

Fabrication of Carbon Doped TiO₂ Nanotubes via *In-situ* Anodization of Ti-foil in Acidic Medium

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Abstract—Highly ordered TiO₂ nanotube (TNT) arrays were fabricated onto a pre-treated titanium foil by anodic oxidation with a voltage of 20V in phosphoric acid/sodium fluoride electrolyte. A pre-treatment of titanium foil involved washing with acetone, isopropanol, ethanol and deionized water. Carbon doped TiO₂ nanotubes (C-TNT) was fabricated 'in-situ' with the same method in the presence of polyvinyl alcohol and urea as carbon sources. The affects of polyvinyl alcohol concentration and oxidation time on the composition, morphology and structure of the C-TN were studied by FE-SEM, EDX and XRD techniques. FESEM images of the nanotubes showed uniform arrays of C-TNTs. The density and microstructures of the nanotubes were greatly affected by the content of PVA. The introduction of the polyvinyl alcohol into the electrolyte increases the amount of C content inside TiO₂ nanotube arrays uniformly. The influence of carbon content on the photo-current of C-TNT was investigated and the I-V profiles of the nanotubes were established. The preliminary results indicated that the 'in-situ' doping technique produced a superior quality nanotubes compared to post doping techniques.

Keywords—Anodization, photoelectrochemical cell, 'in-situ', post doping, thin film, and titania nanotube arrays.

I. INTRODUCTION

TITANIUM dioxide is one of the most attractive metal oxide semiconductors due to its ability to withstand photo-corrosion, non-toxicity and a low cost [1], [2], [3], [4], [5]. Unfortunately, it has a wide bandgap (for anatase 3.2 eV and rutile 3.0 eV), which lead to confined utilization to UV light. UV-radiation is only approximately 4% of the total radiation of the solar spectrum. Therefore, doped titania materials which are sensitive to the visible light have received much interest. A number of material has been used to produce doped titania such as nitrogen [6], [7], [8] and [9], fluorine [10] and [11], sulphur [12] and [13] or carbon [14], [15], [16], [17] and [18] using various methods. These materials showed a good

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response to visible light and exhibited higher photocatalytic activity under solar light irradiation. It has been shown that carbon-doped titania has a surprisingly high activity in the degradation of 4-chlorophenol by visible light [16]. On the other hand, the geometry of titanium oxide (TiO₂) affects the photoactivity and its stability for photoelectrochemical water splitting process [19]. Recently, Ghicov et al., synthesized several kinds of titania nanotubular layers with showed good photoresponse in the visible region by using non-metal dopants [20]. The self-organized titania nanotubular array doped with carbon by thermal acetylene treatment was also explored and noticeably this kind of titania material displayed a significant photoresponse over the whole range of visible light up to the near-IR region [21]. The thickness and morphology of TiO₂ nanotube were controlled by regulating the electrolyzing conditions such as anodization time and electrolyte composition.

This present work investigates the possibility to dope TiO₂ nanotube arrays with carbon via 'In-situ' anodization of Ti foil in acidic electrolyte with variable amounts of carbon dopant sourced from polyvinyl alcohol (PVA) at various duration of anodization and studies their influence to pore morphology, thickness and the elemental compositions of nanotubes films grown on titanium. As far as we know that no one has done the carbon dope by in-situ anodization technique. We also investigate the affects of carbon dopant on the phototcurrent of carbon doped TiO₂ nanotube (C-TNT). The carbon doped and non-doped TiO₂ nanotube (TNT) arrays were characterized with FE-SEM, EDX, and XRD techniques. In addition, the preliminary results of their photoactivity were also reported.

II. EXPERIMENTAL WORK

A. Preparation of C doped TiO₂ Nanotubular Arrays

Titanium (99.99% purity, Aldrich) foils (1.0 × 1.0 cm) of 0.1 mm thickness were cleaned by sonicating them in acetone, *iso*-propanol and ethanol successively, followed by rinsing with deionized water and finally dried with nitrogen gas prior to the electrochemical treatments. The preparation of titania nanotube was similar to previously reported method with a little modification [22]. The TiO₂ and C-TiO₂ NT arrays were grown by anodization of cleaned Ti foils in acidic electrolyte containing 0.5M *ortho*-phosphoric acid (H₃PO₄, 85% in water, A & R marketing, UK), 0.14M sodium fluoride (NaF, 99.5%,

