POSSIBILITIES OF REMOVING THE CRUST FROM THE SURFACE OF HISTORIC STONE WITH NANOPARTICLES I TiO_2

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Abstract

The most common tasks, we encounter during restoration stone historical monument buildings, include mainly cleaning and removing of the crust from their surface. As part of the experimental research of nanomaterials and the widespread use of these materials for the preservation and restoration of stone monuments, the use of TiO_2 is currently being addressed. Applications have shown that this oxide can be used to protect against microorganisms and UV degradation due to its antifungal and antibacterial effects. At the same time, the photocatalytic properties of TiO_2 represent the possibility of chemical decomposition and the creation of a self-cleaning environment and self-sterilization area. Applying lime nanosuspensions with TiO_2 nanoparticles will reduce the rate of deposition of pollutants as a result of photocatalytic phenomena and thus slow the development of degradation processes.

Keywords: Lime nanosuspension, TiO_2, titanium dioxide, self-cleaning surfaces, stone crust, historical material

1. INTRODUCTION

The aging of historical objects and their materials is mainly influenced by degradation processes caused by long-term effects of cyclical weather changes and harmful substances contained in the atmosphere. Among the most important negative factors are, in addition to repeated changes in temperature and humidity, especially carbon dioxide, sulfur dioxide, acid peat and solid particles contained in the atmosphere [1]. The settling of impurities and chemical processes occurring between the components of the external environment and the building material itself lead to the formation of a crust firmly embedded in the surface structure of the material. The formation of crusts damages historical objects not only aesthetically, but above all by the development of surface tensions between the crust and the core of material with different material properties, and chemical processes that influence the composition of the material and, on the other hand, lead to the development of tension in the structure of the material. Last but not least, it provides uneven surface crusts for depositing impurities from the air (resulting in its gradual darkening) and subsequently the broth for the development of microorganisms. The nature and development of degradation processes and their manifestations are influenced in this context also by the type of material (so called lythotype: marble, limestone, travertine, sandstone, granite, etc.), surface grain, material humidity, chemical composition, porosity, structure and texture of materials.

As a result of these negative effects, degradation processes occur in surface layers, which in the case of historical building materials lead to structural breakdown, loss of coherence of individual layers and consequent loss of surface layers [1].

Within the development of the use of nanomaterials in the care of cultural heritage, it has been demonstrated that metal oxides, especially ZnO and TiO_2, can be used as protection against microorganisms and UV degradation due to their antifungal and antibacterial effects [2-4]. Studies show, on one hand, the possibility of incorporating nanoparticles into building materials [5-8], the next route to new applications leads through the incorporation of nanoparticles which either functionalize suspensions themselves or can be functionalized.

Titanium dioxide is one of the most widely known photocatalytic materials used not only in the building industry, but also in other industries, eg for water and air purification, and for its antibacterial properties it is also used as an ingredient in eg tiles, PVC, etc. [9]. It is also known from the studies that nano-TiO_2 coating provides excellent corrosion protection for marine submerged materials [10]. The photocatalytic properties of TiO_2 were discovered by A. Fujishima and K. Honda, who first used titanium dioxide to decompose chemicals [11-13]. The photocatalytic properties of TiO_2 are stimulated by UV radiation and can suppress surface layers by algae and lichens. The intensity of UV radiation with a peak below 385 nm [17-20] is significantly influenced by the effect of TiO_2 [14-17] so that photocatalytic activity is triggered which produces reactive particles capable of oxidative degradation of pollutants.

2. MATERIALS AND METHODS

The research project “Development and Research of Materials, Methods and Technologies for the Restoration, Preservation and Strengthening of Historic Masonry Constructions and Surfaces and Systems of Preventive Conservation of Cultural Heritage Buildings Threatened by Anthropogenic and Natural Hazards“ addresses besides the issues of the care of the historic materials and its surfaces by the different types of lime nanosuspensions. The institutions currently participating in the research project are the Faculty of Civil Engineering, CTU in Prague and the Centre of Polymer Materials, TBU in Zlín.

