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Formation and Mechanistic Study of Self-Ordering ZrO_2 Nanotubes by Anodic Oxidation

Syahriza Ismail, Zainovia Lockman, Zainal A. Ahmad and Andrey Berenov

Abstract— Among all of the one dimensional nanostructures other than titania (TiO_2) and carbon, zirconia (ZrO_2) have started to gain interest due to its potential in catalytic and energy applications. ZrO_2 nanotubes arrays have been prepared using electrochemical anodizing method of Zr foil in fluorine containing glycerol electrolyte. The morphology and structure of the ZrO_2 nanotubes are strongly controlled by the applied electrochemical condition especially voltage. Nanotubes with diameter of 30 to 60 nm has been produced by controlling the anodization voltage from 10 to 40 V. The ZrO_2 nanotubes formed in this method is partially crystalline even without the heat treatment. The wall thickness is ~10 nm. The self-aligned nanotubes produced by this method could be used for phocatalytic application. The degradation of methylene orange under UV light was successful when ZrO_2 nanotubes made in 30 V is used.

***Keywords*:** zirconium oxide, nanotubes, anodization,

I. Introduction

THE emerging of nanosize materials have received significant attraction because of their unique size dependent properties. Many improved technique for the synthesis of such nanomaterials with tuneable properties have been reported recently. Since the pioneering work of Zwilling et al, [1] on the formation of anodic oxide film, anodization [2], [3] has become an interactive method in producing nanoporous materials. Among the nanoporous materials produced by this method, oxide on valve metals has been seen as the potential materials as catalyst and in energy applications especially TiO_2. ZrO_2 on Zr has been produced by anodization. ZrO_2 is a promising candidate for possesses a high ionic conductivity [4] and rather high stability. ZrO_2 is a good catalyst and catalyst support due to its high ion exchange capacity and redox activities [5]. Thus, ZrO_2 is widely used in variety of commercial application such as oxygen sensors, catalyst, and in solid oxide fuel cells. The formation of ZrO_2 nanotubes is motivated by the development of TiO_2 nanotubes [6], [7], [8] which has become the intense subject recently. Furthermore the morphology of well aligned nanotubes is interesting due to the enhancement in surface area and increase in efficiency.

To date, most of the ZrO_2 nanotubes structures fabricated by anodization are using aqueous solution containing F^- electrolyte [9], [10], [11]. However, Zhao and co-workers have produced ZrO_2 nanotubes by using organic electrolyte containing formamide, glycerol and NH_4F [12]. To the best of our knowledge, very little has been reported on the preparation of ZrO_2 nanotubes in glycerol containing F^- electrolyte.

Herein, ZrO_2 nanotubes isproduced by anodization of zirconium in a fluoride-containing glycerol at voltage of 10, 30 and 40 V. Nanotubes of different dimension were obtained in this paper. A possible growth mechanism is presented.

II. Experimental

Zirconium foil (0.1mm thick, 99.8% purity) obtained from Strem. Ammonium fluoride (NH4F, 98%), and glycerol (A.R 85%) obtained from Merk (UK). Zirconium foils were degrease by sonicating in ethanol and DI water, followed by rinsing using DI water and drying in ambient air. Electrochemical anodization of zirconium was carried out at room temperature using two-electrode system. The anodic films were grown on the zirconium foils by anodization process with a platinum foil as counter electrode. During the process the voltage is ramped from the open circuit potential (OCP) to a certain voltage, followed by holding it at a constant

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voltage.

The morphologies of the anodized foils were studied using a field emission scanning electron microscope (FE-SEM) Zeiss Supra 35. Transmission electron microscopy (TEM) (Philips 420T) was used to examine the shape and size of the nanotubes formed. X-ray diffraction analyses (Bruker D8) were done on the samples to determine the crystallinity of the samples.

III. RESULT AND DISCUSSION

Fig. 1 (a), (b) and (c) shows the FESEM images of the as-anodized samples after anodization in glycerol containing 0.07wt% NH_4F at 10, 30 and 40 V for 1 h. Figures marked (i) on the left are the surface morphologies meanwhile figure marked (ii) on the right are the cross section morphologies. It can be seen that, the surface as well as the tubular appearance of the nanotubes become clearer and prominent as the voltage increase. However the length of the nanotubes seemed to decrease from 2 µm to 1 µm.

