

## Silver Doped TiO<sub>2</sub> Photocatalyst for Methyl Orange Degradation

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### Abstract

The photocatalytic efficiency of nanocrystalline TiO<sub>2</sub> is strongly influenced by light sources and recombination of photoinduced electrons and holes. It is known that TiO<sub>2</sub> doped with Ag has self-sterilizing and self-cleaning effects. A study has been carried out on the photocatalytic behavior of silver modified titanium dioxide for decomposition of methyl orange after UV black lamps and solar irradiation treatment. The base nanoparticles were standard photocatalyst TiO<sub>2</sub> (P25). AgNO<sub>3</sub> aqueous solution with the presence of TiO<sub>2</sub> were irradiated with UV black lamps and reduced Ag doped the surface of the TiO<sub>2</sub> nanoparticles. The silver modified titanium dioxide particles were studied by XRD and TEM. Silver ions (Ag<sup>+</sup>) were reduced to Ag<sup>0</sup> as shown by the XRD. Silver particles of about 10 nm in size were detected on the surface of the TiO<sub>2</sub> and partially in the aqueous solution. The presence of Ag<sup>0</sup> on the surface of TiO<sub>2</sub> nanoparticles, after UV black lamps and solar irradiation, highly increased the photocatalytic activity in comparison to the photocatalyst P25. This is explained with the reduced recombination of electrons and holes in the presence of Ag<sup>0</sup>.

*Keywords:* photocatalysis, silver nanoparticles, methyl orange, silver-titania photocatalysis

### 1. Introduction

Nanocrystalline titanium dioxide (TiO<sub>2</sub>) has many important applications such as: solar cells [1], photocatalytic splitting of water to hydrogen and oxygen [2], sensors [3], self cleaning surfaces and degradation of environmental pollutants [4]. Due to the stability of modern dyes, conventional biological treatment methods for industrial waste water are ineffective, resulting often in an intensively colored discharge from the treatment facilities. Recently, a number of researches have dealt with heterogeneous photocatalytic decomposition of many kinds of azo-dyes [5, 6] by UV, visible light and solar irradiation [7]. Methyl orange (MeO) is comparatively stable without photocatalyst under UV and outdoor irradiation. Titanium dioxide has been widely used as a photocatalyst for the degradation of MeO [6, 8, 9]. Photocatalytic efficiency of the nanocrystalline TiO<sub>2</sub> system is strongly influenced by light sources and recombination of photoinduced electrons and holes. It is known that deposited onto TiO<sub>2</sub> surface gold [10] inhibits the recombination of photogenerated electrons and holes. One of the most interesting methods for production of titanium dioxide/metal composites is photocatalytic deposition of metals onto titanium dioxide films. To increase the activity of TiO<sub>2</sub> on the degradation of azo-dyes (incl. methyl orange) combinations with other metals have been used: (Au/TiO<sub>2</sub>) [10], (Ti/TiO<sub>2</sub>) [11],

(Ce/TiO<sub>2</sub>) [12], (Fe/TiO<sub>2</sub>) [13], (Pt/TiO<sub>2</sub>) [14]. Also, it is known that TiO<sub>2</sub> doped with Ag has self-sterilizing and self-cleaning effect. The composites (Ag/TiO<sub>2</sub>) play an important role in sterilization systems, because the OH-radical may be generated on their surface [15, 16]. The great interest to Ag-containing photocatalysts [17-20] is provoked because of their high ion conductivity and possibility to be used in solid state devices.

In this work TiO<sub>2</sub> (P25) is used as a base photocatalytic material. Silver is photocatalytically deposited on the surface of TiO<sub>2</sub> particles. The structure of Ag doped TiO<sub>2</sub> is studied by TEM, SAEDI and XRD methods. The photocatalytic activity of (Ag/TiO<sub>2</sub>) is measured by decomposing MeO in aqueous solution through treatments with UV black lamp and sun irradiation.

