

# Electrochemical Fabrication of Anodic Nanoporous Titania for Photocatalytic Degradation of Pollutants

Amirreza Shayganpour<sup>a</sup>, Andrea Pietro Reverberi<sup>b</sup>, Marco Salerno<sup>a</sup>, Bruno Fabiano<sup>c</sup>

<sup>a</sup> IIT – Istituto Italiano di Tecnologia – Nanophysics Department, via Morego 30, 16163 Genoa (ITALY)

<sup>b</sup> DCCI - Department of Chemistry and Industrial Chemistry, Genoa University, via Dodecaneso 31, 16146 Genoa (ITALY)

<sup>c</sup> DICCA - Department of Civil, Chemical and Environmental Engineering – Polytechnic School, Genoa University, via Opera Pia 15, 16145 Genoa (ITALY)

Photocatalytic dissociation of organic compounds and wastes is currently object of intense investigations for many reasons related to several advantages offered by a combination of chemical conversion with biological aspects, like the bactericidal action, which are irreplaceable in some situations. Moreover, photocatalysis is often easily controllable and does not generally require a continuous feed of reactants as in ordinary chemical abatement. In this work, we have investigated the photocatalytic dissociation of lactose present in milk whey under ultraviolet irradiation of a titanium dioxide substrate produced by anodic oxidation of metallic titanium. Two different forms of photocatalyst have been tested, namely a crude titania electrolytically obtained without any other further surface restructuring and a titania with surface modified by thermal annealing. The results proved the beneficial effects of a surface restructuring in terms of reaction yield. Such results can be interpreted as a preliminary test being a starting point for further surface treatments and process optimization.

## 1. Introduction

Titanium dioxide TiO<sub>2</sub>, shortly titania, is a material largely used in particulate form especially as a white pigment for both paints and food, given its physicochemical stability and biocompatibility (Diebold, 2003). Titania is used as support for innovative bimetallic alloy catalysts e.g. adopted in partial oxidation processes (Fabiano et al., 2015), or in sulphur removal by oxygen enriched Claus processes (Palazzi et al., 2014). In the last decade, many studies were focused on the manufacture of composite materials (Pascariu et al., 2013), owing to their unusual transport properties in heat transfer (Solisio et al., 2012), applied chemistry and pharmaceutical applications (Pastorino et al., 2013). In this field, a commonly adopted technique to make TiO<sub>2</sub>-polymer composites is based on a polymerization process using a monomer dispersion where nanoparticles or colloidal micelles of titania were previously embedded (Dey, 2015). Silicone (Shen et al., 2015), polypyrrole, polyacrylic acids and polyethylene-terephthalate (Fortunato et al., 2014) are examples of polymers where TiO<sub>2</sub> is hosted, often giving transparent composites, provided that the diameters of the dispersed solid phase is below a threshold value.

Thanks to their absorption of UV light, titania nanoparticles are also widely used in sunscreen products, but a major potential application of this property is rather for photocatalysis. Since the observation of water splitting on titania, more than 40 years ago, several applications of the photocatalytic activity of this material have been proposed (Linsebigler et al., 1995). The photocatalytic activity of titania relies upon its peculiarity of absorbing an incident electromagnetic wave making an electron shift from its valence band to the corresponding conduction band, leaving a moving vacancy (“hole”) in the valence band. If electrons and holes reach the titania surface without reciprocal recombination, they may trigger reduction/oxidation reactions on chemical species in contact with the photocatalyst surface, as depicted in Figure 1. A satisfactory yield in redox reactions can thus be achieved by minimizing the aforementioned recombination, a result which is easily obtained when cluster of electron- and hole-scavengers are deposited on the TiO<sub>2</sub> surface.

