

Multipodal formation of TiO_2 nanotubes using anodization

Cite as: AIP Conference Proceedings **2082**, 030019 (2019); <https://doi.org/10.1063/1.5093837>
Published Online: 22 March 2019

Johns Naduvath, Parag Bhargava, and Sudhanshu Mallick



View Online



Export Citation

ARTICLES YOU MAY BE INTERESTED IN

[Rheological characterization of silicone polymer nanocomposites for vibration damping applications](#)

AIP Conference Proceedings **2082**, 030018 (2019); <https://doi.org/10.1063/1.5093836>

[Development of Au doped \$\text{TiO}_2\$ nanofibers for photocatalytic applications](#)

AIP Conference Proceedings **2082**, 030007 (2019); <https://doi.org/10.1063/1.5093825>

[Adsorption studies of hydrothermally synthesized tin oxide nanoparticles](#)

AIP Conference Proceedings **2082**, 030008 (2019); <https://doi.org/10.1063/1.5093826>

AIP | Conference Proceedings

Get **30% off** all
print proceedings!

Enter Promotion Code **PDF30** at checkout



Multipodal Formation of TiO₂ Nanotubes Using Anodization

Johns Naduvath^{1, 2, a)}, Parag Bhargava² and Sudhanshu Mallick²

¹*Department of Physics, St. Thomas College (Autonomous), Thrissur, Kerala, India- 680001*

²*Department of Metallurgical Engineering and Materials Science, Indian Institute of Technology Bombay, Mumbai, India-400076*

^{a)}Corresponding author: johnsnaduvath1@gmail.com

Abstract. The titanium dioxide nanotube arrays with large pore size and multipodal nature have many applications including solar cells applications, three terminal devices, drug delivery and other light harvesting applications. A simple method for the formation of multipodal conical structures by anodization of Ti foil was introduced. During anodization of Ti foil using the electrolytes such as ethylene glycol, glycerol and diethylene glycol with higher water concentrations (from 10 vol% onwards), conical nanotubes of wider pore diameter ~200nm were observed. In order to study the branching of nanotubes in detail, nanotubes with different morphologies were grown in different electrolyte compositions and influence of viscosity and conductivity of electrolyte on multipodal nanotube formation were studied. The mechanism for the formation of bigger conical nanotubes, which contain 3 to 4 nanotubes inside it, was not addressed properly. A detailed study of the formation of these unique nanostructures was performed and proposes a growth mechanism for the same.

INTRODUCTION

Titania has been popular for the various applications solar cells applications¹, three terminal devices², drug delivery³ and other light harvesting applications⁴ due to its n-type nature, band alignment, stability, and non-toxicity. Since titania nanorods and nanotubes provide good conduction path for electrons as compared to nanoparticles, researchers are showing great interest in the synthesis of one-dimensional nanostructures using various experimental methods. Titanium dioxide with different morphologies can be synthesized using hydrothermal process⁵, sol-gel method⁶, alumina template⁷ and anodization method⁸. The third generation of nanotube array synthesis is based on anodization of Ti foil on polar organic electrolytes. In organic electrolytes like formamide (FA), dimethylformamide⁹, dimethyl sulfoxide (DMSO)¹⁰, ethylene glycol¹¹, the chemical dissolution due to fluoride ions is less compared to other electrolytes, which helps in formation of longer tubes.

In this work, a simple method for the formation of multipodal conical structures were introduced and the effect of electrolyte composition on nanotube characteristics such as nanotube diameter, length, shape and separation between the nanotubes were studied. In order to develop a better understanding on the mechanism of nanotube growth, a detailed study was carried out.

EXPERIMENTAL

The synthesis of TiO₂ nanotubes was performed using a two-electrode system. Commercial grade TIMET titanium foils (thickness-0.6 mm, 99.2%) of 2.0 cm x 1.5 cm dimension were used as anode for the anodization experiments. Anodization was performed using cleaned Ti foil of size 2 x 2 cm as counter electrode and anodization voltage 55 V (ramp rate 5 Vmin⁻¹) voltage was applied by a DC power supply (Aplab IT6834, Mumbai). The electrolyte based on diethylene glycol or glycerol containing 0.5 wt% NH₄F (Merck) and DI water. For the studies related to branching of nanotubes in detail, nanotubes were grown in different electrolytes (glycerol and diethylene glycol) with higher water concentrations (from 10 vol% onwards). Additionally, the effect of electrolyte viscosity on anodization was examined by preparing electrolytes with a range of water content in diethylene glycol or glycerol.

