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Porous vs. Nanotubular Anodic TiO\textsubscript{2}: Does the Morphology Really Matters for the Photodegradation of Caffeine?

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Abstract: Herein, the preparation of nanotubular and porous TiO\textsubscript{2} structures (TNS) is presented for photocatalytic applications. Different TNS were prepared in three different types of glycerol- and ethylene glycol-based electrolytes on a large area (approx. 20 cm\textsuperscript{2}) via anodization using different conditions (applied potential, fluoride concentration). Morphology, structure, and optical properties of TNS were characterized by Scanning Electron Microscopy (SEM), X-ray Diffractometry (XRD), and Diffuse Reflectance Spectroscopy (DRS), respectively. All TNS possess optical band-gap energy (E\textsubscript{BG}) in the range from 3.1 eV to 3.2 eV. Photocatalytic degradation of caffeine was conducted to evaluate the efficiency of TNS. Overall, nanotubular TiO\textsubscript{2} possessed enhanced degradation efficiencies (up to 50% degradation) compared to those of porous TiO\textsubscript{2} (up to 30% degradation). This is due to the unique properties of nanotubular TiO\textsubscript{2}, e.g., improved incident light utilization. As the anodization of large areas is, nowadays, becoming a trend, we show that both nanotubular and porous TiO\textsubscript{2} are promising for their use in photocatalysis and could be potentially applicable in photoreactors for wastewater treatment. We believe this present work can be the foundation for future development of efficient TiO\textsubscript{2} nanostructures for industrial applications.

Keywords: nanotubular TiO\textsubscript{2}; porous TiO\textsubscript{2}; anodization; large area; photocatalysis; caffeine

1. Introduction

Electrochemical anodic oxidation (anodization) will soon celebrate 100 years since it was first patented in 1923 by Bengough and Stuart for its use on an industrial scale [1]. In general, the purpose of anodization is to passivate the surface of a material (primarily metals). Thus, the surface of the material develops a protective layer (in the form of oxide), which protects it against future corrosion. Pioneering works were conducted in 1984 [2] and 1995 [3] that allowed the preparation of not only a protective layer, but a unique nanotubular structure of TiO\textsubscript{2} and Al\textsubscript{2}O\textsubscript{3}, respectively, for several applications in several fields including energy, environment, medicine, and technology. Ever since the anodization of metals gained significant attention from the scientific community, thousands of papers have been related to anodization [4–6].

In particular, anodic TiO\textsubscript{2} nanotube layers [7] with unique properties of a 1D material are promising for photocatalysis [8], hydrogen production [9], DSSCs [10], or biomedical applications [11]. This is due to [7]: (i) high specific surface area and enhanced light
absorption due to the materials’ 1D structure, (ii) a vertical transport of the photogenerated charge carriers (electron/holes), and (iii) tunable dimensions of the nanotubes, in particular, their length and diameter. In the last decade, organic-based electrolytes (e.g., glycerol and ethylene glycol) are the most popular for the preparation of TiO$_2$ nanotube layers via anodization [7]. Indeed, in such electrolytes, a high-aspect ratio and smooth nanotubes are prone to form [12]. Nevertheless, there are still major challenges in the synthesis and application of TiO$_2$ nanotube layers in industry. Indeed, layers of several cm$^2$ are necessary and this relates to specific preparation challenges, i.e., when a potential is applied to areas of several cm$^2$, the absolute current flowing between the two electrodes is much higher compared to that of smaller areas (most of the published articles report a laboratory scale of 1 cm$^2$ area) [7]. The flowing high current leads to an increase in the electrolyte temperature and subsequently a dielectric breakdown will occur [13]. To this day, only a few reports deal with the preparation of TiO$_2$ nanotube layers on areas >10 cm$^2$ [9,13–20]. A field-assisted dissolution of titanium supported by fluoride ions is responsible for the formation of a nanotubular structure [7]. Thus, by using optimized anodization conditions, TiO$_2$ nanotube layers are formed. Nevertheless, there is a thin line between the formation of a nanotubular and a porous structure of TiO$_2$. The potential/current induced dissolution of the formed TiO$_2$ in the presence of fluoride ions via [TiF$_6$]$^{2-}$ is well known to the scientific community [21,22]. In case that the dissolution rate is higher than the formation rate, a rather porous structure is formed instead of a nanotubular one. Such a porous TiO$_2$ is often overlooked in the literature, as it is considered an unsuccessful preparation of TiO$_2$ nanotube layers. However, this formed porous TiO$_2$ possesses a high specific surface area and a sufficient number of active sites necessary for, e.g., photocatalysis similarly to nanotubular TiO$_2$. In our recent work [9], we reported that both nanotubular and porous anodic TiO$_2$ nanostructures (TNS) possess efficient properties in the photocatalytic degradation of caffeine and hydrogen production. Therefore, we aim this work as a follow-up to our recent paper. Here, we focus solely on the degradation of caffeine (i.e., liquid phase photocatalysis) by using different types of anodic nanotubular and porous TNS prepared via anodization on a large area to gain knowledge about these two, although, different but in many ways similar materials. We believe that both nanotubular and porous anodic TNS are promising for the application in photo-induced processes including photocatalysis.

