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# 3D nanoporous titania formed by anodization as a promising photoelectrode material

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A B S T R A C T

Nanoscale control of the growth of inorganic metal oxides determines their structures and properties, and leads to development of novel nanostructured materials with fundamental and practical importance from a point of view their further applications. After anodic aluminum oxide, the next nanoporous material which has attracted tremendous interest of researchers around the world, is nanoporous anodic titanium oxide (ATO) formed by anodization. The main objective of this work was to investigate the ability of formation of anodic titanium oxide structures, particularly in the form of $TiO_2$ nanopore arrays on 3D titanium substrates (Ti mesh) in viscous electrolyte containing fluoride ions. Three-dimensional (3D) $TiO_2$ nanopore arrays grown on Ti mesh were prepared via two-step electrochemical anodization process, and the effect of anodizing potential and duration of the process on the formation of ATO layers on titanium mesh were investigated. The 3D $TiO_2$ nanopore arrays on Ti mesh were characterized by using field emission scanning electron microscopy and X-ray diffraction (XRD) technique. The results showed that the optimized anodization conditions for preparation of titanium dioxide nanopore arrays are 40 and 50 V of the applied potential, and 10 min of time processing. The effect of annealing temperature of ATO layers on their morphology and phase composition was also investigated in detail. The amorphous ATO layers on titanium mesh transform to anatase phase at 400 °C and further to rutile phase at 600 °C. However, photoelectrochemical tests demonstrated that the best photoelectrochemical performance of fabricated 3D photoanodes was observed for the samples anodized at 40 V or 50 V for 10 min, and annealed at 400 °C. The photoelectrochemical properties of the mesh-based and typical plate $TiO_2$/Ti electrodes were compared. It was found that the higher photoconversion efficiency was observed for the 3D $TiO_2$/Ti mesh electrode than for a typical plate $TiO_2$/Ti electrode. It is expected that anodizing of three dimensional (3D) Ti substrates will offer an opportunity to enhance various properties of anodic titanium oxide, especially its photoactivity.

## 1. Introduction

Over the last few years, nanotechnology has attracted a great deal of attention due to the fact that miniaturization of objects and devices is often foreseen to be a key for a sustainable future. The improvement offered by nanotechnology allows synthesizing and handling materials on the nanometer scale. In this regard, an important part of the scientific community is currently focused on a very challenging and relevant research direction, which is the fabrication of novel nanostructured materials, especially with nanoporous architecture.

A variety of fabrication methods are used to form nanometer-sized $TiO_2$, but anodic oxidation of titanium in fluorinated electrolytes is a relatively simple method which allows synthesizing porous or tubular nanostructures over a large surface area. A low cost fabrication makes anodization a very attractive and valuable procedure for the synthesis of high quality $TiO_2$ nanopore/nanotube arrays. Moreover, the anodization offers the possibility to control the size of pores/tubes and their surface distribution [1–4]. So far, most nanoporous/nanotubular anodic $TiO_2$ arrays have been prepared on a flat Ti foil and other titanium-covered flat substrates such as glass, aluminum, and silicon [5]. In principle, it is believed that the nanopore/nanotube formation by electrochemical oxidation would be a substrate-independent process and titanium dioxide can grow on any chosen surface. It means that a significant relationship between the surface shape of the titanium anode and formation of anodic titanium dioxide is not expected. However, the morphology of $TiO_2$ formed at the curved surface and its stability can be different from that one observed for Ti plate. Consequently, the effect of oxide morphology on its application performance can be expected. To the best of our knowledge, there is still a lack of detailed information on the formation of titanium dioxide on 3D Ti

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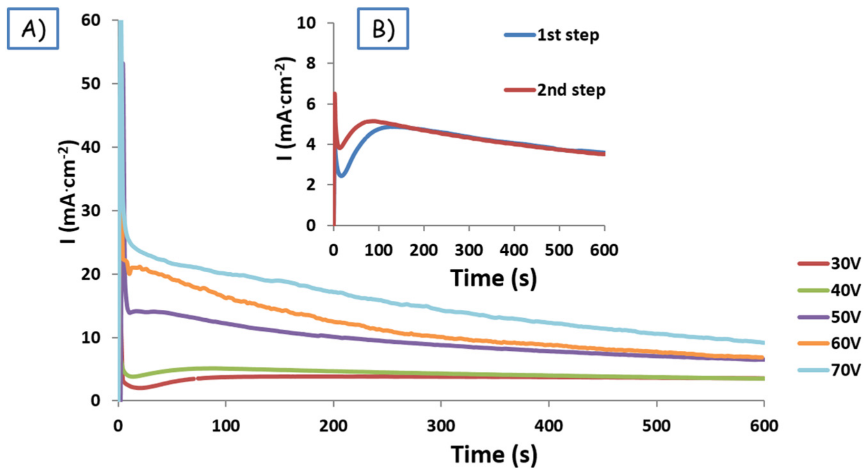


**Fig. 1.** Current density–time curves recorded during the second step of anodization performed at 20 °C in ethylene glycol containing 0.38 wt% $NH_4F$ and 1.79 wt% $H_2O$ at various potential differences ranging from 30 V to 70 V (A) and for different anodizing steps at 40 V (B).

substrates, especially on a Ti mesh.

