



Structural Properties of Photocatalytic Copper Pigmented Anodized titanium

Peter c. Owino^{1*}, Maurice M. Mwamburi¹, David Waswa¹, Margaret E. Samiji², Nuru R. Mlyuka², Grace A. Kinunda², Christopher Maghanga³.

¹Department of Physics, University of Eldoret,
P. O. Box 1125 – 30100, Eldoret, Kenya

²Department of Physics, Department of Chemistry, University of Dar es Salaam,
P. O. Box 35063, Dar es Salaam, Tanzania

³Kabarak University, P.O. Box Private Bag, Kabarok, 20157, Kenya
Tel: +254 722 986 967, Email: cmaghanga@kabarok.ac.ke

*Corresponding author e-mail: owinop3@gmail.com

Abstract

The performance of TiO₂ photocatalyst depends on its surface morphology and the orientation of its crystal structure. In this study, commercial pure grade 1 titanium substrate was anodized at 200V for different anodization times, pigmented and annealed for a period of 450^oC for 4 hours. Structural properties of the samples was done using AFM, XRD and SEM. Prolonging anodization time engineered the formation of pores and eventual pore merging on the surface of the TiO₂ film thereby significantly influencing the surface morphology and crystallinity of the sample. The XRD measurements confirmed the coexistence of both rutile and anatase phases in the samples.

Keywords: TiO₂, Photocatalyst, anodization, pigmentation, structural properties.

Introduction

TiO₂ photocatalysts has been widely studied due to its chemical stability, optical properties, biological and environmental benefits. The photocatalytic performance of TiO₂ materials are determined by the morphology and phase composition of the material. TiO₂ materials exist in three phases namely anatase, rutile and brookite. In their single phase structures, anatase has been reported to have the highest photocatalytic efficiency compared to the other two phases (Hanaor et al, 2011). Anatase is mostly the first phase formed during titanium treatment due to its constrained structural re-arrangement which forms this phase from an amorphous precursor and a lower surface energy compared to the rutile phase (Shin et al, 2005; Zhang and Banfield, 1998). Rutile is deemed to be thermodynamically stable form of the crystal structure at all temperatures, phase transformation from anatase to rutile generally occurs when TiO₂ materials are heated in air in the absence of impurities or dopants at a temperature of 650^oC and above. Dopants such as Cu, Pt and Cr influence the phase transformation from anatase to rutile by changing the oxygen vacancy energy levels and enhancing the structural re-arrangement involved in the transformation (Arroyo et al, 2002). Less research has been carried out on brookite phase due to its reduced photocatalytic activity (Di Paola et al, 2013; Srivatsa et al, 2008). Studies have shown that a mixture of anatase-rutile phase with certain composition ratio exhibits superior photocatalytic performance due to its improved separation of charge carrier



through the trapping of conduction band electrons in the rutile phase (Collins-Martinez et al, 2007; Ohno et al, 2003).

When TiO_2 photocatalyst is illuminated with light of energy higher than the band-gap, an inter-band transition is induced and electron-hole pairs generated. Some of these photogenerated pairs achieve charge separation and diffuse to the TiO_2 surface, react with air or water and eventually generate OH radicals and O^- superanions, which attack the organic compounds adsorbed on the TiO_2 surface, removing them by transforming into CO_2 and H_2O . Thus the surface of TiO_2 photocatalyst converts into a strong oxidizer which attack and clean the water and air by photodestruction of adsorbed contaminants.

Materials and Methods

The pre-treatment processes vary from rinsing, degreasing and etching. Grade 1 titanium foil of 0.3mm thickness was cut in rectangular pieces of 60mm×30mm specimens, the sample was degreased in acetone solution for five minutes at ambient temperature after which etching (Acid activation) followed up. Acid activation was performed in a mixture of nitric acid, hydrofluoric acid and water for 5 seconds to remove the natural titanium oxide layer and surface contaminants after which it was rinsed with distilled water.