The morphology of the nanostructured oxide layers obtained through anodization was characterized using Field Emission Scanning Electron Microscope (FE-SEM, JEOL JSM 7600F). Viscosity of anodization electrolytes was measured using Brookfield R/S plus rheometer. Conductance measurements of anodization electrolytes were performed on conductivity meter (Model: Pico+, Lab India) at 25 °C.

RESULTS AND DISCUSSION

During anodization of Ti foil using the electrolyte composition of glycerol with 30 vol% water content and 0.5 wt% of NH_4F (electrolyte viscosity = 13.7 mPa.s), formation of wider (pore diameter ~200-300 nm) and conical nanotubes was observed. It is further noticed that some of tubes branched to form bipodal structures (Red circles in Fig. 1a). Further, anodization experiments were performed with higher water concentration (40%, 50%) in glycerol electrolyte. But at 40% and 50% water concentration (viscosity = 7.6 mPa.s and 4 mPa.s respectively), entire tubes were etched off and irregular structures were formed though some residual bipodal structure could be observed on the samples (Fig. 1 b and c).

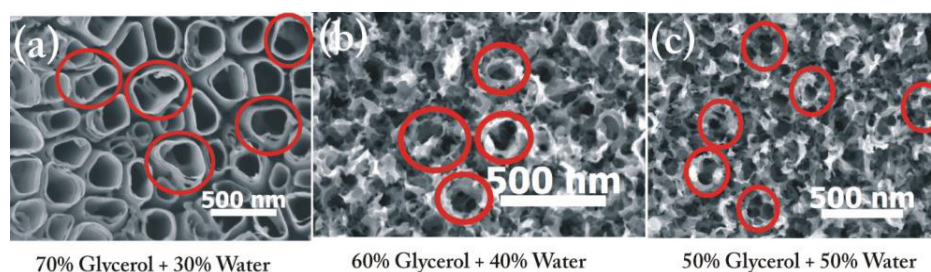


Figure 1. FEG-SEM images of the TiO_2 layer synthesized by anodization of Ti foil in electrolyte containing 0.5 wt% NH_4F and (a) 70%, (b) 60% and (c) 50% of glycerol with 30%, 40%, 50% DI water respectively.

The FEG SEM analysis of TiO_2 nanotubes grown using electrolyte containing 85% glycerol + 15% DI water (electrolyte viscosity= 31.7 mPa.s) revealed the formation of nanoporous films of pore size around 100nm on the surface of nanotubes which were easily removed using ultrasonication. Formation of this nanoporous film is due to the low ionic transport and reduced dissolution reaction in high viscous electrolytes (Fig. 2a). The diffusion coefficients of ions are inversely proportional to the viscosity of the solution. After removal of the nanoporous film, well-separated conical nanotube structures of top inner diameter of 150 nm were observed beneath the film (Fig. 2b). Careful examination of nanotubes showed initial growth of tubular formation on the sidewalls of nanotubes (Blue circle in fig. 2b). But it looks like the growth of tubular structure was not continued through that initial point. Many other bipodal structures were also formed for this electrolyte concentration. If diethylene glycol was used instead of glycerol and ethylene glycol, some unique structures were formed which were entirely different from conventional nanotube structures. The anodization of Ti foil in electrolyte containing 90 % diethylene glycol + 10% DI water (electrolyte viscosity= 19.3 mPa.s) formed conical shape multipodal nanotubes (Fig. 2 c & d).

