Preparation and Microstructure of Ag-Doped TiO₂ Nanotubes by Anodization Method

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Abstract
In this paper, we present the effect of silver (Ag) dopants in titanium dioxide (TiO₂) nanotubes by the electrochemical anodic oxidation of pure titanium in the mixtures of ethylene glycol (EG), ammonium fluoride (NH₄F) and deionized water electrolyte solution containing with different concentrations of silver ions. X-ray diffraction (XRD) was used to study microstructure and scanning electron microscopy (SEM) and atomic force microscopy (AFM) were used to investigate surface morphology of TiO₂. The results showed that the diameters of nanotube arrays were about 92 nm for undoped TiO₂ and about 103 nm for all Ag-doped TiO₂ nanotubes. The peaks for undoped and doped TiO₂ are similar. When the concentration of silver nitrate (AgNO₃) dopants increases, the TiO₂ nanotube arrays cracked and are not well arranged.

Keywords: TiO₂ nanotube arrays, Ag-doped, Anodization, Microstructure.

INTRODUCTION
Titanium dioxide (TiO₂) arrays have attracted increasing scientific and technological attention due to its excellent photocatalytic activity, chemical stability, non-toxicity, favorable optoelectronic property low cost [1] and its importance in a diverse range of applications such as functional materials for energy conversion, photocatalytic, photovoltaic, antibacterial, self-cleaning and sensing applications [2]. Compared with regular particles, TiO₂ in nanoscale dimensions, e.g. nanowire or nanosheets show enhanced properties in photocatalytic activities [3]. In particular, TiO₂ nanotube arrays fabricated by potential anodization of titanium constitute a material architecture that offers a large internal surface area without a concomitant decrease in geometric and structural order. The precisely oriented nature of the nanotube arrays makes them excellent electron percolation pathway for charge transfer between interfaces. TiO₂ nanotube arrays have been found the possess outstanding charge transport and carrier lifetime properties enabling a variety of advanced applications [4]. However, there is a bottleneck that impedes the wide use of TiO₂ due to its large band gap energy (3.2 eV for anatase and 3.08 for rutile) [3], it is only active under UV light spectrum range, which is small fraction (5-6%) of whole solar-light spectrum [5]. In addition, high recombination rate of electron-hole pairs induced by incident photons can also result in its low photocatalytic efficiency [3].

Therefore, doped titanium dioxide nanotube arrays have been extensively investigated due to their capability to narrow band gap and extend the wavelength response of TiO₂ nanotube arrays into the visible light region and inhibits phase transformation [5].

In previous work, there are several methods that have been employed for making of TiO₂ nanostructures because of its potentially wide-ranging application. Recently, M.B. Suwarnkar et al. [6] reported on preparation of pure anatase TiO₂ photocatalyst with different Ag contents by energy efficient microwave assisted method. The average size of optimal Ag doped TiO₂ nanoparticle was found to be 10 nm. The band gap energy was observed to be decreasing from 3.20 eV to 2.98 eV. Agnieszka Hreniak et al. studied about influence of amount of silver on the structural and optical properties of TiO₂ powder obtained by sol-gel method. They found the size of pure TiO₂ particles was in the range 80-300 nm and influence of silver content reduces the light transmission for wavelength above 400 nm. Xiao Fan et al. [3] have synthesized Fe doped TiO₂ nanotube arrays by the electrochemical anodic oxidation of pure titanium in an NH₄F electrolyte solution containing iron ions. Anodization was performed at 40 V for 6 h and then Ag nanoparticles were assembled in Fe/TiO₂ nanotube arrays by microwave-assisted chemical reduction [3]. However, no detailed study has been reported on preparation and microstructure synthesized by containing silver ions in electrolyte and anodization at 50 V for 2 h.

In this paper, we prepare and investigate the microstructure of Ag-doped TiO₂ nanotubes by the electrochemical anodic oxidation of pure titanium in the mixtures of ethylene glycol, ammonium fluoride and deionized water electrolyte solution containing with different silver doping concentrations.

EXPERIMENTAL DETAILS
The titanium foils, 0.25 cm in thickness and more than 99.7% in purity, from Sigma Aldrich, were cut in circular shape with diameter about 1.5 cm. Before anodization, the titanium substrates were degreased ultrasonically in turn in isopropanal, de-ionized water and ethanol [6] for 10 min. The substrates
RESULTS AND DISCUSSION

From our observation, gas bubbles were observed during the anodization. In the first step, the current density between the electrodes was very high and lower when the anodizing time was extended. The gas generation slowed down as the current density decreased [2,9]. This can be ascribed to additional chemical dissolution of electrochemically form oxide layers.

The anodization occurs as follows. The initial oxide layer formed due to interaction of the surface titanium ions (Ti$^{4+}$) with oxygen ions ($O^{2-}$) in the electrolyte can be seen to uniformly spread across the surface. At the anode oxidation of the metal releases Ti$^{4+}$ ions and electron, shows as [4,9]:

$$
Ti + 2H_{2}O \rightarrow TiO_2 + 4H^+ + 4e^- \quad (1)
$$

At the cathode hydrogen evolution occurs:

$$
4H^+ + 4e^- \rightarrow 2H_2 \quad (2)
$$

The overall process of oxidation formation is give by:

$$
Ti + 2H_2O \rightarrow TiO_2 + 2H_2 \quad (3)
$$

Fluorine ions can attack the oxide and hydrated layer; or, the ions being mobile in the anodic layer under the applied electric field, react with Ti$^{4+}$ as described by:

$$
TiO_2 + 6F^- + 4H^+ \rightarrow TiF_6^{2-} + 2H_2O \quad (4)
$$

$$
Ti(OH)_4 + 6F^- \rightarrow TiF_6^{2-} + 4OH^- \quad (5)
$$

$$
Ti^{4+} + 6F^- \rightarrow TiF_6^{2-} \quad (6)
$$

This leads to a higher field a bottom of the pore that drives further oxidation, and field assist dissolution where Ti ions come out of the metal and dissolve in solution. Finally, the current reaches a steady state [9].

