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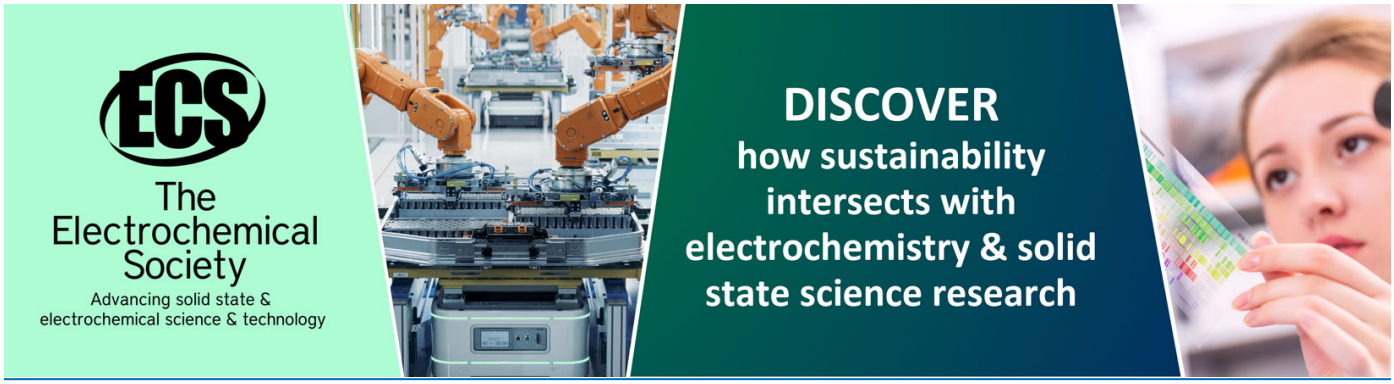

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The effect of NPs addition on the photocatalytic and antibacterial effectivity of composite TiO_2/SiO_2 paint

M Jakubickova[1] M Petrzilkova[1] B Amartuvshin[1] L Kejzlarova[1] and P Kejzlar[1]

[1] Technical University of Liberec, Studentska 1402/2, 461 17, Liberec, Czech republic

michaela.jakubickova@tul.cz

Abstract. TiO_2 in the anatase allotropic modification is well known for its photocatalytic activity. When the anatase is irradiated by UVA light, it forms an electron-hole pair which can participate in redox reaction. Thus, anatase-based layers are suitable for decomposition of organic compounds. Surface self-cleaning ability as well as antimicrobial efficacy are therefore key features for TiO_2 based layers. The present paper deals with a study of ZnO, CuO and Ag NPs addition on the antibacterial and photocatalytic effectivity of TiO_2/SiO_2 paint.

1 Introduction

Building facades, especially at high air humidity and poorly sunlit areas, are under strong attack of microorganisms like bacteria, algae and fungi. These microorganisms cause not only structural disintegration of the facades and subsequent functional malfunction, but often also disrupt the aesthetic appearance of the buildings.

There are few possibilities how to treat such affected areas. The biofilm can be removed physically (e.g. high-pressure water cleaning or mechanical brushing) or chemically (e.g. chlorine-based products). Unfortunately, these methods are effective only in the short term. In addition, often repeated mechanical cleaning destroys the façade itself and the use of chemical products is environmentally harmful. Effective solution offers the use of photocatalytic paints. If the light with appropriate wavelength hits the surface of photocatalytic active substance, electron-hole pairs are created. These pairs further generate free radicals (e.g. hydroxyl radicals OH) which can undergo secondary reactions. These include the gradual oxidative degradation of organic substances including microorganisms. Finally, even the most complex organic molecules are transformed into harmless simple inorganic compound, such as carbon dioxide, water and corresponding mineral acids. [1]

The photocatalytic paint under the name Balclean® used in the present experiment was developed in 2016 on the Technical University of Liberec in cooperation with Czech Academy of Science, BARVY A LAKY TELURIA, s.r.o. and PRAGOTHERM, servis fasad s.r.o. [2]

Key properties of paints used for cleaning of facades include high photocatalytic effectivity and stability under environmental conditions. Effectivity of such paints can also benefit from antimicrobial activity when the coating is not exposed to UV radiation.

