Optical characterization of photocatalytic copper doped thin films of anodized titanium

Julia Rotich 1, Mghendi Mwamburi 2, Njoroge Walter 1, Christopher Maghanga 1, Onesmus Munyati 4 and Sylvester Hatwaambo 1

1 Kenyatta University, Kenya
2 University of Eldoret, Kenya
3 Kabarak University, Kenya
4 University of Zambia, Zambia

E-mail: juliarotich@gmail.com

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Abstract

Titanium oxide is used in a myriad of applications such as in capacitors, insulation paints among others. It is a prime candidate for water splitting due to its photocatalytic properties. In this work, undoped TiO2 thin films were prepared by anodizing titanium foils cut into pieces measuring 60 mm by 20 mm. The specimens were anodized in an electrolyte consisting of 0.5 M H2SO4 and 0.075% wt HF at room temperature. The anodizing voltages ranged from 50 V to 100 V. Anion doping of copper in as anodized TiO2 was done electrochemically. The as anodized Ti foils were dipped in a 1 M Cu2SO4 solution. All samples were annealed at 450 °C for 3 h. Near-normal total reflectance was measured on as anodized and copper pigmented samples in the solar (300–2500 nm) wavelength range. Spectro-photometric reflectance data was analyzed to obtain the absorption coefficient and using the same to determine the band gap of the films. It was noted that the films exhibited reduced solar integrated reflectance for TiO2 samples prepared at lower anodic voltages of 50, 60 and 70 V. The copper pigmented, and annealed, TiO2 samples exhibited both direct and indirect energy band gaps in the ranges, 3.38–3.86 and 2.50–2.74, respectively. Further, annealing and copper doping of the films lead to increased absorption. The photocatalytic activity of the films was assessed by measuring the rate of degradation of 10 ppm methylene blue in UV light source. Copper doped TiO2 exhibited enhanced photocatalytic performance in compared to pure TiO2. An increase in the anodization voltage caused subsequent increase in photocatalytic activity of films with 70 V as the optimum voltage above which photo degradation of methylene blue decreased.

1. Introduction

Titanium dioxide (TiO2) is used in a myriad of applications and is extensively being studied due to its excellent chemical stability and non-toxicity. It is a prime candidate for water splitting due to its photocatalytic activity (Zaleska, 2008). It is also an excellent material which shows most promising prospect in environmental (air) purification and self-cleaning surfaces (Ohko et al 2001). The photocatalytic activity of TiO2 is observed under UV irradiation, but it can only trap 5% of the solar energy that actually reaches the Earth. Several modification strategies for improving the optical and photocatalytic properties of TiO2 have been proposed and adopted including doping with transition metals (Fuerte et al 2001), doping with non-metals (Liu et al 2005) and dye sensitization (Chatterjee and Mahata 2001). Different methods have been used to synthesize copper doped TiO2 thin films such as chemical vapor deposition (Sun et al 2008), sol-gel deposition (Morozova et al 2009), e-beam evaporation (Sun and Hou, 2004), spray pyrolysis (Natarajan et al 1998) and reactive magnetron sputtering (Boukrouh et al 2008). Among all these techniques, anodization is widely used because by controlling the anodization parameters, the surface morphology, structure and thickness of TiO2 films can also be controlled (Mura et al 2009). The characteristics of TiO2 films depend on their crystal structure, orientation and
morphology, therefore control of the phase structure of the films during growth is important. This work aims at investigating the optical and photocatalytic characteristics of TiO₂ thin films that were synthesized by anodization method, chemically modified by incorporation of a metal species (Copper) in the TiO₂ lattice, and annealed at 450 °C so as to increase its photo activity is reported.

2. Theory

2.1. Chemical processes during titanium anodization

In voltaic or galvanic electro-chemical cell, a spontaneous reaction happens and electrons stream from anode (oxidation) to cathode (reduction). Inside an electrolytic cell, a non spontaneous reaction occurs utilizing energy coming out from external sources. Electrons are forced from the external circuit in the cathode to generate the reduction process. They are further attracted to external circuit in the anode pole to generate oxidation process. A number of metals form an oxide coating on the surface as the metal is electrolytically oxidized. As this oxidation happens at the anode pole, the procedure is known as anodizing.

