

Research Article

TiO₂ and ZnO Nanoparticles in Photocatalytic and Hygienic Coatings

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Antimicrobial paints were based on the aqueous acrylic dispersion and various nanoparticles of zinc oxide and titanium dioxide. Antimicrobial ability and photoactivity were assumed in these paints. It was possible to observe the photoactivity thanks to change of organic dyes due to oxidative-reductive reaction. The best photocatalytic effect showed the coating containing the mixture of the first type of TiO₂ and nano-ZnO despite the fact that the first type of TiO₂ was not better in the photocatalytic test than the other types of TiO₂. The agar dilution method was used to test antimicrobial ability. The *Escherichia coli*, *Pseudomonas aeruginosa*, and *Staphylococcus aureus* were chosen as test bacteria and *Penicillium chrysogenum* and *Aspergillus niger* as test molds. The antimicrobial effect of coatings with the mixture of the first type of TiO₂ and nano-ZnO was the best of all the tested samples.

1. Introduction

The worldwide spread of diseases is a great problem of modern society [1]. Infection is a major medical complication associated with health care environments [2]. Infection control is of utmost importance in various places, which require a high level of hygiene as technical applications for antimicrobial coatings include medical products, packaging materials, or filters used in air-conditioning systems. Hospitals, pharmaceutical production units, food factories, and so forth, need to be rigorously disinfected in order to destroy pathogenic microbes [3–5]. Microbial contamination of water poses a major threat to public health too. With the emergence of microorganisms resistant to multiple antimicrobial agents there is increased demand for improved disinfection methods [6]. A promising possibility to overcome these difficulties is the development of a concept to kill bacteria based on physical interactions. It has been proved that the chemicals with positively charged groups, such as quaternary ammonium or phosphonium, can kill bacteria upon

contact [3]. Also coatings containing photocatalytic TiO₂ can be interpreted as contact-active surfaces that kill approaching microbes by light-induced formation of hydroxyl radicals. The threat of device-related infection has become publicized due to recent global events involving MRSA or enterovirus. Unexpected multiplication of germs or other bacteria poses a serious health problem [7, 8].

Nanoparticles seem to be a very good option for antimicrobial additives mostly thanks to their size which is similar to the size of the cells and particles and can pass through the membrane easily. The main mechanism of toxicity of nanoparticles is thought to be via oxidative stress that damages lipids, carbohydrates, proteins, and DNA. Lipid peroxidation is considered the most dangerous as it leads to alterations in cell membrane properties which in turn disrupt vital cellular functions [9–12].

Fujishima and Honda found in 1972 [13] that the photocatalytic properties of certain materials have been used to convert solar energy into chemical energy to oxidize or reduce materials to obtain useful materials including hydrogen

TABLE 1: Characteristics of photocatalytic oxides.

Photocatalytic oxide	ZnO	TiO ₂ I	TiO ₂ II	TiO ₂ III
Appearance	Fine white powder	Fine white powder	Fine white powder	Fine white powder
Crystal form	Zincite	Anatase	Anatase	Anatase
Crystal size (nm)	30–40	550–600	40	10
Specific surface area, BET (m ² /g)	25–35	10	20–30	300
ZnO or TiO ₂ content (%)	99,5	98	97,5	99

and hydrocarbons and to remove pollutants and bacteria [14–16] on wall surfaces and in air and water.

Photocatalytic titanium dioxide (TiO₂) has been developed and extensively applied due to its nontoxicity, high catalytic activity, strong self-cleaning characteristics, and low cost. The photocatalytic process of TiO₂ or ZnO involves the generation of electron-hole pairs during exposure to light. These holes are able to react with nearby molecules to produce oxidants. The reaction of these particles with water produces the hydroxyl radical (OH[•]). In the case of oxygen, the result is the superoxide molecule (O₂^{•-}). Zinc oxide and other semiconductor materials may provide unusual electronic and chemical mechanisms for inhibiting the growth of microorganisms in a similar way to titanium dioxide [17, 18]. These radicals eventually attack bacteria or viruses in terms of inhibiting DNA clonal processing and destroy coenzymes, enzymes in the self-regeneration, and enzymes in the respiratory system. As a result, the radical stops the reproduction of bacteria and molds, thereby inhibiting bacteria growth or preventing virus DNA multiplication [19–21].