### 2. Experimental

#### 2.1 Materials and reagents

Methyl orange and AgNO<sub>3</sub> are obtained from Fluka and used with no further purification. Titanium dioxide used is P25 (anatase 80%, rutile 20%), supplied via Degussa. The structure of methyl orange (C<sub>14</sub>H<sub>14</sub>N<sub>3</sub>SO<sub>3</sub>Na) is characterized by sulphonic groups, responsible for its high solubility in water. Doubly – Fed Induction Generator Modeling

#### 2.2 Preparation of (Ag/TiO<sub>2</sub>)-photocatalysts

The synthesis of (Ag/TiO<sub>2</sub>)-photocatalysts was performed using the following methodology. In a borosilicate

cylinder (inner diameter 35 mm) with volume 0.150 dm<sup>3</sup> TiO<sub>2</sub> powder was imported in an amount providing a concentration 1 g dm<sup>-3</sup>. Diluted aqueous AgNO<sub>3</sub> solution was used with different concentrations to obtain (Ag/TiO<sub>2</sub>)-composites containing different amounts Ag (0.03, 0.1, 0.3 and 0.9 %). Four black lamps (9 inch long), of 6 W power each, were used for UV irradiation. The black lamp peak for the primary wavelength distribution spectrum is at 365 nm and light intensity is 0.35 mW cm<sup>-2</sup>. This composition was magnetically stirred and UV irradiated at room temperature for 24 hours.

### 2.3 Characterization methods

Transmission electron microscopy (TEM) images were taken using a Philips EM 420 microscope with an accelerating voltage of 80 keV and working point resolution of around 0.5 nm. A diffraction contrast in bright field images (BFI) is observed and selected area electron diffraction images (SAEDI) of the samples have also been obtained. X-ray powder diffraction (XRD) spectra were collected at room temperature on a Bruker D8 Advance with Cu K $\alpha$  radiation and SolX detector at 2-theta range from 10 to 80 with a step 0.05 deg 2 theta and counting time 1s/step. The crystalline size was calculated from the peak full-width at half maximum with corrections for instrument line broadening by using the Scherer equation.

The variation of MeO concentration was calculated from optical transmittance measurements.

### 2.4 Photocatalytic degradation experiment

The photocatalytic activity of (Ag/TiO<sub>2</sub>)-photocatalysts was studied by MeO aqueous solution degradation. The concentration of MeO (0.02 g dm<sup>-3</sup>) and its variation is determined from optical transmittance measurements at minimum transmittance (470 nm). The photocatalytic reactor is the same, used for the doping of TiO<sub>2</sub> powder. After exposure, the solutions were filtered, which separated the liquid (MeO solution) from the solid (Ag/TiO<sub>2</sub>)-catalyst phase. The solutions were then spectrophotometrically measured to determine the concentration of methyl orange.

Degradation of MeO was studied in two regimes:

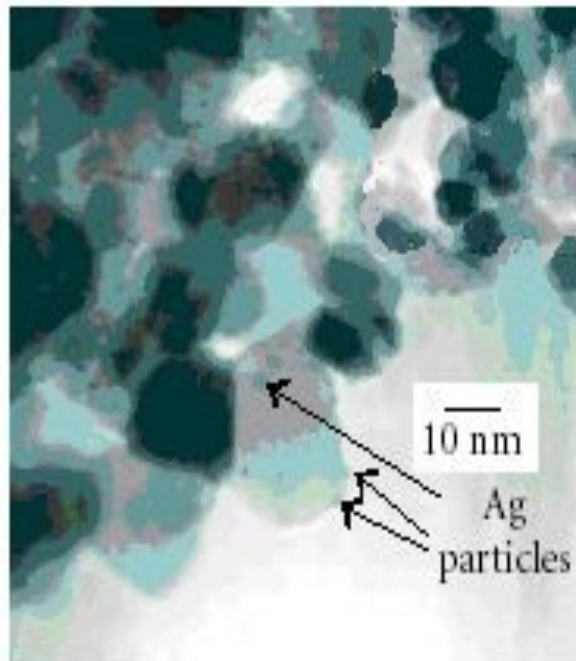
- i) UV irradiation. The borosilicate cylinder with the solution, containing photocatalytic powder (1 g dm<sup>-3</sup>) and 0.02 g dm<sup>-3</sup> MeO was irradiated by four black lamps. Before irradiation the suspension was stirred 10 min in the dark (in order to reach equilibrium state). The sample solutions were irradiated with UV-light for 5 hours at continuous stirring.
- ii) Outdoor sunlight irradiation. This irradiation was carried out with two Pyrex glass reservoirs, placed outside the laboratory building, containing 0.150 dm<sup>3</sup> water with 1 g dm<sup>-3</sup> photocatalyst (TiO<sub>2</sub> powder and Ag doped P25) and 0.02 g dm<sup>-3</sup> MeO. The composition was magnetically stirred. Incident solar radiation was measured with a radiometer (Wm<sup>-2</sup>) in the wavelength range of 285 – 2800 nm.

