



## NANO STRUCTURED ALUMINUM OXIDE BLACK COATING FOR SOLAR PANELS: DOUBLE ANODIZATION USING MUCH IMPROVED ENERGY SAVING PROCESS

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### ABSTRACT

Aluminium oxide coating with highly dense nanopores arranged in ordered close arrays was prepared. The recent two-steps anodization technique has been adopted for this purpose. An improved method for detaching the porous non-regular part from the barrier layer, resulting from the first anodization was suggested. More power saving have been assessed. It also ensures the use of non-toxic species. The nanoporous construction produced shows an extra durability represented by hardness values. Samples with developed nanoporous films were investigated by using SEM and AFM analysis. Plan views and side sections revealed the improvement in the surface morphology and topography. Deep black colored sample was produced using copper sulphate solution 40 g/l.

**Keywords:** composite materials, nanostructures, thin films, electrochemical techniques.

### INTRODUCTION

Nanoporous anodic aluminium oxide (AAO) has been used in several fields such as electronic, photonics, energy storage and nanotechnology [1, 2]. The application of nanoporous AAO for production of solar selective surface extended to 1980 after black coloration, due to its great structural characteristics [3]. The porous films find wide applications as solar panels to heat water for housing, industrial or agricultural uses [4]. Aluminium, as the substrate, has low specific gravity and excellent heat conductivity. So, its alloys may be considered as adequate substrate for solar panels [5]. AAO is produced previously by one-step anodization process. During the anodization process, within an acidic medium, the aluminium surface is oxidized, where the oxide layer consists of a non-organized nanoporous structure. A two-steps anodization process is adopted recently to regulate the nanoporous structure. Since, irregular nanopores are formed after first anodization step, well-ordered nanopores are obtained by detaching almost of the oxide layer with irregular structure and then performing the second anodization steps [6-8]. Hence, the structure of AAO is characterized by high pore density, high structural regularity and uniform nanopores dispersion [3], [9], [10], and [11]. In previous researches, nanoporous AAO produced via double anodization process, the duration time was extended to hours as reported by Moghadam *et al.* [3], or the applied voltage reached to high values as mentioned by Mukhurov *et al.* [1] and Abd-Elnaiem *et al.* [12]. Moreover, Shih *et al.* [13] and most of the other researchers used a solution including chromic acid for detachment process, which is hazardous material. The aim of this work is to find a method for replacing the toxic-chemical detachment step before the second anodization. Moreover, producing a porous layer of efficient pore filling can be obtained. Also, it can lower the highly current density, voltage, and duration time used

usually in the two steps process. The final product obtained during processing before was evaluated through SEM, AFM analysis and hardness measurements.

### EXPERIMENTAL

#### Materials

Samples of dimension 10 x 3 cm were cut from aluminium sheet 99.5 %. Lead electrode was used as counter electrode in both anodization steps. For pre-treatment steps, acetone, sodium hydroxide, nitric acid were used in the appropriate concentrations. Sulphuric acid 170 g/l was prepared and used for anodization. A solution containing 55% phosphoric acid and 14% sulphuric acid was used for electrolytic detachment steps.

#### Set-up and measurements

Cooling system was designed for controlling temperature of electrolytic solution during anodization. The system consists of thermostat, compressor, copper serpentine immersed in water for Freon circulation. DC Power Supply GW Lab GPR-3030 was used as the source of DC current during anodization.

Surface morphology was investigated after each step, using scanning electron microscope device (SEM), QUANTA FEG 250 (FEI). Surface topography was analysed using Atomic Force Microscope (AFM), Shimadzu SPM-9600 Non-Contact Mode, made in Japan. Hardness of the surface was measured using Shimadzu Japan Type - M.

