Tanzania Journal of Science 44(4): 65-76, 2018 ISSN 0856-1761, e-ISSN 2507-7961

Electrophoretic Deposition of TiO_2 Thin Films for Photocatalytic Degradation of Organic Pollutants in Water

Francis W Nyongesa[1*], Bernard O Aduda[1] and Wilson G Nyaga[2]
[1]Department of Physics, University of Nairobi, P. O. Box 30197-00100, Nairobi, Kenya
[2]Kenya Airways, P. O. Box 19002-00501, Nairobi, Kenya
**Corresponding author e-mail: fnyongesa@uonbi.ac.ke*

Abstract

In this study, electrophoretic deposition (EPD) technique was used to deposit titanium dioxide (TiO_2) thin films on conducting glass substrates for application in photocatalytic degradation of organic pollutants in water. Phenol was used as a model pollutant. The EPD suspension related parameters and deposition conditions were first optimized for good quality film deposits. The suspension stability and deposition conditions that result in good adherence of TiO_2 particles to the substrate with homogeneous film coatings are ethanol, a TiO_2 solid loading of 4 wt%, a 0.2 wt% iodine concentration in the solvent and a deposition voltage of 20 V in a time of 3.5 minutes. The photocatalytic activity of TiO_2 thin films decreased exponentially with the ultraviolet light (UV) illumination time and it was also dependent on film thickness, and sintering temperature of the TiO_2 thin films. Highest rate of photocatalytic activity was observed at an optimal film thickness of 95 ± 2 µm sintered at 300 °C. The implications of these results are discussed for design of inexpensive wastewater purification systems for light industries as well for semi urban small communities.

Keywords: Electrophoretic deposition, Titanium dioxide, Photocatalysis

Introduction

Today, the whole world is facing a series of environmental problems such as contaminated ground water and hazardous waste effluents from advanced industrialization which have increased the organic contaminants in natural waterways thereby presenting toxicological hazards to plants, marine and animal lives (Bukowska and Kowalska 2003). There is therefore a need to improve water treatment for human consumption and for proper functioning of the ecosystems. Although several techniques have been employed for water treatment such as adsorption, chemical oxidation and biological treatment, most of these methods are however either slow or non-destructive for some more persistent organic pollutants.

One of the most advanced water purification systems is heterogeneous photocatalysis using solar or UV light and a photocatalyst. Heterogeneous photocatalysis employing semiconductor catalysts (TiO_2, ZnO, Fe_2O_3, CdS, GaP and ZnS) has demonstrated its efficiency in degrading a wide range of organics such as alkanes, haloalkanes, aliphatic alcohols, carboxylic acids, alkenes, aromatics, haloaromatics, polymers, pesticides, and dyes into generally harmless carbon dioxide and water (Lazar et al. 2012, Jin-hui 2012, Atul et al. 2013). Among the semiconductor catalysts, titanium dioxide (TiO_2) nanoparticles offer great advantages for detoxification of wastewater since they are inexpensive, non-toxic, biologically and chemically stable. Titanium dioxide, particularly in the anatase form, exhibits higher photocatalytic activity under ultraviolet (UV) irradiation and has a strong oxidizing power to decompose organic contaminants into environmentally harmless compounds such as water and carbon dioxide as shown in Equation (1) (Mathews 1992, Prihod'ko and Soboleva 2013, Atul et al. 2013). Additionally, complete inactivation of microorganisms such as bacteria, viruses and protozoa can also be achieved (Blake et al., 1999).

$$\text{Organic contaminant} \xrightarrow{TiO_2/hv} CO_2 + H_2O \quad (1)$$

Notably, TiO_2 photocatalyst is mostly used to decompose organic contaminants in suspension forms by directly putting it into water ponds, which makes it impossible to be reused again or requires an extra process of filtration of the catalyst. There is therefore a need to develop ways in which this photocatalyst can be used more effectively. One approach is to grow TiO_2 on a substrate and to pass liquid stream of contaminated water over them. However, since the reaction velocity of this photocatalyst is slow, it is important to obtain the most suitable thin film that will exhibit the highest photocatalytic activity that can allow the application of water purification in large scale and at low cost.

