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Highly ordered and vertically oriented TiO$_2$/Al$_2$O$_3$ nanotube electrodes for application in dye-sensitized solar cells

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Abstract
The surface of long TiO$_2$ nanotube (NT) electrodes in dye-sensitized solar cells (DSSCs) was modified without post-annealing by using atomic layer deposition (ALD) for the enhancement of photovoltage. Vertically oriented TiO$_2$ NT electrodes with highly ordered and crack-free surface structures over large areas were prepared by a two-step anodization method. The prepared TiO$_2$ NTs had a pore size of 80 nm, and a length of 23 μm. Onto these TiO$_2$ NTs, an Al$_2$O$_3$ shell of a precisely controlled thickness was deposited by ALD. The conformally coated shell layer was confirmed by high-resolution transmission electron microscopy, energy-dispersive x-ray spectroscopy, and x-ray photoelectron spectroscopy. The open-circuit voltage ($V_{oc}$) of the DSSCs was gradually enhanced as the thickness of the Al$_2$O$_3$ shell of the TiO$_2$/Al$_2$O$_3$ NT electrodes was increased, which resulted from the enhanced electron lifetime. The enhanced electron lifetime caused by the energy barrier effect of the shell layer was measured quantitatively by the open-circuit voltage decay technique. As a result, 1- and 2-cycle-coated samples showed enhanced conversion efficiencies compared to the bare sample.

Keywords: TiO$_2$/Al$_2$O$_3$ nanotube, dye-sensitized solar cells, atomic layer deposition

(Some figures may appear in colour only in the online journal)

1. Introduction
Since O’Regan and Grätzel reported a high conversion efficiency of 7.12% in 1991 [1], dye-sensitized solar cells (DSSCs) have attracted much attention due to their low production cost, high power conversion efficiency, and ease of manufacturing process [1–3]. A mesoporous TiO$_2$ film typically used in DSSCs is composed of 15 nm diameter TiO$_2$ nanoparticles (NPs). This electrode contains many grain boundaries that can become centers for charge recombination between photoexcited-electrons and the electrolyte [4, 5]. Charge recombination reaction is the main reason to deteriorate photovoltaic performance of DSSCs. One-dimensional structured photoanode materials, such as nanorod (NR), nanotube (NT) materials have merits for the electron transport due to the restricted electron pathway and fewer grain boundaries [6–8]. In particular, vertically oriented TiO$_2$ NT electrodes prepared by anodic oxidation have been actively studied owing to their ideal structure as photoanodes in DSSCs [6–14]. It was reported that TiO$_2$ NT electrodes showed a slower charge recombination rate and enhanced light scattering effect compared to the NP electrodes [7, 8].
However, the general NT electrodes anodized under constant potentials of 50–60 V have smaller surface areas than the NP electrodes at the same thickness. These smaller surface areas reduce the number of adsorbed dye molecules and hence the conversion efficiency [15]. Therefore, for high conversion efficiency, the thickness of NT electrodes should be somewhat larger than that of the NP electrodes. However, as the tube length of the NT electrode becomes longer, the open-circuit voltage ($V_{oc}$) is reduced steeply due to the increased recombination centers [15].

The increased charge recombination rate of long NT arrays can be alleviated by introducing an energy barrier layer. Wide band gap semiconductors such as Al$_2$O$_3$ [16–19], ZnO [10, 20, 21], Nb$_2$O$_5$ [20], SrTiO$_3$ [22], etc, have been introduced as energy barrier shells onto the TiO$_2$ NP in DSSCs. Especially, an Al$_2$O$_3$ layer coated on the TiO$_2$ electrode has been reported to reduce the charge recombination rate due to its insulating nature [17, 18]. However, these studies used solution-based methods that cannot guarantee the conformal coating throughout the mesoporous TiO$_2$ electrode. In addition, these methods require post-annealing, which can deteriorate the photovoltaic performance of NT electrode. Compared to the conventional TiO$_2$ NP electrode, the NT electrode generally has a lower fill factor of DSSCs. The low fill factor is one of the chief limitations of the NT electrode, which resulted from the long-time annealing after anodic oxidation [7, 10–12]. The long-time annealing is inevitable for the crystallization of the anodized NT electrode, however, this also leads to the formation of thick and compact TiO$_2$ barrier in the TiO$_2$ NT/Ti metal interface, which increases internal resistance of the DSSCs. Therefore, when applied to a TiO$_2$ NT electrode, the post-annealing can increase the thickness of compact TiO$_2$ barrier, resulting in the increase of internal resistance in DSSCs and the reduction of fill factor.