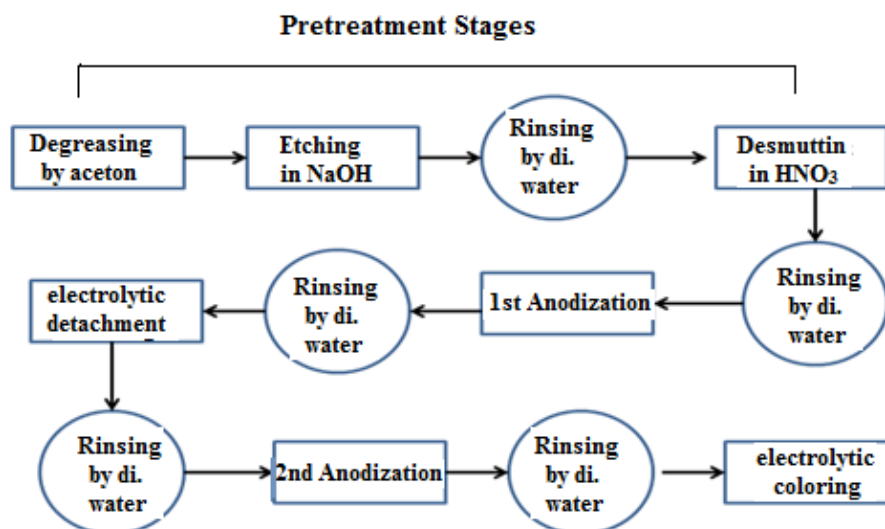
#### Procedure

Multi steps of nanoporous AAO preparation are summarized in the flow chart shown in Figure-1. Aluminium samples were firstly degreased by acetone for



the disposal of grease or oils which may remain over the surface, etching by immersion the sample in a solution of sodium hydroxide 12 %, and then dismuting was done by immersion the sample into a solution of nitric acid. First anodization steps was carried out using electrolytic cell of two electrodes system consisting of DC power supply, connected to working electrode and lead counter electrode in electrolytic solution of prepared  $\text{H}_2\text{SO}_4$  170 g/l. Electric potential 15V was applied and the solution was cooled to 17°C before starting first anodization for 15 min.

Electrolytic detachment steps was used to remove almost of the upper non-ordered irregular layer of anodic coating. It was applied for 1 min. at low current density 0.015 A/cm<sup>2</sup>. Second anodization step was carried out at constant time 30 min. for re-building up of a new regular anodic film with nano size diameter. Finally, the sample was fixed in the electrolytic coloring bath of  $\text{CuSO}_4$  (40g/l) at pH 2, where  $\text{Cu}^{++}$  ions were reduced and deposited within the nanoporous film. A homogeneous black color was formed.



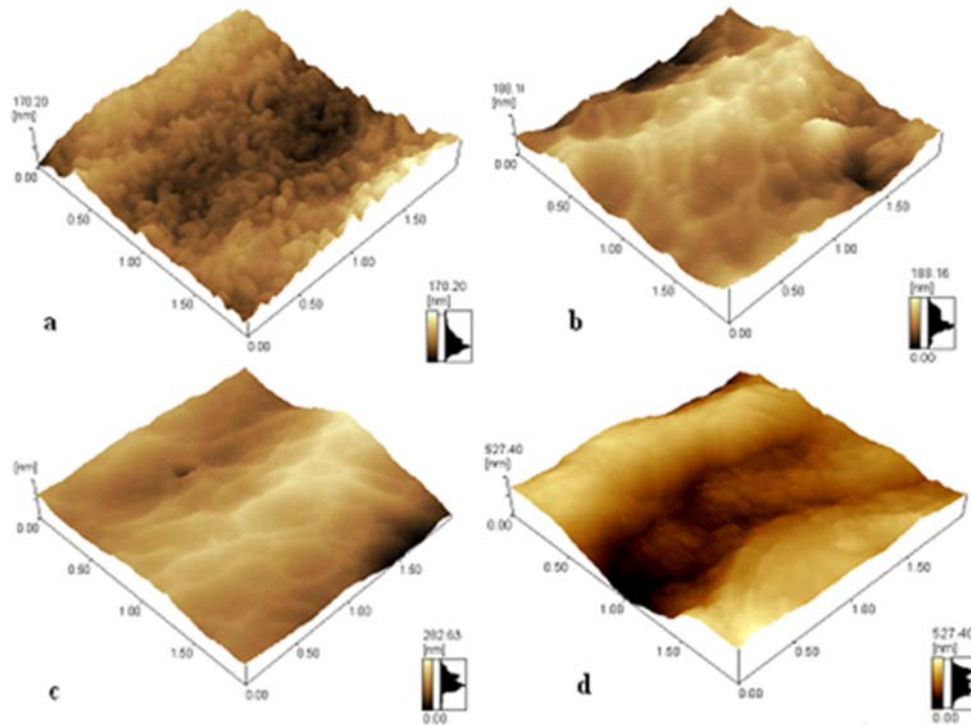
**Figure-1.** Flow chart of two-step anodizing for preparation of nano porous alumina and colouring.