Waterborne coating systems are complex mixtures of polymers, pigments, fillers, and functional additives. The additives are used to improve different appearance or performance characteristics of the final coating. Unexpected synergies or reductions in performance may arise when certain components are included.

The ability of all of these additives to fulfill their roles is greatly impacted by the environment in which they operate. Antimicrobials are one class of additives that is very dependent on what else is in the system formulation [22].

2. Experimental

2.1. Preparation of the Hygienic Paints. Antimicrobial ability and photoactivity were assumed in these interior paints based on aqueous acrylic dispersion and different types of nano-titanium dioxide or nano-zinc oxide. These additives are commercially produced products. The characteristics of oxides are taken from datasheets of products, and they are listed in Table 1.

The first set of paints was formulated with different types of photocatalytic anatase titanium dioxide, and a combination of titanium dioxide and zinc oxide was used too. The content of nano-ZnO was 4 vol.%, and the amount of all different types of titanium dioxide was the same in all samples. The second series of antimicrobial paints was based only on nano-zinc oxide. The content of nano-ZnO was varied from 1 to 4 vol.%. Paint without nanooxides was formulated as control paint.

2.2. Evaluation of Photocatalytic Effect. The photoactivity of nanoparticles TiO₂ and ZnO is dependent on air humidity and ultraviolet (UV) radiation. It is possible to observe the photoactivity thanks to changes in organic dyes due to oxidative-reductive reaction. The interior paints were coated by brush thrice in Petri dishes (diameter 70 mm). These samples were dried for at least 1 week before photocatalytic testing. Then the solution of Orange II (15 g of 0.0014% by wt.) was poured on the surface of coating in the Petri dishes and covered by lids. A control coating without photocatalytic oxide was always tested too. Then, the samples were irradiated with UV lamps (11 fluorescent tubes with power of 11 W) emitting a wavelength of 300–400 nm for 120 min. The distance between the UV lamps and the samples was approximately 29 cm. Samples of Orange II solution were taken at definite time intervals. The absorbance of Orange II solution was measured by means of a photometer (SPEKOL 11, length of cuvette 1 cm) at the wavelength of 485 nm. The same procedure was used for the samples of coatings that were exposed to normal laboratory fluorescent tubes. The samples were irradiated for 72 hours.

2.3. Testing the Antimicrobial Efficiency of Coatings. The tests of antimicrobial efficiency were made on these coatings too. Acrylate coatings were applied in two layers on filter paper (sorte 391), size 5 × 5 cm, which were exposed to UV radiation (300–400 nm) before application for 30 minutes.

Testing microorganisms were *Escherichia coli* CCM 3954, *Staphylococcus aureus* CCM 4223, *Pseudomonas aeruginosa* CCM 3955, *Aspergillus niger* CCM 8189, and *Penicillium chrysogenum* CCM 8034 (Czech Collection of Microorganisms, Brno). Instruments and tested films were sterilized. Suspensions of cultures in solution of NaCl (0,9% by wt.) were prepared (density 10⁶ cells/mL, in fungi 10⁶ spores/mL). Density control of cells in the suspensions was carried out by culture of the suspension for each organism on an appropriate nutrient medium at optimum temperature. Fungi were cultured on agar MALT (HIMEDIA, India) at 24–25°C for 2–5 days and bacteria on nutrient agar no. 2 (HIMEDIA, India) at 37°C for 24–48 hours. The tested coatings, spread on filter paper (5 × 5 cm), were placed on Petri dishes with the appropriate cultivating medium and inoculated with the suspension of the testing microbe (0.1 mL). After incubation at optimum temperature for the optimum time for each microorganism, growths on the surface of the coatings were found out. Inhibition zones around the coatings were observed in some samples. The results are shown in Tables 2 and 3 and Figure 5.