On the other hand, atomic layer deposition (ALD) is an ideal method for conformally coating high aspect ratio nanostructures [23–25] and, in contrast to the solution-based method it does not require any post-annealing for the application targeted in this work. The ALD method can be effectively applied to the NT electrode because of its vertically aligned pore structure; however, this has not been studied yet. Here we report on the surface modification of TiO$_2$ NT electrodes by depositing an Al$_2$O$_3$ thin layer using ALD, which resulted in the enhanced photovoltaic properties in DSSCs. Highly ordered and vertically oriented TiO$_2$ NT electrodes with a thickness of 0.23 μm were prepared by a two-step anodization method. The Al$_2$O$_3$ coating was deposited on the surface of the TiO$_2$ NTs using ALD. Unlike conventional solution-based method for the coating of an energy barrier layer, the ALD process proposed in this study did not require any post-annealing, avoiding further increase of internal resistance in the TiO$_2$ electrode. In addition, conformal and uniform coating of the Al$_2$O$_3$ layer throughout the tube wall with a finely controlled thickness was demonstrated, which may not be possible by solution-based method [18]. The photovoltaic properties of the DSSCs employing TiO$_2$/Al$_2$O$_3$ NT electrodes, especially, the electron lifetimes affected by the surface modification were characterized.

![Figure 1. FE-SEM images of the annealed TiO$_2$ NT electrodes. (a) and (b) surface and (c) and (d) cross-sectional images.](image-url)
2. Experimental details

2.1. Preparation of TiO2 NT electrodes

TiO2 NT electrodes were fabricated by anodic oxidation method. Titanium foil (Goodfellow, 99.6% purity, 0.25 mm thick, 1.5 cm diameter) was anodized in 0.25 wt% NH4F and 2 wt% H2O containing ethylene glycol with a counter electrode of Pt mesh [26]. To obtain highly uniform and smooth structures, we used a two-step anodization process [27]. Firstly, the Ti foil was anodized for 2 h at 60 V, and the produced TiO2 NTs were peeled off by ultrasonication. The pretreated Ti foil was anodized again for 2 h at 60 V. The as-prepared TiO2 NT electrode was annealed at 450 °C for 4 h in air.

2.2. Surface modification of TiO2 NT electrodes by ALD processes

The Al2O3 shell layer was deposited onto the prepared TiO2 NT electrodes in a flow-type ALD apparatus (CN1, Korea), using trimethylaluminum (TMA, Aldrich, purity 97%) and H2O as metal and oxygen sources, respectively, at a deposition temperature of 200 °C. The ALD processes consisted of a given number of the cycles each consisting of: (i) H2O pulse for 0.2 s, (ii) exposure for 5 s, (iii) purging with N2 for 40 s, (iv) TMA pulse for 0.1 or 0.5 s, (v) exposure for 5 s, (vi) purging with N2 for 40 s. The TMA pulse was 0.1 s when only 1, 2, 4 and 6 cycles of the ALD processes were applied, and 0.5 s for 20 cycles. The growth per cycle measured by spectroscopic ellipsometry on Al2O3 deposited onto a silicon wafer was 0.1 nm per cycle.

2.3. Electrode assembly

To prepare the DSSCs, the TiO2/Al2O3 NT electrodes were immersed in a 5 × 10−4 M cis-bis(isothiocyanato)bis(2,2′-bipyridyld-4,4′-dicarboxylato) ruthenium(II) bis-(tetra-butylammonium) (N-719 dye, Dyesol) solution in a mixture of acetonitrile and tert-butyl alcohol (v/v, 1 : 1) for 24 h [28]. The Pt-coated counter electrodes were prepared by spin coating a drop of 5 mM H2PtCl6 in isopropanol on FTO glass followed by annealing at 400 °C for 15 min in air. Then, the dye-adsorbed NT electrodes and the Pt-coated counter electrodes were assembled by using thermal adhesive polymer films (Surlyn, thickness: 50 μm). The electrolyte solution was prepared by mixing 0.60 M 1-butyl-3-methylimidazolium iodide, 0.03 M I2, 0.10 M guanidinium thiocyanate and 0.50 M 4-tert-butylpyridine in a mixture of acetonitrile and valeronitrile (v/v, 85 : 15) [28].

