SILVER NANOPARTICLES LOADED TiO_2 NANOTUBE ARRAYS PREPARED BY PHOTODEPOSITION METHOD FOR PHOTOELECTROCHEMICAL CELL

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Abstract

In this study, TiO_2 nanotube arrays (TNTs) were fabricated by anodizing of Ti foil in NaOH/fluoride/EG electrolyte at 60 V for 60 min while dispersion of Ag nanoparticles on them were performed by photodeposition method. The morphology and crystal structure of pure TNTs and Ag decorated TNTs (Ag/TNTs) were then studied. The assembly was then used as a photoelectrode in the photoelectrochemical cell to measure the photocurrent and generate hydrogen gas. The addition of NaOH into electrolyte resulted in the formation of highly ordered TNTs with the length of 23 μm and diameter of 170 nm. Dispersion of silver nanoparticles through photodeposition was performed in order to enhance photoelectrochemical performance. Enhanced photocurrent of 5.0 mA/cm^2 was achieved using Ag/TNTs compared to 3.2 mA/cm^2 of pure TNTs. The conversion efficiency as measured by solar to hydrogen measurement was found to be 4% for pure TNTs and 6 % for Ag/TNTs. The enhancement thought to be due to enhanced charge separation efficiency and improved electrons transport.

Keywords: Anodization, TiO_2 nanotube arrays, Silver nanoparticles, photoelectrochemical cell

Introduction

Hydrogen is a clean and renewable energy for the consumption as a fuel, converting solar energy into hydrogen is an effective method to resolve the energy crisis for the future. In 1972, Fujishima and Honda first demonstrated the photoelectrochemical cell (PEC) using TiO_2 film as a photoanode due to its low cost, non-toxic, photostability and high photocatalytic activity. Park et al. investigated the performance of PEC using different structures of TiO_2: nanotubes, nanowires, nanorods, nanoporous and P25 nanoparticulate films. The photocurrent density of TNTs was more than 60 times higher than that of TiO_2 mesoporous film with a similar thickness. Furthermore, TNTs exhibited the photocurrent more than 10 times higher than that of a P 25 nanoparticle film. It was found that TNTs can harvest light more efficiently and enhance the photogeneration of electron-hole pairs thus increased solar to hydrogen conversion efficiency than irregular structure under the same illumination. Highly ordered TNTs can be fabricated by using various methods. They are sol-gel method, hydrothermal method and electrochemical anodisation. Among all of these methods, anodization method is relatively simple and easy method to fabricate self-organized nanotube arrays.

The performance of photoelecrochemical cell is depend on their structural characteristics (nanotube length, pore size, wall thickness) which can be easily controlled by the types of electrolytes and their composition as well as by varying anodization parameters such as anodization voltage and time. TNTs with a larger pore size allow better light penetration, thus

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enabling the diffusive transport of photogenerated h^+ to react with OH^- in the electrolyte. In recent years, many studies have been attempted to enhance the performance of PEC using TNTs as a photoanode. However, the photocurrent of PEC using TNTs is still lowed due to its weak light absorption to the visible region and high recombination of photogenerated charge carriers. Therefore studies have been attempted to modify TNTs with noble metals such as copper (Cu), gold (Au) and silver (Ag) to extend light absorption to the visible region and reduce recombination of charge carriers. Among the nobel metals, Ag is one of the most promising metals due to its high conductivity and low cost. Ag nanoparticles (Ag NPs) can be deposited by using different methods such as electrodeposition method, photodeposition method and pulse current deposition methods. Among these deposition methods, the photodeposition method was selected to deposit Ag onto the TNTs due to it was low-cost, simple and easy method. Ag NPs could be extended to the visible light absorption due to surface plasmon effect of Ag NPs, which induces the oscillation of surface electrons when light is exposed to it. In addition, Ag NPs can enhance the separation of the photogenerated charge carriers due to the formation of Schottky barrier at the interface between Ag NPs and TNTs. Recently, Chen et al. investigated the effect of Ag NPs by varying different deposition times on the performance of PEC and found that TNTs with a small Ag NPs exhibited the highest photocurrent which was 3.3 times higher than that of the pure TNTs due to Ag NPs significantly enhanced the light absorption to the visible range and the separation of photogenerated charge carrier in the TNTs. In this present work,rather high amount of NH_4F (0.7 wt%) and NaOH was added as to accelerate the growth rate of TNTsand to increase the pH of the electrolyte. We postulated that higher pH electrolyte can suppress surface etching of the nanotubes, and with an excessive amount of NH_4F, chemical etching within the nanotubes at the bottom part can be made more vigorous and thus long TNTs can be produced at a short time. In this study, the highly ordered and uniform TNTs were successfully fabricated in fluoride/EG electrolyte containing NaOH at 60 V for 60 min. And then the prepared TNTs were modified with Ag NPs using photodeposition method and used as photoanode in PEC cell to assess the performance of their PEC activity.

