TiO$_2$ nanotube layers with metallic nanoparticles

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Abstract. The present work reports the deposition behavior of Pd or Ag particles on TiO$_2$ nanotube layers with an average diameter of 100 nm and length of 500 nm. The deposition of Pd or Ag particles is carried out by photo-induced reduction of metal ions. TiO$_2$ nanotube layers are exposed to UV irradiation in an electrolyte containing Pd ions. Pd deposition behavior strongly depends on the crystal structure of TiO$_2$ nanotube layers. As-anodized nanotube layers are in the amorphous state and can be converted to anatase without any changes in structural integrity. On as-formed amorphous nanotube layer, no Pd particles are deposited whereas in the case of anatase nanotube layer many Pd particles are formed by UV irradiation in PdCl$_2$ electrolyte. However, the size of Pd particles is larger than the diameter of nanotubes and increases with irradiation time. In order to circumvent this problem, TiO$_2$ nanotube layer is immersed in an electrolyte, then rinsed with deionized water, followed by exposure to UV irradiation. This results in the deposition of Ag nanoparticles with the size of 10 nm on and inside nanotubes. Photocurrent measurements reveal that the presence of Ag nanoparticles on TiO$_2$ nanotube layer enhances the absorption efficiency of dye, leading to higher photocurrent.

1. Introduction
Since Masuda et al. reported that the fabrication of aluminum oxide layers with highly ordered parallel-aligned, hexagonally configurated nanopores in 1995 [1], extensive research activities have been achieved due to a wide range of their applications. For example, the highly ordered porous structures have targeted magnetic recording media, optical devices and functional electrodes by filling pores with metals, semiconductors or polymers [2-5]. The highly ordered porous aluminum oxide layers are fabricated by a simple, but optimized electrochemical oxidation, so-called anodization of metallic aluminum in suitable acidic electrolytes such as sulfuric acid, phosphoric acid or oxalic acid. Anodization of other valve metals in these electrolytes results in the formation of flat compact oxide layers or highly random microporous layers depending anodizing voltage. In 1999 Zwilling et al. reported that oxide layers consisting of nanotube arrays can be formed by anodization of titanium in a fluoride containing electrolyte [6]. Since then, the formation of TiO$_2$ nanotube layers has attracted much attention due to many promising applications of TiO$_2$ such as photocatalyst and dye-sensitized solar cells. In order to improve these properties of TiO$_2$, controlling the geometry of TiO$_2$ nanotube layers has been attempted. As a result, as shown in Fig. 1, it becomes clear that tube length and...
diameter can be tuned by tailoring electrochemical conditions. For example, anodization in acidic electrolyte containing a small amount of fluoride ions typically leads to the formation of TiO$_2$ nanotube layers with a thickness up to several hundred nanometers as shown in Figs. 1(a) and 1(d). On the other hand, TiO$_2$ nanotube layers with a thickness higher than 2 µm can be formed in a buffered neutral electrolyte containing NaF and more higher aspect ratio nanotubes with smooth tube walls can be fabricated by using viscous organic electrolytes as shown in Figs. 1(b, e) and 1(c, f), respectively. Key to achieve high aspect ratio TiO$_2$ nanotubes is controlling pH profile and diffusion profile within tubes during anodization [7-11]. Albu et al. also reported that a variety of morphology of TiO$_2$ layers such as nanolace, nano-bamboo and nano-branching can be fabricated by the precise control of electrochemical conditions [12]. These novel nanostructured TiO$_2$ layers, due to their highly defined geometry combined with a large surface area, have shown for example to be highly effective for a range of applications including photocatalysis [13], solar cells [14] and biological interactions with cells [15].

Recently, the presence of metallic particles on TiO$_2$ layers improves photocatalytic properties of TiO$_2$ layers [16, 17]. In the present work we examine loading behavior of metallic particles on TiO$_2$ nanotube layers by different approaches in order to improve functionalities of TiO$_2$ nanotubular electrodes.

**Figure 1.** Top-view (a-c) and cross-sectional (d-f) images of anodic oxide layers by anodization of titanium in different electrochemical conditions; (a, d) anodized at 20 V in 1M H$_2$SO$_4$ + 0.15wt.% HF, (b, e) anodized at 20 V in 1M Na$_2$SO$_4$ + 0.5wt.% NaF, (c, f) anodized at 60 V in ethylene glycol + 0.27M NH$_4$F.