One of the most effective methods for fabrication of ceramic coatings and films from powder suspensions is Electrophoretic Deposition (EPD) (Boccacini and Zhitomisrky 2002). The EPD technique of materials is a simple, fairly rapid and cost effective two-step process for thin film preparation. It involves movement of charged particles in a suspension medium followed by deposition of the particles on a substrate under an applied DC voltage (Sarkar and Nicholson 1996, Van der Biest and Vandeperre 1999, Boccacini and Zhitomisrky 2002, Besra and Liu 2007, Kawakita et al. 2009, Narayan and Raturi 2012, Cabanas-Polo and Boccaccini 2016). With EPD, it is possible to prepare homogeneous coated layers and the thickness of deposited films may be controlled by varying the EPD deposition parameters such as the choice of solvent (suspension), the zeta potential (through the charging mechanism), solid loading of the particles in the suspension and the deposition conditions such as the DC voltage and deposition time (Van Tassel and Randall 2006, Besra and Liu 2007, Radice et al. 2010). Different combinations of EPD deposition parameters have been applied by various authors to deposit TiO_2 thin films for applications in Dye Sensitized Solar Cells (DSCs) (Sarkar et al. 1997, Miyasaka and Kijitori 2004, Put et al. 2004, Yum et al. 2005, Bandy et al. 2011, Chiu et al. 2011, Chiang et al. 2015) in ceramic coatings (Allan 1976, Sarkar et al. 1997, Put et al. 2004) and biomedical applications (Ma and Peng 2003, Boccaccini et al. 2010, Narkevica et al. 2017).

In the present study, the effects of EPD deposition parameters (type of solvent and pH of suspension, concentration of TiO_2 in the solvent, deposition time and the applied voltage) on the quality of deposited films have been investigated to determine the optimal parameters for a homogeneous, good-quality TiO_2 deposits. Photocatalytic activity of TiO_2 nanoparticles deposited at optimal parameters was then explored for decomposition of organic contaminants in wastewater using phenol as a model pollutant.

Materials and Methods

Optimization of EPD suspension related parameters

Glass substrates coated with a conducting layer of fluorine doped tin oxide (FTO) were used as the electrodes in EPD cell. The FTO glass substrates were cleaned using detergent solution in a sonicator for 20 minutes and rinsed with distilled water.

They were then sonicated in ethanol for 20 minutes after which they were again rinsed with distilled water in ultrasonic bath. The EPD apparatus consisted of a cell (Pyrex glass beaker) and a DC power supply (Thurlby Thadar TS30225). The electrodes were partially immersed in suspension containing TiO_2 nanopowder (CAS No. 13463-67-7, Aldrich) dispersed in a solvent as shown in Figure 1. The cross section part of the substrate (cathode) and the counter electrode (anode) that was under the suspension were 1.5×1.5 cm^2 and they were placed 1.5 cm apart. The EPD suspension related parameters were optimized by studying the effects of different solvents, the pH and the solid loading of TiO_2 in the suspension, respectively at a deposition voltage of 20 V for 2 minutes. After deposition, the film qualities were studied to determine the optimal deposition conditions in terms of surface quality, i.e., adherence of TiO_2 particles to the substrate, film homogeneity and uniformity.

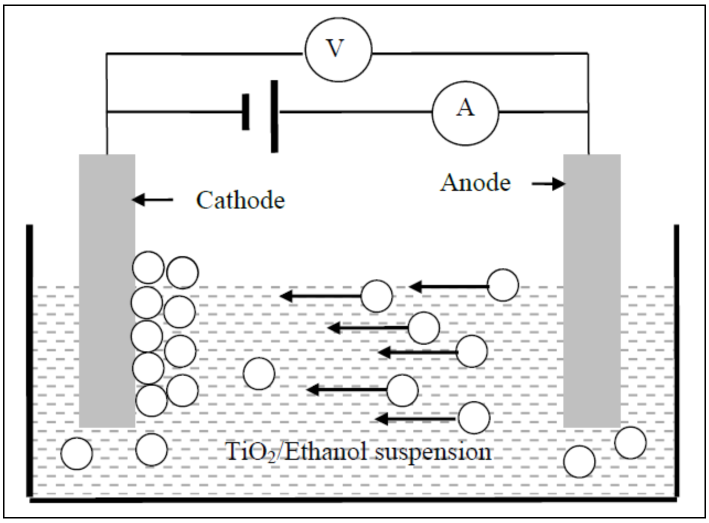

Figure 1: Schematic set-up of the EPD cell.

Different solvents were tested including distilled water, ethanol, 2-propanol (IPA: isopropyl alcohol) and toluene, respectively. The solvents were prepared in glass beakers containing the same solid loading of 3 wt% of TiO_2 nanoparticles. The effect of pH was analyzed using six suspensions with pH values in the range of 1 to 6, obtained by addition of nitric acid to the solvent while keeping the other parameters constant (i.e., 3 wt% TiO_2 solid loading and same solvent as predetermined in previous experiments). The effect of solid loading was investigated by using different TiO_2 solid loadings ranging from 0.1 to 10 wt% TiO_2. The charging mechanism was varied by addition of different amounts of iodine ranging from 01 to 0.80 wt% to the EPD suspension. The amount of iodine is reported as wt% with respect to TiO_2 solid loading in the suspension. For comparison, TiO_2 suspension without any iodine was used as a reference suspension.