2.1. The Lime nanosuspension with titanium dioxide

For the purpose of experimental research, lime nanosuspensions were prepared to further prepare and subsequently test suspensions doped with the active substances for a specific use, ie to clean the surfaces of building materials. Limestone nanosuspensions form nanoparticles of calcium hydroxide scattered in alcoholic environments, which are primarily used to consolidate the surface layers of lime-based building materials. By supplementing these nanosuspensions with other effective nanoparticles (eg TiO_2), there are means that can provide multiple efficiencies - consolidation, self-purification and biocide protection [18]. For this purpose, the synthesis of $Ca(OH)_2$ (Ca4, **Figure 1a**), which was subsequently enriched with titanium dioxide (Ca4-Ti, **Figure 1b**), was developed within the research project.

The basic nanosuspension of Ca4 was made from the weight of calcium methoxide $Ca(OCH_3)_2$ (7.18 g, 70.2 mmol). The charge of calcium methoxide ($Ca(OCH_3)_2$) was dispersed in isopropyl alcohol (150 ml). To this suspension was added 100 ml of distilled water. The reaction time, constant stirring, was 90 minutes. After the reaction, the product was separated by centrifugation and washed with distilled water and isopropyl alcohol. The yield was 4.16 g [19].

To test the self-cleaning effect of titanium dioxide, the TIO_2 nanoparticles were prepared by a procedure known from the literature, an acid-assisted sol-gel method [20]. For the purpose of the research project, the synthesis was modified: Ti_2 was applied as an addition of isopropyl alcohol. Hydrolysis of $Ti(OiPr)_4$ in the presence of acetic acid was carried out by mixing 150 ml of H_2O, 5 ml of $Ti(OiPr)_4$ and 50 ml of CH_3COOH. The reaction was stirred at 70 °C for 3 hours on a magnetic stirrer. The product was separated by centrifugation and dried. To Ca4-Ti nanosuspension 1.0 g of Ti_2 sample was added. After addition of TiO_2, the slurry was dispersed in an ultrasonic bath.

The XRD powder analysis on a Rigaku MiniFlex 600 diffractometer equipped with a CoKα cathode (λ = 1.7903 Å, 40 kV, 15 mA) was used to determine the crystalline structure of the product. The observed diffraction of the TiO_2 nanoparticle sample corresponds to the JCPDS card card for TiO_2 (anatase) 01-071-1169 (**Figure 2**). Diffraction record of $Ca(OH)_2$ forming the initial slurry of Ca4 is also shown in this figure. The TiO2 nanoparticle electron microscope image is shown in **Figure 1b**.

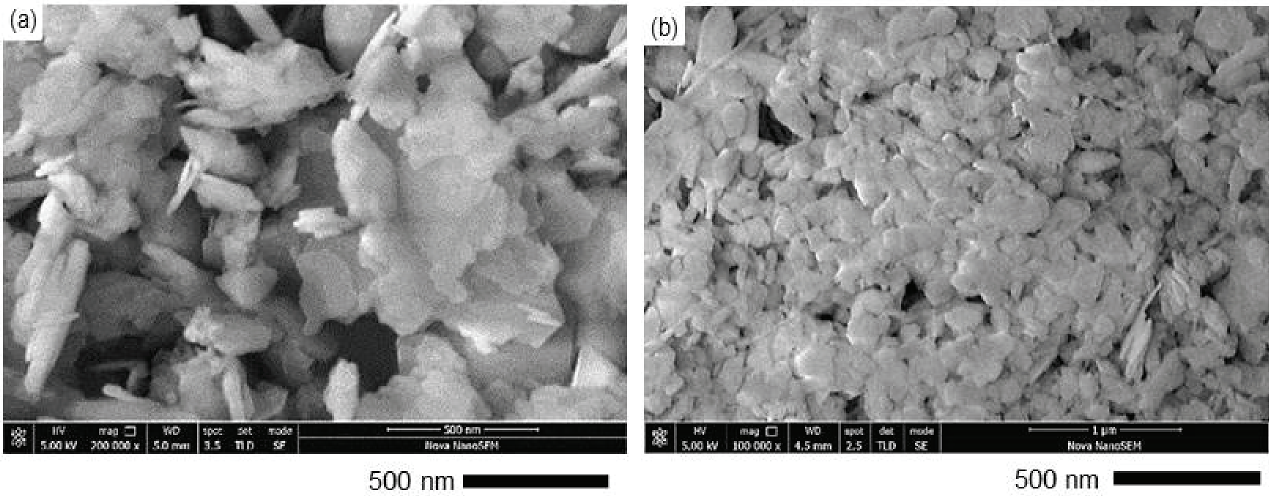

Figure 1 Electron microscope images: a) nanosuspension CA4 ($Ca(OCH_3)_2$ precursor); b) CA4-Ti nanosuspension (Photo CPS UTB)

