

Photocatalytic and Self-Cleaning Properties of Ag-Doped TiO₂

B. Tryba*, M. Piszcz and A.W. Morawski

West Pomeranian University of Technology, 70-322 Szczecin, Poland

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

*Address correspondence to this author at the West Pomeranian University of Technology, 70-322 Szczecin, Poland; Tel: +48 91 449 4730; Fax: +48 91 449 4656; E-mail: beata.tryba@zut.edu.pl

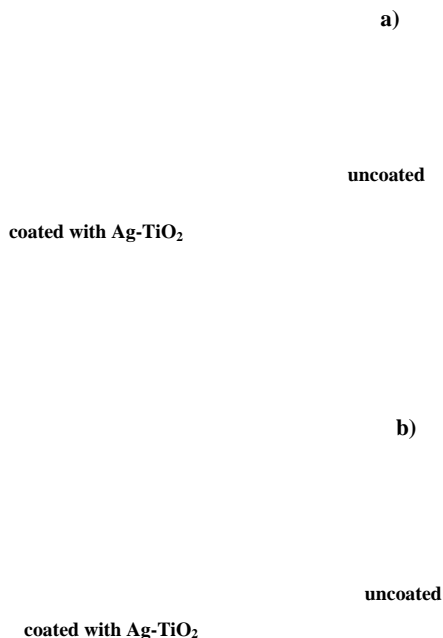


Fig.(4). Photos of the concrete partly coated with titania slurry solution and stained with a dye on the coated and a uncoated parts, **a)** after stained, and **b)** after exposure to solar light.



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

ACKNOWLEDGEMENT

This work was supported by the research project from the Ministry of Science and Higher Education Nr COST/299/2006 for 2007-2010.

REFERENCES

- [1] Fujishima A, Hashimoto K, Watanabe T. TiO₂ photocatalysis fundamentals and applications. BKC Inc 1999.
- [2] Piera E, Tejedor MI, Zorn ME, Anderson MA. Degradation of chlorophenols by means of advanced oxidation processes: a general review. Appl Catal B Environ 2004; 47: 219-56.
- [3] Ohko Y, Utsumi Y, Niwa C, et al. Self-sterilizing and self-cleaning of silicone catheters coated with TiO₂ photocatalyst thin films: a preclinical work. J Biomed Mater Res 2001; 58: 97-101.
- [4] Pratap RM, Venugopala A, Subrahmanyam M. Hydroxyapatite-supported Ag-TiO₂ as *Escherichia coli* disinfection photocatalyst. Water Res 2007; 41: 379-86.
- [5] Zubkov T, Stahl D, Thompson TL, Panayotov D, Diwald O, Yates JT. Ultraviolet light-induced hydrophilicity effect on TiO₂(110)(1×1). Dominant role of the photooxidation of adsorbed hydrocarbons causing wetting by water droplets. J Phys Chem B 2005; 109: 15454-62.
- [6] Gao Y, Masuda Y, Koumoto K. Light-excited superhydrophilicity of amorphous TiO₂ thin films deposited in an aqueous peroxotitanate solution. Langmuir 2004; 20: 3188-94.
- [7] Yuranova T, Mosteco R, Bandara J, Laub D, Kiwi J. Self-Cleaning cotton textiles surfaces modified by photoactive SiO₂/TiO₂ coating. J Mol Catal A Chem 2006; 244: 160-7.
- [8] Sanchez B, Coronado JM, Candal R, et al. Preparation of TiO₂ coatings on PET monoliths for the photocatalytic elimination of trichloroethylene in the gas phase. Appl Catal B Environ 2006; 66: 295-301.
- [9] Hidalgo MC, Sakthivel S, Bahnemann D. Highly photoactive and stable TiO₂ coatings on sintered glass. Appl Catal A Gen 2004; 277: 183-9.
- [10] Hashimoto K, Irie H, Fujishima A. TiO₂ photocatalysis: A historical overview and future prospects. Jpn Soc Appl Phys 2005; 44: 8269-85.
- [11] Sobana N, Murugandham M, Swaminathan M. Nano-Ag particles doped TiO₂ for efficient photodegradation of Direct azo dyes. J Mol Catal A Chem 2006; 258: 124-32.
- [12] Arabatzis IM, Stergiopoulos T, Bernard MC, Labou D, Neophytides SG, Falaras P. Silver-modified titanium dioxide thin films for efficient photodegradation of methyl orange. Appl Catal B Environ 2003; 42: 187-201.
- [13] Vamatheron V, Amal R, Beydoun D, Low G, McEroy S. Photocatalytic oxidation of organics in water using pure and silver-modified titanium dioxide particles. J Photochem Photobiol A Chem 2002; 148: 233-45.
- [14] Szabo-Bárdos E, Czili H, Horváth A. Photocatalytic oxidation of oxalic acid enhanced by silver deposition on a TiO₂ surface. J Photochem Photobiol A Chem 2003; 154: 195-201.
- [15] Dobosz A, Sobczykński A. The influence of silver additives on titania photoactivity in the photooxidation of phenol. Water Res 2003; 37: 1489-96.
- [16] Kato S, Hirano Y, Iwata M, Sano T, Takeuchi K, Matsuzawa S. Photocatalytic degradation of gaseous sulfur compounds by silver-deposited titanium dioxide. Appl Catal B Environ 2005; 57: 109-15.
- [17] Sano T, Negishi N, Mas D, Takeuchi K. Photocatalytic decomposition of N₂O on highly dispersed Ag⁺ ions on TiO₂ prepared by photodeposition. J Catal 2000; 194: 71-9.
- [18] Ilisz I, Dombi A. Investigation of photodecomposition of phenol in near - UV-irradiated aqueous TiO₂ suspensions. II. Effect of charge-trapping species on product distribution. Appl Catal A Gen 1999; 180: 35-45.
- [19] Ishibashi K, Fujishima A, Watanabe T, Hashimoto K. Detection of active species in TiO₂ photocatalysis using the fluorescence technique. Electrochem Commun 2000; 2: 207-10.