EFFECT OF ANNEALING TEMPERATURES ON THE CRYSTALLIZATION AND PHOTOCATALYTIC ACTIVITY OF MICRO-NANOPOROUS TiO_2 FILMS PRODUCED BY ELECTROCHEMICAL ANODIZATION

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ABSTRACT: In this study, micro-nanoporous TiO_2 films were prepared by electrochemical anodization of titanium (Gr-2) in an aqueous solution containing 0.5 wt. % HF solution at a constant potential of 30 V and then annealed in ambient air at 500, 600, 700 and 800 °C for 2 h to obtain crystalline structures. The crystalline phase and surface morphology of the samples were characterized by X-ray diffraction (XRD) and scanning electron microscope (SEM). The photocatalytic performances of the samples were evaluated by the photocatalytic degradation of aqueous methylene blue (MB) solutions under UV light illumination for different periods. XRD results indicated that at annealing temperatures higher than 600°C, anatase started to transform into rutile. Increasing annealing temperatures resulted in reduced micro-nanopores diameter and increased wall thickness. At 800°C, the structure completely disappeared. The results demonstrated that changes in both the crystalline structure and surface morphology have a strong influence on the photoactivity of the nanostructured TiO_2 films.

Keywords: Nanostructured TiO_2; anatase; surface morphology; photocatalytic; methylene blue.

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INTRODUCTION

In 1972, titanium dioxide has been considerable investigated as a semiconductor photocatalyst for solar energy conversion and environmental purification since Fujishima and Honda discovered the photocatalytic splitting of water on TiO_2 electrodes in 1972 [Fujishima and Honda, 1972]. Among various oxide semiconductor photocatalytic materials, TiO_2 is widely used for pollution control because of its high physical stability, chemical inertness, low cost, and non-toxicity and strong oxidizing power under UV light irradiation [Fujishima *et al*., 2000, Linsebigler *et al*., 1995, Chen and Mao, 2007]. TiO_2 has three nature crystallographic phases: anatase (tetragonal), rutile (tetragonal) and brookite (orthorhombic). Among these crystal structures of TiO_2, anatase phase is generally considered to be more active than rutile phase for TiO_2 photocatalysts due to its lower surface energy than rutile [Ahmed, 2012]. Rutile is the most thermodynamically stable phase, whereas anatase and brookite are metastable phases and could be transformed into rutile easily by thermal treatment [Beltran *et al*., 2006].

Nanostructured TiO_2 thin films are usually prepared by sol–gel processing, chemical vapor deposition (CVD), liquid-phase deposition (LPD) methods and ion-beam synthesis methods [Tomandl *et al*., 2000, Yu *et al*., 2003, Komarov *et al*., 2005]. Recently, highly ordered TiO_2 thin films prepared by a simple electrochemical anodization over a titanium substrate in a fluoride containing electrolyte in 2001. This method is a cost effective, versatile, easy, controllable and reproducible technique. This method is also possible to arrange the size and shape of nanopore arrays to the targeted dimensions [Gong *et al*., 2001, Indira *et al*., 2012].

Many new types of TiO_2-based photocatalysts have been reported in recent years, including, nanotubes [Liu *et al*., 2008], nanofibers [Liu *et al*., 2007], nanosheets (TNSs) [Matsumoto *et al*., 2009], porous anodized films [Masahashi *et al*., 2009], nanowire arrays [Yu *et al*., 2009], nanograined thin films [Ryu *et al*., 2008], mesoporous structures [Pan and Lee, 2006] and hierarchical micro- and nanoporous structures [Zhao *et al*., 2008]. It is known that morphology control of TiO_2-based photocatalysts is usually one of the important research directions. This study examines the influence of annealing temperatures on the photocatalytic activity of TiO_2 films grown on titanium substrates by anodization, with the aim of achieving a high photocatalytic performance.

Herein, we prepared the micro-nanoporous TiO_2 films by electrochemical anodization of titanium substrates and then annealed in ambient air at 500, 600, 700 and 800 °C. The

effects of annealing temperature on the crystallization, morphology and photocatalytic activity of TiO_2 films were investigated and discussed. The photocatalytic properties were evaluated using MB as the target pollutant.