The nanoparticles of some metals represent inhibitors of effects for many microorganisms. In particular, ZnO, CuO and Ag nanoparticles are known for their cytotoxicity to eukaryotic and prokaryotic cells. Due to their size, nanoparticles can penetrate through the cell membranes into the cytosol and then target multiple parts of the cell where their action induces complex processes. [3]

In bacterial strains such as E.Coli and S.Aureus, silver nanoparticles attach directly to the cell wall, where increases breathability and subsequently disrupts metabolism. [4,5] CuO nanoparticles are known for their antimicrobial effects (toxic to fungi, viruses and bacteria) and are mainly used as antimicrobial agents. They are effective against both susceptible microorganisms and microorganisms exhibiting resistance to antibiotics used for treatment. They have been shown to have the ability to kill more than 99 % of gram-positive or gram-negative bacteria when exposed for 4 hours when administered at the appropriate dose. CuO nanoparticles show greater cytotoxicity to gram-negative E. coli than gram-positive S. aureus. [6] Another metal oxide which disrupts the cell membrane is ZnO. When the ZnO particles have small size, the specific surface area of the particles increases, promoting their penetration into cells through cell membranes. The penetrated ZnO particles exhibit high solubility in both extracellular and intracellular fluids. Consequently, the metabolism of the cell is impaired, which is attenuated towards the external environment. [7]
The aim of this research is to determine the effect of selected nanoparticles on antibacterial and photocatalytic activity of the Balclean® paint.

2 Experimental

Three types of laboratory prepared nanoparticles were added into the Balclean paint in amount of 1 %. Namely, Ag, ZnO and CuO were selected as suitable materials. For the purposes of Ag nanoparticles was chosen method of chemical reduction of silver nitrate (AgNO3), which is found predominantly on the findings from the work [8]. Sensitive trisodium dihydrates (C6H5Na3O7, 2H2O) as well as formaldehyde (CH2O with stabilizing effect) were used as reducing agents, which can be eliminated from the final product by washing and centrifugation.
Reactions receive equations:

$$12AgNO_3 + 4C_6H_5O_7Na_3 + 6H_2O \rightarrow 12Ag^o + 4C_6H_5O_7H_3 + 12NaNO_3 + 3O_2$$

$$2\ AgNO_3 + H_2O + HCHO \rightarrow 2\ Ag^o + 2\ HNO_3 + HCOOH$$

The chemical precipitation method was chosen for the preparation of ZnO nanoparticles. The exact procedure used in the preparation of ZnO nanoparticles is reported in the paper [9].
The reaction proceeds according to the equation:

$$ZnSO4*7H_2O + 2NaOH \rightarrow Zn(OH)_2 + Na_2SO_4 + 7H_2O$$

$$Zn(OH)_2 + 2H_2O \rightarrow [Zn(OH)_4]^{2-} + 2H^+ \rightarrow ZnO + 3H_2O$$

For the preparation of CuO nanoparticles the chemical precipitation method was also chosen.
The reaction proceeds according to the equation:

$$Cu(NO_3)_2*3H2O + 2NaOH \rightarrow Cu(OH)_2 + 2NaNO_3 + 3H_2O$$

$$Cu(OH)_2 \rightarrow CuO + H_2O$$

The results and structure of the used particles are shown in Figures 1-3. A Bandeline ultrasonic homogenizator was used to homogenize the particles in solution. Using this apparatus, the agglomerates of the particles in solution were separated into individual nanoparticles and at the same time the resulting solution was homogenized. The prepared suspension was subsequently

transferred to an ultrasonic homogenizer where it was further homogenized and dispersed at a frequency of 20 kHz for 5 minutes.