## RESULTS AND DISCUSSIONS

### Atomic Force Microscope analysis (AFM)

As shown in Figure-2(a), AFM analysis of Al substrate reveals the presence of highly average micro roughness 0.967 $\mu\text{m}$  and the crystalline structure of Al metal was appeared. The transfer of the surface to amorphous structure was obtained after first anodization as shown in Figure-2(b) and the surface roughness becomes

about 0.96 $\mu\text{m}$ . The non-ordered porous film of anodic oxide film was removed and regulated after electrolytic detachment step (Figure-2c), where leveling of the surface was improved with low thickness ordered layer, roughness reached to 0.941 $\mu\text{m}$ . Shades of huge numbers of nanopores through nanoporous AAO film shown in Figure-2(d) where the roughness of second anodized sample was 0.991 $\mu\text{m}$ .



**Figure-2.** AFM of different steps ( $2\mu\text{m} \times 2\mu\text{m}$ ) of nanoporous alumina preparation.

(a) Pre-treated Al ( $R=0.967\mu\text{m}$ )

(b) 1st anodized ( $R=0.958\mu\text{m}$ )

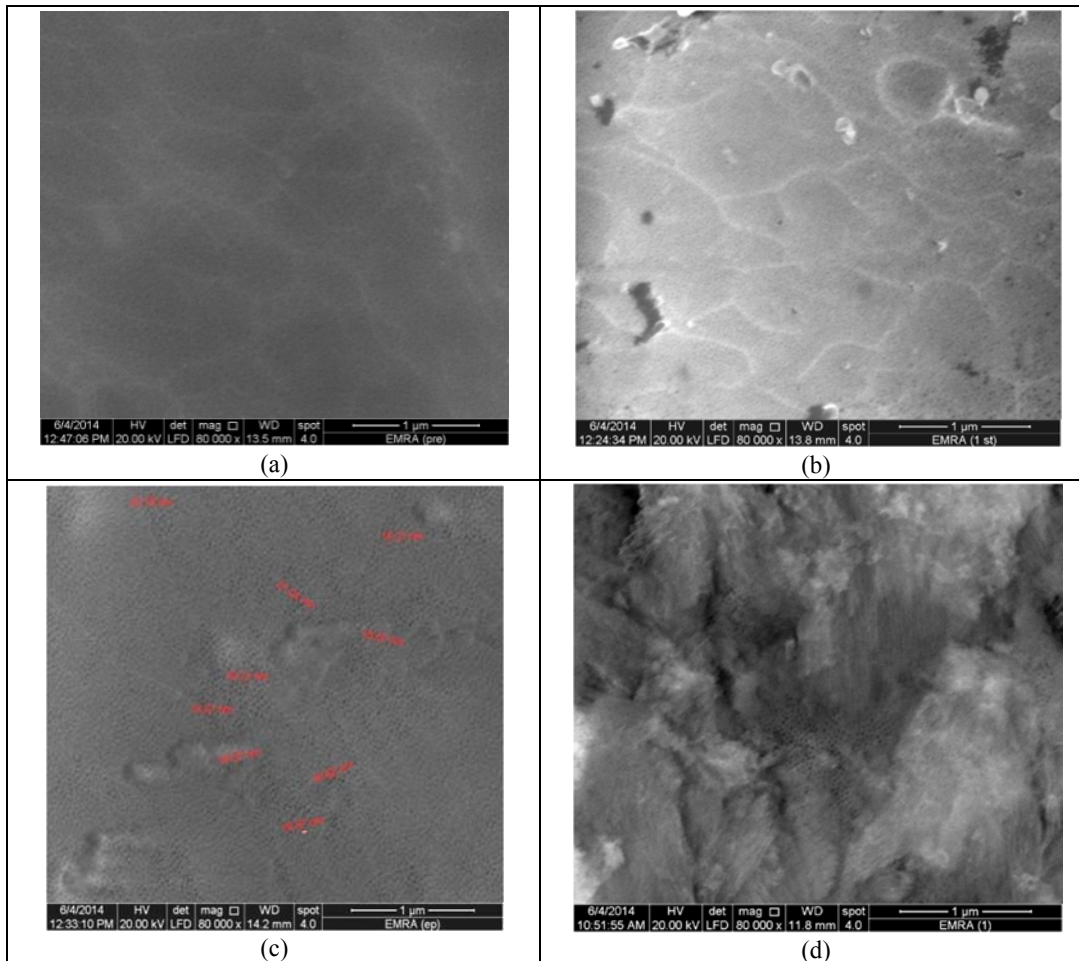
(c) Electrolytic detachment ( $R=0.941\mu\text{m}$ )