The degraded MeO composition was filtered and the filtrate was taken for optical measurements.

## 3. Experimental results

### 3.1 Structural investigations

The separated and dried sediment containing the (Ag/TiO<sub>2</sub>)-phase was investigated by appropriate physical methods (TEM, SAEDI, X-ray diffraction). TEM micrograph of (0.3%Ag/TiO<sub>2</sub>)-photocatalyst, is shown in Fig. 1.



**Fig. 1.** TEM micrograph of (0.3%Ag/TiO<sub>2</sub>) powder.

The TEM analyses have shown the existence of a silver phase in the TiO<sub>2</sub> substrate, even for catalysts with comparatively low Ag contents.

A selected area electron diffraction images (SAEDI) analysis of the samples (TiO<sub>2</sub> and (0.3%Ag/TiO<sub>2</sub>)-catalyst) has been carried out. The SAEDI images (Fig. 2) suggest a poly-crystalline structure, composed from inhomogeneous diffraction maximums (with interrupted to spotted character), which are broadened due to overlapping of close situated single circular diffraction maximums. They are obtained by reflection of electrons from many, accidentally oriented along the electron beam. Nano-crystals for both SAEDI measured the first eight diffraction circles with the smallest radius (named with numbers from one to eight). Because of the broadening shape of the diffraction maximums, the maximal and minimal broadening, as well as width, are measured. The values of the maximal and minimal broadening define the ends of interval where interplanar spacing structured diffraction maximums are situated. This interval is the width of the diffraction maximums. The experimental data from SAEDI show that in both samples the main phase is anatase. The existence of silver in (0.3%Ag/TiO<sub>2</sub>)-sample additionally extends the broadening of 3, 5 and 8 diffraction maximums in comparison to pure TiO<sub>2</sub>.

The XRD patterns of the crystalline phases in the powders TiO<sub>2</sub> and (0.1%Ag/TiO<sub>2</sub>), (0.3%Ag/TiO<sub>2</sub>) and (0.9%Ag/TiO<sub>2</sub>) are given in Fig.3.

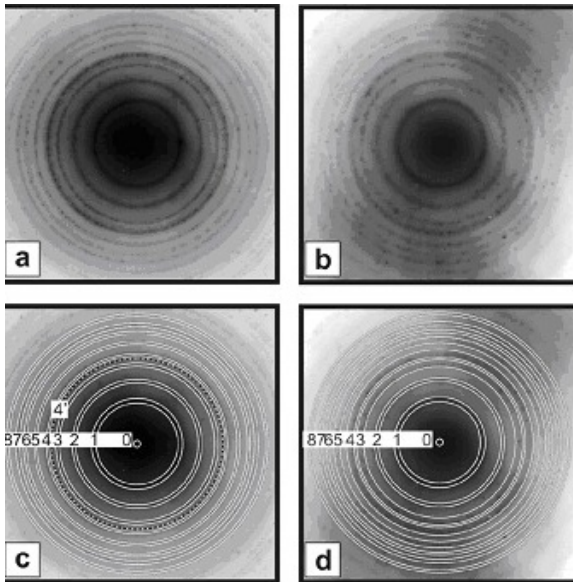


Fig. 2. SAEDI from nanocrystals for samples  $\text{TiO}_2$  (a) and  $(0.3\% \text{Ag}/\text{TiO}_2)$  (b) respectively. Maximal and minimal broadening marked with circumferences placed over the SAEDI for samples  $\text{TiO}_2$  (c) and  $(0.3\% \text{Ag}/\text{TiO}_2)$  (d).

