

PHOTOCATALYTIC ACTIVITY OF SPRAYED TiO₂ FILMS DEPOSITED ON DIFFERENT SUBSTRATES

*I. Stambolova¹, V. Blaskov¹, M. Shipochka¹,
S. Vassilev², A. Loukanov³*

*¹Institute of General and Inorganic Chemistry,
BAS, Acad. G. Bonchev St, bl.11, 1113 Sofia, Bulgaria,
e-mail: stambolova@yahoo.com*

*²Institute of Electrochemistry and Energy Systems,
BAS, Acad. G. Bonchev bl. 10, 1113, Sofia, Bulgaria*

*³Dept. of Engineering geoecology,
University of Mining and Geology, Stoyan Edrev St.,
1700 Sofia, Bulgaria*

ABSTRACT

Thin photocatalytically active TiO₂ films are successfully deposited on glass and alumina foil substrates by spray pyrolysis method. The films are characterized by means of X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), X-ray Photoelectron Spectroscopy (XPS), Thermal Analyses (TG-DTA). The XRD spectra of TiO₂ thin films, treated at 400°C showed formation of nanosize anatase phase. The films were studied with respect to the photo-initiated bleaching of azo dye Reactive Black 5 (RB5) under UV illumination. The influence of the substrate, treatment conditions and pH of the dye solution on the decoloration were investigated. It was found that the films, deposited on alumina foil revealed a better photocatalytic

activity than those on glass substrates, due to the furrowed surface of the alumina substrate. The highest rate of decoloration was obtained at low pH value of the dye solution for films treated at 400°C.

Key words: *TiO₂ films, photocatalysis, spray pyrolysis, azo dye*

INTRODUCTION

In the last decade the interest in photocatalysts applications has greatly grown, especially in the field of water purification. In this case, different wide band gap semiconductors have been studied as photocatalysts such ZnO [1], TiO₂ [2], BiVO₄ [3], Bi₂O₃ [4] etc. Among them, TiO₂ is the most suitable for degradation of organic pollutants in waste water due to its non toxicity, low cost, low water solubility and photochemical stability. The photocatalytic activity of TiO₂ has been found to vary with its structural form and is reportedly higher in the anatase form compared to the rutile form [5].

Up to today, several papers about photocatalytic properties of TiO₂ powders and thin films have been published [6]. The coatings overcome the disadvantage of the powders namely: the need of post-treatment separation in the photocatalytic reactor. Various methods are available for the preparation of TiO₂-based photocatalytic films, such as electrochemical methods [7–9], vacuum arc plasma evaporation [10], chemical vapour deposition (CVD) [11–13], as well as classical [14,15] and modified sol gel [16,17] methods.

Spray pyrolysis is an economical and fast chemical method, which is widely applied for formation of thin layers and particles of different compounds. Seabra et. al. prepared TiO₂ films from mixture of titania powder and polyester ink and studied the degradation of the azo dye Orange II [18]. Spray pyrolysis method have been successfully applied to obtain TiO₂ films, which exhibit good photocatalytic activity [19,20,21]. However, the studies about the technological and operational parameters affecting the photocatalytic performance of sprayed TiO₂ films are quite scarce [21,22].

Azo dyes are the most important class of synthetic organic dyes used in the textile industry. The photodegradation of aqueous solutions of different azo dyes have been reported by Soutsas et.al. [23]. Reactive Black

5 (RB5) dye is often used to colour cellulose fibers, which cause serious environmental problems [24]. This requires the development of effective photocatalysts for the degradation of this dye.

The aim of the present study is to investigate the influence of various parameters of TiO₂ sprayed films on the decoloration of Reactive Black 5 dye.

EXPERIMENTAL PROCEDURES

The alumina foil plates and glass substrates (75 x 25mm) were cleaned successively in hot ethanol and acetone. They were further used for the deposition of thin TiO₂ films. An alcoholic solution (EtOH–98% purity) of titanium tetraisopropoxide (TTIP) (98% purity, Acros) was hydrolyzed by a water-ethanol mixture in molar ratio TTIP:H₂O:C₂H₅OH=1:1:30. Acetyl acetone was added as a complexing agent (solution *A*). The solution *A* was dissolved in a mixture of isopropanol and butyl carbitol (C₄H₉OC₂H₄OC₂H₄OH) and then stirred intensively for 24 h at room temperature. The as prepared mixture were used for the spray procedure onto the heated substrates. After the spray coating procedure, one part of the deposits was progressively treated in air from 20 to 400°C for 1 or 2 hours with heating velocity 5°C/min in order to investigate the effect of thermal treatment temperature on the films properties.