In the present work, TNS on a large area (approx. 20 cm$^2$) were prepared via anodization in different organic-based electrolytes (i.e., glycerol and ethylene glycol) containing fluoride ions. Scanning Electron Microscopy (SEM), X-ray Diffractometry (XRD), and Diffuse Reflectance Spectroscopy (DRS) was conducted to ensure the morphology, crystal structure, and optical properties of the prepared TNS, respectively. Caffeine was employed as a model organic pollutant to evaluate the photocatalytic activity of the prepared TNS. The present work critically discusses the pros and cons of nanotubular and porous anodic TiO$_2$ for application in liquid-phase photocatalysis. It is worthy to note that herein, we do not aim for 100% pollutant degradation, but rather for a fundamental understanding of different TNS for future development in photocatalysis.

2. Materials and Methods
2.1. Synthesis of TNS

Titanium foil (Sigma-Aldrich, Darmstadt, Germany, 99.7% purity, 0.127 mm thickness, 20 cm$^2$ area) was used as a starting substrate for the formation of TNS. According to our previous work [9], a circle of 5 cm in diameter was drawn on the square titanium foil and cut out into three corners to make a drop-like shape which was used as a working electrode (titanium foil of 5 × 2 cm$^2$ was used as a counter electrode). One corner of the electrode was utilized as a handle to fasten the electrode. The distance between the electrodes was kept at 1.6 cm. Anodization was conducted using potential from 20 V to 80 V (20 V step) for 100 min in glycerol- (Central-Chem, Bratislava, Slovakia) and ethylene glycol-based (Central-Chem, Bratislava, Slovakia) electrolytes. To avoid overheating of the electrolyte,
cooling with an ice bath was conducted to possess a constant temperature of 8 °C during anodization. Three different types of electrolytes based on either glycerol or ethylene glycol were used for the synthesis of TNS according to our previous works [9,23]. We also used three optimized electrolyte compositions, which our group often uses [24–30]. Moreover, we varied the concentration of fluoride ions by decreasing it to 75% and 50% of the initial amount (100%), respectively, for each electrolyte. Thus, we obtained altogether 9 different electrolytes and the electrolyte compositions along with the materials’ abbreviations and the used anodization conditions are summarized in Table 1. By these efforts, both nanotubular and porous TiO₂ structures were obtained as required for the purpose of this study. After synthesis, TNS were immersed in isopropanol to remove the electrolyte leftovers from the surface and subsequently annealed in a muffle oven at 400 °C in air (2.21 °C/min heating rate). Afterward, TNS were cooled down inside the oven to room temperature.

