

PAPER • OPEN ACCESS

## Synthesis by anodisation method, characterization by SEM and EDS, and degradable ability of TiO<sub>2</sub> nanotubes.

To cite this article: Bassam RA Al-Abdulaziz *et al* 2019 *J. Phys.: Conf. Ser.* **1294** 072019

View the [article online](#) for updates and enhancements.



**IOP | ebooks™**

Bringing together innovative digital publishing with leading authors from the global scientific community.

Start exploring the collection—download the first chapter of every title for free.

# Synthesis by anodisation method, characterization by SEM and EDS, and degradable ability of TiO<sub>2</sub> nanotubes.

**Bassam RAAI-Abdulaziz<sup>1</sup>, Masara B A Al-Abdulaziz<sup>2</sup>, Zainab TAI-Abdullah<sup>3</sup>, and Faris J M Al-Imarah<sup>4</sup>**

<sup>1</sup>Dept. Chem. and Marine Environ. Poll., Marine Science Centre, Basrah Univ.

<sup>2</sup>Talant School of Basrah, Education Administration of Basrah.

<sup>3</sup>Dept. of Chem., College of Education for Pure Sciences, Basrah Univ.

<sup>4</sup>Vice Dean, Al-Kunooze University College, Basrah - Iraq.

Email : [alimarahfaris1951@gmail.com](mailto:alimarahfaris1951@gmail.com)

**Abstract.** Obtaining of TiO<sub>2</sub> nanotubes could be performed by anodized Ti in fluoride based electrolyte. During the growth of TiO<sub>2</sub> nanotubes within the influence of anodizing process of Ti, a certain parameters are required, electrolyte composition, voltage, and time. The TiO<sub>2</sub> nanotube array was synthesized electrochemically in a fluoride containing electrolyte by anodisation method of a pure titanium plate. The anodisation procedure was carried out in ethylene glycol electrolyte; the applied voltage was 60 volt. The average inner diameter of the nanotube was (67 nm) and the average outer diameter was (80 nm). Characterization of the nanotubes crystal structure, morphology, and oxide composition were performed via field emission scanning electron microscopy (FE-SEM) and energy dispersion spectroscopy (EDS). Elemental analysis by EDS shows the presence of fluoride, and confirm the formation of TiO<sub>2</sub> nanotubes. The results show the possibility of study the distribution of the composition of the tubes elements using the scanning electron microscope-mapping. Synthesized TiO<sub>2</sub> nanotubes were applied for the degradation of organic dye methylene blue as water dye pollutant. It is found that rate of degradation of MB in presence of TiO<sub>2</sub> nanotubes was greater than in case of degradation without TiO<sub>2</sub> nanotubes. It is clear that the main reason for this behavior belongs to the high surface area of TiO<sub>2</sub> nanotubes. For (5) ppm of methylene blue, the degradation in presence of TiO<sub>2</sub> nanotubes has done completely after (5 hours)

**Key Wards:** Anodisation, Nanotubes, EDS-mapping, Degradation of methylene blue dye. TiO<sub>2</sub>

## 1. Introduction

Nanostructures TiO<sub>2</sub> composites are promising materials for advanced application as sensors, dyes, photo electrochemical, environment,...etc. TiO<sub>2</sub> is one of the most widely studied semiconductor photo electrolyte according to ability to catalyze numerous redox reaction (Papoutsis, et al., 1994), high stability, nontoxicity, and low cost (Kment et al., 2010).



Recently TiO<sub>2</sub> nanostructures with the different shapes have received extensive attention due to their unique physical and chemical properties (Ha et al., 2013), and nanostructured titania with tubular shape has been considered one of the most promising materials for the fabrication of gas sensing devices (Zhang, et al., 2012).

Titania nanostructures can be synthesized in a variety of ways. The most common methods include sol-gel (Zhang et al., 2001; Traversa et al., 2000), vapor-solid-liquid (VLS) growth (Lee et al., 2006), template assisted growth [Miao et al., 2002], hydrothermal [Kavan et al., 2004; Yuan and Su, 2004] and electrochemical synthesis [Zwilling et al., 1999; Gong et al., 2001; Macak et al., 2005; Mor et al., 2003].