(d) 2nd anodized ( $R=0.991\mu\text{m}$ )

### Scanning Electron Microscope (SEM)

The surface morphology was strongly dependent on the applied conditions and varied after each steps. Aluminium sample surface was cleaned thoroughly by pretreatment and plain granular surface of aluminium was observed as in Figure-3(a). A layer of porous AAO film was formed after first anodization step and a non-regular porous film was observed by SEM as shown in Figure-3(b) and the measured pore diameter was vacillated between 16 to 19 nm. Electrolytic detachment was used in the

subsequent step to eliminate almost of the non-ordered and irregular oxide film, where an ordered and regular matrix of thin porous oxide layer was predominated after electrolytic detachment with pore diameter ranged between 16 and 21 nm as shown in Figure-3(c). Hence, after second anodization, 3D nano architectural structure and porous nano composite was appeared with measured pore diameter ranged between 18 and 23 nm as shown in Figure-3(d).



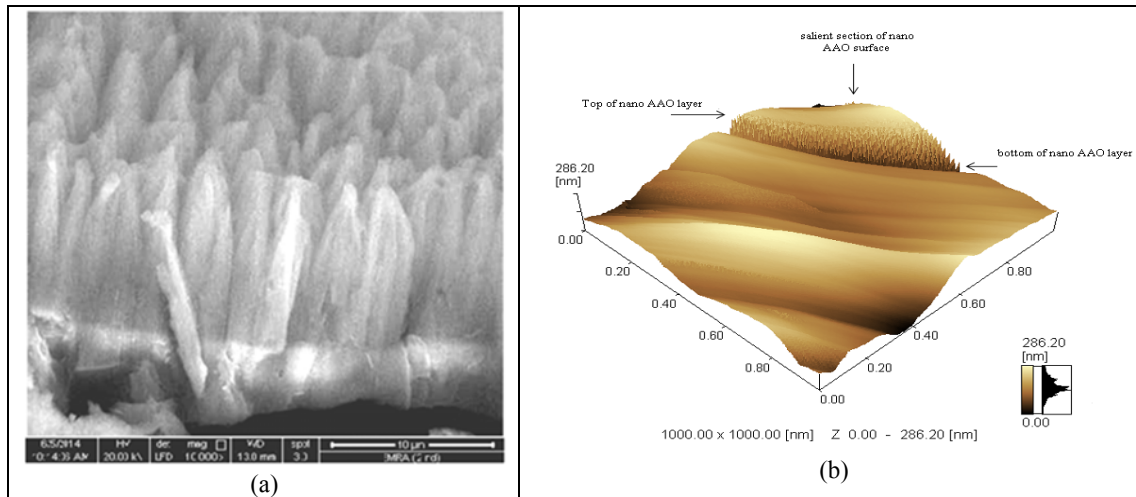
**Figure-3.** SEM images of different steps for nano porous alumina preparation (a) Pre-treated Al (b) 1<sup>st</sup> anodized (c) Electrolytic detachment (d) 2<sup>nd</sup> anodized.

