Synthesis of photocatalytic TiO\textsubscript{2} nanotubes on additively manufactured Ti-alloy substrates

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Abstract. The pursuit of sustainable and clean energy sources has led to the exploration of green hydrogen as a versatile and eco-friendly energy carrier. This research paper focuses on the application of photocatalytic electrolysis, particularly utilizing titanium dioxide (TiO\textsubscript{2}) nanotubes, for efficient hydrogen production. The study investigates the synthesis of TiO\textsubscript{2} nanotubes on additive manufacturing (AM)-produced substrates and explores the effects of post-synthesis annealing and cleaning techniques. The results demonstrate well-organized and uniform nanotubes, with the morphology depending on the annealing ramp rate. X-ray diffraction analysis reveals a phase transformation to anatase with a grain size of approximately 28 nm upon annealing. The study emphasizes the importance of post-synthesis cleaning in achieving desired nanotube surfaces. Cleaning with ethanol followed by 10 vol\% HCl produces well-organized nanotubes of varying sizes. Overall, the research contributes to the understanding of surface modification techniques and nanostructured architectures for optimizing hydrogen photoelectrodes. The study also highlights the potential of AM in advanced fabrication methods for improved photoelectrochemical electrodes and offers valuable insights for future work in this field.

1 Introduction

The pursuit of sustainable and clean energy sources has become increasingly imperative in addressing global energy challenges. One particularly promising solution is green hydrogen, which stands out as a versatile and eco-friendly energy carrier with the potential to revolutionize various sectors, including transportation and energy storage [1,2]. The most common process to produce green hydrogen is through using electricity generated by renewable energy sources such as wind and solar to split water molecules into hydrogen and oxygen. However, an alternative approach, known as photocatalytic electrolysis, utilizes the interaction between a photocatalyst and light to facilitate the water-splitting reaction. This direct solar-to-hydrogen conversion holds the potential for a greener and more sustainable hydrogen production process. Moreover, sun-rich regions like South Africa present an advantageous setting for harnessing solar energy and implementing photocatalysis in hydrogen production. Titanium dioxide (TiO\textsubscript{2}) has emerged as a highly efficient...
allowing for cost-effective and sustainable hydrogen evolution processes [3].

Photocatalytic hydrogen cells, however, face challenges in terms of overall energy efficiency and scalability as the conversion efficiency of solar energy to hydrogen can be relatively low and the catalysts used may have limitations in terms of stability and efficiency [5]. Specifically, the wide band-gap energy of TiO$_2$ (estimated to be 3.0 eV for rutile and 3.2 eV for anatase) limits its photocatalytic activity to ultra-violet (UV) light only [4]. Hence, in recent years, extensive research has been conducted to enhance the visible light absorption capabilities and overall photocatalytic activity of TiO$_2$ by employing increasingly intricate approaches [4]. For example, doping of TiO$_2$ with metal ions, coupling TiO$_2$ with low band gap semiconductor materials, and dye sensitization of TiO$_2$. TiO$_2$ has also been utilized as a support material (i.e., so-called core-shell catalytic design) for noble metals like Pt and Pd, and non-metals such as N, C and S [4,6,7]. The presence of these co-catalysts on TiO$_2$ surfaces facilitates the formation of localized surface plasmon resonances, enabling enhanced visible light absorption and subsequent charge transfer processes [4].

Surface modification techniques – the focus of the current study – involves the manipulation of the photocatalyst's structure to boost activity. A nanostructured architecture, such as nanoparticles and nanotubes, has been shown advantageous for an increase in photocatalytic surface area allowing for more active sites [8]. Nanostructured architectures also improve the reaction kinetics through efficient charge transfer and mass transport during the hydrogen evolution reaction. The shorter diffusion distances for reactants and products at the nanoscale enhance the reaction kinetics, leading to faster and more efficient hydrogen evolution. The high surface area and unique surface chemistry of nanostructured TiO$_2$ catalysts also allow for functionalization by doping with non-metals or noble metal nanoparticle co-catalysts (as previously mentioned) [4]. Nanotubes offer tailorable properties since the catalysts can be precisely engineered and controlled at the nanoscale to manipulate its size and shape. Nanotubes exhibit improved mechanical properties, compared to nanoparticles, such as higher strength and flexibility [9]. Lastly, nanotubes require a smaller amount of material compared to bulk catalysts to achieve the same catalytic activity. This efficient utilization of resources is particularly important for expensive or scarce materials, allowing for cost-effective and sustainable hydrogen evolution processes [3].