Among other methods used for the synthesis of TiO<sub>2</sub> nanostructure, anodic oxidation being a convenient electrochemical method, which can be easily used to grow various oxide layers on titanium surface by using appropriate anodizing conditions (Stoini and Pirvu, 2013). electrochemical synthesis yields the most uniform, highly organized, and oriented nanotube structures, which would be desirable for solar cell applications mentioned. In addition, the nanotubes, as formed, are mechanically and electrically attached to a conducting substrate, which could act as the current collector for many applications. The synthesis method involves immersing a metal substrate in an appropriate electrolyte and anodizing at constant voltage for a set period of time (Nguyen, 2010).

Anodised titanium dioxide (titania, TiO<sub>2</sub>) nanotubes have been widely studied over the last few years, following the discovery in 1999 of nanoporous TiO<sub>2</sub> films prepared via anodisation in aqueous solution containing small quantities of hydrofluoric acid (<http://opus.bath.ac.uk/14370/>).

Characterization of the nanotubes crystal structure, morphology, and oxide composition were performed via cross-sectional and high-resolution Scanning Electron Microscopy (SEM)(Nguyen, 2010). Titania nanotubes have emerged as an exciting new material with a wide array of applications such as sensors, dye sensitized solar cells, and batteries due to their semi-conducting nature, high surface area, and distinct morphology.(Nguyen, 2010).

Titania (TiO<sub>2</sub>) nanotube is considered a very important material due to its promising applications in many fields ranging from energy harvesting to sensors and photocatalytic applications (<http://www.scholarsresearchlibrary.com/articles/the-role-of-anodizing-potentials-in-making-tio2-nanotubes-in-ethylene-glycol--nh4f-water-electrolyte.pdf> ).

The titanium dioxide does not absorb light in the visible region (400-700 nm) but disperse it very efficiently. This is the most broadly commercially used characteristic as white basis for paints, toothpastes, cosmetic products, plastics (Zamudio Torres et al., 2014). TiO<sub>2</sub> is the most photocatalytically active material for the decomposition of organic materials (for example, it is used for degradation of organic pollutants) (Marien et al., 2016). The reason for this high activity are the band-edge positions relative to typical environments (such as water).

Under precise anodic conditions in electrolytes containing fluoride, highly organized arrays of oxide nanotubes can grow on different metals such as Ti (Ghcova, et al., 2005), Zr (Tsuchiyah,2004), and W (Tsuchiyah, et al., 2005). Particularly, TiO<sub>2</sub> nanotubes formed on have attracted great attention in the past years due to their variety of functional properties and potential applications, such as gas sensing ( Paulose, et al., 2006), catalysis ( Macak, et al., 2007), solar cell ( Onodaak,et al., 2007) and biocompatible materials (Oh, et al., 2005). As an effective formation method, the of TiO<sub>2</sub> nanotubes, the anodisation process is beneficial because of simple production and inexpensive.

## 2. Experimental

For the synthesis of TiO<sub>2</sub> nanotubes, the procedure set by Stoian and Pirvu (2013) was adopted in which an electrochemical cell was designed and used with Titanium electrode and one type of aqueous electrolyte was used in this cell. Titanium foils (99% purity) were polished by diamond paste (218-694 USA), degreased prior to anodisation by sonicating in acetone, and then rinsed with deionized water (DI). The electrochemical anodisation set-up was composed of a high-voltage power supply, the electrodes were set at distance (8) cm and Ti surface at (1) cm<sup>2</sup> open to the electrolyte. The iodization was carried out in a two-electrodes electrochemical system at a constant voltage of (60) V and the time of anodisation was (60) min. The Ti plates were used as anode and cathode, immersed in electrolyte contain ammonium fluoride (0.7 wt % NH<sub>4</sub>F), ethylene glycol (97.3 wt % CH<sub>2</sub>OH-CH<sub>2</sub>OH) and water (2 vol % H<sub>2</sub>O) at room temperature ( Feil et al, 2010). The electrochemical cell used through this study is shown in Figure. 1.



