ПЛОВДИВСКИ УНИВЕРСИТЕТ „ПАИСИЙ ХИЛЕНДАРСКИ“ – БЪЛГАРИЯ
НАУЧНИ ТРУДОВЕ, ТОМ 38, КН. 5, 2011 – ХИМИЯ
UNIVERSITY OF PLOVDIV „PAISII HILENDARSKI“ – BULGARIA
SCIENTIFIC PAPERS, VOL. 38, BOOK 5, 2011 – CHEMISTRY

DECOLORIZATION OF REACTIVE BLACK 5 DYE ON TIO$_2$ HYBRID FILMS DEPOSITED BY SOL GEL METHOD

V. Blaskov[1,]*, I. Stambolova [1], M. Shipochka [1],
S. Vassilev[2], N. Kaneva[3], A. Loukanov[4]

[1] Institute of General and Inorganic. Chemistry, BAS,
Acad. G.Bonchev St, bl.11, 1113 Sofia, Bulgaria, vblaskov@abv.bg

[2] Institute of Electrochemisty and Energy Systems, BAS,
Acad. G.Bonchev bl. 10, 1113, Sofia, Bulgaria

[3] Laboratory of Nanoparticle Science and Technology,
Faculty of Chemistry, University of Sofia,
1 J. Bourchier Blvd., 1164 Sofia, Bulgaria

[4] Dept. of Engineering geoecology,
University of Mining and Geology, St. Edrev St.,
1700 Sofia, Bulgaria

ABSTRACT

Photocatalytically active TiO$_2$ films were successfully prepared by sol gel method. The solutions as well as suspensions enriched with Degussa P25 powder were spin coated on glass substrates. The phase composition and crystallite size of the films were characterized by means of X-ray diffraction (XRD). The morphology and chemical composition were studied by Scanning Electron Microscopy (SEM) and X-ray Photoelectron Spectroscopy (XPS). The XRD spectra of TiO$_2$ thin films annealed at 400° C showed a formation of nanosize anatase phase. The decoloration of Reactive Black 5 (RB5) dye, used in the textile industry was investigated at different pH range. The pH of the dye solution influences significantly the photocatalytic properties of TiO_2 films. The films, obtained from suspensions by microwave-assisted drying and/or conventional heating have a rate of the RB5 degradation compatible with those of conventionally treated TiO_2 films.

Key words: *TiO_2 films, photocatalysis, sol gel, hybrid films, azo dye*

INTRODUCTION

Nanosized TiO_2 thin films have many different applications as photocatalysts [1–3], gas sensors [4–6], ceramic membranes [7], optical filters [8] etc. Sol gel method, spray pyrolysis and chemical vapor deposition are widely applied for the preparation of TiO_2 thin films. The sol gel method has many advantages over the other methods due to the possibility of producing materials with controlled porosity, phase and chemical composition on different substrates at relatively low temperatures [9–11]. However, it is difficult to prepare films without cracking. Prominently, the sol gel polymer/inorganic hybrid route is attractive and capable of producing homogeneous crack free films with variety of microstructures.

Only several authors reported about the deposition of composite TiO_2 films using a polymeric matrix which implies hydrolysis and condensation of titanium tetraethoxyde in the presence of hydroxypropylcellulose (HPC) or methylcellulose [4,12,13,14]. Recently our team has proposed a new modified sol–gel processing using $TiCl_4$ and dyethylaminoethylcellulose (DEAE) for the preparation of an oriented pure brookite film [15]. The ethylcellulose, (EC) used in the present study as a polymer modifier, is a long chain and abundant in R-OH and R-O-R bonds. So it can be useful for the enhancement of homogeneity of metal ions in the precursor and thus for preventing the aggregation of particles during the heating.

The hybrid thin films prepared from suspensions of titanium precursor solutions with Degussa P25 powder seem also very promising photocatalysts probably due to the high photocatalytic activity of P25.

We present in this paper the results concerning the preparation of TiO_2 thin films by sol-gel method using solutions and suspensions, deposited onto glass substrates and study the photocatalytic properties of the films.

