Influence of titanium precursor on the photocatalytic properties of TiO$_2$ sprayed films under visible light

V Blaskov$^1$, M Shipochka$^1$, I Stambolova$^{1,*}$, S Vassilev$^2$, A Eliyas$^3$, P Stefanov$^1$ and A Loukanov$^4$

$^1$ Institute of General and Inorganic Chemistry, BAS, Acad. G. Bonchev St, bl. 11, 1113, Sofia, Bulgaria
$^2$ Institute of Electrochemistry and Energy Systems, BAS, Acad. G. Bonchev bl. 10, 1113, Sofia, Bulgaria
$^3$ Institute of Catalysis, BAS, Acad. G. Bonchev, bl. 11, 1113, Sofia, Bulgaria
$^4$ Dept. of Engineering Geocology, University of Mining and Geology, St. Edrev St., 1700 Sofia, Bulgaria

E-mail: stambolova@yahoo.com

Abstract. Thin nano-sized TiO$_2$ films were deposited on aluminum foil substrates by the spray pyrolysis method, using Ti(i-OPr)$_4$ (TIP) and TiCl$_4$ (TC) as precursors. The films were characterized by means of X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and X-ray Photoelectron Spectroscopy (XPS). According to the XRD patterns the as-deposited films appear to be amorphous. The thermal treatment at 400$^\circ$C leads to the formation of anatase nano-crystallites. The XPS analyses showed that the Ti$^{2+}$ broad photoelectron peak of as-deposited TC films indicated a mixture of Ti$^{3+}$ and Ti$^{4+}$ oxidation states. After treatment at 400$^\circ$C the Ti$^{2+}$ peak displays only Ti$^{4+}$ oxidation state for both TIP and TC films. The number of hydroxyl groups on the surface is decreased after the thermal treatment. The photocatalytic activity of the films was studied towards degradation of azo dye Reactive Black 5 (RB5) as model wastewater pollutant under visible light illumination. It was found out that the films obtained from TC were more active than those obtained from TIP films. The thermally treated samples are better photocatalysts than those non-treated, because they possess anatase crystalline phase and stoichiometric TiO$_2$. The TOC measurements showed minimal concentration of total organic carbon in the dye solution after 180 min of visible light irradiation.

1. Introduction

Water pollution due to colored effluents from textile- and paper-industries has attracted much attention among scientists from all over the world. The classical methods for purification of the wastewaters after colorization such as separation, membrane filtration, oxidation etc. are unable to decompose effectively the dyes and can produce some toxic metabolites [1]. In general, photocatalysis is used as a pre-treating step to degrade non-biodegradable organic pollutants to biodegradable compounds. This requires the development of effective photocatalysts for their degradation. Titanium dioxide (TiO$_2$) is a promising photocatalyst for the treatment of polluted air and water [2]. Recently, TiO$_2$ films have been widely studied in photocatalytic degradation of the various textile-colouring dyes, because it overcomes the main disadvantage – the necessity of post-treatment separation in a system and allows longer term operation. The spray pyrolysis method has been applied for the synthesis of TiO$_2$ films with promising photocatalytic activity [3-6]. So far the papers deal mainly with the influence of
deposition temperature and type of the substrate on the photocatalytic activity. There are no available data on the influence of the type of titanium precursor on the properties of TiO$_2$ sprayed films.

The aim of the present study was to investigate both the effects of the type of the titanium precursor and of the thermal treatment on the photocatalytic activity of TiO$_2$ sprayed films.

