

SYNTHESIS AND ACTIVITY OF BI-LAYER TiO₂/WO₃ PHOTOCATALYTIC COATINGS PREPARED BY PULSED CATHODIC ELECTRODEPOSITION

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Abstract: Bi-layer TiO₂/WO₃ coatings (0.4mg/cm² TiO₂ / 0.9mg/cm² WO₃) were prepared by consecutive cathodic electrodeposition in a three-electrode cell on stainless steel (SS) plate specimens (geometric surface area 17.3 cm²), using a platinum counter-electrode and a mercurous sulphate electrode (MSE) as a reference electrode. The coatings were synthesized by the pulsed electrodeposition technique (cathodic pulse time t_{on} was 5 ms) from peroxytungstate and titanium oxosulphate acidic mixed water:ethanol solutions (ratio 1:1). The photocatalytic activity of the coatings was tested in a flat-plate gas-phase continuous flow POLITEF reactor exposing illuminated surface area of 48 cm². The reactor is equipped with a quartz flat-plate illumination window allowing the use of UV-light or visible light with an option to vary the distance to the light source (the illumination intensity). Ethylene was used as a model air pollutant at a feed concentration of 1000 ppm. The C₂H₄ conversion degree was accepted to be the measure of the photocatalytic activity. The highest photocatalytic activity was achieved at the maximum ethylene contact time, when the reaction is occurring in the kinetic region and at optimal 30% humidity of the feed. The contribution of the WO₃ component, activated by visible light, to the overall photocatalytic activity amounts to about 15%.

Keywords: Photocatalytic coatings, electrodeposition, titania, tungsten oxide

1. Introduction

The efforts of both the academic community and the industry in the field of photocatalysis are focused in direction to utilize visible light. One of the promising future alternatives to using pure TiO₂, applied nowadays and activated only by UV light (only 4% of the solar spectrum), is combining the effects of two semiconductors – a wide band gap (TiO₂) and a narrow band gap semiconductor. A series of narrow band gap oxide and sulfide semiconductors have been tested in this respect [1,2]. The present work investigates the option to use TiO₂ and WO₃ layers, synthesized electrochemically, where WO₃ is the narrow band gap semiconductor ($\Delta E = 2.8$ eV, activated by visible light [3]). Among the variety of techniques, used for coating TiO₂ and WO₃ films on various supports, electro-synthesis has also been proposed for preparing TiO₂ and WO₃ bi-layer coatings on stainless steel electrodes as substrates [4-6].

Bi-component WO₃ and TiO₂ materials have shown enhanced UV photocatalytic and photoelectrocatalytic activity with respect to their single component analogues, since their valence and conduction band energy diagrams favour electron injection from the conduction band of TiO₂ to that of WO₃ and hole transfer between valence bands in the opposite direction (Fig. 1) thus enabling their

separation [7]. This, in its turn, reduces electron-hole recombination in the composite material [7-13].

Using pulsed electrodeposition, instead of continuous electrodeposition, coatings having more developed surface area (and consequently enhanced photocatalytic activity) can be obtained. Coating by pulsed electrodeposition, which utilizes short-time-interval potential pulses to nucleate particle growth, provides the possibility to deposit porous, nanoparticulate films of high surface area [14].

An additional way to modify the morphology as well as to improve the stability of the deposition solution is the partial or complete replacement of water by organic solvent [15].

In this respect our aim was to synthesize bi-layer TiO₂/WO₃ porous coatings with high surface area by pulsed electrodeposition and to test their photocatalytic activity under UV and visible light irradiation in the presence of model air pollutant ethylene, evaluating the contribution of the WO₃ component (activated by visible light) of the photocatalytic material to the overall photocatalytic activity.

2. Experimental

Bi-layer TiO₂/WO₃ coatings (0.4 mg/cm² TiO₂/0.9 mg/cm² WO₃) were prepared by consecutive cathodic electrodeposition in a three-electrode cell on stainless steel (SS) plate specimens (17.3 cm²), using Pt as a counter electrode and mercurous sulphate (MSE) reference electrode. An Autolab 30 potentiostat/galvanostat (EcoChimie) was employed. Before the electrosynthesis procedure the SS specimens were degreased ultrasonically in acetone and etched in a 1:1 HCl/H₂O mixture for 60 s.

The bi-layer coatings were synthesized by pulsed electrodeposition from mixed solutions (water : ethanol ratio 1:1) of peroxytungstate and acidic titanium oxosulphate, respectively. Square wave form pulses were ap-

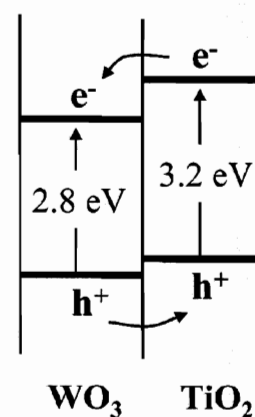


Figure 1. Energy diagram of WO₃ and TiO₂ particles in contact, showing corresponding valence and conduction band positions and UV-photogenerated hole and electron transfer and charge separation.

plied with a duty cycle of 0.5, i.e., the same length time interval was used for t_{on} (cathodic pulse time: 5 ms) as well as for t_{off} (time interval between pulses).