Studies have also found that photocatalytic hydrogen cell performance can be improved by using a 3-dimentional (3D) electrode geometry and conical surface structures [10–12]. Additive manufacturing (AM) is an ideal fabrication method for such electrodes and features since it enables the direct production of complex metal parts layer-by-layer from a computer-aided design model. Li et al. [10] demonstrated the advantages of additive manufacturing (AM) for photocatalysis by using laser powder bed fusion (L-PBF) to manufacture 3D-geometry titanium electrodes with precisely controlled macro-porosity. Similarly, Lee et al. [12] employed L-PBF to manufacture photoelectrodes featuring micro-meter scale conical surface structures. Both studies further enhanced the photoelectrochemical water splitting performance by synthesizing a thin surface-layer of TiO$_2$ nanotubes on the electrodes.

The current study builds upon limited research seeking to leverage the unique advantages offered by both AM and TiO$_2$ nanotubes on hydrogen photoelectrodes. The study firstly aimed to explore the feasibility of manufacturing an AM-built photocatalytic electrode in the form of a titanium core/substrate with a TiO$_2$ nanotubes surface layer. Secondly, to develop understanding of the effects of post-synthesis process variables on the morphology and
composition of TiO\textsubscript{2} nanotubes. To achieve these objectives, the study focuses on the synthesis of photocatalytic TiO\textsubscript{2} nanotubes on L-PBF Ti-6Al-4V substrates and explores the effects of different post-synthesis annealing and cleaning techniques. The paper begins by reviewing the key literature on electrochemical anodization and post-anodization processes. Next, the methodology for manufacturing and characterizing TiO\textsubscript{2} nanotubes on metal AM substrate samples is presented. Subsequently, the anodization and characterization results of the nanotubes are discussed. The paper concludes with a summary of the findings and provides suggestions for future work.

2 Literature review

2.1 Electrochemical anodization

For a detailed review of the synthesis and properties of TiO\textsubscript{2} nanotubes, see [9,13]. Electrochemical anodization (EA) is a widely used technique for the synthesis of TiO\textsubscript{2} nanotubes. This technique involves applying a voltage to a titanium substrate immersed in an electrolyte containing fluoride ions (typically 0.05 – 0.5 wt% F\textsuperscript{–}) [14], which results in the formation of a porous oxide layer on the surface. The structure, morphology and properties of the TiO\textsubscript{2} nanotubes depend on EA parameters, key of which are: anodization voltage, the electrolyte composition ([F\textsuperscript{–}] concentration, pH, viscosity, and water content), and the anodization time [15,16].

The anodization voltage determines the wall thickness (~10–30 nm) and diameter (~10–800 nm) while time controls length (~100 nm – 300 \( \mu \)m) [17,18]. Higher voltages lead to thicker and wider nanotubes, but also increase the risk of breakdown and dissolution of the oxide layer [9,19]. Typically, electrolytes are aqueous, or ethylene glycol (EG) based. The optimal voltage range for TiO\textsubscript{2} nanotube formation is 2–20 V in an aqueous solution [18] and 20–60 V in an EG-based electrolyte [9,19]. When changing the voltage during formation, morphological modifications are possible, for example bamboo-like nanotubes and branching of nanotubes [9].

