

The Photoelectrochemical Response of Various Surface Morphologies of Titanium Anodic Oxide Films

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Abstract: *Anodic oxide films of Titanium (Ti) with different surface morphologies were investigated by controlling the content of NH_4F in EG electrolyte. When Ti was anodised in the low content of NH_4F (1 wt%), a thin TiO_2 compact oxide layer was formed. However, TiO_2 nanoporous structure appeared on the surface of Ti when 3 wt% of NH_4F was added. When NH_4F was further increased to 5 wt%, a self-ordered nanotubular oxide structure was observed. TiO_2 nanotubular structure exhibited higher photocurrent density ($\sim 0.45 \text{ mA cm}^{-2}$) as compared to the nanoporous and compact oxide layer.*

Keywords: Titanium anodic oxide, photoelectrochemical cell, compact oxide layer, nanoporous, nanotubular, photocurrent density

1. INTRODUCTION

Nowadays, energy supply has arguably become one of the most important problems facing humanity.¹ The exponential demand for energy is evidenced by dwindling fossil fuel supplies and record-high oil prices.^{2,3} The increase in world population and energy crisis are further exacerbated by major concerns about global warming due to the consumption of fossil fuel.³⁻⁵ The energy shortage and global warming have significant implications to the future of our society. Therefore, continuous efforts have been carried out to create an alternative renewable energy to sustain the present level of population and economic development.

Recently, a significant progress in the search for clean hydrogen generation has been made.⁶⁻⁹ The hydrogen economy has become a synonym for a sustainable energy system. In this case, hydrogen has to be generated from renewable sources (water and solar light) via water photoelectrolysis.^{5-7,10,11} Thus, photoelectrochemical (PEC) cell has been seen as one of the most promising methods to produce hydrogen.¹²⁻¹⁴ It is the simplest among numerous methods and is comparatively efficient.^{4-6,10-14}

In particular, nano-dimensional titanium dioxide (TiO_2) has been seen as an attractive material and is used as photoelectrode in PEC cell.⁴⁻¹⁴ Thus, the development of more efficient photoelectrode materials, especially self-organised and well-aligned TiO_2 nanotubes is the main objective. The main reason is due to direct path for charge carriers transport and large surface areas for light harvest.¹¹⁻¹⁵ Therefore, good understanding on the formation of nanotubular structure of the anodised Ti surface is important in order to have controlled dimensions for highly efficient PEC response.

Anodisation is an electrochemical technique which can produce Ti anodic oxide layer on Ti substrate.¹⁶⁻¹⁸ This technique has been seen as an effective and economical method in the formation self-organised and well-aligned TiO_2 nanotubes. The most important point ought to be mentioned is anodisation method which is indeed a versatile technique to form nanoporous thin film with controllable dimension.¹⁹⁻²¹ Therefore, in this work, a detailed investigation has been performed to evaluate the morphology of the anodised Ti foil in different contents of ammonium fluoride (NH_4F) in order to develop viable hydrogen fuel cell for sustainable energy system.

2. EXPERIMENTAL

Ti foils with purity of 99.6% from STREM Chemicals were used in this study. The Ti foils were degreased by sonication in ethanol for 30 min before the anodisation process. The anodisation was performed in a two-electrode configuration bath with Ti foil as the anode and platinum foil as the counter electrode. The anodisation process was conducted for 1 h at a constant potential of 60 V using a Keithley DC Power Supply. The electrolyte was ethylene glycol (EG) with different amounts of NH_4F (1 wt%, 3 wt% and 5 wt%). The as-anodised samples were cleaned using acetone and dried in nitrogen stream. Then, these samples were then annealed at 400°C for 4 h in an argon atmosphere.

The morphologies of the TiO_2 nanotubes were characterised through field emission scanning electron microscopy (FESEM) using a Zeiss SUPRA 35VP at working distances down to 1 mm. To obtain the thickness of the nanotube layer, cross-sectional measurements were carried out on mechanically bent samples. The actual length of the tubes was divided by $\cos 45^\circ$. The elemental analysis of TiO_2 nanotubes was determined with energy dispersion X-ray (EDX) equipped in the FESEM. The TEM micrograph was obtained using a FEI CM 12 transmission microscope. The phase determination of the anodic layer was determined via XRD (Philips, PW 1729), operated at 45 kV and 40 mV.