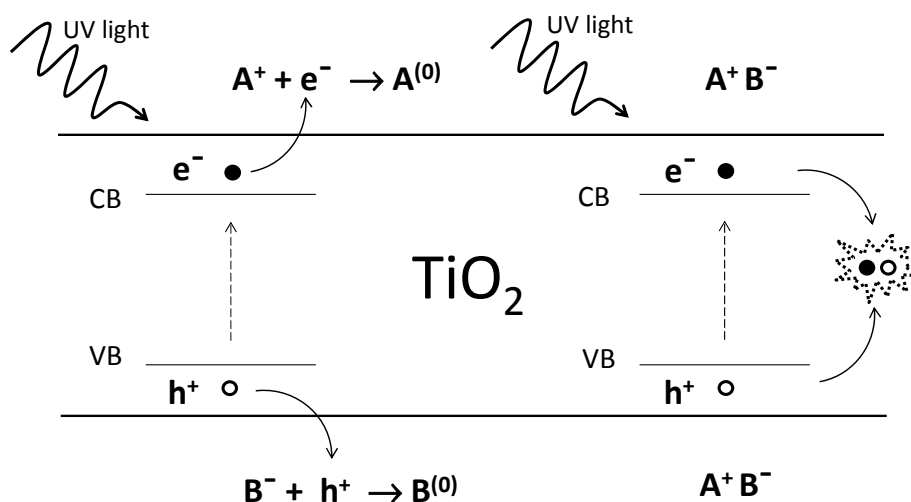


Figure 1: Left snapshot: a photon shifts an electron from the valence band (VB) to the conduction band (CB) producing an electron/hole pair with a redox reaction at the photocatalyst surface. Right snapshot: recombination of an electron/hole pair without giving a redox reaction.

To this purpose, metallic Ag, Au and other weak electropositive elements are used as electron-sink, while metal oxides as RuO<sub>2</sub> are generally adopted as hole-sink (Linsebigler et al., 1995).

In this context, TiO<sub>2</sub> has been successfully used in the abatement of pollutants contained in gaseous and liquid phases, even if further research in the safety area is required to investigate the potential role of nano-TiO<sub>2</sub> during environmental risk assessment (De Rademaeker et al., 2014). Espino-Estévez et al. (2015) investigated the photocatalytic degradation of phenols and non-steroidal anti-inflammatory drugs (NSAIDs) on titania coatings according to their different preparation techniques, based on wet milling or chemical disaggregation.

A band-gap of 3.2 eV for TiO<sub>2</sub> in its pure state makes it excitable only by UV light, and this constraint may represent a drawback limiting its uses in many practical applications. For this reason, many efforts have been focused on how to reduce the aforementioned band-gap in order to promote the sensitivity of titania to visible light. A commonly used technique relies on adding proper electronegative elements (anions) or electropositive elements (cations) as dopants to its composition during the manufacturing process. As for anions, nitrogen (Michalow et al., 2009) and iodine (Song et al., 2013) offer promising result, while boron, an usually undesired element in environment (Tagliabue et al., 2014), is perhaps one of the most efficient doping elements for TiO<sub>2</sub> (Cavalcante et al., 2015). Doping with electropositive elements, though beneficial, often gives minor results.

In recent years, a different type of nanostructured titania has been developed, namely anodic porous titania (APT), which can be readily fabricated on large areas in the form of nanoporous layers, during anodization in an electrochemical cell similar to the most common process applied on aluminium (Gong et al., 2001). In this work we fabricated layers of APT in a teflon cell with inert platinum counterelectrode, under controlled conditions of temperature, electrolyte composition, applied voltage and processing time. Pores with typical size of 450 nm and pore density of almost 10<sup>8</sup>/cm<sup>2</sup> were obtained, as resulting from scanning electron microscope inspection. Post anodization annealing in argon allowed for control of the titania chemical phase and its conversion from amorphous to anatase form.

## 2. Materials and methods

### 2.1 APT Fabrication

An ultrapure (>99.99%) titanium (Ti) plate (Goodfellows, UK) of 1 mm thickness and ~2x5 cm<sup>2</sup> flat surface size was connected to the anode clamp of a high voltage power supply N5751A (Agilent, USA), and dipped vertically in a beaker containing 1.5 M aqueous phosphoric acid (H<sub>3</sub>PO<sub>4</sub>, Sigma Aldrich, Italy). The area in contact with the electrolyte was ~2x4 cm<sup>2</sup> for each side face of the Ti plate (i.e. no protective paint was used for the rear face with respect to the cathode). As the cathode, a platinum-iridium (PtIr) wire (Goodfellows) of 1 mm diameter, curled up to form a spiral with external diameter of ~3 cm, was used, which was placed in

front of the Ti plate at a distance of  $\sim 3$  cm. The beaker was jacketed and in its cavity the cooling liquid Kryo 40 (Lauda, Germany) was circulated, by means of a thermocryostat RP 3530 (Lauda).

