Research Article

Fabrication of TiO₂ Nanotube by Electrochemical Anodization: Toward Photocatalytic Application

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In this study, a self-organized nanotubular titanium dioxide (TiO₂) array was successfully produced by anodizing pure titanium in a mixture of glycerol, distilled water (8% vol.), and ammonium fluoride using a dual electrode system. The size control and distribution of the nanopores were performed in a DC voltage range varying from 30 V to 60 V. The diameter of TiO₂ nanopores varies from 59 to 128 nm depending on the anodizing voltage. Energy-dispersive X-ray spectroscopy (EDX) analysis reveals that the as-prepared films are essentially composed of TiO₂. According to the X-ray diffraction (XRD) and Raman spectroscopy analysis, the nanotubular arrays of TiO₂ annealed at 600°C for 2 hours are composed of a phase mixture of anatase and rutile. Mott-Schottky analysis showed that the TiO₂ nanotubes are consistent with an n-type semiconductor with a donor density of about 10¹⁷ cm⁻³. Preliminary results on the photocatalytic degradation of a pharmaceutical pollutant showed that the TiO₂ nanotubes can be used as a promising material for application in wastewater treatment.

1. Introduction

Recently, owing to the diverse application of titanium dioxide TiO₂, a thorough research and experiments have been devoted to the preparation of titanium dioxide TiO₂ and the considerable number of parameters determining its formation. There is a vast amount of literature on the titanium dioxide application such as photoelectrochemical water splitting [1], water [2, 3] and air purification [4], solar energy conversion [5], medical applications [6], gas sensors [7], and supercapacitors [8]. These applications rely on the specific semiconductor nature of TiO₂, in particular anatase, which is an n-type semiconductor with a large band gap of about 3.2 eV [9].

In the last years, several techniques have received considerable attention for elaborating TiO₂ nanostructures with promising properties. The most often used methods include the sol-gel process [10, 11], the electrochemical anodization of titanium [12], the hydrothermal method [13], and sputtering [14]. Among these methods, titanium anodization is the most effective way to produce highly ordered nanoporous TiO₂ films [15]. It has been now demonstrated that two types of TiO₂ morphology can be obtained by electrochemical anodization: compact TiO₂ films are generally obtained in fluoride free electrolytes, whereas porous films can be prepared in electrolytes containing fluoride ions [16, 17].

The nanostructure of the pores on the titanium surface obtained by electrochemical anodization is strongly affected by several parameters, such as applied potential [12, 18, 19], anodization bath temperature [20], electrolyte composition [21], anodizing time [12, 19, 22], water content in the electrolyte [23, 24], and the fluoride ion concentration [19, 21, 25].

Considerable attention has been directed to study the mechanism of formation of nanotubular TiO₂ films by
electrochemical anodization. Consequently, a number of theories based on field dissolution [26] and localized acidification at the pore bottom that increases chemical dissolution [27, 28] have been proposed to explain some aspects of the mechanism related to the TiO₂ nanotube formation and growth.

The synthesis and properties of one-dimensional tubular arrays have been widely investigated. Lockman et al. [18] reported that in a mixture of Na₂SO₄ (1 M) and 5 wt% NH₄F, the diameters and lengths of the nanotubes increased with increasing anodization voltage from 10 V to 25 V and the average diameters of the nanotubes were about 80 nm, 70 nm, and 50 nm for anodization voltages of 20 V, 15 V and 12 V, respectively. Albu et al. [29] showed that the geometry of the nanotubular layer depends strongly on the applied potential and the fluoride concentration. However, Kulkarni et al. [24] studied the effect of anodization parameters on the morphology of the TiO₂ nanostructure and the mechanism converting the as-formed nanopores to nanotubes.

Very little work has been carried out on the anodization of titanium in glycerol. Indeed, Sreekantan et al. [30] have stipulated that in glycerol containing 6 wt% of ethylene glycol (EG) and 5 wt% NH₄F, in the voltage range from 20 to 60 V, the uniform TiO₂ nanotubes were reached with a voltage less than 30 V. For a potential up to 50 V, the structure of the anodized titanium tended to be irregular.