Anodization was therefore done in an electrolyte consisting of 0.75M H_2SO_4 , 0.075% wt HF and distilled water which was kept in a bath at a temperature of 25°C, magnetic stirring was done at about 800 rpm throughout the anodizing period. Inter electrode distance of 1cm was maintained with the anode to cathode area ratio of 1:4, with aluminium as the counter electrode. Anodization was done at a constant voltage (potentiostatic) of 200Volts from 20seconds to 30minutes after which the samples were rinsed in de-ionised water thoroughly before drying in air and storing for pigmentation.

The electro deposition cell was prepared with 0.1M $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ electrolyte, pigmentation of the anodized plate was done at 12volts for a period of 5 seconds. The anode was made of copper plate fixed at a distance of 1cm from the titanium cathode plate. Annealing of Titanium plates

Annealing was done by Muffle furnace for a period of four hours at $450^\circ\text{C} \pm 5^\circ\text{C}$. The samples were placed inside Petri dishes, placed in the furnace and the door locked tightly to avoid any contact with the outside environment.

Results and Discussion

Atomic Force Microscopy

The AFM images revealed distinct topography for all samples. The morphology and distribution of the pores were found to be affected by the duration of anodization. The AFM images of the un-anodized Ti sample and those anodized at different time intervals of 1 minute, 2 minutes, 3 minutes, 10 minutes and 30 minutes are as shown in figure 1.

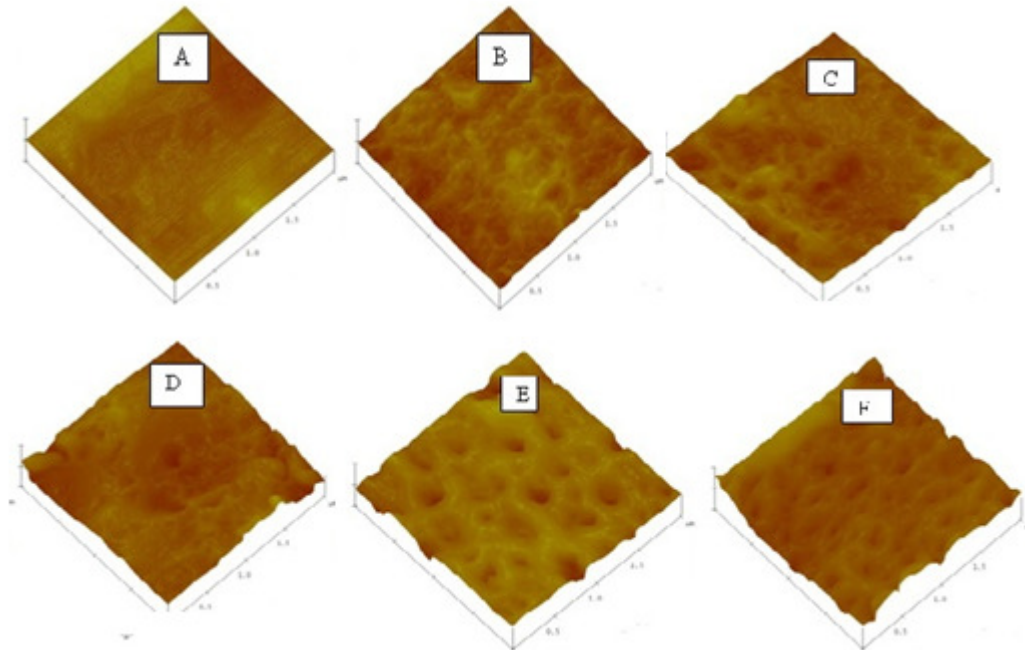


Figure 1: Effect of anodization time on the morphology of the samples, (A) un-anodized Ti (B) 1 minute (C) 2 minutes (D) 3 minutes (E) 10 minutes and (F) 30 minutes.

Before anodization, the surface of metallic titanium sample was smooth and homogeneous as seen in figure 1 A. Figure 1 B, C and D shows that in the initial stages of anodization, there is uneven distribution of the oxide layer on the Ti samples with a low surface roughness. For longer anodization time, the formation of pores becomes more pronounced and unevenly distributed. Each sample scanned at different positions exhibited the same topography but with a slight shift in the surface features. The Ti sample anodized for 30 minutes exhibited unique features as shown in figure 2. The image shows an inhomogeneous distribution of surface features with a continuous oxidation of the surface on some parts of the sample but not on other parts. This finding can be explained based on the three processes namely, field-enhanced oxidation of titanium foil, field-assisted oxide dissolution, and chemical oxide dissolution (Quanet *al*, 2005).