The electrolyte composition affects the chemical stability and uniformity of the TiO\textsubscript{2} nanotubes [20]. The most commonly used electrolytes are aqueous or organic solutions containing fluoride ions, such as NH\textsubscript{4}F/CH\textsubscript{3}COOH, H\textsubscript{2}SO\textsubscript{4}/HF and Na\textsubscript{2}HPO\textsubscript{4}/NaF. [13,20]. The fluoride ions cause localised dissolution of the metal oxide layer, creating the nanotube initiation sites [16]. The concentration of fluoride ions influences the pore size and growth rate of the nanotubes [16]. Higher concentrations lead to faster growth and larger pores, but also increase the chemical dissolution and roughness of the nanotube walls [16].

The type of solvent also plays a role in the morphology and quality of the TiO\textsubscript{2} nanotubes. Organic solvents, such as ethylene glycol or glycerol, tend to produce longer, smoother and better self-organised nanotubes than aqueous solvents, due to their lower conductivity and viscosity [13,16]. However, organic solvents may also introduce carbon impurities into the TiO\textsubscript{2} nanotubes, which can affect their optical and electrical properties [16].

The anodization time determines the length and density of the TiO\textsubscript{2} nanotubes [13]. Longer anodization times result in longer and more densely packed nanotubes, but also increase the possibility of defects and cracks in the oxide layer [13]. The optimal anodization time depends on the desired application and performance of the TiO\textsubscript{2} nanotubes. For example, for photocatalytic applications, longer nanotubes may provide more surface area
and light absorption, but shorter nanotubes may offer faster charge carrier transport and lower recombination losses.

Etching of the tube tops causes the formation of needle- or grass-like morphologies [9]. These tend to collapse or bundle due to their own weight or by capillary forces when drying [9,21]. Annealing can also influence this structurally disordered layer – mechanically unstable and therefore undesired [22]. Authors have developed processes such as polishing the surface pre-EA to avoid the formation of nanograss [22]. An effective method to remove this disordered layer by using a post-synthesis cleaning process, discussed in Section 3.4.

2.2 Post-synthesis annealing

A post-synthesis annealing treatment is a crucial step for improving the properties of TiO$_2$ nanotubes. As-synthesised TiO$_2$ nanotubes are amorphous or poorly crystalline. Annealing in an oxygen-rich environment can induce phase transformation from amorphous to anatase or rutile phases. The crystalline phases enhances the optical and electronic properties of the nanotubes, resulting in improved photocatalytic activity and thermal stability [23]. Annealing TiO$_2$ nanotubes at 300–500 °C leads to crystallization of the as-fabricated amorphous structure into anatase while at >550 °C rutile phase or a mixture of anatase and rutile phases is formed [15]. Anatase generally exhibiting higher photocatalytic activity due to its higher surface reactivity and larger bandgap energy compared to rutile [24].

Annealing may also cause morphological changes such as shrinkage, collapse, or sintering of the nanotubes, which can reduce their surface area and porosity [25]. It has been observed that annealing at higher temperatures can lead to tube collapse or tube-to-particle transformation [15]. The resulting morphological changes can affect the surface area, pore structure, and overall functionality of the nanotubes. Annealing influences the optical properties of TiO$_2$ nanotubes by affecting the absorption spectra and photoluminescence characteristics of the nanotubes [26]. These changes are attributed to crystallinity improvements and the elimination of defects upon annealing. Furthermore, the thermal stability of TiO$_2$ nanotubes can be improved, allowing them to withstand higher temperatures without structural degradation. This property is important for applications requiring elevated temperatures, such as catalysis and solar energy conversion.

The surface chemistry can also be modified through the formation of Ti$^{3+}$ states or O$^{2-}$ vacancies. The presence of these states play a critical role in influencing the electronic and optical properties, as well as surface reactivity [9]. Ti$^{3+}$ content seems to entirely dominate the conductivity of TiO$_2$ crystals.

As-formed nanotubes contain a significant amount of fluoride species. These species can be removed to a large extent by annealing. It induces the formation of surface hydroxyl groups or the removal of adsorbed species (such as F$^-$), which can impact the surface reactivity and adsorption properties [9].

