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INFLUENCE OF THE DECOMPOSED SUBSTRATES ON THE PHOTOCATALYTIC ACTIVITY OF THE TITANIUM DIOXIDE MODIFIED BY SILVER NANOPARTICLES

Photocatalytic activity of Ag/TiO_2 composites obtained by photoreduction treatment (PRT) was investigated. The composite materials, containing 1.0 and 2.1 wt% of silver nanoparticles were obtained by depositing silver on the Evonic–Degussa P25 titania surface. Ag/TiO_2 samples were examined by SEM, XPS and BET techniques. The XPS measurements revealed that silver particles were obtained mainly in metallic form. The photocatalytic activity of pure P25 and Ag/TiO_2 composites was compared in photooxidation reaction of some model compound like: formic acid (FA), rhodamine B (RhB) and methylene blue (MB). Photodecomposition reaction was investigated in a batch reactor containing aqueous suspension of a photocatalyst illuminated by either UV or artificial sunlight (halogen lamp). The tests proved that small amount of silver nanoparticles deposited on titania surface triggers the increase in photocatalytic activity, this increase depends however on the type of substrate. The relation between the type of substrate and the activity of the composite was discussed.

keywords: Titanium dioxide; Photocatalysis; Silver nanoparticles; Organic dyes

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1. INTRODUCTION

Heterogeneous photocatalysis is an economically alternative and environmentally safe technology of advanced oxidation processes (AOP) for removal of organic impurities from water. During that process, the semiconductor illuminated by light of the proper wavelength absorbs light and generates active species, which oxidize the organic compounds dissolved in water. The most popular and promising material for this application is TiO_2 because of its high physical and chemical stability, non-toxicity and low price [1]. However its main drawbacks of low quantum yield and limited photoresponse range (< 380 nm) hinder its application and commercialization [2]. To handle those problems researchers have adopted numerous strategies, including phase and morphological control, doping, sensitizations and semiconductor coupling [3-15]. Recently there has been a great interest in the photoelectrochemical properties of nanostructured TiO_2 films such as photovoltaic [16-17], photocatalytic [18], optical [19] and water splitting ability [2]. Further, several researchers reported that modification of the TiO_2 surface with metals, like Pt, Fe, Ag, Au and Pd is promising as a tool to enhance the photocatalytic activity of TiO_2 and to increase the quantum yield [20-23]. In particular, silver nanoparticles deposited on TiO_2 substrate (Ag/TiO_2) have attracted significant attention because of non-toxicity of the metal with remarkable catalytic and antibacterial activity [24-30]. Moreover silver is particularly suitable for industrial applications due to its relatively low price and the ease of preparation when compared to other metals. Activity of those materials has been tested with many organic compounds like organic dyes [31,32], phenols, ketones [25], carboxylic acids [33] in solid - liquid as well as in solid - gas systems. In that kind of reactions the Ag/TiO_2 composite showed usually higher activity than bare titania. The most common and promising methods of Ag/TiO_2 preparation, which make possible approaching the system of high efficiency and low cost are sol-gel [34, 35], PRT [36,37] and CVD [38] ones.

The aim of this work was the determination of the influence of decomposed substrates on the photocatalytic activity of titanium dioxide modified by silver nanoparticles. The composites were synthesized from organic silver salt (silver acetate). The application of acetate in the PRT reaction allowed synthesizing metallic nanoparticles without any additional reducers (sacrificial reagents). In such photoreaction process the organic anion causes reduction of silver cations to the metallic state. It makes that kind of synthesis simple, fast, relatively cheap and makes possible obtaining pure composites without any impurities what is a big advantage when compared to reduction of $AgNO_3$ [39-41]. The Ag/TiO_2 photocatalysts containing silver particles in two silver concentration (1.0 and 2.1 wt%) were tested in decomposition of selected organic compounds: formic acid (FA), rhodamine B (RhB) and methylene blue (MB) [42]. Results recorded for silver modified titania were

compared with pure P25.

In this paper we would like to take a special note on the photosensitization effect occurring for organic dyes on pure titania and antagonistic effect, the decrease of the Ag/TiO_2 composite activity due to the specific interaction of the dye with silver.