2.4. Characterization and photoelectrochemical measurements

The morphology and structures of the NT electrodes were examined with a field-emission scanning electron microscope (FE-SEM; Carl Zeiss SUPRA 55VP). High-resolution transmission electron microscopy (HR-TEM; JEOL JEM-2010) was used to investigate the morphology and structures. Surface electronic states were examined by x-ray photoelectron spectroscopy (XPS; Thermo SIGMA PROBE) using an Al Kα x-ray source in an UHV system with a chamber base pressure of ~10−10 Torr. Photocurrent–voltage (I–V) measurements were performed using a 500 W xenon lamp (XIL model 05A50KS source measure units and an AM 1.5 filter) at a power of 100 mW cm−2. In order to measure the dye-loading of bare TiO2 and TiO2/Al2O3 NT electrodes, the adsorbed dye molecules on the electrodes were desorbed in 1 M NaOH aqueous solution and examined by UV–vis spectroscopy (Perkin-Elmer Lambda 20). The adsorbed amount of dye per geometric area (1 cm²) was calculated with an extinction coefficient (ε = 3748 cm⁻¹ M⁻¹ at 535 nm) for N-719 dye. UV–vis diffuse reflectance spectra were obtained by using a UV–vis–NIR spectrophotometer (V-670, Jasco). To measure the electron lifetime in DSSCs, the open-circuit voltage decay (OCVD) technique was used [29]. For OCVD measurement, a stationary light was illuminated on the DSSCs and abruptly switched off. Then, the decay of the steady-state photovoltage induced by the stationary light was monitored.
Figure 3. EDX results measured at the four different heights of the TiO$_2$ NTs prepared with 4 ALD cycles.
3. Results and discussion

FE-SEM images of the annealed TiO2 NT electrodes are shown in figure 1. The inner diameter of the NTs was about 100 nm with a wall thickness of about 20 nm. The interconnected macroporous thin layer covered the surface of the electrodes with a NT structure underneath (figure 1(c)). The two-step anodization process afforded highly ordered and crack-free surface structures over large areas (12 μm×8 μm) (figure 1(b)). This highly uniform structure without bundling of the NTs and unwanted precipitate on the surface are advantageous for the light absorption by the dye molecules and electron transport when applied in DSSCs as a photoanode [8, 27]. The thickness of the NT electrode can be controlled by the anodization time. In this study, the anodization was carried out for 2 h resulting in the thickness of about 23 μm, which was confirmed by the cross-sectional FE-SEM image (figure 1(d)).

After the ALD deposition of Al2O3 shell, the TiO2/Al2O3 NTs were characterized by the HR-TEM images as shown in figure 2. The selected area electron diffraction (SAED) pattern (inset of figure 2(a)) is characteristic of the TiO2 anatase phase [30]. Figure 2(b) shows an Al2O3 coating of about 2 nm (i.e. 20 ALD cycles onto the TiO2 NTs), which is smoothly deposited on the surface of the TiO2 NTs. The uniformity of the Al2O3 layer throughout the tube wall of the TiO2 NTs was analyzed using an FE-SEM instrument equipped with energy-dispersive x-ray spectroscopy (EDX). The EDX spectra acquired at the different heights of the NTs coated with 4 Al2O3 ALD cycles (figure 3). In addition, the calculated Al/Ti atomic ratios are listed in table 1. The upper part of the NTs exhibited a slightly higher Al content than the lower part, but this variation in Al content was not considered significant considering the long length of the NTs. This uniform and smooth coating of the Al2O3 shell may effectively reduce the charge recombination in the DSSCs.

XPS measurement was performed to survey the surface chemistry of the TiO2/Al2O3 NTs. Figure 4 shows the XPS spectra of the bare TiO2 NT electrode and the TiO2/Al2O3 NT electrode prepared with 4 ALD cycles. As listed in table 2, the binding energy (BE) of Ti 2p and O 1s were in the range of 458.6–458.7, and 529.9–530.0 eV, respectively, which corresponds to TiO2 [31]. In addition, the measured BE of Al 2p (75.7 eV) and the additional peak located at 532.3 eV in the O 1s spectrum of the TiO2/Al2O3 NTs indicate the presence of Al2O3 [32, 33].