Merck) and different amounts (1.5, 1.0 and 0.5 wt%) of polyvinyl alcohol ($[-CH_2CHOH-]_n$, 99+%, hydrolyzed, Aldrich) at pH 2. All aqueous solutions were prepared with high purity deionized water. The anodization experiments were carried out in a two electrodes home-made cell namely the sample electrodes with an exposed of 0.64 cm^2 (working electrode) and a platinum plate (counter electrode). A high potential ramped from the Open Circuit Potential (OCP) to 20 V in 1 V s^{-1} was applied using DC power supply (Agilent, E3631A) with stirring for 45 minute. The anodized samples were rinsed with deionized water and dried in a N_2 stream at $100 \text{ }^\circ\text{C}$ for 12 hr. The anodized C-TNT arrays were annealed to form an anatase crystal structure using a muffle furnace (PyroTherm Furnace, EUROTHERM 91e) at $500 \text{ }^\circ\text{C}$ for 3 hours in purified air with $5 \text{ }^\circ\text{C}/\text{min}$ of heating rate.

B. Characterizations of C doped TiO_2 Nanotubular Arrays

The morphology of the C-TNT arrays were characterized by field emission scanning electron microscope FESEM (ZEISS, SUPRA 55VD) and the elemental contents was determined by energy-dispersive X-ray analyses (OXFORD Instruments, INCA) at 40V using Cu $K\alpha$ radiation ($\lambda=1.5418 \text{ \AA}$). The crystallinity of the treated samples was established from the XRD spectra collected using Cu $K\alpha$ radiation on a Bruker D8 Advance spectrometer.

C. Photoelectrochemical Measurement

The photoelectrochemical measurement (PEC) was conducted in a standard three-electrode configuration with a Pt plate (counter electrode) and a saturated calomel electrode (reference electrode). The working electrodes TiO_2 and C- TiO_2 NTs have an active area of 0.6 cm^2 . The electrochemical cell was equipped with a quartz glass window. A 450W Xenon lamp was used as the light source. The preparation of TiO_2 and C- TiO_2 NTs samples for PEC analysis has been described in earlier publication [23]. The electrolyte (1M KOH) was purged with a nitrogen gas for 30 minutes before the tests and the scan rate was set at 50 mVs^{-1} . The potential and photocurrent produced by the TiO_2 and C- TiO_2 NTs were recorded using an Ametek Versastat4 potentiostat to establish the I-V profiles.

III. RESULTS AND DISCUSSION

The current density transient was recorded during the anodic oxidation process (see fig 1). All anodization potentials were ramped from OCP to anodization voltage (20V) with a sweep rate of 1 V/s in *ortho*-phosphoric acid/NaF electrolyte with different percentage of polyvinyl alcohol (PVA) for 45 min. The initial exponential current decays refer to high-field TiO_2 formation, which is about 50 nm thick [24]. The mechanism of the C- TiO_2 NT formation are expected to be similar to previous reports [25]. From Fig 1, the current transients' exhibits in all electrolytes, different behaviours with current densities vary with different electrolytes. In the case of increasing PVA percentage, the current density decays were decreasing slowly and smoothly. The highest current density during the anodization was exhibited by 0 and 0.5 wt % PVA in *ortho*-phosphoric acid/NaF electrolyte. This suggested that the PVA content in the electrolyte was affected

reversibly by the flow of anodized current density. It was found that the samples, which were anodized with different amount of PVA in the electrolytes, needed a certain period of time until their nanotube structures become self-organized, in other words until the anodization attained a steady state situation.

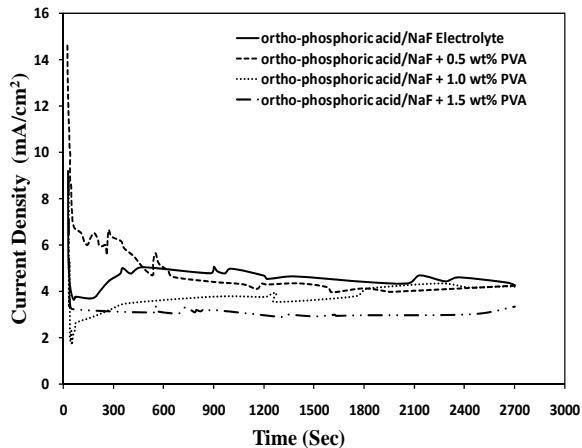


Fig. 1 Current density vs. time plots for anodization of Ti foil with different percentage of polyvinyl alcohol in *ortho*-phosphoric acid/NaF electrolyte during the 45 min anodization process.

