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Effects of $TiCl_4$ Surface Treatment on Photoelectrochemical Response of TiO_2 Nanotube Arrays

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TiO_2 nanotube arrays were fabricated using electrochemical anodization process and post-treated by varying the concentration of the $TiCl_4$ aquous solution (5 to 50 mM) for the surface treatment. Those photoelectrochemical (PEC) performances were significantly influenced by the $TiCl_4$ concentration. The 20 mM $TiCl_4$-treated TiO_2 nanotubes exhibited significantly enhanced PEC response, due to efficient passivation of the surface recombination traps. However, as the $TiCl_4$ concentration increased further to 50 mM, its PEC performance was reduced back, despite higher surface area. It can be attributed to the blocked voids caused by the formation of the TiO_2 nanoparticles between the TiO_2 nanotubes, because it leads to the hindered ion transport.

Keywords TiO_2 nanotube; $TiCl_4$ surface treatment; photoelectrochemical response; surface recombination trap

1. Introduction

Photoelectrochemical (PEC) systems are promising methods of producing H_2 gas using solar energy in an aqueous solution [1–3]. The photoelectrochemical properties of numerous metal oxides have been studied [4] Among them, the PEC systems based on TiO_2 have been extensively studied [1,2,5–7]. Especially, water decomposition technology with photocatalysts consisting of titanium oxide (TiO_2) nanoparticles has great potential to produce low priced and environmentally friendly hydrogen in the future [5–7]. The metal oxides absorb photons with energies larger than the bandgaps and generate electron-hole pairs. Taking into account that n-type semiconductors such as the TiO_2 as the photoanodes, the photogenerated electrons move to the counter electrode where water reduction occurs and the photogenerated holes move towards semiconductor/electrolyte interface where water oxidation takes place [1,2,8–10].

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Nanostructural electrodes can offer significant advantages for applications of photoelectrochemical energy conversion, because of their large surface areas that provide the increased photoelectrochemical reaction sites [11,12] Conventional mesoporous TiO_2 films composed of nanoparticles smaller than 25 nm not only have 3-dimensional network for the electron transport but also do not develop a depletion layer at the interface between the TiO_2 and electrolyte, which causes large recombination reaction of the photogenerated electrons in the TiO_2 [13,14] Suppression of the recombination reaction has recently been attempted by employing 1-dimensional nanostructures (nanotubes, nanorods, *etc.*) with much faster electron transport [11,15–17].

$TiCl_4$ surface treatment has been employed to the mesoporous TiO_2 films in particular for the dye-sensitized solar cells (DSSCs), because it has been reported to increase surface area, improve electron transport, light scattering, purification of TiO_2, and passivate the surface defect traps [15,18,19] Despite many studies of the $TiCl_4$-treated TiO_2 nanotubes for the DSSCs, the effects of the $TiCl_4$ treatments on the TiO_2 nanotubes for the photoelectrochemical water-splitting cells have scarcely been reported [20].

In this paper, the $TiCl_4$ surface treatments were carried out on the TiO_2 nanotube arrays for the photoelectrochemical water-splitting cells by varying the $TiCl_4$ concentration from 5 to 50 mM and those effects on the PEC cells were studied in terms of the passivation of the surface recombation traps, the surface area, carrier transport, and ion transport.

2. Experiment Details

Ti foils (Goodfellow, 0.1 mm thickness, 99.6% purity) were used for the anodic growth of TiO_2 nanotubes. Prior to the anodization process, the Ti foils were roughly ground and cleaned by sonication in acetone and ethanol followed by rinsing in de-ionized water (DI). The constant conditions (60 V for 4 h) and distance ($\sim$4 cm) between the working (Ti foil) and counter electrodes (Pt mesh) were used for electrochemical anodization. The electrolyte consisted of 0.25 wt.% NH_4F in ethylene glycol containing a 1M water. The 20 μm-thick, anodic TiO_2 nanotubes grown on the Ti foils were sonicated in ethanol for 5 min to remove remnants from the surfaces and then dried in an air stream. They were then annealed at 450°C for 4 h in air for improved crystallinity.

Post-treatment with $TiCl_4$ was applied by the TiO_2 nanotube arrays being soaked in different concentration of the $TiCl_4$ aqueous solution (5, 20, and 50 mM) for 30 min at 70°C. After flushing with ethanol and drying, the electrodes were sintered again at 450°C for 30 min.

The photoelectrochemical (PEC) measurements were performed in a three-electrode cell with a flat quartz window to facilitate illumination of the photoelectrode surface. The TiO_2 films (active area: 0.25 cm^2) were used as the working electrodes. A Pt sheet (area: 10 cm^2) and a Ag/AgCl electrode (with saturated KCl) were used as the counter and reference electrodes, respectively. A 1-M KOH basic aqueous solution was used as the electrolyte. The PEC responses were measured using a Xe lamp (150 W) with a light intensity of 100 mW/cm^2, measured by a photodiode power meter. The current-voltage performances under the chopped light on/off illumination were measured with a scan rate of 5 mV/s during the potential sweep. Photocurrent curves with a time for the TiO_2 samples were also measured under light on/off illumination at constant 0 V. The TiO_2 nanotube arrays' morphologies were characterized by scanning electron microscopy (SEM, Hitachi FE-SEM S4800).