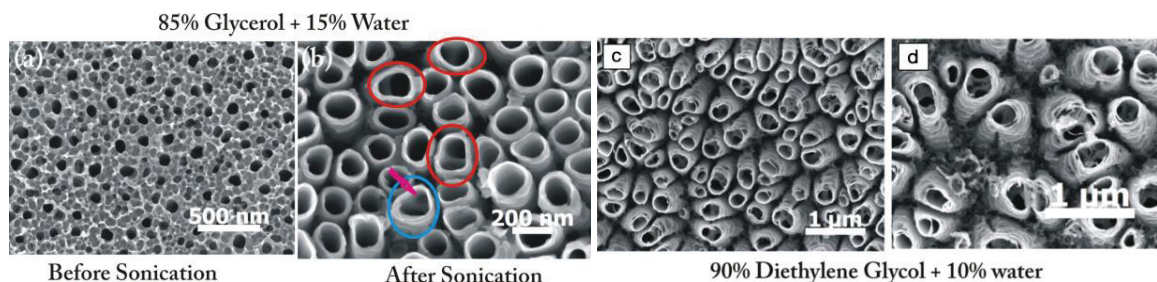


Figure 2. FEG-SEM images of the TiO_2 layer grown by anodization of Ti foil in electrolyte containing 85 % glycerol + 15% DI water and 90% diethylene glycol + 10% DI water

The cross sectional analysis (Figure 3) shows that some tubes tend to form a ‘Y’ shaped and branched structure whereas certain tubes combine together to form bigger tubes. In the case of diethylene glycol based electrolyte, large

conical tubes with base diameter around 600nm were formed. Careful examination of tubes formed in diethylene glycol reveals that each conical tube consists of three or four nanotubes.

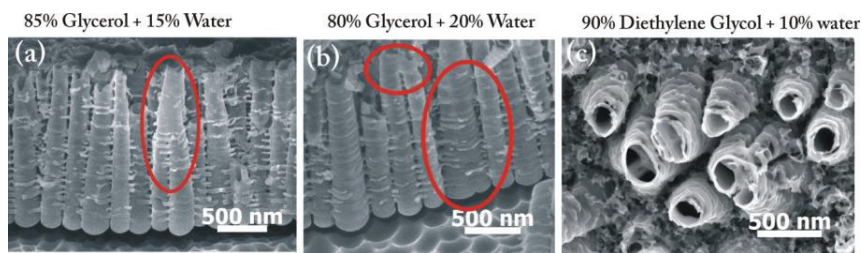


Figure 3. Cross sectional FEG-SEM images of the TiO₂ layer grown by anodization of Ti foil in electrolyte containing (a) 85 % glycerol + 15% DI water (b) 80 % glycerol + 20% DI water (c) 90% diethylene glycol + 10% DI water.

Mechanism for the formation of multipodal TiO₂ nanotubes

It is noticed that the conical nanotube formation occurs only if water content is greater than or equal to 10% in any type of solution irrespective of the nature of the solvent used like diethylene glycol or glycerol. Thus, the first inference that can be drawn from the observations is that higher water concentrations associated with reduced viscosity and increased ionic transport leads to the formation of conical nanotubes. But study of viscosity dependence on the formation of nanotubes reveals that even at same viscosity different type of nanotubes were formed for different electrolytes with different water content. So presence of water is also controlling the dissolution rate and hence the shape of nanotubes. Based on the FEG-SEM observations, a mechanism was proposed for the formation of conical multipodal nanotubes which consist of many nanotubes. When Ti foil undergoes anodization, field assisted oxide formation occur on Ti foil. The field assisted chemical dissolution (due to fluoride ions) leads to the formation of randomly located pores on TiO₂ film. With addition of water, the conductivity of electrolyte increases and also leads to a reduction in viscosity and hence enhances the transport of ions through the electrolyte (Table 1). Initial tube formation must start at a specific viscosity and conductivity of electrolyte. But at higher conductivity and lower viscosity, it was observed that the oxide which is formed dissolves completely without leaving any tubular structure. The hydrogen ions and TiF₆⁻ ions produced due to field assisted oxidation and chemical dissolution may lead to decrease in localized electrical resistance of electrolyte inside the tube. This helps to further increase the rate of oxidation and dissolution inside the nanotubes. Meanwhile due to localized aggressive dissolution, two or more sites are initiated inside the nanotubes for the formation of inner nanotubes (As confirmed from fig. 3.19 b and c). These sites lead to the formation of nanotubes in a multipodal conical structure. Area between the conical nanotubes dissolves very fast and randomly for the formation of well separated nanostructures. So it is concluded that viscosity and conductivity are the main parameters which determines the morphology of nanotubes. The schematic of the proposed mechanism for the formation of multipodal nanotubes is shown in fig. 4.

