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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 (TiO_2) nanotubes by the electrochemical anodic oxidation of pure titanium in the mixtures of ethylene glycol (EG), ammonium fluoride (NH_4F) 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 TiO_2. The results showed that the diameters of nanotube arrays were about 92 nm for undoped TiO_2 and about 103 nm for all Ag-doped TiO_2 nanotubes. The peaks for undoped and doped TiO_2 are similar. When the concentration of silver nitrate ($AgNO_3$) dopants increases, the TiO_2 nanotube arrays cracked and are not well arranged.

Keywords: TiO_2 nanotube arrays, Ag-doped, Anodization, Microstructure.

INTRODUCTION

Titanium dioxide (TiO_2) 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, TiO_2 in nanoscale dimensions, e.g. nanowire or nanosheets show enhanced properties in photocatalytic activities [3]. In particular, TiO_2 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. TiO_2 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 TiO_2 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 TiO_2 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 TiO_2 nanostructures because of its potentially wide-ranging application. Recently, M.B. Suwarnkar et al. [6] reported on preparation of pure anatase TiO_2 photocytalyst with different Ag contents by energy efficient microwave assisted method. The average size of optimal Ag doped TiO_2 nanoparticle was found to be 10 nm. The band gap energy was observes 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 TiO_2 powder obtained by sol-gel method. They found the size of pure TiO_2 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 TiO_2 nanotube arrays by the electrochemical anodic oxidation of pure titanium in an NH_4F electrolyte solution containing iron ions. Anodization was performed at 40 V for 6 h and then Ag nanoparticles were assembled in Fe/TiO_2 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 TiO_2 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

were bound to an electrolytic cell via an o-ring and a copper (Cu) plate. One side of the substrate was in contact with the electrolyte and the opposite side, covered by a Cu plate, was connected to the DC power supply with a conducting wire. The counter electrode was a piece of platinum (Pt) sheet. The spacing between the two electrodes was approximately 2 cm. The electrolyte was the mixture of ethylene glycol (EG) ammonium fluride (0.3 wt% NH_4F), de-ionized water (2 Vol% H_2O) and containing with different concentrations of silver nitrate ($AgNO_3$). The electrolytes were mixed under stirring for 1 h using magnetic stirrer before being used as electrolyte for anodization. The anodizing voltage was set at 50 V and the process was carried out for 2 h. The titanium foil was anodized at room temperature. Then, the samples were subjected to mild ultrasonic treatment in ethanol for 10 min. The nanotubes were crystallized by the annealing at 450 °C for 2 h.

XRD with Phillip X'Pert MPD X-ray diffraction (XRD) was used to investigate crystal structures and phases, scanning electron microsope (SEM) with JEOL JSM-5410 and atomic force microscopy (AFM) with XE-100 Park System were used to study morphology of TiO_2 nanotube arrays.

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]:

$$Ti + 2H_2O \rightarrow TiO_2 + 4H^+ + 4e^- \quad (1)$$

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 2θ peaks shows a major peaks corresponding to reflections of the anatase phase of TiO_2 was apparent at the 2θ angle about 25.3° and 37.8°. Other peaks of smaller intensity, at the angle 2θ 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 TiO2 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 TiO2 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 1 Roughness statistical parameters for undoped TiO2 and Ag-doped TiO_2 nanotube arrays.

Experimental Details	R_{pv}(nm)	R_q(nm)	R_a(nm)	R_z(nm)
Undoped TiO_2	187.157	34.201	27.269	135.110
1.0mM Ag-Doped	119.483	22.974	18.315	96.714
1.5mM Ag-Doped	90.312	18.107	14.706	67.085
2.0mM Ag-Doped	412.420	90.315	73.078	347.354

