

Photocatalytic and Self-Cleaning Properties of Ag-Doped TiO₂

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Abstract: Commercially available TiO₂ of anatase structure produced in the Chemical Factory Police S.A. was modified by doping Ag from AgNO₃ solution *via* photodeposition method. The obtained amount of deposited Ag on TiO₂ was in the range of 0.11 to 0.98 mass %. Deposition of Ag on TiO₂ resulted in the retarding of the recombination reaction and formation of the higher amount of OH radicals on the photocatalyst surface during irradiation with UV light. The photocatalytic activity of samples was tested for the decomposition of phenol and Reactive Black in the water solution under both, UV and artificial solar light radiation. Deposition of Ag on TiO₂ surface increased its photocatalytic activity towards the Reactive Black decomposition but not for phenol. High adsorption of Reactive Black on Ag modified TiO₂ photocatalysts, which was higher than on TiO₂, could enhance the photocatalytic activity of these samples. The solution with 1% slurry of TiO₂-Ag was sprayed on the surface of concrete. For concrete impregnated with TiO₂-Ag slurry the both, fungicidal and self-cleaning effect for dyes were observed.

Keywords: Ag doped TiO₂, self-cleaning, reactive black decolourisation, photocatalysis.

1. INTRODUCTION

TiO₂ has many applications in the environment. TiO₂ under ultraviolet irradiation exhibits photocatalytic activity that enables the oxidative destruction of a wide range of organic compounds (phenols, pesticides, herbicides, dyes, pharmaceuticals, organic acids, alcohols, etc.) and biological species (bacteria, viruses, cyanobacteria, algae, and fungi), causing self-decontamination effect [1-4]. In addition, TiO₂ exposed under UV exhibits photocatalytically induced superhydrophilicity that converts the hydrophobic character of the surface to hydrophilic and forms the uniform water film, which prevents the adhesion of inorganic or organic components on its surface, which retains clean [5, 6]. The powdered TiO₂ may be deployed on the surfaces of various substrates, such as glass, ceramics, metals, textiles, cement, bricks or fibres to provide layer that exhibits self sterilisation and self cleaning properties, when it is exposed to the light [7-10]. This creates a large commercial potential for TiO₂ application: in medicine, automotive and food industries, environmental protection, but especially in the architecture (cultural heritage purposes, facade paints, indoor, wall paper, tiles, etc.).

It has been proved that TiO₂ doped with Ag can sufficiently decompose some dyes and organic acids, such as oxalic and salicylic acids, as well as the other organic compounds, like saccharose, phenol, etc. [11-15]. TiO₂ doped with Ag and mounted on the ceramics can also work as a gas filter for removing some odours like H₂S, CH₃SH or toxic N₂O gas [16, 17]. Ag deposited on the surface of TiO₂ can prevent the recombination reaction between photogenerated holes and electrons, enhancing the yield of photocatalytic activity of the semiconductor [18]. Nanoparticles of Ag can also work as a catalyst in the

photocatalytic reaction [13]. Some of the photocatalytic oxidation reactions are carried out with simultaneous reduction of Ag ions during its deposition on the surface of TiO₂ [14, 15].

In the present work, Ag was deposited on the commercial TiO₂ of an anatase structure by the photodeposition method under UV from AgNO₃ solution under flow of Ar gas. The prepared Ag-doped TiO₂ have been tested for the decomposition of the Reactive Black and phenol under both, UV, and artificial solar light irradiation. The titania slurry with doped Ag have been spread on the concrete of the house and the self-cleaning and fungicidal effects have been observed.

2. MATERIALS AND METHODOLOGY

2.1. Photocatalyst Preparation

Commercially produced TiO₂ in Chemical Factory Police S.A. in Poland has been used for preparation. 3g of powdered TiO₂ has been placed in a quartz beaker together with AgNO₃ solution (75 mL) with different concentrations, 7.4·10⁻³- 4.6·10⁻⁴ mol/L. KOH (0.1 M) was added to obtain pH = 6.3. The mixture was magnetically stirred by 15 min, after that 1 mL of methanol was added and the mixture was rinsed with argon by 45 min. Then UV lamp was switched on and the solution was irradiated for 2h with simultaneous flow of argon gas. The obtained Ag-doped TiO₂ after photodeposition has been filtered through the membrane filter 0.45 μm, rinsed with distilled water and dried in oven at 105°C for 12 h.

