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Research Article

Anodic TiO₂ Nanotube Arrays as Fixed Photocatalyst

¹Ammar Elsanousi, ^{1,2}Oussama Ouerghi and ³Yanming Xue

¹Prince Sattam Bin Abdulaziz University, Al Kahrj 11942, Saudi Arabia

²Pasteur Institute, Tunisia

³School of Material Science and Engineering, Hebei University of Technology, Tianjin 300130, P.R. China

Abstract

In the present study, self-organized TiO₂ nanotube arrays were prepared by anodic oxidation in a viscous electrolyte of ethylene glycol containing NH₄F with a concentration of 1.25% wt. The anodized samples exposes single walled nanotube arrays with an average pore diameter and wall thickness of about 80 and 15 nm, respectively. The photocatalytic efficiency of the nanotube arrays has been investigated and compared to commercial P25 nanopowder by measuring the degradation of methyl orange. The results showed that the nanotube arrays exhibit higher activity towards dye degradation as compared to commercial P25 nanoparticles with a degradation efficiency reaching up to 99.45% after an irradiation time of 60 min. The high surface to volume ratio and the mechanical adhesion makes them suitable as multiple use photocatalysts.

Key words: Anodic oxidation, nanotubes, photocatalytic activity, titanium dioxide, methyl orange

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Corresponding Author: Ammar Elsanousi, Prince Sattam Bin Abdulaziz University, Al Kahrj 11942, Saudi Arabia

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Data Availability: All relevant data are within the paper and its supporting information files.

INTRODUCTION

Titanium dioxide (TiO_2) has received considerable attention due to its unique physical and chemical properties. TiO_2 is an n-type semiconductor, which is chemically stable as well as stable towards photo-oxidation. In addition, it is nontoxic and relatively easy and cheap to produce; therefore, it has been functional in many applications such as solar cells, sensors, photo-catalysts, electrochemical capacitors, rechargeable lithium batteries, etc. (Kasuga *et al.*, 1999; Armstrong *et al.*, 2005).

Recently, TiO_2 nanoparticles have been widely used as traditional photocatalyst for the photodegradation of organic pollutants. It is well known that the photocatalytic performance of TiO_2 photocatalyst is considerably influenced by the semiconductor morphology (Gong *et al.*, 2011; Du *et al.*, 2011; Awate *et al.*, 2011) where a perfect morphology could greatly enlarge the effective surface area for a better contact and reaction of gases or liquids and therefore improve the light response and separation of photogenerated electron-hole pairs (Wu *et al.*, 2010). The TiO_2 nanoparticle photocatalysts are not always suitable for specific applications, due to their high recombination efficiency of photogenerated electron-hole pairs, tendency to aggregate during reaction and their separation problem of suspended nanoparticles for reuse. Therefore, several techniques have been used for the fabrication of fixed photocatalysts on solid support substrate, including sol-gel method (Egerton *et al.*, 2006), template synthesis (Lakshmi *et al.*, 1997), sputtering (He *et al.*, 2006) and anodic oxidation (Mor *et al.*, 2005). Among these techniques, self-organized TiO_2 nanotube arrays fabricated by anodic oxidation on Ti substrate proved to be more effective due its high mechanical adhesion strength, simple fabrication procedure and easy controllable dimensions (Macak *et al.*, 2006; Chen *et al.*, 2007; Tsuchiya *et al.*, 2005; Ruan *et al.*, 2005).

Since the first fabrication of hollow TiO_2 nanotubes on titanium alloy by anodic oxidation by Zwilling *et al.* (1999), many studies have been carried out to improve the structure as well as the functionality of TiO_2 nanotube arrays by tailoring the anodization parameters such as the electrolyte composition, pH, anodization duration and voltage (Mor *et al.*, 2003; Tsuchiya *et al.*, 2006; Beranek *et al.*, 2003; Macak *et al.*, 2005).

Until now, direct comparison studies between the photocatalytic activity of anodic TiO_2 nanotube arrays and commercial TiO_2 nanoparticle powders at the same conditions are very few. However, most studies concerning

the photocatalytic properties of TiO_2 nanotube arrays reported the superiority of these structures as photocatalysts. Roy *et al.* (2011) reported that TiO_2 nanotubes can have higher photocatalytic activity than a comparable nanoparticulate layer. Kontos *et al.* (2010) also reported that an optimum self-assembled titania nanotube structures outperform over standard (P25) TiO_2 nanoparticle films, rendering them very promising for outdoor photocatalytic applications.

The concern in this study was focused on the photocatalytic properties of highly ordered TiO_2 nanotube arrays as fixed photocatalyst investigated by the degradation of Methyl Orange (MO) and the results were compared to conventional TiO_2 nanoparticles powder (P25 Degussa), which is widely used as photocatalyst because of its relatively high levels of activity in many photocatalytic reaction systems.

