

Photocatalytic behaviour of anodised titanium using different cathodes

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In the last decades, titanium dioxide (TiO_2) has been widely researched, because of its applications in photocatalytic environmental pollution removal and in hydrogen generation. Hence, this work deals with the synthesis of titanium dioxide by anodising titanium sheets, however using different cathodes, which may induce differences in the composition and structure of the obtained oxide layers so that these suspected differences can be observed. All specimens were equally thermally treated after anodising to enhance their photocatalytic activity since this step allows the titanium dioxide to crystallise. Their morphology and crystal structure were characterised by X-ray diffraction and FTIR, and optical properties were characterised by ultraviolet-visible absorption spectroscopy. Furthermore, tests of their photocatalytic properties in the degradation of organic dyes were performed in order to have a first evaluation. Indeed, differences in the photocatalytic behaviour of the anodised specimens using different cathodes were found and evaluated.

Keywords: cathode, building, anodising, titanium, photocatalysis, semiconductor

1. Introduction

The Air quality in Europe report of 2014 [1] about pollution regulations and impact concerns us about how essential to both environmental and human health clean air is. For instance, air pollution is the main cause of health issues such as asthma, and new policies should be applied in order to avoid the high number of environmentally related deaths around the world [2]. The limiting values of nitrogen dioxide and monoxide, sulphur dioxide, particulate matter and others given by the European Council Directive 2008/50/EC on ambient air quality and cleaner air for Europe [3] are very low with the aim of improving air quality since traffic rates and industrial activities are increasing the pollution worldwide. A promising approach for fighting the problem of nitrogen oxides (NO_x) is the photochemical conversion of these oxides to low concentrated nitrates thanks to heterogeneous photocatalytic oxidation using a photocatalyst [4-6].

Photocatalysis happens to be a potential answer to air purification, showing the ability of decomposition of organic compounds, sterilisation, self-cleaning among others [7]. Semiconductors such as TiO₂ [8] or others like ZnO, ZnO-TiO₂ [9], ZrO₂, SnO₂, WO₃, CeO₂, Fe₂O₃, Al₂O₃, ZnS and CdS [10] are used as photocatalysts. During this process, an electron (e⁻) is excited and jumps from the valence band to the conduction band, creating a positive hole (h⁺) in the valence band, as long as the semiconductor absorbs a photon with energy $h\nu$ larger or equal to its band gap. Moreover, in the presence of water, •OH radicals are created that together with the positive holes tend to degrade organic compounds such as those found in pollutants and dirt [11]. Besides, the first idea and time of using titanium for the building envelope goes back to 1973 [12], since then its use has increased notably and became especially well-known with the Guggenheim Museum in Bilbao, Spain, probably the most spectacular building clad with titanium so far [12]. Titanium has, moreover, a great corrosion resistance due to the thin natural film of titanium dioxide that appears on its surface [13]. However, the photocatalytic efficiency of this layer is generally negligible if not absent [14]. Yet, the oxide of this metal may show specific functions that find applications in fields such as biomedicine [6, 15], photovoltaics [16], self-cleaning [17] and environmental purification [5-8]. Interestingly, titanium can be anodised in order to get a thicker and more performing TiO₂ layer, whose properties, including photocatalytic activity, depend on its structure, being more efficient if it is in crystalline form like anatase or rutile rather than in the amorphous one [18]. In particular, photocatalytic activity depends on factors such as surface area, crystallinity, phase composition or crystal orientation [19]. Furthermore, anodised titanium presenting a thin oxide layer of more than 300 nanometres presents interference colours that are of particular interest for architectural applications [20,21].