2. EXPERIMENTAL

2.1. Materials and reagents

TiO_2 (P25, 25% rutile and 75% anatase) was kindly supplied by Evonic-Degussa. Silver acetate, 99.99% metals basis was purchased form Sigma-Aldrich. Formic acid (FA, 98.0% p.a.) and methylene blue (MB) were obtained from Fluka. Potassium thiocyanate (99.0%, p.a.), nitric acid (65.0%, p.a), rhodamine B and silver nitrate (p.a) were purchased from POCh Gliwice.

All reagents were used as received without further purification. Deionized water of Millipore Direct Q UV quality was used in all experiments.

2.2. Preparation of Ag/TiO_2

The Ag/TiO_2 nanocomposites were prepared by a photoreduction treatment (PRT). The suspensions (40 ml) were prepared by mixing P25 powder (1 g) with different volumes of CH_3COOAg aqueous solution (0.05 M) and deionized water. Then suspension was sonificated for 10 minutes, agitated (300 rpm) and finally irradiated with a high pressure xenon arc lamp (250 W) for 1 hour in quartz flat bottomed cell. The resulting Ag/TiO_2 nanocomposites were recovered by filtration, rinsed with deionized water several times and finally dried at 40 °C in the dark. The composites were prepared for following Ag/TiO_2 ratios (%) in the synthesis mixture: 2 and 20. The analysis of real silver concentration in composite was performed using Volhard titration method, after digesting composite in nitric acid. In the further text the real concentration of silver, expressed in wt% is given.

2.3. Material Characterizations

The scanning electron microscopy (SEM) images and EDXS analysis were performed with a JEOL JSM-7500F Field Emission apparatus operated at 15 kV. The samples were analyzed without any surface treatment.

The X-ray Photoelectron Spectroscopy (XPS) and X-ray excited Auger Electron Spectroscopy (XAES) measurements were performed using an XPS spectrometer equipped with a hemispherical analyzer (R4000, Gammadata Scienta) using MgKα

(1253.6 eV) radiation. The power of the X-ray source was 240 W and the analyzer pass energy was 100 eV, corresponding to a full width at half maximum (FWHM) of 0.9 eV for the Ag $3d_{5/2}$ peak. The area of the sample analyzed was approximately 3 mm^2. The powder samples were pressed onto indium foil and mounted on a dedicated holder. In a case of Ag/TiO$_2$ suspensions, the drop of liquid sample was dried on the gold sheet surface and then analyzed. The binding energy (BE) was calibrated using Cu, Au and Ag foils as reference materials, according to ISO 15472:2001 procedure.

The Brunauer–Emmett–Teller (BET) surface area of the powder samples was determined with a QuantaChrome Autosorb-1 instrument. The surface area of the samples was obtained from nitrogen adsorption isotherms after outgassing for 18 hours at the temperature of 20°C.

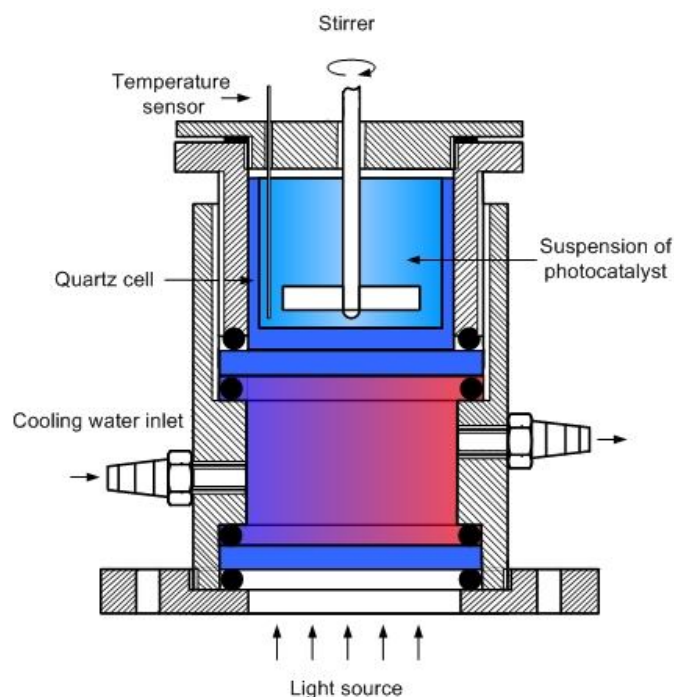### 2.4. Photodegradation experiments

Fig. 1. The scheme of the quartz flat bottomed photoreactor.