EXPERIMENTAL

The glass substrates (26 mm x 76 mm) were cleaned 10 min with ethanol in the ultrasonic bath. Finally they were dried in the furnace at 200°C for 10 min. Two titanium precursor solutions were applied: (i) Titanium tetrachloride $TiCl_4$, (Merck, 98%) dissolved in ethanol (*sol A*) and (ii) alcoholic solution (EtOH–98% purity) of titanium tetraisopropoxide (TTIP) (98% purity, Acros) hydrolized with water-ethanol mixture in a molar ratio $TTIP:H_2O:C_2H_5OH=1:1:30$. Acetyl acetone was added as a complexing agent. The as prepared solution was titled *sol B*. Ethylcellulose $[C_6H_7O_2(OC_2H_5)_3]_n$ solution (1 wt%) dissolved in ethanol and was stirred 24h (*sol C*). This solution was added to *sol A or sol B* under vigorous 3 h stirring.

In order to obtain titania hybrid films powder TiO_2 Degussa P25 (75% anatase and 25% rutile) was used. This powder was added under vigorous stirring to $Ti(OBu)_4$ dissolved in butanol to obtain suspension.

The solutions/suspensions were deposited by spin coating at 1500 rpm. Each coating was treated by different manners. The films deposited from titanium precursor solutions were treated according to path A, while the hybrid films, obtained from suspensions with P25 were treated according to path A, B and B-C. (Fig. 1)

The phase composition and crystallites size of the samples were 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). The measurements were performed in VG ESCALAB II electron spectrometer using AlK_α radiation. A scanning electron microscope (SEM) JSM-5510 of JEOL was used for morphology observations of the films.

The photocatalytic experiments were conducted using an ultraviolet source (UV lamp) with light intensity 5.10^{-5} W/cm^2 located in the centre of a photocatalytic reactor. The latter contained 10 ppm water solution of the RB5. The photocatalytic degradation is evaluated with spectrophotometer type Boeco S26 (the wavelength range from 200 to 1100 nm). The pH of the solutions was adjusted using concentrated HCl before the experiments.

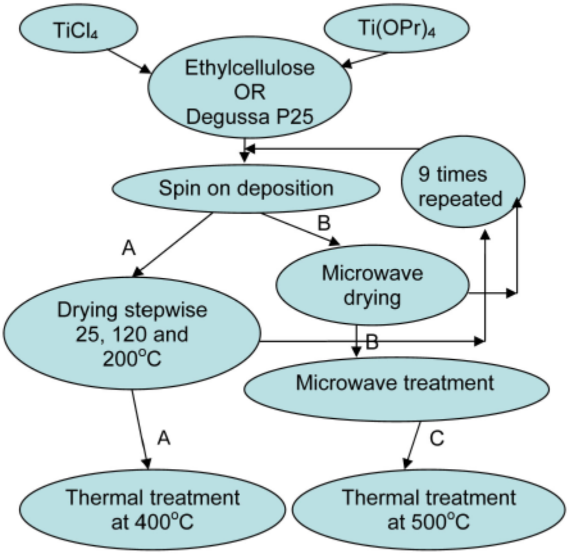


Figure 1. *Scheme of the experimental procedures*

RESULTS AND DISCUSSION

Fig. 2 illustrates XRD patterns of the TiO_2 thin films. The peaks clearly indicate the presence of anatase (crystalline) phase of TiO_2. 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 equation:

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

where D is the crystallite size (nm), λ is the wavelength of CuKα radiation (nm), θ is the Bragg angle (°), K is a constant (0.89) and B is the calibrated width of a diffraction peak at half-maximum intensity (rad).