This idea of first anodising titanium, so that we can take advantage of the potential photocatalytic properties of its oxide layer, titanium dioxide, is quite recent and the simple fact of anodising titanium does not imply or guarantee its efficiency. The composition and morphology of the obtained oxide layer on the titanium surface depend on a variety of parameters and characteristics of the oxidation process, as well as on the used type of titanium or titanium alloy. For instance, it was found out that the use of sulphuric acid as an electrolyte promotes a better photocatalytic efficiency of the samples than using others such as phosphoric acid [20], so that, among all parameters, the type of electrolyte has a very important role. Other known important factors are the applied voltage and current among others. Besides, thermal oxidation is another way of obtaining a titanium dioxide layer, frequently for biomedical purposes and applications [17, 22]. Different crystalline phases may be obtained, especially by thermal oxidation, among which anatase has a better efficiency [23] regarding photocatalytic behaviour, but a mixture of anatase and rutile in a proper proportion, for instance, the relation of approximately 80/20 (anatase/rutile) that can be found in [24] or in [22], obtains better photocatalytic efficiency than oxides containing only anatase. At the same time, the surface area is also known to play a key role in obtaining highly efficient oxides, as demonstrated by several literature works dealing with the production of nanotubular anodic oxides by anodic oxidation. In this case, the crystal phase most commonly achieved is anatase, and given the high specific surface area – orders of magnitude larger than the nominal one – photocatalytic activity is particularly high [20, 25]. Yet, this method of fabrication of TiO₂ coatings is rather complex and not still suitable for large components, as in architectural applications, where anodising is often performed on sheets that are of dimensions in the order of magnitude of square meters. The same applies to high voltage anodising like anodic spark oxidation procedures, which involve

very large current densities in order to allow high oxide crystallinity, with both anatase and rutile phases present [20, 26]. On the contrary, traditional anodising procedures involving the formation of compact oxides can be applied to very large surfaces, and depending on the electrolyte chosen a partial crystallinity may be achieved, in the form of anatase phase [18]. These oxides also present the beneficial aspect of showing interference colours, as previously mentioned.

In this frame, we aim to optimize and simplify the process of obtaining a good photocatalyst in a way never done before to the best of our knowledge, and we present an evaluation of the influence of novel process parameters on the behaviour of anodised titanium presenting both interference colours and photocatalytic activity, as a material of potential interest for the building industry.

2. Materials and Methods

2.1. *Growth of titanium dioxide films*

As already mentioned and known before, some factors in the titanium anodising process, like the applied voltage and current or the type of electrolyte, affect the photocatalytic efficiency. However, the type of the necessary cathode for the anodising process had never been taken into account as a possible factor that influences the photocatalytic activity of the oxide layer. The TiO₂ films tested in this work come, therefore, from three anodising methodologies with three different cathodes: carbon, titanium and platinum. Moreover, they have been also thermally treated after anodising, at 500°C for two hours. All samples were anodised in an aqueous solution of sulphuric acid 0.05M, a maintenance time of one minute was applied after reaching the highest voltage of 60 V and the applied current amounted to 100 mA (10 mA/ cm²).

Hereinafter, samples are abbreviated as or labelled with the symbol of the

corresponding cathode and TT for thermal treatment (C TT: anodised with carbon counter electrode, Ti TT: titanium, Pt TT: platinum) as shown in Table 1.

A sheet of titanium (CAS: 7440-32-6 from Alfa Aesar®) of 1 mm thickness and 99.2% of purity was cut into discs of 2.5 centimetres in diameter. Afterwards, they were degreased with acetone before the process of electrochemical oxidation. Three replicates of each kind of specimen were prepared. The electrolyte was not stirred during anodising, which was carried out at room temperature.

The pieces of titanium working as the anode were connected to each cathode separately (titanium, carbon and platinum) and to a DC power supply TT PLH120. After anodising, thermal treatments were carried out in an oven in air, since they improve the surface morphology regarding photoactivity [27].

2.2. Characterization

Titanium samples were characterised before anodising through X-ray diffraction (XRD) by using a diffractometer X D-5000. Firstly, diffraction has been addressed with 1 mm thick titanium sheets with 99.2% purity and 2.5 centimetres diameter, as if they were a powder for the diffractometer. The type of lamp for the radiation was a Cu-K α , the applied voltage was 40 kV and the current was 300 mA. Furthermore, their patterns were analysed in the 10° to 120° angular range with a 0.02° step size and counting time of 4 seconds each step. Secondly after anodising, samples were further analysed with a Philips PW3020 using a Cu-K α radiation as well. Diffraction patterns were analysed only in the 20°-30° angular range since it contains both anatase and rutile main peaks. The presence of anatase is shown by the presence of a peak at an angle of 25.5° and the visible peak at 27.4° corresponds to rutile phase [28]. SEM analyses were also performed on samples, with a Carl Zeiss AG-EVO® Series 50 instrument.