The photooxidation experiments were performed in two quartz flat bottomed reactors of the same volume as for the preparation of the composite (40 ml). In the first reactor the halogen lamp (150 W, Philips) was used as an artificial sunlight (ASL) source, in the other one, dedicated for ultraviolet, the high pressure xenon arc lamp (250 W, Optel) was applied. Both lamps were used without any cut-off filters, except

the layer of cooling water flowing below the bottom of the cell. The cell illumination was monitored by the radiometer Radiometer RD 0.2/2/100 (Optel). The distance between the source and the sensor was about 25 cm for ASL and 15 cm for UV light and the illumination area was 16.3 cm^2. The irradiation intensity at the bottom of an empty reactor was 68.8 mW/cm^2 for ALS and 48.8 mW/cm^2 for UV source. The photocatalyst suspensions were stirred during the experiments in both reactors with a mechanical stirrer at a constant rate of 300 rpm. During all experiments the temperature in the reactor was stabilized at 25±0.5°C (Fig. 1).

After the photocatalytic experiment three samples of suspension were taken from the reactor, subjected to 25 min of centrifugation at 15000 rpm to separate TiO_2 and analyzed for the contaminant concentration. The concentration changes of different contaminants were determined by UV-VIS spectrophotometery (Analytik Jena – Specord 40). The most characteristic wavelength of maximum light absorption was chosen for all contaminants. After preliminary experiments the following photocatalyst and contaminant concentrations as well as irradiation times were chosen for testing the activity of the Ag/TiO_2 composites, as shown in Table 1.

Table 1. The experimental parameters of the photodegradation experiments.

Contaminant	RhB	MB	FA
$C_{contaminant}$	3×10^{-5} M	3×10^{-5} M	2×10^{-2} M
$C_{photocatalyst}$	500 mg/l	100 mg/l	500 mg/l
Irradiation time	20 min	20 min	60 min
Analytical wavelength	555 nm	665 nm	208 nm

The contaminant concentrations were selected to fit the spectrophotometer absorbance range up to A = 3. The percentage of the decomposed contamination was calculated using following equation (1):

$$\%_{decomp} = \frac{(A_0 - A)}{A_0} \cdot 100 \, , (\%)$$ (1)

where A_0 – is the initial absorbance of the suspension (before irradiation) and A is the suspension absorbance after irradiation.

Obtained results showed photocatalytic activity, when the effect of adsorption was eliminated by differential measurement between the reference kept in the dark and the sample illuminated during the same time. Figure 2 shows the process of sample preparation to the spectrophotometric measurement. Stability of decomposed contaminant was checked in a blank experiment without the photocatalyst. After 1h illumination under ASL and UV light the photodecomposition effect was negligible for all used substrates.
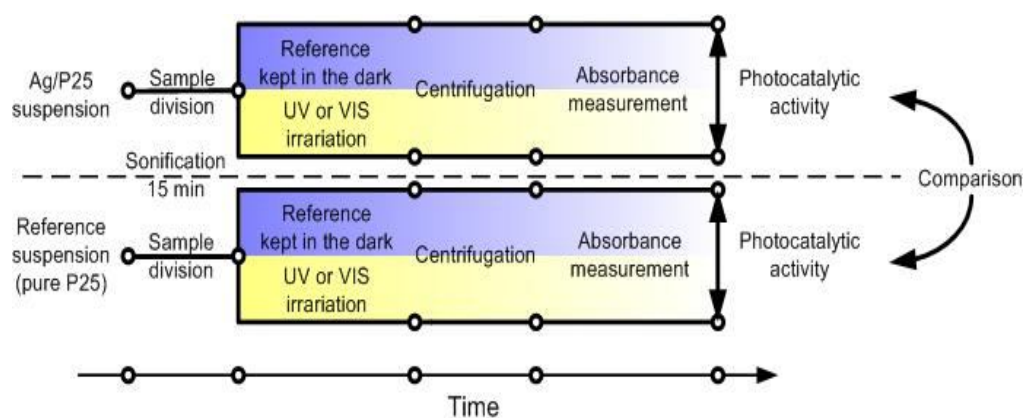
Fig. 2. The process of sample preparation to the spectrophotometric measurement.

3.   RESULTS AND DISCUSSION

3.1. Adsorption effect and photocatalytic activity

Table 2. Adsorption effect registered for different substrates.