WO_3 was deposited by pulsed electrodeposition between -0.5 V and -1.00 V vs. MSE for 30 min from a bath pH=1.4 containing 0.025 M Na_2WO_4 ($\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$; Merck; pro analysis; >99%), 0.03 M H_2O_2 (30% aqueous solution) and 0.05 M HNO_3 (Riedel, 65%).

TiO_2 was electrosynthesized in a subsequent step onto WO_3 -SS electrodes by pulsed electrodeposition between -0.5 V and -2.00 V vs. MSE for 30 min from a solution of pH=1.4 containing 0.02 M TiOSO_4 (Fluka; Assay of Ti (as TiO_2) techn., >29%), 0.03 M H_2O_2 (30% aqueous solution), 0.05 M HNO_3 (Riedel, 65%) and 0.1 M KNO_3 (Merck, pro analysi, >99%).

After deposition of WO_3 , the samples were heated in air at 350°C for 0.5h for crystallization and the final calcination of the bi-layer TiO_2/WO_3 coatings was at 400°C for 1h in air.

Scanning electron microscopy (SEM) was performed using a JSM 733 microscope equipped with an EDS facility to give surface morphology and particle size.

The conditions of the photocatalytic activity testing were the following. The construction of the POLITEF photocatalytic reactor allowed using either UV light or visible light but not the two kinds of illumination simultaneously. In the case of UV light illumination 2 Philips BLB lamps were used (4 watts each one, UV-A polychromatic radiation 320–400 nm with $\lambda_{\text{max}}=365$ nm) or 2 Philips TUV lamps (4 watts each one, the UV-C mono-

chromatic radiation is $\lambda=254$ nm). The lamps were accommodated in the reactor nest above the quartz flat-plate illumination window – at zero distance between the source and the window the illumination intensity is fixed at 0.016 watts/cm² using Al foil reflector. In the case of visible light illumination one Tungsham linear halogen lamp of 500 watts was used giving maximum intensity at zero distance 10.4 watts/cm². An optimal relative humidity of the feed – 30%, established in previous experiments [2] was applied for all the experimental runs. Ethylene was used as a model air pollutant in areas around petrochemical plants and a realistic value of 1000 ppm C_2H_4 for the feed concentration was achieved in the experiments, the oxygen in the feed being in large stoichiometric excess. A maximum contact time of 4 minutes enabled achieving the highest possible ethylene conversion degree (accepted as a measure of the photocatalytic activity), operating in the kinetic region with a laminar flow kind of reactor [16].

3. Results and Discussion

Microscopic characterization of coatings

The SEM micrographs of the obtained bi-layer TiO_2/WO_3 coatings are shown in Figs. 2 and 3. Two different magnifications are shown. The morphology of these coatings is completely different from that of the samples electrosynthesized by continuous electrodeposition from water solution [4,6]. In the back-scattered (BEI) SEM images (Figs. 2b and 3b) bright area is WO_3 and the dark area is TiO_2 .

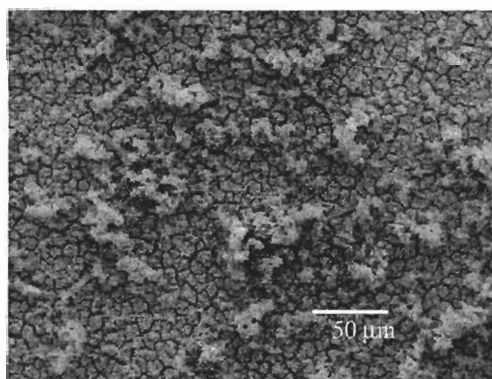


Figure 2a. SEM SEI image of bi-layer TiO_2/WO_3 coating on SS after annealing for 1h at 400°C.

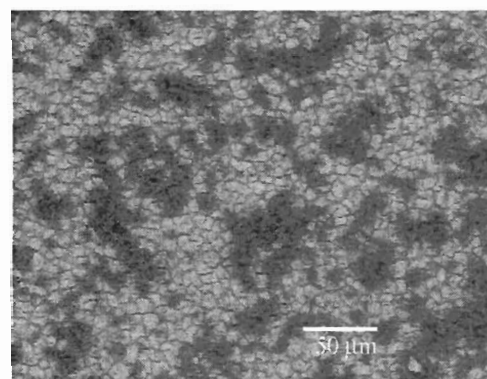


Figure 2b. SEM BEI image of bi-layer TiO_2/WO_3 coating on SS after annealing for 1h at 400°C.

