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Characterization and photocatalytic properties of nanoporous titanium dioxide layer fabricated on pure titanium substrates by the anodic oxidation process

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Abstract

Nanoporous titanium oxide (TiO_2) layers were fabricated on commercially pure titanium (Cp-Ti) substrates by the anodic oxidation method under a potentiostatic regime. Anodic oxidation was performed in an aqueous solution containing 1 wt% hydrofluoric acid at room temperature for 30 min. Subsequently one of the anodized samples was annealed at 480 °C for 2 h in air in order to obtain anatase transformation and increased crystallinity. The average pore diameter of both anodized and anodized+annealed samples were found to be nearly 52 nm and 66 nm, whilst the average inter-pore distances were approximately 65 nm and 76 nm, respectively. Characterization of nanoporous TiO_2 layers was carried out through X-ray diffractometer (XRD), scanning electron microscopy (SEM), atomic force microscopy (AFM) and UV visible spectroscopy. Effects of heat treatment on properties such as crystallinity, morphology and photocatalytic activity were investigated in details. Finally photocatalytic degradation ratios and changes in degradation kinetics under the presence of both anodized and anodized+annealed catalysts were calculated. Depending on the obtained results, the annealed film with anatase structure demonstrated highly efficient photacatalytic performance.

Keywords: Nanoporous titanium oxide; Anatase; Anodic oxidation; Photocatalytic activity; Methylene blue

1. Introduction

Titanium dioxide (TiO_2) has been widely investigated as a key material for photocatalytic, photovoltaic, bio-coating and photoelectrolytic applications due to its non-toxicity, chemical stability, low cost optical, electronic and physiochemical properties [1–5]. Since the discovery of photocatalytic water splitting on TiO_2 by Fujishima and Honda in 1972, the studies performed on TiO_2 as a photocatalyst for purification of groundwater and waste water have grown [6–11]. Nanostrucutured materials have attracted remarkable interest owing to their potential applications in micro-electronics, optical electronics and photocatalysis [12]. Many methods have been developed for the fabrication of TiO_2 nanotubes with larger surface areas, including anodic oxidation, template method, hydrothermal and soft chemical process [13–16]. Anodic oxidation is an effective method for producing TiO_2 nanotubes/nanopores with controllable pore sizes and morphologies because of low cost and simple fabrication [17].

It is well known that TiO_2 has three crystalline forms such as anatase, rutile and brookite. Among these three crystalline forms, anatase phase has been extensively used in photodegradation due to its high photoactivity [18–20]. Post-annealing is an important issue to transform the anodized TiO_2 nanotube

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arrayed films from amorphous in to crystalline structure [17]. In this study, we investigated the photocatalytic activity and the kinetics of amorphous and crystalline nanoporous TiO_2 films formed on pure titanium discs in hydrofluoric acid (HF) aqueous solution via constant voltage on degradation of methylene blue (MB).

2. Experimental details

Commercially pure titanium (Grade 2, Bagsan Co., Turkey) disc (diameter of 15 mm; thickness of 1 mm) was used as a substrate. All substrates were mechanically polished with 80-grit–2000-grit emery paper, and then washed with acetone, ethanol and distilled water in an ultrasonic cleaner. Prior to the experiments, acid activation was performed in a mixture of nitric acid (HNO_3) and hydrofluoric acid (HF) solutions for 10 s to remove the air-formed oxide layer.

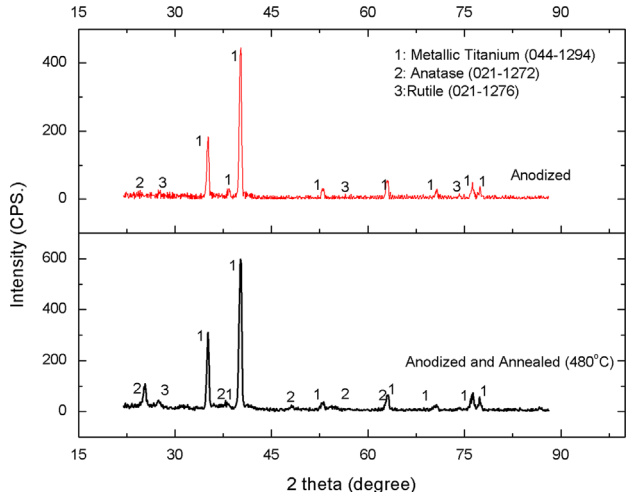

Fig. 1. XRD patterns of the anodized and anodized+annealed samples.