Experimental Section

Materials

Titanium foils (0.127 mm thickness, 99.7 %, Stream Chemicals, USA) were cut into 1 x 3cm and exposed to EG electrolyte ($C_2H_6O_2$, Sigma-Aldrich, USA) containing 0.7 wt % of ammonium fluoride (NH_4F, Sigma-Aldrich, USA) and 5 wt% of sodium hydroxide (NaOH, Wako, Japan).

Methods

Prior to anodization, the foil was ultrasonically degreased in isopropanol, acetone and ethanol for 15 min, rinsed with DI water, and dried in a nitrogen stream. Anodization process was carried out in two electrodescell, with Ti foil as the anode and Pt electrode as the cathode at room temperature. A power supply (Agilent Technologies, USA) was used to supply a DC potential of 60 V for 60 min, and simultaneously recorded the current density transient. The anodized samples were then annealed at 450 ˚C for 3 h in air and then immersed in 0.2 M of silver precursor solution and irradiated with 2 mW the light intensity of UV light.

Materials Characterizations

The morphologies of as-anodized TNTs and Ag NPs deposited TNTswere observed by a field emission scanning electron microscope (FESEM, Hitachi S-4800, Japan). The crystal phases of the TNTs were investigated by X-ray diffraction (XRD) using a Bruker D8 Advanced diffractometer (CuKα radiation, λ = 1.5406 Å). A high resolution transmission electron microscope (HRTEM, JEOL, JEM-2100, Japan) at an acceleration voltage of 200 kV was also used to investigate the morphology and crystallography of TNTs. The optical properties of TNTs were investigated by using by using V-670 ultraviolet/visible spectrophotometer (UV-Vis, Jasco, Japan).

Photoelectrochemical Performance Measurements

The photocurrent measurements were evaluated using a three electrodes PEC cell, with TNTsas the working electrode, platinum rod as a counter electrode, and a saturated Ag/AgCl as the reference electrode. A solution of 1 M KOH used as the electrolyte in this measurement. All three electrodes were connected to the potentiostat (Metrohm μ Autolab III, The Netherlands), and xenon lamp with light intensity of 100 mW/cm^2 (Zolix LSP-X150) was used as a light source for current and voltage measurement sample.

Results and Discussion

The morphologies of pure TNTs and Ag/TNTs were observed by SEM. Figure (1a) shows the surface and cross-section of the pure TNTs formed in NaOH/fluoride/EG electrolyte. As can be seen that highly ordered and uniform pore size were formed in this electrolyte. This result is attributed to the equilibrium reaction between oxidation at metal/electrolyte and dissolution at oxide/electrolyte interface as using higher electrolyte pH. Therefore, 23 μm of long nanotube arrays and 170 nm of larger diameter are resulted. Subsequently, Ag NPs were deposited onto the TNTs via photodeposition method. In the photodeposition process, the TNTs were soaked in 0.2 M Ag-precursor solutionand exposed to light with a light intensity of 2 mW/cm^2. The spherical Ag NPs were formed due to the adsorption of silver (Ag^+) ionson the surface of TNTs are reduced by electronsvia illumination. Fig. 1b shows the SEM images of surface and cross section of Ag NPs/TNTs. It was found that Ag NPs with an average particle size of 10 - 40 nm were uniformly dispersed onto the surface of TNTs, however, small amount of Ag NPs were deposited on the walls of the TNTs.

