O5-coated ZnO electrodes [3].

of the uncoated/heated electrode. This is probably because of the higher surface coverage of Nb2O5.

\( J_{SC} \) of the Nb2O5-coated electrodes, on the other hand, tends to decrease with the coating solution concentration. This is attributable to the lower electron conductivity of the Nb2O5 coating layers [34], judging from the fact that the dye adsorption ability is not changed by the coating. It is also reported that the charge injection efficiency from the Ru(II) complex dye to Nb2O5 is similar to that to ZnO [41]. The thicker coating layer with the higher coverage can possibly disturb the electron transport inside the electrode and decrease \( J_{SC} \) to some extent. For the Nb2O5 (10 mM)-coated ZnO electrode, since both \( V_{OC} \) and \( J_{SC} \) are improved due to the efficient suppression of the recombination and the hindrance of the grain growth, the higher energy conversion efficiency of 5.19% has been achieved. These results suggest that Nb2O5 is more suitable for coating on the ZnO electrodes than SiO2.

In the case of the Nb2O5 coating, the ZnO particle size is kept constant (around 20 nm) regardless of the coating solution concentration. Only the structure of the coating layers is concerned. However, for the TiO2 and the ZrO2 coating, we need to consider both the structure of the coating layers and the influence of the grain growth. It is reported that \( E_{CB} \) of TiO2 is approximately 0–200 meV below \( E_{CB} \) of ZnO, and hence the TiO2 coating layers do not work as the energy barrier for the recombination. Actually, however, slight increase in \( V_{OC} \) is found in the cell using the TiO2-coated ZnO electrodes. As shown in Figure 12(a), the dark current of all the TiO2-coated electrodes is as small as that of the uncoated/heated ZnO electrode. According to Figure 9(b), the size of the TiO2-coated ZnO particles slightly increases by heating, which contributes to the increase in \( V_{OC} \) by the reduction of the recombination sites. Considering that the TiO2-coated ZnO particles are smaller than the uncoated/heated ZnO, the increased \( V_{OC} \) should be explained with the other factor than the grain growth. In other words, the TiO2 coating layer is capable of acting as the energy barrier against our prediction. Actually, there are some reports on the successful TiO2 coatings for improving the performance of DSSCs using ZnO electrodes [42, 43]. The enhancement in \( V_{OC} \) is ascribed to the passivation of the surface defects of the ZnO by TiO2. As a result, the recombination from the ZnO layer is reduced [44]. Further investigations are necessary for TiO2 to clarify the effect or the mechanism of the coating layers.

The decrease in the amount of the adsorbed dye results in the slightly smaller \( J_{SC} \) due to the decrease in the surface area by the slight grain growth of the TiO2-coated ZnO particles. Additionally, the \( ff \) values for all the cells using TiO2-coated ZnO electrode are remarkably smaller than those of the other electrodes. The decrease in \( ff \) is explained with a high intrinsic resistance of the cell [45]. In the present case, the electron transport may be disturbed through the TiO2-coated ZnO particles inside the electrodes due to the small difference in \( E_{CB} \).

ZrO2 is also considered to work as the energy barrier. Similar to SiO2, \( E_{CB} \) of ZrO2 is located at −3.44 eV versus \( E_{VAC} \), which is approximately 0.9 eV above \( E_{CB} \) of ZnO and 0.4 eV above the \( S^* \) state of N719 [38, 39]. The ZrO2 (10 mM)-coated electrode exhibits the highest \( V_{OC} \) value of 0.765 V, which is comparable to that of the TiO2-base
DSSCs. The coverage of the ZrO2 coating layer is considered to be small because the hindrance of the ZnO grain growth is less effective for the ZrO2 coating (Figure 9(b)). In particular, the recorded dark current of the ZrO2 (10 mM)-coated electrode is smaller than that of the uncoated/heated electrode (Figure 12(b)). This result also suggests that both the reduction of the surface recombination sites due to grain growth and the energy barrier constructed by the ZrO2 coating contribute to the increase in VOC. It is found that VOC decreases when the ZnO electrodes are coated with 30 and 50 mM (C3H7O)4Zr solutions. This is because the influence of the decrease in the recombination sites on VOC is diminished by the hindrance of the grain growth due to the higher coverage of the ZrO2 coating. All the ZrO2-coated electrodes show lower JSC than that of the uncoated electrode. As the amount of the adsorbed dye does not change significantly after the ZrO2 coating, the decrease in JSC is due mainly to the interruption of the electron injection. As a result, the energy conversion efficiency of the cells slightly decreases by the ZrO2 coating.

In this paper, the formation of metal-oxide nanocoatings on ZnO is demonstrated to be one of the promising approaches to the enhancement of the cell performance. Since VOC of the cells using the coated ZnO electrodes depends both on the structure of the metal-oxide coating layers and the structure of the ZnO electrode itself, we should control carefully the sol-gel transformation conditions and the following heat treatments. We are now trying to form the ultrathin coating layers which suppress more effectively the recombination and enhance the performance of the ZnO-based DSSCs.

4. Conclusions

The nanoscale coating of four kinds of metal oxides (SiO2, Nb2O5, TiO2, and ZrO2) were performed on the ZnO electrodes to increase VOC of the DSSCs. Metal alkoxide solutions of low concentrations were employed to form nanocoating layers through the dip-coating method, followed by the sol-gel transformation. The SiO2, the Nb2O5, and the ZrO2 nanocoating layers could reduce the recombination rate by constructing the energy barrier at the ZnO/electrolyte interface, leading to the higher VOC values. On the other hand, the TiO2-nanocoating layers were effective to increase VOC due to the reduction of the surface recombination sites by the grain growth of ZnO as well as the surface passivation. The additional effect of the coating layers was found to be the hindrance of the ZnO grain growth. Consequently the coated ZnO films maintained the high surface area to adsorb a large amount of dyes. For the SiO2 and the Nb2O5 coating, the energy conversion efficiency of the DSSCs increased up to 4.80% and 5.19%, respectively. On the other hand, for the TiO2 and the ZrO2 coating, the slight decrease in JSC due to the grain growth led to the lower conversion efficiency. The highest VOC of 0.765 V was recorded for the ZrO2-coated ZnO electrode due to in the present study. Further work is ongoing to enhance the overall cell performance by optimizing the coating conditions.

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References


