A Microfluidic Device Based on Plasma Nitrided Self-Organized TiO₂ Nanotubes for Photocatalytic Reduction Study

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Abstract — Nitrided TiO₂ nanotubes and PDMS microchannel were assembled in a photocatalytic device for organic dyes photo-degradation studies. By integrating a PDMS microchannel with the nitrided TiO₂ nanotubes array, a microfluidic photocatalytic device was obtained and characterized by morphological, chemical, and physical points of view. The fabrication process allows an easy integration of the obtained nitrided TiO₂ nanotubes with a microchannel into a microfluidic device for pollutant photo-degradation. The high surface-to-volume ratio intrinsic of nanotubes structures has functional properties for harvesting light and is responsible for part of the interesting photocatalytic device performance. Another great advantage of nitrided TiO₂ nanotubes compared to just TiO₂ nanotubes, is the lower gap of 2.80 eV achieved by plasma nitriding processes in PECVD reactor, which leads to a 14% increase in the photocatalytic response to sun light. Therefore, the methylene blue reduction efficiency of the microfluidic device fabricated with nitrided TiO₂ nanotubes increased 13% compared to that with just anodized TiO₂ nanotubes.

Index Terms — TiO₂; nanotube; nitriding; photocatalytic; photodegradation.

I. INTRODUCTION

A quest for a better life quality unfortunately brought together an enhanced waste production, which resulted in an increased need for new technologies and devices for pollutant degradation. In this context, utilization of titanium dioxide (TiO₂) as active electrode for water photolysis was discovered by Fujishima and Honda in 1972 [1]. Since then, TiO₂ has attracted interest for wide range applications in technology and general industry such as photocatalytic pollutant degradation, of CO₂ conversion, gas sensors, dye sensitized solar cells (DSSCs), biomedical, paints and sunscreen protection for cosmetics [2–6]. TiO₂ presents three crystalline phases: anatase, rutile and brookite. Each crystalline phase exhibits photocatalytic, optical and electrical properties that best fit certain given applications. For treatment of effluents, photovoltaic and biochemical applications anatase phase presents better results given its greater photocatalytic activity [7–9]. Although anatase has the highest conductivity between the crystalline phases [10], it cannot efficiently use the visible part of the solar spectrum, due to its large band gap 3.2 eV [11], absorbing only 4-5% of the solar light, corresponding to the UV portion of the solar spectrum [12]. Over the last few years, extensive research has been conducted aiming the increase in sunlight absorption by TiO₂. Morphological modification using nanotubes, leads to a larger surface area and so to a higher adsorption, reaction, intercalation processes and light harvesting. TiO₂ nanotubes can be produced by the anodization of Ti foil or thin films, creating a high-organized lattice [13]. Nanotubes also provide a direct path for electronic conduction along them, which does not occur with other one-dimensional materials (i.e. nanowires and nanofibers) [14].

Intending to reduce TiO₂ band gap and charge recombination, doping studies with non-metals such as N, F, C and noble metals and transition metals such as Cr, Co, V, Fe, Z, W have been performed [15–17]. However, till now, the most successful approach for varying its optical and electrical properties remains nitrogen doping (nitriding), which can be conducted using various techniques [18]. Nitriding of TiO₂ can be done in many ways, during the synthesis route or after during some heat treatments, some examples are sputtering, ion implantation, chemical vapor deposition, sol–gel, oxidation of TiN, mechan chemical synthesis, decomposition of N-containing metal organic precursors, CVD nitriding of TiO₂ and other surface treatments [19–21]. At the moment, the most promising form of nitrided TiO₂ nanotubes is heat treatment in the presence of a nitriding gas. However as nitrogen incorporation in TiO₂ is proportional to the increase in treatment temperature [22,23]. Temperatures over 600 °C are required usually leading to phase change, to the undesirable rutile phase, and promoting the collapse of the nanotubes into nanoparticles (NP), that have higher pair electron-hole recombination [24–26]. In this way, lower temperature processes are highly desirable.