#### Surface characterization for second anodized Al sample

After elimination of non-ordered porous AAO film, a new ordered film was built up in regular and arranged architectural structure by applying second anodization step. SEM analysis of cross section of second anodization sample revealed the presence of regular bundles and ordered distribution of nanoporous AAO over the surface. Aluminium oxide nanotubes stem from the bottom barrier layer towards the top of the surface as

shown in Figure-4(a). From Figure-4(a), the diameter is narrow and minute in the top, while it seems to be wider in the bottom. Hence, previous researchers immersed the samples in phosphoric acid after second anodization for widening the nanopore tip.

Highly focusing on second anodized sample (1 x 1 µm) by AFM, it reveals the presence of corrugated surface with longitudinal sections of different planes of nanoporous AAO film as shown in Figure-4(b), each section contains bundles of nanopores.

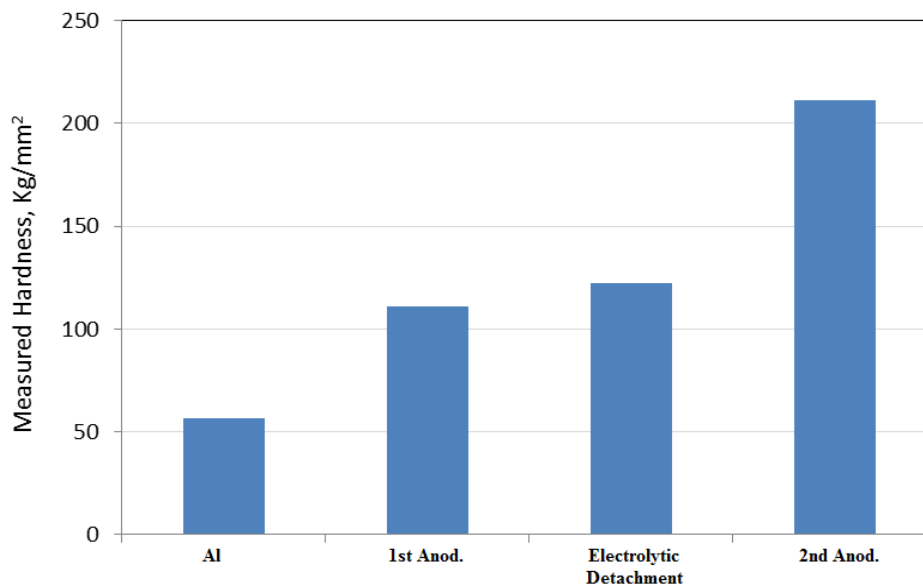


**Figure-4.** (a) SEM of cross section of anodized Al, (b) AFM 1x1  $\mu\text{m}$  zooming graph of anodized Al sample after second anodization step.

## Durability and Hardness

Durability of aluminium samples at various stages of processing was evaluated by hardness measurements. Figure-5 represents the hardness values attained. The hardness was increased appreciably by first anodization. Then, a slight increase was observed after electro-detachment step. Hence, a sudden increase was obviously measured by the second anodization. The hardness values

of the four samples are respectively: 56, 110, 122 and 211 Kg/mm<sup>2</sup>. The durability of aluminium was doubled by first anodization and binary doubled by the second anodization. This is a great proof for the effect of the nanopores and channels in reinforcement of the oxide matrix. Moreover, it represents a new evidence for the great ordering and reclamation of the nanotubes in the second anodization [14-16].