2.3 Post-synthesis cleaning

Post-synthesis cleaning of TiO$_2$ nanotubes is important for the following reasons. During the synthesis process, various contaminants (residual chemicals, impurities, or by-products from the fabrication, such as organic residues, adsorbed molecules, or disordered oxide layers) can be introduced onto the surface of the nanotubes which can form because of exposure to air
or reaction by-products. These surface layers can function as barriers, limiting the access of photons to the nanotube surface or obstructing the adsorption and reaction of target species.

Several research studies have explored different surface cleaning techniques of TiO₂ nanotubes. Zhu et al. [21] demonstrated that cleaning TiO₂ nanotube arrays with ethanol, followed by supercritical CO₂ drying, effectively eliminated structural disorder. Kim et al. [22] proposed a protective top layer approach to prevent structural disorder and bundling of TiO₂ nanotube arrays. However, these methods were found to be costly and complex. Hydrofluoric acid (HF) treatment has also been explored as a cleaning method for effectively removing the precipitated layer on the top surface of nanotubes [27]. However, HF etching of the nanotube surface can result in a serrated and irregular texture, which negatively impacts the photoelectrochemical performance.

To address these challenges, a simple, cost-effective, and environmentally safe cleaning technique has been proposed. This method involves ultrasonic cleaning combined with acetone [4] to effectively remove overlayers on the nanotubes, resulting in the formation of bundle-free and crack-free TiO₂ nanotube arrays without relying on hazardous chemicals such as HF. By using this technique, the nanotube arrays can be effectively cleaned while preserving their structural integrity and avoiding surface irregularities. Cleaning methods applied in this study are based on work by Lai and Sreekantan [4]. The authors found that a 10 min ultrasonic agitation in acetone was effective in removing debris layers from the nanotubes leading to the formation of free-standing TiO₂ nanotube arrays without breaking the tube structure.

3 Experimental methods

3.1 Laser powder bed fusion of Ti-6Al-4V substrates

Twelve cylindrical samples with a diameter of 5 mm and thickness of 1.6 mm were fabricated using laser powder bed fusion (L-PBF). A Concept Laser M2 machine with default printing parameters was used – laser power of 100 W, scan velocity of 600 mm/s, hatch spacing of 105 μm, and layer thickness of 30 μm. Gas-atomized Ti-6Al-4V powder with a particle size in the range of 20 to 50 μm was used. The cylindrical samples were printed with their axis orientated parallel to the build plate.

3.2 Electrochemical anodization of substrates

Substrates were prepared by grinding and polishing using standard Buehler polishing procedures [28] until a mirror-like surface was achieved. A total of twelve sample were anodized. Samples S1 to S10 had an electrode working distance of 15 mm while samples S11 and S12 had a working distance of 30 mm.

A two-step EA process was conducted using an ethylene glycol electrolyte solution containing 0.4 wt% ammonium fluoride and 2 wt% ultrapure water. The first step was performed using a DC voltage of 60 V for 30 to 60 min. This was intended to induce a nanodimples which act as initiation sites for nanotube growth thereby improving adhesion [29]. The resulting thin nanotubes layer was removed with 2 vol% HF, 20 vol% HNO₃ by using as little volume and shortest time possible to limit exposure of the patterned surface to the etchant.
The second step was performed under the same conditions with a fresh electrolyte solution. The current was measured using a digital multimeter via an RS232 interface, Fig. 1.

3.3 Post-synthesis annealing

Two samples were annealed at 450 °C for 2 hours exposed to ambient air. These samples are included in Table 1. To compare the heating rate effects on the nanotubes’ morphology, one sample was placed in the furnace before ramping up the temperature, thereby allowing it to experiencing a slow heating rate, while the other was placed in the furnace at the 450 °C, thereby causing a fast rate. Both samples were cooled slowly at the furnace cooling rate. Furnace heating rate is approximately 5-8 °C per minute.