The crystalline phase composition and size of the crystallites of the samples was studied by X-ray diffraction (XRD) using X-ray diffractometer Philips PW 1050 with CuK_α-radiation. The composition and electronic properties of the films were investigated by X-ray photoelectron spectroscopy (XPS) by VG ESCALAB II electron spectrometer using AlK_α radiation (1486.6 eV). The binding energies were determined with an accuracy of ±0.1 eV. A scanning electron microscope (SEM) JSM-5510 of JEOL was used for morphology observations of the films.

To study the photocatalytic activity of the films, experiments were conducted using an ultraviolet lamp with light intensity 5.10⁻⁵ W/cm² located in the centre of a vessel. The latter contained water solution of dye Reactive Black 5 with concentrations 10 ppm – 80ppm. The photocatalytic degradation is evaluated by taking aliquote of the solution and measuring the residual concentration by spectrophotometer type Boeco S26 in the wavelength range from 200 to 1100 nm at regular time intervals.

RESULTS AND DISCUSSION

Applied experimental way of preparation leads to formation of well crystallized anatase phase according to the X-ray analysis. X-ray diffracton line broadening (XRD-LB) measurements were carried out in order to estimate the TiO_2 crystallite size. Calculation was performed using the Scherrer's equation:

$$D = \frac{k\lambda}{\cos\theta} \quad (1)$$

where D is the crystallite size (nm), λ is the wavelength of $\text{CuK}\alpha$ radiation (nm), θ is the Bragg angle ($^\circ$), K is a constant (0.89) and B is the calibrated width of a diffraction peak at half-maximum intensity (rad).

The average crystallite size of the thin films as determined from half wide of full maximum (HWFEM) intensity of the (101) peak of the films. The average crystallite size, determined by the Scherrer's equation is about 20 nm. The size of the crystallites is typical for the films obtained by spray pyrolysis technique.

All film samples are characterized by X-ray photoelectron spectroscopy and the corresponding spectra are shown in Fig. 1. In the range of the O1s state, the X-ray photoelectron spectrum (Fig. 1a) contains two peaks: the peak at 529.8 eV corresponds to the state of the oxygen atom O^{2-} in the TiO_2 oxide, and the low intensity peak at 531.9 eV characterizes the chemical bond of oxygen ion O^{2-} in the water molecule adsorbed on the surface of the TiO_2 film.

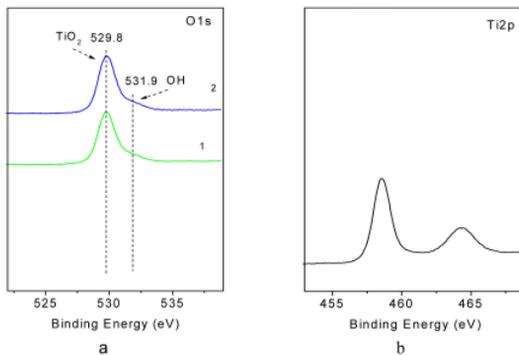


Figure 1. XPS spectra of sprayed TiO_2 film for O1s lines(a) and Ti2p (b).

For the Ti2p state, the spectrum (Fig. 1b) contains two peaks that reflect binding energies for electrons in the states Ti 2p_{1/2} and Ti 2p_{3/2}, respectively. These energies correspond to the Ti⁴⁺ state. The absence of other chemical shifts in the X-ray photoelectron spectrum makes it possible to believe that the synthesized TiO₂ films possess stoichiometric composition.

The XPS results proved that the films on glass substrate contain also Na and Si ions. This could be explained by interaction of the substrate with the films after thermal treatment similarly to the previously obtained by us ZrO₂ [25] and TiO₂-SnO₂ films [26].

Table 1. *Chemical composition of TiO₂ films, deposited on glass substrate*

Sample	O [at%]	Ti [at%]	Na [at%]	Si [at%]
TiO ₂ /glass	77.1	17.0	1.9	4.0

SEM photographs of the sprayed films on alumina foils, thermally treated at 400°C are shown on Fig. 2. The films morphology follows the uneven furrowed metallic plate surface. It consists of pores, which are probably formed by coalescence of several small pores. The structure of the TiO₂ films deposited on glass substrate is almost compact and very smooth (Fig. 3). The difference in the morphology of the films deposited on the glass and alumina foil could be explained with the surface nature of the substrates.

