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Synthesis by anodisation method, characterization by SEM and EDS, and degradable ability of TiO2 nanotubes.

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Abstract. Obtaining of TiO_2 nanotubes could be performed by anodized Ti in fluoride based electrolyte. During the growth of TiO_2 nanotubes within the influence of anodizing process of Ti, a certain parameters are required, electrolyte composition, voltage, and time. The TiO_2 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_2 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_2 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_2 nanotubes was greater than in case of degradation without TiO_2 nanotubes. It is clear that the main reason for this behavior belongs to the high surface area of TiO_2 nanotubes. For (5) ppm of methylene blue, the degradation in presence of TiO_2 nanotubes has done completely after (5 hours)

Key Wards: Anodisation, Nanotubes, EDS-mapping, Degradation of methylene blue dye. TiO_2

1. Introduction

Nanostructures TiO_2 composites are promising materials for advanced application as sensors, dyes, photo electrochemical, environment,...etc. TiO_2 is one of the most widely studied semiconductor photo electrolyte according to ability to catalyze numerous redox reaction (Papoutsi, et al., 1994), high stability, nontoxisity, and low cost (Kment et al., 2010).

Recently TiO_2 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 TiO2 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_2) nanotubes have been widely studied over the last few years, following the discovery in 1999 of nanoporous TiO_2 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_2) 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_2 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_2 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_2 nanotubes, the anodisation process is beneficial because of simple production and inexpensive.

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2. Experimental

For the synthesis of TiO_2 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^2 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_4F), ethylene glycol (97.3 wt % $CH_2OH\text{-}CH_2OH$) and water (2 vol % H_2O) 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_2 nanotubes.

FE- SEM and EDS were employed for the morphological characterization of the TiO_2 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_2 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).

$$\mathbf{Ti + 2H_2O \rightarrow TiO_2 + 4H^+ + 4e^-} \ldots\ldots\ldots\ldots\ldots (\mathbf{1})$$

Then 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).

$$\mathbf{TiO_2 + 6F^- \rightarrow [TiF_6]^{-2}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots \ldots \quad (\mathbf{2})$$

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 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 TiO_2 nanotubular layers. Figure 2 shows the top-view and cross-section of synthesized TiO_2 nanotubes. From the images the inner and outer diameters of TiO_2 nanotubes and also the tubes length can be calculated. In this experiment under the anodisation conditions the inner and outer diameters of TiO_2 nanotubes are (67 nm) and (80nm) respectively and the tubes length (4.5 µm).