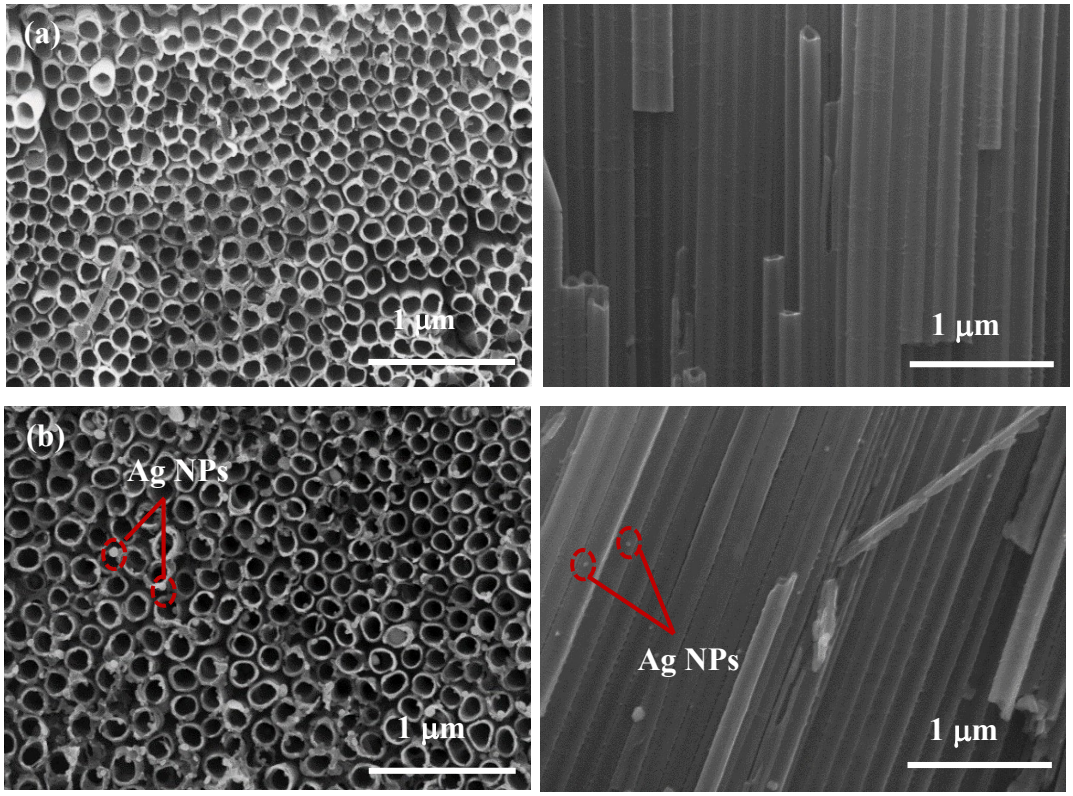

Figure 1 SEM images of (a) pure TNTs and (b) Ag/TNTs.

The morphologies of TNTs were further investigated by TEM to further confirm the existance of Ag NPs. Figure (2) shows TEM images of (a) Pure TNTs (b) surface and (c) cross-section of Ag NPs /TNTs. As can be seen that 20 - 40 nm of Ag NPs are uniformly distributed on the surface of TNTs (Fig. b) and a small amount of Ag NPs are deposited on the walls of TNTs (Fig. c). This result consistent with SEM result. Figure (3A) shows XRD patterns of (a) as-made TNTs (b) annealed TNTs at 450 ˚C and (c) Ag/TNTs. It is found that as-made TNTs are amorphous, only Ti peaks can be seen. After annealing, the crystallinity of anatase peaks detected at 25.4 ˚, 37.8 ˚, 48.5 ˚, 54.0 ˚, 55.2 ˚, 68.9 ˚, and 75.0 ˚ corresponding to (101), (004), (200), (105), (211), (116) and (215) planes of the anatase TiO_2 (JCPDS file no. 21-1272). However, for Ag/TNTs no Ag diffraction peak can be seen. This is attributed to a small size of Ag NPs deposited onto the TNTs.

