Surface passivation of highly ordered TiO₂ nanotube arrays and application to dye-sensitized solar cells using the concept of isoelectric point

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Highly ordered TiO₂ nanotube arrays have attracted much attention in an application to dye-sensitized solar cells (DSCs) due to their superior charge percolation. However, the efficiency of TiO₂-nanotube-based DSCs is 6.89%, which is still lower than that of TiO₂-nanoparticle-based DSCs. In this study, the surface passivation of highly ordered TiO₂ nanotube arrays has been applied to increase the performance of TiO₂-nanotube-based DSCs using the concept of isoelectric point. Both acidic oxide such as WO₃ and basic oxides such as MgO, ZnO have been used as materials for surface passivation. The overall conversion efficiency of DSCs based on surface-passivated TiO₂ nanotube arrays has been improved by these passivating layers.

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1. Introduction

Dye-sensitized solar cells (DSCs) have been highly spotlighted as an alternative device for conventional photovoltaics due to their low cost and easy fabrication.¹⁾ The efficiency of DSCs, which is based on the nanoparticulate TiO₂ photoelectrode, is 11.1%. It is still lower than that of other kinds of photovoltaic devices such as Si solar cell, CIGS, etc.²⁾ The improvement of the overall conversion efficiency of DSCs is one of the important issues to commercialize them. However, the nanoparticulate structure which has a maximum efficiency for DSCs has limitations increasing the cell efficiency. In randomly packed TiO₂ nanoparticulate films, it has been mentioned that electron transport is limited by the structural disorder at the contact between two nanoparticles. This leads to the low efficiency of collecting injected electrons.³⁾

Recently, TiO₂ nanotube structure has received considerable attention to the applications in photocatalysis, sensing, photoelectrolysis and photovoltaics.⁴⁾ In an application to DSCs, highly ordered TiO₂ nanotube arrays have higher charge collection efficiencies than a nanoparticle-based structure due to their faster charge percolation and slower recombination of electrons.³⁾⁻⁵⁾ Shankar et al. made back-side illuminated DSCs based on 20 μ m-thick TiO₂ nanotube arrays and the overall conversion efficiency was 6.89%, which is still lower than that of DSCs based on the TiO₂ nanoparticle structure despite of the advantages of TiO₂ nanotube structure.⁶⁾ More efforts focused on the improvement of photovoltage and photocurrent should be done to increase the efficiency of DSCs based on the TiO₂ nanotube structure.

Surface passivation of TiO₂ photoelectrodes is an effective method which can improve both photovoltage and photocurrent.

This method has been actively studied to increase the overall conversion efficiency of DSCs.⁷⁾⁻¹²⁾ The surface passivating layers act as a barrier layer which inhibits charge recombination between the redox liquid electrolyte and electrons in the TiO₂ conduction band or surface trap sites. Furthermore, they improve dye adsorption due to the increased surface area and their isoelectric points.

In this paper, the concept of isoelectric point was introduced to select materials for surface passivation of TiO₂ nanotube photoelectrodes. One acidic material (WO₃) and two basic materials (MgO, ZnO) were selected to study the effect of isoelectric point of materials for surface passivation. Isoelectric point means the pH at which the oxide surface has a net zero charge.¹³⁾ The oxide surface can be positively or negatively charged according to the pH of the immersing solution. If the isoelectric point of an oxide material is over the pH of the immersing solution, the immersed oxide surface is positively charged and vice versa. The quantity of dye adsorption is expected to be improved by controlling the surface property affected by isoelectric point of materials for surface passivation.

2. Experimental procedure

Highly ordered TiO₂ nanotube arrays were grown by anodic oxidation of 0.25 mm-thick titanium foil (99.5%, Alfar Aesar) at a constant potential 60 V (ramping up to 60 V with 1 V/s) in the ethylene glycol solution containing 0.3 wt% NH₄F and 2 vol% H₂O kept at 30°C for 1 h. The anodized samples were annealed at 500°C for 60 min to crystallize the amorphous TiO₂ nanotube arrays.

Surface passivation of TiO₂ nanotube arrays with MgO,^{8),9)} ZnO,¹¹⁾ and WO₃¹⁰⁾ was done by using Mg(CH₃COO)₂·4H₂O (magnesium acetate pentahydrate, 99%, Junsei Chemical Co., Ltd.), ZnCl₂ (zinc chloride, 98%, Kanto Chemical Co., Inc.), and (NH₄)₁₀W₁₂O₄₁·5H₂O (ammonium tungstate para pentahydrate,

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GR, Wako Pure Chemical Industries, Ltd.) as precursors, respectively. Samples for MgO and WO₃ coating were immersed in aqueous solution by controlling the concentration of each precursor and those for ZnO coating in ethanol solution kept at 65°C for 30 min. While immersing the samples vacuum pumping was done to fill the solution into the pores of TiO₂ nanotubes. The immersed samples in aqueous solution were rinsed with deionized water and those in ethanol solution rinsed with ethanol. Each sample was annealed at 500°C for 1 h to convert hydrous MgO, ZnO, and WO₃ into anhydrous MgO, ZnO, and WO₃ and crystallize those materials.