**Figure-5.** Measurements of hardness of different samples of aluminium.

### Energy consumption and saving

The most important factor in choosing any process for commercial application is energy consumption and consequently the cost. Many processes have been invented for two -steps anodization. However, it depends

mainly on electric power. Electric energy consumption is a function of applied potential, current density and duration time. The goal of this research was mainly to reduce these factors by replacement of the chemical etching by electro-detachment between the two anodizing steps. Table-1 lists





some ranges of the aforementioned factors used in previous researches. According to the conditions applied, the statistical data indicates that the cost of electro-detachment step is highly favored to replace the chemical etching methods. In addition, the total energy of the whole steps comprising, first anodization, electrolytic detachment and second anodization is 0.00227 KWh/cm<sup>2</sup>. This indicates the economic possibilities and the process is

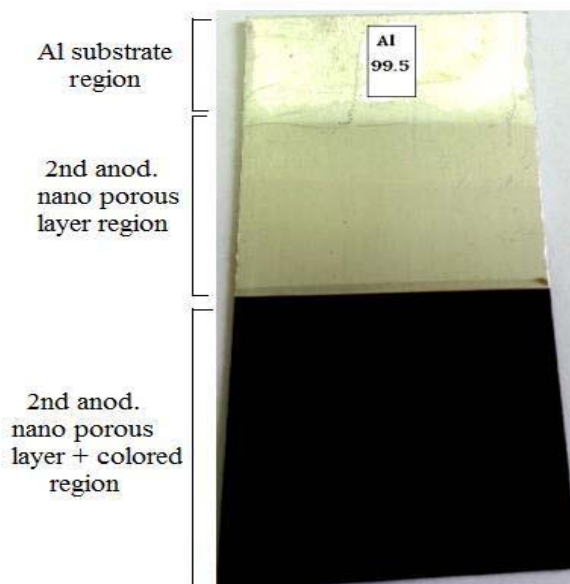
amenable to applications. The present research gives much in more reduction in energy consumption factors as can be deduced from Table-1. Extra refrigeration, required by other researchers, represents additional process costs. The use of the proposed step shows a considerable energy saving, as the total average energy estimated was 0.00125 KWh/cm<sup>2</sup> for first anodization step and 0.00102 KWh/cm<sup>2</sup> for the second anodization step.

**Table-1.** Ranges of variables used in two- step anodization for previous researches.

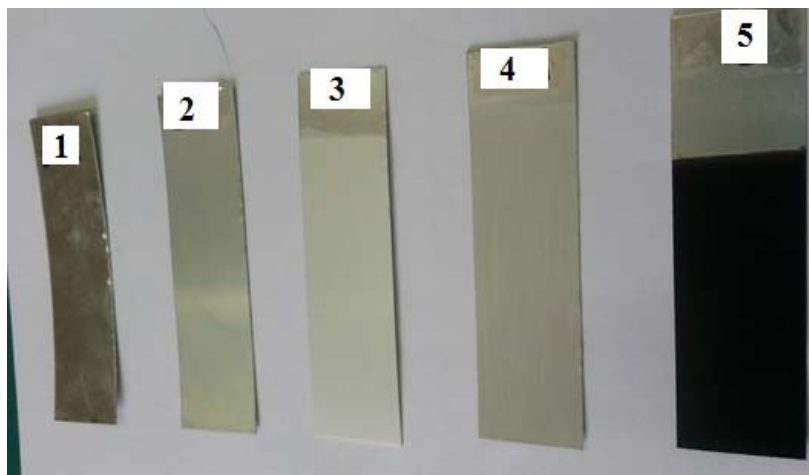
Research author (s) step	Year	Anodization	V, volts	I, mA/cm <sup>2</sup>	t, min.	T, °C
Shih. H .H <i>et al.</i> [13]	2006	First	20-60	-	30	20
		Second	20-60	-	30	20
Zhu. Z <i>et al.</i> [17]	2011	First	40	-	3600	2
		Second	20-60	-	30-60	2
Abbas. M. M [18]	2013	First	8	-	60-180	18
		Second	18	-	60-180	18
Samantilleke. A. P <i>et al.</i> [6]	2013	First	17-20	-	60	5
		Second	17-20	-	120	5
Mukhurov. N. I <i>et al.</i> [1]	2014	First	Up to 110, 160	Up to 70, 80	10	5
		Second	Up to 140, 150	Up to 40, 70	25-45	5
Present Research	2015	First	15	166	15	17
		Second	15	203	30	17