Optimization of EPD process-related parameters

By using the predetermined optimized EPD suspension related parameters from previous experiments, EPD was carried out at constant deposition time of 2 minutes using different applied voltages of 10, 15, 20, 25 and 30 V, respectively. Thereafter, EPD was carried out at a constant applied voltage of 20 V and for varying deposition times ranging from 1 to 5 minutes. After deposition, the TiO_2 coated substrates were carefully extracted from the suspension and the weight of the deposit was determined by weighing the electrodes before and after deposition using a 10^{-4} g precision balance (E. Mettler, Zurrich). Some TiO_2 coated substrates were thermally treated in an electric furnace (Nobertherm LH 15/14) at 300 °C, 400 °C and 700 °C, respectively for 3 hours at a heating rate of 5 °C/min to achieve good adhesion.

The film thickness was measured using ALPHA STEP Q equipment. The surface morphology of the films was investigated using a scanning electron microscope (SEM) in a JEOL 5400 microscope. Structural analysis was conducted using Shimadzu X-Ray Diffractometer with Cu Kα radiation with a scanning range of 2θ from 10° to 60°.

Photocatalytic activity of TiO_2

Different concentrations of phenols were made ranging from 5 parts per million (ppm) to 100 ppm by adding phenol crystals to distilled water in a beaker at room temperature. These are the typical concentrations from many industries although the concentrations may go as high as 500 ppm. Photocatalytic activity of the TiO_2 coatings were evaluated in a laboratory set-up where TiO_2 coated glass substrates at optimized parameters, were immersed in 50 mL phenol solution in a beaker and illuminated by UV lamps (CIGIEMME, ITALY) whose dominant emission was centered at 365 nm. For comparison, illumination on similar coated substrates was also done using direct sunlight. The photocatalytic activity of the titania coatings was evaluated based on the decomposition rate of phenol using bromination method (Sprung 1941). The intensity of the UV light was measured using a digital radiometer (SPECTROLINE DSE-100).

Results and Discussions

Effects of EPD deposition parameters on film quality

Ethanol was found to be a better solvent compared to toluene, 2-propanol or water. This was due to its high dielectric constant, ($\varepsilon = 24.3$). Although water has a higher dielectric constant, it caused electrolysis even at low voltages resulting in gas evolution on the electrodes. Suspension conditions that gave good adherence of the TiO_2 particles to the substrate with homogeneous coatings were a pH value of 3, a solid loading of 4 wt% and 0.2 wt% iodine concentrations in the solvent. For a low pH < 3 and a high pH > 5, formation of agglomerates occurred which reduced the deposit mass. This was attributed to a lower zeta potential (Boccacini and Zhitomisrky 2002). Notably, electrophoretic mobility of the particles was the highest at a pH of 3 such that more particles reached the substrate within a short period of time indicating a high zeta potential. This is an indication that the zeta potential increased with increase in the iodine concentration, reaching a maximum and thereafter it decreased with further increase in the iodine concentration probably because most of the available sites for ion adsorption were saturated. A low iodine concentration less than 0.2 wt% was not enough to charge the particles and agglomeration occurred. On the other hand, higher iodine concentrations > 0.3 wt% resulted in undissolved iodine in the solvent with most of the iodine settling at the bottom of the EPD cell with TiO_2

particles attached to them. Lastly, a high solid loading > 4 wt% caused formation of TiO_2 clusters due to high concentration of particles in the solvent resulting in non uniform deposit.

Figure 2 shows the variation in the TiO_2 film thickness with deposition time at constant low deposition voltages. It is observed that the film thickness increases nearly linearly with deposition time but tends to plateau at high deposition durations. This could be attributed to the increase in the resistance of the film attributed to thick film deposits. Figure 3 shows the variation of the deposit mass with deposition time for various applied DC voltages at the optimal EPD suspension parameters. It is observed that for constant applied DC voltage, the film deposition mass increased, first nearly linearly (indicating a constant deposition rate) followed by a plateau at high deposition times greater than 210 seconds. This was attributed to diminishing amount of the TiO_2 particles in the suspension such that fewer particles were available for deposition after long deposition times. Deposition mass remained constant after 210 seconds for voltages of 20, 25 and 30 V, respectively, indicating saturation.

Notably, higher voltages (> 20 V) caused high currents resulting in rapid deposit formation with growth of TiO_2 clusters as shown in the SEM micrograph of Figure 4a. At the same time, an increase in hydrolysis of the solvent occurred thereby interfering with particle deposition due to undesirable formation and entrapment of bubbles within the deposit. These effects increased the resistance of the film causing a reduction in the current with a subsequent reduction in electrophoretic mobility such that fewer particles reached the substrate. Similar observations have been made by Boccacini and Zhitomisrky (2002) in aqueous slurries. For applied voltages of 20 and 25 V, TiO_2 particles adhered well to the substrates and the coatings were homogeneous as shown in Figure 4b. Consequently, 20 V was chosen as the optimal voltage for coating of TiO_2 with a deposition time of 210 seconds.