UV and visible light spectrum absorbance and Fourier transform infrared (FTIR) analyses were performed using a Cary 60 UV-Vis Spectrophotometer from Agilent Technologies and a Thermo-Nicolet iS10 FT-IR spectrometer with an attenuated total reflectance unit, respectively.

2.3. Photocatalysis

A photocatalysis test is done with titanium samples which have been previously anodised using either carbon or titanium or platinum as the cathode in order to test the differences among them and their efficiency.

This photocatalytic test is based on the degradation of rhodamine-B dye during six hours of irradiation with a lamp whose spectrum is similar to that of natural light. The lamp is an OSRAM ULTRA-VITALUX and its power 300W, the UV intensity was set to 2.5 mW/cm² and measured with a discontinued UM-10 UV radiometer from Konica Minolta. Rhodamine-B [7], like methylene blue and all other dyes, absorbs the visible radiation at given wavelengths: its maximum absorption is at 550 nm. This permits to monitor changes in its concentration due to the TiO₂ photoactivity by measuring the variation in its absorbance by spectrophotometry, as explained in previous works [20]. A Rhodamine-B (C₂₈H₃₁ClN₂O₃, RhB hereafter) solution is prepared with concentration 10⁻⁵ M in distilled water and the photocatalysts samples are immersed in beakers containing 10 ml of this RhB solution for each measure.

The beakers are covered with a smooth piece of quartz, which not only allows the UV light pass through it but avoids that water evaporated by the heat of the lamp causes a concentration of the RhB solution.

The concentration is measured at 30 minutes intervals in 6 hours starting from time zero (t₀). To do this, a Thermo Scientific™ Spectronic 200 spectrophotometer was used.

3. Results and Discussion

3.1. *Samples anodising*

Differences among the specimens were already noticed in the anodising process, and specifically in the time required to arrive at the desired voltage, which was approximately 1 minute with a titanium or carbon cathode, whereas it was approximately 2 minutes with platinum. Cathode potentials are consistent with the materials used, being carbon and platinum nobler than titanium, while anode potentials only show few tens of mV of difference, which is a normal value dispersion in different samples of the same material. The observed variation in the oxide growth rate cannot be explained by measured potential values. Table 2 shows the measurements performed on one of the anodising batches, showing that the electrochemical differences observed concern the initial potential of the cathode, which is lower for titanium, and more interestingly the residual current that still flows in the circuit at the final voltage ΔE_f , i.e., the imposed 60 V. In fact, when ΔE_f is reached the oxide grown in presence of the platinum cathode allows a larger current flow, almost double, with respect to those obtained with titanium and carbon, likely indicating higher dissipations in the process such as oxygen evolution, which would justify the longer anodising time as it subtracts current from oxide growth [29]. Higher dissipations are generally associated with an oxide that is not completely amorphous nor stoichiometric, since compositional defectiveness and crystal nuclei would enhance its electronic conductivity and therefore allow oxygen anions to intervene as oxidation process reactant, evolving oxygen as a result. Considering the cathode material, different overpotentials for the cathodic reaction may also be responsible for the higher dissipations. In fact, it is well known that platinum allows very easy hydrogen evolution reactions, meaning that overpotentials for this reaction are rather low compared to other materials. Considering

that the voltage that builds up in the cell is proportional to reaction overpotentials, following the relationship:

$$V = RI + \eta_a + \eta_c \quad (\text{Eq. 1})$$

where R is the electrolyte resistivity, I the current circulating, η_a and η_c the anodic and cathodic overpotentials, respectively; and considering that, operating at constant current density, both RI and η_a terms are constant in the three cases, the only parameter that may change in presence of different cathodes is η_c . Specifically, with Pt lower η_c values are observed, consequently, the same amount of current flowing in the system will build up a smaller voltage V across the cell, therefore explaining the need for longer anodising time (i.e., higher overall charge) in presence of Pt electrode when working in a galvanostatic regime.

3.2. *Samples characterization: crystal phase analysis*

The XRD spectra of the specimens previous to anodising only show peaks related to metallic titanium of α -phase, as expected due to the use of commercial purity titanium as a substrate for anodising (Figure 1). On the contrary, after anodising also the oxide phases are observed, and specifically, diffraction patterns show the presence of anatase peaks at an angle of 25.5° (Figure 2). The visible peak at 27.4° corresponds to rutile phase [28]. There are no big differences among all thermally treated oxides.