Two anodizations with similar Ti plates were carried out, both lasting 10 min and with target voltage and current of 150 V and 0.5 A, respectively, but at different anodization bath temperatures of 5 and 25°C. After each process, the area not anodized was cut away and the anodized area was cut into two halves of  $\sim 2 \times 2$  cm<sup>2</sup> each. One half was used as fabricated, and another half after annealing in a tubular oven under an inert argon stream at 900°C overnight ( $\geq 8$  h at the target temperature), namely using an equipment analogous to the one adopted for pyrolysis processes at laboratory scale (Chiarioni et al., 2006).

## 2.2 Photodegradation of test compound.

The four APT samples (corresponding to the two combinations of fabrication temperature and post fabrication annealing) were used as a substrate for catalytic enhancement of the photodegradation of selected test molecules by means of UV light irradiation. The target compound chosen for these tests was lactose (C<sub>12</sub>H<sub>22</sub>O<sub>11</sub>, MW=342.3), present in the milk whey samples here utilized as a waste of dairy industry. The lamps used were CN-15 (Vilber Lourmat, France), with nominal total power of 60 W, with UV line at 365 nm wavelength. Starting from whey samples with a lactose concentration of 15 mM, we used sterile polystyrene Petri dishes (diameter 2.54 cm) with the APT substrate of choice on the bottom, and poured 5 mL of lactose solution in whey on it, which made a depth of liquid of  $\sim 1.0$  cm. The Petri dish was placed under the light of the lamp, held on its original stand, and both were on top of the plate of an agitation system Rotamax 120 (Heidolph, Germany) set at low speed of 20 rpm, in order to mix the liquid during irradiation without perturbing the exposure of the substrate. Five different irradiation times were tested, up to 10 h with sampling times every 2 h, for a total of 2 substrates. Lactose identification and concentration was performed by high performance liquid chromatography (model 1100, HPLC Agilent, Palo Alto, CA, USA) using a UV detector and a C18 reverse-phase-column (model 201TP54, Vydac, Hesperia, CA, USA), according to standard procedure. All results are expressed as the mean of three replicates.

## 3. Results and discussion

For the anodization process, the power supply worked in such a way that both current and voltage were ramped up towards the target values, and the first one of the two that was reached was then maintained constant. As a result, usually a transient current peak appeared first, which was limited by the current target value, and then (after some seconds) the target voltage was reached, and maintained for the rest of the anodizing time (mainly potentiostatic process). In Figure 2 the chronopotentiometric and chronoamperometric profiles of the fabrication processes for the two plates at different temperature are presented.

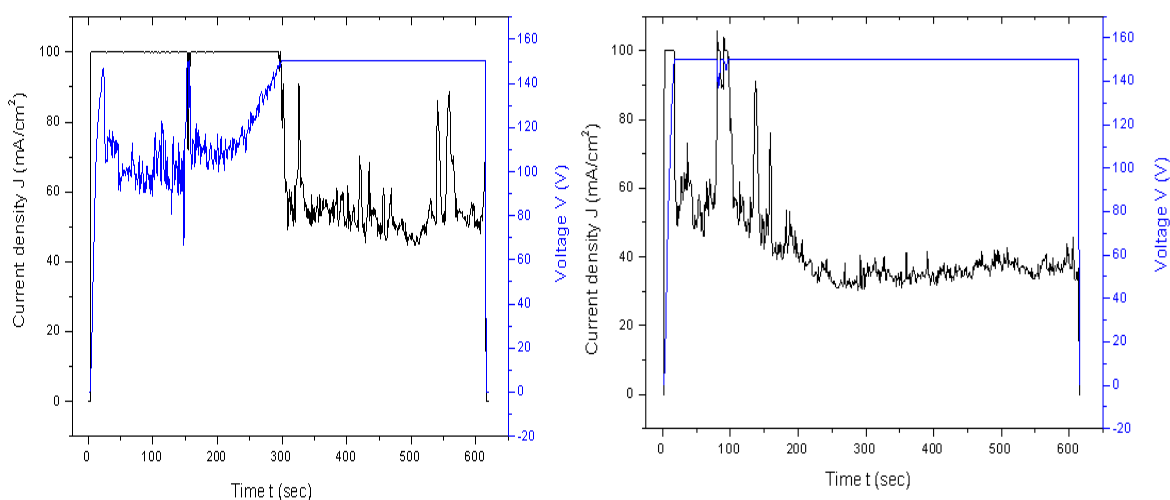


Figure 2: Profiles of current and voltage acquired during the anodizations of the Ti plates at two different temperatures: left 5°C, right 25°C.