Table 1. Summary: electrolyte abbreviation, composition, and applied potential.

| Electrolyte | Electrolyte Composition | Electrolyte | Electrolyte Composition | Electrolyte | Electrolyte Composition | Applied Potential (V) |
|-------------|------------------------|-------------|------------------------|-------------|------------------------|----------------------|
| EL100%      | 2 g NH₄F; 100 mL glycerol; 100 mL H₂O | EL200%     | 1.3 g NH₄F; 197 mL ethylene glycol; 3 mL H₂O | EL300%     | 1.1045 g NH₄F; 180 mL ethylene glycol; 20 mL H₂O | 20 |
| EL175%      | 1.5 g NH₄F; 100 mL glycerol; 100 mL H₂O | EL275%     | 0.975 g NH₄F; 197 mL ethylene glycol; 3 mL H₂O | EL375%     | 0.83 g NH₄F; 180 mL ethylene glycol; 20 mL H₂O | 40 |
| EL150%      | 1 g NH₄F; 100 mL glycerol; 100 mL H₂O | EL250%     | 0.65 g NH₄F; 197 mL ethylene glycol; 3 mL H₂O | EL350%     | 0.55 g NH₄F; 180 mL ethylene glycol; 20 mL H₂O | 60 |

2.2. Characterization and Photocatalytic Activity of TNS

Morphology and structure of the TNS layers was studied using Scanning Electron Microscopy (SEM, Lyra 3 Tescan, Tescan, Brno, Czech Republic, at 10 kV) equipped with Energy-Dispersive X-ray Spectroscopy (EDS) and X-ray Diffractometer (20°–60° 2 Theta; XRD, PANalytical Cu Kα radiation, λ = 1.5418 Å, Malvern-Panalytical, Malvern, United Kingdom), respectively. Optical properties were studied via Diffuse Reflectance Spectroscopy in the wavelength range from 200 nm to 800 nm (DRS, Shimadzu UV-2600, Shimadzu, Kyoto, Japan) equipped with an integrating sphere 2600 Plus.

Photocatalytic degradation of caffeine (CAF, Reagent Plus, Sigma-Aldrich, Darmstadt, Germany) aqueous solution (10 ppm, 50 mL) was evaluated in a home-made photoreactor, which consisted of a circular glass dish with a diameter of 8 cm. A sample carrier was placed at the bottom of the glass dish. Prior to the photocatalytic measurements, the whole assembly (along with TNS) was placed in the dark for 20 min to achieve the adsorption/desorption equilibrium. Afterwards, an 8W Hg lamp (Ultra-Violet Products Inc. UVP, Upland, CA, USA, λₘₐₓ = 365 nm) was used as the radiation source. The degradation of CAF was monitored for 3 h at 20 min intervals. The solution was withdrawn (0.5 mL) with a micropipette and mixed with 0.5 mL of distilled water. The concentration of CAF was determined by UV-VIS spectrophotometer (Jasco V530, Kyoto, Japan), according to our previous work [9]. To confirm the good stability of all TNSs, the photocatalytic activity measurements were repeated 3 times for each sample, and the differences in the overall photocatalytic performance did not exceed ±5%.

3. Results and Discussion

Anodization of a 20 cm² area Ti was conducted using fluoride-containing glycerol- and ethylene glycol-based electrolytes to obtain the herein-presented materials. The an-
odization conditions that we used led to the formation of both nanotubular and porous TiO$_2$ structures. Therefore, to avoid any confusion, we abbreviated the prepared materials as TNS (TiO$_2$ nanostructures).

Representative SEM images of TNS prepared in EL1, EL2 and EL33 with different concentrations of fluoride ions (according to Table 1) at 60 V are shown in Figure 1. Using similar conditions (voltage and anodization time), both nanotubular and porous structures were formed, depending primarily on the electrolyte composition. We conducted the SEM analysis on all the prepared TNS according to Table 1; however, we did not include all the SEM images in the manuscript (not to overload the manuscript with plenty of SEM images). The surface of each prepared TNS possess similar surface morphology as seen in Figure 1. Nevertheless, we summarized the morphological features (tube/pore diameter and thickness of the layer) of each TNS in Table 2, i.e., TNS prepared in different electrolytes (glycerol- or ethylene glycol-based ones), with different concentrations of fluoride ions (according to Table 1), at different applied potentials (from 20 V to 80 V). In general, electrolyte composition and applied conditions during anodization are crucial factors that affect the final morphology of TNS. Fluoride ions present in electrolytes act as etching agents and are directly responsible for the formation of either nanotubular or porous structures [21,22,31–33]. Generally, when the dissolution rate is higher than the formation rate, a rather porous structure is formed instead of a nanotubular one [34]. Thus, the mechanical stability of the formed nanotubular structure is disturbed, and as a result, a collapse of the tubes’ mouth is observed. Nevertheless, both nanotubular and porous structures possess good adhesion to the underlying Ti substrate, i.e., the formed layers do not peel off the substrate after bending. Moreover, both structures are efficient in applications such as photocatalysis and hydrogen production [9].