TiO₂ nanotube photoelectrodes with and without surface-passivating layer were immersed for ~1 d in an ethanol solution containing 3×10^{-4} M cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium (II) bis-tetrabutylammonium (N719) dye. The dye-adsorbed photoelectrodes were rinsed with ethanol and dried at room temperature. The liquid electrolytes consisted of 0.6 M 1-hexyl-2,3-dimethyl-imidazolium iodide (C6DMIIm), 0.05 M iodine (I₂), 0.1 M lithium iodide (LiI) and 0.5 M 4-tert-butylpyridine in 3-methoxypropionitrile. A Pt counter electrode was prepared by spin-coating H₂PtCl₆ solution (7 mM in isopropyl alcohol) onto the FTO glass; this was then sintered at 450°C for 30 min. The electrode of TiO₂ nanotube arrays and the counter electrode were spaced and sealed by 60 μ m-thick hot melt film as a spacer.

Photocurrent-voltage characteristics (*J-V* curves) were measured under AM 1.5 illumination (Keithley Model 2400 source measure unit). A 1000 W xenon lamp (Oriel, 91193) was used as a light source. XRD (X-ray Diffractometry, Rigaku D/MAX-RC, Cu K α radiation) analysis was done to confirm the crystallinity of TiO₂ nanotubes and the formation of surface-passivating layers. The length, pore size, and wall thickness of highly ordered TiO₂ nanotube arrays were determined by scanning electron microscope (SEM) analysis.

3. Results and discussion

Figure 1 shows the SEM images of TiO₂ nanotube arrays which have been fabricated in ethylene glycol solution containing 0.3 wt% NH₄F and 0.2 vol% H₂O. The images of as-anodized TiO₂ nanotube arrays are shown in Figs. 1(a) and (b); those of

Fig. 1. SEM images of TiO₂ nanotube arrays by anodic oxidation process at a constant voltage 60 V in 0.3 wt% NH₄F and 0.2 vol% H₂O contained ethylene glycol solution kept at 30°C for 1 h: (a), (b) cross-sectional images of as-anodized TiO₂ nanotube arrays; (c), (d) cross-sectional images of annealed TiO₂ nanotube arrays.

annealed TiO₂ nanotube arrays are shown in Figs. 1(c) and (d). As shown in Figs. 1(a) and (c), both the wall thickness and the pore size of as-anodized and annealed TiO₂ nanotube arrays were nearly same. The wall thickness and the pore size were 25 nm and 60 nm, respectively. However, the length of TiO₂ nanotube arrays was increased from 3.17 μ m to 4.58 μ m as shown in Figs. 1(b) and (d). It is assumed that the rearrangement of Ti and O atoms led to the increase of the length of TiO₂ nanotube arrays during the heat treatment at 500°C.

Figure 2 shows the XRD result of bare TiO₂ nanotube arrays. As-anodized TiO₂ nanotube arrays initially have amorphous phase. Because only surface part of Ti foil is anodized into amorphous TiO₂ nanotube arrays, XRD data result of those samples showed only Ti metal peaks (XRD data result is not shown here). After the annealing at 500°C for 1 h, the amorphous TiO₂ nanotube arrays were crystallized and transformed into anatase phase. Annealed TiO₂ nanotubes had polycrystalline anatase structures characterized with (101), (103), (200), (105) and (211) orientations as shown in Fig. 2. **Figure 3**(a), (b) and (c) shows the XRD results of MgO, WO₃ and ZnO coated TiO₂ nanotube arrays, respectively. It was very difficult to find the

Fig. 2. XRD result of annealed TiO₂ nanotube arrays: annealed TiO₂ nanotubes had polycrystalline anatase structures characterized with preferred (101) orientation with (103), (200), (105) and (211) orientations.