The influence of Ag doping on the microstructure of the film was analyzed through X-ray diffraction and the results are presented in Fig. 1 the XRD pattern of undoped TiO$_2$ and Ag doped TiO$_2$ nanotubes arrays with different concentration of silver nitrate (AgNO$_3$). The dopants were varied from 1.0 mM, 1.5 mM and 2.0 mM of AgNO$_3$ and annealed at 450 °C for 2 h. The X-ray spectra of both undoped TiO$_2$ and Ag doped TiO$_2$ nanotube arrays show anatase and titanium structures with a dominance of anatase structure. In Fig. 1, the 20 peaks shows a major peaks corresponding to reflections of the anatase phase of TiO$_2$ was apparent at the 20 angle about 25.3° and 37.8°. Other peaks of smaller intensity, at the angle 20 about 48.0°, 54.0°, 55.1°, 76.2° and 77.3°. The peaks for undoped and doped TiO$_2$ are appear similar, but in case of Ag doped TiO$_2$ samples, there was some noticeable reduction in peak intensity. This suggests that some desired phases or lower crystallinity take place in anatase structure after introduction of Ag ions [10-11]. The diffraction patterns of all the samples do not show any diffraction peak of silver or silver compounds, which shows that there is dispersion of metal ions on TiO$_2$, which can be attributed to very low amount of dopants in these samples or replacement of Ti ions by Ag ions into TiO$_2$ matrix.

The detailed morphological characterization of Ag doped TiO$_2$ were examined by scanning electron microscopy (SEM). SEM images in figure 2 show that the diameters of nanotubes were about 92 nm for undoped TiO$_2$ and about 103 nm for all Ag doped TiO$_2$ nanotubes. When the concentration of silver nitrate (AgNO$_3$) increases, the TiO$_2$ nanotube arrays cracked and are not well arranged.

More details obtained by atomic force microscopy (AFM) analysis, figure 3, which showed a significant match the SEM images. Also AFM scans revealed information on the surface roughness of the TiO$_2$ nanotube arrays. The statistical parameters of roughness distribution are reported in Table 1.

<table>
<thead>
<tr>
<th>Experimental Details</th>
<th>$R_{pV}$(nm)</th>
<th>$R_q$(nm)</th>
<th>$R_a$(nm)</th>
<th>$R_z$(nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Undoped TiO$_2$</td>
<td>187.157</td>
<td>34.201</td>
<td>27.269</td>
<td>135.110</td>
</tr>
<tr>
<td>1.0mM Ag-Doped</td>
<td>119.483</td>
<td>22.974</td>
<td>18.315</td>
<td>96.714</td>
</tr>
<tr>
<td>1.5mM Ag-Doped</td>
<td>90.312</td>
<td>18.107</td>
<td>14.706</td>
<td>67.085</td>
</tr>
<tr>
<td>2.0mM Ag-Doped</td>
<td>412.420</td>
<td>90.315</td>
<td>73.078</td>
<td>347.354</td>
</tr>
</tbody>
</table>

$R_{pV}$ = peak-to-valley, $R_q$ = root mean square, $R_a$ = roughness average, $R_z$ = ten point height.

$\text{Ti}(\text{OH})_4 + 6\text{F}^- \rightarrow \text{TiF}_6^{2-} + 4\text{OH}^-$
Figure 1. XRD patterns of TiO$_2$ prepared under undoped and Ag-doped: (a) pure TiO$_2$, (b) 1.0mM Ag-doped TiO$_2$, (c) 1.5mM Ag-doped TiO$_2$ and (d) 2.0mM Ag-doped TiO$_2$. A = Anatase
Ti = Titanium
Figure 2. SEM images of TiO$_2$ prepared under undoped and Ag-doped: (a) pure TiO$_2$, (b) 1.0mM Ag-doped TiO$_2$, (c) 1.5mM Ag-doped TiO$_2$ and (d) 2.0mM Ag-doped.

Figure 3. AFM images of TiO$_2$ prepared under undoped and Ag-doped: (a) pure TiO$_2$, (b) 1.0mM Ag-doped TiO$_2$, (c) 1.5mM Ag-doped TiO$_2$ and (d) 2.0mM Ag-doped.
CONCLUSIONS

In summary, TiO$_2$ nanotube arrays undoped and doped with different contents of silver nitrate were successfully fabricated by anodization method. The XRD patterns of undoped and Ag doped TiO$_2$ appear similar, but in cause of Ag-doped TiO$_2$ samples, there was some noticeable reduction in peak intensity due to lower crystallinity of TiO$_2$ nanotubes. This suggests that some perturbation takes place in anatase structure after introduction of Ag ions [10-11]. The SEM and AFM images of the nanotube arrays show that the diameters of nanotube arrays were about 92 nm for undoped TiO$_2$ and about 103 nm for all Ag-doped TiO$_2$ nanotube arrays. When the concentration of silver nitrate (AgNO$_3$) increases, the TiO$_2$ nanotube arrays break and are not well organized.

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