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

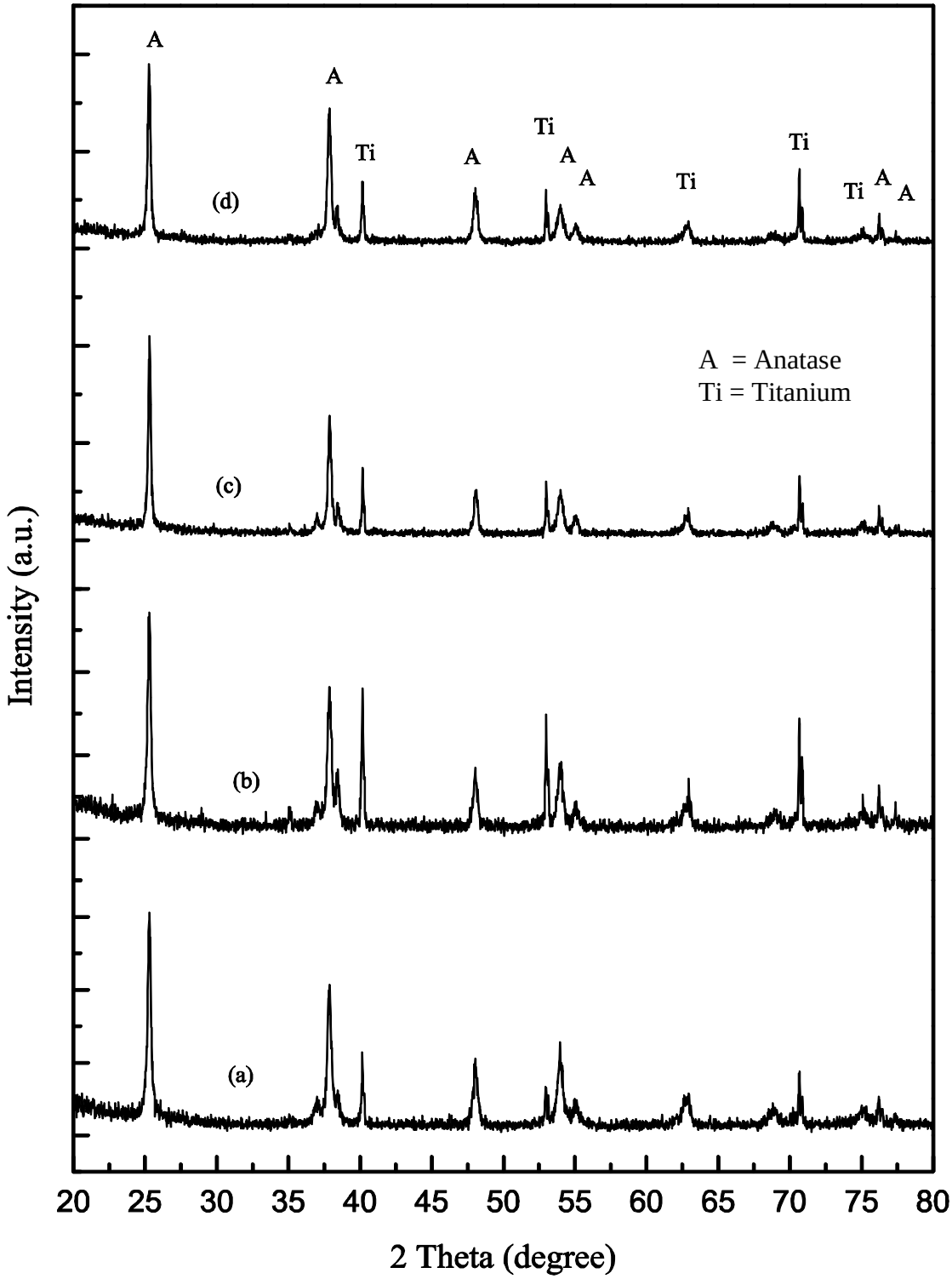

Figure 1. XRD patterns of TiO_2 prepared under undoped and Ag-doped : (a) pure TiO_2,(b) 1.0mM Ag-doped TiO_2, (c) 1.5mM Ag-doped TiO_2 and (d) 2.0mM Ag-doped