**2. Experimental**

In the present work we used TiO$_2$ nanotube layers with an average diameter of 100 nm and length of 500 nm as shown in Fig. 1(a, d). The detail for preparation of the layers is as follows. Samples were titanium (99.6 % purity) in the form of foils with a thickness of 0.1 mm. Prior to anodization, the samples were degreased by sonication in acetone, isopropanol and methanol, successively, then rinsed with deionized water and dried with a nitrogen stream.

For the anodization, an electrochemical cell with a three-electrode configuration was used. The samples were contacted by a Cu plate and then pressed against an O-ring in the electrochemical cell, exposed to an electrolyte. A platinum plate and a Ag/AgCl electrode are served as a counter electrode and a reference electrode, respectively. The electrolyte used for the tubular layer formation was 1M H$_2$SO$_4$ containing 0.15 wt.% HF, prepared from reagent grade chemicals and deionized water. The
anodization consists of a potential sweep from the open circuit potential to 20 V, followed by holding the potential at 20 V for several hours. The anodization was carried out using a high-voltage potentiostate (Hokuto denko, H-3001A) at room temperature under an aerated non-stirred condition. After the anodization, the samples were rinsed with deionized water and dried with a nitrogen stream. In the present work we tried photo-assisted deposition in order to load metallic nanoparticles on the TiO$_2$ nanotube layers. The TiO$_2$ nanotube layers were soaked in electrolytes containing metal ions for some period, and then exposed to UV irradiation to induce photocatalytic reduction of metal ions to metal in the form of nanoparticle. For morphological characterization of the samples, a field-emission scanning electron microscope (FE-SEM, JEOL JSM-6500) and a transmission microscope (TEM, Hitachi-800) were used. Cross-sectional images of nanotube layers were obtained from mechanically scratched samples, at locations where some pieces of the layers on the samples cracked off.

We evaluated photoresponse of metallic nanoparticle loaded, dye-sensitized TiO$_2$ nanotube layers in order to evaluate effects of metallic nanoparticles. For dye-sensitization, the TiO$_2$ nanotube layers with and without metallic nanoparticles were sensitized for several hours in N3 dye dissolved in methanol with a concentration of 300 $\mu$M. After the sensitization, photocurrent spectra were recorded at 500 mV$_{Ag/AgCl}$ with a step of 10 nm in the range from 500 nm to 800 nm. The electrolyte for the photocurrent measurements was acetonitrile containing 1.5 mM I$_2$ and 15 mM KI.

3. Results and discussion

We have examined a variety of metals for metallic nanoparticles deposition on TiO$_2$ nanotube layers. In the present work we targeted especially on Pd and Ag. Figure 2 shows top-view SEM images after UV irradiation for 30 minutes onto as-formed TiO$_2$ nanotube layer in 0.2M PdCl$_2$ electrolyte containing a small amount of methanol. It is clear that no nanoparticles can be observed, that is, no reduction of Pd ions to metallic Pd takes place. This can be attributed to the crystal structure of as-formed TiO$_2$ nanotube layer. Figure 3(a) shows XRD pattern obtained for as-formed TiO$_2$ nanotube layer. It is apparent that as-formed layer shows only the peaks from a titanium substrate. Therefore, as-formed TiO$_2$ nanotube layer is in amorphous state and therefore exhibits low photocatalytic reactivity due to fast recombination of electron-hole pairs. However, as-formed amorphous TiO$_2$ nanotube layer can be converted to crystalline by annealing. Figure 3(b) shows XRD pattern after annealing at 450 °C for 3 hours. The annealed TiO$_2$ nanotube layer exhibits clearly the crystalline signature of anatase. Note that even after annealing and conversion to anatase, TiO$_2$ nanotube layer retains its structural integrity [18]. Figure 4 exhibits Pd loading behavior on anatase TiO$_2$ nanotube layer in the same electrolyte. As apparent in Fig. 4(a, b), Pd particles are successfully deposited on the anatase TiO$_2$ nanotube layer after 30 min. UV irradiation. The size of the Pd particles is approximately 2 µm and larger than the diameter of nanotubes. Further irradiation does not affect the number of Pd particles deposited on the layer, but increases the size of the particles as shown in Fig. 4(c, d). Cross-sectional TEM
observations also revealed that no trace of Pd deposition inside nanotubes was detected. From these results one can deduce that once metallic nanoparticles are initiated on TiO$_2$ nanotube layer, the nanoparticles act as photo-excited electron collection sites, leading to the situation in which more reduction of Pd ions to metallic Pd can occur at the sites and as a result the particles can increase their sizes without increasing the number of Pd particles. In order to circumvent this problem, TiO$_2$ nanotube layers were soaked in electrolytes containing metal ions, then slightly rinsed with deionized water, finally followed by exposure to UV irradiation. This approach resulted in highly dispersed metal nanoparticle deposition on TiO$_2$ nanotube layers. A variety of metallic nanoparticles such as Pd, Pt and Ag were successfully deposited on TiO$_2$ nanotube layers. One example obtained for Ag deposition is shown in Fig. 5. Figures 5(a) and 5(b) are top-view SEM and cross-sectional TEM images of anatase TiO$_2$ nanotube layer after Ag deposition, respectively. It is clear from Fig. 5(a) that Ag nanoparticles with a diameter of approximately 10 nm are deposited on the nanotube layer in highly dispersed manner. Cross-sectional TEM observation reveals that the nanoparticles are deposited not only on the top of the tubes but also inside the tubes. Therefore, it is found that Ag nanoparticles can be successfully deposited on TiO$_2$ nanotube layer. Figure 6 shows photocurrent spectrum for Ag nanoparticle loaded TiO$_2$ nanotube layer. Spectrum obtained for nanotube layer without Ag nanoparticles is also included in the figure as comparison. Both layers were dye-sensitized for 1 hour. It is clear that the photocurrent spectra showed a peak at a wavelength of 570 nm and photocurrent was drastically enhanced by the presence of Ag nanoparticles on TiO$_2$ nanotube layer. The enhanced photocurrent by Ag

