

## Effect of post-synthesis acid activation of TiO<sub>2</sub> nanofilms on the photocatalytic efficiency under visible light

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**Abstract.** Nanosized TiO<sub>2</sub> films were deposited by spray pyrolysis and thermally treated at 400°C. Then the films were dipped in 1M aqueous solution of HCl. The activated samples were divided into two parts – one part was dried (A) and another was annealed (AT) in air. The photocatalytic degradation of Reactive Black (RB5) textile dye under visible light was tested. The following instrumental methods: X-ray diffraction (XRD), Raman spectroscopy and X-ray photoelectron spectroscopy (XPS) were applied for the phase and surface characterization of obtained samples. According to Raman and XRD analyses all films are anatase. The XRD showed that activated films are better crystallized than non activated TiO<sub>2</sub> film. The presence of chlorine at 200.3 eV was registered for acid activated samples by X-Ray photoelectron spectroscopy. The acidic activated films exhibited higher rate of dye photodegradation than that of the reference TiO<sub>2</sub> sample. The photocatalytic efficiency decreases in the order A > AT > non activated TiO<sub>2</sub> films. The degradation rate constant for acid activated films is two times higher than those of the reference film. The hydroxyl content in TiO<sub>2</sub> acidic activated films is greater than that of the non- activated films, which results in significant increase in the photocatalytic activity. In addition, the presence of chlorine may also lead to enhancement in efficiency.

### 1. Introduction

The uncontrolled release of colored waste water contaminated with dyes from textile, paper, rubber and plastic industries is resulting in serious environmental pollution [1]. Recent studies have shown that heterogeneous semiconductor photocatalysis can be an alternative method to the conventional ones (flocculation, sedimentation, absorption etc.) for the removal of dye pollutants from water [2]. The heterogeneous photocatalytic process consists of making use of the near ultraviolet band of the solar spectrum to photoexcite a semiconductor catalyst in contact with water in the presence of oxygen. Oxidizing species (hydroxyl radicals) which attack oxidizable contaminants are generated producing CO<sub>2</sub>, H<sub>2</sub>O and diluted inorganic acids. Titania exhibits outstanding decomposition ability for many organic compounds induced by illumination with UV light [3]. Various methods are available for the preparation of nanostructured TiO<sub>2</sub>-based photocatalytic films, such as electrochemical method [4], chemical vapour deposition (CVD) [5] as well sol gel methods [6]. Nevertheless, most of them are complicated, expensive and not suitable for practical production of high-effective catalyst. Among the



chemical films deposition methods the spray pyrolysis is promising for industrial applications, due the possibility to obtain thin films with desired morphology and thickness on large-area substrates [7].

There are many approaches, proposed to increase the photocatalytic activity such as doping with transition metals, non metals [8], mixing with other semiconductor oxides [9]. Recently the acid treatment is applied to enhance the photocatalytic performance of TiO<sub>2</sub> powders and films, but the studies are quite scarce in the available literature. Liang et. al. have revealed the positive effect of HCl treatment on the activity of TiO<sub>2</sub> thin films [10]. Another scientific groups have improved the photocatalytic properties of TiO<sub>2</sub> powders by treatment in different acids [11, 12].

The aim of this study is to investigate the effect of the HCl activation of sprayed TiO<sub>2</sub> film on the surface features and the rate of photocatalytic degradation of real textile di-azo dye under Visible light.

## 2. Experimental details

### 2.1. Preparation of the films

The aluminium foil plates (75 x 25mm, thickness 0.3 mm) were used for the deposition of thin TiO<sub>2</sub> films. The substrates were cleaned successively in hot ethanol and acetone. The solution of TiCl<sub>4</sub> (0,4 M) was diluted with a mixture of isopropanol and butyl carbitol (C<sub>4</sub>H<sub>9</sub>OC<sub>2</sub>H<sub>4</sub>OC<sub>2</sub>H<sub>4</sub>OH). The aerosol of precursor solution was generated by pneumatic glass nebulizer to the heated substrate at 300-400°C. All samples were thermally treated at 400°C (label T). One part of T films was dipped in 1M aqueous solution of HCl. After acidic activation the samples were divided into two parts – one part was dried at 100°C (label A) and another was annealed at 400°C in air (label AT).