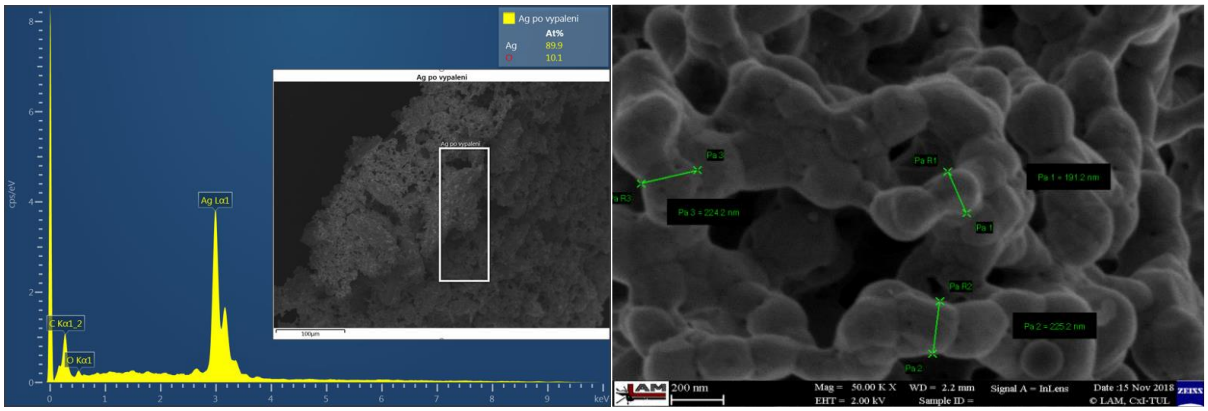

Figure 1. EDS analysis and SEM image showing the structure of Ag nanoparticles.

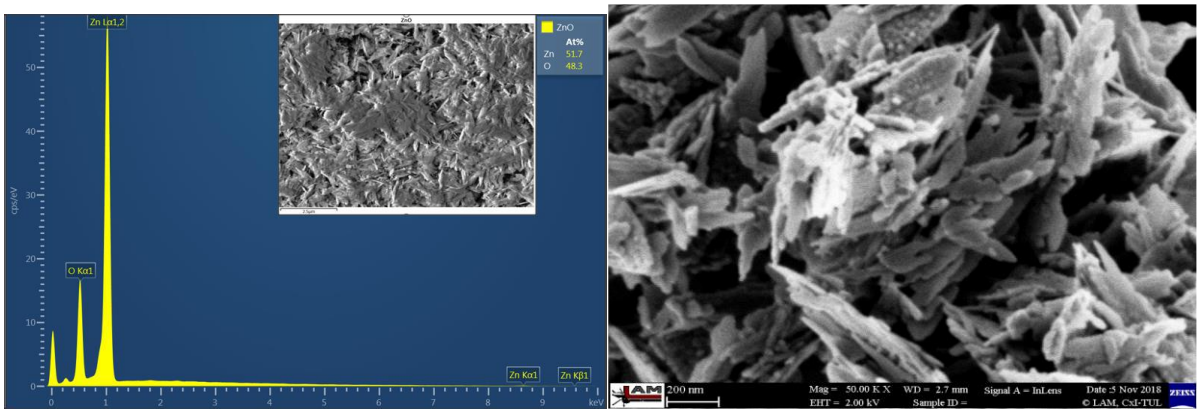

Figure 2. EDS analysis and SEM image showing the structure of ZnO nanoparticles.

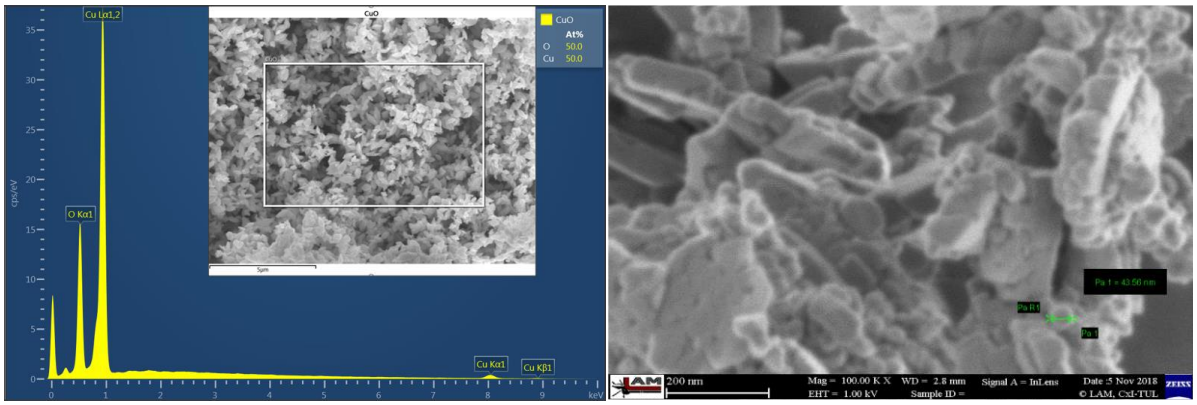

Figure 3. EDS analysis and SEM image showing the structure of CuO nanoparticles.

