Au-Nanoparticle-Embedded Open-Ended Freestanding TiO₂ Nanotube Arrays in Dye-Sensitized Solar Cells for Better Electron Generation and Electron Transport

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ABSTRACT: Freestanding TiO₂ nanotube arrays (TNTAs) were prepared by an electrochemical method, and dye-sensitized solar cells (DSSCs) were fabricated with the open-ended freestanding TNTAs incorporated with Au nanoparticles (NPs). Open-ended freestanding TNTAs were prepared by etching the barrier layer of closed-ended freestanding TNTAs using an ion milling method, and Au NPs were incorporated into the channel of the open-ended freestanding TNTAs by an electrodeposition method. The Au-NP-embedded open-ended freestanding TNTAs were applied to DSSCs to improve the energy conversion efficiency (ECE) by better electron generation and electron transport. The ECE of DSSCs based on the closed-ended freestanding TNTAs with Au NPs increased to 6.116% from 5.502% for DSSCs based on the closed-ended freestanding TNTAs without Au NPs, an enhancement of 11.16% because of better electron generation by the plasmonic and charging effects of the Au NPs. However, the ECE of DSSCs based on the closed-ended freestanding TNTAs incorporated with Au NPs for 40 s decreased from 6.116 to 5.336% because aggregation of the Au NPs led to a decrease in the open-circuit voltage (Voc) and fill factor. For enhanced ECE of DSSCs, the barrier layer of closed-ended freestanding TNTAs was etched by an ion milling method for 0, 30, 60, or 90 min to provide “open-ended freestanding TNTAs”. Then, Au NPs were incorporated into the open-ended freestanding TNTAs. After the barrier layer was completely removed by the ion milling method for 90 min, the ECE of the DSSCs reached 7.120% because the electron transport and electrolyte diffusion were improved by the elimination of the barrier layer of the freestanding TNTAs.

1. INTRODUCTION

Dye-sensitized solar cells (DSSCs) are an application of the photosynthesis principle so the special dyes in the cell generate current like the chloroplasts in the plant generate oxygen and it flows to external electrodes. DSSCs have a lower efficiency than crystalline silicon solar cells, but their manufacturing process is simple and raw materials are cheap so their production costs is reduced. The first successful development is known to be that by Michael Grätzel in 1991.1 Since then, scientists have worked on overcoming the shortcomings of DSSCs to achieve better efficiency. DSSCs consist of a conducting glass, dye-coated TiO₂ electrode, electrolyte that contains a redox couple reagent, and counter electrode coated with Pt. The dye-coated TiO₂ electrode is the most important part in DSSCs because it determines the electron generation and transport, which affect the energy conversion efficiency (ECE).

The TiO₂ electrode section can be largely divided into nanoparticles (NPs) and nanotubes. The TiO₂ electrode with nanoparticles has the advantage of being able to produce many electrons because of the large surface area of the nanoparticles for the adsorption of dyes; however, a limitation is the low electron transport because of a mesoporous structure due to disorderly connections between the nanoparticles.2–5 As an alternative, by synthesizing TiO₂ nanotubes, the electrons of the TiO₂ electrode can be prevented from being lost while moving toward the transparent electrode, thereby increasing the ECE.6–11 The synthesis methods for nanotubes are hydrothermal synthesis and electrochemical synthesis. In hydrothermal synthesis, large quantities of nanotubes can be synthesized, but there is a downside in the vertical arrangement. For electrons to travel well within a solar cell, vertically arranged nanotubes are needed. Consequently, an electrochemical synthesis method that can synthesize vertically arranged nanotubes must be used, even though a large amount of nanotubes cannot be obtained. However, a barrier layer exists in the bottom part of the vertical array nanotubes made by electrochemical synthesis methods.12,13 This barrier layer interferes with the electron transport and the electrolyte diffusion inside the DSSCs. Through an ion milling method, the barrier layer can be removed completely.