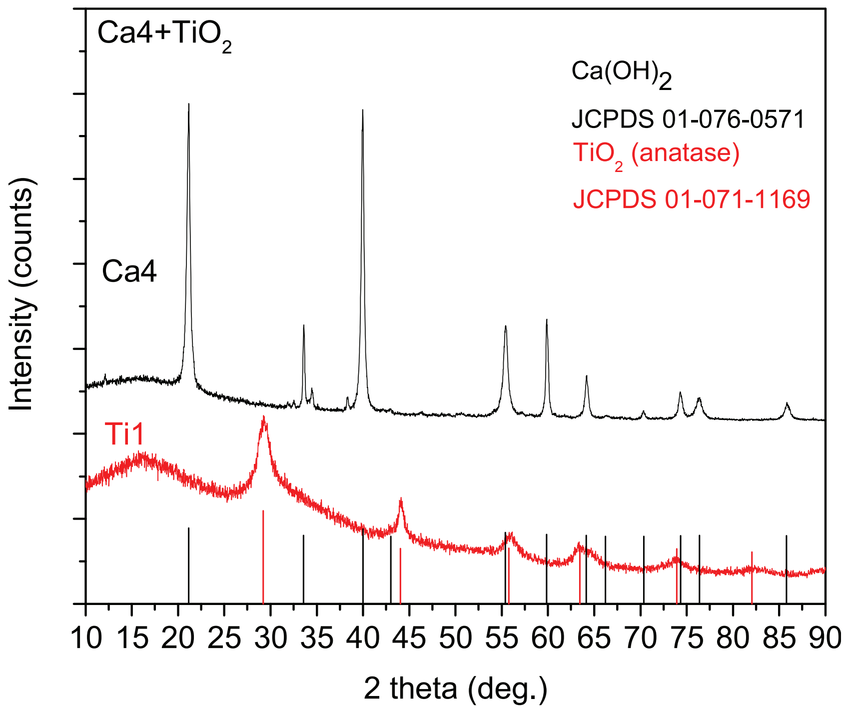

Figure 2 XRD diffractogram of prepared TiO_2 nanoparticles and Ca4 nanosuspension

2.2. Application of nanomaterials on stone samples

The application of Ca4-Ti nanosuspension was performed in situ on stone (marlite) walls in Prague, the surface of which is degraded by surface crust and massively contaminated by microorganisms (**Figure 3**). In a place exposed to sunlight, dry stone blocks were used to apply nanosuspension so that a photocatalytic reaction could take place. On their surface, the tested nanosuspension (Ca4-Ti) was applied sequentially using the sprayer. The application of nanosuspension Ca4-Ti with a total volume of 20 ml was repeated with the sprayer, where the individual applications followed successively after application of the applied composition, without its significant leakage on the surface.