During field-enhanced oxidation, titanium metal undergoes a process of oxidation leading to the growth of an oxide layer on the metals' surface, as the oxygen ions in the electrolyte solution move towards the interface of the metal and the oxide layer. During field-assisted oxide dissolution, the oxide layer dissolves into the electrolyte due to the movement of titanium ions from the metal-oxide interface through the oxide layer into the solution. The presence of hydrofluoric acid (HF) in the electrolyte helps in accelerating the rate of dissolution of the oxide layer by consuming titanium ions in solution (Gonget *al*, 2001). Since this process has no restriction to the occurrence of pores and pore widening, the extensive dissolution of the oxide layer taking place when the anodization period is prolonged results to pore merging and the eventual loss of the pore structures as seen in figure 2.

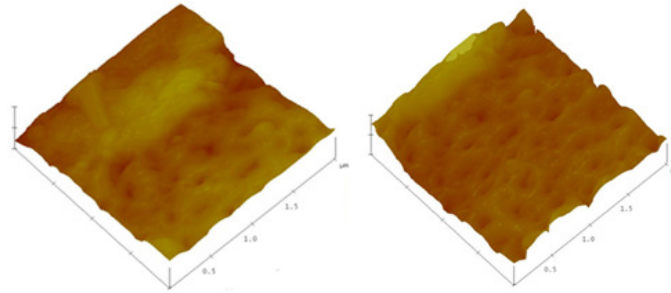


Figure 2: Surface morphology of sample taken at different positions and anodized for 30 minutes.

Surface roughness

Surface roughness is an important characteristic of the oxide film and significantly affects its properties. In order to investigate the effect of anodization on the surface roughness of the oxide film, the average surface roughness (Ra) and root mean square of the sample roughness (Rms) were obtained by allowing the software to scan through different sections of two-dimensional AFM samples' morphology. It can be seen from figure 3 that the Ra and Rms of the oxide film on the surface of the sample anodized for 1 minute, 2 minutes, 3 minutes, 10 minutes and 30 minutes are 18.87 and 24.63, 21.46 and 33.04, 39.17 and 51.27, 40.95 and 55.71, 77.08 and 90.81, respectively, which indicates that the roughness of the oxide film increased with the increase of anodization time.

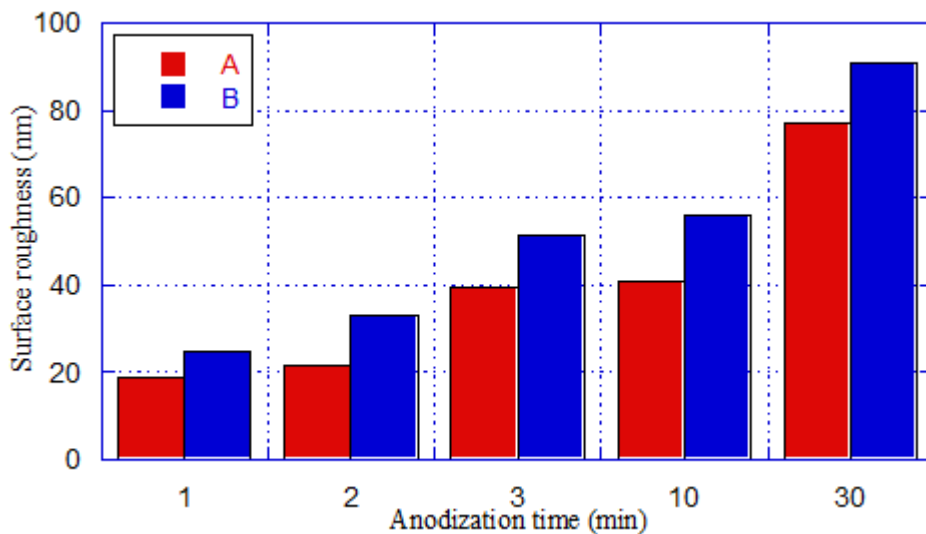


Figure 3: Comparison of sample's surface roughness against anodizing time A) the average surface roughness (Ra) and B) root mean square of the sample roughness (Rms)