The photocatalytic studies showed that pH of the dye solution is very important parameter for the effective decoloration of the RB5 (Fig. 4). In our case the most suitable value of pH is 2. The catalyst also reveals relatively fast decoloration at pH=4. The reaction rate is very slow at pH 6. Similar dependence of degradation rates vs pH of azo dye by TiO₂ powders is proved by Augugliaro et.al. [27]. In the heterogeneous photocatalysis pH is very important operating parameter affecting the charge of the surface of the films and the positions of conductance and valence bands. The variation in the operating pH is known to influence the isoelectric point (PZC) and the surface charge of the photocatalyst used. The surface charge of TiO₂ is zero or neutral at pH_{pzc} in the range of pH 4.5–7.0, depending on the catalysts used, according to [28] At PZC of TiO₂, the interaction between the photocatalyst particles and water contaminants is minimal due to the absence of any electrostatic force. At low pH (pH < pH_{pzc}), TiO₂ particles possess positive charge, while a negative charge is expected at higher pH (pH > pH_{pzc}).

The majority of the reactive dyes (anionic dyes) found in the wastewater have water solubilizing sulfonic ($-\text{SO}_3^-$) groups, which are negatively charged. Therefore, acidic conditions would favor the electrostatic attraction between the positively charged TiO_2 surface and the reactive dyes, which would result in increased absorption and consequently in increased degradation of dyes.

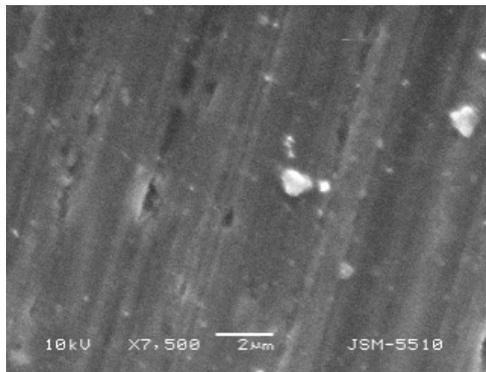


Figure 2. SEM photograph of TiO_2 film, deposited on alumina foil.

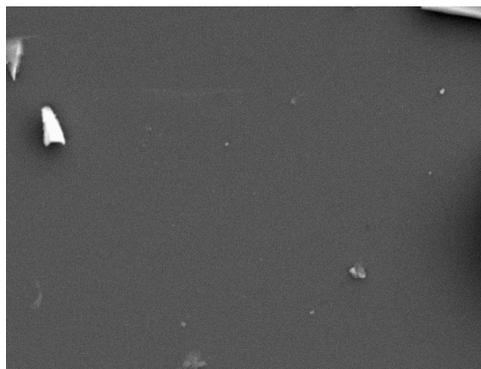


Figure 3. SEM photograph of TiO_2 film, deposited on glass substrate.

Fig. 5 shows the relationship between the decoloration rate and the volume of the sprayed solution. As can be seen the decrease in the sprayed volume leads to enhancement of the photocatalyst efficiency in the chosen interval.

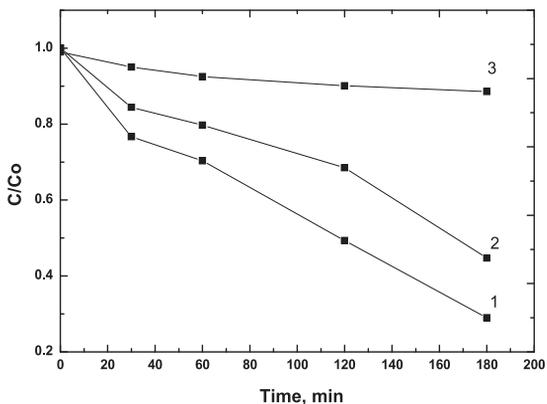


Figure 4. Kinetic curves of RB5 decoloration in coordinates $(C/C_0) = f(t)$ at different pH of the dye solution: pH=2 (1), 4 (2) and 6 (3). Films are deposited by spray of 25 ml solution, treated at 400°C.