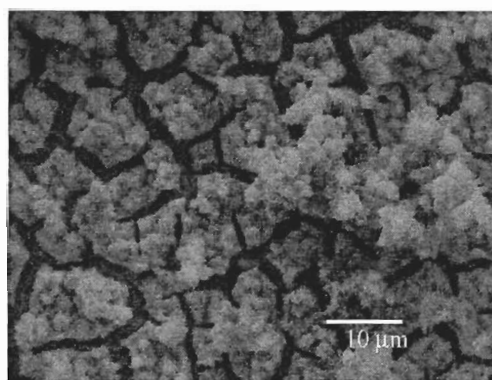


Figure 3a. SEM SEI image of bi-layer TiO_2/WO_3 coating on SS after annealing for 1h at 400°C.

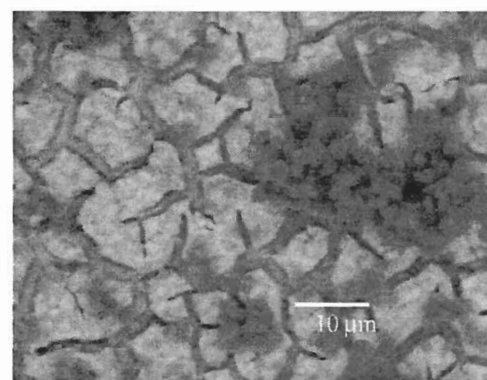


Figure 3b. SEM BEI image of bi-layer TiO_2/WO_3 coating on SS after annealing for 1h at 400°C.

This chemical contrast is due to the higher yield of electrons, back-scattered by the element with greater atomic mass (in our case W). On the top coatings nanometer-sized particles are seen grouped in randomly distributed clusters (Figs. 3a, 3b). The WO₃ under-layer is also particulate with cracks. This morphology is due to the fact that during a single pulse cycle the growth of new small particle nuclei is more favored than growth and coalescence of existing larger particles.

Photocatalytic activity testing

The photocatalytic activity testing was carried out with the newly constructed POLITEF photocatalytic reactor, designed as an improvement of the previous reactor, which was operating only with UV-light. The POLITEF reactor (Figure 4) is equipped with a flat quartz glass

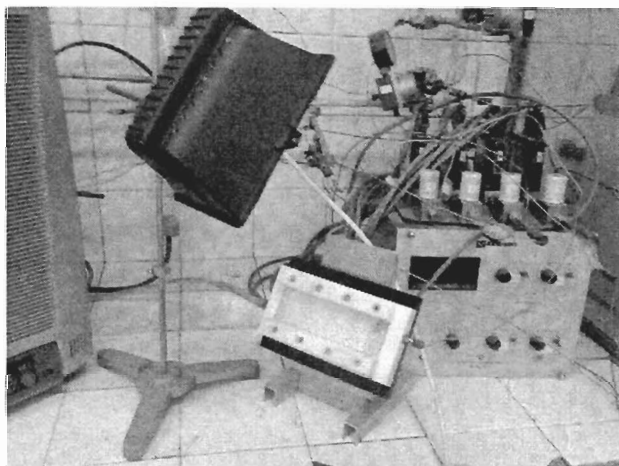


Figure 4.

illumination window, penetrable to both UV and visible light. This enables operation with both kinds of light and characterizing composite photocatalytic materials in regard to their visible light component contribution to the overall photonic efficiency. This reactor belongs to the flat-plate continuous laminar flow reactors (LFR). The time interval for reaching steady state operation conditions and the contact time and photocatalyst loading for achieving kinetic region were the object of another investigation [16]. The present activity testing was carried out in the kinetic region after achieving steady-state conditions of operation. The illuminated surface area is 48 cm². The three kinds of illumination were applied – UV-A, UV-C and visible light artificial illumination. The Tungstam 500 watts lamp was mounted on a stand, which allows varying the distance between the illumination source and the quartz glass illumination window from 0 to 50 cm i.e. varying the illumination intensity (decreasing with the square of the distance). At the closest distance of 20 cm, applied in this study in view of safety precautions (the heat flux, emitted by the lamp is too strong) the illumination intensity was 8.9 watts/cm². Ethylene – air mixtures are potentially dangerous because of their explosiveness upon heating. Ethylene is selected as model air pollutant as this is a large-scale chemical, produced in petrochemical works, polluting the air in industrial sites. A feed concentration of 1000 ppm C₂H₄ was estimated to be realistic

for the air pollution around the Petrochemical works of Bourgas. The maximum contact time of 4 min guarantees carrying out the measurements in the kinetic region. The optimal relative humidity of 30%, established in previous works [16] was used in all the experimental runs. The results are represented in Table 1. Operation with UV-light reveals the activity of the TiO₂ component of the coating – 21.7% conversion with UV-A light, and 10.3% conversion with UV-C light. This result is surprising as the photon energy in the second case is higher. Operating upon visible light illumination reveals the contribution of the WO₃ component of the coating – 3.5% conversion, which means that the share of WO₃ in the overall photocatalytic activity would not be higher than 15% in case of combined UV-vis light illumination.