Table 2. Morphological features of the prepared TNS in different electrolytes.

| Electrolyte | Applied Potential (V) | Structure Type | Pore Diameter (nm) | Layer Thickness (µm) |
|-------------|-----------------------|----------------|-------------------|---------------------|
| EL1$_{100\%}$ | 20 | Nanotubular | 30–60 | 3–4 |
| | 40 | Nanotubular | 40–70 | 6–8 |
| | 60 | Porous | 50–100 | 7–9 |
| | 80 | Porous | 50–100 | 9–12 |
| | 20 | Nanotubular | 20–40 | 6–8 |
| | 40 | Nanotubular | 50–80 | 6–8 |
| | 60 | Nanotubular | 50–100 | 6–8 |
| | 80 | Porous | 50–100 | 6–8 |
| | 20 | Nanotubular | 10–20 | 2–4 |
| | 40 | Nanotubular | 30–50 | 4–8 |
| | 60 | Porous | 50–100 | 4–5 |
| | 80 | Porous | 50–100 | 5–6 |
| EL2$_{100\%}$ | 20 | Porous | 10–30 | 7–8 |
| | 40 | Nanotubular | 20–50 | 12–17 |
| | 60 | Nanotubular | 30–40 | 13–17 |
| | 80 | Nanotubular | 40–60 | 14–17 |
| | 20 | Porous | 10–20 | 4–6 |
| EL2$_{75\%}$ | 40 | Nanotubular | 30–50 | 4–8 |
| | 60 | Nanotubular | 40–50 | 8–9 |
| | 80 | Nanotubular | 40–50 | 9–12 |
| | 20 | Porous | 5–20 | 1–2 |
| EL2$_{50\%}$ | 40 | Nanotubular | 20–40 | 1–2 |
| | 60 | Nanotubular | 30–40 | 2–3 |
| | 80 | Nanotubular | 30–40 | 3–4 |
Table 2. Cont.

| Electrolyte | Applied Potential (V) | Morphological Features |
|-------------|-----------------------|------------------------|
|             |                       | Structure Type | Pore Diameter (nm) | Layer Thickness (µm) |
| EL3_{100%} | 20                    | Nanotubular      | 30–50              | 3–5                  |
|             | 40                    | Porous           | 30–70              | 3–5                  |
|             | 60                    | Porous           | 50–80              | 4–7                  |
|             | 80                    | Porous           | 60–80              | 6–9                  |
|             | 20                    | Nanotubular      | 20–40              | 2–3                  |
|             | 40                    | Porous           | 50–80              | 4–6                  |
|             | 60                    | Porous           | 60–80              | 4–8                  |
|             | 80                    | Porous           | 50–80              | 4–8                  |
| EL3_{75%}  | 20                    | Nanotubular      | 20–40              | 2–3                  |
|             | 40                    | Porous           | 50–80              | 4–6                  |
|             | 60                    | Porous           | 60–80              | 4–8                  |
|             | 80                    | Porous           | 50–80              | 4–8                  |
| EL3_{50%}  | 20                    | Nanotubular      | 10–20              | 1–2                  |
|             | 40                    | Porous           | 10–30              | 1–3                  |
|             | 60                    | Porous           | 50–80              | 2–5                  |
|             | 80                    | Porous           | 50–90              | 4–7                  |

Figure 1. Representative SEM images of TNS prepared in different electrolytes (according to Table 1) at 60 V: (a–c) EL1_{100%}, EL1_{75%}, and EL1_{50%}, respectively; (d–f) EL2_{100%}, EL2_{75%}, and EL2_{50%}, respectively; and (g–i) EL3_{100%}, EL3_{75%}, and EL3_{50%}, respectively.