A. FESEM Characterizations of C doped TiO_2 NTs

A field emission scanning electron microscope was used to characterize the morphologies and micro-structure of the samples. Fig. 2 showed a cross-sectional and bottom view, Fig. 3 showed the surface and EDX results of the samples anodized at 20 V with different percentages of PVA in *ortho*-phosphoric acid/NaF medium for 30, 45 and 60 minutes.

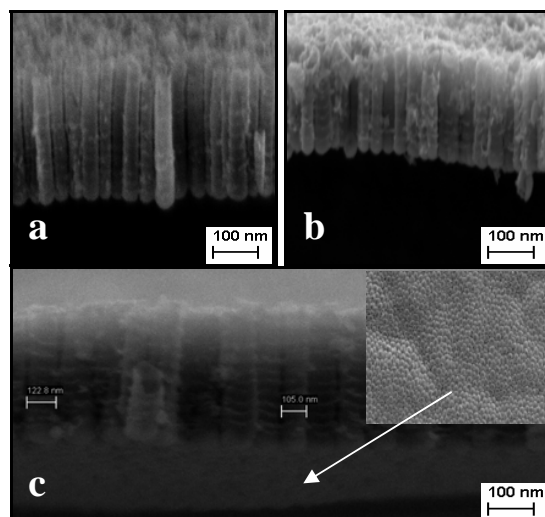


Fig. 2 Cross-sectional view of C- TiO_2 (C-TNT) prepared by anodization in the *ortho*-phosphoric acid/NaF electrolyte with different percentage of polyvinyl alcohol (a) 0.5 wt% (b) 1.0 wt% (c) 1.5 wt% of PVA (inset: the bottom surface of C-TNT arrays).

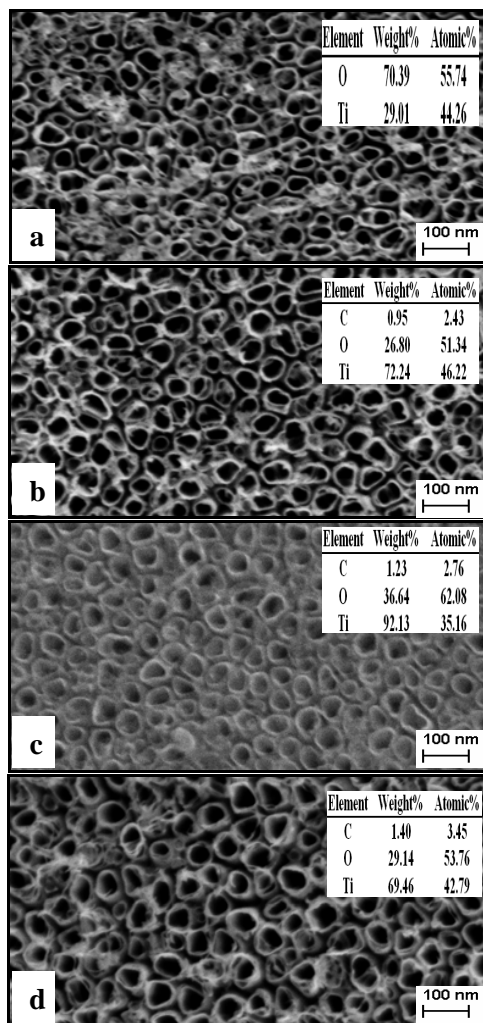


Fig. 3 Surface view and elemental compositions of C-TiO₂ nanotube array prepared by anodization in phosphoric acid/NaF electrolyte at 20V with different amounts of PVA content (a) 0 wt (b) 0.5 wt% (c) 1.0 wt% and (d) 1.5 wt% of PVA.

From these figures, we can conclude that the 'in-situ' anodization technique was able to produce a self-ordered nanotubular structure in the presence of PVA. The C-TNT arrays appeared clean compared to specimen without PVA. The lengths of C-TNT were approximately 0.320 to 0.471 μm . The diameter ranges from 96 to 165 nm for samples which were anodized in *ortho*-phosphoric acid/NaF electrolyte with different amounts of PVA. The EDX results showed all C-TNTs contains Ti, O and C elements (fig. 4 (a), (b) and (c)). The C content increases upon introduction of PVA. It was observed that a longer anodization time increases the C content much further.

Fig. 5 and 6 showed the affects of PVA content and anodization time on diameter and length of C-TNT arrays. The diameter of C-TNTs and the length decreases with increase in anodization time. On other hand, the affects of PVA content on the morphology and microstructure was not straight forward and difficult to understand.