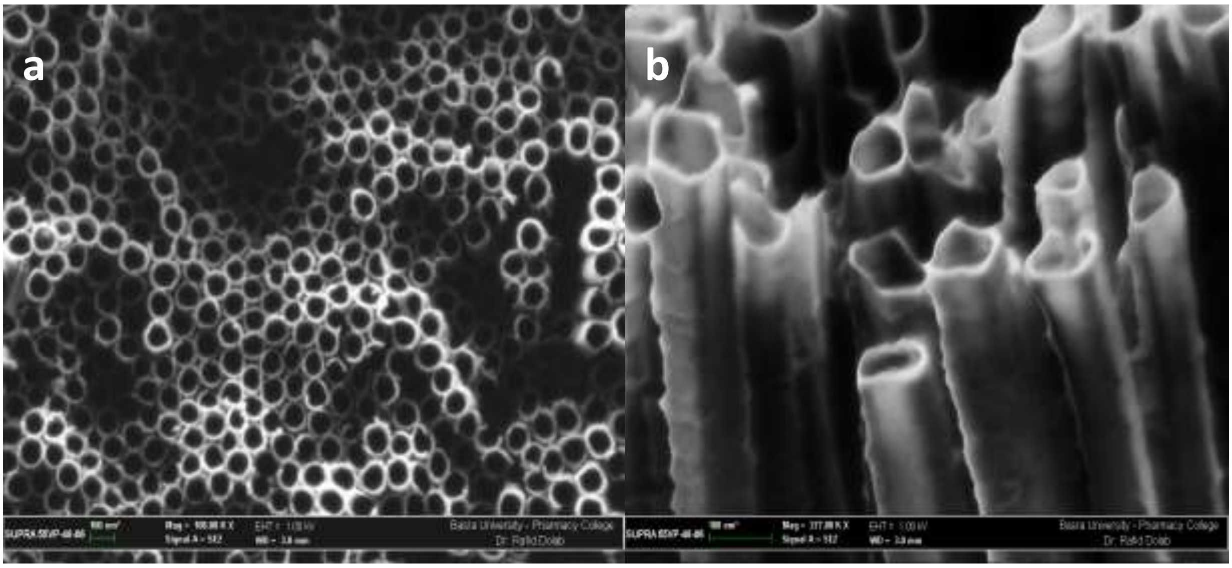

Figure 2. FE-SEM images show (a) top-view (b) side-view of synthesized TiO_2 nanotubes.

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_2 morphology which prepared by anodisation.

It is found that the elemental weight percentage for the synthesized TiO_2 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_2 nanotubes.

The distribution of TiO_2 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_2 nanotubes.

Element	Series	UNN, C [W%]	Norm.C [W%]	Atom.C [W%]	Error (3 Sigma) [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 %	

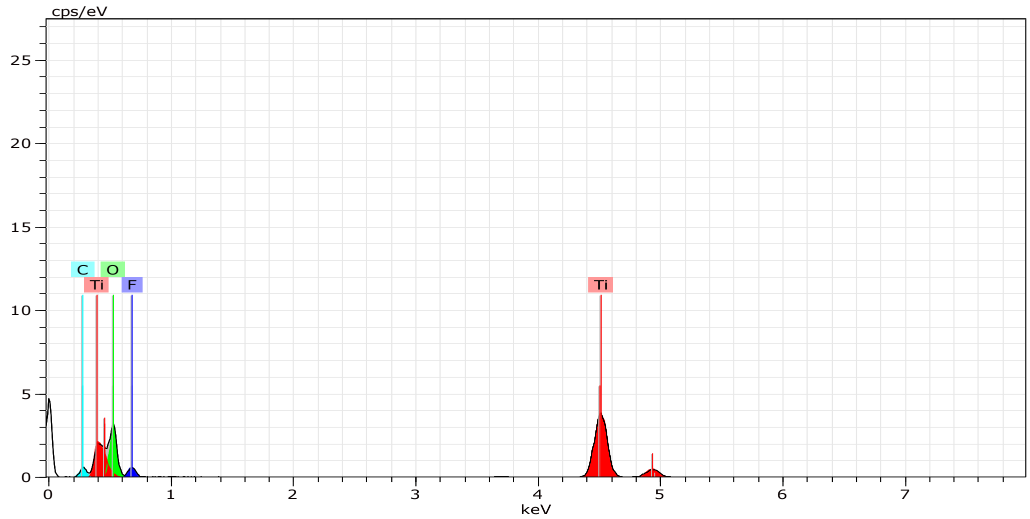

Figure 3 illustrates the elemental analysis of the synthesized TiO_2 nanotubes using EDS.

Morphological characterisation by EDS showed images of a typical TiO_2 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_2 nanotubes as seen in figure 4 was taken for more qualitative analysis.