Several trends were observed from the obtained data summarized in Table 1 and are as follows: In all types of electrolytes, the pore diameter and thickness of the nanotubular...
or porous TiO$_2$ layer increased with the increased potential. This is in accordance with the plethora of reports on the effect of anodization conditions on the morphology of the layers [7,35–37]. In general, at higher potentials (i.e., 60 V and 80 V), rather a porous structure is formed instead of a nanotubular one. Indeed, the etching rate is higher at increased potentials; thus, a porous structure formation is present. At lower potentials (i.e., 20 V and 40 V) a nanotubular structure is prone to form. Nevertheless, in the case of EL2, the porous structure was observed at 20 V, and nanotubular structures were formed at 40 V, 60 V, and 80 V. This is due to the low content of distilled water in the electrolyte (3 mL); thus, higher potentials are required for nanotubular structure to be obtained [7]. Indeed, the viscosity of the electrolyte that contains 197 mL of ethylene glycol and 3 mL of distilled water inhibits the migration of fluoride ions present in the electrolyte during anodization.

Figure 2 shows XRD patterns of annealed TNS; XRD was performed on all the TNS (a total of 36 samples), but the applied potential during anodization (20 V–80 V) and electrolyte composition has no impact on the phase composition of the material after annealing, and all the TNS possess similar phase composition. Therefore, we included representative XRD patterns for each electrolyte type (according to Table 1) prepared at 60 V. In all TNS, two different phases were identified, i.e., tetragonal anatase TiO$_2$ (P4$_2$/mm; ICCD 01-086-1157) [38,39] and hexagonal metallic Ti (P6$_3$/mmc; ICCD 00-044-1294) [23]. The visible diffractions of metallic Ti stem from the underlying Ti substrate and are visible due to the penetration of X-rays. Nevertheless, the prepared nanotubular and porous TiO$_2$ structures consist solely of anatase TiO$_2$. The XRD patterns show typical diffractions of anodically prepared TiO$_2$ layers [9,23].

![Figure 2. XRD patterns of TNS prepared in different electrolytes (according to Table 1) at 60 V. A—anatase; T—titanium.](image)

UV-VIS DRS spectra and the corresponding Kubelka–Munk curves were recorded to determine the reflectance and the indirect optical band gap energy ($E_{BG}$) of TNS (Figure 3). Although DRS measurements were performed on all TNS, we show representative spectra of TNS prepared at 60 V (similarly to SEM in Figure 1 and XRD in Figure 2). All TNS (36 different ones) possess similar optical properties with $E_{BG}$ in the energy range from 3.1 eV to 3.2 eV. The obtained values of the indirect $E_{BG}$ are in good agreement with previous reports on TiO$_2$ materials composed solely of the anatase phase [40–43]. Indeed, the appeared reflectance edge at ~400 nm is attributed to the anatase phase with $E_{BG}$ ~3.2 eV [44], and no substantial differences were observed in the different TNS. Both nanotubular and porous structures contain solely anatase TiO$_2$, thus their $E_{BG}$ are similar.
Although the degradation rates were calculated, we decided to add the conversion efficiency (\( \text{efficiency} \)). A clear trend appeared wherein by the obtained SEM data (Figure 1) show clear differences in the pore diameter; thus, it from the underlying substrate and proceed with the BET measurements. Nevertheless, herein, Brunauer–Emmett–Teller (BET) theory \([46]\) is not applicable in the case of TNS, the pore diameter is another crucial factor that directly affects the specific surface area. The thickness substantially increased and reached approx. 17 \( \mu \text{m} \) in EL2-365 nm at 60 V. The obtained values of the indirect \( E_B \) are in good agreement with previous reports on TiO\(_2\) and no substantial differences were observed in the different TNS. Indeed, the unique properties of the nanotubular structures. Indeed, the unique properties of nanotubular TiO\(_2\) structures, such as improved charge carrier transport along the nanotube walls and overall enhanced incident light utilization is responsible for this outcome. The most efficient TNS (EL2-100\%) at prepared 40 V) degraded approx. 50\% of the pollutant. A clear trend appeared wherein by decreasing the amount of fluoride ions during anodization, the photocatalytic degradation efficiency decreased. Indeed, fluoride ions are responsible for the formation of nanotubular and porous TiO\(_2\) structures; thus, by lowering the total amount of fluorides, the etching rate during anodization is low. As a result of the low content of fluorides, thinner layers are obtained during anodization in EL1-365 nm, as seen in Table 2 (\textit{with a maximum thickness of approx. 5 \( \mu \text{m} \)}). With the increasing of the fluoride content in the electrolytes (EL1-375%–100%), the thickness substantially increased and reached approx. 17 \( \mu \text{m} \) in EL2-100\%. Moreover, the pore diameter is another crucial factor that directly affects the specific surface area. Herein, Brunauer–Emmett–Teller (BET) theory \([46]\) is not applicable in the case of TNS, as it is challenging to measure BET on our kind of samples, i.e., to remove the layers from the underlying substrate and proceed with the BET measurements. Nevertheless, the obtained SEM data (Figure 1) show clear differences in the pore diameter; thus, it indirectly confirms a high surface area of the material, in general. As the degradation