3.4 Post-synthesis cleaning

To investigate the effect of cleaning methods on the morphology of TiO2 nanotubes, different cleaning procedures, durations and chemical solutions were used. The cleaning methods are tabulated in Table 1. A two-step method, step (a) followed by (b), was applied to S5 in which it was first sonicated in ethanol followed by submerging in 10 vol% HCl. All samples cleaned using HCl (S5, S9, S10) were rinsed with ethanol afterwards. The control sample (S6) did not undergo any post-synthesis processes.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Method (duration)</th>
<th>Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>Slow ramp, 450 °C (2 hrs)</td>
<td>-</td>
</tr>
<tr>
<td>S2</td>
<td>Fast ramp, 450 °C (2 hrs)</td>
<td>-</td>
</tr>
<tr>
<td>S3</td>
<td>Ultrasonicate (5 s)</td>
<td>Acetone</td>
</tr>
<tr>
<td>S4</td>
<td>Ultrasonicate (5 s)</td>
<td>Acetone</td>
</tr>
<tr>
<td>S5</td>
<td>a. Ultrasonicate (20 min)</td>
<td>Ethanol</td>
</tr>
<tr>
<td></td>
<td>b. Submerge (20 s)</td>
<td>10 vol% HCl</td>
</tr>
<tr>
<td>S6</td>
<td>Control</td>
<td>-</td>
</tr>
<tr>
<td>S7</td>
<td>Ultrasonicate (2 min)</td>
<td>Acetone</td>
</tr>
</tbody>
</table>

**Table 1.** Post-synthesis processes: annealing and cleaning procedures.
not undergo any post using HCl cleaning.

To 3.4 Furnace heating rate is approximately experiencing a sample was included in Two samples were annealed at 450 °C for 2 hours.

<table>
<thead>
<tr>
<th></th>
<th>Method (duration)</th>
<th>Solution</th>
</tr>
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<tbody>
<tr>
<td>S8</td>
<td>Ultrasonicate (2 min)</td>
<td>Acetone</td>
</tr>
<tr>
<td>S9</td>
<td>Submerged (30 min)</td>
<td>1 vol% HCl</td>
</tr>
<tr>
<td>S10</td>
<td>Submerged (60 min)</td>
<td>1 vol% HCl</td>
</tr>
<tr>
<td>S11</td>
<td>Ultrasonicate (5 min)</td>
<td>Acetone</td>
</tr>
<tr>
<td>S12</td>
<td>Rince until clean (5-10 s)</td>
<td>2 vol% HF, 20 vol% HNO₃</td>
</tr>
</tbody>
</table>

3.5 Characterisation of TiO₂ nanotubes

Nanotube morphology was imaged using a secondary electron detector on a Zeiss MERLIN field emission scanning electron microscopy (SEM). Chemical composition and crystal structure were evaluated using energy dispersive spectroscopy (EDS) and X-ray diffraction (XRD) techniques. Wide angle 20 XRD scans were done using a Bruker D2 PHASER machine. The X-ray generator was set at 30 kV and 10 mA, while a CuKα (1.541838 Å) radiation source was used. The XRD scan hold time was 1 second at the step size, 0.02°. Bragg peak analysis was done using software XPowderX [30] and MAUD [31]. The XRD patterns of the samples were compared to data base file CIF file 9015929 and CIF 9008517 for anatase and titanium respectively.

The crystallite sizes (d) were calculated using Scherrer’s formula: \( d = \frac{k\lambda}{B\cos\theta} \), where k is a dimensionless constant having a value of 0.9, \( \lambda = 0.15406 \) nm, \( \theta \) is the diffraction half angle in radians and B is the full width at half maximum (FWHM). The crystallite size of the anatase phase, was obtained from fitting and measuring the width of the (011) peak. The anatase unit cell parameters were calculated by using the tetragonal formula [26]:

\[
\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2},
\]

where d, is the interplanar distance, a and c are lattice constants and h, k, l are the Miller indices. The lattice parameters were calculated by using the (004) and (200) peaks in order to obtain comparable results to [26].

4 Results and discussion

4.1 Anodization current density

A plot of current density-vs-time is given in Fig. 2. The difference between individual plots is likely due to local effects such as temperature, sample size and sample surface roughness. Noise in the data was likely caused by a combination of sensitive measuring equipment and local fluctuations in electrolyte ion concentration due to agitation by the magnetic stirrer. Three stages in nanotubes’ formation are identifiable from this plot as described according to the oxidation-dissolution model based on findings of Roy, Berger and Schmuki [9].