Photocatalytic activity of TiO_2

The photocatalytic activity of TiO_2 was found to be dependent on film thickness and sintering temperature among other factors such as the intensity of the UV light. Figure 5 shows the variation in the decomposition rate of phenol with UV illumination, using TiO_2 films of varying thicknesses and sintered at 300 °C. It is observed that the decomposition rate decreased nearly exponentially with increase in illumination time irrespective of the film thickness. On the other hand, for a given illumination time, photocatalytic activity increased with increase in film thickness up to an optimal film thickness of 95 ± 2 µm, beyond which, the effect decreased with further increase in film thickness. This is an indication that very large TiO_2 film thickness has the effect of reducing the light penetration depth into the film through absorption and scattering such that less light reaches the TiO_2 particles at the bottom of the film. Consequently, this causes a reduction in the number of electron–hole pairs produced, resulting in less photocatalytic effect. A similar observation was made by Chen and Ray (1999), for a slurry reactor. Complete oxidation of phenol was observed after 10 hours using a film thickness of 95 ± 2 µm.

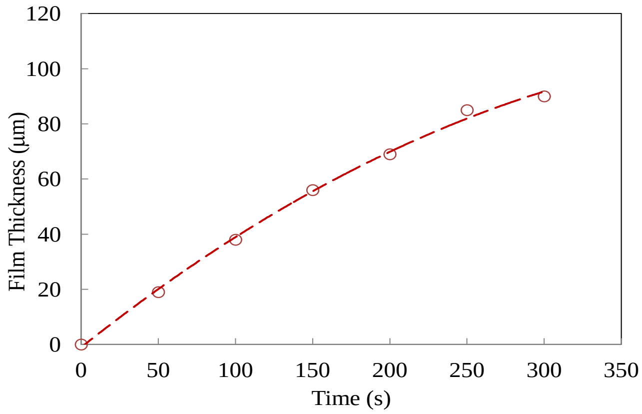

Figure 2: Variation in film thickness of TiO_2 films with EPD deposition time.

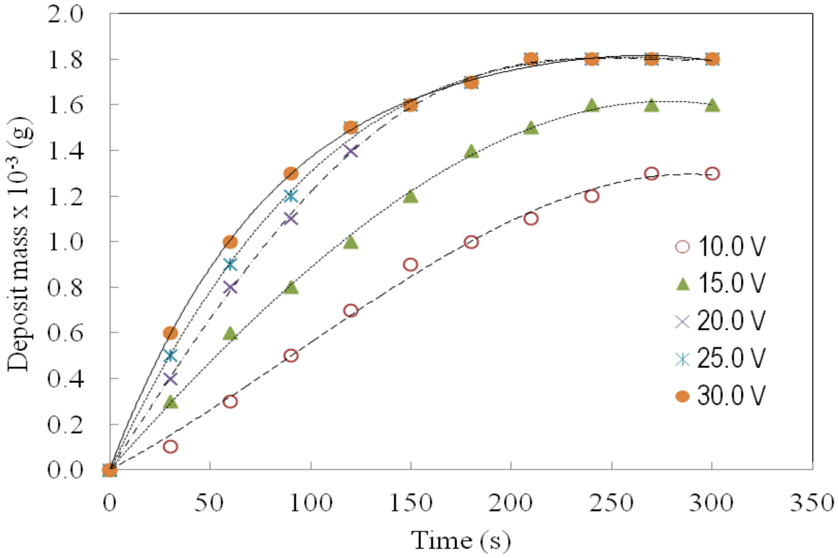

Figure 3: Variation of deposition mass with deposition time for different deposition voltages and a solid loading of 4 wt %.

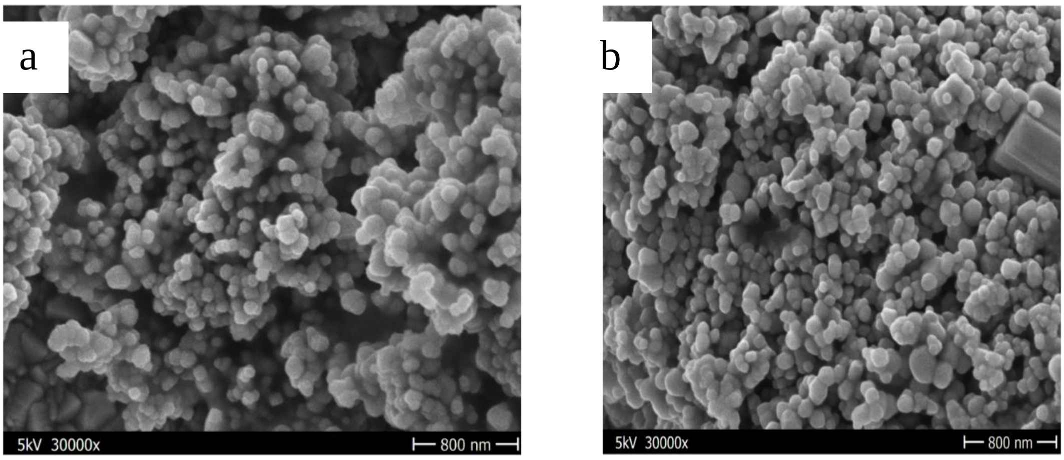

Figure 4: SEM of TiO_2 deposited films (a) at 30 V for 210s showing TiO_2 clusters and (b) at 20 V and 210s showing uniform film coating.