Substrate	Time [h]	Adsorption on pure P25, %	Adsorption on Ag/TiO$_2$, %
MB	1.5	3.1	40.4
	3	1.6	40.3
	6	1.7	41.4
	12	1.5	40.2
RhB	1.5	1.7	6.9
	3	1.0	8.9
	6	1.2	9.0
	12	0.9	9.5
FA	1.5	3.3	1.9
	3	1.7	1.0

In the first stage of the experiments the adsorption of investigated substances on TiO$_2$ and Ag/TiO$_2$ composites was determined (Table 2). The adsorption was expressed as the % decrease in the concentration of the contaminant in relation to the initial concentration after various times of contact.

Significant adsorption of both RhB and MB on Ag/TiO_2 composite was observed, but the decrease of concentration of FA was very low and similar for TiO_2 and composite. Note that none of the investigated compound adsorbed in a significant degree on pure TiO_2.

As the first model contaminant rhodamine B (RhB) was used. In the case of 2.1 wt% Ag/TiO_2, after UV illumination (Figure 3) RhB got degraded by only 12 % more than in the case of pure P25. ASL light illumination of the silver enriched titania showed no effect on RhB oxidation (1.0 wt% sample) or even some decrease of the reactivity (2.1 wt% sample).
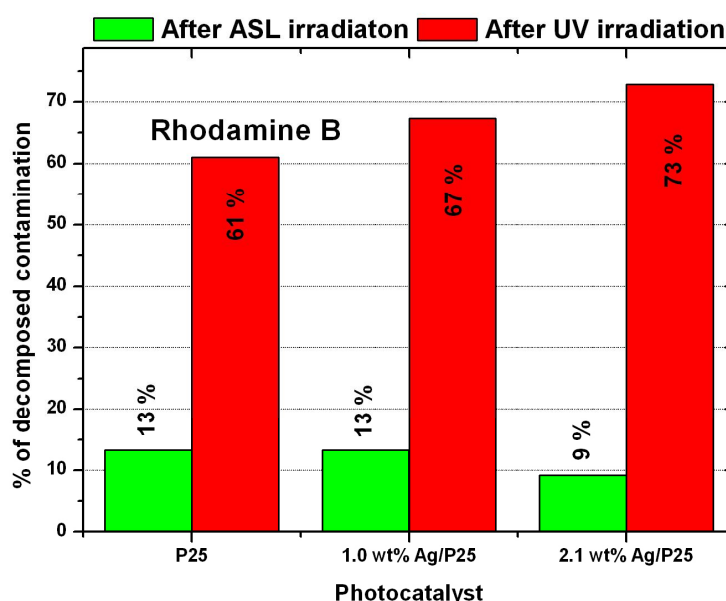

Fig. 3. Photocatalytic degradation of RhB on the pure P25 and silver modified photocatalyst

Methylene blue was also tested. For that compound a decrease of the photoactivity of Ag/TiO_2 as compared to pure TiO_2 was observed under ASL and UV irradiation. Note that decrease of the photoactivity is roughly proportional to the silver concentration on the P25 surface (Figure 4).