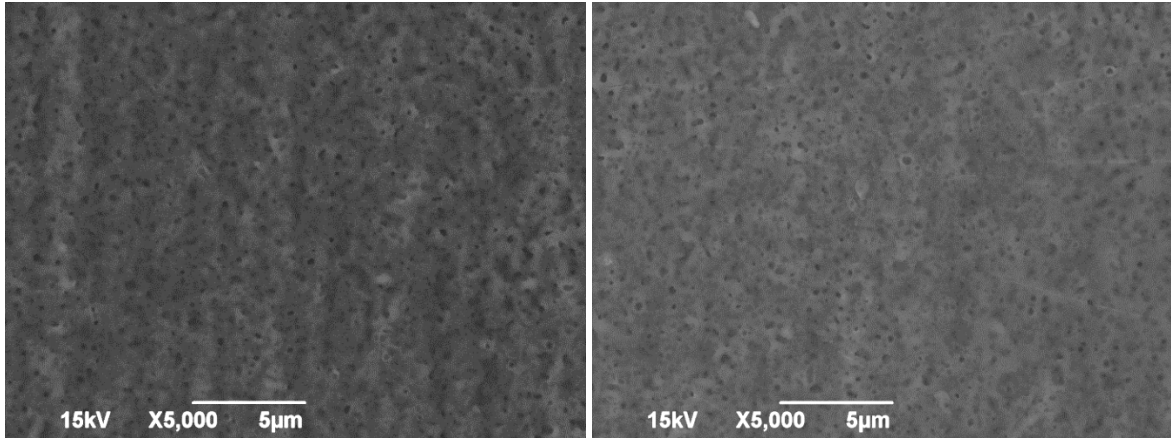


Figure 3: Top-view SEM images of the APT surfaces resulting from anodization: 'cold' as-fabricated sample (left) and 'hot' sample after annealing (right), do not show in any case significant modifications of surface morphology.

When imaged by means of SEM Model (JEOL, Japan), the surfaces of both types of Ti plates (i.e. 'cold' and 'hot' anodized) clearly showed pores. Whereas it was expected that the 'hot' sample will be made with higher current and present higher density of pores, in fact, similarly to the current profiles shown in Figure 2, there was only a little difference between the two samples, see Figure 3, and both presented a pore size and density of  $(450 \pm 90)$  nm (mean  $\pm$  standard deviation) and  $9.5 \times 10^7$  cm<sup>-2</sup>, respectively. Also for the crystalline phase, Raman measurements revealed no significant difference, and both samples appeared to be amorphous titania before the annealing (data not shown), and were converted into anatase crystalline phase after annealing.

In Figure 4, the scaled concentration of lactose has been reported versus time in semi-logarithmic plot, for the case of the 'hot' sample only. The 'cold' sample presented results that were very close and largely overlapping with those of the 'hot' sample and thus have not been included in the plot for the sake of clarity. The scatter datapoints in Figure 4 refers to samples obtained by lactose photodegradation in whey on both annealed and non-annealed TiO<sub>2</sub>. The plots have been interpolated with a linear fitting, according to the well-known simplified Langmuir-Hinshelwood kinetic law (Kumar et al., 2008):

$$\frac{dC}{dt} = -\frac{k_r KC}{1 + KC} \quad (1)$$

where  $C$  is lactose concentration,  $k_r$  is the maximum asymptotic reaction kinetics for  $C \rightarrow \infty$ ,  $K$  is the equilibrium constant for lactose adsorption on solid substrate, and  $t$  is time.

If we assume  $KC \ll 1$ , we can integrate the previous expression reported by Eq (1) from  $t=0$  to a running time, obtaining:

$$\ln \frac{C}{C_0} = -k_r Kt \quad (2)$$

In Figure 4 it is noteworthy noting that the data points for both sets of annealed and non-annealed TiO<sub>2</sub> collapse onto single lines with slopes  $k_r K = 0.03805$  and  $0.02043$ , respectively, proving a superiority of annealed titania in terms of lactose conversion. This result can be explained by taking into account that an annealing process leads to a higher crystallinity in the substrate, with a decrease in the number of defects acting as recombination sites for the electron/hole pairs generated by an incident photon. As a consequence, the probability for a single electron or hole to reach the surface and to trigger a redox reaction is higher for the annealed photocatalyst, thus giving a better reaction yield.