Table 1. Photocatalytic activity of TiO₂- WO₃ bi-layer coated SS plate at maximum contact time (4 min), optimal humidity 30%, excess of oxygen in the feed upon various illumination and 1000 ppm feed concentration of ethylene

C ₂ H ₄ conversion, %	Kind of illumination	Illumination intensity	Illumination distance
21.7	UV-A	0.016 watts/cm ²	0 cm
10.3	UV-C	0.016 watts/cm ²	0 cm
3.5	Visible light	8.4 watts/cm ²	20 cm

4. Conclusions

1. Bi-layer TiO₂/WO₃ porous coatings with high surface area were synthesized by pulsed electrodeposition from mixed solutions (water vs. ethanol ratio 1 to 1) of peroxytungstate and acidic titanium oxosulphate, respectively.
2. Electrosynthesized TiO₂/WO₃ samples have shown photocatalytic activity both under UV and visible light irradiation in the presence of model air pollutant ethylene. The conversion degree under UV light illumination is higher than that under visible light irradiation.
3. The ethylene conversion degree over the TiO₂/WO₃ porous coatings varies depending on the type of illumination applied and the distance of illumination (respectively intensity of illumination). The highest conversion degree was measured with the UV-A polychromatic illumination at zero distance and highest intensity of illumination 0.016 watts/cm². The contribution of the visible-light-active component WO₃ to the overall photocatalytic activity in case of combined UV-vis illumination would not exceed 15%.

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References

- [1] U. Diebold, *Surface Science Reports*, **48** (2003) 53.
- [2] L. Petrov, V. Iliev, A. Eliyas, D. Tomova, G. Li Puma, *J. Environ. Prot. & Ecology*, **8** (2007) 881.
- [3] V. Keller, P. Bernhardt, F. Garin, *J. Catal.*, **215** (2003) 129.
- [4] J. Georgieva, S. Armyanov, E. Valova, Ts. Tsacheva,

- I.Poulios and S.Sotiropoulos, *J. Electroanal. Chem.*, **585** (2005) 35.
- J.Georgieva, S.Armyanov, E.Valova, I.Poulios and S.Sotiropoulos, *Electrochim. Acta*, **51** (2006) 2076.
- J.Georgieva, S.Armyanov, E.Valova, I.Poulios, S.Sotiropoulos, *Electrochem. Commun.*, **9** (2007) 365.
- M.Miyauchi, A.Nakajima, T.Watanabe and K.Hashimoto, *Chem.Mater.*, **14** (2002) 4714.
- T.He, Y.Ma, Y.Cao, X.Hu, H.Liu, G.Zhang, W.Yang and J.Yao, *J.Phys.Chem. B*, **106** (2002) 12670.
- I.Shiyanovskaya and M.Hepel, *J. Electrochem. Soc.*, **146** (1999) 243.
- J.Luo and M.Hepel, *Electrochim.Acta*, **46** (2001) 2913.
- [11] C.R.Chenthamarakshan, N.R. de Tacconi, K.Rajeshwar and R.Shiratsuchi, *Electrochem.Commun.*, **4** (2002) 871.
- [12] N.R. de Tacconi, C.R.Chenthamarakshan, K.Rajeshwar, T.Pauporte and D.Lincot, *Electrochem. Commun.*, **5** (2003) 220.
- [13] S.Somasundaram, C.R. Chenthamarakshan, N.R. de Tacconi, N.A.Basit and K.Rajeshwar, *Electrochem. Commun.*, **8** (2006) 539.
- [14] S.H.Baeck, T.Jaramillo, G.D.Stucky, and E.W.McFarland, *Nano Letters*, **2** (8) (2002) 831.
- [15] P.K.Shen, J.Syed-Bokhari, and A.C.C.Tseung, *J.Electrochem. Soc.*, **138** (1991) 2778.
- [16] A. Eliyas, K. Kumbilieva, L. Petrov, „Application of various criteria for conditions of operation of photocatalytic reactors using nanosized photocatalyst particles”, in press in „Nanoscience and Nanotechnology” Science Series, Issue 9, Eds. E. Balabanova, I. Dragieva, Academic Publishing House „Prof. Marin Drinov” (2009) 45.