Recently, a polymer called polydimethylsiloxane (PDMS) has been implemented in many microfluidic devices for a wide range of applications, due to its interesting physical and chemical properties, such as elasticity, optical transparency, flexible surface, high dielectric properties and low cost [27–29]. Moreover, the integration of TiO₂ nanostructures with PDMS for photocatalytic devices has increased in the last few years, attempting to reduce these nanostructures disposal on the environmental [30,31]. These attempts to reduce nanostructure disposal are important, mainly for TiO₂ NP and SiO₂ NP, since they are certainly the most relevant materials in terms of worldwide production volume. Being wastewater the dominating emission pathway to the environment, and TiO₂ NP correspond to 85% of the total emission [32].

In this work, the integration of nitrided TiO₂ nanotubes arrays, produced by Ti thin films on microscope slides anodization followed by Nitrogen plasma treatment, with reduced gap of 2.80 eV, [33] and PDMS microchannels into a microfluidic photocatalytic device is proposed. The performance of the fabricated microfluidic system and the
photocatalytic efficiency of the proposed devices were evaluated by UV-Vis measurements of methylene blue (MB) reduction. This study provides a new approach on the use of TiO$_2$ nanotubes in microfluidics offering a practical solution to photocatalytic reactions.

II. MATERIALS AND METHODS

A. Formation of TiO$_2$ nanotubes by Ti anodization

The self-organized TiO$_2$ nanotubes were prepared by anodizing thin titanium films deposited on glass microscope slides and titanium foils, both in slices 1x0.5-inch. Titanium thin films 0.5-µm thick were deposited by RF magnetron sputtering from a 99.995% purity Ti target onto glass microscope slides. Titanium foils were cut from a brushed plate 0.5-mm thick and 99% purity, in sequence were chemically polished in an HNO$_3$ + HF + CH$_3$COOH solution on 3:1:1 vol. rate. The anodization process was carried in a two-electrode electrochemical system using platinum helical wire as cathode and the samples with Ti as anode maintained at a distance of 8 cm. The electrolyte was an ethylene glycol solution containing 0.25 wt.% of NH$_4$F and 2 vol.% of water, kept constantly at 25 °C using a water cooled system. Samples were anodized with 80 V. The Ti foils for 10 min and Ti thin films anodized until the current came to zero (around 55 s) for the total conversion of Ti into TiO$_2$ and 2 vol.% of water, kept constantly at 25 °C using a water anode maintained at a distance of 8 cm. The electrolyte was an ethylene glycol solution containing 0.25 wt.% of NH$_4$F and 2 vol.% of water, kept constantly at 25 °C using a water cooled system. Samples were anodized with 80 V. The Ti foils for 10 min and Ti thin films anodized until the current came to zero (around 55 s) for the total conversion of Ti into TiO$_2$ nanotubes. Samples in microscope slides with sputtered Ti as anodized and after nitrided can be seen in Fig. 1 (a).

B. Nitriding TiO$_2$ nanotubes

The nitriding processes were carried out in a PECVD (Plasma Enhanced Chemical Vapor Deposition) reactor used in the usual diode configuration. A RF (Radio Frequency) plasma source of 13.56 MHz with variable power was used. The reactor was operated at a pressure of 2 Torr in N$_2$ atmosphere during the heating ramp from room temperature to 320 °C in 1 h. Then the N$_2$ flow was released and the desired pressure adjusted with the valves. After the pressure stabilized (around 3 min), the plasma was turned on for the 2 h nitriding processes. A pressure of 1.0 Torr and 80 W of RF power were used.

The choose of these nitriding parameters were due to previously work of the group, which determined the nitriding processes parameters to nitriding TiO$_2$ nanotubes efficiently reducing the bandgap without surface corrosion by plasma nor generating morphology changes [33].