Scanning Electron Microscopy

Figure 4 shows SEM images for samples anodized at 200 V, pigmented and annealed at 450°C for 4 hours at different time intervals of 1 minute, 2 minutes, 3 minutes, 10 minutes and 30 minutes. It is clear that the structure and morphology of the oxide layers on Ti samples change when the duration of anodization is prolonged.

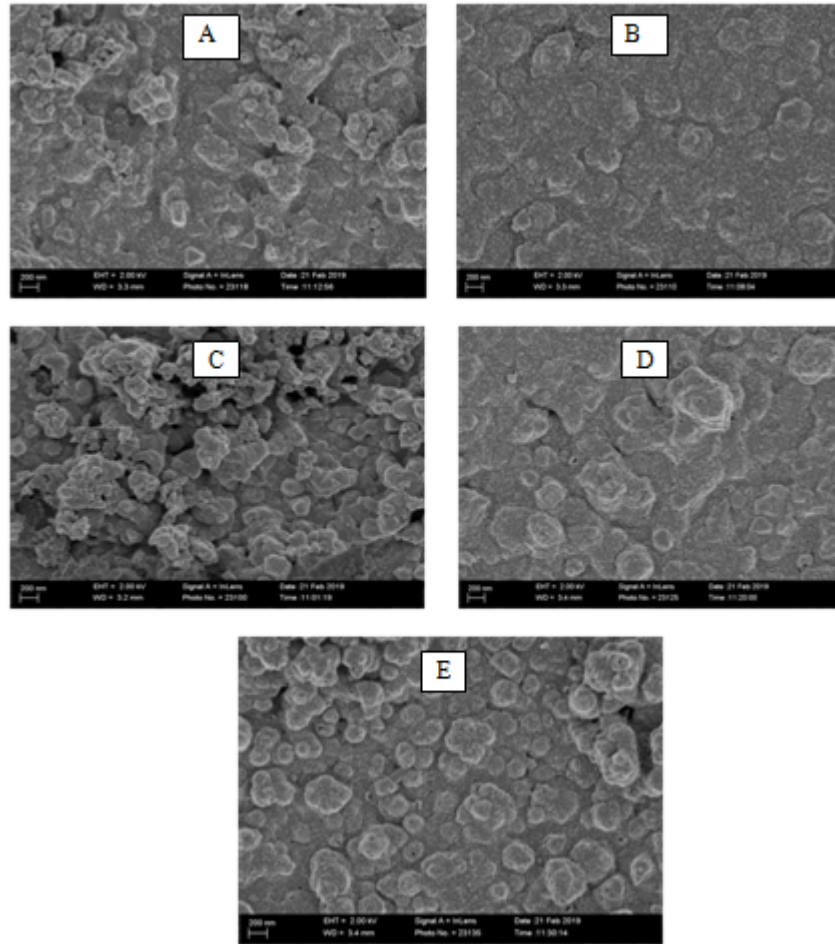


Figure 4: SEM images for samples anodized at 200 V, pigmented and annealed for 450°C for 4 hours. (A) anodized for 1 min, (B) 2 min, (C) 3 min, (D) 10 min and (E) 30 min.

The sample shown in Figure 4(A) exhibited hilly like features which represents the formation of the metal oxide layer with porous structure, implying that Ti starts to be oxidized to Ti^{4+} ions at the surface layer of the Ti metal sample at this stage. Figure 4(B) shows an almost compact and smooth surface morphology after anodization period of 2 minutes. It is interesting to note that by prolonging the anodizing time to 3 minutes, a layer of flower shaped features with irregular grains forms and covers the top layer of the TiO_2 sample as seen in Figure 4 (C). Figure 4 (D) showed irregular grains with tiny cracks as samples are anodized for 10 minutes. In Figure 4 (E), the surface structure appears to be compact with formation of hill like structures in some sections of the sample. The whole process of grain and pore formation is due to the Electric field dissolution which is induced under applied potential, which eventually produces pores and grain

like structures. It is noteworthy that field-assisted oxidation and dissolution involves the formation of an oxide layer and the dissolution of that oxide.