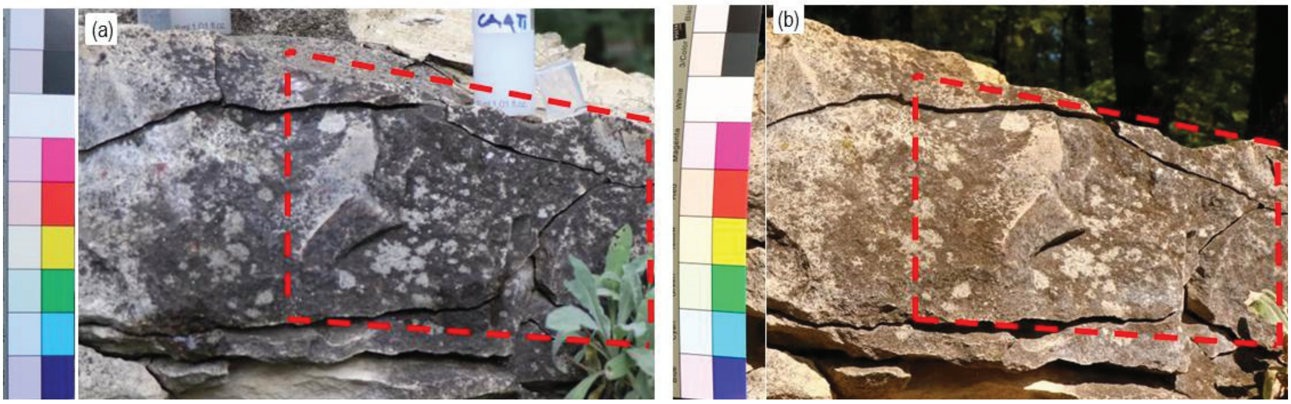

Figure 3 Detail of the stone block before application of the nanosuspension of Ca4-Ti (stone - marlite - wall in Prague): a) before application; b) after application

Skins and scraps for laboratory bioassay were also performed. From the samples taken, the microorganisms were transferred to nutrient agar (Czapek Dox agar), which was cultured for 7 days at 23 ± 3 °C. The molds were isolated to individual species from which microscopic native preparations were prepared. Mold identification was performed on the Olympus BX41 microscope according to significant characters (in conformity with Fassati (1979), Singha, Frisvalda, Thrane Mathura (1991) and Samson, Houbraken, and Thrane (2010) microscopes). To determine the presence of algae, a 50 μl culture medium was inoculated with stone granulate (weight approximately 0.5 gram). Cultivation was carried out on a Ika vibrax shaker (150 rpm) for 14 days at 25 °C ± 5 °C. The illumination intensity was 1.5 kLux with a cycle of 18 : 6 (day : night). At the end of the 1st week of cultivation, bacteria were identified on the samples on 50 % of the area and mold on 30-40 % of the area.

2.3. Efficacy assessment of nano - titanium dioxide preparations

After 3 weeks of application, control documentation, skins and scraps were performed. The collected samples were transferred to Czapek Dox agar broth and allowed to cultivate for 7 days at 23 ± 3 °C. After a week of cultivation, significant algae and mold loss (only 10-15 % of the sample area), increased bacteria (up to 50 % of the sample area) were observed in all the samples studied. By visual comparison and by laboratory analysis, no change in the extent, character and color of the surface crust has been demonstrated.

3. CONCLUSION

The titanium dioxide suspensions were partially proven to be directly applied to areas with a massive presence of microorganisms (algae, bacteria, fungi). TiO_2-doped nanosuspension results show that mold and algae growth at Czapek Dox agar has decreased by about 20-30 %. However, experimental tests of nanosuspension doped with TiO_2 nanoparticles did not clearly show a significant results of the selfcleaning effect. The possibility of removing gypsum crusts using prepared lime nanosuspension with TiO_2 nanoparticles has not been demonstrated.

The results obtained have been influenced, among other things, by the particle size, concentration and stability of the suspension, the carrier media, the presence of ballast substances which suppress the self-cleaning and biocidal effect, etc. As mentioned above, the mineralogical composition also has a significant effect on the activity of the antifungicide and antibacterial agent material, its pH value and porosity.

These results were also limited to a relatively small number of in situ and laboratory tests. Obtaining fully objective results requires more extensive experimental research so that the results are statistically evaluable. At the same time, the need for further research stems from the need to eliminate the potential risk of failure and damage, especially on listed buildings. In addition to verifying any modified functional nanomaterials, it will be necessary to address the requirements of durability, long-term reliability, and last but not least reversibility requirements.

ACKNOWLEDGEMENTS

This article was written as part of the NAKI DG16P02M055 research project "Development and Research of Materials, Methods and Technologies for the Restoration, Preservation and Strengthening of Historic Masonry Constructions and Surfaces and Systems of Preventive Conservation of Cultural Heritage Buildings Threatened by Anthropogenic and Natural Hazards (2016 - 2022, MK0/DG)".

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