Fig. 3. XRD results of heavily coated TiO₂ nanotube arrays with MgO, WO₃, and ZnO: diffraction peaks for each coating material were marked with different symbols. This indicates that the crystallized surface-passivating layers were formed on the TiO₂ nanotube arrays by immersing the bare samples in each precursor solution and annealing them at 500°C for 1 h.

diffraction peaks of coating materials if the concentration of precursors for surface passivation is too low (~ 0.01 M for MgO, ZnO and ~ 0.00001 M for WO₃). For this reason, highly ordered TiO₂ nanotube arrays were heavily coated to confirm the formation of MgO, ZnO and WO₃ surface-passivating layers (~ 1.0 M for MgO, ZnO and ~ 0.1 M for WO₃). Diffraction peaks for each coating material were marked with different symbols in Fig. 3(a), (b) and (c). This indicates that the crystallized surface-passivating layers were formed on the TiO₂ nanotube arrays by immersing the bare samples in each precursor solution and annealing them at 500°C for 1 h.

Figure 4 shows the performance comparison of the DSCs based on bare, 0.02 M MgO coated, 0.00001 M WO₃ coated and 0.03 M ZnO coated TiO₂ nanotube arrays. These coating concentrations of each precursor are optimized values to maximize the performance of DSCs. The concentration of each precursor solution affects the performance of DSCs, because it is closely related to the thickness of surface-passivating layers. If the thickness of surface-passivating layers is too thin, the blocking effect of charge recombination by surface passivation is very weak. On the other hand, if it is too thick, the charge injection into photoelectrodes is hindered. Therefore, the thickness of surface-passivating layers should be properly controlled by maximizing reduced charge recombination and minimizing hindered charge injection. It is difficult to define the optimum thickness of surface-passivating layers to improve the performance of DSCs. However, it has been reported that the optimized coating thickness is only a few angstroms.⁷⁾ In this study, the optimized thickness could not be measured by TEM or SEM analysis, hence, the exact coating thickness is not possible to be mentioned.

The performance data are summarized in **Table 1**. Photocurrent, photovoltage, fill factor and efficiency for the DSCs consisting of bare TiO₂ photoelectrodes were 0.70 mA/cm², 0.81 V, 0.56 and 0.31%, respectively. For MgO coated TiO₂-nanotube-based DSCs, the photovoltage was hardly changed compared to that of bare TiO₂-nanotube-based DSCs. However, the photocurrent was greatly increased from 0.70 mA/cm² to 2.51 mA/cm². The overall conversion efficiency was improved from 0.31% to 1.06% by MgO surface-passivating layers. For WO₃ coated TiO₂-nanotube-based DSCs, the photocurrent was increased from 0.70 mA/cm² to 1.14 mA/cm²; however, the photovoltage was decreased from 0.81 V to 0.62 V. In spite of the

Fig. 4. Performance comparison of the DSCs based on bare, 0.02 M MgO coated, 0.00001 M WO₃ coated, and 0.03 M ZnO coated TiO₂ nanotube arrays: The overall conversion efficiencies of DSCs consisting of surface-passivated TiO₂ nanotube arrays were improved compared to that of DSC consisting of bare TiO₂ nanotube arrays.

photovoltage degradation, the improved conversion efficiency could be obtained by the increased photocurrent. For ZnO coated TiO₂-nanotube-based DSCs, both photocurrent and photovoltage were increased from 0.70 mA/cm² and 0.81 V to 1.98 mA/cm² and 0.88 V, respectively. The overall conversion efficiency was improved from 0.31% to 0.41% by ZnO surface-passivating layers.

The overall conversion efficiencies of the DSCs based on surface-passivated TiO₂ nanotube arrays were improved compared to that of the DSC based on the bare TiO₂ photoelectrode. **Figure 5** shows the schematic mechanism of performance improvement by surface passivation. The injected photoelectrons, which are generated from dye molecules, diffuse across the TiO₂ layer by trapping and detrapping at the surface states. Therefore, the diffusing electrons usually reside at the surface states. Charge recombination usually occurs at the interface between the surface states and I_3^-/I^- redox couple system. The coating layers of TiO₂ photoelectrodes usually retard the charge recombination due to the formation of energy barrier and the passivation of surface states as shown in Fig. 5. They also improve the dye adsorption because of the increased surface area and their isoelectric points.