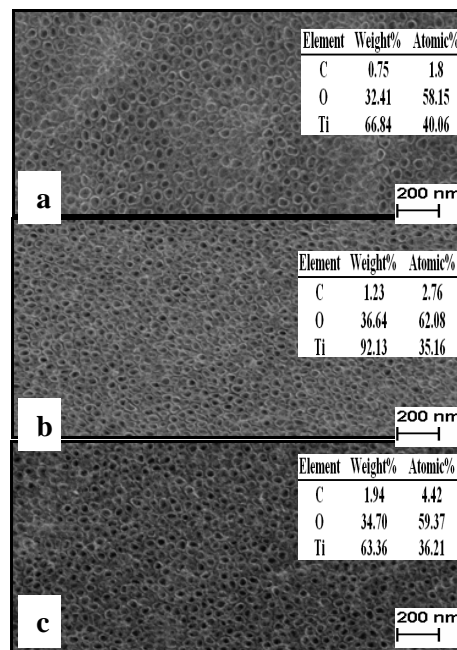


Fig. 4 FESEM micrographs showing the surface morphology and elemental compositions of C-TiO₂ nanotube array prepared by anodization in the phosphoric acid/NaF electrolyte containing 1.0 wt% PVA at different time; (a) 30 min, (b) 45 min and (c) 60 min.

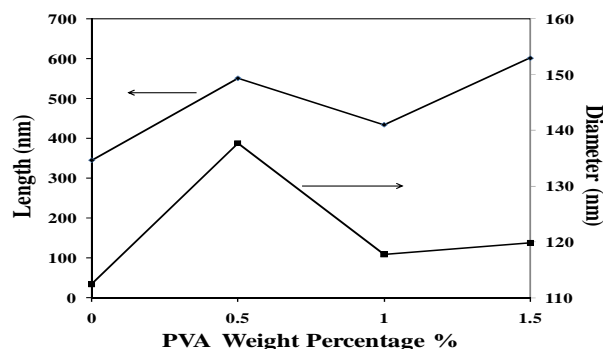


Fig. 5 The effects of PVA content on C-TNT arrays diameter and length for samples anodized in *ortho*-phosphoric acid/NaF electrolyte at 20V.

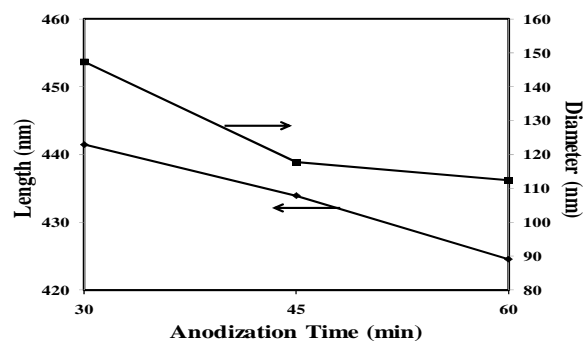


Fig. 6 The effects of anodization time on C-TNT arrays diameter and Length for samples anodized in *ortho*-phosphoric acid/NaF electrolyte with 1 wt% of PVA at 20V.

B. X-Ray Diffraction Analysis

The degree of crystallinity and crystal phases of the C-doped TiO₂ nanotube were determined by examining the X-ray diffraction (XRD) diffractograms at a scanning rate of 0.025°/min from 20° to 80°. The samples were annealed at temperature 500 °C. A closer examination of the XRD diffractogram revealed that all three phases namely anatase, rutile and titanium were observed at various angles with Ti peaks were due to the substrate. All samples were exhibited high degree of crystallinity with preference for a Rutile phase at low PVA content. However, at higher PVA content the anatase phase became more prevailed due to its stability. It is worth to note that the crystalline phase was affected by the PVA content during the anodization process as shown in Fig. 7.

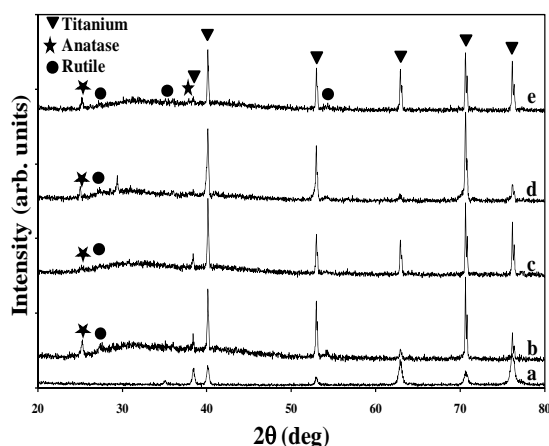


Fig. 7 XRD diffractograms C-TNTs arrays anodized with different wt% of PVA in Phosphoric acid/NaF electrolyte (a) Ti foil, (b) 0 wt%, (c) 0.5 wt%, (d) 1.0 wt% and (e) 1.5 wt% PVA.