The same photocatalytic tests as for RhB and MB were performed for formic acid. Significant increase of activity for Ag modified sample, as compared to pure TiO_2 was observed in the case of UV irradiation (Figure 5). In the case of ASL irradiation of the composites containing 1.0 and 2.1 wt% of Ag the decomposition of FA was practically negligible. The increase of silver concentration to 2.1 wt% resulted in significant increase of the FA degradation under UV irradiation when compared to 1 wt% of Ag.
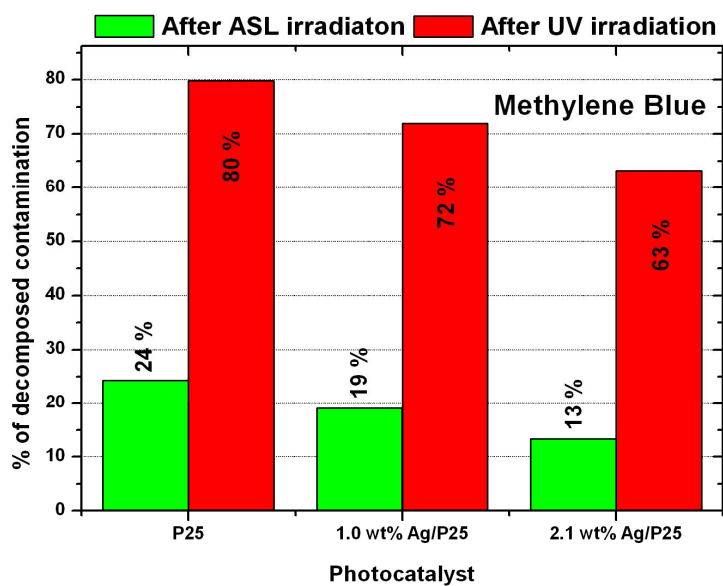
Fig. 4. Photocatalytic degradation of MB on the pure P25 and silver modified photocatalyst.
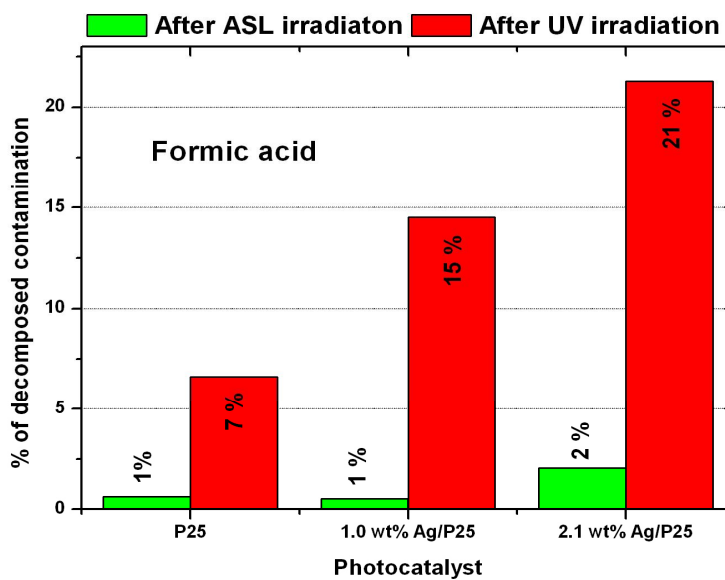

Fig. 5. Photocatalytic degradation of FA on the pure P25 and silver modified photocatalyst

3.2. XPS analysis

The chemical composition of Ag/TiO$_2$ composite before the photocatalytic tests was analyzed by the XPS method (Table 3, 4). The chemical state of silver in the composite was obtained by analysis of Ag 3d core excitation and Auger spectrum (XAES). The Ag 3d peaks of all composite samples were slightly asymmetric. Good fit was obtained when two doublets were applied in the spectrum fitting procedure. The exemplary spectrum of the just prepared composite is shown in Figure 6.

Table 3. XPS, and EDXS analysis of Ag/TiO$_2$ – 2.1 wt% composite freshly synthesized,
A – ratio of the intensity of the Ag 3d emission line that may be ascribed to metallic silver,
B – ratio of the higher BE component .

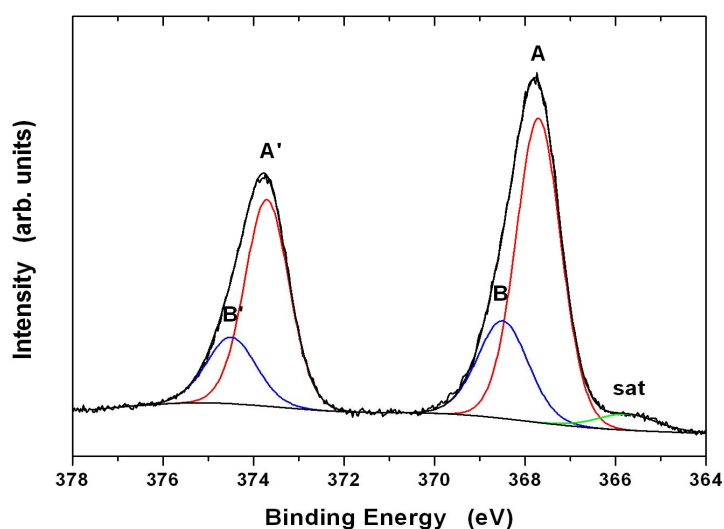| Ag 3d$_{5/2}$ (A)		Ag 3d$_{5/2}$ (B)		Ag L$_4$N$_{45}$N$_{45}$ (eV)	α' (eV)	XPS Ag/Ti
BE (eV)	%	BE (eV)	%			
367.7	78.2	368.6	21.8	358.4	726.1	0.081

Fig. 6. The deconvoluted spectrum of Ag 3d core excitation obtained for Ag/TiO$_2$ composite (2.1 wt%).