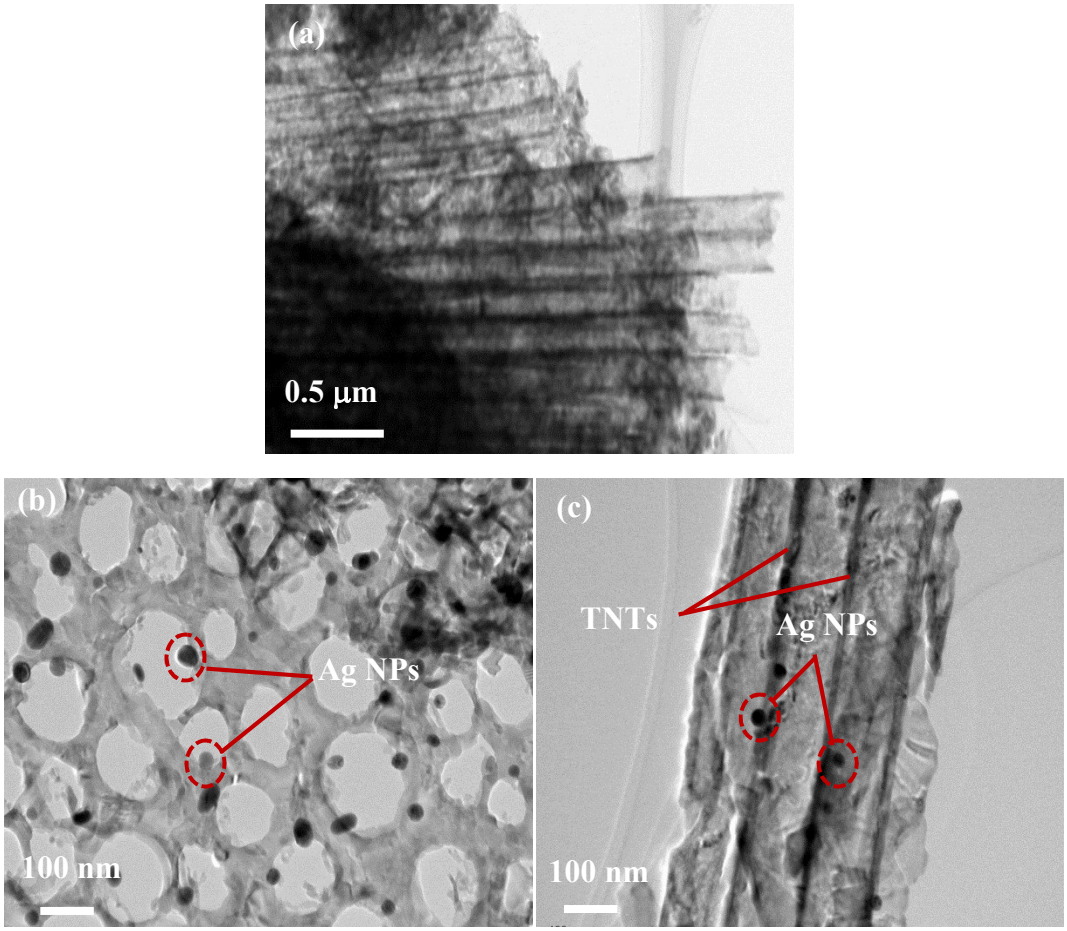

Figure 2 TEM images of (a) pure TNTs (b) surface and (c) cross section of Ag NPs/TNTs.

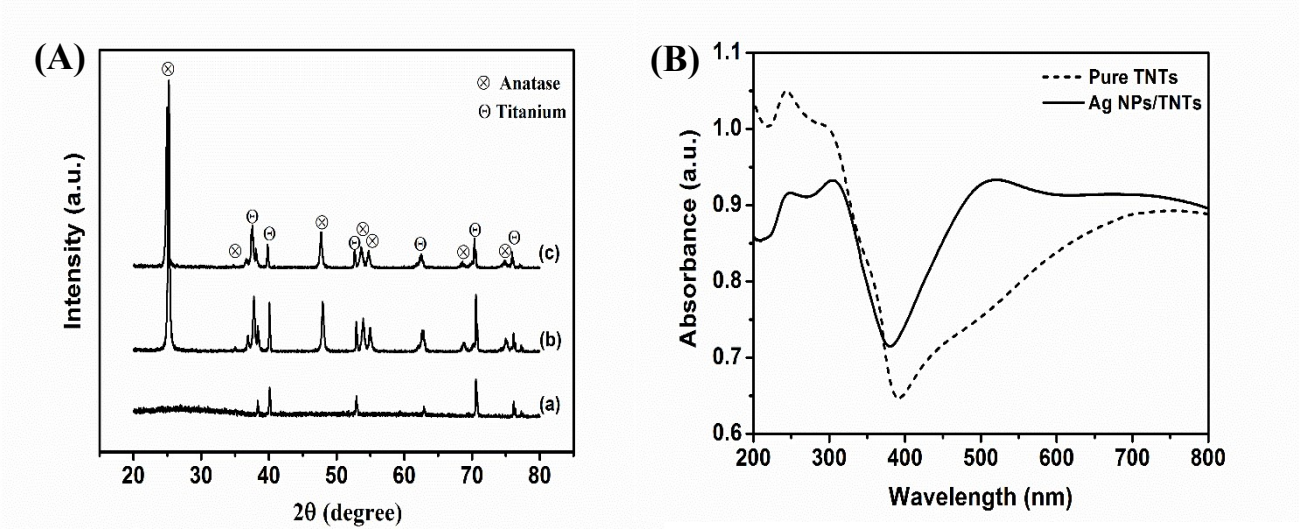

Figure 3A XRD patterns of (a) as-made (b) annealed TNTs at 450˚C for 3 h (c) Ag/TNTs (3B) UV-Vis absorption spectrum of pure TNTs and Ag/TNTs