TEM was used to further investigate the microstructural characterization of the cross section view. As seen in the fig. 2 (a), hollow nanotubes are revealed with the outer diameter of about 40 nm, whereas the wall thickness is about 10 nm. Fig. 2 (b) is a selected area diffraction pattern of the ZrO_2nanotubes, indicating the crystalline structure of the as-anodized nanotubes.

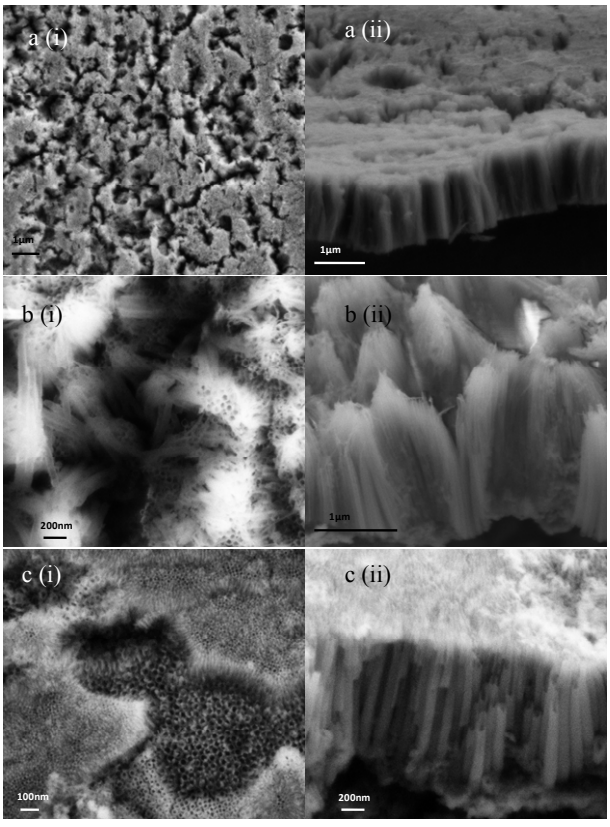

Fig.1 FESEM images of as-anodized zirconia nanotubes in glycerol containing 0.07 wt% NH_4F electrolyte at (a) 10 V, (b) 30 V and (c) 40 V. (i: surface morphology and ii: cross-sectional)

Fig. 3 shows the current transients (I-t curved) recorded during the anodization process at 3 different voltages: 10, 30 40 V. As shown in the figure, all the curves have a similar pattern. The steep increase at the initial stage is due to the potential sweep from 0 V to the subsequent constant voltage. The current density gradually decrease as the constant potential anodization is reached. The current drop was due to the formation of oxide films which elevated the resistance and reduces the current densities.

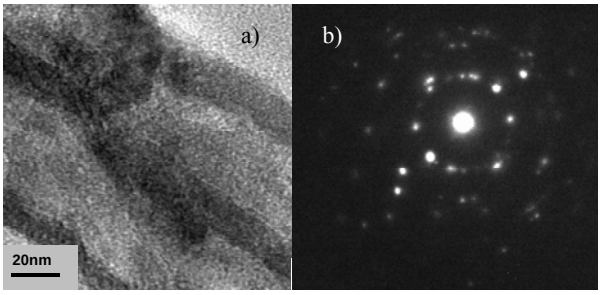

Fig. 2 TEM images (a) and selected area diffraction pattern (b) of zirconia nanotubes formed in glycerol containing 0.07 wt% NH_4F electrolyte