Figure 3. UV-VIS DRS spectra and the corresponding Kubelka–Munk curves (as insets) of TNS prepared in different electrolytes (according to Table 1) at 60 V: (a) EL1-50\%–EL1-100\%, (b) EL2-50\%–EL2-100\%, and (c) EL3-50\%–EL3-100\%.

Photocatalytic degradation of caffeine (CAF) was explored under UVA light irradiation \( (\lambda_{\text{max}} = 365 \text{ nm}) \) on all TNS, and the results are summarized in Figure 4, along with the illustration of the photoreactor that was used. Photocatalytic degradation of CAF follows the first-order reaction typical for TiO\(_2\) photocatalysts and an organic pollutant \([45]\). Although the degradation rates were calculated, we decided to add the conversion efficiency of CAF in % for an easier and more understandable interpretation of the results \((\text{to avoid 36 different rate constants that would confuse the reader})\). The conversion efficiency was calculated directly from the degradation extents after 3 h, i.e., from the initial and final concentration of CAF. Overall, the most efficient CAF degradation was obtained using nanotubular structures. Indeed, the unique properties of the nanotubular TiO\(_2\) structures, such as improved charge carrier transport along the nanotube walls and overall enhanced incident light utilization is responsible for this outcome. The most efficient TNS (EL2-100% at 60 V) degraded approx. 50\% of the pollutant. A clear trend appeared wherein by decreasing the amount of fluoride ions during anodization, the photocatalytic degradation efficiency decreased. Indeed, fluoride ions are responsible for the formation of nanotubular and porous TiO\(_2\) structures; thus, by lowering the total amount of fluorides, the etching rate during anodization is low. As a result of the low content of fluorides, thinner layers are obtained during anodization in EL1-365 nm, as seen in Table 2 (\textit{with a maximum thickness of approx. 5 \( \mu \text{m} \)}). With the increasing of the fluoride content in the electrolytes (EL1-375%–100%), the thickness substantially increased and reached approx. 17 \( \mu \text{m} \) in EL2-100%. Moreover, the pore diameter is another crucial factor that directly affects the specific surface area. Herein, Brunauer–Emmett–Teller (BET) theory \([46]\) is not applicable in the case of TNS, as it is challenging to measure BET on our kind of samples, i.e., to remove the layers from the underlying substrate and proceed with the BET measurements. Nevertheless, the obtained SEM data (Figure 1) show clear differences in the pore diameter; thus, it indirectly confirms a high surface area of the material, in general. As the degradation
of CAF proceeds at the TNS/CAF interface, surface area (or porosity) is a crucial factor. The interplay of morphology (SEM, Figure 1), structure (XRD, Figure 2), and optical properties (DRS and Kubelka–Munk plots, Figure 3) are in favor of the photocatalytic efficiency of the herein-presented TNS prepared in glycerol- and ethylene glycol-based electrolytes with higher concentration of fluoride ions. The porous TiO$_2$ structures showed approx. 2 times lower degradation efficiencies. This is due collapse/distortion of the nanotubular structures during anodization by the applied conditions. The pores are denser, thus providing fewer active sites for CAF to be adsorbed and subsequently degraded. Nevertheless, a satisfactory degradation efficiency of CAF (approx. 30%) was obtained by using porous TiO$_2$ (EL3$_{100\%}$ prepared at 60 V). All in all, both nanotubular and porous TiO$_2$ structures prepared via anodization are promising for application in photoreactors for wastewater treatment. Nevertheless, there are still major challenges of synthesis such nanostructures on large area, and such synthesis is necessary for industrial applications of these nanomaterials. At last, Table 3 shows the comparison of our TNS with reports on anodic TiO$_2$ based nanostructures for caffeine photocatalytic degradation.