**Figure 1:** Anodisation unit used for preparing of TiO<sub>2</sub> nanotubes.

FE- SEM and EDS were employed for the morphological characterization of the TiO<sub>2</sub> nanotubular layers formed on the Ti plate. FE- SEM instrument used was Make:Carl Zeiss ULTRA Plus, Germany/ Location at College of Pharmacy/ Basrah University, together with the EDS and Mapping.

Synthesised nanotubes were applied for the degradation of methylene blue dye using LED (15watt) and the distance between the light and the sample was fixed as (14cm). The methodology involved measuring the absorbance at a fixed period of (15 min) by using UV-Vis spectrometry at maximum absorbance of methylene blue (663) nm. The initial concentration of MB dye is (5ppm) and the volume of degradable dye solution is (25 ml) without using stirring.

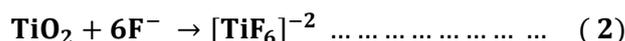
## 3.Result and Discussion

**3-1. Anodisation process,** Growth mechanism of TiO<sub>2</sub> nanotubes can be explained as two processes which happened in the same time the first process called oxidation and the second process is dissolution which was explained earlier by Zamudio Torres et al., (2014) and stated as follows:

In the first anodisation process water in the solution reacts with the titanium metal surface leading to formation of oxide layer (oxidation) under an applied electric field as shown in equation (1).



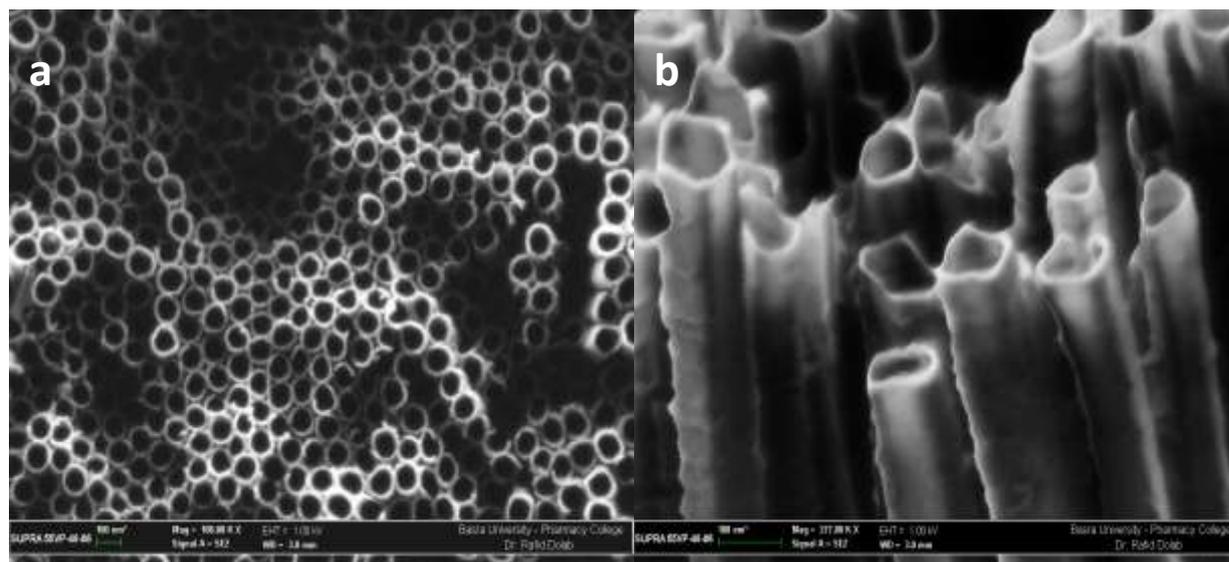
Then  $\text{TiO}_2$  oxide layer will be etched by fluoride ion from the electrolyte. The presence of fluoride ions in the oxide layer causes chemical dissolution as shown in equation (2).