The development of novel more efficient $TiO_2$ photoactive layers is extremely important in order to improve the conversion efficiency of Dye-Sensitized Solar Cells (DSSCs). Highly ordered $TiO_2$ nanopore/nanotube arrays, formed by anodization, are particularly attractive for applications in DSSCs because they can provide an intuitive one-dimensional electric channel and a large internal surface area as compared to a random nanocrystalline particle network. Many literature explorations have shown that the use of $TiO_2$ nanopore/nanotube arrays in conventional planar DSSCs can effectively improve the charge collection efficiency [6–11]. It is worth emphasis that anodizing of the titanium wire or titanium mesh is a promising method for the preparation of $TiO_2$ nanopore/nanotube arrays in a form of flexible electrode for applications in dye-sensitized solar cells [12–16]. After annealing, the anodized Ti wire/mesh can be directly used as the flexible anode for DSSCs. Compared with planar foils, anodic titanium dioxide formed on curved surfaces (wires and meshes) can provide higher aspect ratio and higher surface accessibility for outer sunlight and pollutants. In the wire or mesh-based cell with a 3-D array of porous/tubular $TiO_2$, the accessible surface for incoming photons is oriented in all directions ranging from parallel to perpendicular.

On the other hand, the $TiO_2$/Ti mesh electrode fabricated by anodization can be used for the water purification and wastewater treatment as a novel photoelectrode with improved photocatalytic performance [17–21]. It was proven that the fabricated electrode provides a higher efficiency for the degradation of methyl orange. The observed enhancement in the degradation efficiency was about 22% and 38% per mass and per area, respectively. The significant improvement in photocatalytic activity can be ascribed to the better light absorbance by the nanotubes formed over Ti mesh. Recently, has been also showed that anodized titanium could also improve the air purification process [22]. The strong oxidation ability of $TiO_2$ photocatalyst has received growing attention, and such photocatalysts are expected to be applied soon in environmental purification systems. For the photocatalytic air purification, various filter materials are available now, but there is a strong limitation in difficult handling of the filter material. Ochiai et al. [22], proposed an easy-to-handle photocatalytic filter, based on $TiO_2$ nanoparticles sintered on the anodized Ti-mesh, successfully applied for the environmental air purification. Due to the highly-ordered three-dimensional structure, the fabricated $TiO_2$ nanoparticles/$TiO_2$ mesh filter provides excellent air pass through and maintains a high level of surface contact.

What is more, Zhang et al. [23] have paved the way for using $TiO_2$/Ti mesh electrodes in lithium-ion batteries with a high capacity per unit area and outstanding mechanical behavior by tuning the geometric parameters of the $TiO_2$/Ti mesh and anodization time. 3D $TiO_2$ nanotube arrays grown on Ti mesh after 600 min of anodizing showed good capacity retention and high specific area capacity due to their high surface area, high substrate utilization, and a large active material loading rate per unit area. Moreover, such a system is not required to use a current collector or binder.

Additionally, Gulati and co-workers [24] have recently reported a new approach for the preparation of drug-eluting Ti implants in the form of Ti wires covered with a nanotubular $TiO_2$ layer. Titania nanotube arrays on Ti wires for potential applications as bone fixative tools and orthopaedic implants were fabricated via anodization followed by a loading of common antibiotic drug (gentamicin) into the nanotubes. The drug loading and release were characterized to reveal a drug-eluting characteristic of the proposed implant. It should be mentioned that the anodized Ti wire, as the orthopaedic implant, can be easily inserted inside bones. This opens up new possibilities for the enhanced bone fixation/repair and targeted treatment in bone cancer, osteomyelitis and other related orthopaedic diseases.

As can we seen, the controlled anodization of titanium wire/mesh that results in nanoporous/nanotubular $TiO_2$ layer on titanium substrate is a very important issue for achieving better-performance of many devices for diverse applications from photovoltaics and photocatalysis to biomedical applications. However, the number of publications regarding the electrochemical synthesis of porous/tubular $TiO_2$ layers on different 3D Ti substrates is limited. Therefore, in order to address the existing knowledge gap the principal goal of this work was focused on the possibility of fabricating 3D nanoporous $TiO_2$ on Ti mesh via electrochemical oxidation. In this work, we investigated in detail the properties of $TiO_2$/Ti mesh electrodes formed at different anodizing potentials and process durations. Moreover, the prepared 3D $TiO_2$/Ti mesh samples after the appropriate thermal treatment were used as nanostructured electrode materials for photoelectrochemical tests. The early photoelectrochemical investigations showed that amorphous $TiO_2$