PHOTODEGRADATION AND WETTABILITY OF THIN TITANIA LAYERS CONTAINING GOLD, SILVER AND COPPER

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The influence of noble metals (gold, silver, copper) on photocatalytic properties of thin titania layers prepared on glass was followed. The layers were prepared by sol-gel method from tetra-n-butyl orthotitanate, isopropanol, acetylacetone, water and mineral acid as catalyst. Metal additives were added in form of water solution of appropriate salt – $AuCl_3$, $AgNO_3$ and Cu_2Cl_2. Layers were applied on microscopic slides by dip-coating technique. The influence of composition of initial sol and the amount of metals on photodegradation effect and wetting angle was followed. Photodegradation ability and wetting angle of layers containing metal additives were lower in comparison with pure titania layers. The wetting angle values on metals containing layers were not measurable which can be considered as superhydrophilic behavior (zero contact angle) of the layers surface. This effect was observed on the surface of metals containing layers without necessity of previous UV irradiation.

INTRODUCTION

Thin titania layers embodying photocatalytic properties show many possible applications that can be used in industry processing. Degradation of some pollutants in water or air and also electrochemical properties useful in electronics and energetics (solar cells) are of interest in the last decade [1]. Photodegradation ability of anatase layers is well known for several decades [2], [3]. Titanium dioxide produces very reactive radicals when irradiating by the UV light. These radicals are responsible for the degradation ability and also can affect the electrochemical properties. Some of these properties can be changed or improved by modification of basic titania matrix. There are two main procedures used to modify the basic matrix. Microstructure of the matrix can be influenced by optimizing of preparation conditions which are used to produce pure titania layers. Addition of some oxides or other compounds was also suggested to affect titania layers properties [3]. Noble metals addition is considered as a way how the photoactivity and optical properties of the layer can be improved. According to some authors [4,5], the presence of gold produces selective absorption in visible or near IR region of light. Also doping by copper embodies light absorption properties and according to Trapalis et al. [6] evoke antibacterial effect of titania layers. Similar effect can be achieved also by silver adding [7,8,10]. Another advantage of metal addition is in a preparation of material not only with specific photoactivity properties but also with catalytic abilities on several kinds of chemical reactions [6], [9-11].

This work is focused on the measurement of photodegradation effect and wettability determination of thin titania layers prepared on glass substrate. The influence of initial sol composition and addition of gold, silver and copper on those properties is followed.

EXPERIMENTAL

Initial sols were prepared in different ratio of components with regard to determine the influence of titania precursor (tetra-n-butyl orthotitanate) content and also amount of water on final layers properties. A few drops of hydrochloric acid were added as catalyst. The composition of initial sols is presented in Table 1, in which TiBu means tetra-n-butyl orthotitanate, AcAc acetylacetone, BzAc benzoylacetone and Triton X100 denotes commercial tenside.

The prepared sols were deposited on washed (with detergent and hot water) and dried (at 60°C for 10 mins) microscopic slides ($75 \times 25 \times 1$ mm^3) by dip-coating technique. Dipping speed was 200 mm/min, delay in sol set on 30s and pulling speed was 60 mm/min. The films were fired at 550°C for 2 hours with temperature increase of 2°C/min. This increase is sufficient for drying of the layer without its deformation or cracking.

Table 1. Composition of initial sols.

	TiBu (ml)	AcAc (ml)	BzAc (g)	dil. HCl (1:2) (ml)	conc. HCl (ml)	Triton X100 (ml)	i-propanol (ml)	H_2O (ml)
T 1	26	10	0.1	2	0.25	5	4	5.5
T 2	23	10	0.1	2	0.25	5	7	5.5
T 3	20	10	0.1	2	0.25	5	10	5.5
T 4	17	10	0.1	2	0.25	5	13	5.5
T 5	14	10	0.1	2	0.25	5	16	5.5
T 11	26	10	0.1	2	0.25	5	4	1.4
T 12	26	10	0.1	2	0.25	5	4	2.8
T 13	26	10	0.1	2	0.25	5	4	4.1
T 14	26	10	0.1	2	0.25	5	4	5.5
T 15	26	10	0.1	2	0.25	5	4	6.9

The photocatalytic degradation of the fired layers was tested using water solution of orange II (OII) or methylene blue (MB). The concentration of the solution was 2.85×10^{-5} mol MB/dm3 and 1.56×10^{-5} mol OII/dm^3, respectively. The samples were immersed into 20 ml of dye solution and irradiated for different period of time by UV light source with dominant wavelength of 365 nm. The degradation of the organic dyes was evaluated by spectrophotometric determination of OII and MB solution absorbance using spectrophotometer Shimadzu UV-2450. The decrease of absorbance in visible range with time of irradiation was measured.