### 2.2 Films characterization

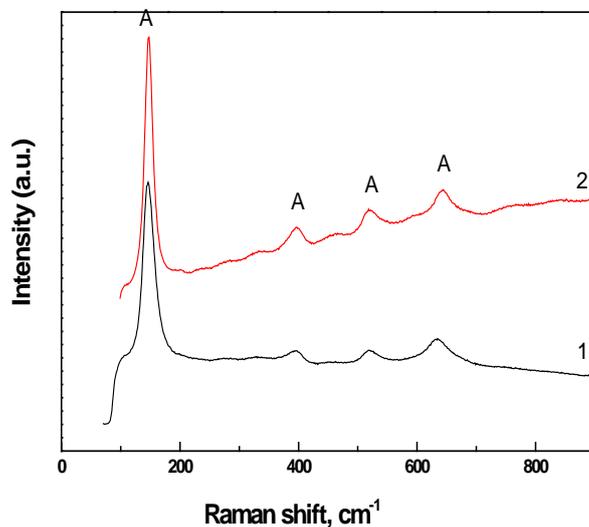
The phase composition of the samples was studied by X-ray diffraction (XRD) with CuK<sub>α</sub>-radiation (Philips PW 1050 apparatus). The composition and electronic properties of the films were investigated by X-ray photoelectron spectroscopy (XPS). The measurements were performed in VG ESCALAB II electron spectrometer using AlK<sub>α</sub> radiation with energy of 1486.6 eV. The binding energies were determined with an accuracy of ±0.1 eV utilizing the C1s line at 285.0 eV (from an adventitious carbon) as a reference. The chemical composition of the films was investigated on the basis of peak areas and binding energies of O1s, Ti2p and Cl2p photoelectron peaks (after linear subtraction of the background and Scofield's photoionization cross-sections). The Raman spectra were obtained using a LabRAMHR visible single spectrometer.

### 2.3. Photocatalytic tests

The photocatalytic experiments were conducted with powerful visible-light irradiation source (TUNGSRAM 500W lamp). The TiO<sub>2</sub> coated substrate was placed into the vessel and covered completely with 150 ml solution of Reactive Black 5 dye with 20 ppm concentration and stirred continuously with a magnetic stirrer at a constant magnetic stirring rate (400 rpm) under oxidative conditions at room temperature. 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.

## 3. Results and discussion

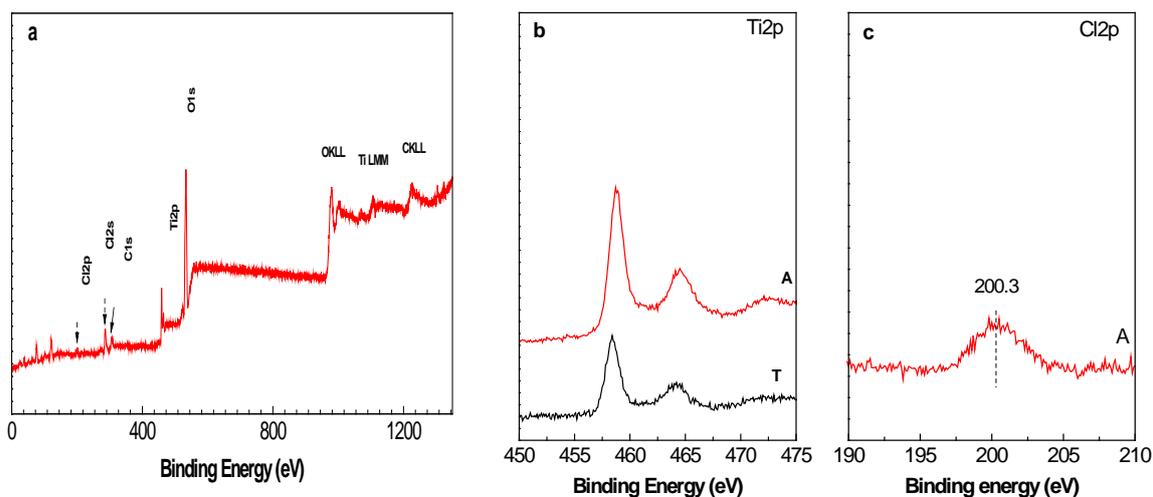
We have applied Raman spectroscopy for more precise phase analysis, because this technique is more surface sensitive, while XRD is applied for bulk analysis. The Raman spectra of non activated and acid activated TiO<sub>2</sub> films have shown the presence of anatase phase (figure 1).