TABLE 2: Amount of bacteria/mold growth (%) on the coatings with various types of TiO₂ or mixture of nano TiO₂ I and nano ZnO.

	<i>Escherichia coli</i>	<i>Staphylococcus aureus</i>	<i>Pseudomonas aeruginosa</i>	<i>Penicillium chrysogenum</i>	<i>Aspergillus niger</i>
Control	80	90	95	100	100
TiO ₂ I	0	0	80	80	80
TiO ₂ II	70	80	100	100	90
TiO₂ I + ZnO	0	0	80	30	0
TiO ₂ III	100	100	80	100	100

TABLE 3: Amount of bacteria/mold growth (%) on the coatings containing nano ZnO in various concentrations.

	<i>Escherichia coli</i>	<i>Staphylococcus aureus</i>	<i>Pseudomonas aeruginosa</i>	<i>Penicillium chrysogenum</i>	<i>Aspergillus niger</i>
Control	80	90	95	100	100
1% ZnO	0	0	80	100	90
2% ZnO	0	0	80	100	80
3% ZnO	0	0	40	95	15
4% ZnO	0	0	25	95	5

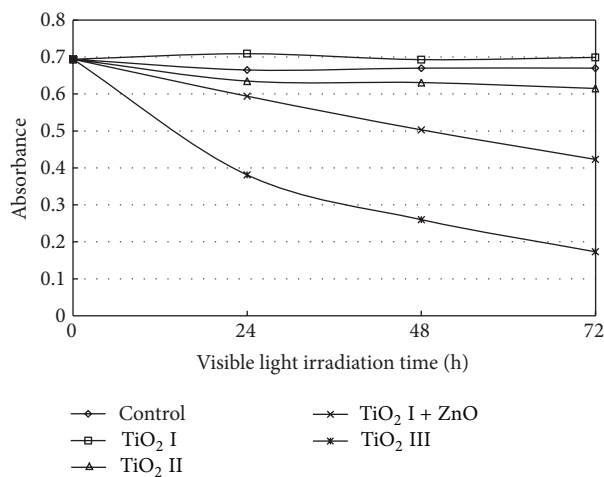


FIGURE 1: Absorbance of Orange II solution versus visible light irradiation time for various nanophotocatalytic oxides.

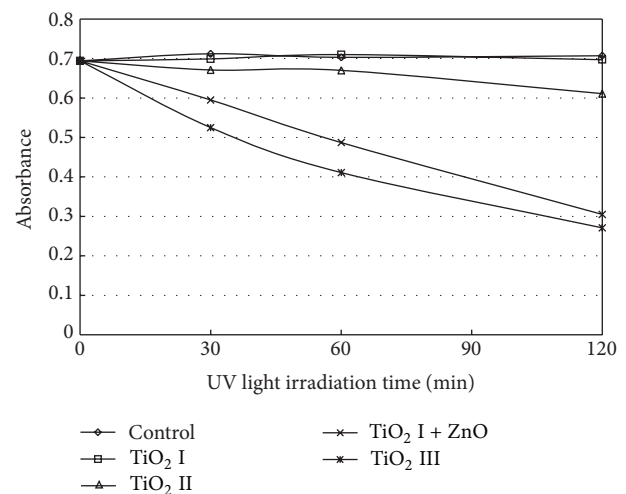


FIGURE 2: Absorbance of Orange II solution versus UV irradiation time for various nano photocatalytic oxides.