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DSSCs are devices that use the principle of turning light into electricity. While there are some ways to physically eliminate obstacles to increase efficiency, there are other ways to maximize the benefits of these devices. One method of improving the light-harvesting ability of DSSCs is the introduction of metal nanoparticles. By using metal nanoparticles, the absorption of light is increased by the surface plasmonic resonance phenomenon that occurs by the interaction between a negative dielectric constant from a metal and a positive dielectric constant from a medium. Generally, presynthesized metal nanoparticles are mixed with TiO₂ nanoparticles for plasmonic DSSCs. However, it is difficult to introduce the presynthesized metal nanoparticles into the vertically arranged TiO₂ nanotube arrays (TNTAs) because of aggregation and interaction. By using electrochemical methods, metal nanoparticles can be introduced easily into TiO₂ nanotube arrays because the solution that contains the metal precursor easily penetrates into the channels of TiO₂ nanotube arrays.

In this study, the barrier layer of TiO₂ nanotube arrays was etched by an ion milling method for better electron transport and Au nanoparticles were introduced by an electrochemical method for better electron generation to improve the ECE of DSSCs. To the best of our knowledge, Au nanoparticles were first incorporated into open-ended freestanding TiO₂ nanotube arrays and fabricated DSSCs with Au-nanoparticle-embedded open-ended freestanding TiO₂ nanotube arrays. Moreover, we investigated the plasmonic and charging effect by the amount of Au nanoparticles in DSSCs.

2. RESULTS AND DISCUSSION

2.1. Overall Scheme of Preparation of DSSCs. The preparation of Au-NP-embedded open-ended freestanding TiO₂ nanotube arrays (TNTAs) and fabrication of DSSCs are represented in Figure 1. The TNTAs were prepared by two times anodization of Ti plate. After the 1st anodization and an annealing step at 500 °C, the “1st TNTAs” were produced, and these have crystallinity. The 1st TNTAs are stable in acidic or basic conditions; however, the barrier layer can be removed by a chemical method or a physical method. With a chemical method, the barrier layer can be removed by chemical reagents, but the chemical reagents will damage the TNTAs. However, by using a physical method such as ion milling, the barrier layer can be removed without any damage to the TNTAs. To increase the ECE in the DSSCs, the barrier layer of the freestanding TNTAs was removed by an ion milling method. The resulting TNTAs are called “open-ended freestanding TNTAs” and are shown in Figure 1c. The open-ended freestanding TNTAs were attached to fluorine-doped tin oxide (FTO) glass with TiO₂ paste and connected by an annealing step at 500 °C under the ambient condition, as shown in Figure 1d. The FTO glass with open-ended freestanding TNTAs was dipped in Au solution and a constant voltage of 5 V DC was applied to incorporate the Au NPs from the Au precursor into the open-ended freestanding TNTAs as shown in Figure 1e. Finally, the DSSCs were fabricated using the FTO glass with the Au-NP-embedded open-ended freestanding TNTAs. In the completed DSSCs, the Au-NP-embedded open-ended freestanding TNTAs act as a “working electrode” and Pt-coated FTO acts as a “counter electrode”. The electrolyte was injected between the working electrode and the counter electrode, and the fabricated DSSCs are shown in Figure 1f.

Figure 1. Overall scheme of DSSCs. (a) Anodization of Ti plate, (b) Preparation of closed-ended freestanding TNTAs, (c) Preparation of open-ended freestanding TNTAs, (d) Transfer of open-ended freestanding TNTAs on FTO glass, (e) Synthesis of Au NPs, and (f) Fabrication of DSSCs.
The pore diameter of the TNTAs is approximately 100 nm. FE-SEM images of the side view of the TNTAs are shown in Figure 2b, and the length of the TNTAs is approximately 18 μm. The Au NPs are well-incorporated into the TNTAs as shown by the transmission electron microscopy (TEM) images in Figure 2c. The vertical lines are the wall of the TNTAs and the black dots are Au NPs embedded in the TNTAs. The size of the Au NPs is different in the single phase because the position of the Au NPs is also different. However, the average size of the Au NPs is approximately 60 nm. The images of element mappings are shown in Figure 2d,e. The green elements represent the position of TNTAs, and the shape is a vertical line, while the red elements are the Au NPs. The positions of TNTAs and Au NPs shown by the element mappings are the same as their positions in the TEM images.