The sol with the highest degradation effect was selected for testing of influence of additives on photocatalytic properties of thin titania layers. Water solutions of auric chloride ($AuCl_3$), silver nitrate ($AgNO_3$) and cuprous chloride (Cu_2Cl_2) were used as a source of these additives. The quantity of metals in resulting layer was 0.01, 0.5, 1.0 and 2.0 wt.%. The amount of water added to the sol was kept at the same level as for initial sol without additives. In the case of silver additive, the small amount of nitric acid instead of hydrochloric was used as catalyst to avoid the precipitation of silver chloride.

The hydrophilic properties of prepared layers were tested using water drop colored by methylene blue for better visibility. Photo images of the drops were then evaluated with software for image analysis NIS-Elements AR 2.30. Titania layers were observed by scanning electron microscopy (HITACHI S4700), thickness of layers was determined by contact profilometry (Hommel tester T1000).

RESULTS AND DISCUSSION

Table 2 shows comparison in photodegradation effect of different samples prepared from sols based only on titania precursor. Increasing photodegradation of both model solutions (MB, OII) with increasing amount of titania precursor was observed. Water added to initial sols has no significant influence on the photodegradation ability of prepared layers (Table 3).

The sol with the highest photodegradation ability (T 13) was used to determine an influence of addition of different amount of metals. Following Figures 1 and 2 and Table 4 show photodegradation effect of layers prepared from those sols containing various amount of Au, Ag and Cu and from the original sol T 13. Decreasing photodegradation effect by adding of metals was found. This could be related to the property of metallic structure. The higher amount of metal present in titania layer can lead to capturing of electrons released by UV irradiation. The possibility to create reactive radicals, which are responsible for the photodegradation effect, is than decreased so the photodegradation also decreases (Table 4). However there is no simple relationship between photodegradation and the content of metals in the layers. The dependence is not linear or smooth and the maximum decrease of model solutions absorbance is different for the metals used as additives.

The highest photodegradation ability after 8 hours irradiation with UV light source was found for layers containing 0.5 wt.% of gold (sample TA 0.5), 1.0 wt.% of copper (sample TC 1.0) and 2.0 wt.% of silver (sample TS 2.0). However, all these samples have lower degradation effect on both model solutions than the value found for the initial sol (sample T 13 in Table 4).

Table 2. Decrease of absorbance of layers prepared from sols with different amount of titania precursor after 2 hours of UV light irradiation.

Sample	T 1	T 2	T 3	T 4	T 5
OII absorbance decrease (%)	27.3	20.1	16.6	21.3	19.8
MB absorbance decrease (%)	59.6	56.4	54.5	55.2	56.4

Table 3. Decrease of absorbance of layers prepared from sols with different amount of water after UV irradiation of 2 hours for MB and 8 hours for OII.

Sample	T 11	T 12	T 13	T 14	T 15
OII absorbance decrease [%]	81.0	79.6	84.6	76.9	84.9
MB absorbance decrease [%]	46.6	57.1	63.8	54.5	60.0

The influence of additions of optimal amount of metals on photodegradation appears to be very similar and the increase of MB absorbance in comparison with the pure titania layer is obvious (Figure 1). In the case of Orange II absorbance (Figure 2), the difference was remarkable only for the layer containing gold.

Table 4. Photodegradation effect of layers with different content of metals - decrease of absorbance (in %) of model solution after 8 hours of UV irradiation.

Sample	T 13	TA 0.05	TA 0.5	TA 1.0	TA 2.0
OII [%]	84.6	56.0	70.3	65.3	62.6
MB [%]	96.1	95.3	90.6	90.5	84.9

Sample	T 13	TC 0.05	TC 0.5	TC 1.0	TC 2.0
OII [%]	84.6	63.8	68.4	79.6	31.2
MB [%]	96.1	95.6	89.5	90.0	82.9

Sample	T 13	TS 0.05	TS 0.5	TS 1.0	TS 2.0
OII [%]	84.6	65.7	68.9	79.6	80.5
MB [%]	96.1	96.8	90.3	88	88.9

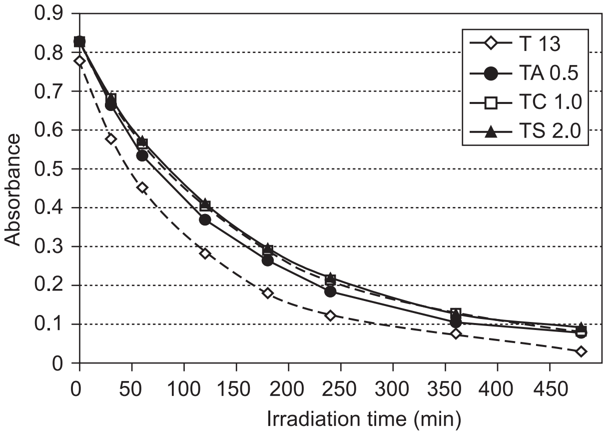


Figure 1. Photodegradation of MB by different layers - decrease of absorbance vs. time of UV irradiation.