Figure 4. Top-view SEM images of anatase TiO$_2$ nanotube surfaces after the Pd deposition treatment for (a, b) 30 min. and (c, d) 3 hours.

Figure 5. (a) Top-view SEM and (b) cross-sectional TEM images of TiO$_2$ nanotube layers after the Ag deposition treatment. The arrows in (a) indicate the deposition sites of Ag particles.
nanoparticles may be attributed to the increased absorption efficiency of dye induced by plasmon resonance effect of Ag nanoparticles. Photocurrent spectra increased with increasing sensitization time due to the increased amount of chemisorbed dye. However, the increment of maximum photocurrent significantly decreased at the short sensitization time and then leveled off. Actually, extended sensitization led to the increased amount of chemisorbed dye. However, the increased amount of dye thickens the chemisorbed dye layer even on Ag nanoparticles. The thick chemisorbed layer attenuates the plasmon resonance effect of Ag nanoparticles, resulting in the decrease of photocurrent. In order to improve solar energy conversion efficiency, the surface area of TiO₂ layer should be increased. Therefore, the effect of surface area is considered using longer nanotubes with the same diameter of 100 nm. As mentioned above, the length of nanotubes can be controlled by tailoring electrochemical conditions. In the present work TiO₂ layer consisting of longer nanotubes was grown in 1M Na₂SO₄ containing 0.5 wt.% NaF for 3 hours, leading to 1.5 μm thick TiO₂ nanotube layer. After the growth of the layer, Ag nanoparticles were deposited under the same condition. Photocurrent spectrum obtained for dye-sensitized 1.5 μm thick TiO₂ nanotube layer with Ag nanoparticles is plotted in Fig. 6(b). As comparison, photocurrent spectrum for Ag nanoparticle loaded, 500 nm thick nanotube layer is also included in the figure. It is clear that the longer nanotube layer exhibits larger photocurrent as expected. Therefore, it is found that by a combination of the high surface area of TiO₂ electrode and the presence of Ag nanoparticles higher solar energy conversion efficiency can be obtained. However, optimizations are required in terms of length, diameter of nanotubes and size of Ag nanoparticles in order to obtain higher conversion efficiency.

![Figure 6](image.png)

**Figure 6.** (a) Photocurrent spectra obtained from 500 nm thick TiO₂ nanotube layers with and without Ag nanoparticles. (b) Effect of tube length on photocurrent spectrum obtained from Ag-nanoparticle loaded TiO₂ nanotube layer.

### 4. Conclusions

In the present work, we examined the deposition behavior of metallic particles on anodic TiO₂ nanotube layers by photo-induced reduction of metal ions. The deposition behavior strongly depended on the crystal structure of nanotube layers – on as-formed amorphous layer, no deposition took place whereas on annealed anatase nanotube layer metallic particles were formed on the entire surface. However, when the deposition was carried out in an electrolyte, the size of deposited metallic particles was larger than the diameter of nanotubes. On the other hand, in the case that TiO₂ nanotube layers were rinsed with deionized water after removing from an electrolyte, then exposed to UV irradiation,
metallic particles with the size of 10 nm were deposited on and inside nanotubes. The presence of Ag nanoparticles strongly enhanced photocurrent spectrum of dye-sensitized TiO$_2$ nanotube layers. The increment of photocurrent was varied depending on the sensitization time and the length of nanotubes.

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