C. Photoelectrochemical Analysis

The comparisons of the photocurrent density vs. applied potential curves of the TiO₂ and C-TiO₂ photoanode in the dark and under Xenon illumination showed in Fig. 8. The observed dark current densities were found to be negligible (approach to zero). The photocurrent densities of C-TiO₂ photoanode are varied by PVA content in the electrolyte. This indicates that the C-doped TiO₂ photoanodes produced have the potential to increase the visible light photoresponse (fig. 8 f). However, the current density of all sample with PVA increase rapidly, except for sample with 1.0 wt % PVA. (Fig. 8f) the photocurrent increases slowly with bias potential zero until the voltage reached 0.1V vs. SCE, then the current decreases rapidly. The best photocurrent response was recorded by photoanode with 1.0wt % PVA and 30 min anodization period.

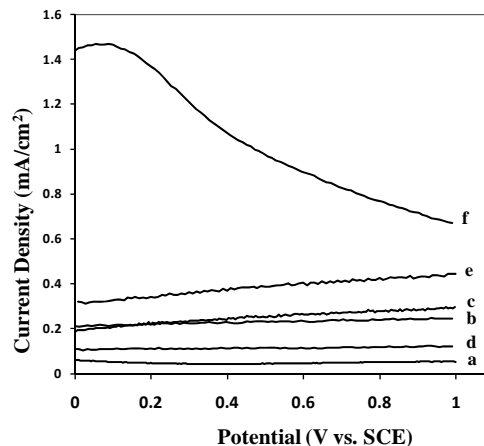


Fig. 8 Current density of C-doped TiO₂ nanotube arrays (a) dark current, (b) 0.5 wt% PVA, (c) 1.0 wt% PVA, (d) 1.5 wt% PVA for 45 min anodization time, in 1M KOH electrolyte, (e) 60 min (1.0 wt% PVA) and (f) 30 min (1.0 wt% PVA).

IV. CONCLUSION

A highly ordered carbon-doped titania nanotube arrays was successfully fabricated from Ti foil by adding different amounts of polyvinyl alcohol (PVA) as carbon source to the anodization electrolyte (0.5M *ortho*-phosphoric acid and 0.14 M sodium fluoride, NaF) at 20 V. The anodized samples were annealed at 500 °C in purified air for 3 hours. A C dopant sourced from different amounts of PVA was incorporated into the titania nanotube during the anodization process. The diameter (96 to 165 nm) and length (0.320 to 0.471 μm) of the C-TNTs were influenced by PVA content and anodization time. The best photocurrent density was recorded for C-TNTs with 1.0 wt% PVA with anodization period of 30 min in phosphoric acid/NaF electrolyte with Xenon light illumination.

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REFERENCES

- [1] J. R. Bolton, "Solar photoproduction of hydrogen: a review," *Solar Energy*, vol. 57, pp. 37-50, 1996
- [2] V. M. Aroutiounian, V. M. Arakelyan, and G. E. Shahnazaryan, "Metal oxide photoelectrodes for hydrogen generation using solar radiation-driven water splitting," *Solar Energy*, vol. 78, pp. 581-592, 2005
- [3] M. Gratzel, "Dye-sensitized solar cells," *J. Photochem. Photobiol. C: Photochemical Review*, vol. 4, pp. 145-153, 2003
- [4] M. Ashokkumar, "An overview on semiconductor particulate systems for photoproduction of hydrogen," *International Journal Hydrogen Energy*, vol. 23, pp. 427-438, 1998
- [5] M. Gratzel, "Photoelectrochemical cells," *Nature*, vol. 414, pp. 338-344, 2001
- [6] R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, and Y. Taga, "Visible-light photocatalysis in nitrogen-doped titanium oxides," *Science*, vol. 293, pp. 269-271, 2001
- [7] H. Irie, Y. Watanabe, and K. Hashimoto, "Nitrogen-concentration dependence on photocatalytic activity of TiO_{2-x}N_x powders," *J. Phys. Chem. B*, vol. 107, pp. 5483-5486, 2003