MATERIALS AND METHODS

Preparation of TiO_2 nanotube arrays: Self-organized TiO_2 nanotube arrays were prepared by anodization in a two-electrode electrochemical cell as illustrated in Fig. 1. All the anodization experiments were carried out at room temperature using commercially available Ti foil (98.7% purity, 0.3 mm thickness) as a working electrode and a graphite plate as a counter electrode. Before anodization, the Ti foil was cleaned with acetone, ethanol and distilled water sequentially in ultrasonic bath. The anodization process was performed in a viscous electrolyte of ethylene glycol containing ammonium fluoride (NH_4F) with a concentration of 1.25 wt% at constant voltage of 20 V for 30 min using a direct current voltage source (DH1722, Dahua Co., Beijing, China). The anodized sample was then washed several times with distilled water and annealed at 450°C for 1 h with heating and cooling rates of $20^\circ\text{C min}^{-1}$.

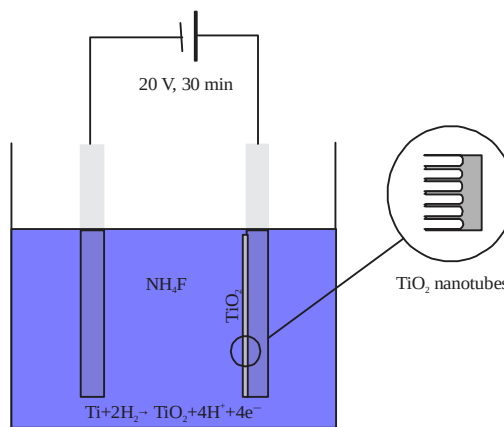


Fig. 1: Illustrative diagram of the anodization process

Characterization: The surface morphology and dimension characterization (top-view and cross-section view) of the anodized samples were observed by Scanning Electron Microscopy (SEM, JEOL JSM-6700F). The cross-section images were taken from mechanically cut samples. The phase structure of the anodized sample was analyzed by X-ray diffraction (XRD; D/max-RB) before and after annealing using Cu K α radiation ($\lambda = 1.54178 \text{ \AA}$).

Photocatalytic activity measurements: The photocatalytic measurement was carried out by immersing the TiO₂ nanotube arrays film in 20 mL glass beaker containing Methyl Orange (MO) solution with the concentration of 20 mg L⁻¹. Prior to irradiation, TiO₂ nanotube arrays film was soaked in MO solution for 30 min in a dark environment to achieve the equilibrium of adsorption and desorption. A UV-lamp ($\lambda = 360 \text{ nm}$) was fixed about 10 cm above the surface of the solution as light source and small quantities of the solution were withdrawn after various radiation time intervals (0, 10, 20, 40 and 60 min). Each sample solution was centrifuged for 10 min in order to separate the catalyst particles from the solution. The absorption spectra were measured using a UV-vis spectrophotometer and the residual concentration of MO was determined by measuring the maximum absorption peak value of each sample solution at approximately 464 nm. For comparison the photocatalytic activity of commercial TiO₂ nanoparticles (P25 Degussa) composed of anatase and rutile crystallites, with a primary particle size of about 21 nm was also tested under identical conditions.

RESULTS AND DISCUSSION

Figure 2 shows the top and side view SEM images of the anodized sample. The anodized foil sample exposes single walled nanotube arrays with an average pore diameter and wall thickness of about 80 and 15 nm, respectively (Fig. 2a) and an average nanotube length of about 1 μm (Fig. 2b).

The proposed growth mechanism of the nanotube arrays can be described from the current density/time curve shown in Fig. 3. A rapid reduction in the current density can be observed at the beginning of the anodization process, which is attributed to the poor electrical conductivity of the layer due to the formation of a thin titanium (IV) layer on the surface of the titanium sheet according to the following chemical reaction as in Eq. 1:

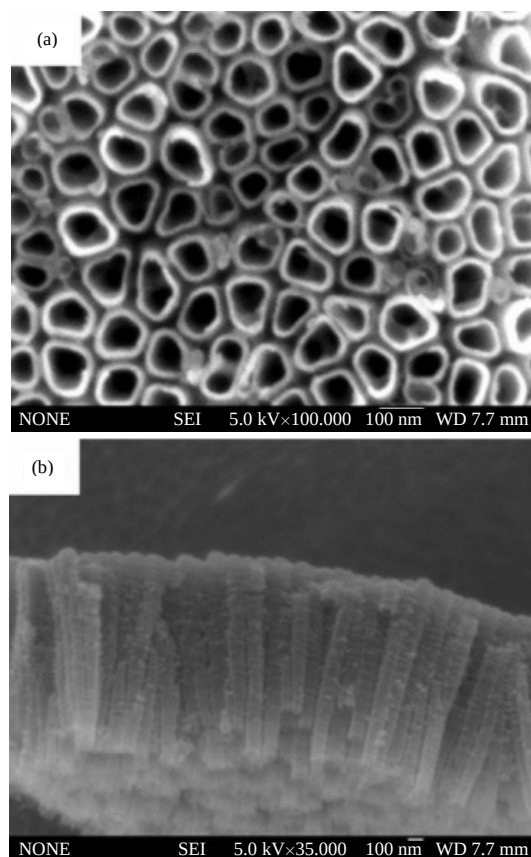
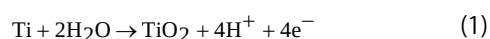