This work reports on the effect of anodization voltage on the morphology of nanotubular TiO₂ on the pure titanium surface and their electrochemical, structural, optical, and electrical properties. Different approaches are thoroughly investigated with the aim of producing a nanotubular titanium dioxide including current time transients, SEM along with EDX, X-ray diffraction, Raman spectroscopy, and impedance measurements.

2. Experimental

2.1. Chemicals. Titanium foil (99.99% pure, 2 mm thick), glycerol (99.8%, anhydrous), ammonium fluoride (98%), acetic acid (99.98%), HF (40%), H₂SO₄ (96%), and carbamazepine (99% purity) were purchased from Sigma-Aldrich (St-Louis, USA).

2.2. Elaboration and Characterization. To obtain reliable and reproducible results, the pure titanium sample underwent, before each test, a pretreatment consisting of polishing the electrode surface with an increasingly fine grade emery paper (SiC #400, #1200, #2000, and #4000), followed by rinsing with distilled water and then drying under airflow.

Afterwards, the sample was electrolytically polished in a solution containing hydrofluoric acid (18% v/v), sulfuric acid (40% v/v), and acetic acid (42% v/v) at a voltage of 11 V for 30 s. Samples are then abundantly rinsed with distilled water.

The anodization of pure titanium foils was carried out in an electrolytic bath consisting of a mixture of glycerol-distilled water (92:8% v/v) and ammonium fluoride (0.4 M) for 60 min, at a voltage ranging from 30 to 60 V, using a two-electrode cell with the titanium sample as the anode and a platinum electrode as the counter electrode.

Later with the intention of enhancing the crystallinity of as-synthesized nanoporous TiO₂ films, the anodized samples were annealed in a muffle furnace at 600°C for two hours with a heating ramp of 10°C/min.

The electrochemical study was performed in a 0.1 M Na₂SO₄ solution using a conventional three-electrode cell consisting of an anodized TiO₂ as the working electrode (WE), a saturated calomel electrode (SCE) as the reference electrode, and a platinum sheet (4 cm²) as the counter electrode [31]. The measurements were performed using a VoltaLab potentiostat (PGZ301) controlled by the VoltaMaster 4 software. To perform the EIS experiments at steady state, the rotational speed of the stirrer was set at 200 rpm. The temperature was controlled in jacketed glass at 293 K using a bath thermostat (±1°C). The Mott-Schottky (MS) analysis was performed at a frequency of 1 kHz in wide voltage range (from -1 V to 1 V/SCE).

The morphology of the anodized samples and the elemental composition of the oxide films are examined by scanning electron microscopy (SEM) along with energy-dispersive X-ray spectroscopy (EDX). The crystal structure of the oxide films was determined by X-ray diffraction (XRD) (Rigaku, SmartLab SE, Cu Ka1, λ = 1.5418 Å) and Raman spectroscopy (Confotec MR520) with laser of wavelength λ = 532 nm. Pore diameter measurement is performed using the image processing software ImageJ.

The irradiation system used is equipped with an Ultra-Vitalux lamp at 300 W with high-pressure tungsten filament. A double-jacketed glass reactor allowed maintaining the temperature at 25°C of the solution during the irradiation time.

3. Results and Discussion

3.1. Current Time Transient Measurements. During the anodizing process, the variation of the current density as a function of time is monitored. Figure 1 shows the anodizing current density/time curves during the anodization at different potentials. The observed transients share similar trends. Three stages are typically observed in these curves related to the typical current density-time curve of the porous oxide formed under constant voltage. The kinetic trend consists of an initial fast drop (stage A), a steady increase (stage B), and a quasisteady state current density (stage C).