### Black coloration of AAO films

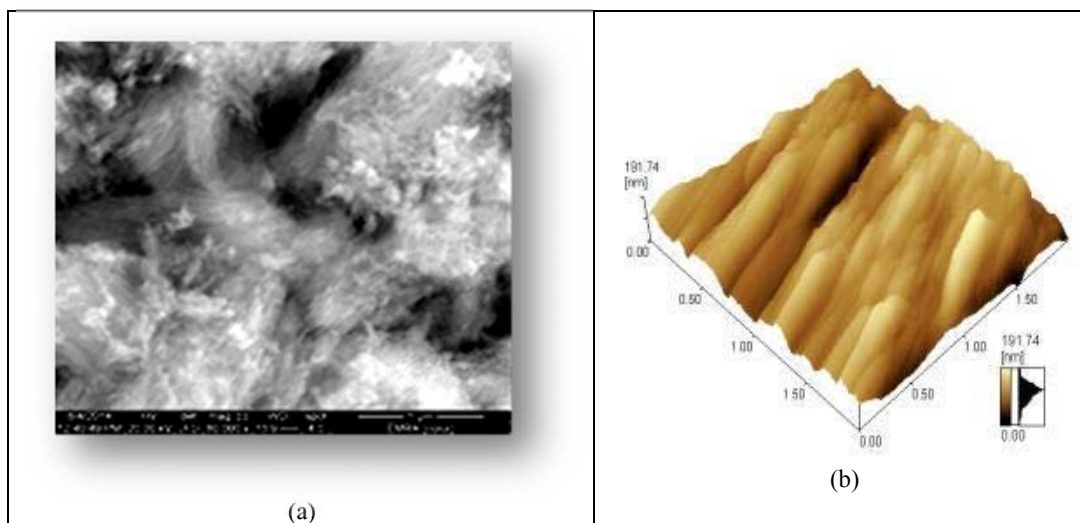
Figure-6 reveals the coloured sample with three different regions, Al substrate, second anodized and coloured regions. Highly ordered nanoporous AAO coating was prepared by anodic oxidation of aluminium surface in 170 g/l sulphuric acid. Figure-7 reveals the variation of the surface aspects after each step; aluminium surface was modified by multi steps including preliminary treatment, first anodization, electrolytic detachment and second anodization. Low cost and low hazardous electrolytic detachment step was suggested to eliminate almost of non-ordered porous AAO after first anodization step. As shown in Figure-8, it is focusing on the blackened sample which shows deep coloured film with homogenous and smooth texture.



**Figure-6.** Different regions of coloured aluminium sample.



**Figure-7.** Different steps of prepared samples: (a) Aluminium sample (b) 1<sup>st</sup> Anodized sample (c) Electro- detached sample (d) 2<sup>nd</sup> Anodized sample (e) electrolytic ally coloured sample.



**Figure-8.** (a) and (b) SEM and AFM of nanoporous coloured AAO.

## CONCLUSIONS

A new step for nanoporous oxide film preparation was developed to aluminium substrate in two-steps anodization process. It was elucidated in an electrochemical detachment of almost the porous oxide film after first anodization. This proposed step causes a great reduction in electric energy consumption in the process of two steps anodization. More power saving was affected in refrigeration requirements during the process. The toxic chromic acid used previously for chemical detachment step was avoided. Hence a great benefit in environmental impact was attained. The nanoporous construction produced shows an extra durability represented by hardness values. Moreover, the prepared nanoporous AAO film is suitable for extra quality deep black coloration as efficient solar energy panels.

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## REFERENCES

- [1] N. I. Mukhurov, I. V. Gasenkova, I. M. Andruhovich. 2014. Ordered Growth of Anodic Aluminum Oxide in Galvanostatic and Galvanostatic- Potentiostatic Modes, J. of Materials Science and Nanotechnology. 1: 1-6.



