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Preparation and study of TiO_2-WO_3-$ZnWO_4$ film heterostructures on titanium

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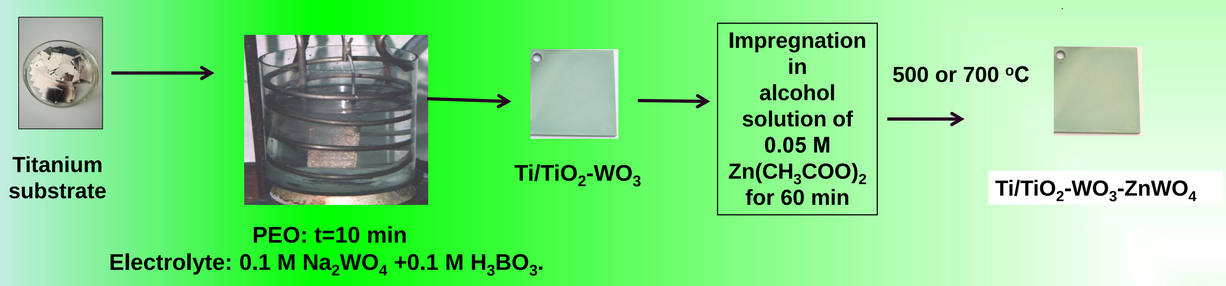
Introduction

$ZnWO_4$ and WO_3 are important inorganic compounds which extensively studied as heterogeneous photocatalysts for the degradation of organic pollutants. A promising method for obtaining films of complex oxide compounds with good adhesion to the substrate is plasma electrolytic oxidation (PEO). PEO is the formation of oxide coatings on metals under electric spark and/or arc discharges at the metal/electrolyte interface.

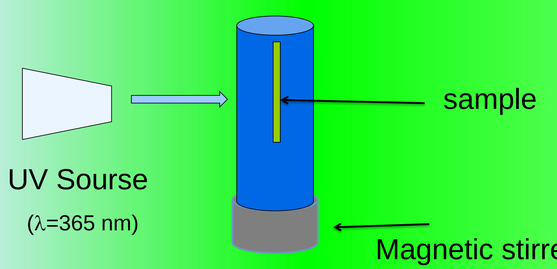
The objective

This report presents the results of a study of Zn-, W-containing coatings on titanium obtained by a combination of PEO in electrolyte containing Na_2WO_4 with addition of H_3BO_3 and impregnation in solutions containing zinc acetate followed by high-temperature annealing.

Sample preparation



Photocatalytic tests



The absorbance of the IC solution before (A_0) and after reaction time (A) was studied using a UNICO-1200/1201 spectrophotometer at λ=610 nm. The conversion of IC was calculated by formula:

$$\chi = \frac{A_0 - A}{A_0} \cdot 100\%$$

Solution: Indigo Carmine (IC) (10 mg/L) pH 5.9

Results and discussion

Table I. Phase and Elemental Composition of the Composites

Sample	Phase	Elemental composition (at.%)				
		C	O	Ti	Zn	W
Ti/W	WO_3	13.3	69.0	7.0	-	10.7
Ti/W/Zn-500	TiO_2 (anatase) WO_3, ZnO, $ZnWO_4$	-	75.7	7.4	2.6	16.3
Ti/W/Zn-700	TiO_2 (anatase), WO_3, $ZnWO_4$	-	68.8	9.7	1.6	19.9

After annealing the Ti/W/Zn sample at 500°C, the numerous elongated nanocrystals about 20 nm thick and no more than 100 nm long cover its surface (Fig. 1a). According to EDX, such nanocrystals contain 3-4 at.% Zn, 15-18 at.% W, and 60-67 at. % O. Raising the annealing temperature to 700°C leads to the deformation of nanocrystals due to their melting and the formation of large crystals, whose composition (25.0 at.% W, 70.0 at.% O, and 0.6 at.% Zn) corresponds to tungsten trioxide (Fig. 1b, c). The melted nanostructures formed after annealing at 700°C (Fig. 1c) are similar in composition to the nanocrystals in Fig. 1a. Thus, the nanostructures formed on the surface of the samples contain elevated concentration of Zn and W compared to their average concentrations. This suggests that such nanostructures are a mixture of zinc tungstate and tungsten oxide.