The prepared TiO2/Al2O3 NT electrodes were applied in DSSCs as photoanodes combined with conventional counter electrodes (Pt-coated FTO glasses). Photocurrent–voltage (I–V) measurements were performed using an AM 1.5 solar simulator (100 mW cm−2). The I–V characteristics of the DSSCs with an active area of 0.30 cm² are shown in figure 5(a) and summarized in table 3. One of the merits of the ALD method is that the thickness of the coated layer can be controlled with high resolution. Therefore, we could confirm the photovoltaic performance of the TiO2/Al2O3 electrodes with various Al2O3 shell thicknesses. The Al2O3 coating was deposited by 1–6 ALD cycles (nominal thickness of 0.1–0.6 nm). The open-circuit voltage (Voc) was notably enhanced with increasing Al2O3 layer thickness, which was attributed to the insulating nature of the Al2O3 which reduced the charge recombination rate between the photoelectron in the TiO2 NTs and the electrolyte [18, 19]. As a consequence, the short-circuit photocurrent density (Jsc) was also slightly increased in the 1- and 2-cycle-coated samples [34]. As listed in table 3, the adsorbed amount of dye was nearly the same regardless of the thickness of Al2O3 layer. In addition, diffuse reflectance was also not greatly affected by the Al2O3 layer as shown in figure 5(b), indicating that the light

![Figure 4](image-url)  
XPS spectra of the bare TiO2 NT electrode and the TiO2/Al2O3 NT electrode prepared with 4 ALD cycles.

<table>
<thead>
<tr>
<th>Height (μm)</th>
<th>Al/Ti atomic ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>20.2</td>
<td>6.60 × 10⁻³</td>
</tr>
<tr>
<td>15.5</td>
<td>6.68 × 10⁻³</td>
</tr>
<tr>
<td>10.7</td>
<td>5.25 × 10⁻³</td>
</tr>
<tr>
<td>5.1</td>
<td>6.00 × 10⁻³</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ti 2p/Al 2p</th>
<th>O 1s</th>
<th>Al 2p</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO2</td>
<td>458.6 eV</td>
<td>529.9 eV</td>
<td>—</td>
</tr>
<tr>
<td>TiO2/Al2O3</td>
<td>458.7 eV</td>
<td>530.0 eV</td>
<td>75.7 eV</td>
</tr>
</tbody>
</table>

Table 1. Atomic ratios of Al/Ti at the four different heights of the TiO2 NTs determined from EDX results.

Table 2. Binding energy (BE) values obtained from XPS analysis for the bare TiO2 NT electrode and the TiO2/Al2O3 NT electrode prepared with 4 ALD cycles.
scattering effect was not enhanced by the Al2O3 layer. Therefore, it is reasonable that the increases in Voc and Jsc for the 1- and 2-cycle-coated samples mainly resulted from the reduced charge recombination by the Al2O3 shell layer. The reduced charge recombination due to the Al2O3 shell was confirmed from the I–V curves in the dark state. As shown in figure 5, the dark current was gradually decreased with increasing Al2O3 layer thickness, while the onset potential was not shifted. This implies that the Al2O3 shell did not shift the conduction band potential of the TiO2 NT electrode, however served as an insulating barrier that reduced the electron loss by the charge recombination [20]. However, more than 2 cycles of the ALD process resulted in steeply decreased Jsc, because of the reduced electron injection from the sensitizers into the conduction band of TiO2 [18, 19, 35]. As a result, only 1- and 2-cycle-coated samples showed enhanced conversion efficiencies compared to the bare TiO2 NT electrode. It is noticeable that the photovoltaic properties of the DSSCs were significantly affected by the Al2O3 shell layer in spite of its small thickness (less than 1 nm). This may be attributed to the uniform and conformal coating as already confirmed by EDX data. Antila et al also reported that the photovoltaic properties of the DSSCs employing the conventional TiO2 NP electrodes can be greatly affected by the thin Al2O3 shell layer coated with less than 5 ALD cycles [35]. Their study showed that especially the electron injection efficiency and the charge recombination were significantly decreased by the thin energy barrier layer.