EXPERIMENTAL

The commercially pure titanium (Cp-Gr 2) substrates with diameters of 25 mm and 5 mm thickness were used as anode. After polishing process, the samples were cleaned ultrasonically in ethanol, acetone and deionized (DI) water for each 15 min and finally washed by distilled water. Prior to the anodization process, the samples were degreased in a mixture of nitric acid and hydrofluoric acid solutions for ten seconds to remove the air-formed oxide layer.

The anodization was performed in a solution consisting 0.5 wt. % HF solution at 30 V for 30 min in two-electrode configuration connected to a DC power supply at room temperature. After electrochemical anodization, all the anodized films were calcined at 500, 600, 700 and 800 °C in air for 2 h.

X-ray diffraction patterns of all samples were recorded to identify the phase structures with the aid of an X-ray diffractometer having a CuK_α characteristic radiation source (XRD, Thermo-Scientific, ARL K_α). Diffraction patterns were acquired in the range of 10° to 80° with a scanning rate of 2°/min. The X-ray radiation of Cu-K_α was set at 45 kV and 44 mA. The surface morphology and microstructure of the samples were characterized by a scanning electron microscope (SEM, COXEM EM-30 Plus).

The photodegradation of MB experiments were exploited in a homemade reactor which was surrounded a cooling system to keep the photocatalytic reaction system at room temperature. All tests were performed using a light source (Osram, UltraVitalux E27, 300W). The films were placed into beakers containing 30 ml of MB aqueous solution. The initial concentration of MB is 3 mg/L corresponding to 10^{-5} M (pH = 8). The distance between the lamp and the beakers was kept at 20 cm for all specimens. During the whole reaction, 3 ml of the MB aqueous solution from each beaker was extracted at an interval of 1 h in order to measure the absorption spectra of MB. The absorption of the MB solutions was conducted and analyzed by a UV-1240 Shimadzu spectrophotometer based on the characteristic absorption of MB peak at 664 nm.

RESULTS AND DISCUSSION

Fig. 1 depicts the XRD patterns of the micro-nanoporous TiO_2 films annealed at different temperature. It was observed that the microporous layers exhibited mixed crystalline structures consisting of anatase, rutile and metallic Ti from the substrate. It was observed that the main diffraction peaks at 25.38 (101) and 37.96 (004) which correspond to crystal structure of anatase for the samples annealed at 500 °C and 600 °C [Kenanakis, *et al*., 2015]. When the annealing temperature increased, the intensity of anatase decreased in the samples and crystalline phase of micro-nanoporous TiO_2 films was predominantly rutile. It must also be noted that metallic titanium peaks observed in patterns that can be associated to X-ray penetration into the substrates on which surface modifications were made.

It is known that surface morphology is of great influence on catalysts' photocatalytic activity. Fig.2 shows the SEM micrographs of the micro-nanoporous TiO_2 films. The shapes of TiO_2 micro- and nanopores exhibited a noticeable change with increasing annealing temperature. With further increasing of the annealing temperature to 800 °C, pores were destroyed and started to disappear.

As mentioned before, the MB dye was used to assess the photocatalytic performance of the prepared micro-nanoporous TiO_2 films annealed at different temperature.

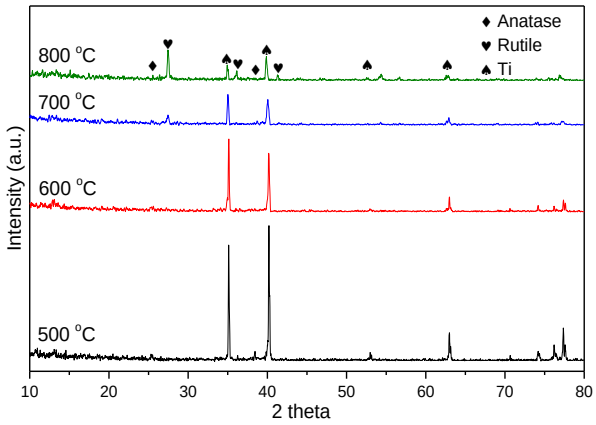

Figure 1: XRD patterns of the micro-nanoporous TiO_2 films annealed at different temperatures.