2.3. FE-SEM Images of Barrier Layer of TNTAs. When the DSSCs were fabricated by Au NPs embedded in the closed-ended freestanding TNTAs, the ECE was improved because the Au NPs are able to enhance the electrons generated by plasmonic and charging effects in the DSSCs. However, the barrier layer portion of the closed-ended TNTAs interrupts the electron transport and electrolyte diffusion inside the completed DSSCs. To overcome this problem and improve the ECE, the bottom surface of the TNTAs was removed by ion milling, a physical method, as shown in Figure 3. The SEM image of the closed-ended freestanding TNTAs before ion milling is shown in Figure 3a, and the SEM images of the ion-milled TNTAs are shown in Figure 3b–d, filmed at a time interval of 30, 60, and 90 min, respectively. The etching process of the bottom surface is shown as time increases, with the pores being gradually exposed after 30 and 60 min of the ion milling process. After 90 min, the pores of the TNTAs were completely etched as shown in Figure 3d to produce open-ended freestanding TNTAs, and these were used to fabricate DSSCs.

2.4. X-ray Diffraction (XRD) of TNTAs and Au NPs. The crystal phase structure of the TNTAs and Au NPs was confirmed by X-ray diffraction (XRD). The XRD patterns of each of FTO, TNTAs, and TNTAs incorporated with Au NPs are shown in Figure 4. In the XRD patterns of the FTO, the blue line (a) of Figure 4, the peaks such as the (110), (101), (111), (211), (002), and (112) planes are represented. In the XRD patterns of the anatase TNTA phase, the red line (b) of Figure 4, the peaks such as the (101), (200), (105), (211), (204), (116), (220), and (215) planes are represented at 2θ = 25.35, 47.95, 54.05, 55.15, 62.80, 69.05, 70.40, and 75.10°, respectively. In the XRD patterns of the anatase TNTAs incorporated with Au NPs, the black line (c) of Figure 4, the peaks such as the (111), (200), and (220) planes are represented at 2θ = 38.30, 44.25, and 64.45°, respectively. The XRD measurements were used to verify the success of the steps required for the introduction of the metal (Au) NPs to the TNTAs, and it was confirmed that Au NPs were well-incorporated into the TNTAs by the electrochemical method.

2.5. UV–vis Spectra Result of TNTAs and Au NPs. The UV–vis spectra results of TNTAs with Au NPs incorporated by the electrodeposition method for 0, 10, 20, 30, and 40 s are shown in Figure 5. Without Au NPs embedded in the...
freestanding TNTAs, a smooth graph is shown through 400–800 nm as shown in Figure 5a. The extinction peaks of the Au NPs from 5 to 80 nm are 514–550 nm,28–30 which is wellmatched to the N719 dye in the DSSCs whose absorbance range is from 340 to 540 nm.18,31 When the Au NPs were incorporated into the TNTAs by an electrodeposition method for 10 s, a special peak is represented at 530 nm as shown in Figure 5b. By increasing the electrodeposition time from 10 to 30 s, the signal of the special peak becomes stronger as shown in Figure 5b–d. The amount of Au NPs is controlled by the reduction time during the electrodeposition and the strongest signal is confirmed at 530 nm for 30 s, as shown in Figure 5d. This is because of the aggregation of the Au NPs whose extinction is not matched to the absorbance of the N719 dye.32