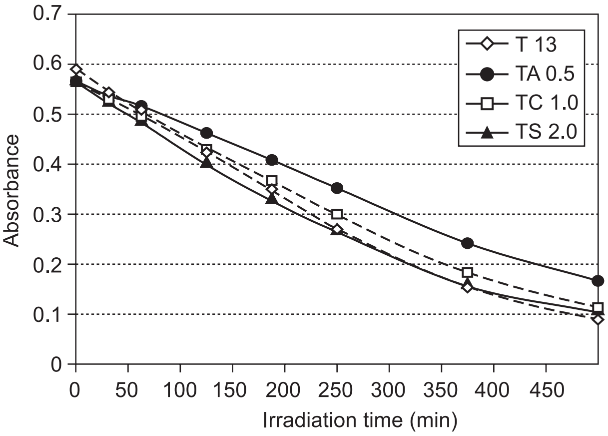
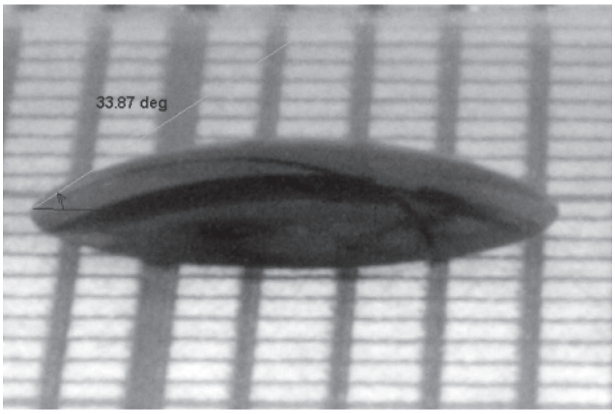


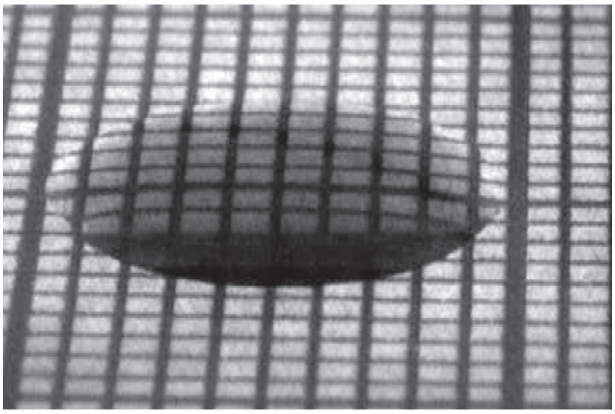
Figure 2. Photodegradation of OII by different layers - decrease of absorbance vs. time of UV irradiation.

The wettability of prepared layer was also tested (Figures 3, 4). The contact angle was measured and evaluated on water drop of 10 μl colored by methylen blue which was put on the layer. The superhydrophilicity (zero contact angle) was found even without necessity of previous irradiation by UV light source. This can be caused by presence of noble metals in titania matrix that can lead to decreasing of energetic gap and sensitizing of the samples on visible region of light.

The electron microscopy images (Figures 5, 6) were used to determine the nature and thickness of the layers. The anatase crystals were found in all layers examined. Metals particles were identified only in the case of gold. The amount and distribution of anatase crystals depend on the amount of water in the starting sol (Figure 5). The thickness of prepared layers calculated from SEM images varies in the range of 323-347 nm and did not depend on the metals content. These values are in a very good agreement with values obtained by using contact profilometry (330-350 nm).



a) before irradiation (33.9°)



b) after irradiation for 1 hr (angle immeasurable)

Figure 3. Wettability of the T13 layer.

CONCLUSIONS

Thin titania layers described in this paper embody photodegradation and superhydrophilic properties. The effect of gold, silver and copper on photodegradation and wettability of titania coatings was tested. It was found that these metals are decreasing photodegradation ability of titania layers. The increasing wettability of layers doped by those metals is occurring without necessity of previous UV irradiation by a source of UV light. The layers prepared are composed of fine anatase crystals. Metals particles were identified only in case of gold. The thickness of prepared layers were determined by contact profilometry and confirmed with SEM images. Thickness values vary in the range of 323-350 nm.

