Preparation and characterization of high aspect ratio TiO₂ nanotube powders using rapid anodization method in chloride-based electrolytes

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This new method describes, for the first time, the application of rapid anodization in chloride-based electrolytes to quickly synthesize high quality, high-aspect ratio and robust titanium dioxide nanotube powders. This titania nanotubes powder produced from potentiostatic anodization of titanium foil in an electrolyte containing perchlorate or chloride ions. This would result in a more efficient usage of the titanium foil and in the production of large quantities (of the order of grams) titanium oxide tubes in less than 1 h. Further optimization of this route may provide a fast alternative method for the production of titanium oxide nanotube powders, now routinely synthesized via a hydrothermal method derived from the one pioneered by Kasugai et al. Various characterization techniques (viz., TEM, FESEM, XRD< DRUV-Visible, XPS) are used to study the morphology, phase, band gap and chemical composition.

Keywords: Titania Nanotube, powders, Rapid anodization

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1. INTRODUCTION

During the past decade, scientists have developed techniques for synthesizing many new materials with one dimension on the nanoscale, including nanoparticles, nanolayers, and nanotubes. Still, the synthesis (or fabrication) of nanoscale materials with controlled properties is a significant and ongoing challenge within nanoscience and nanotechnology. Among the most promising material is titanium dioxide (TiO₂), which has led to many promising applications in areas ranging from photovoltaics and photocatalysis to photo-/electrochromics and sensors. Various methods have been used to synthesis TiO₂ nanostructures like sol-gel, hydrothermal, solvothermal, direct oxidation, CVD, PVD, sonochemical, electrodeposition and microwave method. Many groups have used the hydrothermal method to prepare TiO₂ nanotubes [1, 2].

Electrochemical synthesis routes provide an attractive alternative to the standard methods of synthesizing nanomaterials. Electrochemical anodic oxidation has been widely used to synthesize TiO₂ nanotubes on titanium metal surface. Recently, an anodization of Ti foil in an electrolyte containing chloride or perchlorate ions can produce high aspect ratio TiO₂ NTs in very short time (~ 50 μm in < 1 min), which the main advantage of this kind of anodization that known as “rapid breakdown anodization” [3]. Based on the aforementioned, the high reactivity and ultra speed of the reaction can be used to produce the TiO₂ NTs powders. The electrochemical anodization method, to the best of our knowledge, is the first time to use for preparation of nanotube powders. Therefore, this study presented the synthesis of TiO₂ NTs powders by using rapid anodization method.

2. EXPERIMENTAL

Electrochemical anodization was performed in a simple two electrode cell at room temperature by using potentiostat (Amel 7050, Italy). The titanium sheet of size (5x5 cm) was used as anodic electrode and a platinum sheet of size (1x2 cm) as counter electrode. A voltage of 20 V was applied for 40 min to completely anodize this size of Ti sheet. The anodization was carried out in 0.3 NaCl or 0.1 M HClO₄ as electrolyte. After anodization the powders were washed with deionized water and collected by centrifugation then filtered. Finally, the TiO₂ NTs powders were dried in an oven at 60 °C overnight. The as-formed powder is amorphous structure, to obtain the crystalline structure by annealing. Different annealing temperature was done.

3. Results & Discussion

Figure 1a shows the current-time behavior 55 min of the constant voltage anodization of Ti sheet in 0.1 M HClO₄ aqueous electrolyte. This is the typical characteristic curve of TiO₂ NTs, which composed of three characteristics regions of strong current decay followed by an increase in the current then gradually changes to plateau at a steady-state value indicating the balance between oxide formation and oxidative dissolution. Fig.1b shows the amount of the powder obtained in the end of anodization process that about 4.0 g for I sheet of dimensions (10 x 10 x 0.1) cm² in less than 3 h. Figure 2 shows the morphology and microstructure of as-
formed TiO\textsubscript{2} NTs powders. It is seen that the length of nanotubes > 15 \textmu m and the outer diameter ~ 40 nm, as observed from the TEM image. However, interesting results also from Uv/visible spectra measurements, the as-formed and annealed samples (E\textsubscript{g} = 3.13); as expected, the absorption edge shows a significant red-shift with respect to the pure anatase structure (E\textsubscript{g}=3.25 eV).

4. Conclusions
In summary, we demonstrated the synthesis of titanium dioxide nanotubes powders by using electrochemical anodization, for the first time. The reaction yield was 4.0 g TiO\textsubscript{2} NTs in less than 3 h. The band gap of the nanotubes powder of significant red shift (E\textsubscript{g}=3.13), which may improves their performance as photoanode in DSCS or as a photocatalyst. This study suggests that this method of preparation can be qualify to replace the conventional methods used for preparation of titania nanotubes powders.

![Fig1](image1.png)

**Fig1.** The current-time behavior seen during preparation of TiO\textsubscript{2} powders by rapid anodization of Ti foil at 20 V in 0.1 M HClO\textsubscript{4} electrolyte (a) and the micrograph shows the amount of powder at the end of anodization of Ti sheet of (5x5 cm\textsuperscript{2}) (b).

![Fig2](image2.png)

**Fig2.** FE-SEM micrograph (a) and HRTEM image show the nanotubular structure of the as-formed TiO\textsubscript{2} NTs powders.

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