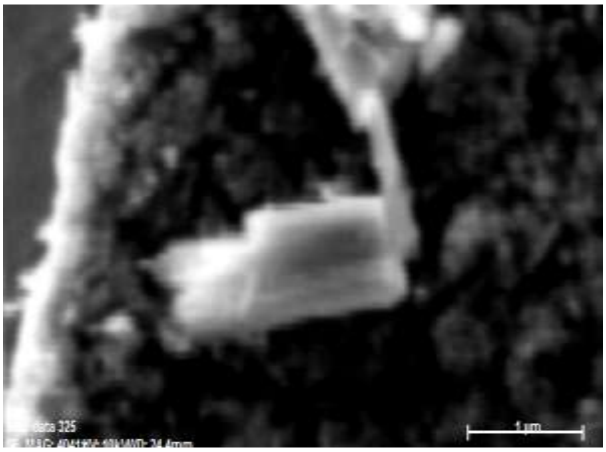

Figure 4 EDS-mapping image of piece of TiO_2 nanotubes.

EDS- mapping was used for the identifying the TiO_2 nanotubes compositions with element coding and shown in figure 5

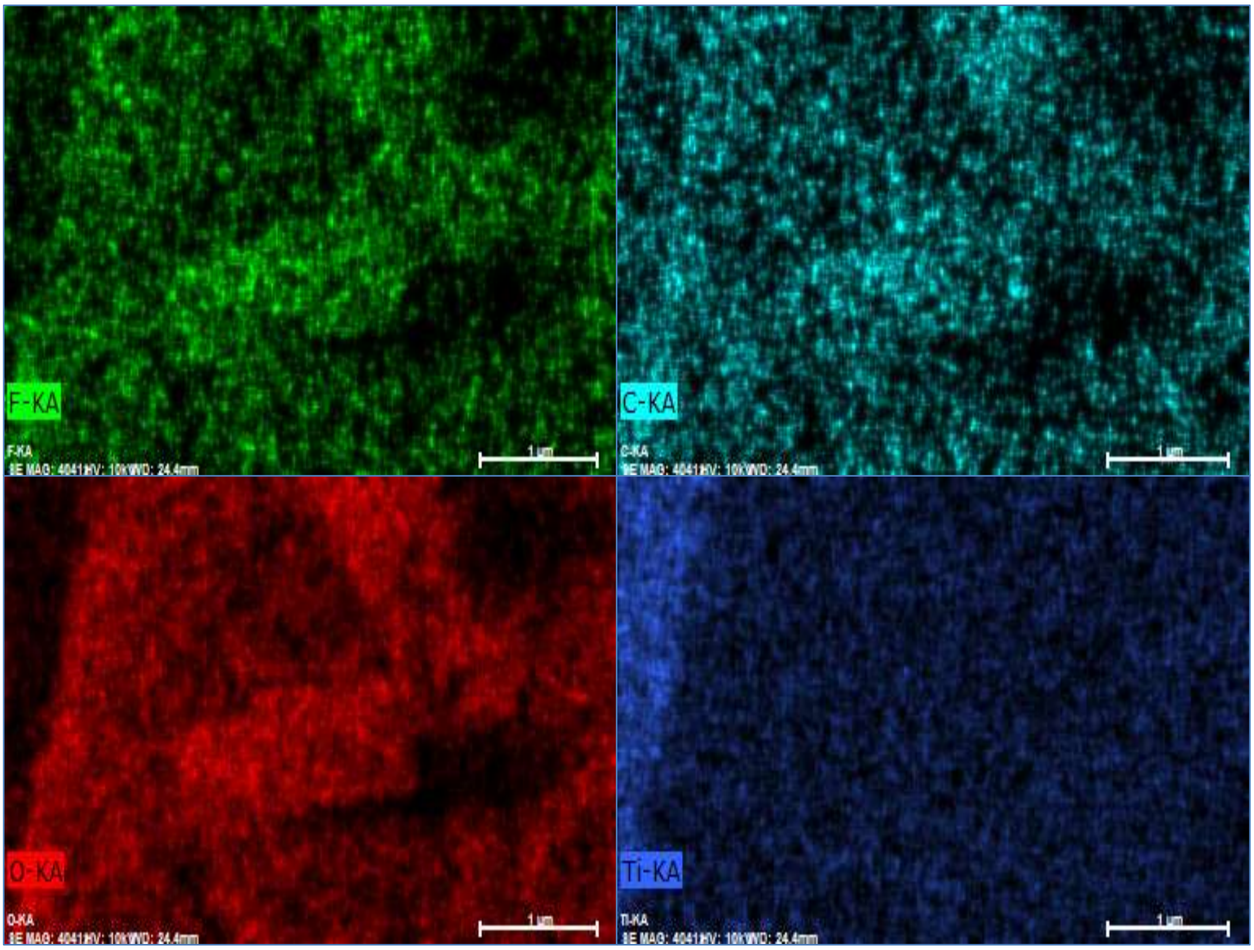

Figure 5 EDS-Mapping of TiO_2 nanotubes composition with element-coding.

3.3. Degradation of methylene blue (MB) using synthesized TiO_2 nanotubes

Highly ordered TiO_2 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_2 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_2 nanotubes array. From this figure it is clear that the rate of degradation is more when using TiO_2 nanotubes array. The reason is that using TiO_2 nanotubes with high surface area to volume ration enhances the surface of degradation. Therefore, TiO_2 nanotubes function in a beneficial rule as a photocatalyst The initial concentration