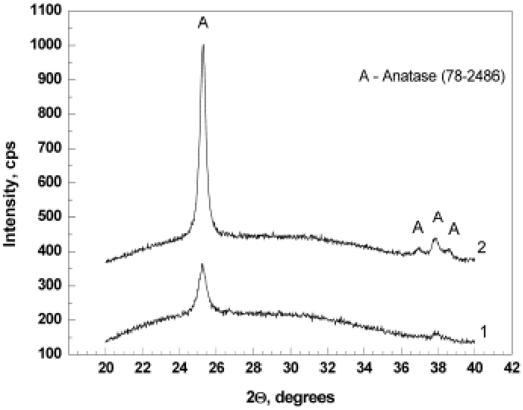


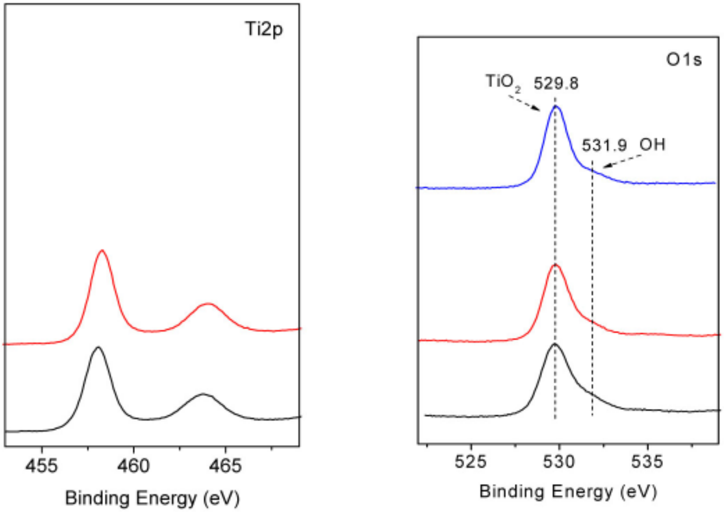
Figure 2. *XRD of TiO_2 films obtained from: $Ti(OPr)_4$ /EC (1) and $TiCl_4$/EC (2) solutions*

The average crystallite size of the thin films as determined from half width of full maximum (HWFM) intensity of the (101) peak of the films, obtained from $Ti(OPr)_4$/EC and $TiCl_4$/EC solutions are: t_{101}=16.1 nm and t_{101}=22.8 nm, respectively.

The typical XPS spectrum of the TiO_2 films contains two peaks corresponding to states Ti $2p_{1/2}$ and Ti $2p_{3/2}$ (Fig. 3a). These energies correspond to the Ti^{4+} state. In the range of the O 1s state the peak at 529.8 eV corresponds to the state of the oxygen atom O^{2-} in the TiO_2 oxide. 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. The presence of OH – group is characteristic of the TiO_2 catalysis with developed specific area. The chemical composition of the films obtained from both titanium precursor solutions as well as corresponding O/Ti relations (in atomic percent) are shown in Table 1.

Table 1 *Chemical composition of the TiO_2 films, according to XPS analyses*

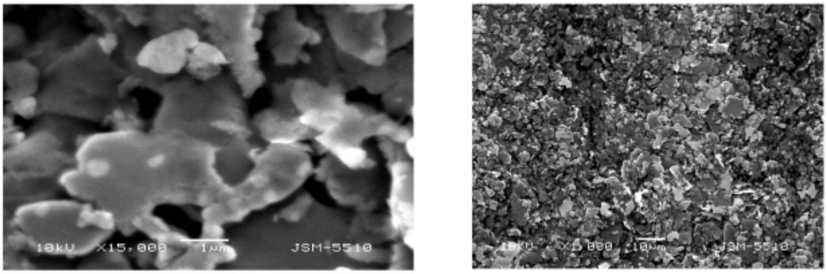
Solution composition	C [at.%]	O [at.%]	Ti [at.%]	Si [at%].	O/Ti
$TiCl_4$/EC	27.9	50.8	18.0	3.3	2.82
$Ti(OPr)_4$/EC	20.9	56.9	22.2	-	2.56



a **b**

Figure 3. *XPS spectra of Ti2p line (a) and O1s line (b) of* TiO_2 *sol gel layers*

The SEM micrographs of the films form $TiCl_{4,}$ treated at 400°C is shown in Fig. 4. The films posses flake like structure, which consists of fine particles agglomerates



a **b**

Figure 4. *Morphology of* TiO_2 *films with 9 successive coatings from* $TiCl_4$ *and ethylcelulose, treated at 400°C, magnification 15000 (a) and 1000 (b)*

The films have slightly different chemical composition. The samples prepared from $TiCl_4$/EC solution contain also small quantity of Si ions. Probably in the analyzed spot of the monochromatic X-rays the films are thinner. Consequently in the final composition we were observed ions from the substrate. This could be explained by interaction of the substrate with the films after thermal treatment, similarly to the previously obtained by us ZrO_2 [16] and TiO_2-SnO_2 films [17].