The PEC properties of the samples were characterised using a three-electrode PEC cell with TiO₂ nanotube arrays as the working photoelectrode, platinum rod as the counter electrode and saturated calomel electrode (SCE) as the reference electrode. A solution of 1 M KOH with 1 wt% EG was used as the electrolyte in the PEC cell. The role of 1 wt% EG in 1 M KOH electrolyte was acted as a potential hole scavenger (electron donor) to minimise the recombination of charge carriers. All three electrodes were connected to a potentiostat (μ Autolab III). A 150 W xenon lamp (Zolix LSP-X150) with an intensity of 800 W m⁻² was used to produce a largely continuous and uniform spectrum. The light was transmitted by the quartz glass as the xenon lamp shone on the photoanode. The xenon lamp was switched on after the three electrodes were connected to the potentiostat and the photocurrent was measured during the voltage sweeping (5 mV s⁻¹).

3. RESULTS AND DISCUSSION

3.1 Surface Morphology of Titanium Anodic Oxide Films

In this part of experiments, the effect of different amount NH₄F on the morphology of Ti anodic oxide films is discussed. The NH₄F plays an important role in the formation of the nanotubular structure of Ti anodic oxide films.^{22,23} The formation of TiO₂ nanotube arrays in fluorinated electrolyte was the result of three simultaneously occurring processes: (1) field-assisted oxidation of Ti metal to form TiO₂; (2) field-assisted dissolution of Ti metal ions into electrolyte; and (3) chemical dissolution of Ti and TiO₂ in the presence of H⁺ and F⁻ ions.²³ In general, it can be concluded that the content of NH₄F is one of the important factor for the formation of self-organised and well-aligned TiO₂ nanotubes.

Figure 1 shows the micrographs of surface morphology of the anodised Ti foils in EG containing different concentration of dissolved NH₄F for 1 h. The amount of NH₄F was varied from 1 wt% to 5 wt%. Insets are the cross-sectional morphology of the oxides. From those FESEM images [Figure 1(a) to (c)], the appearance of the anodic oxides on the Ti foils was dependent on the content of NH₄F in the electrolyte. Anodisation of Ti in a bath containing 1 wt% NH₄F resulted in a thin TiO₂ compact oxide layer formed on the surface of Ti as shown in Figure 1(a). The overall thickness of the oxide is approximately 500 nm. This result indicates that a low F⁻ concentration is insufficient in forming a pit on the oxide layer due to the inactive chemical dissolution reaction.