A huge advantage of anodisation is their capability to regulate the shape and size of nanotubular arrays on diverse kinds of materials, viz., metals and metal alloy substrates, to obtain accurate dimensions, satisfying the demand of particular applications by use of controlled anodic oxidation. It can be classified as one of the most straight-forward, cost-effective and basic approaches to establish an ordered porous nanostructures under convenient conditions. The initiation step is crucial not only for the growth processes that proceed during anodisation, but also for the organization of the pores that result from synthesis. (Nguyen, 2010)

### 3-2. Characterization and morphology for the synthesized $\text{TiO}_2$ nanotubes by using FE-SEM and EDS-Mapping

The field emission scanning electron microscope (Germany Model, Make Carl Zeiss ULTRA Plus in College of Pharmacy/ Basrah University) was employed for the morphological characterization of the  $\text{TiO}_2$  nanotubular layers. Figure 2 shows the top-view and cross-section of synthesized  $\text{TiO}_2$  nanotubes. From the images the inner and outer diameters of  $\text{TiO}_2$  nanotubes and also the tubes length can be calculated. In this experiment under the anodisation conditions the inner and outer diameters of  $\text{TiO}_2$  nanotubes are (67 nm) and (80nm) respectively and the tubes length (4.5  $\mu\text{m}$ ).



**Figure 2.** FE-SEM images show (a) top-view (b) side-view of synthesized  $\text{TiO}_2$  nanotubes.

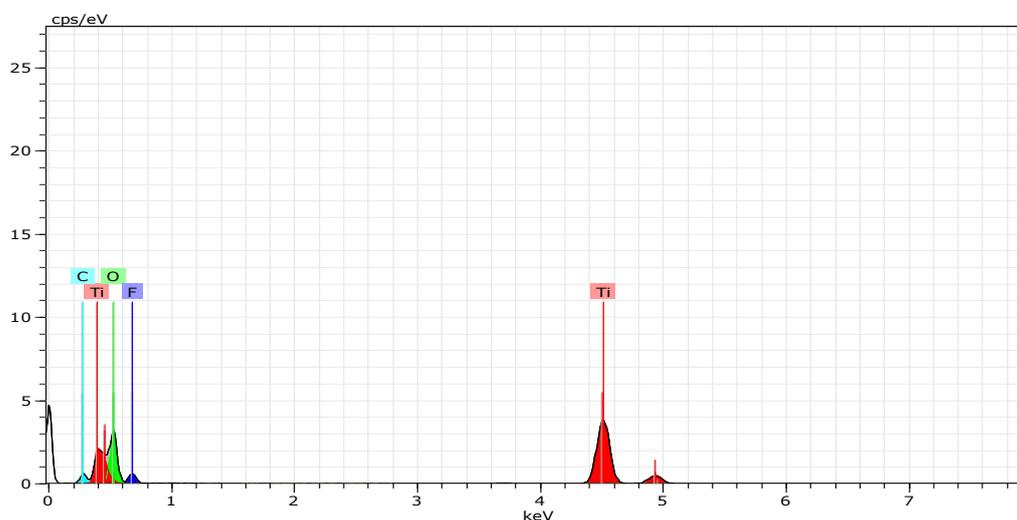
Through FE-SEM imaging, the steps that occur during the anodizing process, forming a first layer of titanium oxide on the surface of Ti, then under influence of the electric field and the presence of fluorine chemical attack occurs is established, which causes fractures and pores subsequently grow into nanotubes by the effect of the electric field. It was also possible to establish the influence of the current during this process (Zamudio Torres et al., 2014). Moreover, EDS was applied for elemental analysis of TiO<sub>2</sub> morphology which prepared by anodisation.

It is found that the elemental weight percentage for the synthesized TiO<sub>2</sub> nanotubes composition as following, 36.64 wt % of Titanium, 49.64 wt % of Oxygen, 7.21 wt % of Fluorine and 6.50 wt % of Carbon which are tabulated in table 1 . Hence, the total amounts of atoms are 100%. Figure 3 illustrates the EDS analysis for the synthesized TiO<sub>2</sub> nanotubes.

The distribution of TiO<sub>2</sub> nanotubes composition is prove that the major amounts of tube composition is oxygen then Titanium with small amount of fluorine and carbon with is from anodisation electrolyte.