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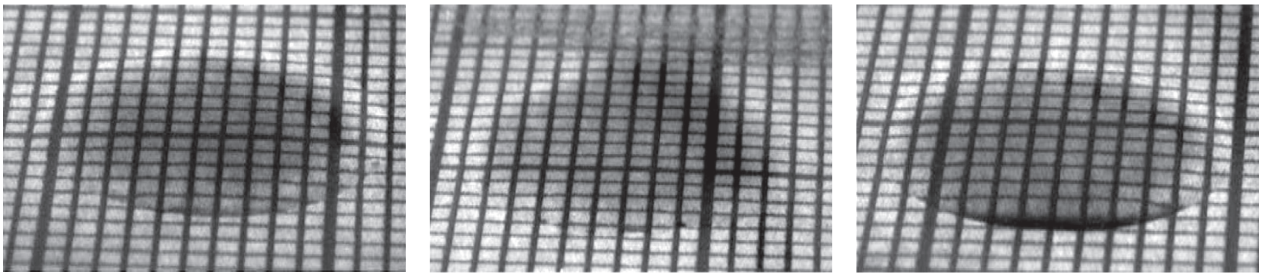
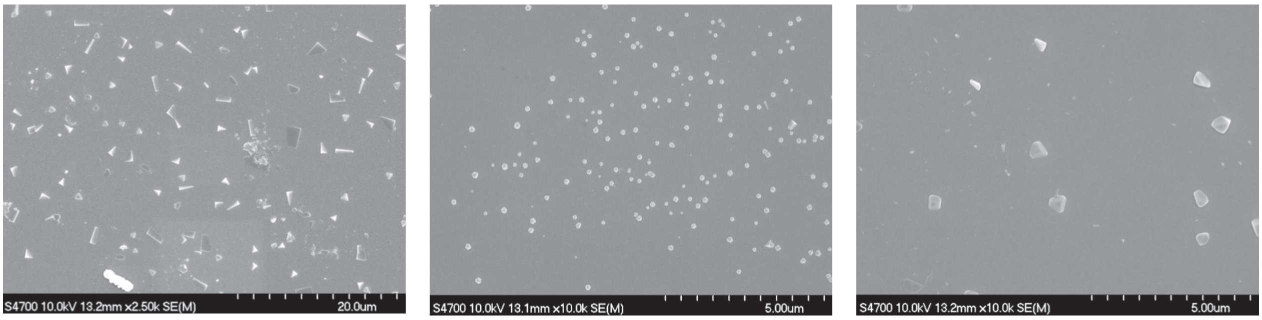
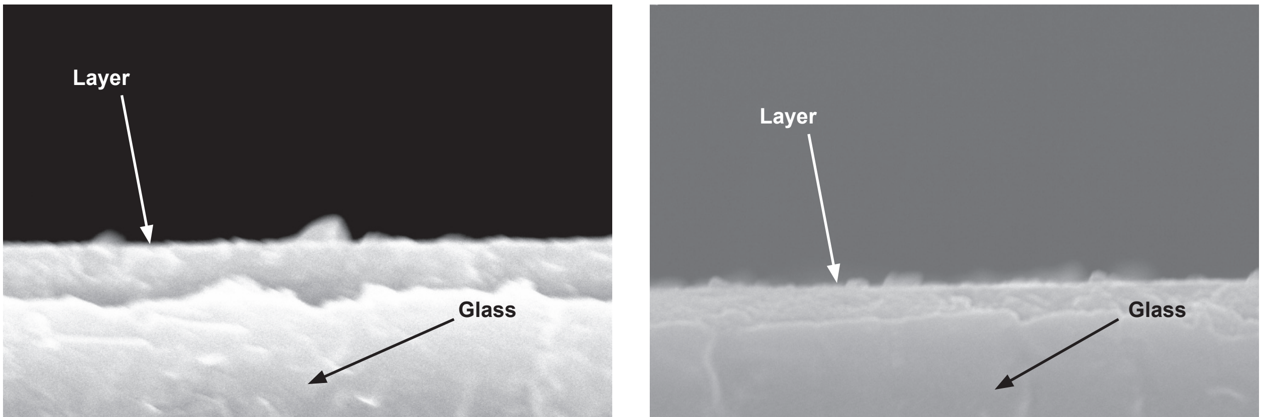

a) layer TA 0.5 (angle immeasurable)
b) layer TC 1.0 (angle immeasurable)
c) layer TS 2.0 (angle immeasurable)

Figure 4. Wettability of layers containing some metals before irradiation.



a) sample T 11
b) sample T 15
c) sample TS 2.0

Figure 5. SEM figures of thin titania layers with different amount of water.



a) layer TC 0.05
b) layer T 13

Figure 6. Thickness calculated from SEM

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