2. Experiment

2.1. Films deposition

Two types of titanium precursor solutions were prepared for the spray pyrolysis procedure. Titanium tetraisopropoxide (TIP) was hydrolyzed in a water-ethanol mixture at molar ratio TIP:H$_2$O:C$_2$H$_5$OH=1:1:30. Acetyl acetone (AcAc) was added as a complexating agent in such amount that one obtains the ratio TIP:AcAc =1:1 (solution A). Titanium chloride (TiCl$_4$) was used as inorganic titanium precursor and it was diluted in ethanol (solution B). Each one of the solutions A and B was diluted with a mixture of isopropanol and butyl carbitol (C$_4$H$_9$OC$_2$H$_4$OC$_2$H$_4$OH) and then stirred intensively for 1h at room temperature. The as-prepared mixtures were used for the spray procedure. The aluminum foil sheets (76mm x 25mm) were cleaned successively in hot ethanol and then in acetone. The aerosol of the precursor solution was generated by pneumatic glass nebulizer and transported to the heated substrate. The spray coating process was repeated 5 times for each film at 10 sec interval. Afterwards, one part of the deposits was treated in air raising progressively the temperature from 20 to 400$^\circ$C for 1 or 2 hours, another part remained untreated. The theoretically estimated TiO$_2$ content in the films was 2.2 mg/cm$^2$.

2.2 Characterization

The phase composition of the samples was studied by X-ray diffraction (XRD) with CuK$_\alpha$-radiation (Philips PW 1050 apparatus). The crystallite size was estimated based on the XRD spectra. The composition and electronic properties of the films were investigated by X-ray photoelectron spectroscopy (XPS). The measurements were performed in VG ESCALAB II electron spectrometer using AlK$_\alpha$ radiation with energy of 1486.6 eV. The binding energies were determined with an accuracy of ±0.1 eV. The chemical composition of the films was investigated on the basis of peak areas and binding energies of O1s, Ti2p and Al2p photoelectron peaks (after linear subtraction of the background and Scofield’s photoionization cross-sections). A scanning electron microscope (SEM) JSM-5510 of JEOL was used for morphology observations of the films.

2.3. Photocatalytic tests

The photocatalytic experiments were conducted with powerful visible-light irradiation source (TUNGSRAM 500 W lamp, 9700 Lm). The photocatalytic reactor contained aqueous solution of Reactive Black 5 dye (20 ppm concentration), which was being stirred continuously. The TiO$_2$ coated substrate was placed into the vessel and covered completely with 150 ml dye solution. The photocatalytic degradation was evaluated by taking aliquot of the solution and measuring the residual concentration using spectrophotometer UV-1600PC in the wavelength range from 200 to 800 nm at regular time intervals.

2.4 Total organic carbon measurements

Total Organic Carbon (TOC) analyzer, made by Shimadzu Co. (Japan), model VCSH, is based on total combustion of the organics, contained in the aqueous solution and the result is expressed in milligrams of carbon per liter of water. The use of TOC analyzer allows us to follow the course of the reaction by evaluating the concentration (mg C/L) based on the decreasing absorbance of the dye solution with the time. The analysis of a solution of unknown concentration was done by 5 injections and taking the mean value – in most cases 5 injections were sufficient to obtain a value of the coefficient of variation below 2% (after the microprocessor of the TOC excludes automatically the outliers). Only for the initial solution the deviation was higher, which necessitates some additional manual injections.
3. Results and discussions
X-ray diffraction patterns revealed that the sprayed thin films without any additional treatment are amorphous. The thermal treatment leads to a formation of well crystallized anatase phase with average crystallites size about 20-23 nm.

![Graph of O1s peaks](image)

**Figure 1.** Deconvolution of O1s peaks of TC films not treated (a), TC films, treated at 400°C, (b) TIP films, not treated (c), TIP films treated at 400°C (d).