Titanium foil is oxidized (anodized) by the following reaction.

\[
\text{Ti} + 2\text{H}_{2}\text{O} \rightarrow \text{TiO}_2 + 4\text{H}^+ + 4\text{e}^-
\]

So that one can know process of anodic oxide formation, a simplified model of chemistry is involved. The outer anodic layer (partially uncovered to the electrolyte) has a supply of hydroxyl ions in contrast to the inner layer (Macak, et al 2006) and is believed to be Ti(OH)₄. Inner layer, where de-hydroxylation of film (water releasing) has happened is symbolised as TiO₂. There can be a concentration gradient across the film, that can be recorded as TiO₂, xH₂O, to signify the internal (dry) and external (hydrated) anodic oxide. The reactions which happen at the anode were:

(i) Oxidation of the metal that discharge Ti⁴⁺ ions and electrons,

\[
2\text{Ti} \rightarrow 2\text{Ti}^{4+} + 8\text{e}^-
\]

(ii) Combination of Ti⁴⁺ ions with OH⁻ and O²⁻ species provided by water.

\[
\text{Ti}^{4+} + 4\text{OH}^- \rightarrow \text{Ti(OH)}_4
\]

\[
\text{Ti}^{4+} + 2\text{O}^{2-} \rightarrow \text{TiO}_2
\]

Equations (3) and (4) given above describe the hydrated oxide layer and the anodic layer. Extra oxide is generated during the period when hydrated anodic layer discharge water by a condensation reaction equation 5 below,

\[
\text{Ti(OH)}_4 \rightarrow \text{TiO}_2 + 2\text{H}_2\text{O}
\]

At cathode, there is evolution of hydrogen,

\[
8\text{H}^+ + 8\text{e}^- \rightarrow 4\text{H}_2
\]

By adding up the equations from (1) to (5), the whole procedure of oxide generation is denoted as:

\[
\text{Ti}^+ + 2\text{H}_2\text{O} \rightarrow \text{TiO}_2 + 2\text{H}_2
\]

The production of oxygen at anode (equation (7)) has been earlier described as a side reaction in the development of a barrier layer (Rahim 1995) and nano-tubular anodic titania (Paulose et al 2006)

\[
2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{e}^- + 4\text{H}^+
\]

The oxide coatings in the titanium, nevertheless, operate as a diffraction grating and divides white light into its colours so that no dyeing is required. The surface colour relies on the thickness of oxide layer in the surface that is controlled by voltage applied in the anodizing procedure.

2.2. Band gap determination/absorption coefficient

The optical energy band gap of pure and copper doped TiO₂ was determined using the tauc plot extrapolation method. From the equation;

\[
\alpha \cdot h \cdot \nu = B(h \cdot \nu - E_g)^n
\]

Where \( \alpha \) is the absorption coefficient which is proportional to the absorbance, \( h \) is the Planck’s constant (J.s), \( B \) is the absorption constant, \( E_g \) is the band gap energy, \( \nu \) is the light frequency (s⁻¹) and \( n \) is a constant related to the electronic interband transition. \( n = 2 \) for an indirect allowed transition (plotted as \((\alpha \cdot h \cdot \nu)^{1/2} \) versus \( E \)), \( n = 3 \) for an indirect forbidden transition, \( n = 1/2 \) for a direct allowed transition (plotted as \((\alpha \cdot h \cdot \nu)^2 \) versus \( E \)).
Plotting $(\alpha h\nu)^{1/n}$ or $(\alpha h\nu)^n$ as a function of photon energy (E), the band gap energy value is obtained by extrapolating until $(\alpha h\nu)^{1/n} = 0$ or $(\alpha h\nu)^n = 0$ the linear section of this spectra. Considering TiO$_2$ as both direct and indirect allowed transition, the band gap energy obtained for pure TiO$_2$ and copper doped TiO$_2$ samples are as shown in tables 3 and 4.

2.3. Integrated reflectance
The integrated reflectance is evaluated by averaging the spectral-reflectance data over the standard AM1.5 solar-irradiance data $G(\lambda)$ (ASTM G173-03 2012) using the formula by Dufﬁe and Beckman (1991);

$$R = \frac{\int_{300}^{2500} G(\lambda)R(\lambda)d\lambda}{\int_{300}^{2500} G(\lambda)d\lambda}$$

Where $R$ is the integrated reflectance, $G(\lambda)$ is the standard AM 1.5 solar irradiance data and $R(\lambda)$ is the spectral reflectance data.