of MB is (5 ppm). The area of TiO_2 nanotube array that contains the film is about (2 cm^2).The photocatalytic was done without use of any kind of stirring.

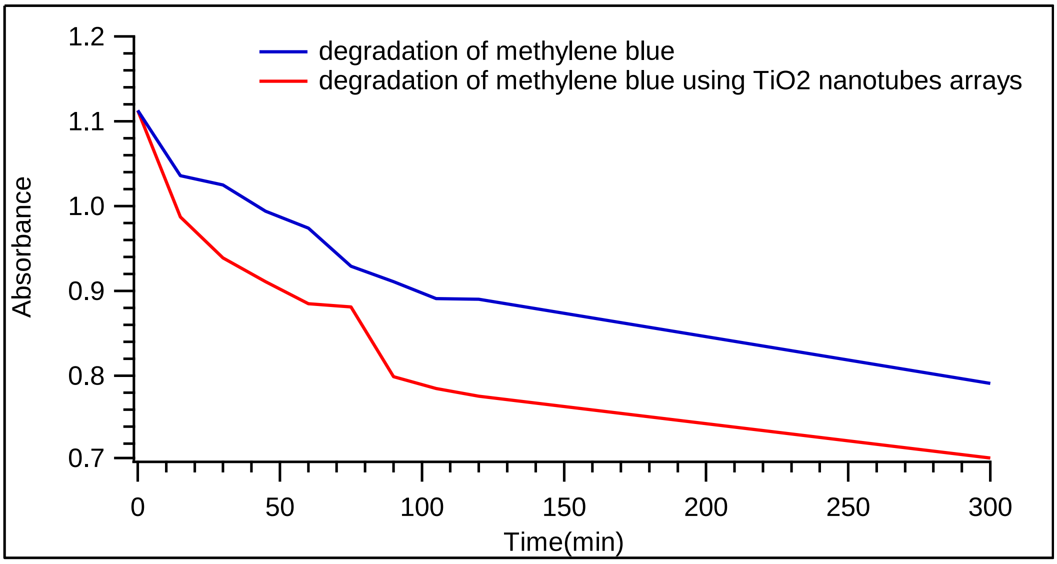

Figure (6) shows degradation of MB using TiO_2 nanotubes array as photocatalytic layer.

The concentration of MB in the presence of the TiO_2 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 photodegradatio of MB without the presence of TiO_2.

4. Conclusion

Anodisation method is very good method for creation of TiO_2 nanotubes because of its fast, reproducible and low-cost method. Using EDS is useful for qualitative and quantitative analysis of TiO_2 nanotubes and mapping is a new technique can be used for confirm the distribution of element on TiO_2 nanotubes wall. Under the experiment condition

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