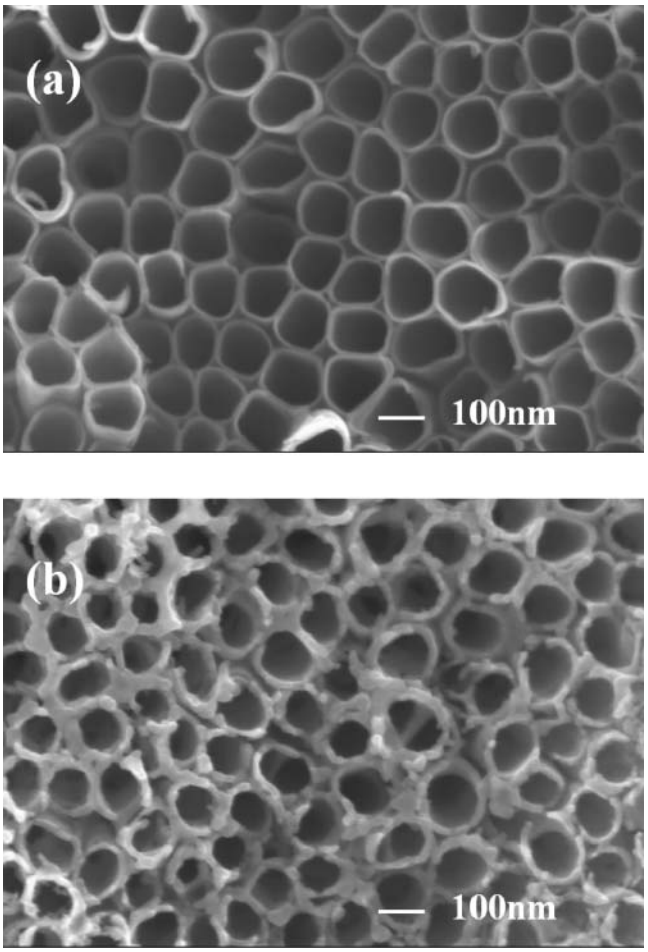

Figure 1. SEM images viewed from the top of the (a) untreated and (b) 50 mM $TiCl_4$-treated TiO_2 nanotube arrays.

3. Results and Discussion

Figure 1 shows the scanning electron microscopy (SEM) images viewed from the top of the (a) untreated and (b) 50 mM $TiCl_4$-treated TiO_2 nanotube arrays, respectively. The TiO_2 nanotube arrays comprised separated nanotubes with average diameter and wall thickness of 80 ($\pm$6) nm and 9 nm, respectively. The TiO_2 nanotubes post-treated by the 5 and 20 mM $TiCl_4$ solution exhibited no apparent morphological difference in the SEM images (not shown here), due to the use of low concentration of the $TiCl_4$ solution. On the contrary, high concentration of the $TiCl_4$ solution (50 mM) for the surface treatment of the TiO_2 nanotube arrays led to the formation of the TiO_2 nanoparticles on the surface, leading to the higher surface area. However, the voids between the nanotubes were partially blocked by the nanoparticles.

Figure 2 shows the current-voltage curves of the untreated TiO_2 nanotube and the 5, 20, and 50 mM $TiCl_4$-treated TiO_2 nanotube arrays measured under the chopped light on/off illumination. The voltage was applied to the samples from 0.4 V to -1 V with a scan rate of 5 mV/s. In order to confirm whether the photocurrent was specifically generated only by the absorbed photons without any dark current contribution, the photoelectrochemical

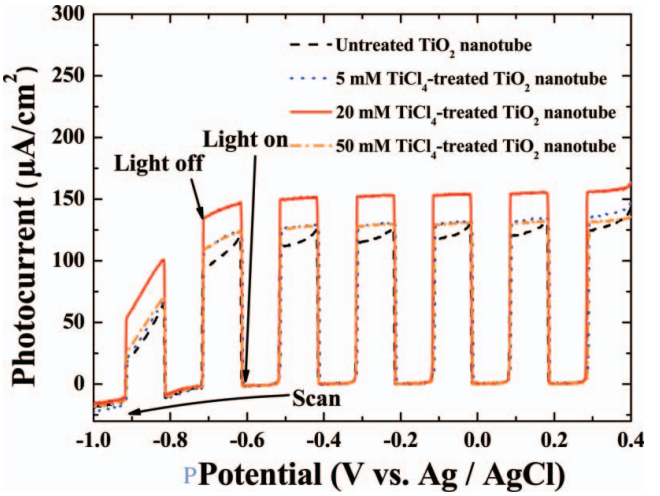

Figure 2. Photocurrent-voltage curves of the untreated TiO_2 nanotube and the 5, 20, and 50 mM $TiCl_4$-treated TiO_2 nanotube arrays measured under the chopped light on/off illumination.