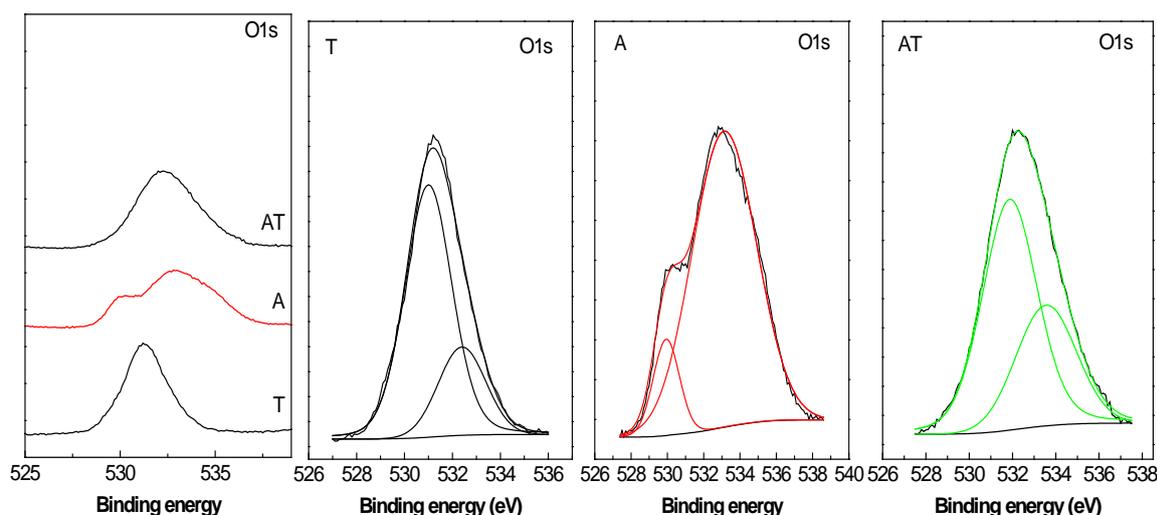
**Figure 1.** Raman spectra of non activated (1) and acid activated (2) TiO<sub>2</sub> film.

According to the literature the main bands of anatase monocrystal were registered at 144, 197, 320, 399, 519, 639 cm<sup>-1</sup> [13]. It has to note that the anatase main bands of the T films are broadened and high frequency shifted with respect to the values of bulk crystal due to the lack of long range order, which is typical for nanocrystalline materials [14]. The X-ray diffraction analyses have proved that the main phase in the films is the anatase and the acid modification leads to a better crystallization of A and AT films. The crystallites size of T, A and AT films are 20 nm, 18 and 17 nm, respectively.

According to the XPS analyses the films are non-stoichiometric and on their surface are present hydroxyl groups, which were proved by the deconvolution of the O1s peaks.



**Figure 2.** (a) XPS survey spectrum of acid treated TiO<sub>2</sub> films; (b) Ti2p core level spectra of the films T, A and AT; (c) Cl2p photoelectron spectrum of acid treated TiO<sub>2</sub> films.