To characterize the reduced charge recombination rate quantitatively, the electron lifetime was measured using the OCVD technique [29]. Figure 6(a) shows the OCVD curves for Table 3. Summarized I–V characteristics and the adsorbed amount of dye for the TiO2/Al2O3 NT electrodes according to the variation of ALD cycles.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Voc (V)</th>
<th>Jsc (mA cm$^{-2}$)</th>
<th>Fill factor (%)</th>
<th>Efficiency (%)</th>
<th>Adsorbed amount of dye ($\times10^{-7}$ mol cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare</td>
<td>0.675</td>
<td>9.90</td>
<td>59</td>
<td>3.95</td>
<td>2.00</td>
</tr>
<tr>
<td>1 cycle</td>
<td>0.690</td>
<td>10.72</td>
<td>59</td>
<td>4.37</td>
<td>1.93</td>
</tr>
<tr>
<td>2 cycles</td>
<td>0.700</td>
<td>10.20</td>
<td>60</td>
<td>4.26</td>
<td>1.94</td>
</tr>
<tr>
<td>4 cycles</td>
<td>0.705</td>
<td>7.34</td>
<td>59</td>
<td>3.05</td>
<td>1.97</td>
</tr>
<tr>
<td>6 cycles</td>
<td>0.720</td>
<td>6.08</td>
<td>60</td>
<td>2.63</td>
<td>1.98</td>
</tr>
</tbody>
</table>

Figure 5. (a) Photocurrent–voltage (I–V) characteristics in the illuminated (light intensity: 100 mW cm$^{-2}$, AM 1.5 filter, and illumination area: 0.30 cm$^2$) and dark states (a), and UV–vis diffuse reflectance spectra (b) of the TiO2/Al2O3 NT electrodes according to the variation of ALD cycles.

Figure 6. (a) Open-circuit voltage decay (OCVD) curves of the TiO2/Al2O3 NT electrodes according to the variation of ALD cycles, and (b) electron lifetime as a function Voc(V).
each cell. The rate of $V_{oc}$ decay is proportional to the charge recombination rate. Therefore, the electron lifetime can be calculated according to the following equation (1) [29]:

$$\tau_e = \frac{k_B T}{e} \left( \frac{dV_{oc}}{dt} \right)^{-1},$$

(1)

where $k_B T$ is the thermal energy, $e$ the positive elementary charge, and $dV_{oc}/dt$ the derivation of $V_{oc}$. The electron lifetime as a function of $V_{oc}(V)$ is shown in figure 6(b). The plotted curves show a linear relationship on a logarithmic scale, which indicates that the charge recombination reaction has a first-order dependence on the electron concentration of the TiO$_2$ NT electrodes [10]. As shown in figure 6(b), the electron lifetime was gradually enhanced with increasing number of ALD cycles, indicating that more photocurrents could survive from the back-reaction with increasing Al$_2$O$_3$ shell layer thickness. This alleviated charge recombination reaction was attributed to the insulating nature of the coated Al$_2$O$_3$ shell. The prolonged electron lifetime resulted from the Al$_2$O$_3$ shell layer may contribute to improving not only $V_{oc}$ but also $J_{sc}$ for the 1- and 2-cycle-coated samples [34]. These results support the conclusion that the Al$_2$O$_3$ ALD shell effectively acts as an energy barrier layer and thereby enhances the photovoltaic performances of the TiO$_2$ NT electrodes in DSSCs.

4. Conclusions

In this study, we have prepared vertically oriented TiO$_2$ NT electrodes with highly ordered and crack-free surface structures over large areas. Onto these TiO$_2$ NTs, an Al$_2$O$_3$ shell of a precisely controlled thickness was deposited without post-annealing by using ALD. The electron lifetime and the $V_{oc}$ of the DSSCs was gradually enhanced as the thickness of the Al$_2$O$_3$ shell of the TiO$_2$/Al$_2$O$_3$ NT electrodes was increased due to the energy barrier effect of the Al$_2$O$_3$ shell. Therefore, we believe that the ALD deposition of the Al$_2$O$_3$ shell is an effective method to alleviate the charge recombination reaction at the surface of TiO$_2$ NT electrodes in DSSCs.

Acknowledgments

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References

[30] Pattern No. 21-1272, JCPDS 1996