Figure 6 shows the effect of the isoelectric point of surface-passivating layers. As mentioned previously, isoelectric point means the pH at which surface oxide has a net zero charge. When

Table 1. Performance Comparison of the DSCs Based on Bare, 0.02 M MgO Coated, 0.00001 M WO₃ Coated, and 0.03 M ZnO Coated TiO₂ Nanotube Arrays: The Overall Conversion Efficiencies of DSCs Consisting of Surface-passivated TiO₂ Nanotube Arrays were Improved Compared to that of DSC Consisting of Bare TiO₂ Nanotube Arrays

Electrode	J_{sc} (mA/cm ²)	V_{oc} (V)	Fill Factor	Efficiency (%)
(a) Bare TiO ₂ nanotube	0.70	0.81	0.56	0.31
(b) MgO coated TiO ₂ nanotube	2.51	0.80	0.53	1.06
(c) WO ₃ coated TiO ₂ nanotube	1.14	0.62	0.58	0.41
(d) ZnO coated TiO ₂ nanotube	1.98	0.88	0.40	0.70

Fig. 5. Schematic mechanism of the performance improvement by surface passivation: Charge recombination usually occurs at the interface between the surface states and the redox couple systems in liquid electrolyte. Surface-passivating layers not only retards the charge recombination but also enhances dye adsorption.

Fig. 6. Effect of the isoelectric point of surface-passivating layers: (a) the surface-passivating layers with basic materials have a positive charge because the isoelectric point of basic materials is higher than the pH of ethanol. The coating layers attract N719 dye molecules more strongly than the bare TiO₂ layers; (b) the surface-passivating layers with acidic materials are negatively charged because the isoelectric point of acidic materials is lower than 7.

Table 2. Isoelectric Points of TiO₂, MgO, WO₃, and ZnO:¹³⁾ the Isoelectric Point Means the pH at which Surface Oxide has a Net Zero Charge. The Isoelectric Points of TiO₂, MgO, WO₃, and ZnO are 6.2, 12.4 ± 0.3, 0.5, and 9.2–9.7, Respectively

Material	Isoelectric point
TiO ₂	6.2
MgO	12.4 ± 0.3
WO ₃	0.5
ZnO	9.2–9.7

the pH of solvent is higher than the isoelectric point of the solute, the solute material has a negative charge and vice versa. Dye adsorption is done by immersing the TiO₂-nanotube-based photoelectrodes in 3×10^{-4} M N719 ethanol solution. The pH of ethanol is around 7 and the isoelectric point of N719 dye molecule is lower than 7 due to the carboxylic chains of N719. Therefore, N719 dye molecules are assumed to have a negative charge in ethanol solution. The isoelectric point of acidic materials is below 7, and that of basic materials is over 7. As shown in Fig. 6(a), the surface-passivating layers with basic materials have a positive charge because the isoelectric point of basic materials is higher than the pH of ethanol. The coating layers attract N719 dye molecules more strongly than the bare TiO₂ layers. In this way, the dye adsorption is assumed to be improved by surface-passivating layers with basic materials. On the other hand, as shown in Fig. 6(b), the surface-passivating layers with acidic materials are negatively charged because the isoelectric point of acidic materials is lower than 7. In this case, the attraction between coating layers and N719 dye molecules becomes worse, hence, the dye adsorption is assumed to be deteriorated.

As shown in Table 2, the isoelectric points of TiO₂, MgO, WO₃, and ZnO are 6.2, 12.4 ± 0.3, 0.5, and 9.2–9.7, respectively.¹³⁾ While the MgO and ZnO surface-passivating layers are assumed to be positively charged in N719 ethanol solution during dye adsorption, the WO₃ surface-passivating layers are assumed to be negatively charged. Therefore, the surface passivation with basic materials such as MgO, ZnO was expected to improve dye adsorption more than acidic materials such as WO₃. As shown in Fig. 4 and Table 1, we can find that the performance data coincides with our expectation. Photocurrents of DSCs

based on MgO, ZnO (basic materials) coated TiO₂ nanotube arrays were improved more than that of DSC based on WO₃ (acidic material) coated TiO₂ photoelectrodes. Photocurrent of the WO₃ coated sample was increased from 0.7 mA/cm² to 1.14 mA/cm² compared to the bare TiO₂ sample. This is probably due to the increase of surface area by WO₃ coating. Furthermore, the photovoltage of the WO₃ coated sample was decreased from 0.8 V to 0.62 V. It is assumed that the conduction band of TiO₂ is shifted to positive direction by WO₃ coating due to the low isoelectric point of WO₃ because it has been reported that the surface passivation with basic materials shift TiO₂ conduction band to negative direction.¹²⁾ While the photovoltage was increased from 0.81 V to 0.88 V by ZnO coating, the effect of band shift by MgO coating was very weak.

4. Conclusion

The surface passivation of highly ordered TiO₂ nanotube arrays with basic materials such as MgO, ZnO has enhanced the photocurrent of DSCs more strongly than acidic materials such as WO₃. This result indicates that basic materials have higher isoelectric points than acidic materials, thus, the dye adsorption is more improved by surface passivation with basic materials than that with acidic materials. In this study, we could conclude that the basic materials had better effects on the performance of DSCs as surface-passivating materials.

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