Typical formation of a dense oxide layer occurs in stage I which is characterised by an exponential decay in current density as the oxide layer increases electric resistance. Dissolution of the dense oxide by F⁻ species (stage II) reduces the resistance and slightly increases the current density. The dissolution of the compact oxide layer by fluoride ions causes the formation of Ti⁴⁺ which undergoes immediate complexation (solvatization) arriving at the oxide–electrolyte interface (producing titanium hexafluoride). Irregular nanoscale pores are initially formed that penetrate the initial compact oxide layer by fluoride ions arriving at the oxide

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4.2 Microscopy imaging

SEM imaging revealed samples with well organised and uniform nanotubes and provides measurement of their morphology. Samples with partially and unorganised nanotubes morphology are also presented and discussed. The correlations between post-synthesis processes and morphology are discussed.

4.2.1 As-synthesised nanotubes sample

The control sample (S6), Fig. 3, showed nanotubes covered with collapsed, bundled and fragments of nanotubes debris. This is likely the top part of the nanotubes that have thinned to etching effects and have collapsed. This therefore highlights the necessity of post-synthesis cleaning.

4.2.2 Annealed nanotubes samples.

A slow ramping rate resulted in well organised, uniform nanotubes, Fig. 4(a & b). Fig. 4(a) depicts large grain-like clusters of nanotubes, while Fig. 4(b) depicts the individual
morphology of nanotubes at a high magnification. Nanotubes morphology measured an approximate inner diameter of 100 nm, a wall thickness of 15-35 nm and a length in the order of 10 µm, as measured on Fig. 4(e). A micrograph of the closed bottom-ends of the nanotubes (previously attached to the substrate surface) is depicted in Fig. 4(f). A fast ramp rate resulted in thin-walled, collapsed nanotubes, Fig. 4(c & d), which was likely caused by temperature-induced mechanical stresses as the nanotubes contracted / expanded. These findings are consistent with previous studies, which have demonstrated that the morphology of tubes formed in ethylene glycol strongly correlates with the ramping rate [9].

Fig. 4. Micrographs of samples (a) S1 low mag., (b) S1 high mag., (c) S2 low mag, (d) S2 high mag. (e) S1 side view, (f) S1 closed-ends of nanotubes’ bottom.

4.2.3 Cleaned nanotubes samples.

Acetone
Fig. 5 depicts micrographs of samples cleaned with acetone. While acetone cleaning was able to remove the debris-like fragments observed in Fig. 3, distorted nanotube bundles can still be observed. Such structure is believed to be caused by the capillary stress created during the evaporation of liquids from the nanotubes [20]. The unbalanced capillary stress within the interior and exterior of the pores accelerates the distortion of the pore structure near the ends of the nanotube, collapsing to produce an overlayer that covers the opening of the nanotubes. These distorted top-layer films are comparable to results obtained by [21]. By comparing the surface areas of the nanotubes in the micrographs of Fig. 5(a-f), a larger number of nanotubes are visible for samples with increased acetone exposure time. Fig. 5(b) appears to show the presence of anatase particles (as indicated by the arrows).

![SEM micrographs of samples cleaned with acetone.](image)

Fig. 5. SEM micrographs of acetone ultrasonicated samples, (a & b) 5 seconds, (c & d) 2 min and (e & f) 5 min.

**1 vol% HCl**

SEM micrographs of samples submerged in 1 vol% HCl for 30 and 60 min are depicted in Fig. 6(a) and Fig. 6(b), respectively. By comparing the number of nanotubes between images...
(a) and (b) at the same magnifications, a larger number of nanotubes are visible for a longer exposure time. As with cleaning with acetone for up to 5 min, the investigated submerged exposure times in 1 vol%, for up to 60 min, were not effective in fully removing clustered and bundled top surface layer. Longer exposure did, however, show to cause a larger number of nanotubes to become visible.