3. Results and Discussion

The photocatalytic activity was investigated for the coatings containing nano-ZnO, nano-TiO₂, mixture of these nanooxides, and coatings without nanooxides after exposure to UV radiation and VIS radiation. The absorbance changes in Orange II solution were measured, and the results are showed in Figures 1, 2, 3, and 4.

The paints based on aqueous acrylic dispersion doped by different nanooxides showed the photoactivity in case of the ultraviolet irradiation and also visible light irradiation. The control coating and coating containing TiO₂ I did not have any photocatalytic effect. The coating that included TiO₂ III showed the highest amount of photoactivity. There was a visible influence of nano-ZnO on the paint where the combination of nano-ZnO and TiO₂ I was used compared to coating containing only TiO₂ I.

Because of this result the photoactivity was also tested on the samples containing a various amount of nano-ZnO.

Photoactivity of samples after 24-hour irradiation of visible light changed quickly and then was nearly constant. The photoactivity of coatings after UV irradiation was relatively high but it was not as high as the photoactivity of nano-TiO₂ III. It was obvious that the photoactivity of coatings containing the mixture of TiO₂ I and nano-ZnO was higher than the photoactivity of coatings with 4 vol.% nano-ZnO. This synergic effect was observed in the case of UV radiation and also by exposure to visible light.

The antimicrobial efficacy of coatings containing nano-TiO₂, nano-ZnO and control coating without both nanoparticles is showed in Tables 2 and 3. It is obvious that coatings containing nano-TiO₂ showed poor antimicrobial efficacy compared to coatings with mixture of TiO₂ I and nano-ZnO and also compared to coatings with nano-ZnO. The antimicrobial effects of coatings with combination of TiO₂ I and nano-ZnO against bacteria *Escherichia coli* and *Staphylococcus aureus* and fungi *Aspergillus niger* were excellent.

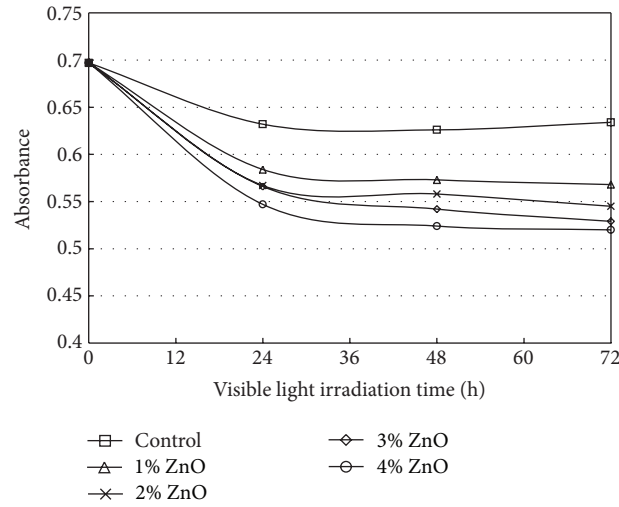


FIGURE 3: Absorbance of Orange II solution versus visible light irradiation time for various nano-ZnO pigment volume concentrations.

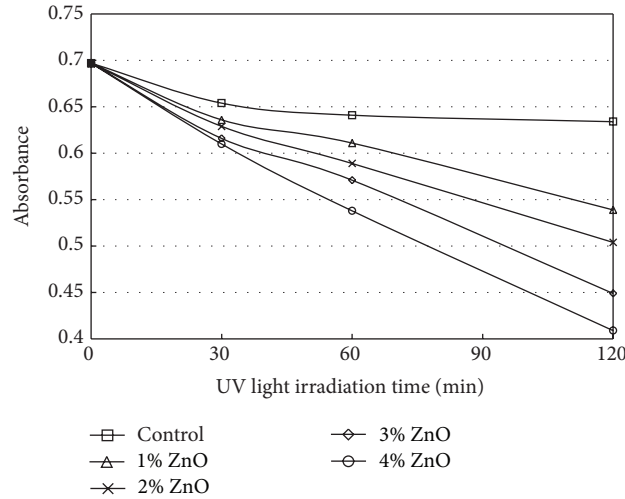


FIGURE 4: Absorbance of Orange II solution versus UV irradiation time for various nano-ZnO pigment volume concentrations.