**Figure 3.** Deconvolution of the O1s photoelectron spectra of non activated (T), acid treated (A) and acid activated and thermally treated at 400°C (AT) films.

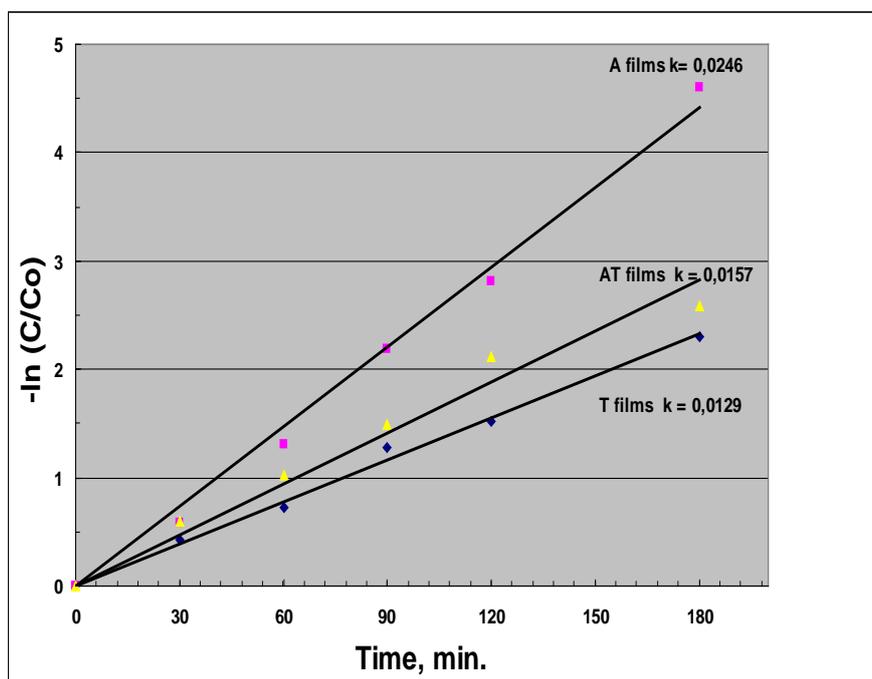
Figure 2 shows the XPS survey spectrum, Ti2p core level spectrum of non treated and acid treated TiO<sub>2</sub> films and Cl2p photoelectron spectrum of acid treated TiO<sub>2</sub> films. The Ti2p spectra of sample T and A are sharp and symmetric and have a maximums at 458.4 eV and 458.8 eV, respectively, typical for TiO<sub>2</sub>. For sample AT the concentration of titanium strongly reduces. The presence of chlorine at 200.3 eV was registered for acid activated samples (figure 2-c). Figure 3 shows the deconvolution of the O1s photoelectron spectra of the TiO<sub>2</sub> films, obtained by different treatments. The O1s peaks are wide and asymmetric and deconvoluted by Lorentzian–Gaussian curve fitting into two components [15]. The first component with the lower binding energy is attributed to O<sup>2-</sup> ions in the TiO<sub>2</sub> lattice and the second one with the higher binding energy is ascribed to oxygen atoms in hydroxyl groups. The shape of O1s peaks for not activated films and acid activated films is different, showing that the amount of adsorbed OH<sup>-</sup> groups is increased for samples A. After temperature treatment at 400°C amount of OH<sup>-</sup> groups is decreased (sample AT).