responses were measured under light on/off illumination. The dark current under light-off conditions hardly changed across the potential range, when compared to the photoresponse under light-on conditions, indicating that the photocurrents of the TiO_2 nanotube films were generated only by the absorbed photons under light illumination without the contribution of the dark current. The PEC response was significantly enhanced as the concentration of the $TiCl_4$ increased up to 20 mM. However, the TiO_2 nanotubes treated by high concentration of the $TiCl_4$ (50 mM) exhibited much lower PEC performance, despite higher surface area. It indicates that the PEC performances of the $TiCl_4$-treated TiO_2 nanotubes were influenced by different factors including the surface area.

Figure 3 shows photocurrent curves with a time for the untreated TiO_2 nanotube and the 5, 20, and 50 mM $TiCl_4$-treated TiO_2 nanotube arrays under light on/off illumination at 0 V. Inset in the Fig. 3 shows the photocurrent behavior with a time for the mesoporous TiO_2

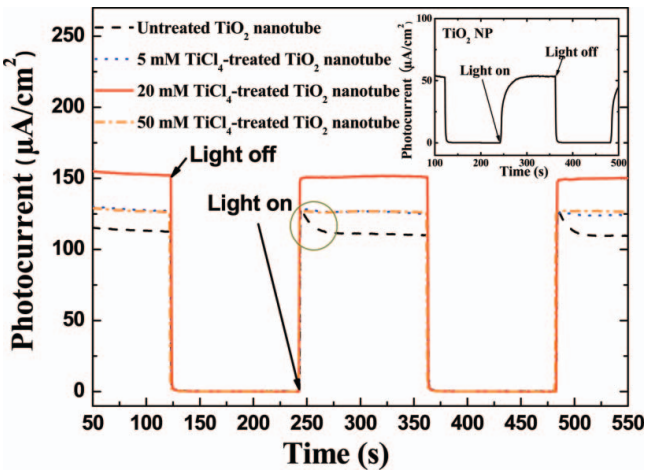

Figure 3. Photocurrent curves with as time for the untreated TiO_2 nanotube and the 5, 20, and 50 mM $TiCl_4$-treated TiO_2 nanotube arrays measured under light on/off illumination at constant voltage of 0 V.

film, which was prepared by doctor-blading the TiO_2 nanoparticle (P25)-containing TiO_2 pastes on the FTO (F-doped SnO_2) transparent conducting oxide followed by calcination at 450°C for 30 min. The mesoporous TiO_2 film composed of the TiO_2 nanoparticles is refered to as the TiO_2 NP for the simplicity. When the illumination was switched on, the photocurrent of the TiO_2 NP was gradually increased with a time. On the contrary, all of the TiO_2 nanotube arrays exhibited sharply increased photocurrent with the light on, indicating that the 1-dimensional TiO_2 nanotube arrays provided much faster carrier transport than the 3-dimensional nanoparticle-based mesoporous film, due to smoother carrier transport pathway. The untreated TiO_2 nanotube exhibited initial photocurrent decay with light on illumination (See the circle in the Fig. 3). The photocurrent decay is an indicative of recombination of photogenerated charge carriers through the surface traps [9] However, there were no photocurrent decays for all of the $TiCl_4$-treated TiO_2 nanotube arrays, indicating that the $TiCl_4$ surface treatment passivated the the surface defect traps efficiently. Therefore, the significantly improved PEC response of the 20 mM $TiCl_4$-treated TiO_2 nanotubes can be owing to the effectively passivated surface recombination traps. However, the TiO_2 nanotubes treated by the much higher $TiCl_4$ concentration (50 mM) exhibited the reduced PEC response, despite higher surface area. As seen in Fig. 1, the 50 mM $TiCl_4$-treated TiO_2 nanotube arrays exhibited the formation of the TiO_2 nanoparticles on the surface, resulting in the partial blocking of the voids between the nanotubes. The blocked voids may hinder the ion transport through the voids, which is responsible for the reduced PEC response.

4. Conclusion

The TiO_2 nanotube arrays were post-treated by the different concentrations of the $TiCl_4$ solution (5, 20, and 50 mM) for the photoelectrochemical water-splitting cells. Although the TiO_2 nanotubes treated by low concentration of the $TiCl_4$ solution (5 and 20 mM) exhibited no apparent morphological difference when compared with the untreated nanotube array, the PEC performances were significantly enhanced, due to the efficiently passivated surface recombination traps. However, the use of much higher $TiCl_4$ concentration (50 mM) caused the formation of the TiO_2 nanoparticles on the surface, leading to the partially blocked voids between the nanotubes. The hindered ion transport caused by the blocked voids resulted in the reduced PEC performance of the 50 mM $TiCl_4$-treated TiO_2 nanotubes. We expect that these results should provide a good insight on the surface treatment for the nanostructural electrodes for the PEC applications.

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