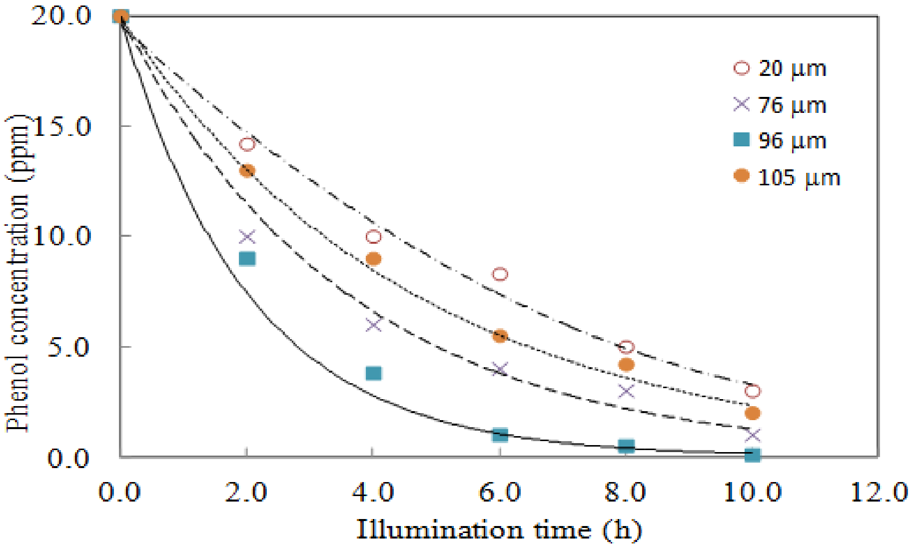

Figure 5: Variation of phenol concentration with illumination time on TiO_2 films of varying thicknesses heated at 300 °C.

Figure 6 shows the effect of sintering temperature of TiO_2 films on photocatalytic activity of phenol using film thickness of 33 ± 2 µm. It is observed that the photocatalytic activity decreased with increase in the sintering temperatures of TiO_2 films. This could be attributed to the change in phase when TiO_2 is heated in the temperature range of 600 to 800 °C, where an irreversible conversion of the anatase to rutile phase occurs (Allan 1976). Since anatase is more efficient in photocatalytic activity than rutile, this conversion causes a reduction in photocatalytic activity for films heated above 600 °C. This phenomenon is evidenced by the XRD results of Figure 7 which show an increase in the peak intensities of rutile with when heated at 700 °C.

From Figure 7, the XRD pattern of the unheated TiO_2 powder shows the peaks of anatase and rutile at 2θ = 25.42° and 27.50°, respectively. The composition of the respective phases such as rutile in the original powder of TiO_2 was calculated using Equation 2 (Allan 1976).

$$x = \left(1 + 0.8\frac{I_A}{I_R}\right)^{-1} \qquad (2)$$

Where: x is the weight fraction of rutile in the powder, while I_A and I_R are the x-ray peak intensities of anatase and rutile, respectively. The results indicated that there was 23.84% rutile in the unheated samples. Heating at 300 °C and 400 °C for 3 hours resulted in virtually no change in phases of TiO_2. However, at 700 °C, an increase in the rutile content from 24.59% to 45.21% occurred indicating that rapid transition of anatase to rutile occurs at high temperatures. Similar observation was made by Allan (1976) who noted that high temperatures above 600 °C favour the conversion of anatase into rutile. This explains the decrease in the decomposition rate of phenol for films heated at high temperatures.

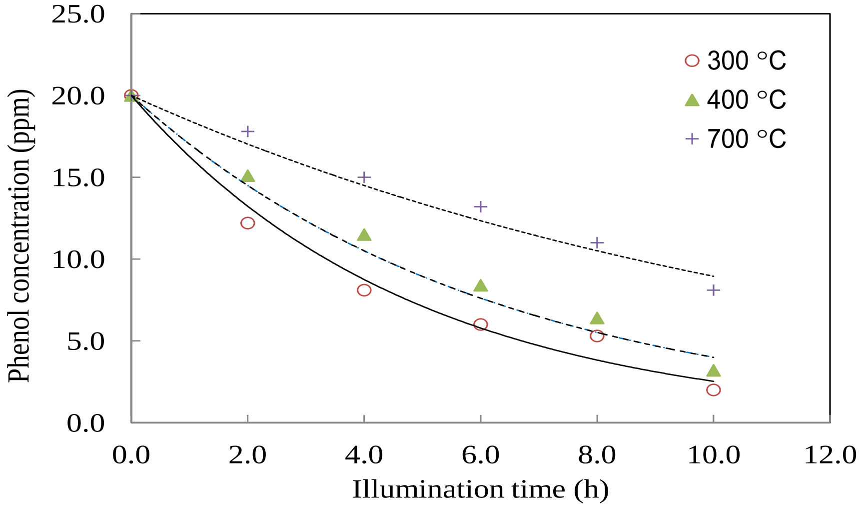

Figure 6: Decomposition of phenol for films sintered at different temperatures showing reduction in photocatalytic activity with sintering temperature.