SEM imaging of the as anodized sample (Figure 3a) revealed a rather smooth surface, with few small craters due possibly to the fast growth of the oxide and to the beginning of anodic spark deposition phenomena, which are still in a very early stage. The oxide surface was modified after annealing (Figure 3b): in fact, small features appeared on the surface of the oxide, which were interpreted as formation of crystal

phases, as also attested by XRD. On the other hand, no significant difference was noticed as a function of the cathode employed.

UV and visible light absorbance spectrum of the anodised and thermal treated titanium samples are reported in Figure 4. Spectra of the three different samples are quite similar but different from pure titanium sheet spectrum. Commercially used TiO₂ Sigma-Aldrich P-25 has been also tested as a reference, as it is the most commonly used photocatalyst for air and water purification purposes [30, 31]; this oxide, available in the form of nanopowders, contains both anatase and rutile phases. The common absorbance of TiO₂ Sigma-Aldrich P-25 is high in the UV-light range, but it decreases with wavelength in the visible light range after a jump in the UV and visible light threshold showing its band gap. In the case of the different samples, the band gaps resulting from the extrapolation happen to be in the range 3-3.2 eV, which is coherent with typical crystalline TiO₂ band gap values. While P-25 shows a flat absorbance spectrum in visible light, anodised samples present a sinusoidal shape, as observed in the zoom in Figure 4. This depends on the fact that, as mentioned in the introduction, anodic oxides show interference colours, i.e., they are not grey but – in this specific case – present a light blue hue that is caused by interference between the nanometric oxide film and light [29]. It is interesting to observe that the sample that showed the most different behaviour during anodising, i.e., that anodised in presence of platinum cathode, is the one which shows the highest absorbance among anodised ones, meaning that the colour is less intense. The cause may be found in the same differences that led to higher dissipations and longer anodising time, i.e., lower oxide homogeneity, likely caused by compositional and structural defects that would also be responsible for a loss in transparency and, hence, for a decreased colour intensity.

Additionally, the oxidation state of the anodised titanium surfaces was evaluated by Fourier transform infrared (FTIR) analysis. All anodised samples show a significant peak in the pattern at an approximate wavenumber of 670 cm^{-1} , whereas the pure titanium sample does not follow this behaviour. This peak is characteristic of TiO_2 crystallisation in the form of either rutile or anatase. Besides, characteristic peaks of anatase appear on the studied samples at approx. 1630 cm^{-1} and 2900 cm^{-1} as well (Fig. 5), confirming XRD results.

3.3. Photocatalysis

Photocatalytic performance has been assessed with tests aimed at the degradation of a dyes model pollutant. Figure 6 shows the results of the photocatalysis test done with the three different samples and a reference Rhodamine B solution that did not contain any photocatalyst. This test has been repeated giving good reproducibility.

The mechanism of their photocatalytic activity can be understood as explained in the introduction section. Electrons in the titanium dioxide particles of the samples were excited and jumped from the valence band to the conduction band, since they absorbed photons with energy $h\nu$ larger or equal to their band gap, in our case in the range 3-3.2 eV, typical of crystalline TiO_2 and electron-hole pairs are created. In the presence of water and in the presence of oxygen, hydroxyl ($\bullet\text{OH}$) and superoxide ($\bullet\text{O}_2^-$) radicals were created [27] and both degraded the organic dye of the test verifying the photoactivity of all of the samples. Specifically, they achieved a notable reduction of more than 44% of dye concentration, comparing to the reference one which obtained a mean of 7%, representing the sole photolysis of the dye due to UV exposure. However, differences among all of them were noticed in the extent of Rhodamine-B degradation. Anodising with platinum counter electrode resulted in the lowest photoactivity, a degradation extent of 44%, and with titanium in the better photoactivity, 74% of