X-ray diffraction measurement

Figure 5 shows a typical XRD pattern of TiO₂film anodized at different time intervals, pigmented and annealed for duration of 450 °C for four hours. The samples had diffraction peaks at 2θ values of 27.9°, 37.0°, 61.81° and 69.5°, that can be readily attributed to (110), (101), (002) and (112) planes which correspond to a tetragonal crystal structure of rutile phase, while the peak at 38.8°, 51.75° and 75.1° can be attributed to the (004), (105) and (215) plane of anatase TiO₂. This confirms the coexistence of both rutile TiO₂ and anatase TiO₂ phases in the annealed samples. The diffraction peak at 61.81° identified the presence of CuO coordinated to the metal cation Ti⁴⁺.

The intensity of the (101) peak is the strongest in all peaks corresponding to rutile phase which indicates that the growth of TiO₂ is highly oriented along the (101) plane. Diffraction peaks (110) and (004) grew in intensity compared to the unanodized TiO₂ sample with peak (110) being more intense at anodization time of 1 min.

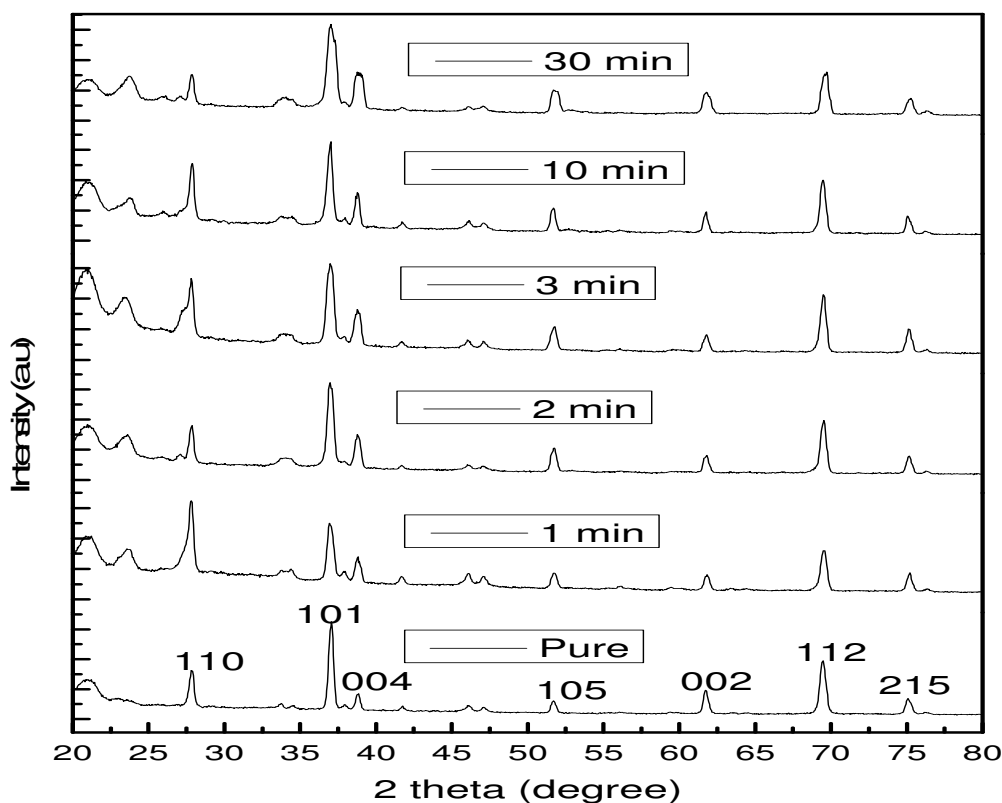




Figure 5: XRD patterns of TiO₂ anodized at 200 V, pigmented and annealed at 450 °C for 4 hours with anodizing time of 0min for pure sample, 1 minute, 2 minutes, 3 minutes, 10 minutes and 30 minutes.