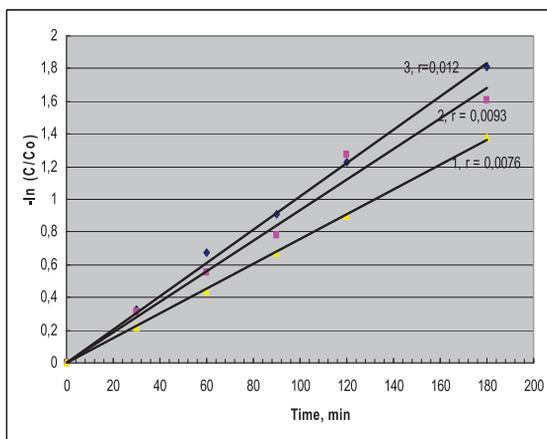


Figure 5. Kinetic curves of RB5 decoloration in coordinates $-\ln(C/C_0) = f(t)$ for films obtained by spraying of: 35 ml solution (1), 25 ml (2) u 15 ml(3); r is rate constant.

Deposition of the larger spray volume probably covers even deep grooves of the metallic surface leads to a formation of smoother film with

less number of active centers. For this reason the thin films (spray of 15 and 25 ml) are better catalysts than the thicker films, deposited by spraying of 35 ml, regardless of their lower TiO_2 content.

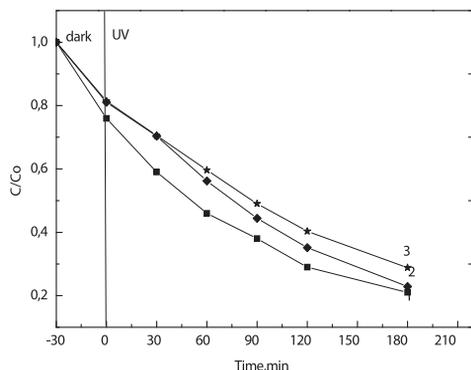


Figure 6. Kinetic curves of RB5 decoloration in coordinates $C/Co = f(t)$ The TiO_2 films are treated at $400^\circ\text{C}/1\text{ h}$ (1), $400^\circ\text{C}/2\text{ h}$ (2) not treated (3), RB5 concentration – 50 ppm

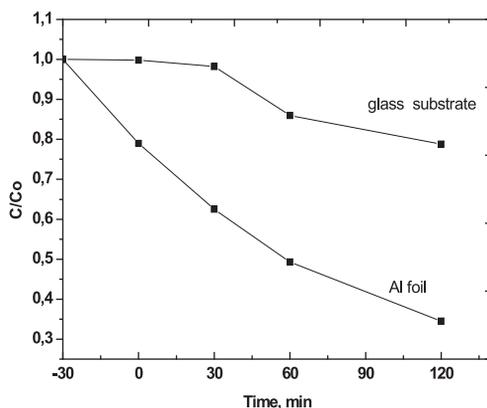


Figure7. Kinetic curves of RB5 decoloration in coordinates $C/Co = f(t)$ for TiO_2 films deposited on glass and Al foil.

The post deposition thermal treatment of the films has pronounced effect on the dye decoloration process (Fig 6). The films which are no treated

thermally after spray deposition have weaker efficiency than the treated films. The best results were obtained for the films treated at 400°C for 1 h, probably due to the better crystallization of the films. The prolongation of the isothermal heating up to 2 hours is not so effective due to the sintering effects.

The effect of the substrate used is shown on Fig. 7. The TiO₂ films on alumina foil are more effective photocatalysts than the films, deposited on glass substrate. This effect can be explained with the surface of the foil, which is not so smooth as the glass surface (Fig. 3 and Fig. 4). The uneven furrowed metallic surface causes better adsorption and adhesion of the dye. Another reason could be the temperature treatment of the glass substrate. It leads to a presence of Na and Si ions in the film, as was proved by XPS analysis (Table 1). According to the literature data [29] this element has detrimental effect on the photocatalytic efficiency.

CONCLUSIONS

Thin TiO₂ nanosize anatase films are prepared by spray pyrolysis of Ti(i-OPr)₄ solution. The films revealed high photocatalytic activity for decoloration of Reactive Black 5 azo dye and are effective at relatively high concentrations (up to 80 ppm). It was proved that the studied technological and operating parameters affect the photocatalytic properties. The pH of the dye solution influences considerably the photocatalytic activity. It was established that the films were most effective for the dye degradation in acidic medium (pH=2–4). The alumina foil seems to be more suitable than the glass substrate.

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