- [2] N. N. Bwana. 2008. Synthesis of Highly Ordered Nanopores on Alumina by two-steps Anodization Process, *J. Nanopart Res.* 313-319.
- [3] H. Moghadam, A. Samimi, A. Behzadmehr. 2013. Effect of Nanoporous Anodic Aluminium oxide (AAO) Characteristics on Solar Absorptivity. *Transport Phenomena in Nano and Micro Scales.* 1: 110-116.
- [4] F. Kadirgan. 1999. Electrochemical Characterization of  $\text{Al}_2\text{O}_3$ -Ni Thin Film Selective Surface on Aluminium, *Turk. J. Chem.* 23: 381-391.
- [5] F. J. Monteiro, F. Oliveira, R. L. Reis, O. C. Paiva. 1992. The morphology and Optical Characteristics of Black Solar Selective Coatings. *Plating and Surface Finishing.* 79: 46-52.
- [6] A. P. Samantilleke, J.O. Carneiro, S. Azevedo, T. Thuy, V. Teixeira. 2013. Electrochemical Anodizing, Structural and Mechanical Characterization of Nanoporous Alumina Templates, *J. of Nano Research.* 25: 77-89.
- [7] D. Nemes, V. Moldovan, E. Bruj, N. Jumate, I. Vida-Simiti. 2011. Porous Anodic Alumina Films Obtained by Two steps Anodization. *Bulletin of the Transilvania University of Braşov Series I: Engineering Sciences.* 4(53) No. 2.
- [8] J. Zhou, Jian-Ping, G. Zhao, C. Zhang, J. Zhao, H. Hu. 2007. Alumina Nanostructures Prepared by Two-steps Anodization Process, *Trans. Nonferrous Met. SOC. China.* 17: 82-86.
- [9] C. H. Huang, H. Y. Lin, Y. Tzeng, C. H. Fan, C. Y. Liu, C.Y. Li, C.W. Huang, N.K. Chen, H.C. Chui. 2012. Optical Characteristics of Pore Size on Porous Anodic Aluminium Oxide Films with Embedded Silver Nanoparticles, *J. of Sensors and Actuators A: Physical.* 180: 49- 54.
- [10] S. Shingubara. 2003. Fabrication of Nanomaterials Using Porous Alumina Templates, *J. of Nanoparticle Research.* 5: 17-30.
- [11] F. Li, L. Zhang, and R. M. Metzger. 1998. on the Growth of Highly Ordered Pores in Anodized Aluminium Oxide, *Chem. Mater.* 10: 2470-2480.
- [12] A. M. Abd-Elnaiem, A. M. Mebed, A. Gaber, M.A. Abdel-Rahim. 2013. Effect of the Anodization Parameters on the Volume Expansion of Anodized Aluminium Films. *Int. J. Electro chem. Sci.* 8: 10515-10525.
- [13] H. H. Shih, S. L. Tsai, T. T. Wang. 2006. The Study of Electrolytic Coloring after the Second Anodic Treatment of Aluminium Sheet. Thesis for Master of Science Department of Chemical Engineering Tatung University.
- [14] J. Malzbender, J. M. J. Den Toonder, A. R. Balkenende, G. de with. 2002. Measuring mechanical properties of coatings: a methodology applied to nanoparticle-filled sol-gel coatings on glass, *Mater. Sci. Eng.: R: Reports.* 36, 47 47-103.
- [15] J. M. Moon, A. J. Wei. 2005. Uniform Gold Nanorod Arrays from Polyethylenimine-Coated Alumina Templates, *Phys. Chem B.* 109(49): 23336-23341.
- [16] B. O. Odera. 2012. Electrolytic Etching of Platinum-Aluminium Based Alloys, *Platinum Metals Rev.* 56(4): 257-261.
- [17] G. Zhu, R. Cheng, C. Chang, W. Wang, B. Wei, L. Ge. 2011. Growth of alumina oxide nanowires in an aluminium anodization process. *Chinese Sci Bull.* 56(18): 1947-1950.
- [18] A. A. Abbas. 2013. Electrochemical Self-Assembly of Nanoporous Alumina Templates Title. *Advances in Materials Physics and Chemistry.* 3: 244-248.