The electron binding energy (BE) of the most intense peak (A) was found in the range of 367.5-368.0 eV for all studied samples. The Auger parameter (α'= Ag 3d$_{5/2}$

(BE) + Ag $L_4N_{45}N_{45}$ (KE)) showed values above 725 eV. Analysis of Ag $3d_{5/2}$ BE and α' parameters showed that metallic silver is main silver species present in the composite [43]. Additionally, because the BE of the Ag 3d core excitation depends on the particle size [44, 45], the presence of the second peak (B) at BE of 368.5-369.2 eV in the XP spectra suggests that part of silver at the TiO_2 surface forms nanoparticles.

Table 4. Silver concentration in 1.0 and 2.1 wt% Ag/TiO_2 composites obtained by XPS and EDXS analysis.

Sample	XPS measurements		EDXS measurements	
	Ti at% XPS	Ag at% XPS	Ti at% EDXS	Ag at% EDXS
Ag/TiO₂ 1.0 wt%	96.0	4.0	98.2	1.8
Ag/TiO₂ 2.1 wt%	92.5	7.5	96.1	3.9

XPS analysis allowed calculation of the Ag to Ti atomic ratio (Table 4). The XPS analysis depth for Ag and TiO_2 was estimated to 5.2 and 7.4 nm, respectively [46]. The results showed that surface occupied by silver nanoparticles proportionally increase with the concentration of silver in composite. It means that applying higher concentration of silver salt during synthesis do not trigger the agglomeration or nanoparticles growth. This result was confirmed by EDXS analysis (Table 4) although lower values of the Ag/Ti were found. The EDXS analysis depth is much larger comparing to the XPS, it can approach 1 μm. Taking above into account it may be stated that Ag clusters/nanoparticles decorate the TiO_2 surface.

3.3. SEM and EDXS analysis

Figure 7 presents the SEM images obtained for the Ag/TiO_2 composite containing 1.2 wt% of the silver nanoparticles. The image 7a shows morphology of the composite. In Figure 7b, the back-scattered electrons (BSE) were used to obtain the SEM image sensitive to the larger atomic number (Z). In this picture, the bright spots were identified as the silver nanoparticles. Most of the Ag particles show rather low diameter (up to 20 nm) although there is a small number of relatively large particles (more then 50 nm). The titanium and silver concentrations in the EDXS analyzed points (Fig. 7b) are collected in Table 5. The Ag concentration shows nonuniform distribution over the sample that varies from 1.67 to 5.24 wt%.
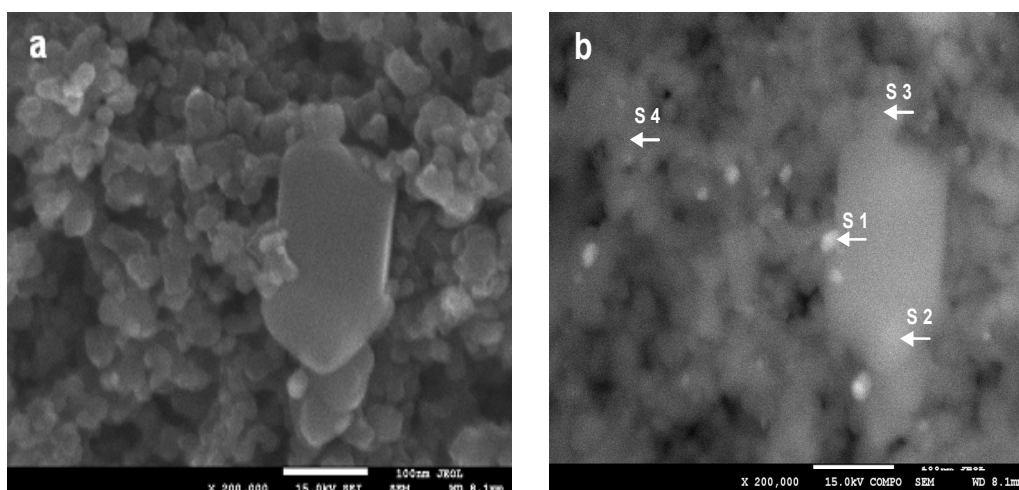
Fig. 7. SEM (a) and BSE (b) images of Ag/TiO$_2$ composite (1.2 wt%)

