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Structure and Photocatalytic Properties of TiO\textsubscript{2}-WO\textsubscript{3} Composites Prepared by Electrophoretic Deposition

Ineta Liepina\textsuperscript{1}, Gunars Bajars\textsuperscript{1}, Marcis Rublans\textsuperscript{2}, Janis Kleperis\textsuperscript{1}, Andrejs Lusis\textsuperscript{1}, Evalds Pentjuss\textsuperscript{1}

\textsuperscript{1}Institute of Solid State Physics, University of Latvia, Latvia
\textsuperscript{2}Faculty of Physics and Mathematics, University of Latvia, Latvia
liepina.ineta@gmail.com

Abstract. In this work TiO\textsubscript{2}–WO\textsubscript{3} composite films containing different oxide concentrations were prepared by electrophoretic deposition on steel substrates. Composite coating structures were analyzed by X -ray diffraction, Raman spectra and scanning electron microscopy. The results showed an even distribution of WO\textsubscript{3} particles in the entire composite layer. Light absorption measurements were used for photocatalytic properties evaluation. It was found that the removal ratio of methylene blue depends on the (TiO\textsubscript{2}): (WO\textsubscript{3}) concentration ratio. The most effective photodegradation was determined for the sample that was electrophoretically deposited from the suspension with the molar content ratio n(TiO\textsubscript{2}):n(WO\textsubscript{3}) 2:1.

1. Introduction
Due to its photocatalytic capability, low cost and chemically inert properties, TiO\textsubscript{2} is a promising material for water and air contamination treatment technologies [1-3]. Most of investigations have been devoted to the pure TiO\textsubscript{2} films because of its reusability. However, practical application of such films is limited by recombination of photo-induced hole-electron pairs. Coupling TiO\textsubscript{2} with other inorganic oxides such as SiO\textsubscript{2}, SnO\textsubscript{2}, WO\textsubscript{3}, In\textsubscript{2}O\textsubscript{3}, (Sr,La)TiO\textsubscript{3}+\textsubscript{δ} and ZnFe\textsubscript{2}O\textsubscript{4} can increase the energy range of photo-excitation and this will change the photocatalytic efficiency [4].

Electrophoretic deposition (EPD) method has been widely applied to obtain pure TiO\textsubscript{2} thin films as well as doped TiO\textsubscript{2} thin films with transition elements. Advantages of electrophoresis over other coating methods are the homogeneity of thin films on large substrates, as well as better control of particle size and shape [5, 6].

In this work we focus on the preparation of TiO\textsubscript{2}–WO\textsubscript{3} composite film using EPD method. WO\textsubscript{3} is a suitable photo-electron storing material to couple with TiO\textsubscript{2} because WO\textsubscript{3} has a more narrow band gap (3.0 eV) than that of TiO\textsubscript{2} (3.25 eV for anatase) to allow the transfer of photogenerated electrons from TiO\textsubscript{2} to ensure effective charge separation. Photocatalytic properties of coatings were determined with measurements of methylene blue decomposition under UV irradiation.

2. Experimental
The first part of this work includes electrophoretic deposition that was carried out using suspension of pure TiO\textsubscript{2} (Sigma-Aldrich, 98%) or TiO\textsubscript{2}:WO\textsubscript{3} mixtures (molar ratio in suspension 1:1, 2:1, 3:1 and 1:2) in isopropanol (Fluka Analytical, 97%). To improve conductivity of dispersion media, pH of the suspension was adjusted with 1 mL HCl (Fluka Analytical, 98%). Each suspension was sonificated for 30 min. For the electrophoretic growth two 3x3 cm\textsuperscript{2} stainless steel (grade 316)
electrodes were used. Distance between electrodes was 1 cm. A constant voltage of 100 V was applied between the electrodes by DC Power Supply (Agilent Technologies N5772A) and held for 10 min. The deposited coatings were gradually heated (5 ºC/min) and annealed at 500 ºC for 2 h.

Photocatalytic measurements were carried out using methylene blue (MB) solution under UV irradiation. Each sample was placed in 80 mL of 0.43 mg/L MB solution in a quartz beaker and illuminated with Hg lamp from 30 cm distance. Each composite was used to obtain MB solution sample series after 0; 0.5; 1; 3 and 6 hours of photodegradation. Light absorption measurements (Jenway 6300, 1 cm quartz cell) were used to calculate MB concentration after photodegradation had occurred.