C. PDMS microchannel

The PDMS microchannels were made by 90-µm thick film of SU-8 photosist in lithography process over a Si wafer, conducting to a circle with 8.4 mm diameter. After that, liquid PDMS was spilled over the microchannel and then heated at 80 °C for 30 min for curing. In sequence, the PDMS was cut and removed from the template being ready to be attached onto the samples surface creating a reservoir with approximately 5 µL of volume. A real image of the device is shown in Fig. 1 (b) and a schematic of PDMS microchannel production and integration with the nitrided TiO$_2$ nanotubes can be seen in Fig. 2.

D. Characterization

The nitrided TiO$_2$ nanotubes were characterized by a FEI Inspect F50 – High Resolution SEM (Scanning Electronic Microscope) to visualize any changes in the morphology of the TiO$_2$ nanotubes caused by the nitriding processes. The nitrided TiO$_2$ nanotubes crystalline structure was determined by microRaman spectroscopy and XRD (X Ray Diffraction). A microRaman spectroscopy (WITEC, Confocal Raman Microscope Alpha300 R) by a Nd:YAG laser (λ = 532 nm) with a maximum power of 25 mW and x50 lens to focus the laser beam was used to obtain the crystalline phase after the nitriding processes, since we already know that the as-formed TiO$_2$ nanotubes are amorphous as mentioned before. A XDR (Shimadzu ERX- 6000 teta-2theta) with Cu target 40 KV and 30 mA, a scan ranges 20-80 and scan speed 1.0000 (deg/min) was also utilized to verify changes in the crystalline structure. The absorbance spectra from 300 nm to 700 nm for the UV-Vis measurements of methylene blue (MB) reduction after the anodization processes were evaluated.

![Fig. 1](image1.png)

**Fig. 1**(a) Samples in microscope slides with: sputtered Ti (with apiezon edge to guarantee the conductivity in the anodization processes), as anodized (the transparent area) and after nitrided respectively. (b) PDMS microchannel coupled into nitrided TiO$_2$ nanotubes forming a photocatalytic device.

![Fig. 2](image2.png)

**Fig. 2** PDMS microchannels production and the assembling with nitrided TiO$_2$ nanotubes into the device: (a) A slide of Si wafer. (b) SU-8 photosist deposited over Si. (c) and (d) Lithography processes to expose the desired microchannel form. (e) Liquid PDMS spilled over the microchannel mold and cured. (f) After the cure, the PDMS is ready to be detached from Si. (g) and (h) Device production by integration of the PDMS microchannel with the nitrided TiO$_2$ nanotube on microscope slide.
1100 nm for all TiO$_2$ nanotubes films of on glass slides produced in this work were obtained by UV-Vis (Ultraviolet to Visible) spectroscopy. From these data, Tauc extrapolation technique was utilized to extract the band gap value enabling sample comparison before and after nitriding and thus process effectiveness. A 26 µM MB solution was used to fill the microchannel device, then the reduction was conducted under equivalent AM 1.5 illumination and the solution absorbance spectra was taken at different times in order to quantify the increase in photocatalysis, comparing the as anodized with the nitrided TiO$_2$ nanotubes. An EDS (energy dispersive X-ray spectroscopy) coupled to the SEM was utilized to determine qualitatively the elements concentration in the samples.

**III. RESULTS AND DISCUSSION**

Fig. 1 (a) shows the slides with Ti deposited, as anodized nanotubes (the TiO$_2$ nanotubes are in the translucent region of sample) and after nitriding. The anodization processes of Ti in microscope glass slides leads to formation of nanotubes with diameter and length around 130 nm and 500 nm respectively, as it can be appreciated in Fig. 3. The diameter is as expected, from previous works, according to the used voltage, while the length is limited by the deposited Ti film thickness. Fig. 3 presents SEM images for nanotubes arrays before and after the nitriding process. As can be observed, the nanotubes morphology remains the same, without plasma corrosion processes or cracks due to thermal expansion. The detached nanotubes that can be seen in the images were purposely made to reveal the length and the base of nanotubes. Raman spectroscopy was conducted to analyze the crystalline phase change in the samples. As Fig. 4 shows, they crystallized in anatase form, keeping the desired electrical properties for photocatalytic and photovoltaic devices. The spectrum also shows the contamination with amorphous carbon that is originated from the thermal decomposition of the organic residues from the anodization solution. There is no sign of any other TiO$_2$ phase.