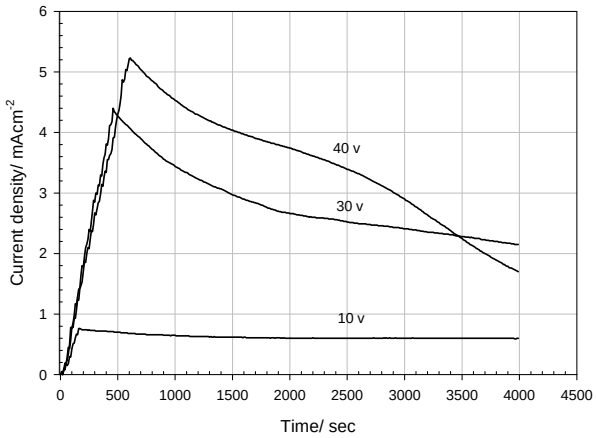

Fig 3 I-t curve recorded during the anodization process

Fig. 4 shows the XRD pattern of anodized ZrO_2 in glycerol at 3 different voltages. As seen in the figure there is a broad peak at $2\theta = 30^o$. This peak indicates that there is a trace of T/C crystal phase. The existence of T/C is due to the oxygen vacancies that held in the samples. Oxygen ion vacancies are responsible for the stability of the phase structure of ZrO_2 [13]. The nano-size effect has also contributed to the stabilization of C/T ZrO_2 in generating the excess oxygen vacancies. It cause the metal-oxygen bonds become weaker, which resulting in desorption of the lattice oxygen ions. Hence, greater number of oxygen vacancies is created.

Fig. 5 depicts the growth stages of the nanotubular layer schematically. The growth mechanism of ZrO_2 nanotubes is firstly by forming ZrO_2 film on the zirconium surface. This oxide formation is due to the interaction of Zr^{4+} with O^{2-} from the electrolyte. As the process of anodization proceeds, the compact ZrO_2

become thicker resulting higher volume stress and reaction heat become difficult to be released. At the same time, the applied electric fields that exist across the film will weaken Zr-O bonds, polarizing and weakening it. This is one of the reasons for the microcracks to form on the surface of electrolyte|oxide interface in order to reduce the internal energy (Fig. 5(a)). The process is known as electric field dissolution and pits formed on the surface of the ZrO_2 oxide. The Pits formed is deepening by F^- migration from the solution inwards forming porous structure at metal|oxide (Fig. 5(b)).

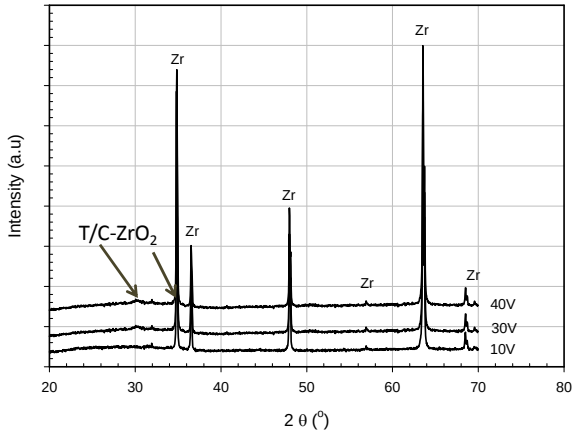

Fig 4 XRD patterns of anodized ZrO_2 nanotubes in glycerol for 1 at 10, 30 and 40 V.

These pits increase the electric field intensity across the barrier layer and provide easier route for more O^{2-} migration towards the metal|oxide layer. Therefore, further metal (Zr) oxidation occurs. The simultaneous process between anodization and dissolution, forming more uniform pore structures, if both the electrical and chemical dissolution processes are balanced. As the pores become deeper, the electric field in those protruded ZrO_2 area increase. The electric dissolution is increase and at the same time the abruption occurs between the two pores forming well aligned nanotubes (Fig. 5(d)).

During the nanotubes growth, the thickness of the tubular structure stop to increase when the dissolution rate at the pore mouth and anodization rate becomes equal at the bottom part of the tubes.

The formation of nanotubes is voltage dependent whereby the diameter and length are controlled by the applied voltage. However the length change only gradually but the diameter change from 30 nm to 60 nm. Two important key during the nanotubes formation are the rate of pits nucleation and the rate of pits growth. At high voltage, lots of small pits appear to occur on the oxide surface as the oxide thickens due to higher rate of pits nucleation. Whilst the high growth rate of pits enlarge the pits into pores. The vigorous F^- etching provides the pore growth to occur vertically and laterally.