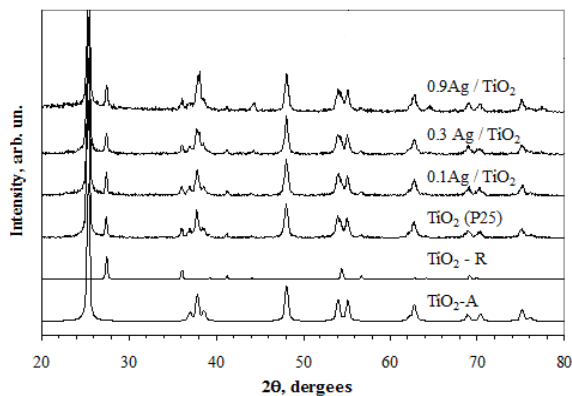


Fig. 3. XRD patterns: calculated:  $\text{TiO}_2/\text{A}$  (anatase) and  $\text{TiO}_2/\text{R}$  (rutile) and experimental:  $\text{TiO}_2$  (P25),  $(0.1\% \text{Ag}/\text{TiO}_2)$ ,  $(0.3\% \text{Ag}/\text{TiO}_2)$  and  $(0.9\% \text{Ag}/\text{TiO}_2)$ .

The  $2\theta$  peaks in the base material ( $\text{TiO}_2$ ) correspond to anatase and rutile, both for the tetragonal crystal modification. The presence of Ag phase does not change the crystalline structure of the  $\text{TiO}_2$  substrate. The registered peaks of the Ag phase suggest a cubic crystalline modification

### 3.2 Photocatalytic experiments

Photocatalytic activity of  $(\text{Ag}/\text{TiO}_2)$ , depending on Ag content is studied. In all experiments  $1 \text{ g dm}^{-3} \text{ TiO}_2$  (P25) and  $0.2 \text{ g dm}^{-3} \text{ MeO}$  are used. The weight percentage in the  $(\text{Ag}/\text{TiO}_2)$  system is calculated from the quantity of Ag which takes part in the photocatalytic reduction process. Four  $(\text{Ag}/\text{TiO}_2)$ -composites were investigated, containing different quantities (% Ag) silver (0.03, 0.1, 0.3 and 0.9). Photocatalytic activity of the  $(\text{Ag}/\text{TiO}_2)$  is compared to the activity of pure  $\text{TiO}_2$  powder (P25). The concentration (C) of MeO is measured using the Beer's law at the absorption maximum (475 nm). In order to illustrate the impact of the silver concentration in

$(\text{Ag}/\text{TiO}_2)$ -catalyst Fig.4 presents data for 5 h UV-irradiation, at  $20^\circ\text{C}$ . The obtained results show that the increase of the silver amount in  $(\text{Ag}/\text{TiO}_2)$ -catalysts, with other conditions being equal, leads to an increase of the degradation degree of MeO. Titanium dioxide doped with silver ions, exposed to UV radiation, is a more efficient photocatalyst than pure  $\text{TiO}_2$ .

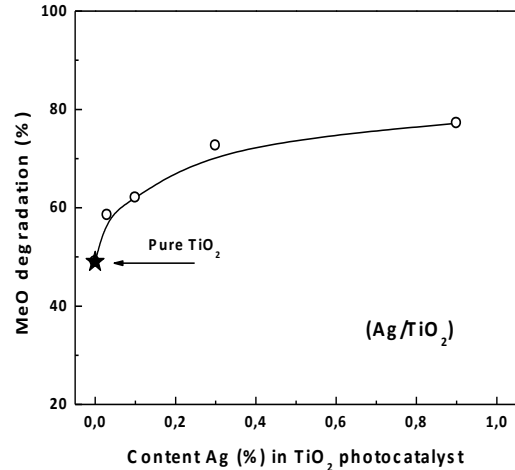


Fig. 4. Dependence of the MeO degradation degree on silver content in  $(\text{Ag}/\text{TiO}_2)$ -catalysts.