Fig. 2(a-b): SEM images of the self-organized TiO₂ nanotubes grown on titanium foil, (a) Top view and (b) Side view

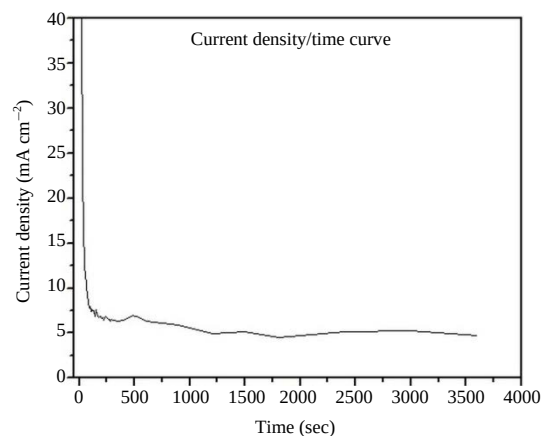


Fig. 3: Current density-time curve of the anodized sample

After that, the current density reaches a quasi-steady state due to the chemical dissolution of the oxide layer forming soluble fluoride complexes according to the following reaction as in Eq. 2:

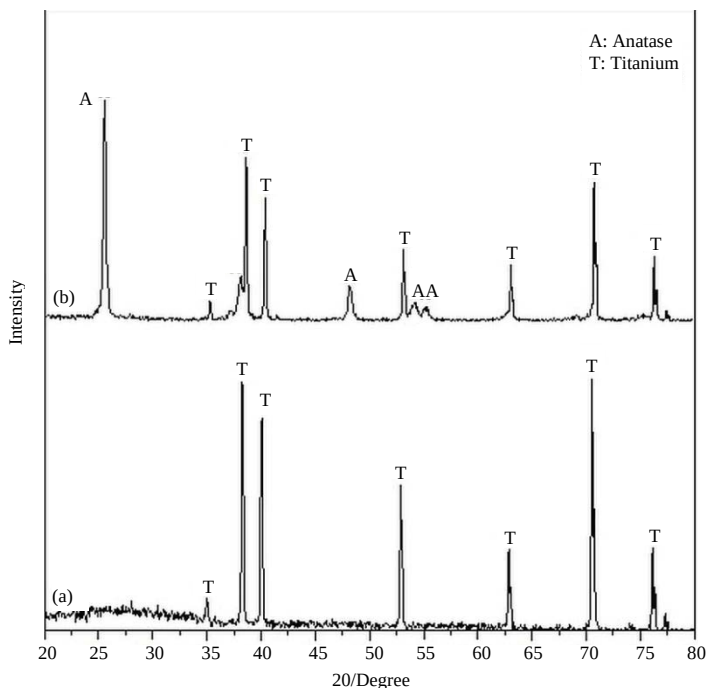


Fig. 4(a-b): XRD patterns of anodized sample, (a) Before annealing and (b) After annealing at 450 °C

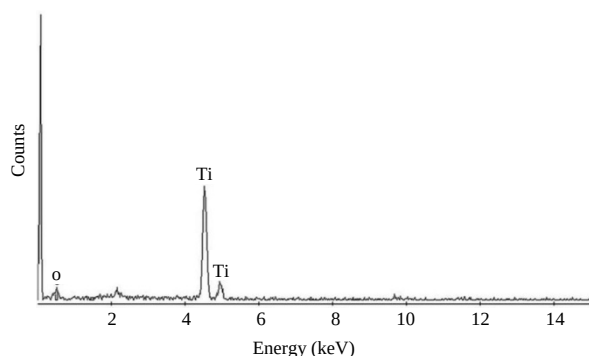
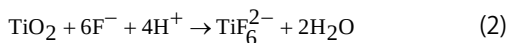


Fig. 5: EDX spectrum of the anodized sample



As a result fine pores are formed at the surface. Under sufficient applied voltage magnitude, field-assisted oxidation occurs at the TiO_2/Ti interface, where the oxygen ions (O^{2-}) are transported from the solution to the oxide layer. At the same time, titanium ions (Ti^{4+}) are transported from the titanium to the oxide/solution interface and dissolve into the solution, leading to a continuous increase in the depth of the porous structure and thus the formation of ordered nanotubes oriented vertically to the substrate (Elsanousi *et al.*, 2008; Yang *et al.*, 2008).