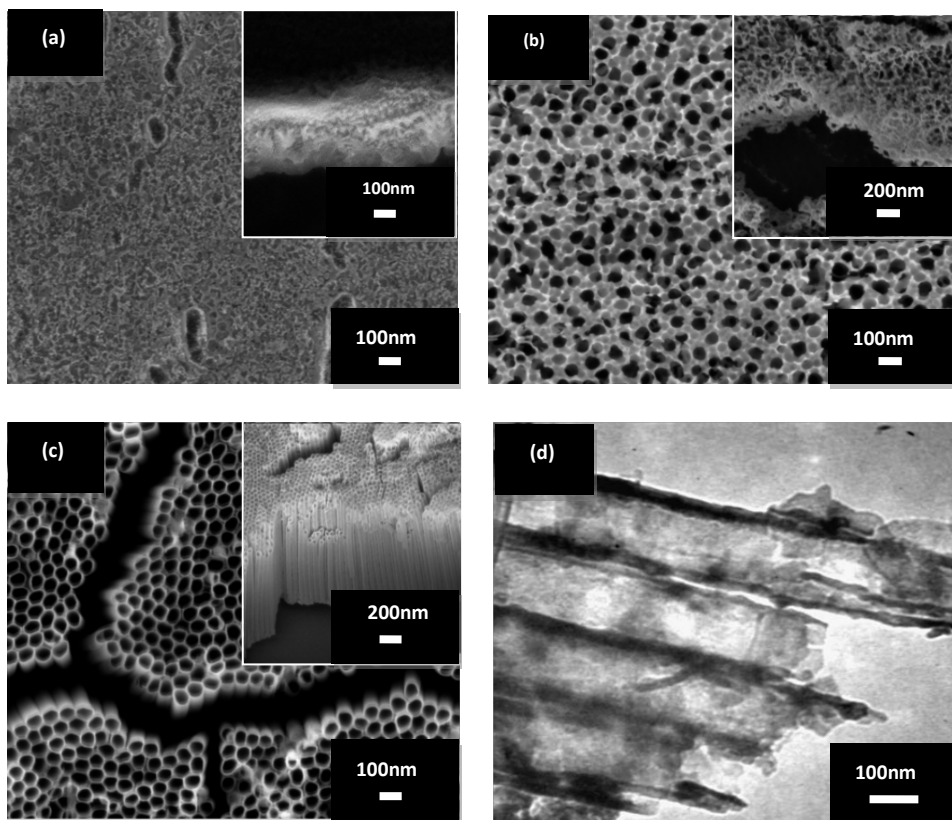


Figure 1: FESEM images of TiO_2 anodic oxide film anodised in EG containing different content of NH_4F at 60 V for 1 h: (a) 1 wt%, (b) 3 wt% and (c) 5 wt%. 1 (d) shows TEM images of TiO_2 nanotubes.

Figure 1(b) shows the FESEM image of the sample prepared in EG containing 3 wt% of NH_4F . The Ti surface contained irregular features and a porous oxide instead of ordered nanopores. The pore sizes were in the range of 25–100 nm and the thickness of the porous oxide layer was approximately 600 nm. The inadequate concentration of F^- might be caused by incomplete chemical dissolution and oxidation at the interface between Ti and the barrier layer. Thus, formation of irregular features and nanoporous TiO_2 layer in this condition.

For the 5 wt% NH_4F , self-organised and well-aligned TiO_2 nanotubes were successfully synthesised, which inferred that the concentration of F^- present in the EG was sufficient to increase the chemical dissolution. This condition led to further acidification to develop a nanotube structure, as shown in Figure 1(c). The TiO_2 nanotubes with diameters of approximately 90 nm, and lengths of 3 μm were formed when the F^- concentration was increased upto 5 wt%. Based on the

results, the optimum fluoride content identified in our electrolyte was 5 wt%. Subsequently, TEM images further confirmed the existence of TiO₂ nanotubes [Figure 1(d)]. The TEM images show that all TiO₂ nanotubes exhibited a hollow tube opening.

3.2 Current Density Studies

The difference in morphology of the anodic TiO₂ nanostructures under different amounts of NH₄F can be explained by referring to the current density profile, as shown in Figure 2. The current density curve increases as a function of NH₄F. The current density was increased up to 0.008 A cm⁻² when amount of NH₄F was 5 wt%. This was attributed to the high diffusivity and the ion concentration in the EG electrolyte because of the increasing of F⁻ species, which led to enhanced conductivity of the solution.^{24,25}