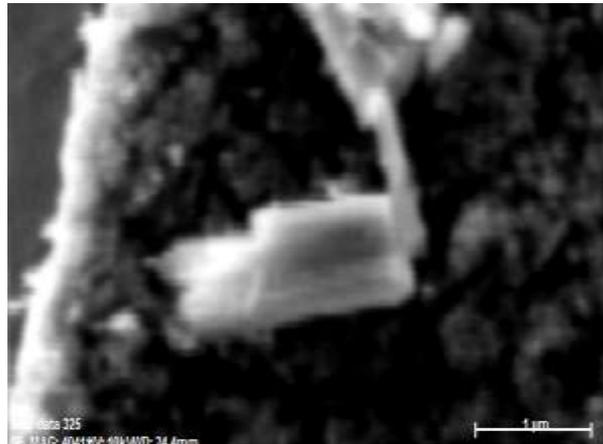
**Table 1.** EDS analysis of TiO<sub>2</sub> nanotubes.

| Element  | Series   | UNN, C<br>[W%] | Norm.C<br>[W%] | Atom.C<br>[W%] | Error (3 Sigma)<br>[W%] |
|----------|----------|----------------|----------------|----------------|-------------------------|
| Titanium | K-series | 64.36          | 63.48          | 36.64          | 6.75                    |
| Oxygen   | K-series | 29.13          | 28.73          | 49.64          | 11.00                   |
| Fluorine | K-series | 5.03           | 4.96           | 7.21           | 2.42                    |
| Carbon   | K-series | 2.87           | 2.83           | 6.51           | 1.43                    |
|          |          | 100 %          | 100 %          | 100 %          |                         |



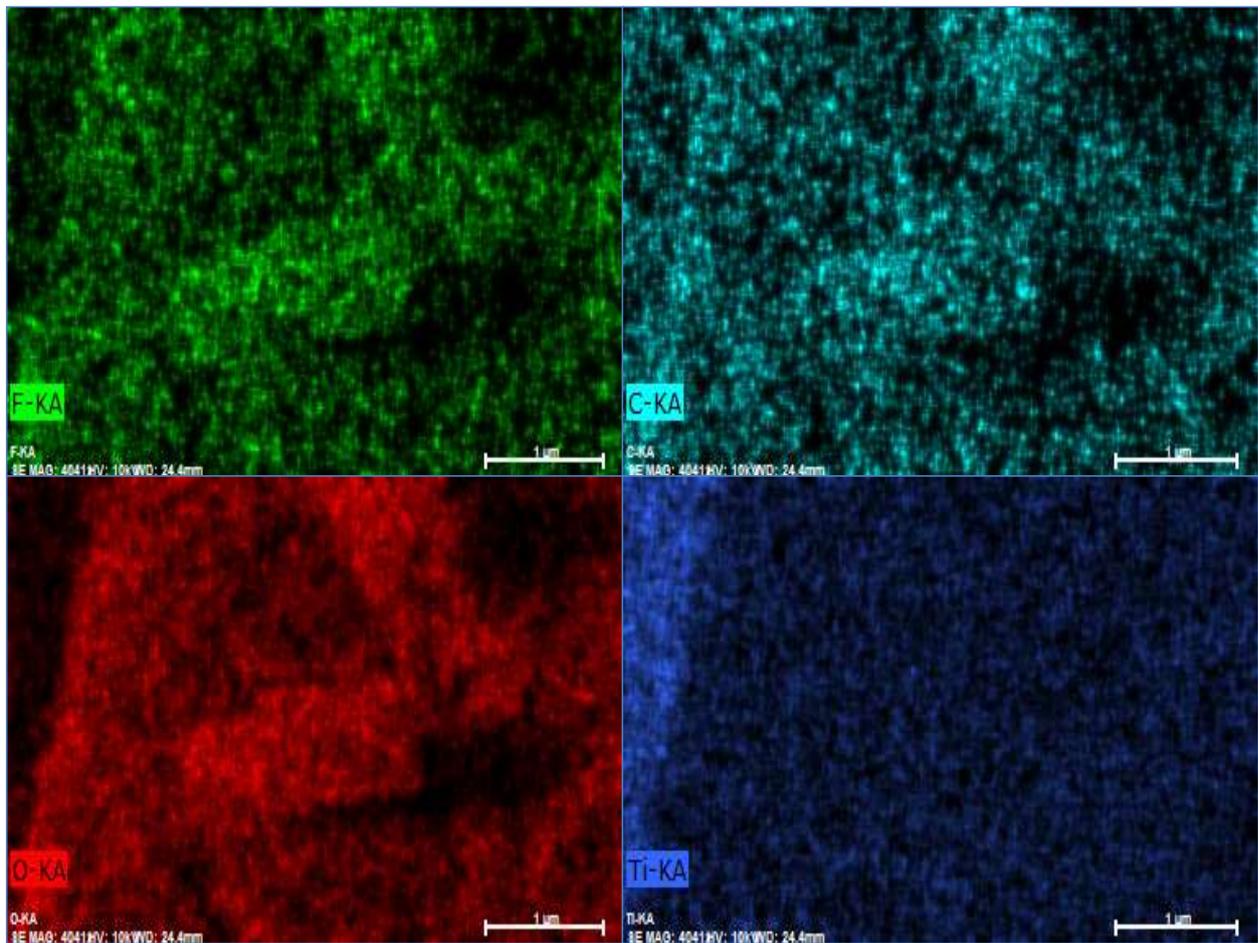
**Figure 3** illustrates the elemental analysis of the synthesized TiO<sub>2</sub> nanotubes using EDS.