At stage A, the anodizing process begins, and the current quickly decreases to a minimum value because of the formation of a high resistance compact oxide layer on the surface by the interaction of the Ti³⁺ ions with the oxygen O²⁻ ions in the electrolyte according to the following reaction [32]:

\[ \text{Ti} + 2\text{H}_2\text{O} \rightarrow \text{TiO}_2 + 4\text{e}^- + 4\text{H}^+ \]  

At stage B, the current subsequently rises to a maximum as the pore formation progresses. This is due to the chemical dissolution of the oxide layer by fluoride ions that is
promoted by an electric field created between the cell electrodes. Small pits are formed on the surface of the compact layer followed by the formation of a nanoporous structure according to the following reaction [32, 33]:

\[
\text{TiO}_2 + 6\text{F}^- + 4\text{H}^+ \rightarrow \text{TiF}_6^- + \text{2H}_2\text{O}
\]

At the final stage, the current density attains a constant value when a steady state is reached owing to the formation of TiO$_2$ nanotubes [34].

3.2. Morphological and Composition Characterization. For the morphological analysis of TiO$_2$ nanotubular layers formed on the titanium substrate at different potentials, a
scanning electron microscope TESCAN VEGA 3 was used. SEM top images and cross-sections of nanotube arrays produced in glycerol-distilled water (92:8% v/v) and NH₄F (0.4 M) for 60 min at different anodizing potentials are given in Figure 2.

The electrochemical anodization of titanium under these conditions leads to the formation of an ordered nanotubular array on the titanium surface. For the anodized sample at 30 V, there are areas where the oxide formed is compact. In addition, other areas have an ordered distribution of medium-sized nanotubes of about 59 nm in diameter. For voltages above 30 V, the surface of the samples is made up of neat TiO₂ nanotubes. The average diameters of the nanotubes are about 80 nm and 128 nm for an applied voltage of 40 V and 60 V, respectively.

In addition, the lengths of the nanotubes were measured by scanning electron microscope observation of cross-sections of the films. The result showed that the length of the TiO₂ nanotube obtained on the surface of the titanium metal increases with the increasing anodization potential to reach approximately 1.5 μm at 60 V.

Figure 3 shows the evolution of nanotubular internal diameter as a function of the anodizing voltage. It is clearly seen that the nanotube diameter increases linearly with the...
Figure 5: XRD spectra of samples anodized at different anodization potentials in glycerol-distilled water (92:8% v/v) and NH₄F 0.4 M.

Figure 6: Raman spectra of anodized simples at different anodization potentials in glycerol-distilled water (92:8% v/v) and NH₄F 0.4 M.

anodizing potential with a good correlation coefficient $R^2$ that is close to 1 (0.97). It should be noted that for a potential of 30 V, the internal diameter of the nanotubes is about 59 nm, while it reached 128 nm for a potential of 60 V.

3.3. Composition Analysis by EDX. For the elemental characterization of the obtained nanotubular layers, energy-dispersive X-ray analysis is conducted using an acceleration voltage of 10 kV. The characteristics of the emitted X-rays from the anodized substrate produced at different conditions are presented in Figure 4. The EDX spectrum indicates the presence of the TiKα peak at 4.58 eV and O peaks at 0.5 eV, as well as F and C peaks in the anodized sample. The obtained percentages of Ti (26.5 at%) and O (41.4 at%) yield a Ti/O ratio of about 0.5 indicating that the structure of the formed oxide is TiO₂ with the
presence of fluorine that arises from the solution during the anodization process [35] and carbon which comes from the metallization process using graphite.

3.4. XRD Structural Characterization. The crystal phases of as-prepared and annealed samples were identified by XRD using Cu Kα radiation. As shown in Figure 5, the formed TiO$_2$ nanotubular film consists of a mixture of anatase and rutile phases. The anatase phase was identified from the peaks at ca. 25.03°, 48.05°, 54.85°, and 55.30° characteristic of the planes (101), (200), (105), and (211), respectively, according to JCPDS file no. 21-1272. In addition, the rutile phase is revealed by peaks at 27.4°, 36.07°, 41°, 43.6°, and 56.9°, corresponding to planes (110), (101), (110), (111), (210), and (220) (JCPDS card no. 21-1276), respectively. XRD spectra of annealed oxides reveal that TiO$_2$ peaks become more intense when the anodizing potential increases.