2.6. Photovoltaic Properties of DSSCs Based on Closed-Ended TNTAs with Au NPs. The photovoltaic properties of DSSCs based on the closed-ended TNTAs with Au NPs were measured under the one sun condition. To determine the optimum amount of Au NPs to produce the best efficiency, we measured DSSCs based on the closed-ended TNTAs with Au NPs incorporated for 40 s at 10-second intervals. The results are shown in Figure 6 and the values for each short-circuit density (Jsc), open-circuit voltage (Voc), fill factor (ff), and energy conversion efficiency (ECE, η) are summarized in Table 1. The ECE of DSSCs with Au NPs incorporated for 10 s increased slightly to 5.678% from 5.502% for the DSSCs without Au NPs because of an increase in the Voc and in spite of a similar Jsc. It means that electrons are generated by the Au NPs, and this affects the electron density of the TNTAs. The higher electron density affects the Fermi level of the TNTAs, and then the Voc is increased by the "charging effect."17 The ECE of DSSCs with Au NPs incorporated for 30 s increased to 6.116% from 5.502% for the DSSCs without Au NPs and showed the highest efficiency. In this case, the Jsc, Voc, and ff are increased, and this affects the ECE. Especially, there is a large increase in the Jsc from 10.626 to 11.828 mA cm\(^{-2}\), which means that many electrons are generated by the "plasmonic effect"; however, some electrons are recombined with the Au NPs because of the decreased electron density of the TNTAs. The decreasing electron density means a decreasing Fermi level of the TNTAs, which affects the ff and Voc and has a negative effect on the photovoltaic properties of the DSSCs. When the DSSCs were fabricated with Au NPs incorporated for 40 s, the ECE immediately decreased. For the DSSCs with Au NPs incorporated for 40 s, the Jsc, Voc, and ff also decreased because the generated electrons from the dye were recombined by the Au NPs, and the electron density also decreased in the active layer of the TNTAs because of the aggregation of the Au NPs as shown in Figure 5e.

2.7. Photovoltaic Properties of DSSCs Based on Open-Ended TNTAs with Au NPs. The photovoltaic properties of DSSCs based on the open-ended TNTAs with...
Au NPs were measured under the one sun condition (Figure 7), and the values of \( J_{sc} \), \( V_{oc} \), \( \eta \), and \( \eta \) are summarized in Table 2.

![Figure 7. I–V curves of DSSCs based on the TNTAs with Au NPs incorporated by electrodeposition method for 40 s and whose bottom layer is etched by ion milling method for (a) 0 min, (b) 30 min, (c) 60 min, and (d) 90 min.](Image)

Table 2. Photovoltaic Properties of DSSCs Based on the TNTAs with Au NPs Incorporated by Electrodeposition Method for 30 s and Whose Bottom Layer Is Etched by Ion Milling Method

| DSSCs based on bottom layer etched TNTAs by ion milling method | \( J_{sc} \) (mA cm\(^{-2} \)) | \( V_{oc} \) (mV) | \( \eta \) (%) | \( \eta \) (%) |
|---------------------------------------------------------------|-------------------------------|-----------------|----------------|----------------|
| (a) for 0 min                                                | 11.828                        | 0.753           | 0.687          | 6.116 ± 0.284  |
| (b) for 30 min                                               | 12.493                        | 0.767           | 0.698          | 6.688 ± 0.397  |
| (c) for 60 min                                               | 12.603                        | 0.794           | 0.703          | 7.031 ± 0.453  |
| (d) for 90 min                                               | 12.723                        | 0.797           | 0.702          | 7.120 ± 0.418  |

The bottom layer of the freestanding TNTAs was etched by the ion milling method for 0, 30, 60, or 90 min, and Au NPs were incorporated by the electrodeposition method for 30 s. The ECE value gradually increased to 6.116, 6.688, 7.031, and 7.120% with increased ion milling time. The ECE value of 7.120% is one of the highest for DSSCs based on the open-ended freestanding TNTAs whose bottom part is completely removed as shown in Figure 3d. Among the photovoltaic properties, \( J_{sc} \) and \( V_{oc} \) are also gradually increased with the decrease in the barrier layer until finally the ECE reached 7.120%. This means that the electron generation of all the DSSCs is similar, but the electron transport and electrolyte diffusion are improved by the removal of the barrier layer of the TNTAs.