A matt glass with dimensions of 50 x 50 x 1 mm was selected as a suitable substrate. 100 µl from prepared nanoparticle suspensions was pipetted onto the surface of the glass plate cleaned by ethanol. The solution was spread over the substrate using a brush.
The antibacterial activity was measured according to ISO 27447/2009. The antibacterial properties of the samples were measured using a Gram-negative bacterial culture of Eschericha coli CM 3954.

Using McFarland dilutions, the initial cell concentration was 3×108 cells/ml. Appropriate inoculated samples were placed in Petri dishes. 150 µl of prepared inoculum was pipetted onto the samples and spread evenly over the surface of the sample. Petri dishes were covered with a transparent film. Half of the Petri dishes with inoculated test samples were incubated in the dark while the other half were incubated under the UVA lamp (intensity 0.25 mW / cm2). Samples for direct rinsing were processed without incubation for 4 hours, after which the inoculum was applied to the glass plate, immediately rinsed with 10 ml of saline and diluted in decimal series. After the exposure period, samples were transferred to shaking tubes. The samples were then rinsed with 10 ml saline and mixed thoroughly on a Vortex shaker. By decadic series, samples of bacteria concentrations were diluted. This procedure is shown in figure 4. Subsequently, 1 ml was pipetted into Petri dishes. Then, these Petri dishes were embedded with Nutrient agar and incubated in a thermostat at 37 °C for 48 hours. After 48 hours, Petri dishes were removed from the thermostat and viable bacteria count (CFU) was performed. In addition, an agar inoculum was inoculated to control whether the bacterial culture was vital.

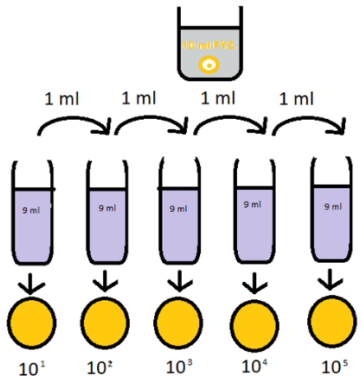

Figure 4. Schematic procedure of decimal dilution.

Methylene blue degradation was measured according to ISO 10678; 2010. Prior to testing, samples were exposed to UV radiation. The irradiation lasted 23 hours at an intensity of 1 mW / cm^2. Samples were placed in dishes with 80 ml of 20 µmol/dm^3 methylene blue (MB) solution and left in the dark for 16 hours. After 16 hours, 3 ml of MB solution were removed from each dish. Consequently, the concentration was measured with a UV / VIS spectrophotometer at a wavelength of 665 nm till the MB concentration dropped below 10 µmol/dm^3.
Subsequently, in all dishes, the old MB solution was replaced with 80 ml of a new 10 µmol/dm^3 MB solution and the dishes were covered with a transparent plastic lid.
The plates (glass plates with photocatalytically active layer and 10 µmol/dm^3 MB solution) were sequentially placed at a distance of 15 cm from the sample surface under an UV lamp (intensity 2 mW/cm^2), while the reference sample was kept in the dark. Subsequently, from the beginning of exposure to the first sample, after 20 minutes, 3 ml of MB solution were taken from each plate together with the reference sample and their concentration was measured by UV/VIS spectrophotometer at a wavelength of 665 nm. The exposure time of the sample was 3 h under UV.

