NANOTECHNOLOGY IN THE CULTURAL HERITAGE - INFLUENCE OF NANOSPENSIONS ADOPTED BY NANOPARTICLES OF TiO_2 FOR CLEANING THE SURFACE OF HISTORICAL PLASTERS

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ABSTRACT

The continuous development of nanostructure and the study of physico - chemical processes in the nanometer range lead to new methods that can slow down the degradation processes of a work of art, or even restore damage caused, for example, by an inappropriate restoration process. The use of nanosuspensions based on calcium hydroxide is probably the most widespread application of nanomaterials in heritage care, especially in the field of hardening of lime building materials (plaster, limestone, etc.). In combination with titanium dioxide, it should be a successful suspension in the fight against biological agents, surface contamination or in the protection of UV-resistant building materials.

KEYWORDS

Calcium hydroxide, TiO_2, fotocatalysis, nanosuspension, cleaning, antimicrobial

INTRODUCTION

Between the most common tasks encountered in the restoration of historic buildings, belongs the purification, desalting and consolidation of various types of construction materials. The biocorosis of construction materials can be caused by bacteria, algae, lichens, plants and animals. These living organisms are able to adapt to a wide range of documents and their growth is not only affected by climatic conditions, but also by the surface moisture, chemical composition, structure and texture porosity materials.

In recent decades, nanotechnologies have become increasingly important in the area of cultural heritage care, which can facilitate the cleaning of contaminated surfaces, run self-cleaning processes and act antimicrobically, or protect the material from the negative effects of UV radiation and others. The application of nanomaterials in the care of monuments has been verified in the last approximately 15 years mainly in the form of nanosuspensions, resp. nanoemulsions based on hydroxides (especially calcium, barium, magnesium, etc.), carbonates and, in some cases, sulphates [1-3]. The advantage of the application of nanomaterials is the possibility of achieving a high penetration depth into the structure of the materials (mainly depending on the pore system and the moisture content of the material) and high efficiency while preserving the original material matter.

The use of nanomaterials is proven in practice in the deacidification of movable artworks (paper, textiles, leather [4-7]), cleaning of surfaces of historical monuments (eg. titanium hydroxide nanosuspension, nanoemulsion of organic solvents in water etc. [8-10]) and for the consolidation of porous materials (eg. plasters, limestone or eg wall paint etc., nanodispersion of calcium hydroxide [1-3]). Successful applications of nanomaterials in crack injection or in the remediation of building materials found in humid or chemically contaminated environments and other are also documented in foreign practice [11-12].

Within the development of nanomaterials, metal oxides, especially ZnO and TiO_2, have been shown to be useful for protection against microorganisms and UV degradation due to their antifungal and antibacterial effects [13-15]. From foreign publications is known the efficiency of titanium coatings deposited on historic architectural stone surfaces as self-cleaning [16-18]. Experience in the application of oxides with different physical properties and the principles of their effects on restored materials have only recently appeared in the literature and the development of these materials is at the beginning.

The photocatalytic properties of TiO_2 were discovered by Fujisima and Honda, who first used titanium dioxide to decompose chemicals [19-20]. Titanium dioxide (TiO_2) is one of the most important and commercially available photocatalysts due to its excellent efficiency (even under low solar irradiation), low cost, compatibility with a large number of materials and good stability, where the use of photocatalytic reactions decompose the most inorganic and organic pollutants due to UV radiation. Titanium dioxide is a semiconductor material and is mainly used in atanase form. Due to its antibacterial effects, it is applied in various fields, such as water and air purification, paintings, glasses, or the cosmetics industry.

The TiO_2 nanocrystals, in the form of anatase, have a particle size in the range of several nm to 30 nm. Due to light with a shorter wavelength than 388 nm, they activate and remove oxygen atoms from some TiO_2 molecules. Next to each other coexist the hydrophilic regions depleted by oxygen and hydrophobic, unchanged (uncharged) regions. Due to the close proximity of these areas (these are areas in the order of several hundred nm^2), the water droplets lose their spherical shape and form a continuous film that prevents adhesion of the pollutant to the surface [21]. This synergy of effects allows to maintain aesthetic properties, improve surface properties and slow degradation processes caused by dirt.

The photocatalytic effect of titanium dioxide produced by ultraviolet light is influenced by the size and shape of the particles and their specific surface. It is necessary to emphasize that UV radiation is absolutely necessary for the course of the reaction and that TiO_2 has a catalyst function and therefore does not decrease. However, to maintain long-lasting high efficiency, it is necessary to maintain surfaces (treated with TiO_2) and remove reaction products (eg. by water or rain).

The TiO_2 nanoparticles themselves are chemically inert, very stable over time and, according to their current knowledge, non-toxic to humans. The presence of metal oxides such as WO_3, ZrO_2, MoO_2, or also CdS and the doping of TiO_2 by nitrogen can significantly affect the course of photocatalysis [22]. However, the problem of dispersed TiO_2 nanoparticles in the nanocoating is the tendency to form clumps after a certain period of time in the liquid environment. This leads to enlargement of the average particle size of TiO_2 and the photocatalytic potential decreases.