Anodization was performed in a two-electrode configuration under a constant 20 V anodic potential for 0.5 h at room temperature by a DC power supply (CRS Power, Turkey) and 1 (wt%) HF as an electrolyte. The distance between the anode and cathode was kept at about 40 mm. After the anodic oxidation, one of the anodized substrates was annealed at 480 °C for 2 h under air ambient to improve the crystallinity and anatase transformation.

X-ray diffraction (XRD, Rigaku D/MAX-2200/PC) patterns of the specimens were determined to identify phase structure by means of a diffractometer with a CuK_α irradiation. The surface morphology of the specimens was characterized by a scanning electron microscopy (SEM, JEOL 6060) and an atomic force microscopy (AFM, EasyScan2, Nanoscience) in contact mode.

Photocatalytic degradation experiments of the specimens were performed using a setup including aquous MB solutions for both catalysts and a UV light source (Osram, UltraVitalux E27, 300 W). In order to record catalyst-free degradation of MB under radiation an arbitration sample of the solution was also prepared. In this study, MB was supplied from Merck in the laboratory grade and used without further purification. 30 mL of MB solutions ($C_0 = 1.28 \times 10^{-5}$ mol/L) were poured into beakers and catalysts were placed across to the light source with a distance approximately 200 mm. As denoted in

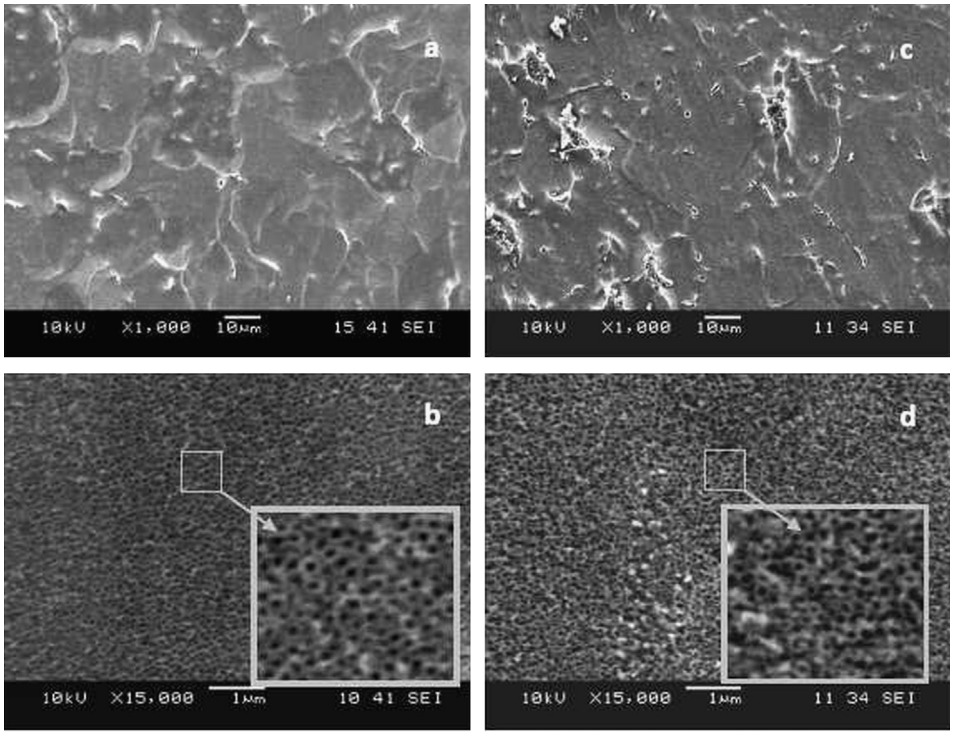

Fig. 2. SEM micrographs of the samples from (a) top view of anodized sample, (b) high-magnification top view of anodized sample, (c) the annealed sample at 480 °C after anodizing and (d) high-magnification top view of the annealed sample at 480 °C after anodizing.