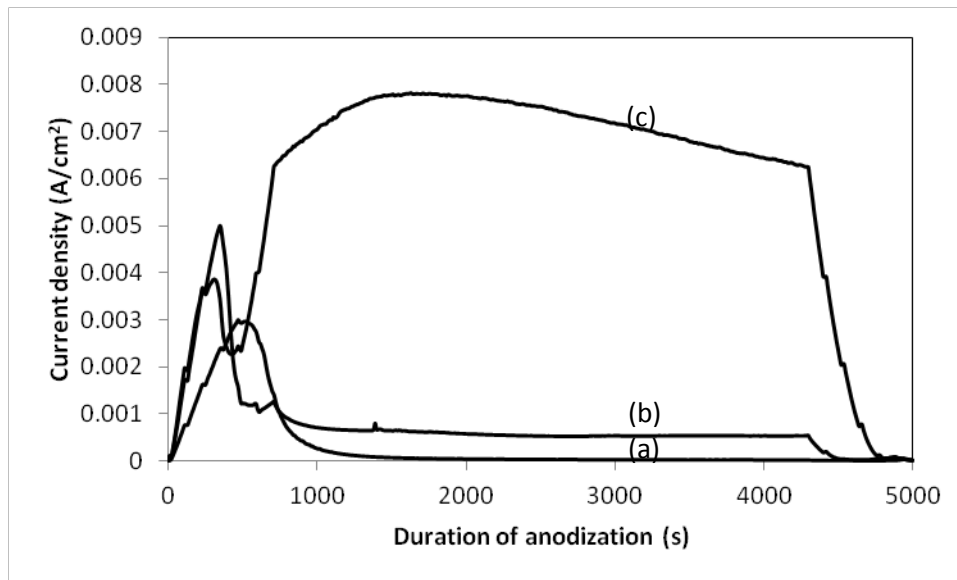


Figure 2: Current density against time plot for anodised Ti foils at 60 V for 1 h in EG containing different amount of NH₄F: (a) 1 wt%, (b) 3 wt% and (c) 5 wt%.

3.3 EDX Analysis of the Anodised TiO₂ Nanotubes

The EDX analysis was carried out in order to identify the atomic and weight percentage of the elements presents in the TiO₂ nanotubes. The EDX spectrum is shown in Figure 3. The peaks of Ti, O and C could be observed from the EDX spectrum, which indicate the existence of Ti, O and C elements in the TiO₂ nanotubes. The TiO₂ nanotubes comprised the carbonate species, which

resulted from the organic electrolyte of EG ($C_2H_6O_2$) during potentiostatic anodisation.

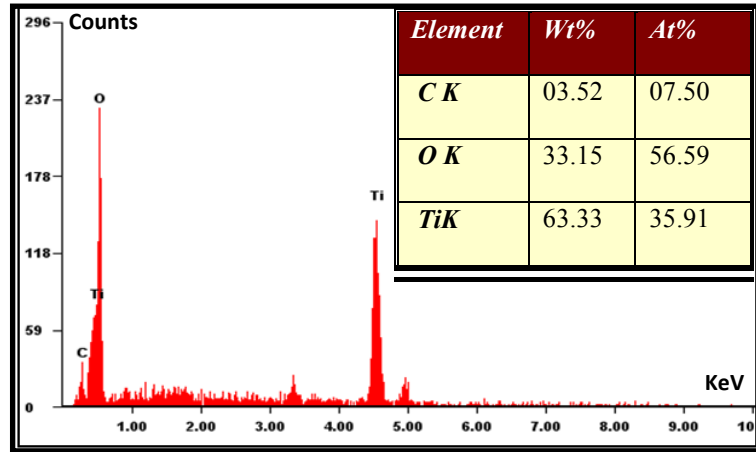


Figure 3: EDX spectrum of the TiO_2 nanotubes anodised in EG containing 5 wt% NH_4F at 60 V for 1 h.

3.4 XRD Analysis of the Anodised TiO_2 Nanotubes

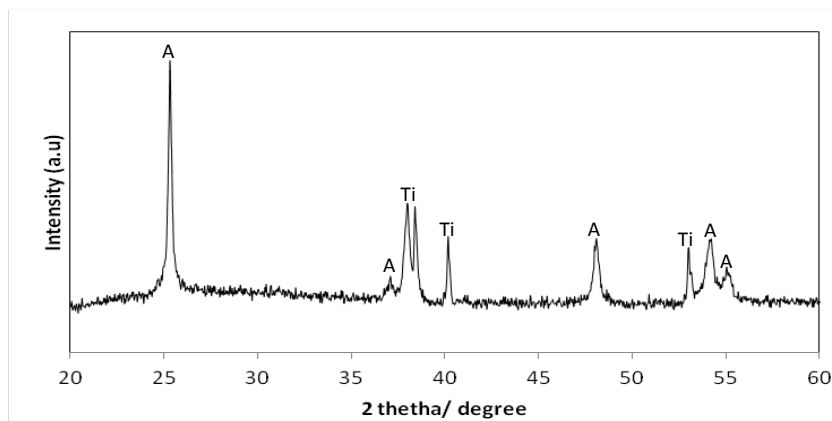


Figure 4: XRD patterns of annealed TiO_2 nanotubes at $400^\circ C$ in argon atmosphere for 4 h (A = anatase TiO_2 , T = titanium).