Figure 4. Photocatalytic degradation of caffeine using TNS prepared in different electrolytes (according to Table 1): (a) EL1-3$_{100\%}$, (b) EL1-3$_{75\%}$, (c) EL1-3$_{50\%}$, and (d) illustration of the photocatalytic reactor. T—nanotubular; P—porous.
Table 3. The comparison of anodic TiO$_2$ based nanostructure for caffeine photocatalytic degradation. Anodization condition, target pollutant (and its concentration), rate constant, and time duration were taken from the literature.

| Material | Anodization Conditions | Caffeine Concentration | Rate constant (k)/Conversion Efficiency (%) | Time (min) | Ref |
|----------|------------------------|------------------------|---------------------------------------------|------------|-----|
| TiO$_2$  | Glycol electrolyte with 0.3 wt % NH$_4$F and 2 vol % DI-H$_2$O (60 V for 6 h); 2g NH$_4$F + 100 mL DI-H$_2$O in glycerol-based electrolyte (20 V for 100 min). | 50 mg L$^{-1}$ | 44% | 180 | [47] |
| TiO$_2$  | NH$_4$F (1.3 g) in EG (197 mL) and DI-H$_2$O (3 mL). | 20 ppm | 0.0069 min$^{-1}$ | 120 | [9] |
| V- TiO$_2$ | 98% ethylene glycol, 2% DI-H$_2$O and 0.3 wt % NH$_4$F; EG and a solution of 0.3 wt % NH$_4$F. | 20 ppm | 46% | 120 | [48] |
| TiO$_2$  | NH$_4$F in 2 vol % DI-H$_2$O (60 V for 3 h); 1.3 g NH$_4$F; 197 mL EG; | 15 mg L$^{-1}$ | 51% | 240 | [49] |
| EL$_{100}$% | 3 mL H$_2$O (40 V for 100 min); 0.975 g NH$_4$F; 197 mL EG; | 10 ppm | 2.12 $\pm$ 0.13 $\times$ 10$^{-2}$ min$^{-1}$ | 180 min | [50] |
| EL$_{75}$% | 3 mL H$_2$O (80 V for 100 min) | 10 ppm | 50% | 180 min | This study |

4. Conclusions

Anodization of an approx. 20 cm$^2$ Ti area was conducted to prepare nanotubular and porous TiO$_2$ structures for comparison in the photocatalytic degradation of caffeine under UVA. A variety of conditions were conducted to obtain a total of 36 different TNS: (i) three different electrolytes based on glycerol and ethylene glycol, (ii) three different concentrations of fluoride ions in each type of electrolyte, and (iii) different applied potentials from 20 V to 80 V for each type of electrolyte. Depending on the different conditions, nanotubular and porous TiO$_2$ structures were formed with thickness up to 17 µm and pore diameter up to 100 nm, and subsequently annealed at 400 °C to obtain crystalline anatase TiO$_2$. All TNS possess E$_{BG}$ in the range from 3.1 eV to 3.2 eV. Overall, both nanotubular and porous TNS lead to efficient degradation extents of caffeine after 3 h, although nanotubular TNS showed enhanced photocatalytic activity (reaching degradation up to 50%) compared to that of porous TNS. Indeed, the unique properties of 1D nanotubular structures are responsible for the improved photocatalytic activity. The degradation efficiency of both nanostructures is due to their high surface area associated with a sufficient number of active sites for caffeine to adsorb on the surface of TNS and subsequently degrade the pollutant. As the anodization of large areas is, nowadays, becoming a trend, we show that both nanotubular and porous TiO$_2$ are promising for their use in photocatalysis and could, potentially, be applicable in photoreactors for wastewater treatment. We believe this present work can be the foundation for future development of efficient TiO$_2$ nanostructures for industrial applications.

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