2.2. Photocatalytic Activity

The activity of photocatalysts in both visible and UV light was conducted in a beaker filled with 500 ml of phenol (0.1 g/L) or Reactive Black (0.03 g/L) solutions and photocatalyst (0.1 g/L). In case of phenol solution, there was observed almost no adsorption on the photocatalyst surface and reaction was carried out under irradiation for 5 h. In case

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of Reactive Black solution a marked adsorption on the photocatalyst surface has been observed, therefore the photocatalytic reaction has been carried out for 4 h in the dark until saturation with Reactive Black adsorption, and then the following process of photocatalysis was started by switching the lamp. During adsorption and photocatalytic decomposition the solutions with photocatalyst have been simultaneously mixed with the magnetic stirrer. The concentrations of the phenol and Reactive Black solutions have been analysed in UV-Vis Spectrophotometer by the measure of the absorption light at $\lambda_{\text{max}} = 270$ and 597 nm for phenol and Reactive Black, respectively. Turbidity of the titania slurry solution has been measured each time after photocatalytic process and 10 min of sedimentation. The prepared Ag-doped TiO₂ slurry (1%) has been painted on the concrete outdoor of the living house. The concrete surface has been cleaned up before painting, moss has been removed. The painting part with Ag-doped TiO₂ and the non-painting part have been stained with a dye – Reactive Black. This concrete has been exposed to sunlight. The observations of self-cleaning effects have been done and some photos have been taken to evident this process.

2.3. Analytical Methods and Techniques

Content of silver in prepared Ag-doped TiO₂ photocatalysts was determined by using inductively coupled plasma atomic emission spectroscopy (ICP-AES) method in ICP-AES Spectrometer (by Jobin - Yvon). The recombination reaction of TiO₂ and Ag-doped TiO₂ powders was measured by photoluminescence spectra at temperature of liquid nitrogen at excitation wavelength $\lambda = 330$ nm. The spectra were taken in the Fluorescence Spectrometer Hitachi F-2500 equipped with low temperature sample compartment accessory. Hydroxyl radicals have been detected by using fluorescence technique. Terephthalic acid can easily react with hydroxyl radicals to form highly fluorescence compound, 2-hydroxyterphthalic acid, which is determined in the Fluorescence Spectrometer Hitachi F-2500. For these measurements the photocatalyst samples have been irradiated under UV in the terephthalic acid solution ($2 \cdot 10^{-3}$ M) and then the solution, after separation from a photocatalyst was taken to analysis. The fluorescence measurements have been done at the excitation wavelength of 314 nm and the emission of 330-600 nm with maximum peak at 425 nm. The detailed procedure has been described elsewhere [19].

3. RESULTS AND DISCUSSION

Ag-doped TiO₂ samples after photodeposition turned to brown colour, which was more intensive when higher concentration of AgNO₃ solution was used. After exposition to air, these Ag-doped TiO₂ samples became white, probably due to the oxidation process.

In Table 1 are presented the results from the ICP measurements, together with the sample names and starting concentration of AgNO₃ solutions used for photodeposition. Higher concentration of AgNO₃ solution resulted in higher amount of deposited Ag on TiO₂ surface.

Photoluminescence spectra of TiO₂ and Ag-TiO₂ photocatalysts measured in a spectrofluorimeter after excitation at $\lambda = 330$ nm are shown in Fig. (1). For comparison Ag-doped TiO₂ samples with the highest and the

lowest contents of Ag were shown. A very broad peak with maximum at around 515 nm can be observed. The intensity of this peak decreases in the samples with Ag deposition. It is caused by the retarding of the recombination due to the capture of electrons by the Ag deposited on TiO₂ surface. In Fig. (2) the results from the measurements of OH radicals formation on the photocatalysts surface under UV irradiation are presented. Amount of OH radicals is increasing with the time of UV irradiation. Insignificant higher amount of OH radicals was formed on the surface of Ag-doped TiO₂ than on the not modified TiO₂. Increase of OH radicals formation on Ag-doped TiO₂ samples can be caused by the better separation of free carriers (retarding the recombination reaction in the semiconductor through the capture of electrons by silver deposited on TiO₂) and enhanced yield of reaction between photogenerated holes and adsorbed water molecules on the photocatalyst surface.