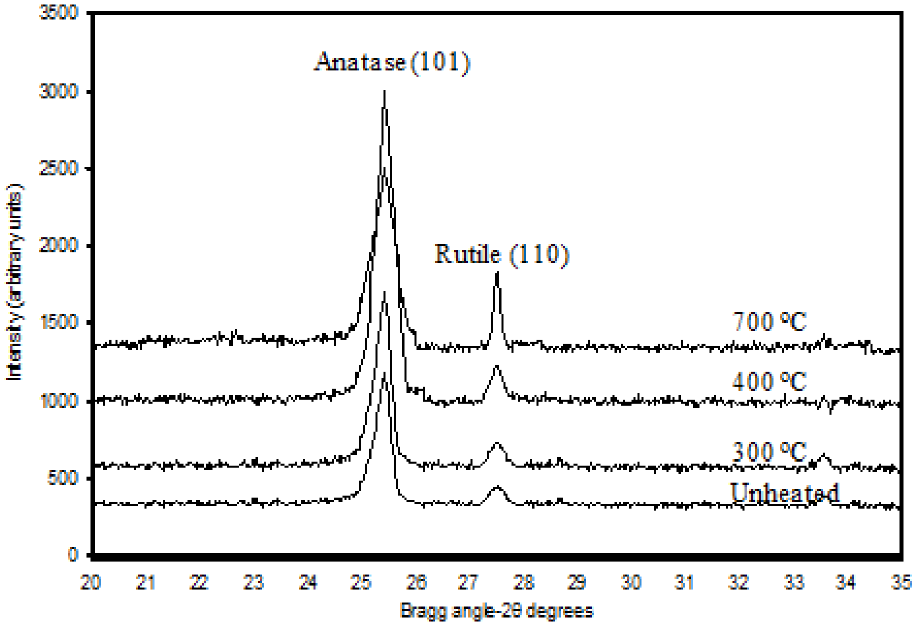

Figure 7: XRD patterns of unheated and heated samples of titanium dioxide showing increase in rutile phase at 700 °C.

An important feature to point out is that these phase changes are also accompanied by a reduction in the surface areas of the TiO_2 particles due to the micro-cracking associated with the mismatch in the thermal expansion coefficients between anatase and rutile. Rutile has a higher thermal expansion coefficient ($\alpha_R = 6.99 \times 10^{-6}$ K^{-1}) compared to anatase ($\alpha_A = 4.47 \times 10^{-6}$ K^{-1}). As such, during cooling, the differential contraction between these phases causes micro cracking in the TiO_2 matrix resulting in reduction in the surface area of the TiO_2 particles. Consequently, there are fewer sites for adsorption of the contaminant particles leading to reduced photocatalytic activity. This phenomenon is shown in Figure 8 where it is observed that lower sintering temperature (400 °C) causes less micro cracking in the matrix in the matrix (Figure 8a) compared to samples heated at higher temperatures (700 °C) (Figure 8b) due to the differential thermal expansion coefficients between anatase and rutile phases.