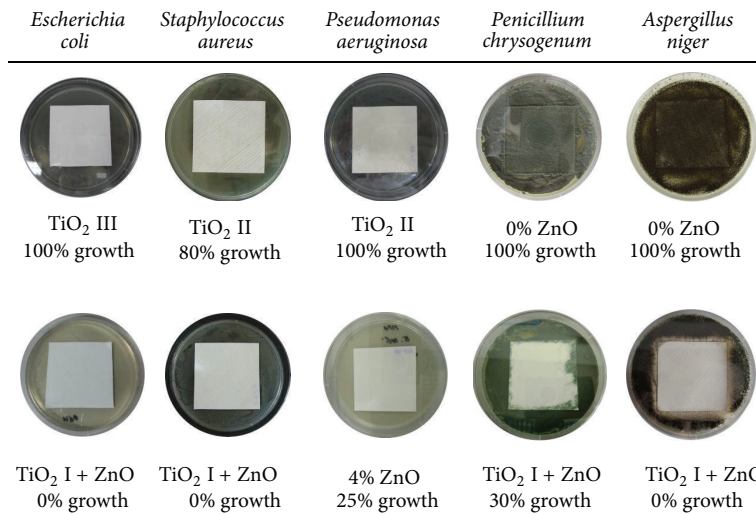


FIGURE 5: Photos of Petri dishes containing samples of coatings after growth of bacteria/mold.

The lowest concentration of nano-ZnO in the coating was effective against bacteria *Escherichia coli* and *Staphylococcus aureus*. Higher content of nano-ZnO improved inhibition against bacteria *Pseudomonas aeruginosa* and fungi *Aspergillus niger*. It could be caused by the toxic influence of nano-ZnO to the microbial cell. Nanosized particles can pass through the microbial cell, and they can damage organelles [12].

The effectiveness of the combination of TiO₂ I and nano-ZnO was somewhat better than that of the highest amount of nano-ZnO. Unfortunately the efficacy against *Pseudomonas aeruginosa* and *Penicillium chrysogenum* was poor in all cases. The better results were obtained for a combination of nanosized titanium dioxide and nanosized zinc oxide. This is probably caused by the influence of nanosized zinc oxide as written previously.

Very good antimicrobial effects of zinc oxide are consistent with the results published by Sawai and Kathirvelu [23, 24]. According to Chen et al., the antimicrobial activity of oxides depends on many factors such as humidity, temperature, UV light irradiation time, surface treatment, and morphology of nanoparticles [25]. In their work, Akiyama et al. using ZnO confirmed the inhibition of *S. aureus*. They found that 5% ZnO inhibited the growth of this bacterium [26].

Further experiments involving various concentrations of TiO₂ and ZnO nanoparticles or their mixtures to improve the antimicrobial efficacy could be tried. Maybe a mixture with organic biocides could show an interesting result.

4. Conclusion

The lowest concentration (1 vol.%) of nano-ZnO in the coating was effective against bacteria *Escherichia coli* and *Staphylococcus aureus*. Higher nano-ZnO content in coatings improved inhibition of bacteria *Pseudomonas aeruginosa* and fungi *Aspergillus niger*. However even the highest tested amount of ZnO was not sufficient to inhibit fungi *Penicillium chrysogenum*. The coatings containing a mixture of the first type of TiO₂ and nano-ZnO did not show the best photocatalytic effect, but the antimicrobial efficacy against *Escherichia coli*, *Staphylococcus aureus*, and *Aspergillus niger* was excellent.

Conflict of Interests

There was no conflict of interests present regarding the use of commercial products; all products used in this study were purchased from the market.

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