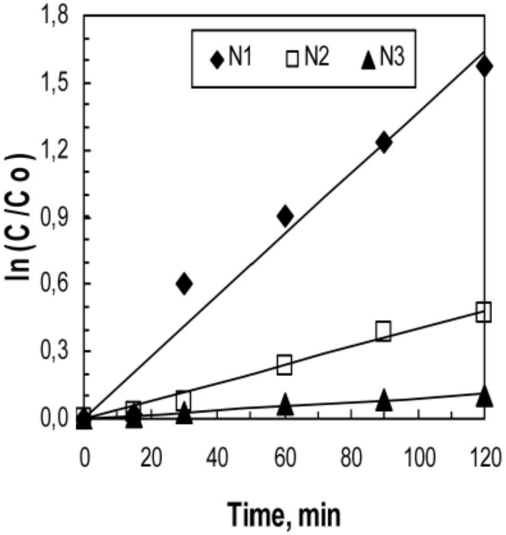


Figure 5. *Kinetic curves of RB5 decolorization in coordinates – ln(C/Co) =f (t) for films, deposited from Ti(OPr)$_4$/EC at different pH: pH=2 (N1), pH=4(N2) and pH=6(N3)*

The kinetic curves of RB5 decoloration on the TiO_2 films (where C_o is initial concentration of RB5), deposited from $Ti(OPr)_4$ and $TiCl_4$ solutions at different pH of the dye solution under UV radiation are shown in Fig. 5 and Fig. 6. The degradation of the dye enhances with decreasing of the pH. This tendency is valid for the films obtained from both titanium precursor solutions. Similar dependence of degradation rates *vs* pH of the azo dye by TiO_2 powders is proved by Augugliaro et.al. [18]. 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) or the surface charge of the photocatalyst used. The surface charge of TiO_2 is zero or neutral in the pH range of 4.5–7.0 according to [19]. At PZC of TiO_2, the interaction between the photocatalyst particles and water contaminants is minimal due to the absence of any electrostatic force. At low pH (pH < pHpzc), TiO_2 particles possess positive charge, while a negative charge is expected at higher pH (pH > pHpzc). The majority of the reactive dyes possess water solubilizing sulphonic ($-SO_3^-$) groups which are negatively charged. Therefore, acidic conditions would favor the electrostatic attraction between the positively charged TiO_2 surface and the sulphonic groups of the dyes, which would results in increased absorption and degradation of dyes.

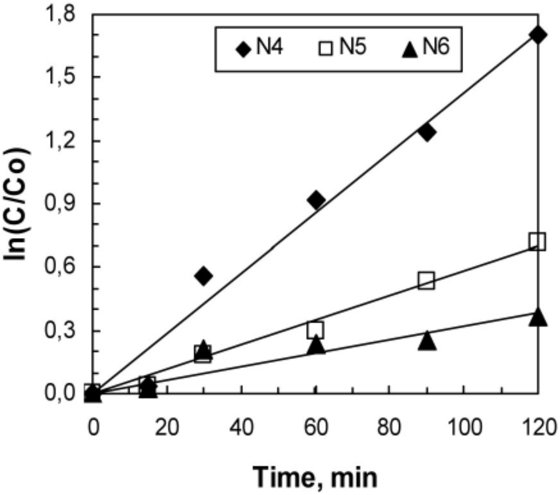


Figure 6. *Kinetic curves of RB5 decolorization in coordinates – ln(C/Co) =f (t) for films, deposited from $TiCl_4$/EC at different pH=2(N4);pH=4(N5);pH=6 (N6)*

The photocatalytic properties of hybrid TiO_2 films are presented on Fig 7. It was established that the drying/heating way of the films influences significantly their characteristics. When the microwave oven is used in drying and heating stage the films relatively slow degrade the dye, may be due to the incomplete incineration of the organics and low degree of crystallization. The films, dried in microwave oven and treated conventionally showed photocatalytic behaviour similar to those, obtained by conventional treatment. Application of microwave heating in sol gel method seems promising way to obtain photocatalytic active films at reduced temperatures and time, giving possibility to use substrates with low thermal stability (plastic etc.).