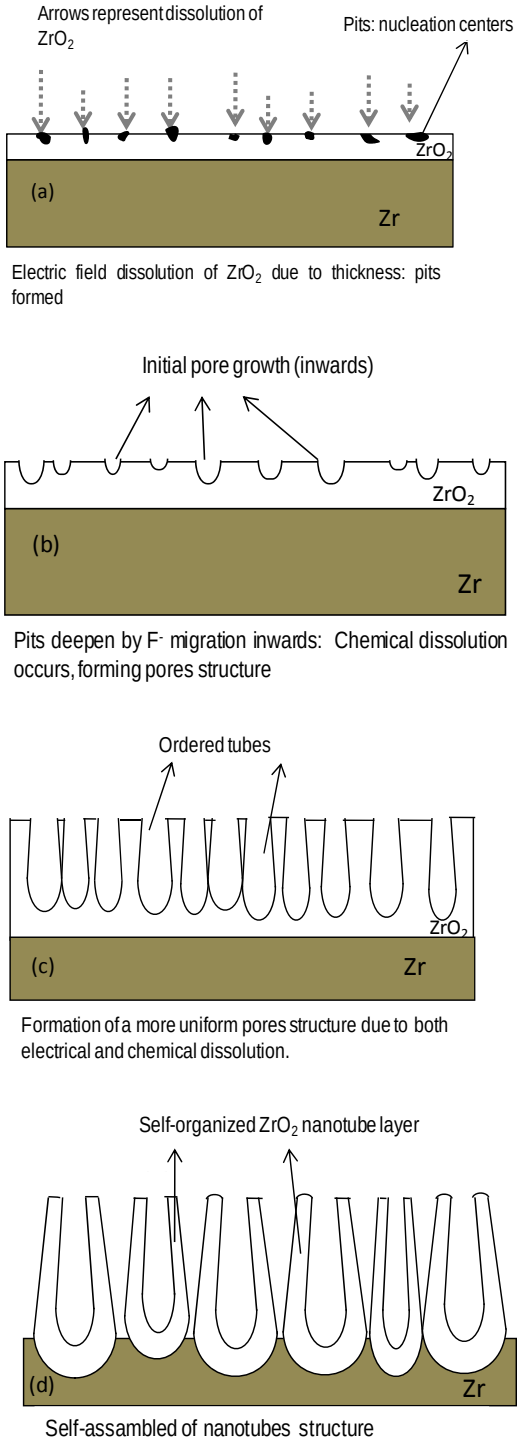

Fig 5 Schematical illustration to show the different stages of the ZrO_2 nanotubes layer formation.

The degradation activity of ZrO_2 nanotubes was studied by the photo degradation of methyl orange in aqueous solution under UV radiation. Fig 6 shows the use of ZrO_2 nanotubes as the photocalyst which was produced in glycerol at 20 V. As seen in the figure, ZrO_2 nanotubes can successfully be used as photocatalyst as it shows swift reduce in the methyl orange concentration.

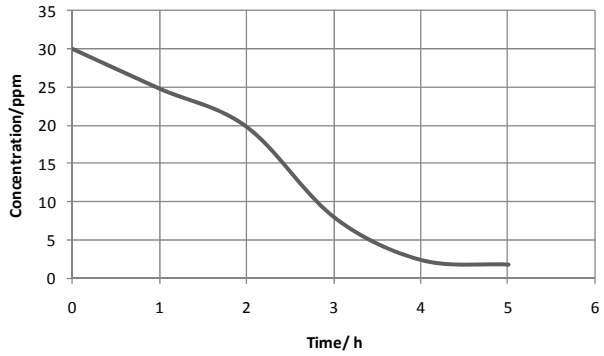

Fig 6 Photocatalytic degradation of methyl orange under UV radiation with ZrO_2 nanotubes

CONCLUSION

Self-organized ZrO_2 nanotubes layer are fabricated by electrochemical anodization of zirconium in glycerol electrolyte containing F^-. The morphology of the anodized oxide layer changes along with the applied voltage. ZrO_2 nanotubes with diameter ranging from 30 to 60 nm and length of 3 μm were formed. The as-grown zirconia nanotubes have a T/C-ZrO_2 phase. The mechanism of the ZrO_2 nanotubes is also proposed and the degradation of methyl orange was successful in the presence of ZrO_2 nanotubes.

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