3. Experimental methods

3.1. Anodization
Commercially pure Titanium Grade 1 foil (TiGr1-FL-080-01-03) was selected as experimental material for this study (William Gregor Ltd shop). The foil was cut into pieces measuring 60 mm by 20 mm. The titanium specimens were ultrasonically cleaned in acetone for 15 min after which they were subjected to chemical etching for 5 s (89% distilled water + 69% Nitric acid + 49% HF respectively). Finally they were again cleaned in acetone, rinsed with distilled water and dried in air. Anodization was carried out in an electrolytic cell with the prepared sample (Ti) as anode and aluminium plate whose acreage was four times that of the anode was used as the cathode. Electrode distance of 10 mm was kept constant throughout the anodization process using an electrode separator.

The specimens were anodized in an electrolyte consisting of 0.5 M H$_2$SO$_4$ and 0.075% wt HF at room temperature. Magnetic stirring at about 800 rpm was done throughout the anodizing period. The anodizing voltages applied were arranged from 50 V to 100 V. For each anodizing potential, current was recorded using a multimeter connected to the anodizing equipment. Two anodized titanium specimens were prepared at each 10 V increment. Anodization was done for a period of 120 s after which the specimens were removed from the anode, rinsed with deionized water, dried in air and stored for characterization.

3.2. Copper pigmention/doping
Anion doping of copper in as anodized TiO$_2$ was done by electrochemical technique. The as anodized Ti was dipped in 1 M Cu$_2$SO$_4$ electrolyte for 3 s after which they were annealed at 450 °C in a Carbolite 301 furnace with a ramp dwell programme for temperature control. The temperature was raised to 450 °C at a rate of 3 °C min. They were kept at that temperature for 2 h followed by a natural cool down. After cooling, the samples were removed and stored for further characterization.

3.3. Optical characterization

3.3.1. Reflectance
Near-normal reflectance for all the samples; as anodized and copper pigmented were measured in the 300 < $\lambda$ < 2500 nm range by use of a UV/VIS/NIR Perkin-Elmer Lambda 19 double-beam spectrophotometer equipped with an integrating sphere. A barium sulphate film was used as a reflectance standard.

3.3.2. Film thickness estimation
TiO$_2$ film thickness values were obtained using the drude model of the SCOUT software. From the computer simulated reflectance data, the various film thickness values were obtained.

3.3.3. Optical band gap and optical constants
Tauc’s extrapolation method was used to determine the optical band gap of the TiO$_2$ thin films. The computer simulated data was fitted into the experimental data to obtain the optical constants. SCOUT (Theiss 2002) changes the model parameters to produce a reflection spectra that match up to experimental reflection spectra as shown in figure 1. The required optical constants were then obtained from the fit parameters and were used to calculate the band gap energies for the different TiO$_2$ thin films.
3.4. Photocatalytic characterization

The photocatalytic activity of copper doped TiO$_2$ was assessed through degradation of Methylene Blue (MB) which was in aqueous solution under UV light. Methylene Blue aqueous solution was considered as the standard pollutant to check the photocatalytic activity. Before each photo-degradation experiment, the TiO$_2$ catalyst films (both Cu-doped and pure TiO$_2$) were immersed into 40 ml solution of MB with concentration of 10ppm and magnetic stirring in darkness for 1 h to determine adsorption—desorption equilibrium. The films were then irradiated with UV light from a CAMAG UV Cabinet showing main emission line at 366 nm for 5 h to decompose the contaminant. 1 ml solution samples were drawn at 30 min intervals for the decolourization of Methylene Blue solution at its optimum absorption wave length (664 nm) to be measured and recorded through UV–vis spectrophotometer (SP-3000nano, OPTIMA with wavelength spanning from 190 ~ 1100 nm) as a function of exposure time. The experimental outcomes were the mean of three experiments that were repeated. For comparison, dye solution (Methylene Blue) without catalyst was performed within similar conditions. This was done to estimate the rate of photolysis of MB in UV light.