The XRD analysis was used to investigate the effect of crystal growth and phase transition on the TiO_2 nanotubes. The XRD patterns of the annealed TiO_2 nanotubes are shown in Figure 4. It could be observed that the diffraction peaks of the entire samples are ascribed to the TiO_2 with anatase phase [JCPDS no. 21-1272]. The diffraction peaks allocated at 25.37° , 38.67° , 48.21° , 54.10°

and 55.26° are corresponding to (101), (112), (200), (105) and (211) crystal planes for the anatase phase, respectively.

3.5 PEC Response of Titanium Anodic Oxide Films

To evaluate the PEC response, anodic samples with different surface morphologies were used as a photoanode in PEC cell. The I - V characteristic transient was recorded under darkness and under illuminated conditions, with a light intensity of approximately 800 W m^{-2} . Under dark conditions, all samples exhibited insignificant photocurrents less than $10^{-6} \text{ A cm}^{-2}$ (not shown). This indicates that less photo-induced electron were transported through the sample and inactive of the photoactivity of TiO_2 . However, the photocurrent density increased under illumination as shown in Figure 5. Thus, the TiO_2 is a good photo-response semiconductor for the transfer and decay of the photo-induced electrons when exposed to the illumination.

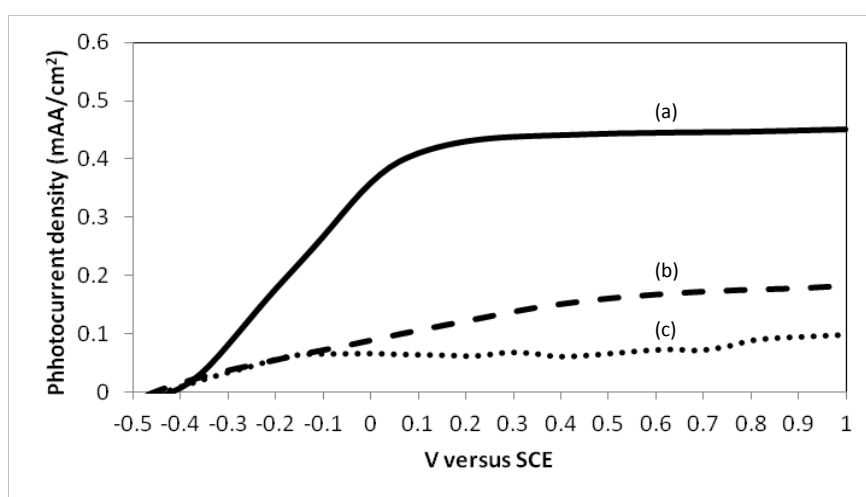


Figure 5: The I - V characteristics of different surface morphologies of anodic TiO_2 photoanode, (a) nanotubes, (b) nanoporous and (c) compact oxide layer.

Based on I - V characteristic, the photocurrent density increased under illumination. A maximum photocurrent density of up to 0.45 mA cm^{-2} was observed from the anodic TiO_2 nanotubes as compared to the nanoporous and compact oxide layer [Figure 5(a)]. TiO_2 nanoporous structure and TiO_2 compact oxide layer exhibited decreased photocurrent densities, that are approximately 0.18 mA cm^{-2} [Figure 5(b)] and 0.08 mA cm^{-2} [Figure 5(c)], respectively. The reason is due to the availability of larger active reaction sites in TiO_2 nanotubes to trigger the PEC reaction. In addition, both sides of the tube walls and the entire tube sidewalls can act as PEC reaction sites for generating more photo-induced electrons and transferring to counter electrode (platinum) to reduce the H^+ ions

into hydrogen gas.^{12,25-28} Therefore, TiO₂ nanotubes have better PEC response among the samples.

4. CONCLUSION

The present study demonstrated that high surface area of anodic TiO₂ nanotubes was successfully synthesised in EG containing 5 wt% of NH₄F. It is shown that anodic TiO₂ synthesised in EG containing less 5 wt% will result in the formation of nanoporous structure and compact oxide layer. The anodic TiO₂ nanotubes generated higher photocurrent response of 0.45 mA cm⁻². The main reason could be attributed to the larger active surface area in nanotubular structure for better photon absorption and released more photo-induced electrons, thus, it exhibited good PEC response.

5. ACKNOWLEDGEMENTS

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