Figure 4 shows the XRD patterns of the TiO_2 nanotube arrays produced by anodic oxidation before and after

annealing. Before annealing (Fig. 4a), the as-grown nanotube arrays exposes an amorphous structure, where only diffraction peaks from the titanium substrate can be seen. After annealing at 450 °C (Fig. 4b), the structure of the nanotube arrays converts into crystalline structure, where sharp peaks of anatase phase can be observed. These results are well consistent with the previous reports by Liao *et al.* (2012).

Varghese *et al.* (2003) also studied the stability of TiO_2 nanotubes on Ti substrate at the elevated temperature and found that the anatase to rutile phase transition started at 430 °C and completely transform to rutile at 620 °C, which is also to some extent consistent with our results.

Elemental analysis using the Energy Dispersive X-ray (EDX) diffraction technique reveals that Ti and O are the major elements without the existence of any impurity peaks as can be seen from Fig. 5. The quantitative analysis shows that the atomic ratio of Ti:O is about 1:2, which confirms the composition of TiO_2 .

The photocatalytic activity of the nanotube arrays and the commercial TiO_2 nanoparticle powder (P25) were tested by measuring the degradation of MO after different time intervals as can be seen from Fig. 6. From this figure it is apparent that the TiO_2 nanotube arrays exhibited higher photocatalytic activities than P25 nanopowders. The results are in good agreement with previous reports by Roy *et al.* (2011) and Kontos *et al.* (2010).

It was noticed that the degradation efficiency of TiO_2 nanotubes is at least 5% higher than that of P25 nanopowders

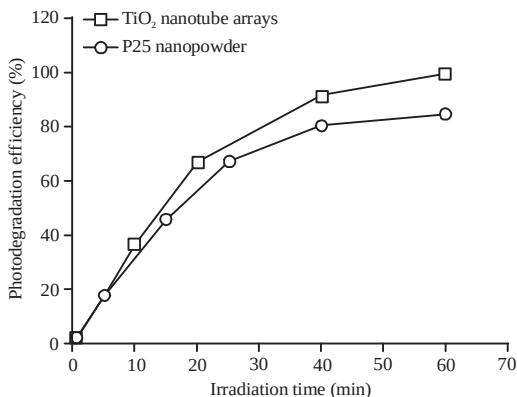


Fig. 6: Photodegradation efficiency as a function of irradiation time for the nanotube arrays and P25 nanopowder

and it reaches 99.45% after 60 min under UV irradiation while P25 nanopowders reaches only 84.45% at the same irradiation time. This can be ascribed to the high surface area of the nanotube arrays compared to P25 nanoparticles, since their wall thickness (≈ 15 nm) is smaller than the mean diameter of the P25 nanoparticles which is about 21 nm. Hoffmann *et al.* (1995), Lai *et al.* (2006) and Yu *et al.* (2006) reported that titania in the anatase form has a better catalytic performance than the mixtures of anatase and rutile, which could be another reason for the enhanced photocatalytic activity of the pure anatase phase TiO₂ nanotube arrays compared to P25 nanoparticles, since they are composed of anatase and rutile crystallites.

It was also noticed that the photodegradation of MO in both samples obeys the first order reaction kinetics, which can be expressed as in Eq. 3:

$$\ln (C/C_0) = k t \quad (3)$$

where, k is the reaction rate constant, t is the irradiation time, C_0 and C are the initial and reaction concentrations of MO aqueous solutions, respectively. The k value of MO for the nanotube arrays has a maximum value of $6 \times 10^{-2} \text{ min}^{-1}$, whereas it is only $4 \times 10^{-2} \text{ min}^{-1}$ for P25 nanoparticles. These results indicate that the nanotube arrays can be more beneficial as photocatalysts than P25 nanopowders, since they exhibit remarkably enhanced photocatalytic activity, besides their ability to be reused several times.

CONCLUSION

Highly ordered TiO₂ nanotube arrays were grown by electrochemical anodization in a viscous electrolyte of ethylene glycol containing NH₄F with a concentration of 1.25% wt. The photocatalytic activity of the synthesized

nanotube arrays was investigated by measuring the degradation of methyl orange at different time intervals and the results showed that the nanotube arrays exhibit higher activity towards dye degradation as compared to commercial P25 nanoparticles with a degradation efficiency of at least 5% higher than P25 at short irradiation time.

According to these results, the nanotube arrays proved to be more effective as active materials for the waste water treatment than traditional nanopowder photocatalysts due to their ideal morphology with its high effective surface, allowing a better contact and reaction of liquids and thus improving the light response and separation of the photogenerated electron-hole pairs, besides their mechanical adhesion strength allowing the possibility for multiple use.

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