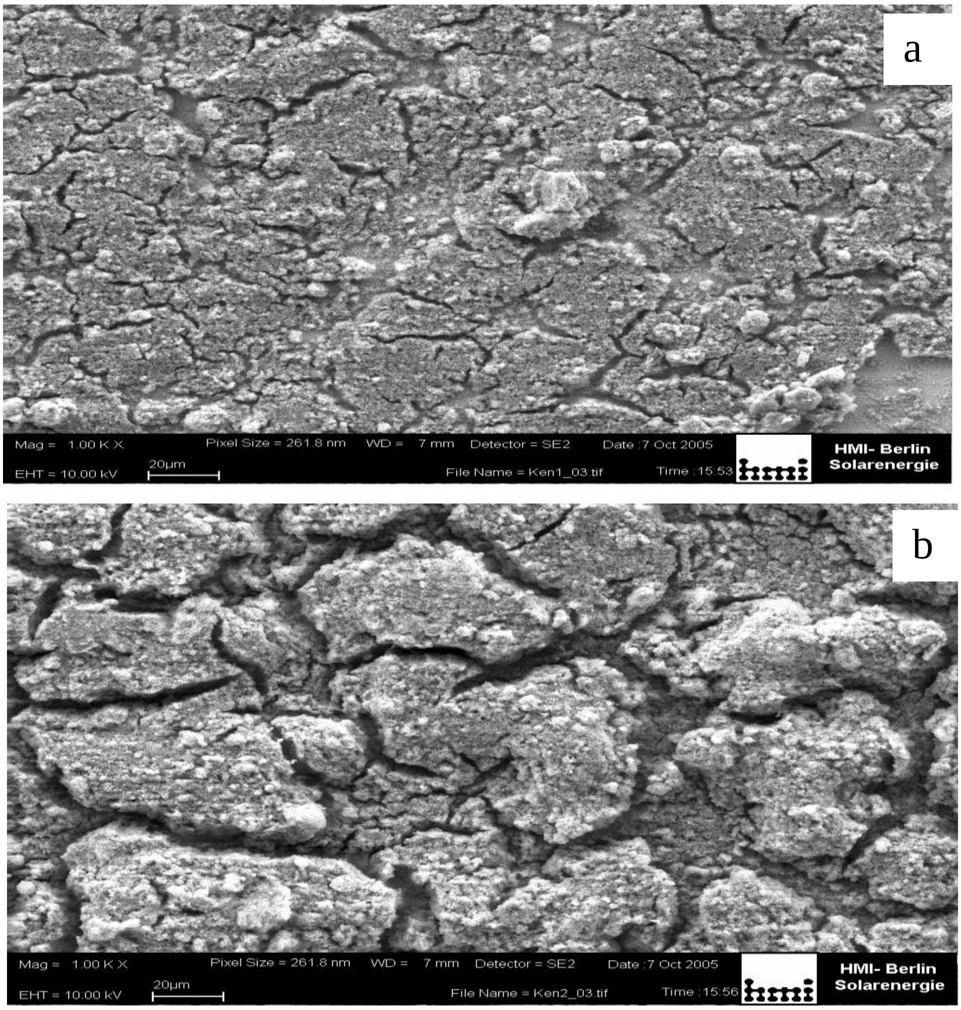

Figure 8: SEM of TiO_2 thin films heated at (a) 400 °C and (b) at 700 °C.

Effect of UV intensity on photocatalytic activity

Table 1 shows the effect of UV light intensity on the photocatalytic activity of phenol. It was observed that doubling the UV intensity increased the photocatalytic effect although not by the same proportions. This implies that the rate of photo-excitations of the TiO_2 particles to form OH radicals responsible for photocatalytic oxidation is also dependent on other process related factors apart from the amount of UV intensity alone. Also shown in the table is the data for natural sunlight which shows very little photocatalytic effect since sunlight contains only about 4–5% of UV light (although this may vary from place to place). As such, there is little photo-excitation of TiO_2 particles to form OH radicals responsible for photocatalytic oxidation.

Table 1: Variation in the concentration of phenol (ppm) after illumination with UV light of different intensities for various time durations

	Illumination intensity (mW/cm^2)			
Time (h)	Sunlight	1.8	3.6	5.4
0	20 ± 0.1	20 ± 0.1	20 ± 0.1	20 ± 0.1
2	20 ± 0.1	17 ± 0.1	16 ± 0.1	14 ± 0.1
4	20 ± 0.1	14 ± 0.1	12 ± 0.1	9 ± 0.1
6	20 ± 0.1	10 ± 0.1	9 ± 0.1	6 ± 0.1
8	19 ± 0.1	8 ± 0.1	7 ± 0.1	3 ± 0.1
10	19 ± 0.1	4 ± 0.1	3 ± 0.1	1 ± 0.1

Conclusions

The implications of the current work are quite significant. First, this study demonstrated EPD as an inexpensive method for thin film coating. However, it is necessary to optimize the suspension and deposition conditions for good quality film deposits. The zeta potential is the most important parameter to monitor since it determines the suspension stability. It is necessary to select the appropriate solvent, pH value and dispersant concentration necessary to attain high zeta potential. The control of deposition voltage and time is also important for good quality thin films deposits. Furthermore, this study shows that the EPD technique can be applied in the design of inexpensive wastewater purification systems for light industries before discharge into the ecosystems.

References

Allan M 1976 The crystallization of anatese and rutile from amorphous titanium dioxide under hydrothermal conditions. *Am. Mineral.* 61: 419-424.

Atul VW, Gaikwad GS, Dhonde MG, Khaty NT and Thakare SR 2013 Removal of organic pollutant from water by heterogenous photocatalysis: a review. *Res. J. Chem. Environ.* 17(1): 84-94.

Bandy J, Zhang Q and Cao G 2011 Electrophoretic deposition of titanium oxide nanoparticle films for dye-sensitized solar cell applications. *Materials Sciences and Applications* 2(10), 1427-1431.

Besra L and Liu M 2007 A review of fundamentals and applications of electrophoretic deposition (EPD). *Prog. Mater. Sci.* 52(1): 1-61.