Morphological characterisation by EDS showed images of a typical TiO<sub>2</sub> nanotubes array grown on Ti plate in an ethylene glycol / ammonium fluoride solutions ( Feil et al., 2010), as shown in Figure 4. EDS-Mapping for cross-section fragment of TiO<sub>2</sub> nanotubes as seen in figure 4 was taken for more qualitative analysis.



**Figure 4** EDS-mapping image of piece of TiO<sub>2</sub> nanotubes.

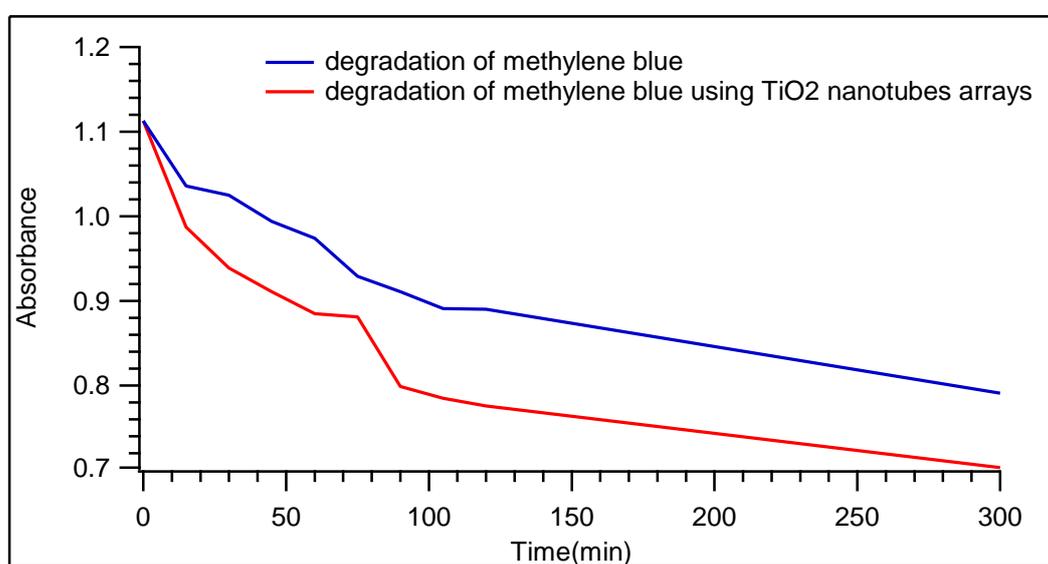
EDS- mapping was used for the identifying the TiO<sub>2</sub> nanotubes compositions with element coding and shown in figure 5