The crystallite size is an important factor to determine the stability of nanotubular TiO$_2$ crystalline phases [1, 36]. The average crystallite size of nanotubular TiO$_2$ samples is calculated using the Scherrer equation

$$D = \frac{0.9\lambda}{\beta \cos \theta},$$

where $D$ is the grain size, $\lambda$ (1.548 Å) is the wavelength of X-ray radiation used, $\theta$ is the Bragg diffraction angle obtained from XRD peak, and $\beta$ is the full width at half maximum of the diffraction peak [37]. Using the width of the (101) peak for anatase and the width of the (110) peak for rutile, crystallite sizes were obtained in the ranges 7.3 to 8.5 nm and 8.2 to 9.7 nm for anatase and rutile phases, respectively.

On the other hand, the phase composition of TiO$_2$ has a crucial impact on the photocatalytic activity. The effect of the anatase/rutile ratio is discussed in many controversial works. It is reported that a mixture of anatase and rutile phases was found suitable for photocatalytic oxidation of organic pollutants in water [38]. Nevertheless, Tayade et al. [39] suggested that only the anatase phase has attracted considerable attention as a photocatalyst for the chemical treatment of organic pollutants. In our conditions, the relative amounts of anatase and rutile were estimated at 82% and 18%, respectively. This result is similar to that for the commercial TiO$_2$, Degussa P25, which exhibits a strong photocatalytic activity and has an anatase-rutile mass fraction of 80:20.

3.5. Structural Characterization by Raman Microscopy. The TiO$_2$ films obtained at different anodizing voltages were also characterized by Raman spectroscopy after thermal annealing at 600°C. Figure 6 shows the Raman spectra of the different anodized samples at different anodization potentials in a glycerol-distilled water mixture.

For the as-anodized sample, we noticed the absence of Raman peaks indicating the amorphous nature of the formed oxide [40]. However, the Raman spectra of all

| Tension (V) | $E_{FB}$ (V/SCE) | $N_D \times 10^{-17}$ (cm$^{-3}$) |
|------------|-----------------|---------------------------------|
| 30         | -0.13           | 1.95                            |
| 40         | -0.16           | 3.37                            |
| 50         | -0.10           | 2.45                            |
| 60         | -0.14           | 4.25                            |

**Figure 7:** Mott-Schottky plots obtained for the formed nanotubular TiO$_2$ layers in 0.1 M Na$_2$SO$_4$ solution.
annealed samples depict a similar trend and show a very intense band at 143 cm$^{-1}$ and four others at 195, 394, 515, and 637 cm$^{-1}$. These bands can be attributed to the vibrational modes $E_g^{(1)}$, $E_g^{(3)}$, $B_{1g}$, or $A_{1g}$ (superposition of $A_{1g}$ and $B_{1g}$), and $E_g$ of anatase, respectively. The observed bands confirm the predominance of anatase as the crystalline phase in the structure [41]. However, peaks of about 447 and 619 cm$^{-1}$ indicate the presence of a certain amount of rutile and their intensities increase with the anodizing potential. These vibration modes are shifted by 2 to 4 cm$^{-1}$ due to the variation in grain size and stoichiometric defects present in TiO$_2$ structures as reported by Bassi et al. [42]. These structural observations are in good agreement with the XRD analysis.

3.6. Mott-Schottky (MS) Analysis. Electrochemical capacitance measurements were carried out to characterize the semiconductor nature of the films and to determine the donor density $N_D$ of the formed TiO$_2$ layers, as well as to estimate the flat band potential ($E_{FB}$) of the anodized samples at different potentials. MS analysis was performed in Na$_2$SO$_4$ 0.1 M at 1 kHz in the potential range of -1 to 1 V/SCE. Figure 7 shows the variation of $1/C^2$ as a function of potential $E$ (V/SCE).
As shown in Figure 7, a quasilinear behavior of the variation of $1/(C_s^2)$ as a function of the potential was observed. All curves have a positive slope corresponding to an n-type semiconductor [43]. The parameters $N_D$ and $E_{FB}$ can be determined from the slope of the linear regions in the Mott-Schottky plot and its intersection with the $x$-axis, respectively, according to the Mott-Schottky relationship:

$$\frac{1}{C_s^2} = \frac{2}{\varepsilon_0 \varepsilon S e N_D} \left( E - E_{FB} - \frac{kT}{e} \right), \quad (3)$$

where $C_s$ is the space charge layer capacitance, $e$ the electron charge ($1.60 \times 10^{-19}$ C), $\varepsilon_0$ the permittivity of free space ($8.85 \times 10^{-14}$ Fcm$^{-1}$), $\varepsilon_S$ the dielectric constant of TiO$_2$, which is assumed to be 100 Fcm$^{-1}$ [44], $E$ the applied potential, $k$ the Boltzmann constant ($1.38 \times 10^{23}$ JK$^{-1}$), and $T$ the absolute temperature. The values of the $N_D$ and $E_{FB}$ of the different samples are summarized in Table 1.

Table 1 shows clearly that the $N_D$ values increase with anodizing potential, and the values obtained are in the order of $10^{17}$ cm$^{-3}$. The $N_D$ values obtained are in good agreement with those reported in the literature for nanotubular TiO$_2$ [45]. Generally, the growth of the anodized oxide films is always nonstoichiometric with an excess/deficiency of metal cations or oxygen anions [40]. According to the Point Defect Model (PDM), the n-type semiconductor behavior of an anodic passive film indicates that the defects in all samples are due to the oxygen deficiencies and/or interstitial titanium ions [46]. Somehow, Peng [47] reported that the predominance of oxygen deficiency is due to the low formation energy of oxygen vacancy compared to the interstitial titanium.

### 3.7. Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopy (EIS) technique was used to study the electrochemical behavior of the interface of TiO$_2$ nanotubular film. Figures 8(a) and 8(b) present the Nyquist and Bode diagrams of the EIS data obtained for the TiO$_2$ films with their fitting adjustments obtained using EC-Lab software with the suggested equivalent circuit (inset in Figure 8(a)).

The Bode diagrams of Figure 8(b) reveal the presence of more than two time constants in the lower and intermediate frequency ranges. This behavior can be attributed to the presence of an inner compact layer and an outer porous TiO$_2$ nanotube layer [48]. In addition, the decrease in phase angles at a high frequency is related to the porous nature of the outer layer [35]. At intermediate frequencies, the spectrum $\log |Z|$ vs. $\log(\text{freq})$ is a straight line with a slope ranging from -0.78 to -0.88 that exhibits capacitive behavior.

Table 2: Parameters obtained by fitting the impedance spectra of the anodized samples at different applied potentials.

| Potential | $R_s$ ($\Omega \times \text{cm}^2$) | $C_1$ ($\mu\text{F/cm}^2$) | $R_i$ ($\Omega \times \text{cm}^2$) | $Q_1$ ($\mu\text{F s}^{-1/2}$) | $a_2$ | $R_2$ (k$\Omega \times \text{cm}^2$) | $Q_3$ (mF s$^{-3/2}$) | $a_3$ | $R_3$ (k$\Omega \times \text{cm}^2$) |
|-----------|-------------------------------|-----------------|---------------------|-------------------------------|--------|---------------------|---------------------|--------|---------------------|
| 30 V      | 7.74                          | 19.9            | 127.20              | 86.18                         | 0.44   | 4.38                | 0.55                | 0.97   | 9.35                |
| 40 V      | 23.08                         | 23.76           | 25.63               | 95.42                         | 0.45   | 1.31                | 0.11                | 0.70   | 21.76               |
| 50 V      | 10.13                         | 47.89           | 0.29                | 56.64                         | 0.29   | 1.02                | 0.23                | 0.60   | 5.67                |
| 60 V      | 14.99                         | 23.52           | 0.56                | 76.49                         | 0.56   | 4.31                | 0.92                | 0.68   | 19.65               |

Figure 9: Photocatalytic activity of TiO$_2$ nanotubular- (formed at 60 V and annealed at 600°C) simulated sunlight irradiation (300 W).
The Nyquist diagrams shown in Figure 8(a) represent incomplete semicircles at low frequencies. Different equivalent circuits have been proposed in the literature to model the TiO$_2$/electrolyte interface [40, 49]. In our case, Nyquist spectra are adjusted using the following equivalent electrical circuit as $R_s + C_1/(R_1 + Q_2/R_2 + Q_3/R_3)$.