Table 5. Distribution of Ag nanoparticles

Spectrum	Spectr. 1	Spectr. 2	Spectr. 3	Spectr. 4	Mean	Std. dev.	Max.	Min.
	Weight%							
Ti	94.8	98.2	98.3	97.7	97.2	1.7	98.3	94.8
Ag	5.2	1.8	1.7	2.3	2.8	1.7	5.2	1.7

3.4. Analysis BET

The surface area obtained for 2.1% Ag/TiO$_2$ (49.4 m^2/g) was smaller then for pure P25 (56.6 m^2/g). Probably silver nanoparticles are deposited in the cracks and holes of agglomerates of TiO$_2$.

4. DISCUSSION

Interpretation of the organic dyes behavior in the photodecomposition reactions requires the consideration of the photosensitization effect. In the case of RhB degradation photoactivity increased with the increases in silver concentration slightly and only under UV irradiation (see Figure 3). On the other hand silver composites under ASL light illumination showed no effect on RhB oxidation (1.0 wt% of Ag) or even

some decrease of the reactivity (for 2.1 wt% sample). That behavior can be, at least partially, explained by the occurrence of photoinduced activation (photosensitization mechanism) [17]. Organic dye adsorption modified photocatalyst surface and shifted TiO_2 light absorption to the visible region what increased activity due to wider light spectrum available. The photosensitization is correlated with the effective surface area of TiO_2. Thus the composites with larger amount of silver have smaller active area due to the surface blocking what results in the decrease of activity. In the case of UV light photosensitization mechanism is not so important because the excitation energy is high enough to initiate the photocatalytic process. So, the synergic influence of the silver nanoparticles and titania substrate is stronger than photosensitization effect caused by organic dye which resulted in the increase of photocatalytic activity under UV irradiation. Note, that because photosensitization occurs on bare TiO_2 surface both effects (photosensitization and activation by Ag) interfere with each other. So, in the case when sensitization plays an important role in the photocatalytic process the influence of activation by depositing metal particles on the surface would be masked in the systems where photosensitization occurs.

In the case of MB the decrease of photoactivity were observed under both ASL and UV irradiation when silver was deposited at the surface. Besides the influence of photosensitization this behavior can be explained by blocking of the silver surface by MB due to the creation of Ag-S bond between sulfur atom contained in MB molecule and the surface of silver, which results in poisoning of silver containing composites. So, that part of the surface of TiO_2 which is occupied by silver becomes inactive. Therefore, the more silver at the TiO_2 surface the stronger surface poisoning and the stronger decrease of the photocatalytic process efficiency. Strong adsorption of MB at the surface of silver was confirmed by adsorption measurements. The rate of MB decomposition on TiO_2 was generally very high, much higher then in the case of RhB which is evidently due to the photosensitization effect.

Elimination of the photosensitization mechanism was done by applying colorless substrate, FA. Photodecomposition of that compound in the presence of Ag/TiO_2 composited showed significant increase of activity under UV irradiation (see Figure 5). It means that decomposition of FA could be possible only under UV light irradiation, so the pure photodegradation mechanism was observed only for FA.

4. CONCLUSIONS

The Ag/TiO_2 composites containing various concentrations (1.0 and 2.1 wt%) of the silver nanoparticles on the titania surface were tested as a potential photocatalyst for the removal of organic contaminations from water. It was proved that small amount of silver nanoparticles (2.1 wt%) greatly increase photocatalytic activity, this effect

depends however on the substrate studied. The Ag/TiO$_2$ composite showed oxidation activity significantly higher than pure P25 in the case of FA. However for RhB the activity of the composite was only slightly higher than the activity of pure TiO$_2$ and in the case of MB bare P25 was slightly better than the obtained composite. According to our opinion the difference between dyes and other substrates is caused by the interference of the photosensitization effect which neutralizes the influence of silver. So, it may be concluded that organic dyes, commonly applied as testing substances in photocatalytic experiments may not be recommended as testing species in the case of surface-modified titania. What is more, substrate containing sulfur in the molecule could deactivate Ag/TiO$_2$ composite.

ACKNOWLEDGEMENT

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