**Figure 5** EDS-Mapping of TiO<sub>2</sub> nanotubes composition with element-coding.

### 3.3. Degradation of methylene blue (MB) using synthesized TiO<sub>2</sub> nanotubes

Highly ordered TiO<sub>2</sub> nanotubes have attracted a lot of attention for the photocatalytic removal of organic pollutants. A few studies demonstrated that the tube morphology plays a key role on the photocatalytic activity (Marien et al., 2016). Within his study the synthesized TiO<sub>2</sub> nanotubes were used as a photocatalysis of degradation of organic compounds, in this work methylene blue was used as an example of water dye pollutant. Figure (6) shows the degradation of MB with and without TiO<sub>2</sub> nanotubes array. From this figure it is clear that the rate of degradation is more when using TiO<sub>2</sub> nanotubes array. The reason is that using TiO<sub>2</sub> nanotubes with high surface area to volume ration enhances the surface of degradation. Therefore, TiO<sub>2</sub> nanotubes function in a beneficial rule as a photocatalyst. The initial concentration of MB is (5 ppm). The area of TiO<sub>2</sub> nanotube array that contains the film is about (2 cm<sup>2</sup>). The photocatalytic was done without use of any kind of stirring.



**Figure (6)** shows degradation of MB using TiO<sub>2</sub> nanotubes array as photocatalytic layer.

The concentration of MB in the presence of the TiO<sub>2</sub> nanotubes gradually decreased as a function of LED exposure time. After a 300-min exposure of the nanotubes to LED light, concentration of MB was continually decreased to reach values lower in comparison with photodegradation of MB without the presence of TiO<sub>2</sub>.

## 4. Conclusion

Anodisation method is very good method for creation of TiO<sub>2</sub> nanotubes because of its fast, reproducible and low-cost method. Using EDS is useful for qualitative and quantitative analysis of TiO<sub>2</sub> nanotubes and mapping is a new technique can be used for confirm the distribution of element on TiO<sub>2</sub> nanotubes wall. Under the experiment condition

## 5. References

- [1] Feil, A. F., Migowski, P., Scheffer, F. R., Pierozan, M. D., Rodrigo R. Corsetti, R. R., Melissa Rodrigues, M., Pezzi, R. P., Machado, G., Livio Amaral, L., Teixeira, S. R., Weibel, D. E., and Dupont, J. (2010). Growth of TiO<sub>2</sub> nanotube arrays with simultaneous Au nanoparticles impregnation: photocatalysts for hydrogen production. *J. Braz. Chem. Soc.*,21(7):1-16.