4. Results and discussion

4.1. Reflectance

The UV–vis reflectance spectra for the sample that is; as anodized (Pure TiO$_2$), copper doped TiO$_2$ is shown in figure 2. Compared with the reflectance of pure TiO$_2$, it was observed that Cu-doped TiO$_2$ have a higher light harvest performance as shown by the decrease in integrated reflectance and increase in its UV absorption peaks. This shows that visible absorption is closely related to incorporating metal ions in the host lattice (titanium) as reported by Vu et al (2010). The longer wavelength absorption can be assigned to the formation of impurity level within the band gap of TiO$_2$ (Cong et al 2007) where Cu$^{2+}$ ions in the host lattice of TiO$_2$ create oxygen vacancies due to the charge compensation effects and this may shift the optical absorption of Cu–TiO$_2$ in the Visible light region as reported by Sahu, M., & Biswas, P. (2011).

4.1.1. Integrated reflectance

Integrated spectral data for all TiO$_2$ samples prepared using 50 V, 60 V, 70 V, 80 V, 90 V and 100 V anodic voltages were computed as shown in table 1. The integrated reflectance values for copper doped TiO$_2$ samples are lower compared to pure TiO$_2$ samples as shown in table 1. This shows that doping decreases the reflectance hence making the films more absorbing. A significant drop in the integrated reflectance is observed for copper doped samples fabricated at 50 V, 60 V and 70 V while slight drop is observed for samples fabricated at 80 V, 90 V and 100 V. An increase in the anodization voltage results to a decrease in the roughness factor of the films which can lead to the decrease in the size of the nanopores of the films and therefore dopants of copper cannot be well incorporated into the TiO$_2$ lattice.
4.2. Estimated thickness

Table 2 shows the summary of the estimated thicknesses obtained.

| Sample         | Thickness (nm) |
|----------------|----------------|
| TiO₂ (50 V)    | 148.1          |
| TiO₂ (60 V)    | 151.3          |
| TiO₂ (70 V)    | 173.7          |
| TiO₂ (80 V)    | 188.4          |
| TiO₂ (90 V)    | 193.9          |
| TiO₂ (100 V)   | 197.3          |

4.3. Optical constants

4.3.1. Optical Constants; extinction coefficient, $k$ and refractive index, $n$

Figures 3 and 4 show the variation in extinction coefficient and refractive index of the films with wavelength of the anodized (pure) and Cu-doped TiO₂ films synthesized at different anodization voltage respectively. Both optical constants $n$ and $k$ increase with doping and the values decrease with increasing wavelength in the UV region. The decrease in the values of extinction coefficient with wavelength can be attributed to the films normal dispersion behavior. These findings confirm that there is a decrease in the loss of light with increase in wavelength due to scattering and absorbance.

For pure TiO₂, the extinction coefficient value is close to zero, meaning that the film is transparent in the visible region. Band-to-band excitations which is the fundamental transition, causes the change in the extinction coefficient values of the films at lower wavelengths.
The values of the refractive index obtained for pure and doped TiO$_2$ are lower than those obtained before in literature (Bass et al 2009). This can be attributed to difference in thin film structures obtained by different methods. Additionally, refractive index is affected by crystallinity, electronic structure, lattice point defects and/or stresses (Lu et al 1997, Sonmezoglu et al 2013). Based on Pasikhani et al (2016), structural analysis for pure TiO$_2$ obtained by anodization method showed formation of nanotubes with regular honeycomb surface structures with many ordered hexagonal imprint patterns. Structural analysis for pure TiO$_2$ obtained by sol-gel method (Sonmezoglu et al 2016) in this work showed formation of tetragonal anatase form of TiO$_2$.

4.4. Absorption coefficient

To study the optical behavior of anodized (pure) and copper doped TiO$_2$ films, absorption coefficients were obtained from the fitted reflectance spectra (figure 1) and were plotted as a function of wavelength as presented in figure 5. Absorption decreases with increase in wavelength and copper doping increased the absorption coefficient of the films with absorption peaks in the visible light region. This shows that copper helps to expand absorption light spectra to longer region (Yang et al 2015).
4.5. Optical band gap

Figures 6 and 7 illustrates the estimation of band gap energies for two samples by extrapolating the straight line to the E (eV) axis. The band gap energies obtained for TiO$_2$ thin films synthesized by different anodization voltages ranges from 3.79 eV to 3.92 eV for direct allowed transition and 3.08 eV to 3.44 eV for indirect allowed transition. The calculated indirect $E_g$ values for copper doped annealed TiO$_2$ anodized at 50 V, 60 V, 70 V, 80 V, 90 V and 100V are 2.53 eV, 2.52 eV, 2.50 eV, 2.65 eV, 2.74 and 1.79 eV respectively.