Table 1. Content of Ag in Ag-Doped TiO₂ and Initial Concentrations of AgNO₃ Solution Used for Photodeposition

Concentration of AgNO ₃ [mol/L]	Content of Ag [mass %]	Sample Name
$7.40 \cdot 10^{-3}$	0.98	Ag1
$3.70 \cdot 10^{-3}$	0.68	Ag2
$1.85 \cdot 10^{-3}$	0.39	Ag3
$9.25 \cdot 10^{-4}$	0.18	Ag4
$4.62 \cdot 10^{-4}$	0.11	Ag5

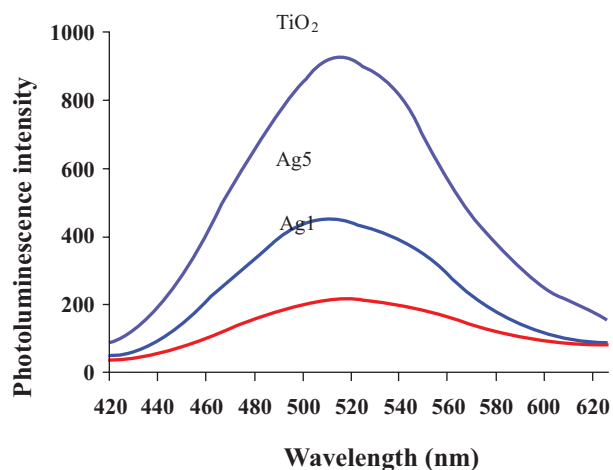


Fig. (1). Photoluminescence spectra of TiO₂ and Ag-doped TiO₂ photocatalysts.

The photocatalytic decomposition of phenol has been performed on the prepared photocatalysts under UV and artificial solar light irradiation. Results are listed in Table 2. Phenol has been poorly decomposed, either under UV or solar light irradiation, modification of TiO₂ by Ag deposition did not enhance the photocatalytic activity of TiO₂.

In Fig. (3) the adsorption and photocatalytic decomposition of Reactive Black under UV and artificial solar light irradiation are presented. High adsorption of

Reactive Black on the photocatalysts surface has been observed. Modification of TiO₂ by silver deposition increased amount of adsorbed dye in Ag-doped TiO₂ samples and therefore accelerated the process of dye decomposition. The highest adsorption ability towards Reactive Black had sample Ag3, which also showed the highest rate of Reactive Black decolourisation under UV irradiation. However, under artificial solar light irradiation, Ag1, Ag2, and Ag3 samples showed higher rate of Reactive Black decomposition than Ag4 and Ag5 but all of them showed higher decomposition than TiO₂.

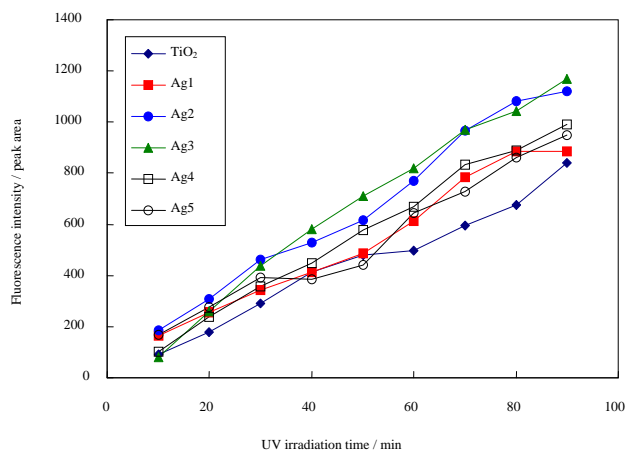


Fig. (2). Formation of OH radicals on the photocatalysts surface with time of UV irradiation.

Table 2. Phenol Decomposed After 5 h of UV and 24 h of Artificial Solar Light Irradiation

Photocatalyst	Phenol Decomposition [%]	
	UV Light (5 h)	Artificial Solar Light (24 h)
TiO ₂	13.1	11.9
TiO ₂ -Ag1	14.2	8.9
TiO ₂ -Ag2	13	10.2
TiO ₂ -Ag3	11.3	9.5
TiO ₂ -Ag4	8.2	10.8
TiO ₂ -Ag5	14.2	11.3

The solution with 1% slurry of Ag-doped TiO₂ has been used for coating of concrete. The concrete has been stained with a Reactive Black solution on both, the coated and uncoated part and then the self-cleaning effect has been monitored with the time of its exposure in the sunlight. In Figs. (4, 5), the photos of the concrete are shown. Both, fungicidal and decolourisation effects can be observed, the part coated with Ag-doped TiO₂ became clean with the time of sunlight exposure and also no any moss grew up as it was observed on the uncoated part of concrete in Fig. (5).