3. Results and Discussion
TiO$_2$–WO$_3$ composite films were obtained from suspension with the following n(TiO$_2$):n(WO$_3$) ratio: 1:1 (a), 2:1 (b), 3:1 (c), 1:2 (d) and pure TiO$_2$ (e). The X-ray diffraction (PANalytical X"Pert PRO Cu Ka, $\lambda = 0.15418$ nm) pattern for sample d is shown in Figure 1. Characteristic peaks at 2$\theta$ 25.35°, 48.05°, 54.05° and 55.10° of the composite coating indicate that after thermal treatment TiO$_2$ has crystallized in anatase form with average crystallite size 200 nm (Scherrer equation) and WO$_3$ has monocline structure (characteristic peaks at 2$\theta$ 23.72° and 33.65°) with crystallite size 80–90 nm.

![Figure 1. X-ray diffraction pattern of annealed d sample composite on a steel substrate](image)

The concentration of WO$_3$ in the obtained composites was also determined from X-ray diffraction patterns - 18.2 wt.% (a), 17.8 wt.% (b), 16.6 wt.% (c) and 19.9 wt.% (d). As it is seen, the coating compositions don’t have the same TiO$_2$:WO$_3$ ratio as their corresponding suspensions. This might be caused by the van der Waals force that affected coagulation of WO$_3$ particles near the electrode.

Figure 2 shows the Raman spectrum of annealed composite coating. The vibrational bands at 150 cm$^{-1}$ ($E_g$), 400 cm$^{-1}$ ($B_{1g}$), 515 cm$^{-1}$ ($A_{1g}$) and 633 cm$^{-1}$ ($E_g$) confirm phase transition of
electrophoretically deposited TiO$_2$ to anatase phase [6]. The bands sited at 274, 327, 716 and 806 cm$^{-1}$ are typical Raman peaks of crystalline WO$_3$ of monoclinic phase [7].

![Raman spectrum of annealed composite coating of sample b](image)

**Figure 2.** Raman spectrum of annealed composite coating of sample b

Scanning electron microscopy (SEM) images in Figure 3 show the cross-section and surface of c (top row) and d (bottom row) using both – scattered and back scattered detectors for imaging. As it is seen, c and d samples show an even distribution of WO$_3$ particles (seen as bright spots because of stronger backscattering) in the entire composite layer. This was observed as a common trend for all the composite samples.

![SEM images of composite coatings of c (top row) and d (bottom row) samples annealed at 500 °C](image)

**Figure 3.** SEM images of composite coatings of c (top row) and d (bottom row) samples annealed at 500 °C
Figure 4 shows that the size of WO$_3$ crystallites can be estimated about 200–400 nm, while X-ray diffraction showed notably lower crystalline size.

![SEM images of composite coatings](image)

**Figure 4.** SEM images of composite coatings c (left) and d (right) annealed at 500 °C

Photocatalysis graph (Figure 5) shows that in the first hour photo degradation occurs at a slower rate. This can be explained with the absorption and dissociation of water molecules in contact with oxygen bridges in TiO$_2$ structures. Only after reduced oxygen was formed on composite surface the noticeable photodegradation of MB was observed. As expected a sample of clear stainless steel substrate (control) has no effect on MB decomposition. Most effective photodegradation occurred with the sample b (n(TiO$_2$):n(WO$_3$) ratio = 2:1) with the resulting content of WO$_3$ 17.8 wt.% - after 6 hours of UV irradiation MB had decomposed to less than 10% of its initial concentration. Slightly slower photodegradation was observed for the samples a and c where the concentration of WO$_3$ in films were somewhat higher or lower than that for the sample b (18.2 wt.% and 16.6 wt.%) respectively.

The sample d (n(TiO$_2$):n(WO$_3$) ratio = 1:2) with the highest resulting content of WO$_3$ (19.9 wt.%) showed a considerably slower photodegradation rate of MB. Even a sample of pure TiO$_2$ (e) showed more effective photocatalytic properties than d sample. This can be explained with the instability of WO$_3$ – unlike the inert TiO$_2$, tungsten trioxide undergoes a transformation to WO$_4^{2-}$ in a solution that has pH over 4 [8].

![Photocatalysis graph](image)

**Figure 5.** Photodegradation rate of MB using composite coatings under UV irradiation
Conclusions

Uniform TiO$_2$-WO$_3$ coatings have been successfully obtained by electrophoretic deposition method on stainless steel substrates. X-ray diffraction patterns confirmed the crystallization of anatase TiO$_2$ with average particle size 200 nm and monocline WO$_3$ with particle size 80-90 nm, while scanning electron micrographs showed WO$_3$ size distribution of 200–400 nm. The removal ratio of methylene blue depends on the (TiO$_2$): (WO$_3$) concentration ratio. The most effective photodegradation was determined for the sample that was electrophoretically deposited from the suspension with the molar content ratio n(TiO$_2$):n(WO$_3$) 2:1 with the resulting content of WO$_3$ 17.8% - after 6 hours of UV irradiation MB had decomposed to less than 10% of its initial concentration.

Acknowledgments

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