- [8] O. Diwald, T. L. Thompson, E. G. Goralski, S. D. Walck, and J. T. Yates, "The effect of nitrogen ion implantation on the photoactivity of TiO₂ rutile single crystals," *J. Phys. Chem. B*, vol. 108, pp. 52-57, 2004
- [9] J. L. Gole, J. D. Stout, C. Burda, Y. B. Lou, and X. B. Chen, "Highly efficient formation of visible light tunable TiO_{2-x}N_x photocatalysts and their transformation at the nanoscale," *J. Phys. Chem. B*, vol. 108, pp. 1230-1240, 2004
- [10] C. Yu J., J. G. Yu, W. K. HO, Z. T. JIANG, and L. Z. ZHANG, "Effects of F-doping on the photocatalytic activity and microstructures of nanocrystalline TiO₂ powders," *Chem. Mater.*, vol. 14, pp. 3808-3816, 2002
- [11] A. Hattori, M. Yamamoto, H. Tada, and I. Seishiro, "A promoting effect of NH₄F addition on the photocatalytic activity of sol-gel TiO₂ films," *Chem. Letter*, vol. 27, pp. 707-708, 1998
- [12] T. Umabayashi, T. Yamaki, H. Itoh, and K. Asai, "Band gap narrowing of titanium dioxide by sulfur doping," *Appl. Phys. Lett.*, vol. 81, pp. 454-456, 2002
- [13] T. Umabayashi, T. Yamaki, S. Yamamoto, and A. Et, "Sulfur-doping of rutile-titanium dioxide by ion implantation: photocurrent spectroscopy and first-principles band calculation studies," *J. Appl. Phys.*, vol. 93, pp. 5156-5160, 2003
- [14] H. Irie, Y. Watanabe, and K. Hashimoto, "Carbon-doped anatase TiO₂ powders as a visible-light sensitive photocatalyst," *Chem. Lett.*, vol. 32, pp. 772-773, 2003
- [15] S. U. M. Khan, M. Al-shahry, and W. B. Ingler, "Efficient photochemical water splitting by a chemically modified n-TiO₂," *Science*, vol. 297, pp. 2243-2245, 2002
- [16] S. Sakthivel and H. Kisch, "Daylight photocatalysis by carbon modified titanium dioxide," *Angew. Chem. Int. Ed.*, vol. 42, pp. 4908-4911, 2003
- [17] Y. Choi, T. Umabayashi, and M. Yoshikawa, "Fabrication and characterization of C-doped anatase TiO₂ photocatalysts," *J. Mater. Sci.*, vol. 39, pp. 1837-1839, 2004
- [18] C. Xu, R. Killmeyer, M. L. Gray, and S. U. M. Khan, "Photocatalytic effect of carbon-modified n-TiO₂ nanoparticles under visible light illumination," *Applied Catalyst B: Environ.*, vol. 64, pp. 312-317, 2006
- [19] I.-D. Kim, A. Rothschild, B.-H. Lee, D.-Y. Kim, S.-M. Jo, and H. L. Tuller, "Ultrasensitive chemiresistors based on electrospun TiO₂ nanofibers," *Nano Letter.*, vol. 6, pp. 2009-2013, 2006
- [20] A. Ghicov, J. M. Macak, H. Tsuchiya, and A. Et, "Ion implantation and annealing for an efficient N-doping of TiO₂ nanotubes," *Nano Letter.*, vol. 6, pp. 1080-1082, 2006
- [21] R. Hahn, A. Ghicov, J. Salonen, V. P. Lehto, and P. Schmuki, "Carbon doping of self-organized TiO₂ nanotube layers by thermal acetylene treatment," *Nanotechnology*, vol. 18, p. 1, 2007
- [22] V. K. Mahajan, S. K. Mohapatra, and M. Misra, "Stability of TiO₂ nanotube arrays in photoelectrochemical studies," *International Journal of Hydrogen Energy*, vol. 33, pp. 5369-5374, 2008
- [23] N. A. Kelly and T. L. Gibson, *International Journal of Hydrogen Energy*, vol. 31, pp. 1658 - 1673, 2006
- [24] L. Taveira, J. M. Macak, H. Tsuchiya, L. F. P. Dick, and P. Schmuki, "Initiation and Growth of Self-Organized TiO₂ Nanotubes Anodically Formed in NH₄F(NH₄)₂SO₄ electrolyte," *J. Electrochem. Soc.*, vol. 152, pp. B405-B410, 2005
- [25] J. W. Schultze, M. M. Lohrengel, and D. Ross, *Electrochim. Acta*, vol. 28, p. 973, 1983