- [2] Ghicov A., Macak. T. H., and Schmukip, J. M., (2005). Titanium oxide nanotubes prepared in phosphate electrolytes. *J. Electrochem. Comm.*, **7**:505-509.
- [3] Gong, D., C. Grimes, O. Varghese, W. Hu, R. Singh, Z. Chen, and E. Dickey, (2001). *Journal of Materials Research*, **16**:3331- 3338.
- [4] Ha, T.J., Hong, M.H., Park, C.S., and Park, H.H., (2013). Gas sensing properties of ordered mesoporous TiO<sub>2</sub> film enhanced by thermal shock induced cracking. *Sens. Actuators B Chem.* **181**:874–879.
- [5] <http://opusbath.ac.uk/14370/>
- [6] <http://www.scholarsresearchlibrary.com/articles/the-role-of-anodizing-potentials-in-making-tio2-nanotubes-in-ethylene-glycol--nh4f-water-electrolyte.pdf>
- [7] Kavan, L., M. Kalbac, M. Zikalova, I. Exnar, V. Lorenzen, R. Nesper, and M. Graetzel, (2004). *Chemistry of Materials*, **16**:477-483.
- [8] Kment, S.; Kmentova, H.; Kluson, P.; Krysa, J.; Hubicka, Z.; Cirkva, V.; Gregora, I.; Solcova, O.; Jastrabik, L. (2010). Notes on the photo-induced characteristics of transition metal-doped and undoped titanium dioxide thin films. *J. Colloid Interface Sci.* , **348**:198–205.
- [9] Lee, J., K. Park, T. Kim, H. Choi, and Y. Sung, (2006). *Nanotechnology*, **17**:4317-4322.
- [10] Macak, J., Tsuchiya, H., and Schmuki, P., (2005). *Angewandte Chemie International Edition*, **44**, 2200-2106.
- [11] Macak, J. S.-S.F., Schmuki, P., (2007). Efficient oxygen reduction on layers of ordered TiO<sub>2</sub> nanotubes loaded with Au nanoparticles. *J. Electrochem. Comm.*, **9**:1783-1787.
- [12] Marien, C.B.D., Cottineau, T., Robert, D., and Drogui, P., (2016). TiO<sub>2</sub> Nanotube arrays: Influence of tube length on the photocatalytic degradation of Paraquat, *Appl. Cataly. B: Environ.* **194**: 1-6
- [13] Miao, Z., D. Xu, J. Ouyang, G. Guo, X. Zhao, and Y. Tang, (2002). *Nano Letters*, **2**:717-720.
- [14] Mor, G., O. Varghese, M. Paulose, N. Mukherjee, and C. Grimes, (2003). *Journal of Materials Research*, **18**:2588-2562.
- [15] Nguyen, Q.A. (2010). *Electrochemical Synthesis and Structural Characterization of Titania Nanotubes*. D. Ph. Thesis in Materials Science and Engineering University of California, Berkeley.
- [17] Oh, H. J., L.J.H., Jeong, Y., Kim, Y. J., and Chi, C. S., (2005). Microstructural characterization of biomedical titanium oxide film by electrochemical method. *J. Surface and Coating Tech.*, **198**: 247-252.
- [18] Onoda, N.S., Fujieda, T., Yoshikawa, S., (2007). The superiority of Ti plate as the substrate of dye-sensitized solar cells. *J. Solar Energy Materials and Solar Cells*, **91**:1176-1181.
- [19] Papoutsi, D.; Lianos, P.; Yianoulis, P.; Koutsoukos, P., (1994). Sol-gel derived TiO<sub>2</sub> microemulsion gels and coatings. *Langmuir*. **10**:1684–1689.
- [20] Paulose, M., V.O.K., Mor, G. K., Grimes, C. A., and Ong, K., (2006) Unprecedented ultra-high hydrogen gas sensitivity in undoped titania nanotubes. *J. Nanotechnology*, **17**:398-402.
- [21] Stoini, A. B., and Pirvu, C. (2013). Synthesis and characterisation of TiO<sub>2</sub> nanotubes with EC-AFM. *B. Sci. Bull., Series B*, **75**(2):43-54.
- [22] Traversa, E., M. Di Vona, S. Licocchia, M. Sacerdoti, M. Carotta, M. Gallana, and G. Martinelli, *Journal of Sol-Gel Science and Technology*, **19**, 193, 2000.

- [23] Tsuchiyah, S.P., (2004). Thick self-organized porous zirconium oxide formed in H<sub>2</sub>SO<sub>4</sub>/NH<sub>4</sub>F electrolytes [J]. *Electrochemistry Communications*, **6**:1131-1134.
- [24] Tsuchiyah, M.J.M., Sieber, T., Taviral, Ghicov, A., and Sirotanek, S.P. (2005). Self-organized porous WO<sub>3</sub> formed in NaF electrolytes [J]. *Electrochemistry Communications*, 2005. **7**:295-298.
- [25] Yuan, Z., and B. Su, (2004). *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 241, 173-179.
- [26] Zamudio Torres, I., Pérez . Bueno, J.J., and Meas Vong, Y. (2014). Process of growth TiO<sub>2</sub> nanotubes by anodization in an organic media . *Microscopy: advances in scientific research and education* , Méndez-Vilas, A., Ed., Formatex, pp:887-893.
- [27] Zhang, M., Bando, Y., and Wada, K., (2001) *Journal of Materials Science Letters*, 20, 167, 2001.
- [28] Zhang, X.X.; Zhang, J.B.; Jia, Y.C.; Xiao, P.; Tang, J. (2012). TiO<sub>2</sub> nanotube array sensor for detecting the SF<sub>6</sub> decomposition product SO<sub>2</sub>. *Sensors*, 12:3302–3313.
- [29] Zwillig, V., E. Darque-Ceretti, A. Boutry-Forveille, D. David, M. Perrin, and M. Aucouturier, (1999). *Surface and Interface Analysis*, 27:629–637.