The reaction kinetics is represented by plotting the natural logarithm of the concentration ratio as a function of the illumination time. The experimental results show that the photocatalytic decoloration of the dye with the films under UV-light irradiation follows a pseudo first order reaction kinetics, expressed by the equation:

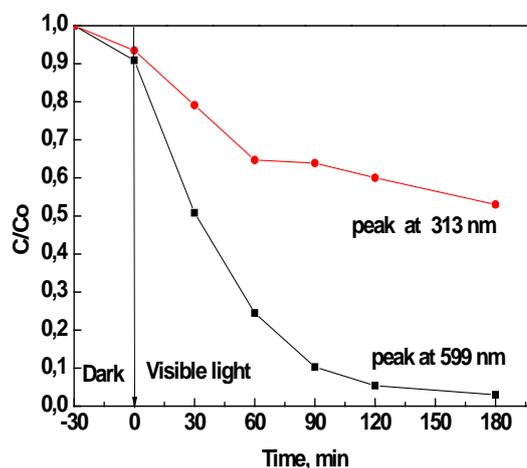
$$\ln(C/C_0) = -kt \quad (1)$$

where  $C_0$  is the initial concentration of the dye,  $C$  is the concentration of the dye after irradiation during a selected time interval  $t$  and  $k$  is the rate constant.

The photocatalytic studies have proved that the kinetic curves for RB5 degradation follow the pseudofirst order kinetics of the Langmuir - Hinshelwood model as confirmed by plotting of  $\ln(C/C_0)$  vs reaction time  $t$ . (figure 4). A straight line with  $R^2$  (correlation coefficient) higher than 0.9 is obtained. It can be seen that the activated TiO<sub>2</sub> films show higher photocatalytic activity than non activated films. The thermal treatment after acid activation has strong influence on the photocatalytic efficiency. Samples A possess faster rate of dye degradation than AT films. The photocatalytic behavior of the acid activated films can be explain as follows: (i) Surface of the TiO<sub>2</sub> films is protonized as a result of the treatment with HCl. The amount of OH groups on the surface considerably increase (as was proved by XPS analysis) in order to maintain the equilibrium OH/H<sup>+</sup> and the photocatalytic degradation of the dye increases [11]. (ii) the presence of Cl<sup>-</sup> on the surface of activated TiO<sub>2</sub> films leads to more efficient degradation of the dye in the visible region due to the red shift. Xu et al. [16] have found that the doping of chlorine resulted in red shift of absorption and higher acidity, which were the reasons for higher photocatalytic activity.



**Figure 4.** Kinetic curves of RB5 degradation for TiO<sub>2</sub> films, non activated (T), activated in HCl and dried at 100°C(A), activated in HCl and treated at 400°C (AT).



**Figure 5.** Concentration changes vs time of illumination for samples A, for the peak at 599 nm (corresponding to azo-bond) and at 313 nm (corresponding to naphthalene-ring).

The photocatalytic measurements have shown that the adsorption peaks corresponding to the N=N bond (at 599 nm) and to naphthalene rings (at 313 nm) decrease with the time (figure 5). The peak at 313 nm not only diminishes, but it is shifted to lower values with the time, due to the destruction of naphthalene structure. The plot C/C<sub>0</sub> versus time (where C<sub>0</sub> and C are initial absorbance

and absorbance of the photolyzed solution at time  $t$ , respectively) displayed a considerably degradation rate for azo groups. The stability of the unsaturated six-membered ring leads to slower rate of degradation.

#### 4. Conclusions

The effect of HCl acid activation of TiO<sub>2</sub> nanosize sprayed films on their photocatalytic efficiency was investigated. One part of the samples was dried (A) and another was annealed (AT) in air. The photocatalytic degradation of Reactive Black (RB5) textile dye under visible light was tested. The activated films are better crystallized than non activated TiO<sub>2</sub> films. The acidic activated films exhibited higher rate of dye photodegradation than reference TiO<sub>2</sub> sample. This photocatalytic behavior can be explain as follows: (i) Surface of the TiO<sub>2</sub> films is protonized as a result of the activation with HCl. The amount of OH groups on the surface considerably increase (as was proved by XPS analysis) in order to maintain the equilibrium OH/H<sup>+</sup> and the photocatalytic degradation of the dye increases and (ii) the presence of chlorine on the surface of activated TiO<sub>2</sub> films leads to more efficient degradation of the dye in the visible region due to the red shift.

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