Results and discussion

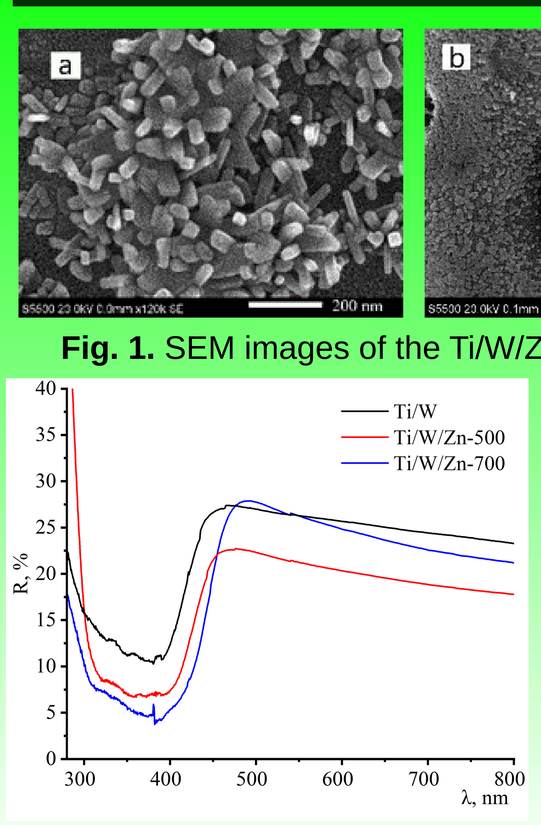


Fig. 1. SEM images of the Ti/W/Zn annealed at 500°C (a) and 700°C (b, c).

Fig. 2. Reflection spectra for different samples

Table II. Direct (n=1/2) and Indirect (n=2) Band Gaps E_g of the Composites

Sample	E_g (eV)	
	n=1/2	n=2
Ti/W	3.02	2.82
Ti/W/Zn-500	2.97	2.78
Ti/W/Zn-700	2.98	2.74

Figure 2 shows the diffuse reflectance spectra of oxide layers on titanium in the range of 200–800 nm. The E_g values of the formed samples are shown in Table II. Various compounds (TiO_2, WO_3 and $ZnWO_4$) in the coating composition form the direct and indirect band gaps. Impregnation and annealing of the Ti/W samples leads to a slight decrease in the band gap of the composites, probably due to an increase in the crystallization of WO_3 and $ZnWO_4$.

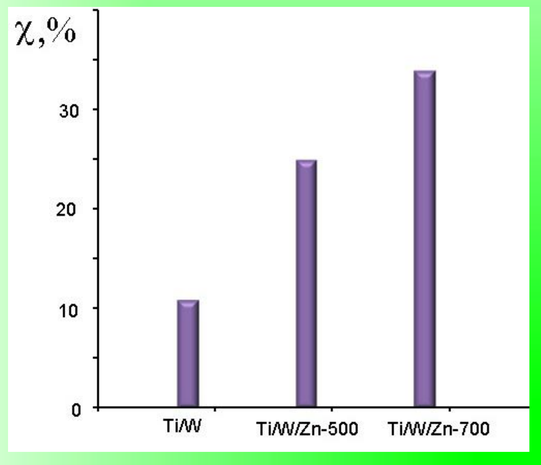


Fig. 3. IC degradation under UV irradiation

Under UV irradiation (Fig.3), unmodified composites exhibit a certain photocatalytic activity, which slightly increases after their impregnation and annealing. An increase in activity after annealing can be associated with an increase in the crystallinity of the films and the formation of mixed nanocrystals, which can contribute to the separation of photogenerated charges.

Conclusions

The Ti/TiO_2-WO_3-$ZnWO_4$ composites were formed by combination of plasma electrolytic oxidation and impregnation followed by air annealing at the temperature of 500 and 700°C.

The morphology and phase composition of the modified composites depend on the annealing temperature. The modification of composites leads to a decrease in the band gap. With an increase in the annealing temperature, the photocatalytic activity of the samples slightly increases, which may be due to the improvement in the separation of electrons and holes in various semiconductors.

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