2.8. Electrochemical Impedance Spectra (EIS) of DSSCs Based on Open-Ended TNTAs with Au NPs. To confirm the effects on electron transport and electrolyte diffusion by the barrier layer in DSSCs, the DSSCs were measured by electrochemical impedance spectroscopy. The resulting electrochemical impedance spectra (EIS) for the DSSCs based on the TNTAs whose barrier layer was etched by the ion milling method for 0, 30, 60, or 90 min are shown in Figure 8, and the fit parameters are summarized in Table 3. Each spectrum contains two different semicircles. The series resistance \( R_s \) is caused by the parallel resistance of the FTO, and it corresponds to the value of the x-axis where the small semicircle begins. The value of \( R_s \) is similar with increasing ion milling time because the barrier layer may have very little effect on \( R_s \). The small semicircle that has high frequency contains the parallel resistance and capacitance at the Pt-FTO/electrolyte and the FTO/TNTAs. The sum of the interfacial resistance of the FTO/TNTAs and Pt/electrolyte represents the value of \( R_s \). The value of \( R_s \) decreases with increasing ion milling time because of the change in the interfacial property of the FTO/TNTAs with reduction in the thickness of the barrier layer, which means that electron transport and transfer will be improved by the elimination of the barrier layer under the TNTAs. The larger semicircle that has low frequency contains the sum of the transfer resistance at the dye-absorbed TNTAs/electrolyte interface and transport resistance in the TNTAs. The sum of the transfer resistance at the dye–TNTAs/electrolyte interface and the transport resistance in the TNTAs represent the value of \( R_s \). The value of \( R_s \) decreases significantly with increasing ion milling time, which means that the electrolyte may penetrate into the channel of the TNTAs. From the EIS fit parameters, it is shown that the electron transport and transfer and electrolyte diffusion are improved by the elimination of the barrier layer under the TNTAs in the DSSCs.

![Figure 8. Electrochemical impedance spectra of DSSCs based on the freestanding TNTAs etched by ion milling for (a) 0 min, (b) 30 min, (c) 60 min, and (d) 90 min.](Image)

Table 3. Fit Parameters of Electrochemical Impedance Spectra of DSSCs Based on the Freestanding TNTAs

| fit parameters of DSSCs based on the freestanding TNTAs etched by ion milling | \( R_s \) (Ω) | \( R_s \) (Ω) | \( C_1 \) (F) | \( C_2 \) (F) |
|-------------------------------------------------------------------------------|------------|------------|-------------|-------------|
| for 0 min                                                                      | 9.519      | 1.174      | 2.6175 × 10\(^{-5}\) | 10.01 | 0.0086 |
| for 30 min                                                                      | 9.437      | 1.142      | 2.5773 × 10\(^{-5}\) | 8.919 | 0.0101 |
| for 60 min                                                                      | 9.521      | 1.027      | 3.9125 × 10\(^{-5}\) | 7.845 | 0.0114 |
| for 90 min                                                                      | 9.532      | 1.012      | 3.2028 × 10\(^{-5}\) | 7.169 | 0.0121 |

\(^\text{Note:} R_s: \text{ohmic series resistance}; R_s: \text{sum of small semicircles at high frequency}; C_1: \text{constant phase element 1}; C_2: \text{sum of large semicircles at low frequency}; C_2: \text{constant phase element 2.}\)

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3. CONCLUSIONS

In summary, the barrier layer of closed-ended freestanding TNTAs is well-removed by an ion milling method and Au NPs were successfully incorporated into open-ended freestanding TNTAs by an electrodeposition method. The barrier layer of the closed-ended freestanding TNTAs was gradually etched by increasing the ion milling time until the barrier layer was perfectly removed and opened. The amount of Au NPs was controlled by the electrodeposition time, and the extinction of Au NPs was well-matched to the absorbance of dye (N719). DSSCs based on the open-ended TNTAs with Au NPs were fabricated, and an ECE of 7.120% was achieved because of improved electron transport and electron generation due to the elimination of the barrier layer and presence of Au NPs. Our research has great potential for other solar cells by suggesting a way to improve electron transport and electrolyte diffusion through the removal of the barrier layer of TNTAs and increase in the light-harvesting availability through introducing Au NPs and has many applications such as photocatalyst, display, biology, Li-ion batteries, gas sensor, or supercapacitor.