Table 1. Viscosity and conductivity measurements of anodization electrolyte at different combinations of solvent and water with 0.5 wt% NH₄F

	85% Glycerol + 15% DI water	80% Glycerol + 20% DI water	70% Glycerol + 30% DI water	60% Glycerol + 40% DI water	50% Glycerol + 50% DI water	90% Diethylene glycol + 10% DI water
Viscosity at 25 °C (mPa.s)	31.7	21.8	13.7	7.6	4.0	19.3
Conductivity μS	594	932	1481	1990	2450	555

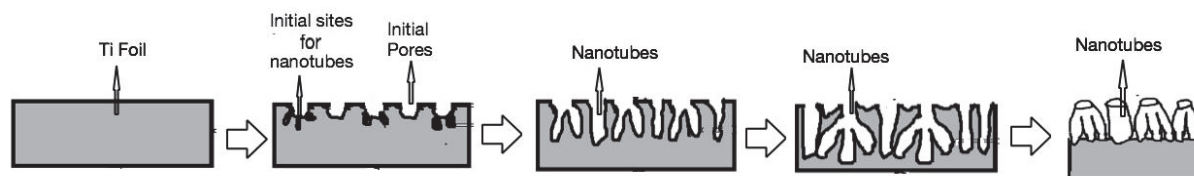


Figure 4. Schematic of the formation of conical multipodal TiO₂ nanotubes

CONCLUSION

In summary, well aligned, ordered TiO₂ nanostructures of different diameter and morphologies were synthesized on Ti substrate. The formation of TiO₂ nanostructures of mainly depends on amount of water and conductivity of electrolyte. These parameters control the transport of ions through the electrolyte. The mechanism for multipodal, conical nanotube formation during anodization has been proposed.

ACKNOWLEDGMENTS

The authors would like to acknowledge DST, NCPRE, and SERIUS for financial support and SAIF, IIT Bombay, for the experimental facilities.

REFERENCES

1. K. Shankar, G. K. Mor, H. E. Prakasam, O. K. Varghese, C. A. Grimes, *Langmuir* **23**, 12445-12449 (2007).
2. A. Mohammadpour, P. R. Waghmare, S. K. Mitra, K. Shankar, *ACS Nano* **4**, 7421-7430 (2010).
3. L. Peng, A. D. Mendelsohn, T. J. LaTempa, S. Yoriya, C. A. Grimes, T.A. Desai, *Nano Lett.* **9**, 1932-1936 (2009).
4. Y. Rambabu, M. Jaiswal, S. C. Roy, *J. Phys. D: Appl. Phys.*, **48**, 295302-295311 (2015).
5. D. V. Bavykin, V. N. Parmon, A. A. Lapkin, F. C. Walsh, *J. Mater. Chem.* **14**, 3370-3377 (2004).
6. T. Kasuga, M. Hiramatsu, A. Hoson, T. Sekino, K. Niihara, *Langmuir*, **14**, 3160-3163 (1998).
7. M. S. Sander, M. J. Cote, W. Gu, B. M. Kile, C. P. Tripp, *Adv. Mater.* **16** 2052-2057 (2004).
8. P. Roy, S. Berger, P. Schmuki, *Angew. Chem. Int. Ed.* **50**, 2904-2939 (2011).
9. J. M. Macak, H. Tsuchiya, L. Taveira, S. Aldabergerova, P. Schmuki, *Angew. Chem. Int. Ed.* **44**, 7463 -7465 (2005).
10. J. M. Macak, P. Schmuki, *Electrochim. Acta*, **52** 1258-1264 (2006).
11. H. E. Prakasam, K. Shankar, M. Paulose, O. K. Varghese, C. A. Grimes, *J. Phys. Chem. C*, **111**, 7235-7241 (2007).