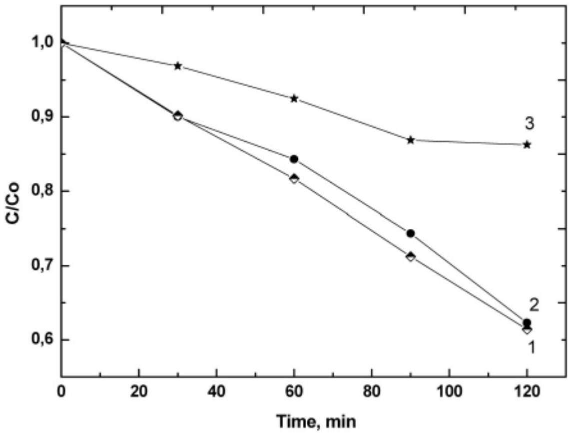


Figure 7. *Kinetic curves of RB5 decolorization in coordinates C/Co =f (t) for hybrid films, deposited from suspensions Ti(OPr)$_4$ – Degussa P25 by: conventional drying and treatment at 500^o (1), microwave drying and conventional treatment at 500^{o}C (2) and microwave drying and treatment (3).*

CONCLUSIONS

Thin TiO_2 photocatalytic active films were obtained from polymer modified solutions and suspensions. The films treated at 400◦C possess nanosize anatase phase.

It was established that the acidity of the dye solution influences significantly the photocatalytic activity towards degradation of the azo dye Reactive Black 5. The catalysts degrade faster the dye in acidic than in neutral medium. The films deposited from $TiCl_{4,}$ showed better activity than the films, obtained from titanium iso-propoxide solutions.

The TiO_2 hybrid films, obtained from suspensions and treated under microwaves, following by conventional treatment revealed degradation rate compatible with those of conventionally treated films. The TiO_2 thin films prepared by us are promising as efficient photocatalyst for degradation of Reactive Black 5 azo dye.

ACKNOWLEDGEMENTS

The authors thank to the Bulgarian Ministry of Science and Education for the financial support by project DVU 02/36 (2010).

REFERENCES

1. Dong F.,W. Zhao, Z. Wu, S.Guo, J. Hazard. Mater., 162, 2009, 163.
2. Saylikan F., M. Asiltürk, N.Kiraz, E. Burunkaya, E. Arpaç, H. Sayılkan, J. Hazard. Mater., 162, 2009, 1309.
3. Yu J., X. Zhao, Mater. Res. Bull., 35, 2000,1293.
4. Garzella G., E. Comini, E.Tempesti, C. Frigeri, G. Sberveglieri, Sens Act. B, 68, 2000, 189.
5. Ruiz M., G. Sakai, A. Cornet, K. Shimanoe, J. R. Morante, N. Yamazoe, Sens. Act. B, 93, 2003, 509.
6. Liu H.-M.,Ch-H Keng, Ch.-Y Tung, Nanostr. Mater., 9, 1997,747.
7. Yan Y., S. R. Chaudhuri, A. Sarkar, J Amer. Ceram. Soc.,79, 1996, 1061.
8. Zhai J.,T. Yang, L. Zhang, X. Yao, Ceram. Int., 25, 1999, 667.
9. Brinker C. J., M. S. Harrington, Sol. Energy Mater. Soll. Cells 5, 1981, 159.
10. Vicente G. S., A. Morales, M. T. Gutierrez, Thin Solid Films 391, 2001, 133
11. Fan Q., B. McQuillin, A. K. Ray, M. L. Turner, J. Phys. D, Appl. Phys., 33, 2000, 2683
12. Кim K., H. Kim, J. Eur. Ceram. Soc. 23, 2003, 833

13. Nagpal V., R. Davis, S. Desu, J. Mater. Res.,10, 1995, 3068.
14. Habibi M. H., M. Nasr –Estafani, T.A. Egerton, J. Mater. Sci. 42, 2007,6027
15. Kuznetsova I. N., V. Blaskov, I. Stambolova, L. Znaidi, A. Kanaev, Mater. Lett. 59, 2005, 3820
16. P. Peshev, I. Stambolova, S. Vassilev, P. Stefanov, V. Blaskov, K. Starbova, N. Starbov, Mater Sci. Eng. B 97,2003, 106.
17. I. Stambolova, V. Blaskov, S. Vassilev, M. Shipochka, C. Dushkin, J Alloys Comp. 489,2010, 257.
18. Augugliaro V., C. Baiocchi, A.B. Prevot, E. Garcia-Lopez, V. Loddo, S. Malato, G. Marci, L. Palisano, M. Pazzi, E. Pramauro, Chemosphere, 49, 2002, 1223
19. Chong M. N., B. Jin, Ch. W. K. Chow, Ch. Saint, Water Research 44, 2010, 2997.