It was of interest to determine the kinetic law by which the process of MeO degradation occurs. For this purpose, the kinetic curves have been presented in the appropriate coordinates. Figure 5 presents the  $(\log C_0/C)$  vs. time (t) of UV treatment dependence for  $\text{TiO}_2$  and  $(\text{Ag}/\text{TiO}_2)$ -catalysts with different Ag amounts. The plot of  $[-\log(C_0/C)]$  versus time (t) is a straight line, the slope ( $\tan \theta$ ) of which upon linear regression equals the apparent first-order rate constant ( $k = 2.303 \tan \theta$ ). The first-order kinetics for MeO photocatalysed degradation, has also been established by other authors [21, 22].

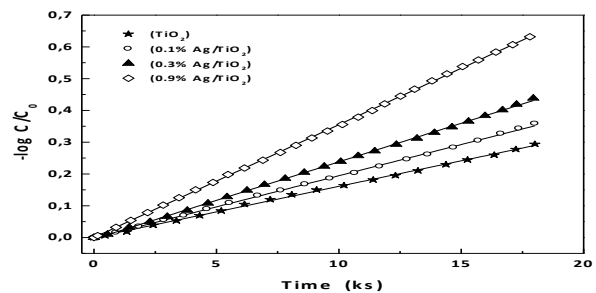


Fig. 5. Methyl orange UV degradation in the presence of  $\text{TiO}_2$  (P25) and  $(\text{Ag}/\text{TiO}_2)$ -photocatalysts with different Ag contents

It was of interest to provide a qualitative assessment of the catalytic ability of  $(\text{Ag}/\text{TiO}_2)$ -catalysts by irradiating the solution with solar light. This assessment has a relative nature, as the sunlight is not constant during the day. For the measurements is taken into account the spectral dispersion of the solar energy (AM2) which is characteristic for the present geographic location.

Comparative data for one of the catalysts (0.3%Ag/TiO<sub>2</sub>) and pure TiO<sub>2</sub> are presented in Table 1.

**Table 1.** Solar irradiation degradation of MeO

Photo catalyst	Solar radiation (Wm <sup>-2</sup> )	Outdoor Temperature (°C)	Degradation (%)
TiO <sub>2</sub>	320	16	31.2
(0.3%Ag/TiO <sub>2</sub> )	320	16	41.1
TiO <sub>2</sub>	720	23	57.3
(0.3%Ag/TiO <sub>2</sub> )	720	23	87.2

Irradiation of samples was carried out with the same duration (2 hours), at two temperatures and two different light intensities.

The results reconfirmed the fact that in all cases the presence of silver in the TiO<sub>2</sub>-catalyst increases the amount of degraded methyl orange.

#### 4. Conclusions

Silver can be deposited on the surface of TiO<sub>2</sub> (P25) using aqueous AgNO<sub>3</sub> solution and a UV photocatalytical process. The increase of AgNO<sub>3</sub> content in the solution, results in higher Ag amounts in the structure. Photocatalytical decomposition of methyl orange by

(Ag/TiO<sub>2</sub>) depends on Ag content in the structure. Elevated Ag content brings to higher rate of methyl orange decomposition. The probable mechanism might be recombination of UV irradiation induced electrons and holes. As a result the rate of methyl orange decomposition on (Ag/TiO<sub>2</sub>) substantially grows as compared to the standard substrate P25. High photocatalytic activity for the MeO reduction using lamps of low energy UV emission ( $\lambda = 365$  nm) was obtained for the (Ag/TiO<sub>2</sub>)-catalysts, improving the rate constant of reduction with up to 3 times compared to TiO<sub>2</sub> alone (reference). These results evidence a very important role of Ag in photoreduction reactions for organic compounds, in this particular case for the reduction of MeO. The methyl orange photocatalytic decomposition corresponds to a first order reaction. These catalysts exhibit a significant efficiency by the methyl orange decomposition even under solar irradiation only. The physical methods used show the presence of a silver phase (TEM), a polycrystalline structure (SAEDI), and lack of change of the structure and composition of modified with silver TiO<sub>2</sub> (XRD).

As conclusion, the reported results indicate that (Ag/TiO<sub>2</sub>)-catalysts can be successfully used for the complete degradation of azo-dyes.

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