The band gap energy decrease with copper doping and decreases even more with annealing as shown in tables 3 and 4. These results suggest that Cu doping certainly causes absorbance of visible light by TiO$_2$. Doping with transition metals can extend the absorption edge of TiO$_2$ to visible light due to its electronic characteristics by inserting new electronic states into the original band gap (Wang et al 2014), which is why electrons can be excited from the defect state to the TiO$_2$ conduction band by photons of less energy.

4.6. Photocatalytic characterization of TiO$_2$ films

Since the concentration of methylene blue is in a linear relationship with absorbance, its final concentration was established through a linear calibration curve (concentration vs. absorbance) as shown in figure 8.
Figure 9 illustrates the photocatalytic activity of pure and Cu-doped TiO₂ films with different anodization voltages on degradation of 10ppm methylene blue. It was observed that the Cu-doped anodized TiO₂ exhibited enhanced photocatalytic activity in relation to that of anodized (pure) TiO₂ and sample anodized at 70 V showed the best photocatalytic performance among them.

The degradation of MB follows the order: MB (without catalyst) < pure TiO₂ < Cu–TiO₂ (50 V) < Cu–TiO₂ (60 V) < Cu–TiO₂ (70 V) > Cu–TiO₂ (80 V) > Cu–TiO₂ (90 V) > Cu–TiO₂ (100 V). Photodegradation of MB follows first order reaction kinetics which is expressed as:

\[ \ln\left(\frac{C_0}{C}\right) = kt \]

Where; \( C_0 \) is the initial concentration, \( C \) is the concentration at time \( t \), \( k \) is the reaction rate coefficient (RRC) or rate constant (hr\(^{-1}\)) and \( t \) is the reaction time. Table 5 gives the degradation rate constant \( k \) of different TiO₂ films obtained from linear fitting of \( \ln(C_0/C) \) versus irradiation time graph shown in figure 10. For the Cu-doped TiO₂ anodized at 70 V, \( k \) was found to be 0.035 h\(^{-1}\) which was 2.3 times higher when evaluated against pure TiO₂ (\( k = 0.015 \) h\(^{-1}\)) and 3.9 times higher than MB without a catalyst (\( k = 0.009 \) h\(^{-1}\)).

As shown in table 5, the best photocatalytic degradation recorded was of the sample fabricated at 70 V which had the highest reaction rate constant (0.035 h\(^{-1}\)) and the highest photo-degradation of MB (18.10%) compared to other samples. From figure 11, it is observed that, an increase in anodization voltage from 50 V to 70 V.

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**Table 3. Summary of Direct Band Gap Values (eV).**

| Anodization Voltage | A   | AP  | APA |
|---------------------|-----|-----|-----|
| 50 V                | 3.79| 3.73| 3.63|
| 60 V                | 3.80| 3.76| 3.59|
| 70 V                | 3.86| 3.75| 3.38|
| 80 V                | 3.89| 3.85| 3.70|
| 90 V                | 3.92| 3.88| 3.86|
| 100 V               | 3.60| 3.05| 2.97|

**Table 4. Summary of Indirect Band Gap Values (eV).**

| Anodization Voltage | A   | AP  | APA |
|---------------------|-----|-----|-----|
| 50                  | 3.44| 3.26| 2.53|
| 60                  | 3.33| 2.71| 2.52|
| 70                  | 3.08| 3.06| 2.50|
| 80                  | 3.40| 3.14| 2.65|
| 90                  | 3.31| 3.02| 2.74|
| 100                 | 3.39| 2.33| 1.79|

Figure 7. Indirect band gap plot of anodized TiO₂ (A), Cu-pigmented (doped) TiO₂ (AP) and Cu-pigmented annealed TiO₂ (APA) anodized at 90 V.
Figure 8. MB calibration curve and absorbance peak intensity.

Figure 9. Photocatalytic degradation of MB under UV irradiation.