The proposed equivalent circuit takes into account the different time constants. The TiO$_2$/electrolyte interface can be represented by the Helmholtz capacitance ($C_1$). As shown in the equivalent circuit, this capacitance ($C_1$) is in parallel with a resistance coupled to the constant phase element ($R_1/Q_1$) and ($R_2/Q_2$), corresponding, respectively, to the porous (outer) and barrier (inner) layer. Constant phase elements ($Q_i$) are used to take into account the surface heterogeneity, nonideality of capacitance, and frequency dispersion [50, 51]. The values of the circuit elements are summarized in Table 2.

For all the studied potentials, the calculated $R_s$ and $C_1$ parameters vary slightly compared to the other parameters. It is interesting to note that the resistance of the barrier layer $R_3$ is higher than $R_1$ of the nanotubes. The $a_1$ values of the tubular layers are ranging from 0.29 to 0.56, while the $a_3$ values of the barrier layers are between 0.60 and 0.97 for all samples which can be associated with a distribution of relaxation times due to the heterogeneities at the surface. The $a_2$ values indicate that the tubular layers of all samples have a nonideal capacitive behavior. Values in the order of 0.30 and 0.50 have been reported in the literature for porous materials [52].

### 3.8. Photocatalytic Activity.

To value the photocatalytic activity of nanoporous TiO$_2$ formed in our conditions, the TiO$_2$ nanotube arrays formed at 60 V and annealed at 600°C are evaluated for the degradation of a pharmaceutical pollutant known for its photochemical stability, carbamazepine (CBZ) [49]. Figure 9 shows the degradation curve of CBZ in an aqueous solution with an initial concentration of 5 ppm in the presence of the TiO$_2$ nanotubes and under simulated sunlight irradiation (300 W). As it can be clearly observed, the anodized TiO$_2$ in these conditions can effectively degrade 96% of CBZ within 10 h of irradiation. This may be due to their large surface area the TiO$_2$ nanotubes and to their crystalline size and phase composition. Under these anodization conditions, TiO$_2$ nanotube arrays were characterized by a pore diameter of 128 nm, a tube depth of 1.5 μm, and a maximum donor charge of about 4.25 $10^{17}$ cm$^{-3}$. With this tube length, in combination with minimal radial dimensions, the incident illumination can be effectively captured near the surface of the nanotubes, providing facile separation of a photogenerated charge. Our results are promising, and further work is underway to study the influence of other parameters on the photocatalytic activity of titanium dioxide nanotubes.

### 4. Conclusion

The electrochemical anodizing method was used to produce amorphous TiO$_2$ nanotubes converted by annealing into crystalline nanotubes. The nanotubes of significantly different diameters were obtained in a voltage range from 30 V to 60 V. The variation in anodizing voltage did not modify the chemical composition of the TiO$_2$. In addition, their crystalline structure shows the presence of a mixture of anatase and rutile phases. The electrochemical study reveals that the oxide formed under these conditions is an n-type semiconductor with a donor density on the order of $10^{17}$ cm$^{-3}$. Our results are promising, and further work is underway to study of the photocatalytic properties of the produced titanium oxide nanotubes.

### Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

### Additional Points

**Highlights.** (i) Nanotubular titanium dioxide (TiO$_2$) array was produced by the anodization method; (ii) applied potential significantly affects the nanotube diameter; (iii) the anodic TiO$_2$ was analyzed by SEM, XRD, Raman spectra, Mott-Schottky analysis, and EIS measurements; (iv) photocatalytic degradation of a pharmaceutical pollutant was achieved.

### Conflicts of Interest

The authors declare that they have no conflicts of interest regarding the publication of this paper.

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