The XRD spectrum in Fig. 5 shows that nitriding processes does not change the crystalline structure of the TiO$_2$ nanotubes. As can be seen it only exhibits the TiO$_2$ anatase crystalline planes and Ti from the substrate. No peaks of TiN are found in the XRD spectra nor in Raman spectroscopy analyses, revealing that nitriding processes lead to substitutional nitrogen in the TiO$_2$ crystal lattice, been incorporated in material oxygen vacancies.

EDS spectrum in Fig. 6 was acquired from samples after the nitriding process and a quantitative evaluation was performed giving the following percentage of the constituent atoms: nitrogen 11.4% titanium 25.85%, oxygen 51.71%, carbon 8.32% and fluorine 2.72%. This proves that nitriding processes were successful in nitrogen incorporation.

The optical gap obtained from the UV-Vis absorbance spectra data by the Tauc extrapolation technique, Fig. 7, gave a gap value of 2.80 eV for nitrided samples, indicating a 14% reduction in comparison to the standard TiO$_2$ band gap value around 3.24 eV. It is important to remember that TiO$_2$ nanotubes as prepared absorb only 5% of the AM 1.5 solar spectrum, while with the obtained band gap for nitrided TiO$_2$ nanotubes, a double energy range can be absorbed.

The absorbance spectra for the MB solution, Fig. 8, was taken at different times in order to accompany the reduction of the solution. The photocatalytic device completely reduced the 5 µL of MB solution in about 12 min. The reduction rate is approximately linear, giving a value about 130 µM/h for the nitrided devices, instead of the 115 µM/h rate obtained for the device with as prepared TiO$_2$ nanotubes. Therefore, the nitriding treatment lead to a 13% increase in MB reduction efficiency. A good result, since recent works...
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[15] M. Pelaez, N.T. Nolan, S.C. Pillai, M.K. Seery, P. Falaras, A.G. Kontos, P.S.M.M. Dunlop, J.W.J.J. Hamilton, J.A.A. Byrne, K. O’Shea, M.H. Entezari, D.D. Dionysiou, A review on the visible nanotubes morphology has advantages over other forms such as higher electron conductivity, less charge recombination and higher surface area. The integration of PDMS microchannel to glass slides with the nitrided TiO2 nanotubes to form a photocatalytic device was performed in an easy way, since the PDMS has a great adhesion on the nanotubes surface. This mechanism allowed limiting a specific volume of solution for the study of the photodegradation efficiency of the methylene blue dye over the nitrided TiO2 nanotubes resulting in an increase of 13% than as prepared TiO2 nanotubes.

IV. CONCLUSION

The nitriding process of TiO2 nanotubes in a PECVD reactor allowed the production of nitrogen doped TiO2 nanotubes presenting a lower gap 2.80 eV than the 3.24 eV for non-treated NT. This gap reduction doubles the ability of absorbing solar photons from 5% of the solar spectrum to 10%. It is important to note that this reduction was achieved with a low temperature process compared to the current CVD processes. The plasma assisted nitriding processes in PECVD reactor allowed a higher nitrogen incorporation in the nanotubes keeping the desirable anatase crystalline phase. The nitriding processes also did not generate changes in morphology of the nanotubes, what is great, since the demonstrated that TiO2 still is one of the best compounds for solar photocatalytic degradation of effluents, in spite of the difficulty in separation and reuse when nanostructures dispersed in solution are utilized [34,35]. Considering this, nitried TiO2 nanotubes, used in this work, present another advantage over other TiO2 nanostructures since they exhibit higher surface adhesion to substrates, which greatly reduces its disposal together with the photodegraded material.

It is also important to take into account, the wide conditions in geometries, dimensions, and working conditions when comparing results of similar device systems [30,36,37], since there is no standard method to develop these measurements.