The surface composition and chemical state of the TiO₂ films were investigated by XPS analyses. The O1s peaks of TC and TIP films are wide and asymmetric and could be divided. They are deconvoluted by Lorentzian–Gaussian curve fitting into two components at 530.0 eV and 531.6 eV, respectively (figure 1). The first component at 530.0 eV is related to O²⁻ ions in the TiO₂ crystal lattice. The second component at 531.6 eV is attributed to oxygen atoms in hydroxyl groups. A decrease in the number of the hydroxyl groups on the films surface after treatment is also seen in the figure. Figure 2 shows the Ti2p photoelectron spectra of the films obtained from both titanium precursors. The Ti 2p₃/₂ peaks of TiO₂ films, obtained from TiCl₄, are located at 458.6 eV for the as-deposited film and 458.8 eV for the film treated thermally at 400°C. The as-deposited film exhibited broad Ti2p photoelectron peak, corresponding to a mixture of Ti³⁺ and Ti⁴⁺ oxidation states. After treatment at 400°C, the binding energy and the shape of the Ti2p peak became characteristic of Ti⁴⁺ oxidation state. The position of Ti 2p₃/₂ peaks of TiO₂ films, prepared from titanium isopropoxide are at 458.8 eV, which is typical for TiO₂.
Figure 2. Ti2p core level spectra of the surface of the non-treated TC films (a), TC films treated at 400°C (b), non-treated TIP films (c), TIP films treated at 400°C (d).

Figure 3. Decolorization of the dye after visible light illumination for 90 minute period. The photocatalyst is TC film, treated at 400°C.
Figure 3 illustrates the typical spectrum of the dye, decolorized by TiO$_2$ sprayed film, obtained from TiCl$_4$. It is seen in the figure that the process of its degradation can be observed by the changes in the position and intensity of the peaks, corresponding to aromatic ring at 313 nm and azo bond at 599 nm.

Photocatalytic activity tests with the films showed strong influence of the type of the precursor solution (figure 4 and figure 5). The films, obtained from inorganic precursor (TC) are more efficient photocatalysts than those obtained from titanium isopropoxide. The films, obtained from organic precursor probably have greater extent of carbon-compound contaminations (originated from TIP and AcAc) than TC films. Duminica et al. [6] have proved that the carbon residues in the titania films are detrimental for the photocatalytic activity. The thermal treatment after spray pyrolysis affects also the films properties. As a rule the photocatalyst samples treated thermally at 400°C are the better ones than those non-treated, because they possess anatase crystalline phase with stoichiometric composition.

An exception appear to be the non-treated TC films (figure 4, curve 5), which exhibit behavior similar to the treated TC films, regardless of their amorphous nature. The films probably have higher surface area and contain mixtures of Ti$^{4+}$ and Ti$^{3+}$ ions (figure 2), which could be the reason for their activity.

The TOC measurements showed that the concentration of total organic carbon content in the sample after 180 min of photocatalytic activity testing is 2.26 mg/L and 23 mg/L for TC and TIP films, respectively. This result revealed that the inorganic titanium precursor is more suitable for preparation of efficient photocatalyst films for azo dye degradation in aqueous solutions.

4. Conclusions
Nanosized TiO$_2$ films were prepared by spray pyrolysis method. The films treated thermally possess crystalline anatase phase, while those non-treated are amorphous. According to XPS analysis the peak, corresponding to Ti2p state indicates only Ti$^{4+}$ oxidation state after thermal treatment of the films at 400°C. The photocatalytic properties towards degradation of textile dye in aqueous solution depend both on the type of the titanium precursor and on the thermal treatment. The samples obtained from TiCl$_4$ precursors showed higher photocatalytic activity than the films, prepared from Ti(i-OPr)$_4$. As a rule the films treated thermally are more active photocatalysts, than those non-treated. This result can be explained with formation of anatase crystalline phase with stoichiometric composition of the
treated TiO$_2$ films. TOC measurements showed minimal concentration of total organic carbon in the dye solution after 180 minutes visible light irradiation.

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References
[1] Saquib M Muneer M 2003 Dyes Pigments 56 37
[2] Hoffmann H Martin S Choi W and Bahnemann D 1995 Chemical Reviews 95 69
[3] Lopez A Acosta D Martinez A I and Santiago J 2010 Powder Technol 202 111
[4] Abou-Helal M O and Seeber W T, 2002 Applied Surface Science 195 53
[5] Uzunova-Bujnova M Kralchevska R Milanova M Todorovska R Hristov D and Todorovsky D 2010 Catalysis Today 151 14
[6] Duminica F D Maury and F Abisset S 2007 Thin Solid Films 515 7732