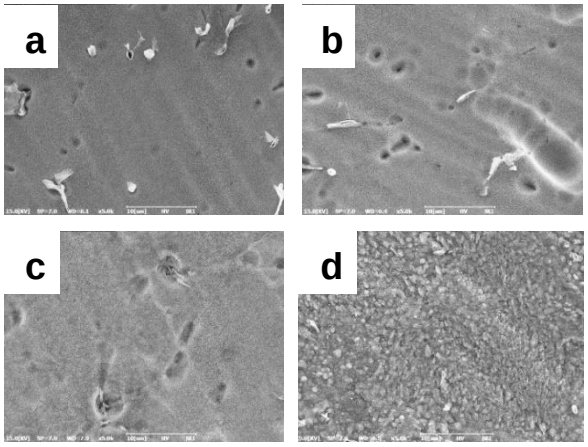

Figure 2: SEM images of TiO_2 films annealed at (a) 500 °C (b) 600 °C (c) 700 °C and (d) 800 °C.

Fig. 3 shows the photocatalytic degradation of MB by the micro nanoporous TiO_2 films annealed at different temperatures. Considering the annealing temperatures of the films, the sample annealed at 600 °C has the best photocatalytic activity and SEM photographs support these results. Fig 4 shows the photocatalytic kinetics of the TiO_2 films micro-nanoporous TiO_2 films annealed at different temperatures. Photocatalytic degradation kinetics were calculated from Langmuir–Hinshelwood kinetics model that express the first order reaction kinetics for the samples. With this approach, it can be inferred that the higher the slope of the linear plot, the higher the degradation reaction rate.

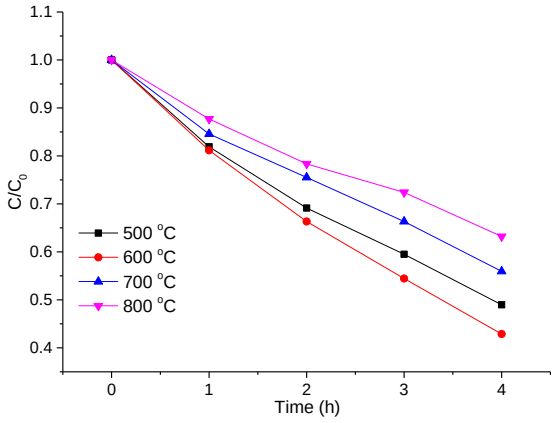

Figure 3: Photocatalytic degradations of the TiO_2 films micro-nanoporous TiO_2 films annealed at different temperatures.

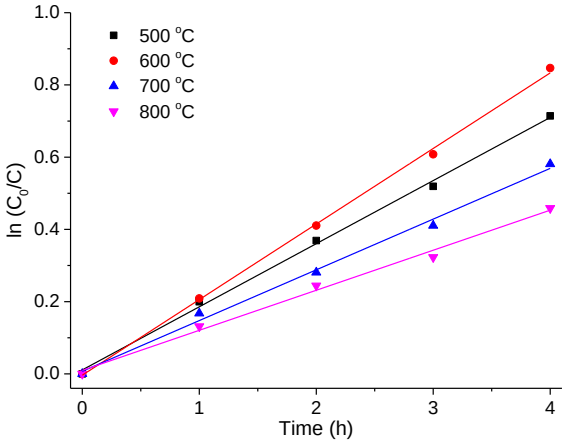

Figure 4: Photocatalytic kinetics of the TiO_2 films micro-nanoporous TiO_2 films annealed at different temperatures.

Table 1: Photocatalytic parameters of the samples.

Annealing temperature (°C)	Kinetic rate constant (k) (h^{-1})	R^2
500	0.1748	0.9971
600	0.2093	0.9985
700	0.1405	0.9935
800	0.1109	0.9916

It can be understood from the Fig. 4; all samples are good agreement with the first order kinetics. The photocatalytic parameters of the samples were given in Table 1. The film annealed at 600 °C proved to be the best photocatalyst among the samples annealed from 500 °C to 800 °C. The photocatalytic activity of TiO_2 structures depends on several factors such as surface area, crystallinity, phase composition and crystal orientation [Dikici *et al*., 2015].

CONCLUSION

It can be concluded that the structural properties of the films determined the best photocatalyst in this work. Annealing temperature of the 600 °C for 2 h in air is the best heat treatment regime that the anatase phase is predominant and rutile is the newly formed for the sample with higher surface area. Low anatase/rutile ratio is better for the photoactivity of micro-nanoporous TiO_2 films.

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