degradation. On the other hand, anodising with carbon as a cathode performed a 57% reduction of the concentration of Rhodamine-B. This means that the counter electrode not only affects the oxide growth rate and defectiveness, which is responsible for higher current dissipations in the process, but also the oxide photoactivity in spite of a similar crystallinity. In this case, it takes approximately 2 minutes to arrive at the desired voltage, as compared to the 1 minute in the other two samples. It is known that the faster the half-reaction that occurs at the auxiliary or counter electrode is, the better for the process (anodising) at the working electrode so that it sounds sensible that the formed oxide layer of the samples anodised with platinum is more defective and therefore, less photoactive due to recombination of charge carriers at the oxide defects. Moreover, samples which showed similar behaviour in the anodising process (with titanium and carbon counter electrodes) also resulted in slightly different photoactivity. The reason could lie in the contamination of the oxide by carbon, partly dissolved in the acid electrolyte used in anodising and could then be incorporated in the oxide during the growth process, therefore affecting its chemistry and, with it, its electronic properties. However, other authors stated that the impurity doping (carbon) probably improved photoactivity under visible light [32].

3.4. Differences in the photocatalytic behaviour of the samples

In order to analyse if there are statistically significant differences between the obtained results, a statistical approach is used. Moreover, another batch of samples was performed subsequently (see Table 3 below) and the photocatalysis was as well tested twice to add more data to the statistical analysis.

Specifically, the F-test (Fisher's test) was applied with a 95% of confidence level, testing the null hypothesis of equality of means. This procedure compares several

samples and tests whether there are any significant differences amongst them. The P-value evaluates how well the data support the argument that the samples have different photocatalytic behaviour if the P-value (Probability value) is lower than 0.05. The results of this test showed that there is a statistically significant difference between the means of the 4 different samples at the 5% significance level since the P-value is 0.0002. Furthermore, the Multiple Range Test was applied to determine which means are significantly different from which others, indicating that the six possible pairs show statistically significant differences at the 95.0% confidence level. The applied Kruskal-Wallis Test obtained a P-value of 0.0012, which is less than 0.05 and shows as well significant difference amongst the medians at the 95% confidence level.

4. Conclusions

After having coated the different samples and addressed the photocatalysis tests, the following conclusions have been drawn:

- Oxide layers that achieve an important photocatalytic activity are obtained with all of the different treatments.
- All these oxides show a nice and uniform colour which is due to interference phenomena, which makes them even more appealing as environmentally friendly, depolluting materials for architectural applications.
- Differences among samples were found depending on the cathode used in the anodising process, as the hypothesis pointed out. The most efficient sample results to be the one anodised with titanium as a cathode. On the other hand, the samples anodised with platinum as the cathode show the lowest photocatalytic efficiency and at the same time their production requires the highest amount of current, i.e., the least efficient anodizing process. Further investigations are

needed to better understand this variation in the oxide behaviour, but it appears to be due to the extent of defectiveness of the oxide, which adversely affects photocatalytic activity. This approach can lead to energy savings and economic benefits.

- Future investigations about the photocatalytic activity under visible light of the samples may indicate if they are also efficient in such conditions, which would be of great interest for architectural applications, and to which extent the cathode material influences such behaviour.

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Label	Electrolyte	Voltage-Time	Current	Thermal Treatment	Cathode
C TT	Sulphuric acid	60 V - 1'	100 mA	500°C – 2 h	Carbon
Ti TT	Sulphuric acid	60 V - 1'	100 mA	500°C – 2 h	Titanium
Pl TT	Sulphuric acid	60 V - 1'	100 mA	500°C – 2 h	Platinum

Table 1. Overview of the conditions of each sample and their labels

Cathode	Platinum	Carbon	Titanium
Cathode potential at t=0	460 mV	457 mV	250 mV
Anode potential at t=0	220 mV	160 mV	220 mV
Time to reach 60V	2 min 16 sec	1 min 3 sec	1 min
Final voltage ΔE_f	59.7 V	58.8 V	60 V
Residual current after reaching ΔE_f	57.4 mA	34.8 mA	37.4 mA

Table 2. Current and voltage measured during the anodising of the different samples

Sample	Rhodamine B degradation (%)				Statistical data	
	First batch		Second batch		Mean	Standard deviation
	First test	Second test	Third test	Fourth test		
Reference RhB	8.6	5.4	7.1	8.1	7.3	1.4
C TT	58.1	56.0	52.0	44.1	52.5	6.2
Ti TT	75.3	73.1	63.5	72.1	71.0	5.2
Pt TT	44.1	43.8	34.3	46.9	42.3	5.5

Table 3. Overview of the percentage reduction of each sample in the first, second and third test after 6 hours of irradiation

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Figure 1.