Results and discussion

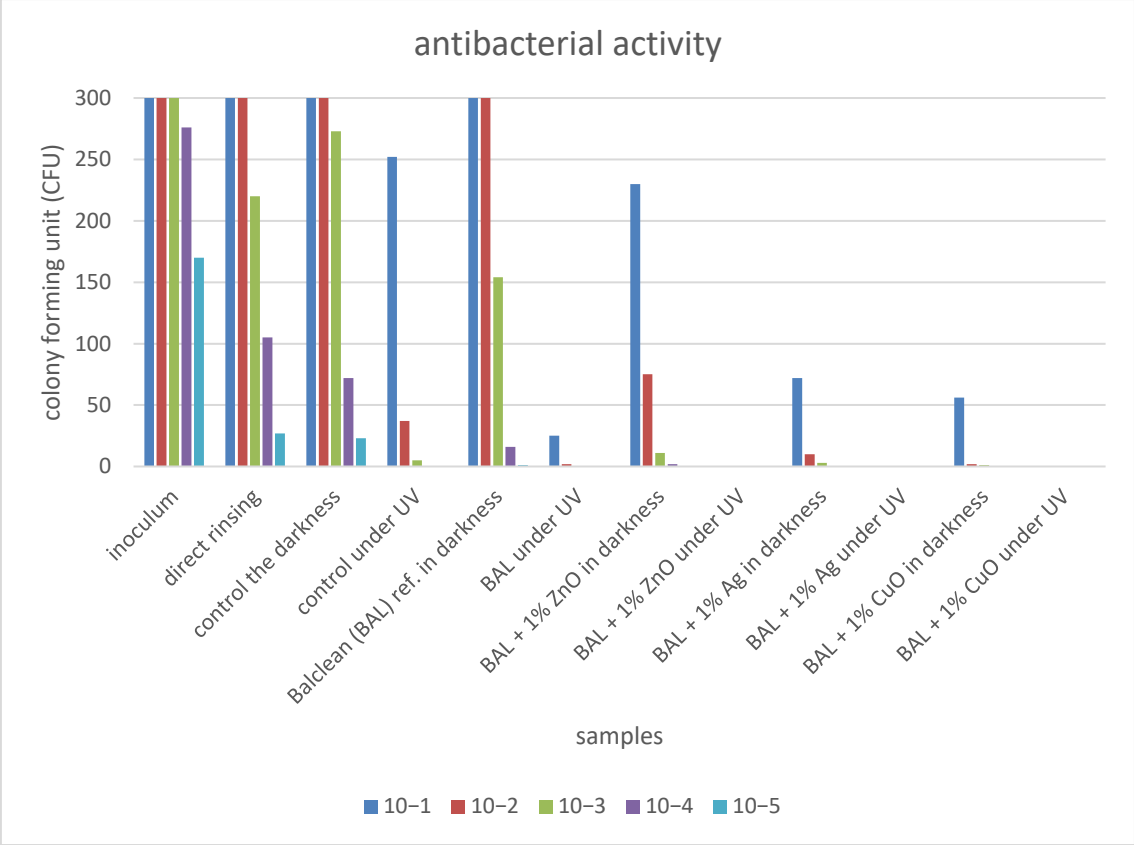

Figure 5. antibacterial activity of samples.

The results of antibacterial activity tests are summarized in figure 5. The samples left in the dark show a significant decrease in CFU compared to the reference sample (RS), suggesting the bactericidal properties of the added nanoparticles.

The result from the inoculum confirmed that the bacterial strain E. coli is viable or vital when cultured on Nutrient agar. In the direct rinse sample (glass plate without photocatalytic coating), we observe a high amount of bacterial colonies surviving about 300 to a dilution of 10^{-3}, which is comparable to the control glass sample (without photocatalytic coating) incubated in the dark. The same results showed a reference coat named Balclean incubated in the dark, showing that there was no photocatalytic effect. However, a significant decrease in the number of bacterial colonies was observed in the control incubated under UV lamp at all dilutions compared to the control incubated in the dark. This suggests that a UV lamp at 0.25 mW/cm^2 produced a germicidal effect on the bacteria and thereby killed, requiring a reduction in radiation intensity.

In a sample coated with a Balclean reference paint incubated under a UV lamp, we observe a noticeable bacterial death compared to its reference sample incubated in the dark, due to the photocatalytic properties of the Balclean paint. For other samples (Balclean with 1% Ag, Balclean with 1% ZnO and Balclean with 1% CuO) complete bacterial mortality was recorded in case of incubation under UV lamp. These samples also killed bacteria even when incubated in the dark. This can be explained by the toxic effects of Ag, CuO and ZnO nanoparticles, since these nanoparticles all have a germicidal effect on E. coli.