Figure (3B) shows the light absorption spectra of pure TNTs and Ag/TNTs. As can be seen from the absorption spectra that pure TNTs exhibit better absorption in the ultraviolet and also could absorb to the visible region. This may be attributed to better crystallization of TNTs and the present of carbon in the prepared TNTs. After deposition Ag NPs onto the TNTs, which

exhibits a significant absorption to the visible regions. The absorption band of Ag/TNTs observed at ~ 480 nm due to the surface plasmon resonance effect of Ag NPs to TNTs that strongly absorbs and scatters light.

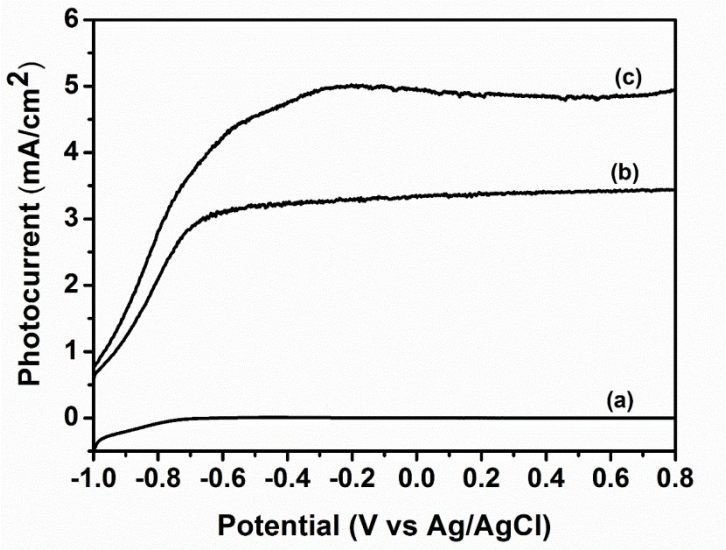

Figure 4 Current-voltage curve of (a) under dark condition (b) pure TNTs and and (c) Ag (0.2 M) /TNTs under light condition

The photoelectrochemical properties of pure TNTs and Ag/TNTs were evaluated by the I-V transient under the solar simulated light shown in Figure(4). This figure shows the photocurrent of pure TNTs is 0 mW/cm^2 under the dark condition and 3 mA/cm^2 under light illumination. Ag NPs deposited TNTs shows the highest photocurrent of 4.5 mA/cm^2 due to both of the faster electrons transport from Ag NPs to the CB of TNTs. Moreover, Ag NPs facilitates the separation of charge carriers due to the formation of Schottky barrier at the interface between Ag NPs and TNTs and also it can trap electrons, accumulated on the surface of Ag NPs. These accumulated electrons shift the position of Fermi level closer to the conduction band of TNTs thus promote interfacial charge transfer process. It was found that Ag NPs deposited TNTs not only increase the absorption to the visible region but also improve the separation of charge carriers due to its surface plasmon effect of Ag NPs. The solar to hydrogen (STH) conversion efficiency of these samples were calculated by using the following equation,

$$\eta_{STH} = \frac{1.23\, J_T}{E_T} \times 100$$

Where, J_T is the hydrogen current density and E_T is the incident light intensity. The STH conversion efficiency of pure TNTs is 4 %, while the STH of Ag/TNTs is 6 %.

Conclusion

In this study, highly ordered and uniform TNTs with a naotube length of 23 μm and diameter of 170 nm were successfully fabricated in NaOH/fluoride/EG electrolyte and a suitable size of Ag NPs are successfully deposited onto the TNTs. These samples were used as photoelectrodes in PEC andevaluated the generation of photocurrent and hydrogen gas of their samples. The Ag NPs deposited TNTs show the highest photocurrent and solar to hydrogen

conversion efficiency than that of the pure TNTs due to surface plasmon effect of Ag NPs, which can extend light absorption and reduce the recombination of photogenerated charge carriers.

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