Qualitatively analogous results can be found in the study of Dikici et al. (2014), where nanoporous titania synthesized by anodic oxidation of titanium foil was tested in the photodissociation of methylene blue.

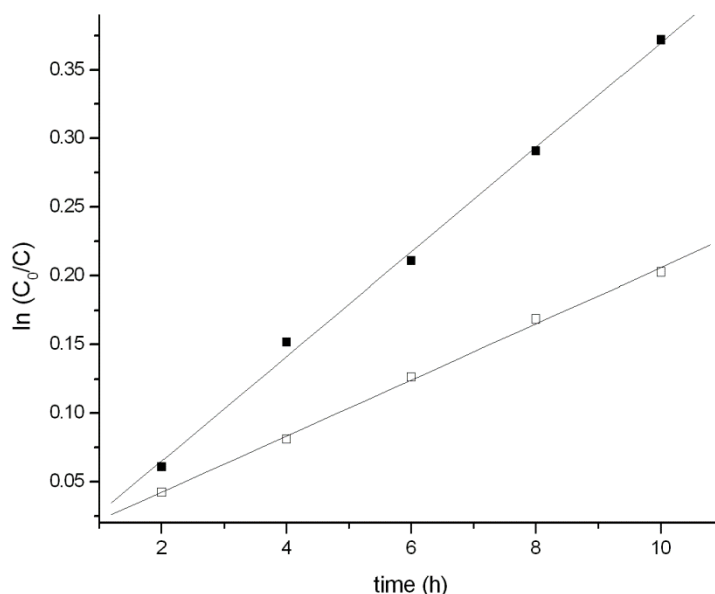


Figure 4: Plot of scaled concentration of lactose versus time for annealed titania (solid squares) and non-annealed titania (hollow squares) for the case of the 'hot' sample.

Nevertheless, we notice that the conversion in the present case study, with or without TiO<sub>2</sub> annealing, is acceptable but significantly lower than expected when compared to the yield of the same photocatalyst in degrading dyes (Zhang et al., 2007), or other organic compounds.

This phenomenon can be ascribed to a multiplicity of factors, namely:

- lactose, being a reducing sugar, is particularly active as electron-donor. Hence, we expect that its dissociation kinetics is correlated to its hole-capturing kinetics. Admittedly, the use of an electron-scavenger (here not employed) as a mild oxidizing agent in solution would have been indirectly beneficial towards lactose dissociation, thus removing electrons from likely recombination and leaving more holes at disposal for other lactose oxidations;
- whey has a multiplicity of components, relatively inert towards redox reactions, acting as fouling agents damping the reaction kinetics by inertization of surface active sites;
- whey and its dissociation products may act as UV adsorbers, giving a progressive surface deactivation.

In the present study, we have intentionally avoided the addition of oxidizing agents such as nitrates or hydrogen peroxide often adopted in literature, to avoid side reactions, which might superpose to the pure photocatalytic process. Additionally, this choice is in line with the up-to-date trend inspired by the concept of Inherently Safer Design, to address environmentally friendly design of industrial processes by reducing or eliminating the use and/or generation of hazardous substances (Primerano et al., 2015).

#### 4. Conclusions

We have proposed a photocatalytic method aiming at dissociating lactose contained in whey using anodic porous titania. Two different forms of photocatalyst have been employed and the thermal annealing proved to be beneficial in terms of reaction yield. We are currently investigating the activation of titania surface with anions contained in the electrolytic bath to improve the conversion and to enhance the sensibility of the as-prepared photocatalyst to visible light.

#### References

- Cavalcante R.P., Dantas R.F., Bayari B., González O., Giménez J., Esplugas S., Machulek A. Jr., 2015, Synthesis and characterization of B-doped TiO<sub>2</sub> and their performance for the degradation of metoprolol, *Catalysis Today* 252, 27-34.