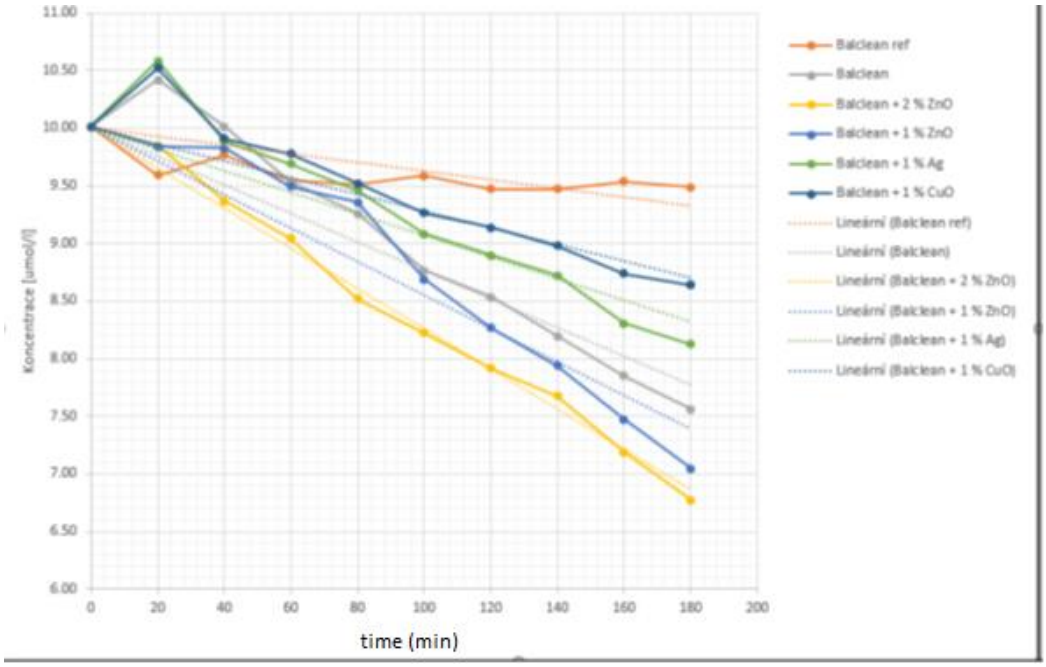

Figure 6. Graph of photocatalytic MB degradation.

MB degradation results are summarized in figure 6. In some cases there was observed slight increase in MB concentration after 20 minutes which was caused by MB desorbtion. The results clearly demonstrate high photocatalytic activity of BAL and BAL with ZnO sample. With the addition of CuO and Ag we observed a decrease of photocatalytic activity, which may be caused by an increase in the proportion of photocatalytically inactive particles (shading effect). In addition, the silver particles were too large (see figure 1).

3 Conclusion

The application of photocatalytically active coatings seems to be a very effective alternative for the reduction of undesirable ingrowth of facades, plasters and other surfaces by microorganisms. Nanoparticles of Ag were synthetized used chemical reduction method. For the preparation of ZnO and CuO nanoparticles, we chose the precipitation method, which successfully synthesized oxidic nanoparticles with the corresponding ratio of element Zn and Cu to oxygen, which has been confirmed by EDS analysis. A significant increase in the antimicrobial activity was achieved. With regard to the elimination of the number of CFUs in the samples left in the dark, it can be concluded that there was a significant germicidal effect of the added particles. A significant decrease in the incidence of bacterial colonies was also observed in samples exposed to UV radiation, which can be attributed to a combination of photocatalytic effect of the layer and germicidal effect of the added particles.

The negative effect of Ag and CuO addition on photocatalytic activity was confirmed also by methylene blue decomposition tests. Here, an increase in photocatalytic efficiency was observed in the case of ZnO addition, which can be explained by an increase in the total photocatalyst proportion in the resulting SiO_2 / TiO_2 / ZnO composite system. The increase in photocatalytic activity in the composite system is probably due to the fact that the coupling of the two catalysts results in a heterotransition between TiO_2 and ZnO, resulting in an increase in the recombination time and hence the photocatalytic efficiency of the system. The results of methylene blue digestion tests also confirmed the negative effect of CuO and Ag addition.

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