Table 5. Rate constant, \( k \) (hr\(^{-1}\)) and MB degradation (%).

| Sample                     | Rate constant, \( k \) (hr\(^{-1}\)) | Degradation (%) |
|----------------------------|--------------------------------------|-----------------|
| MB (Without catalyst)      | 0.009                                | 6.00            |
| Pure TiO\(_2\)             | 0.015                                | 9.50            |
| Cu–TiO\(_2\) (50 V)        | 0.029                                | 15.80           |
| Cu–TiO\(_2\) (60 V)        | 0.032                                | 16.40           |
| Cu–TiO\(_2\) (70 V)        | 0.035                                | 18.10           |
| Cu–TiO\(_2\) (80 V)        | 0.024                                | 13.80           |
| Cu–TiO\(_2\) (90 V)        | 0.022                                | 11.90           |
| Cu–TiO\(_2\) (100 V)       | 0.018                                | 10.80           |
resulted to an increase in reaction rate constant. Percentage degradation of methylene blue was computed using the formula,

\[
\left( \frac{C_o - C}{C_o} \right) \times 100
\]

Where \(C_o\) is the initial concentration of methylene blue and \(C\) is the concentration at time \(t\).

An increase in the anodization voltage results to an increment in porosity (Pasikhani et al 2016) which is an efficient blocking layer that prevents the recombination of electrons that are photo generated (Kim et al 2014) leading to the enhanced photo degradation of methylene blue. Based on figure 11, it is also observed that a reduction in the anodization voltage from 100 V to 70 V leads to an increase in the reaction rate constant of the photocatalytic degradation of MB. Based on Pasikhani et al (2016), a reduction in anodization voltage resulted to an increase of the roughness factor of nanotubes. The roughness factor articulates the real surface area improved by the photocatalyst and provides more active sites for photocatalytic reactions and this explains the increase in the photocatalytic activity with the decrease in voltage from 100 V to 70 V.

Cu-doped TiO₂ exhibits improved photocatalytic performance in comparison to that of pure TiO₂ as seen table 5. From the reflectance spectra of Cu-doped TiO₂ (figure 2), a shift to longer wavelengths (red shift) in absorption is observed and this enables much additional light energy to be utilised for photocatalysis i.e. copper help to expand absorption light spectra to longer region. The outcomes are in Yang et al (2015) research findings.
However, a blue shift was observed in the reflectance spectra for the sample fabricated at 90 V and 100 V and this explains the decrease in photo-degradation of methylene blue. Doping produces impurity levels in the band gap of semiconductors and could reduce the band gap. Nonetheless, if these states are available deep in band gap they could act as recombination centres (Molina-Reyes et al 2020) for the photo generated carriers which would prevent the development of hydroxyl radical (OH which is produced with the manifestation of holes in the valence band of the catalyst) and this interaction would reduce the photocatalytic activity related with the holes as observed for samples fabricated at 90 V and 100 V. Since photocatalytic activity is determined by the competition between charge carrier promotion and the recombination rate, photo generated carriers do not get sufficient time to be involved in redox reactions at the surface if the recombination rate is too high (Rehman et al 2009). Inducing impurity energy level through doping TiO₂ with Cu also performs a significant performance in the efficient separation of photo induced electron-hole pair (Sahu and Biswas 2011). Because the valence of Cu²⁺ ions is less than that of Ti¹⁺, doping of Cu would induce oxygen vacancies that act as the active sites for dissociation of water on the surface of TiO₂ and may also capture the holes to prevent the recombination of hole-electron pairs. Hence, the photocatalytic performance is improved as observed for the samples synthesized at 50 V, 60 V, 70 V and 80 V.

5. Conclusion

Anodic films of titanium were successfully formed using sulfuric acid electrolyte. The fabricated TiO₂ thin films depicted improved optical properties as reflected in the increase in the absorption coefficient values for the copper pigmented samples. This shows that copper plays a critical role in expanding the absorption of light to longer region. The thickness of the films increases with increase in the anodization voltage. An increased absorption should lead to an increased photocatalytic efficiency. In this paper, anodization at lower voltages of 50, 60 and 70 V compounded with copper pigmenting and annealing yield the best results. The thickness of the films increases with increase in the anodization voltage. An increase in the anodization voltage also caused an increase in photocatalytic activity of films with 70 V as the optimum voltage above which photo degradation of methylene blue decreased. Structural and morphological characteristics of the fabricated TiO₂ films need to be done so as to co-relate the properties to the optical and photocatalytic behaviour of these films.

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ORCID iDs

Julia Rotich  @ https://orcid.org/0000-0002-5573-6168
Christopher Maghanga  @ https://orcid.org/0000-0002-5311-3346

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