Blake DM, Maness PC, Huang Z, Wolfrum EJ, Huang J and Jacoby WA 1999 Application of the photocatalytic chemistry of titanium dioxide to disinfection and the killing of cancer cells. *Sep. Purif. Methods* 28(1): 1-50.

Boccaccini A, Klein S, Ma R, Li Y and Zhitomirsky I 2010 Electrophoretic deposition of biomaterials. *J. Royal Soc. Interface* 7(5): S581-S613.

Boccacini A and Zhitomisrky I 2002 Application of electrophoretic and electrolytic deposition techniques in ceramic processing. *Curr. Opin. Solid State Mater. Sci.* 6: 251-260.

Bukowska B and Kowalska S 2003 The presence and toxicity of phenol derivatives-their effect on human erythrocytes. *Curr. Top. Biophys.* 27(1-2): 43-51.

Cabanas-Polo S and Boccaccini A 2016 Electrophoretic deposition of nanoscale TiO_2: technology and applications. *J. Eur. Ceram. Soc.* 36(2): 265-283.

Chen D and Ray KJ 1999 Photocatalytic kinetics of phenols and its derivatives over UV irradiated TiO_2. *Appl. Catal. B: Environ.* 23: 143-157.

Chiang WT, Lee PT and Hsu RQ 2015 Study on preparation of flexible semiconductor electrode for dye-sensitized solar cells by EPD. *Manufact. Sci. Technol.* 3(4): 170-176.

Chiu W-H, Lee K-M and Hsieh W-F 2011 High efficiency flexible dye-sensitized solar cells by multiple electrophoretic depositions. *J. Power Sources* 196: 3683-3687.

Jin-hui Z 2012 Research on UV/TiO_2 photocatalytic oxidation of organic matter in drinking water and its influencing factors. *Proc. Environ. Sci.* 12: 445-452.

Kawakita M, Uchikoshi T, Kawakita J and Sakka Y 2009 Preparation of crystalline-oriented titania photoelectrodes on ITO glasses from a 2-propanol-2,4-pentanedione solvent by electrophoretic deposition in a strong magnetic field. *J. Am. Ceram. Soc*. 92(5): 984-989.

Lazar M, Varghese S and Nair S 2012 Photocatalytic water treatment by titanium dioxide: Recent updates. *Catalysts* 2: 572-601.

Ma J, Wang C and Peng KW 2003 Electrophoretic deposition of porous hydroxyapatite scaffold. *Biomaterials* 24: 3505-3510.

Mathews RW 1992 Photocatalytic oxidation of organic contaminants in water: An aid to environmental preservation. *Pure Appl. Chem.* 64(9): 1285-1290.

Miyasaka T and Kijitori Y 2004 Low-temperature fabrication of dye-sensitized plastic electrodes by electrophoretic preparation of mesoporous TiO_2 layers. *J. Electrochem. Soc.* 151(11): A1767-A1773.

Narayan MR and Raturi A 2012 Deposition and characterization of titanium dioxide films formed by electrophoretic deposition. *Int. J. Mater. Eng. Innov.* 3(1): 17-31.

Narkevica I, Stradina L, Stipniece L, Jakobsons E and Ozolins J 2017 Electrophoretic deposition of nanocrystalline TiO_2 particles on porous TiO_{2-X} ceramic scaffolds for biomedical applications *J. Eur. Ceram. Soc.* 37: 3185-3193.

Prihod'ko RV and Soboleva NM 2013 Photocatalysis: Oxidative processes in water treatment. *J. Chem*. 2013: 1-8.

Put S, Biest O, Anne G and Vleugels J 2004 Microstructural engineering of FGMs by elecrophoretic deposition. *J. Mater. Process. Technol.* 143-144: 572-577.

Radice S Bradbury C Michler J and Michler S 2010 Critical particle concentration in electrophoretic deposition. *J. Eur. Ceram. Soc.* 30(5): 1079-1088.

Sarkar P and Nicholson P 1996 Electrophoretic deposition (EPD): Mechanisms, kinetics and applications to ceramics. *J. Am. Ceram. Soc.* 79 (8): 1987-2002.

Sarkar P, Datta S and Nicholson PS 1997 Functionally graded ceramic/ceramic and metal/ceramic composites by electrophoretic deposition. *Composites Part B* 28(1): 49-56.

Sprung MM 1941 Bromination of phenols by means of bromide-bromate solution. *Ind. Eng. Chem. Anal. Ed.* 13 (1): 35-38.

Van der Biest O and Vandeperre L 1999 Electrophoretic deposition of materials. *Ann. Rev. Mater. Sci.* 29(1): 327-352.

Van Tassel J and Randall C 2006 Mechanisms of electrophoretic deposition. In *Key Eng. Mater.* 314: 167-174, Trans Tech Publications.

Yum JH, Kim SS, Kim DY and Sung YE 2005 Electrophoretically deposited TiO_2 photo-electrodes for use in flexible dye-sensitized solar cells. *J. Photochem. Photobiol. A: Chem.* 173: 1-6.