



# Electrochemical growth of porous titanium dioxide in a glycerol-based electrolyte at different temperatures

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## ABSTRACT

Anodic TiO<sub>2</sub> layers on Ti were prepared via a three-step anodization in glycerol containing NH<sub>4</sub>F (0.38 wt%) and H<sub>2</sub>O (1.79 wt%) at the constant anodizing potential of 40V and temperatures ranging from 10 to 40 °C. It was confirmed that TiO<sub>2</sub> growth is thermally activated and transport of oxygen species across the titanium dioxide layer at the pore bottoms is a rate-limiting step of anodization. The morphological characterizations of received anodic layers were performed for all studied temperatures. The structural features of anodic TiO<sub>2</sub> such as pore diameter, cell diameter, porosity, pore density and pore circularity were investigated for various anodizing temperatures. It was found that the oxide thickness, pore diameter, cell diameter and porosity of formed TiO<sub>2</sub> layers increase gradually with increasing temperature. The pore density and their arrangement analyses showed that the nanoporous anodic titania layer with the lowest density of pores and best pore arrangement was synthesized at 20 °C. In addition, photoelectrochemical properties of formed TiO<sub>2</sub> layers were investigated as well.

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## 1. Introduction

Nowadays, nanotechnology is considered as a key strategy to improve conventional and develop new technologies by exploring novel nanomaterials and nanoscale processes. Over the last years, the anodic formation of nanostructured TiO<sub>2</sub> with ordered, straight and parallel tubes/channels, and a narrow distribution of their diameter has received significant scientific and technological attention. The exploitation of unique functional properties of nanostructured TiO<sub>2</sub> holds outstanding promise for the achievement of significant breakthroughs in various areas of applications ranging from photovoltaics and photocatalysis to sensors and deposition of templates for secondary nanomaterials [1–3]. The increasing research interest in these fields has demonstrated that nanostructured TiO<sub>2</sub> will play in the future an important role in the environmental and energy sectors. These include protection of

the environment and development of renewable and clean energy technologies [1,4].

Indeed, nanoporous/nanotubular anodic TiO<sub>2</sub> has been successfully used as an efficient photocatalyst for water splitting [5,6], hydrogen generation [7,8], degradation of pollutants [9,10], and electrocatalytic oxidation of methanol [11,12]. Moreover, other potential technological applications of anodic TiO<sub>2</sub> include dye-sensitized solar cells [13–15], energy storage systems [15–17], humidity sensors [18], gas sensors [19,20], biosensors [21,22], and biocompatible bone grafting materials [23,24]. Similarly to porous anodic alumina, anodic TiO<sub>2</sub> has been recently utilized as a porous template for synthesis of metal nanowires and nanoparticles [25,26], as well as conducting polymer nanowires and nanopore arrays [27,28].

The effectiveness of above mentioned applications depends evidently on the morphology of TiO<sub>2</sub> layers. It is therefore not surprising that over the past years, many researchers have focused their studies on the fabrication of nanostructured titania [3]. In 1999, Zwilling et al. [29] first reported fabrication of nanotubular TiO<sub>2</sub> through anodization of titanium in a mixture of chromic acid and hydrofluoric acid. Since then, researchers continuously studied and developed this approach to form porous/tubular TiO<sub>2</sub>. The first-generation of anodic TiO<sub>2</sub> nanotube arrays grown in acidic

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aqueous solutions had a length not exceeding 500 nm, because of a high dissolution rate of oxide in HF-based electrolytes [30]. The second generation of nanotubes were grown in neutral fluoride-based aqueous solutions, where the dissolution of TiO<sub>2</sub> was considerably reduced, and thus, the nanotube length increased to approximately 7 μm [31,32]. Afterwards, the most crucial improvement to the method was to use fluoride-containing polar organic electrolytes such as formamide [33], dimethylsulfoxide (DMSO) [34,35] or ethylene glycol [36,37]. It was found that the water presence in electrolytes used for anodization of titanium play an appreciable role in the dissolution of formed oxide. Consequently, water as a main constituent of anodizing electrolytes was replaced by organic liquids with low water contents, and accordingly, the third-generation TiO<sub>2</sub> nanotube arrays with lengths of up to 1000 μm and a smooth surface morphology were achieved in ethylene glycol containing NH<sub>4</sub>F and H<sub>2</sub>O [38].