Fig. 6. SEM micrographs of 1 vol% HCl ultrasonicated samples for, (a) 30 min, and (b) 60 min.

**Ethanol + 10 vol% HCl**

The cleaning process for sample S5 resulted in uncovering the uniform honeycomb-like nanotubes, Fig. 7(a & b). Fig. 7(a) depicts large grain-like clusters of nanotubes, while Fig. 7(b) depicts the individual morphology of nanotubes at a high magnification. Nanotubes had an approximate inner diameter of 590 nm, and wall thickness that varied between 60–150 nm, Fig. 4(b).

The measured nanotubes are larger in diameter than those measured of the annealed sample (S1) in Fig. 4(b). Since the morphology of the nanotubes is known from literature to be thicker towards the base and thinner towards the top of the nanotubes, [9], it is likely that what is being observed is the lower cross-section of the nanotubes towards the bottom. If this is the case, it means that this cleaning method removed a larger portion of nanotubes compared to the other cleaning methods.

Fig. 7. SEM micrographs of Ethanol + 5 vol% HCl ultrasonicated samples (a) low mag., and (b) high mag.
4.3 Electron dispersive spectroscopy

Fig. 8(a) depicts the SEM image with labelled points while Fig. 8(b) depicts the wt% of Ti, O, and F of each measurement point. The point measurement closest to the bottom of the nanotubes (i.e., closest to the substrate) is labelled as measurement number 8, while the topmost point measurement is labelled measurement number 1.

From the trend in concentration, as suggested by curves on Fig. 8(b), oxygen decrease from the top to the bottom of the nanotubes, while F increases towards the bottom of the nanotubes. This concentration gradient is caused by the relative diffusion of elements during EA and in agreement with literature [15,32].

![Element concentration plot](https://doi.org/10.1051/matecconf/202338805006)

Fig. 8. Chemical composition along the length of nanotubes (S1). (a) SEM micrograph of side view of nanotubes with measured locations labelled 1-8, (b) plot of chemical composition for each measurement location.

4.4 X-ray diffraction

XRD results plotted in Fig. 9 compares the lattice structure of the as-synthesised nanotubes sample (S4) to the slow-ramp annealed nanotubes sample (S1). The as-synthesised sample revealed Bragg peaks that correspond to a $\alpha$-titanium (hcp) lattice structure. The annealed sample produced peaks that correspond to both anatase (A) and $\alpha$-titanium peaks. The existence of no crystallised TiO$_2$ phases in the as-synthesised nanotubes confirms that these have an amorphous structure, while the anatase peaks in the annealed nanotubes sample indicated a crystallisation from an amorphous to anatase structure. XRD results agree with that found by other studies [15,20,25,26]. The crystallite size of the anatase phase, was obtained from fitting and measuring the width of the (101) peak, Fig. 9(b). The Scherrer grain size (neglecting strain effects) was calculated as 28 nm. This is in agreement with [26]. The anatase cell parameters were calculated as $a = 3.776$ Å, and $c = 9.436$ Å.

To determine if the $\alpha$-titanium peaks were caused by diffractive reflections of the underlying substrate, the X-ray penetration depth was calculation. X-ray penetration depth was calculated using the Beer-Lambert law, expressed as $I(x) = I(0)e^{-\mu x}$, in which $I(x)$ is the intensity at depth $x$, $I(0)$ denotes the initial intensity of the incident rays, and $\mu$ corresponds to the mass attenuation coefficient. The value of $\mu$ is influenced by the energy of the incoming rays, which, in turn, relies on the wavelength. The energy of K$_{\alpha1}$ rays generated by a Cu tube is 8.047 keV [33]. Additionally, $\mu$ is often given as $\mu/\rho$, and for Ti this ratio equals 202.3 cm$^2$/g for waves with an energy of 8 keV [33]. For Ti-6Al-4V, the
penetration depth or attenuation length to which \( I(x) \) falls to \( 1/e \) of the incoming intensity \( I(0) \) is then around 11 \( \mu \)m. Since \( \text{TiO}_2 \) is less dense than \( \text{Ti-6Al-4V} \ (4.23 \text{ vs } 4.43 \text{ g/cm}^3) \), the oxide layer has a higher penetration depth than \( \text{Ti-6Al-4V} \) and more than \( \sim 11 \mu \)m. Since the measured length of the nanotubes are in the order of 10 \( \mu \)m, Fig. 4(c), and assuming their porous nature makes allows some X-ray diffusions, the \( \alpha \)-titanium Bragg peaks are observed in both samples are likely due to the substrate and not surface effects.