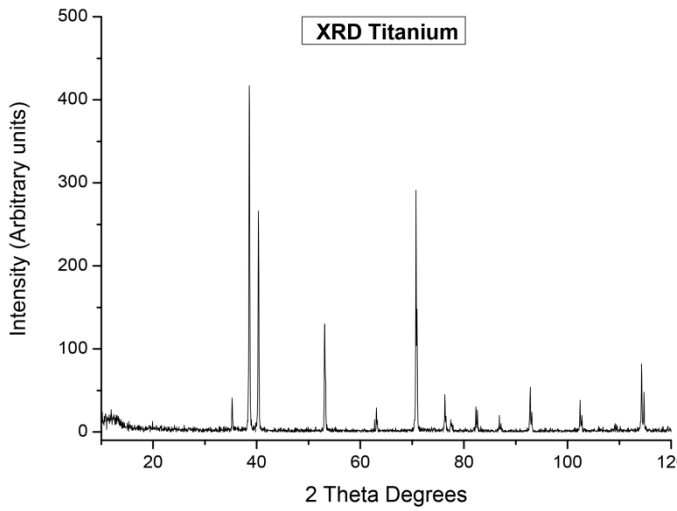


Figure 3.

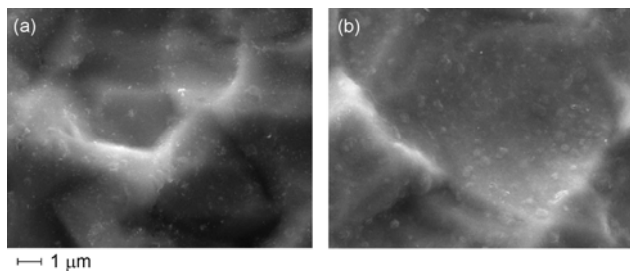


Figure 4.

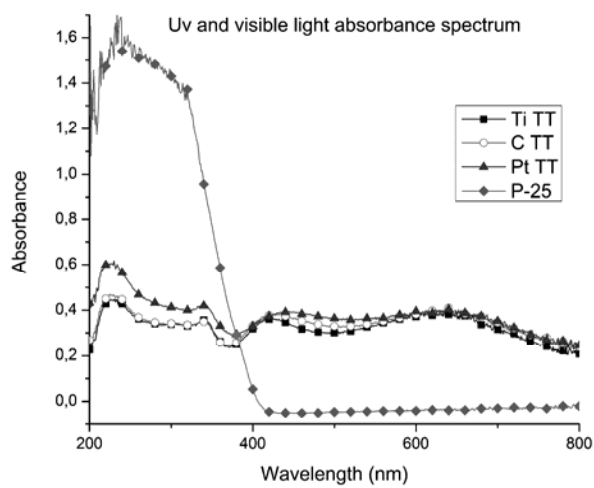


Figure 2.

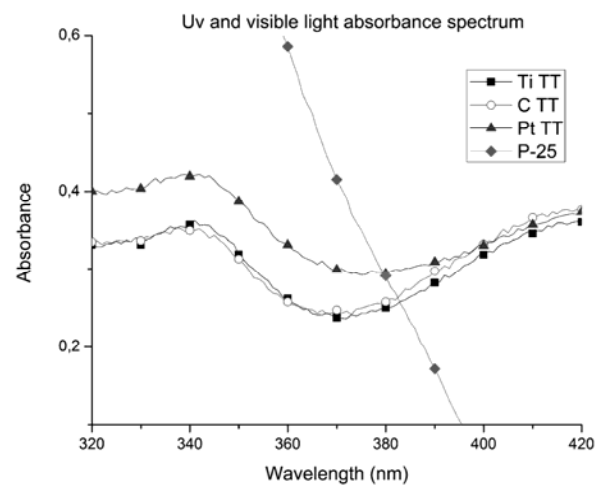
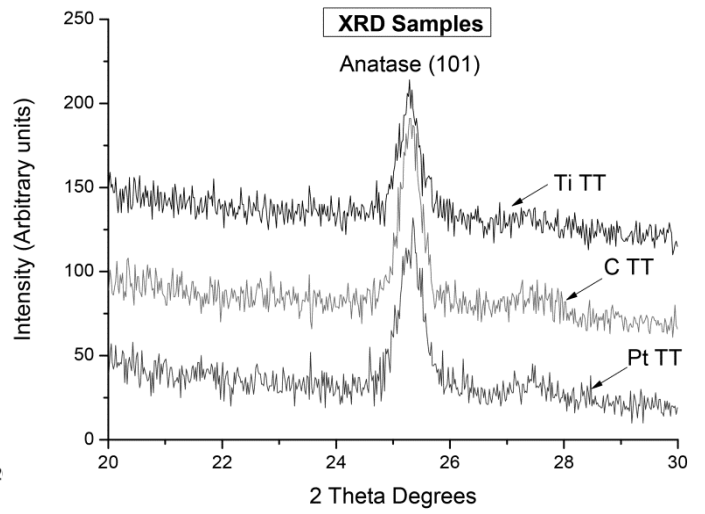