4. EXPERIMENTAL SECTION

4.1. Preparation of Freestanding TNTAs. TNTAs were fabricated by anodizing Ti plate purchased from Alfa Aesar with a purity of 99.7% and thickness of 0.25 mm. The electrolyte was composed of 0.8 wt % of NH₄F and 2 vol % H₂O in ethylene glycol, and a 1st Ti anodization was carried out at 25 °C with a constant applied voltage of 60 V DC for 2 h. The 1st TNTAs formed on the Ti plate were annealed at 500 °C for 1 h under ambient air to improve their crystallinity. After the 1st anodization, a 2nd Ti anodization was carried out at a constant applied voltage of 30 V DC for 15 min, and then the plate was dipped in 10% H₂O₂ to separate the TNTAs from the Ti plate. The barrier layer of the TNTAs was removed by ion milling with Ar⁺ bombardment for various time intervals. After the ion milling step, the open-ended TNTAs were prepared.

4.2. Fabrication of DSSCs. A TiO₂ blocking layer was formed on fluorine-doped tin oxide (FTO) glass by spin-coating with 5 wt % of titanium di-isopropoxide bis(acetylacetonate) in butanol. This was then annealed at 500 °C for 1 h under the ambient condition for crystallinity. The TiO₂ paste was coated on the TiO₂ blocking layer by the doctor blade method, and then open-ended freestanding TNTAs were transferred to the TiO₂ paste layer. The size of TNTAs is 0.5 cm × 5 cm, and the active area of DSSC is 0.25 cm². To enhance the adhesion between the FTO glass and TNTAs, the substrate was annealed at 500 °C for 1 h under ambient condition. Au NPs were incorporated into the open-ended freestanding TNTAs with 10 mM HAuCl₄ in an H₂O and ethanol (50:50, v/v) solution by an electrodeposition method at a constant applied voltage of 5 V DC. After the electrodeposition process, the Au-embedded open-ended freestanding TNTAs were coated with TiCl₄ at 50 °C for 30 min and annealed at 500 °C for 1 h to prevent the redox reaction between Au NPs and electrolyte. The prepared substrate was immersed in a dye ((Bu₄N)₂Ru(dobpyH)₂(NCS)₂; N719, Solaronix) solution at 50 °C for 8 h, and then a counter electrode (Pt-sputtered FTO glass) covered the working electrode. Also, the electrodes were separated by a 60 μm thick hot-melt sheet. After that, the electrolyte, which consisted of 0.7 M 1-butyl-3-methylimidazolium iodide, 0.03 M I₂, 0.1 M guanidium thiocyanate, and 0.5 M 4-tert-butylpyridine in acetonitrile and valeronitrile (85:15, v/v), was injected between the electrodes.

4.3. Characterization. The morphology, thickness, and pore size of freestanding TNTAs were confirmed by using field emission scanning electron microscopy (FE-SEM; JSM-6330F, JEOL Inc.). The incorporation of Au NPs into the freestanding TNTAs was confirmed by using Cs-corrected field emission transmission electron microscopy (Cs-TEM; JEM-ARM-200F, JEOL Inc.) at the Center for University-Wide Research Facilities (CURF) at Jeonbuk National University. The current density–voltage (J–V) characteristics of the DSSCs were confirmed by an electrometer (Keithley 2400) under AM 1.5 illumination (100 mW cm⁻²) that was provided by a solar simulator (1 kW xenon). The electrochemical impedance spectra were measured with a potentiostat (Solartron 1287) equipped with a frequency response analyzer (Solartron 1260), with the frequency ranging from 10⁻² to 10⁶ Hz. The applied bias voltage and ac amplitude were set at the open-circuit voltage (Vₒｃ) of the DSSCs and 10 mV under AM 1.5 one-sun light illumination. Also, the electrochemical impedance spectra were analyzed by using Z-View software (Solartron Analytical) with the aid of an appropriate equivalent circuit.

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Notes
The authors declare no competing financial interest.

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