It is well known, that the most common electrolyte used today for electrochemical oxidation of Ti is ethylene glycol (ethane-1,2-diol) containing fluoride ions. Glycerol (propan-1,2,3-triol) as an anodizing electrolyte is much less often used for the synthesis of nanotubular/nanoporous TiO<sub>2</sub> compared to ethylene glycol. So far, research efforts were focused mainly on controlling the morphology of grown TiO<sub>2</sub> nanotube/nanopore arrays and various parameters of electrochemical oxidation in glycerol-based electrolytes [39–56]. These include the studies on Ti anodization at various anodization voltages [44–53], electrolyte compositions and different values of pH [42,44,47,48,54,55], different hydrodynamic conditions [55], and anodizing times [44,46,48,53]. As it was shown for other anodizing electrolytes, temperature affects considerably the morphology and geometrical parameters of anodic TiO<sub>2</sub>. However, the temperature influence on ATO layers formed in glycerol-based electrolytes has attracted attention only a few researcher groups. The earliest work on the effect of electrolyte temperature on the diameter and length of formed nanotubes has been reported by Macak et al. [40]. They reported self-organized nanotubular ATO layers with high aspect ratios up to 150 formed at the temperatures of 0, 20 and 40 °C. The temperature of 20 °C was recommended as the best one for the nanotube growth. Moreover, it was found that for the glycerol electrolyte containing 0.5 wt% NH<sub>4</sub>F, the current efficiency of nanotube formation is close to 100%, which is significantly higher than that reported for water-based solutions. Then, Wang and Lin performed anodizations of titanium in glycerol containing 0.25 wt% NH<sub>4</sub>F at room temperature and in an ice bath [56]. It was shown that anodizing temperature markedly affects nanotube dimensions, while the applied voltage does not influence the diameter of nanotubes. Next, Lee et al. [51] reported the fabrication of the self-ordered nanochannel TiO<sub>2</sub> structure by anodization in a hot glycerol electrolyte (180 °C) containing 10 wt% K<sub>2</sub>HPO<sub>4</sub>. Furthermore, the effect of bath temperature on the dimension of fabricated TiO<sub>2</sub> nanotube arrays was studied by Wang and Chen [57]. They anodized Ti at 30 V in a mixture of glycerol and water (40 wt%) containing 0.5 wt% NH<sub>4</sub>F at temperatures ranging between 10 and 80 °C. The titania nanotubes were observed at the bath temperatures between 40 and 80 °C, while below 40 °C the formation of nanotubes was not detected. They claimed also that the inner diameter of nanotubes increased from 170 to 210 nm as bath temperature increased from 40 to 50 °C. Above 50 °C, comparable nanotube diameters were observed. On the other hand, the average length of nanotubes decreased from 2.10 to 0.94 μm with increasing bath temperature, while above 60 °C the formed nanotubes had similar lengths.

The listed above works give only limited information about the role of electrolyte temperature in the fabrication of nanoporous/nanotubular anodic TiO<sub>2</sub> and many questions and issues are still open to discussion. In this context, the main purpose of this work was to evaluate how the electrolyte temperature

affects the morphology and growth of ATO layers in glycerol containing 0.38 wt% NH<sub>4</sub>F and 1.79 wt% H<sub>2</sub>O. To the best of our knowledge, the influence of the electrolyte temperature on growth of ATO layers was not studied in glycerol solutions containing less than 2 wt% of water. In addition, photoelectrochemical properties of formed TiO<sub>2</sub> films were studied as well.

## 2. Experimental

The titanium foil of 0.25 mm thickness and 99.5% purity from Alfa Aesar was used. Prior to anodizations, Ti substrates (1.5 × 2.5 cm) with a selected working area of 0.8 cm<sup>2</sup> were degreased in acetone and ethanol, then dried in the air. The specimens were electrochemically polished at 20 °C in a mixture of acetic acid (99.5 wt%), sulfuric acid (98 wt%), and hydrofluoric acid (40 wt%) (60:15:25 in volume) at a constant current density of 1.4 A cm<sup>-2</sup> for 1 min, followed by chemical polishing carried out in a mixture of HF (40 wt%) and nitric acid (65 wt%) (1:3 in volume) for 10 s until mirror finish was observed. The anodization was performed in a two-electrode configuration with the Ti foil as the anode and a platinum grid as the cathode. The electrochemical oxidation process was carried out in a home-made Teflon electrochemical cell (volume of 100 cm<sup>3</sup>), where the anodized samples laid horizontally on the metallic cooled plate. The anodic TiO<sub>2</sub> films were prepared via a three-step anodization in a glycerol solution containing NH<sub>4</sub>F (0.38 wt%) and H<sub>2</sub>O (1.79 wt%) at the constant anodizing potential of 40 V and temperatures ranging from 10 to 40 °C. The duration of the first and second anodizing steps was 3 h. After the first and second anodizations, the grown oxide layers were removed. Then, immediately, the samples were re-anodized typically for 1 h. The resulting thicknesses of the oxide layer were 175, 602, 1434, 2615 nm for the temperatures of 10, 20, 30 and 40 °C, respectively. In case when the fixed 1-μm thick of ATO layers were synthesized (Fig. S1, supplementary content), the anodizing durations were selected to be 344, 100, 42 and 23 min for the corresponding temperatures 10, 20, 30 and 40 °C. After anodizations, the as-prepared samples were rinsed with water and dried in the air at room temperature.

The structural and morphological characterizations of anodic TiO<sub>2</sub> were performed for all studied temperatures, and include an extensive study of the ATO morphology by field emission scanning electron microscopy (FE-SEM, Hitachi S-4700) and evaluation of structural features of ATO layers (cell diameter, pore density and regularity of pore arrangement) by using software [58,59].

Before photoelectrochemical measurements, the anodic titania films were calcined (in the air) at 400 °C for 2 h using a muffle furnace (Czylok, FCF5-SHM). The photoelectrochemical characterization was performed using a photoelectric spectrometer (Instytut Fotonowy) equipped with the 150 W xenon lamp and coupled with the EG&G 273A (Princeton Applied Research) potentiostat. The photoelectrochemical experiments were carried out in a Teflon cell with a quartz window (35 × 35 mm) using a three-electrode configuration with a platinum foil as the counter electrode, a Haber-Luggin capillary with a saturated calomel electrode (SCE) as the reference electrode and nanoporous TiO<sub>2</sub> as the working electrode. The photocurrent vs. time curves were recorded at 0.5 V vs. SCE in a 0.1 M KNO<sub>3</sub> aqueous solution under pulsed UV illumination in 5 and 10 s for a light and dark cycles, respectively. A wavelength step of 10 nm was applied in the range of 300–400 nm.

## 3. Results and discussion

Fig. 1 shows the surface morphology, bottom and cross-sectional views of anodic TiO<sub>2</sub> layers obtained after 1 h of the third anodization performed in a glycerol solution containing NH<sub>4</sub>F (0.38 wt%)

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