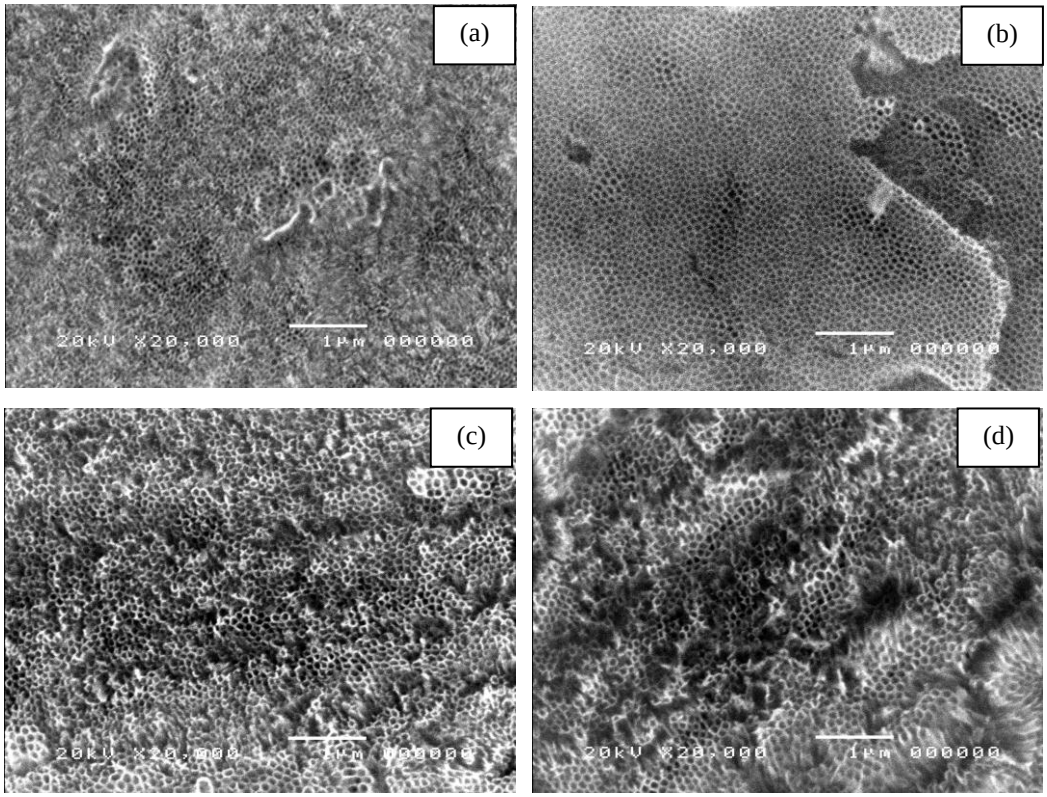

Figure 2. SEM images of TiO_2 prepared under undoped and Ag-doped : (a) pure TiO_2,(b) 1.0mM Ag-doped TiO_2, (c) 1.5mM Ag-doped TiO_2 and (d) 2.0mM Ag-doped

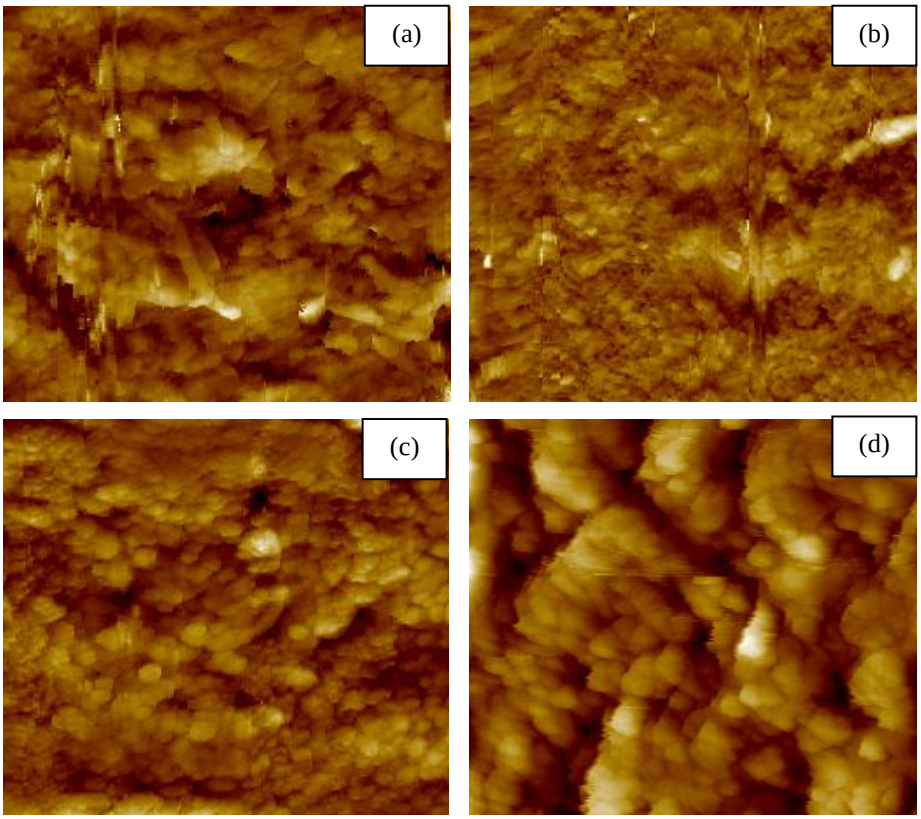

Figure 3. AFM images of TiO_2 prepared under undoped and Ag-doped : (a) pure TiO_2,(b) 1.0mM Ag-doped TiO_2, (c) 1.5mM Ag-doped TiO_2 and (d) 2.0mM Ag-doped

CONCLUSIONS

In summary, TiO_2 nanotube arrays undoed 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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