Figure 5.

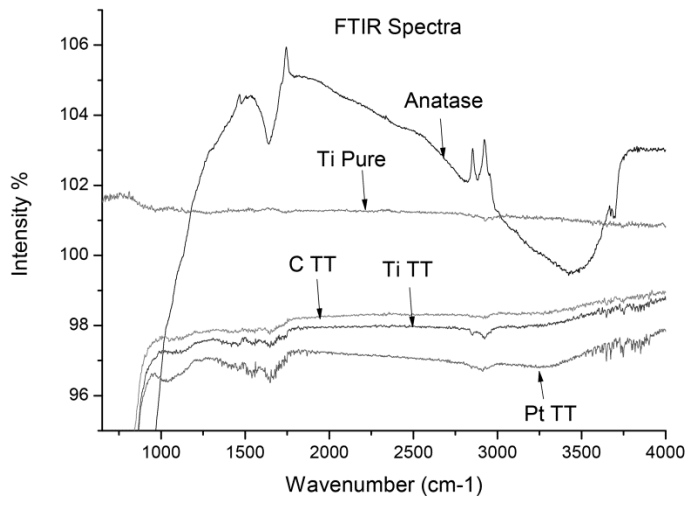
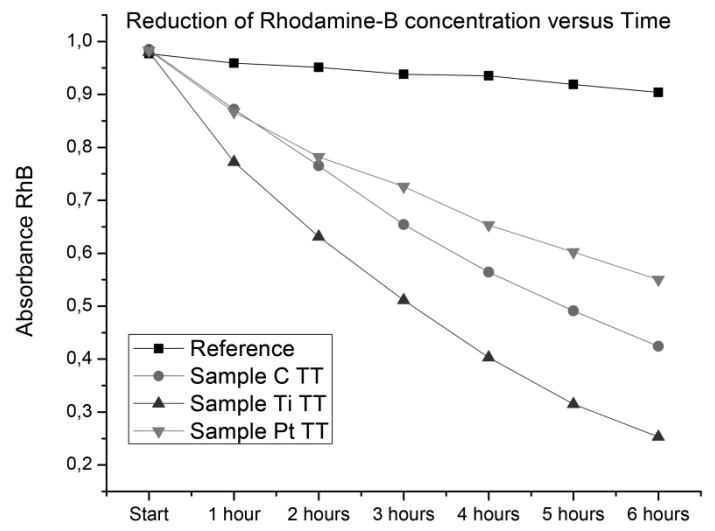


Figure 6.



List of figure captions

Figure 1. X-ray diffraction pattern with the X Siemens D-5000; the ranges in the x-axis go from 10 to 120 grades (angle of diffraction 2θ) and the intensity in the y-axis is shown in arbitrary units

Figure 2. XRD pattern of Ti TT, C TT and Pt TT samples

Figure 3. SEM images of anodized sample (a) before and (b) after annealing

Figure 4. UV and visible spectrum of different anodised titanium samples (Ti TT, C TT and Pt TT) comparing to pure titanium and the commercially used TiO₂ Sigma-Aldrich P-25

Figure 4. FTIR spectrum of the anodised titanium samples (Ti TT, C TT and Pt TT) comparing to pure titanium and anatase phase crystalline titanium dioxide as comparison

Figure 5. Degradation of Rhodamine B solutions in contact with samples Ti TT, C TT and Pt TT