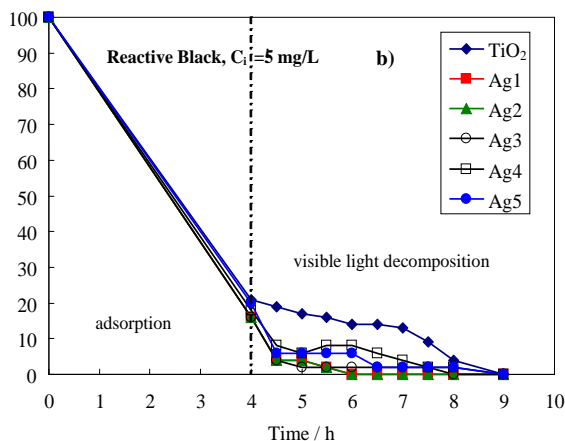
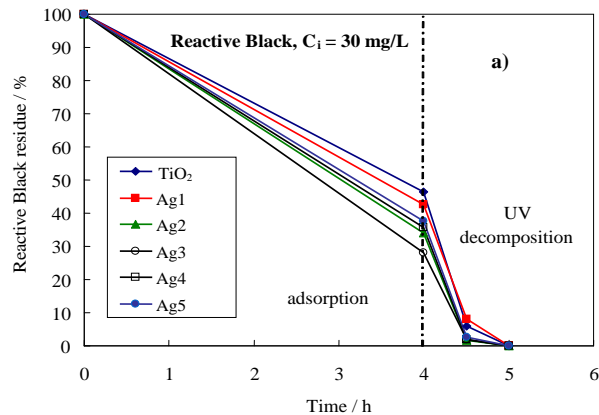


Fig. (3). Reactive Black decomposition on TiO₂ and Ag-doped TiO₂ photocatalysts under irradiation of a) UV light, and b) artificial solar light.

4. CONCLUSIONS

TiO₂ was modified by the deposition of Ag from AgNO₃ solution in the amount of 0.11-0.98 mass %. The presence of Ag on the surface of TiO₂ caused retarding the recombination reaction which occurs after excitation of semiconductor with UV light. Increase of the OH radicals formation during UV irradiation in Ag-doped samples was observed due to the better separation of free carriers, however there was no linear relation of the photocatalyst ability to OH radicals formation on the content of Ag in TiO₂. It was probably resulted from the different hydrophilicity of the samples and the quantity of the adsorbed water molecules on their surface. Deposition of Ag on TiO₂ photocatalyst did not enhance the phenol decomposition, however increased the Reactive Black adsorption on the photocatalyst surface and its decomposition under both, UV and artificial solar light irradiation. It was proved that prepared Ag-doped TiO₂ samples can be efficiently used for self-cleaning surfaces, especially for decomposition of stained surfaces, because of their good ability for adsorption of organic dyes and good photocatalytic effects. Sterilizing effect of Ag-doped TiO₂ is also a great advantage of this photocatalyst.

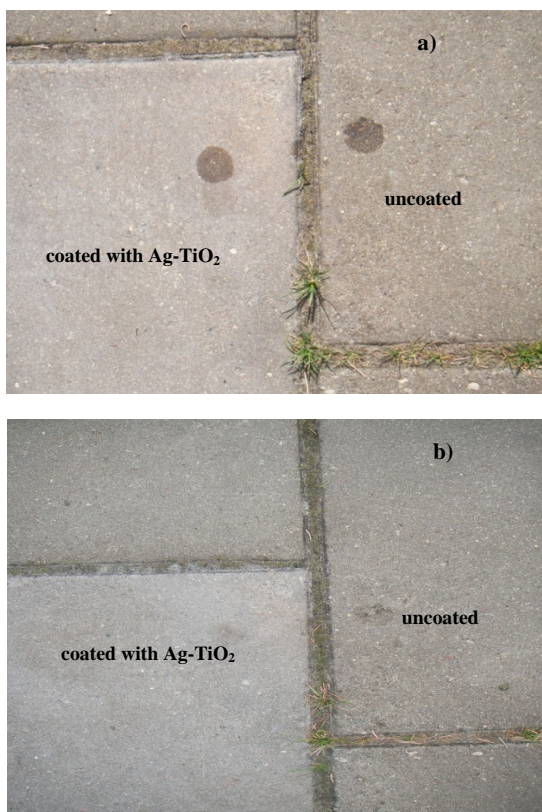


Fig.(4). Photos of the concrete partly coated with titania slurry and stained with a dye on the coated and a uncoated parts, **a)** after stained, and **b)** after exposure to solar light.



Fig. (5). Photo of concrete partly coated with titania slurry solution (1% of Ag-TiO₂).

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