Fig. 9. (a) XRD Bragg peak plots of as-synthesised & annealed samples (A – anatase, T – Titanium) and (b) enlarged image of (101) peak fit.

5 Conclusions

Green hydrogen production through photocatalytic electrolysis offers a promising avenue for a more sustainable method of hydrogen generation. The study described the utilization of titanium dioxide (\( \text{TiO}_2 \)) nanotubes as an efficient photocatalyst to enhance the performance of hydrogen cells. Additive manufacturing (AM) further demonstrates the potential for advanced fabrication methods in optimizing photoelectrochemical electrodes. We demonstrated the relatively undemanding synthesis of TiO\(_2\) nanotubes on AM-produced substrates and investigated the effects of post-synthesis annealing and cleaning. The study aimed to contribute to the limited knowledge on the application of AM to photoelectrodes and advance the understanding of surface modification techniques and nanostructured architectures for efficient hydrogen evolution reaction kinetics.

Results from micrographs revealed well-organized and uniform nanotubes. The morphology of annealed samples varied depending on the ramp rate used, with a slower ramp rate producing highly organized and uniform nanotubes. Hence, precise control over the annealing ramp rate was identified as a crucial factor in obtaining the desired nanotube morphology. XRD analysis revealed that the as-synthesized nanotubes had an amorphous structure. When annealed at 450 °C for 2 hours, a phase transformation to an anatase with an approximate grain size of 28 nm was achieved. EDS measurements along the longitudinal length of nanotubes showed a concentration gradient of oxygen and fluoride, confirming diffusion during the anodization process.

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The control sample showed nanotubes covered with collapsed and fragmented debris, emphasizing the importance of post-synthesis cleaning. Cleaning with acetone (for the period investigated) was effective in removing debris-like nanotube fragments, but ineffective in fully removing the distorted, bundled surface layer. An increase in cleaning time correlated with an improved nanotubes surface and it is therefore predicted that a longer cleaning time would fully remove the distorted surface layer. Cleaning with ethanol followed by 10 vol% HCl produced well-organized nanopores with varying pore sizes.

Valuable insights have been gained regarding the application of AM to hydrogen photoelectrodes. By synthesizing TiO$_2$ nanotubes on AM-produced substrates and investigating post-synthesis annealing and cleaning steps, the study has contributed to the understanding of optimal design and fabrication processes hydrogen photoelectrodes. The findings highlight the importance of surface modification techniques and nanostructured architectures in improving the overall efficiency and kinetics of the hydrogen evolution reaction.

6 Future work & recommendations

To gain a more comprehensive understanding of the process-property relationships of TiO$_2$ nanotubes, future studies are intended to broaden the research scope by incorporating additional process variables. This expansion will enable a more detailed investigation and provide a more comprehensive picture of the subject matter. For example, temperature control during nanotube synthesis has been shown to impact on nanotube quality [13], and would therefore be an important process variable to control in the future. Additional morphology characterisation techniques are also planned. For example, High Resolution Transmission Electron Microscopy imaging would provide additional or more detailed insights into nanotube morphology [25].

Electrochemical characterisation methods to establish the performance of photoelectrodes are planned (well documented by [34]). These include voltammetry and chronocomperometry, as well as more advanced techniques such as (photo-)electrochemical impedance spectroscopy. Furthermore, measuring the absorption and transmission of light in the ultraviolet (UV) and visible (Vis) regions via a UV-Vis Spectrophotometer is envisioned.

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