The mean crystallite size of TiO₂ films was calculated using the Scherrer’s formula

$$D = \frac{K\lambda}{\beta \cos\theta} \tag{1}$$

Where, D is the average crystallite size, λ is the X-ray wavelength, β is the full width at half maximum (FWHM) of the dominant peak and θ is the Bragg angle. The pure unanodized TiO₂ film exhibited a crystallite size of 0.37 nm which was higher than the anodized ones. At 1 minute, 2 minutes, 3 minutes, 10 minutes and 30 minutes there crystallite size was 0.19 nm, 0.22 nm, 0.25 nm, 0.26 nm and 0.18 nm. This trend shows an increase in the crystallite size from 1 minute of anodization then an abrupt decrease towards anodization time of 30 minutes.

The dislocation density was calculated using the relations

$$\delta = \frac{1}{D^2} \tag{2}$$

From the calculation, the dislocation density decrease with increase in anodization time which implies a decrease in lattice imperfection due to the increase in crystallite size. At anodization time of 30 minutes, the dislocation density increases.

The micro strain was calculated using the relations

$$\varepsilon = \frac{\beta \cos\theta}{4} \tag{3}$$

The strain gets lower for increasing anodization time but increases at 30 minutes.

Table 1 shows the effect of anodization time on the average crystallite size (D), dislocation density (δ) and micro strain (ε) of the samples

Anodization Time	Average Crystallite size (D)	Dislocation Density (δ)	Micro Strain (ε)
1 minute	0.19	27.7	0.186
2 minutes	0.22	20.7	0.166
3 minutes	0.25	16.0	0.142
10 minutes	0.26	14.8	0.139
30 minutes	0.18	30.9	0.199



Conclusion

Prolonging the anodization time engineers the formation of pores, pores merging and eventual loss of pore structure of the TiO₂ film thereby significantly influencing the surface morphology and crystallinity of the sample.

The XRD measurements confirmed the coexistence of both rutile and anatase phases in TiO₂ samples anodized at 200V, pigmented and annealed at a temperature of 450⁰C for 4 hours.

Acknowledgement

The authors wish to thank Kabarak University, University of Dare salaam and International Science Programme (ISP) of Uppsala, Sweden for supporting this work.

References

- Arroyo R, Cordoba G, Padilla J and Lara V. (2002), *Materials Letters*, 54, 397-402.
- Collins-Martinez V, Ortiz A and Elguezabal A. (2007), Influence of the anatase/rutile ratio on the TiO₂ photocatalytic activity for the photodegradation of light hydrocarbons. *International Journal of Chemical Reactor Engineering*. 5.
- Di Paola A, Bellardita M and Palmisano L. (2013), Brookite, the least known TiO₂ photocatalyst. *Catalysts*. 3(1): p. 36-73.
- Gong D, Grimes C, Varghese O, Hu W, Sing R, Chen Z and Dickey E. (2001). Titanium oxide nanotube arrays prepared by anodic oxidation, *J.Mater.Res.*,16, 3331.
- Quan X, Yang S, Ruan X, and Zhao H. (2005). Preparation of titania nanotubes and their environmental applications as electrode, *Environ.Sci.Technol.* 39, 3770-3775.
- Srivatsa K., Bera M and Basu A. (2008), Pure brookite titania crystals with large surface area deposited by plasma enhanced chemical vapour deposition technique. *Thin Solid Films*. 516(21). 7443-7446.
- Hanaor D, Triani G, Sorrell C. (2011), *Surface and Coatings Technology* 205(12), 3659-3664.
- Ohno T, Tokieda K, Higashida S and Matsumura M. (2003), *Applied Catalysis A*,244, 383-391.
- Shin H, Jung H, Hong K and Lee J. (2005), *Journal of Solid State Chemistry*, 178,15-21.
- Zhang H, and Banfield J. (1998), *Journal of Materials Chemistry*, 8, 2073-2076.