- Chiarioni A., Reverberi A.P., Fabiano B., Dovi V.G., 2006, An improved model of an ASR pyrolysis reactor for energy recovery, *Energy* 31(13), 2124-2132.
- Dey A., 2015, Electrical transport in titania nanoparticles embedded in conducting polymer matrix, *Nanotechnology Reviews* 4(5), 429-437.
- De Rademaeker E., Suter G., Pasman H.J., Fabiano B., 2014, A review of the past, present and future of the European Loss Prevention and Safety Promotion in the Process Industries, *Process Safety and Environmental Protection* 92(4), 280-291.
- Diebold U., 2003, The surface science of titanium dioxide, *Surface Science Reports* 48, 53–229.
- Dikici T., Erol M., Toparli M., Celik E., 2014, Characterization and photocatalytic properties of nanoporous titanium dioxide layer fabricated on pure titanium substrates by the anodic oxidation process, *Ceramics International* 40, 1587-1591.
- Espino-Estévez M.R., Fernández-Rodríguez C., González-Díaz O.M., Navío J.A., Fernández-Hevia D., Doña-Rodríguez J.M., 2015, Enhancement of stability and photoactivity of TiO<sub>2</sub> coatings on annular glass reactors to remove emerging pollutants from waters, *Chemical Engineering Journal* 279, 488-497.
- Fabiano B., Pistrutto F., Reverberi A., Palazzi E., 2015, Ethylene–air mixtures under flowing conditions: a model-based approach to explosion conditions, *Clean Techn Environ Policy* 17, 1261-1270.
- Fortunato G., Tenniche A., Gottardo L., Hufenus R., 2014, Development of poly(ethylene terephthalate) masterbatches incorporating highly dispersed TiO<sub>2</sub> nanoparticles: Investigation of morphologies by optical and rheological procedures, *European Polymer Journal* 57, 75-82.
- Gong D., Grimes C.A., Varghese O.K., Hu W., Singh R.S., Chen Z., Dickey E.C., 2001, Titanium oxide nanotube arrays prepared by anodic oxidation, *Journal of Materials Research* 16, 3331–3334.
- Kumar K.V., Porkodi K., Rocha F., 2008, Langmuir–Hinshelwood kinetics – A theoretical study, *Catalysis Communications* 9, 82–84.
- Linsebigler A.L., Lu G., Yates J.T., 1995, Photocatalysis on TiO<sub>2</sub> surfaces: principles, mechanisms, and selected results, *Chemical Reviews* 95, 735–758.
- Michalow K.A., Logvinovich D., Weidenkaff A., Amberg M., Fortunato, G., Heel, A., Graule, T., Rekas, M., 2009, Synthesis, characterization and electronic structure of nitrogen-doped TiO<sub>2</sub> nanopowder, *Catalysis Today* 144, (1-2), 7-12.
- Pascariu V., Avadanei O., Gasner P., Stoica I., Reverberi A.P., Mitoseriu L., 2013, Preparation and characterization of PbTiO<sub>3</sub>-epoxy resin compositionally graded thick films, *Phase Transitions* 86, 715-725.
- Palazzi E., Currò F., Reverberi A.P., Fabiano B., 2014, Development of a theoretical framework for the evaluation of risk connected to accidental oxygen releases, *Process Saf Environ* 92(4), 357-367.
- Pastorino L., Erokhina S., & Erokhin V., 2013, Smart nanoengineered polymeric capsules as ideal pharmaceutical carriers, *Current Organic Chemistry* 17(1), 58-64.
- Primerano P., Milazzo M.F., Risitano F., Matarazzo A., 2015. Sustainable improvement of the tetrabromoethylcyclohexane synthesis using Amino ILs as Catalysts in Water. A facile and environmentally-friendly procedure, *J. of Chemical Technology and Biotechnology* DOI 10.1002/jctb.4717
- Shen Y., Wang L., Zhang H., Wu T., Pan H.Y., Preparation and characterization of titania/silicone nanocomposite material, *Global Conference on Polymer and Composite Materials, PCM 2015; Beijing; China, IOP Conference Series: Materials Science and Engineering* 87(1), 2015, Article number 012021.
- Solisio C., Reverberi A.P., Del Borghi A., Dovi V.G., 2012, Inverse Estimation of Temperature Profiles in Landfills Using Heat Recovery Fluids Measurements, *Journal of Applied Mathematics* vol. 2012, article number 747410.
- Song S., Hong T., Fang H., He Z., Chen J., 2013, Preparation and photocatalytic mechanism of visible-light-driven iodine doped titanium dioxide photocatalyst, *Chinese J. Environmental Engineering* 7(1), 1-6.
- Tagliabue M., Reverberi A.P., Bagatin R., 2014, Boron removal from water: Needs, challenges and perspectives, *Journal of Cleaner Production* 77, 56-64.
- Zhang G., Huang H., Zhang Y., Chan H.L.W., Zhou L., 2007, Highly ordered nanoporous TiO<sub>2</sub> and its photocatalytic properties, *Electrochemistry Communications* 9, 2854-2858.