MATERIALS AND METHODS

The goal of laboratory research was to create a multifunctional nanoparticle and titanium dioxide based compound that would give very good results to historic surfaces (especially plaster and stone) in the mean of self-cleaning surface and simultaneously to add the missing binder. Applying nanomaterial would not change the original appearance, as a result of the photocatalytic phenomenon would reduce the rate of deposition of pollutants and thus slow the development of degradation processes. TiO_2 nanoparticle suspension allows thin transparent coatings on the surface of the treated material to act as a preventive protective system activated by solar UV radiation while reducing existing pollution and retarding degradation processes.

The incorporation of TiO_2 into nanosuspension of calcium hydroxide was carried out within the framework of the NAKI research project in cooperation with the TBU Polymer Systems Center in Zlín.

For the preparation of nanosuspesions were used the following chemicals: Calcium methoxide ($Ca(OCH_3)_2$, 97 %, M_w = 102,15 g mol^{-1}), Titanium(IV) isopropoxide ($Ti(OC_3H_7)_4$, 97 %, M_w = 284,22 g mol^{-1}) and isopropyl alcohol (p.a.) were purchased by Sigma-Aldrich.

The nanosuspension of $Ca(OH)_2$ (Ca1) was produced by hydrolysis of calcium methoxide $Ca(OCH_3)_2$ (average particle size according to DLS 298 nm, Figure 1, Table 1, [23]). The nanosuspension sample CaTi1 was prepared by hydrolysis of $Ca(OCH_3)_2$ and $Ti(OC_3H_7)_4$ mixture in isopropyl alcohol/water solvent. The reaction mixture was stirred at room temperature, the obtained suspension was separated by centrifugation and washed with water and isopropyl alcohol. The final product was dried in the oven at 80 °C for 1 hour. Yield = 4,21 g (81 %), (theoretical yield 5,20 g). See the Table 1 for more details.

The nanolime suspension was prepared by dissolving 0.75 g of the product in 250 ml of isopropyl alcohol. To increase the homogeneity of the resulting dispersion, the suspension was placed in an ultrasonic bath for 1 hour.

Table 1 - Precursor amounts and product yields

sample	precursor	m precursor (g)	n precursor (mmol)	yields (g)
Ca1	$Ca(OCH_3)_2$	7,18	70,2	4,21
CaTi1	$Ca(OCH_3)_2$	5,79	56,6	4,95
	$Ti(OC_3H_7)_4$	5,61	19,7	

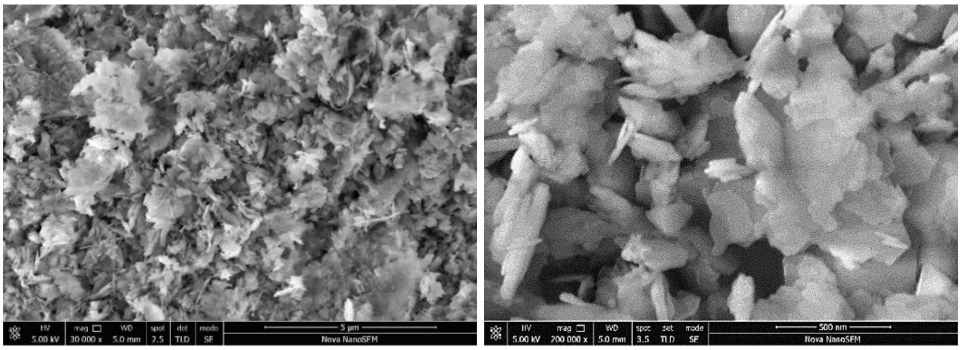

*Fig. 1 - SEM images of the test product of nanosuspension Ca1 without dopant TiO_2. There are well visible hexagonal, very thin (approx. 50 nm) platelet crystals on the images (*Nova NanoSEM (FEI) with Schotky field emission electron source (0.02–30 keV) and TLD detector, *Photo CPS UTB Zlín)*

For the identification of crystalline phases and confirmation of presence of $Ca(OH)_2$ in prepared products powder XRD diffraction analysis was employed. Powder XRD patterns were recorded on Rigaku MiniFlex 600 equipped with a CoK_λ (λ = 1.7903 Å) X-ray tube (40 kV, 15 mA). Diffraction patterns are displayed in Figure 2. All diffractions are assigned to $Ca(OH)_2$ phase and they correspond to the JCPDS database card number 076-0571. In the case of sample CaTi1 with the titanium, no diffractions related to TiO_2 were detected. The absence of TiO_2 diffractions means that titanium species are presented in the amorphous form. This amorphous form is characterized most probably by oligomeric titanium oxo clusters with tetracoordinated and hexacoordinated titanium atoms.

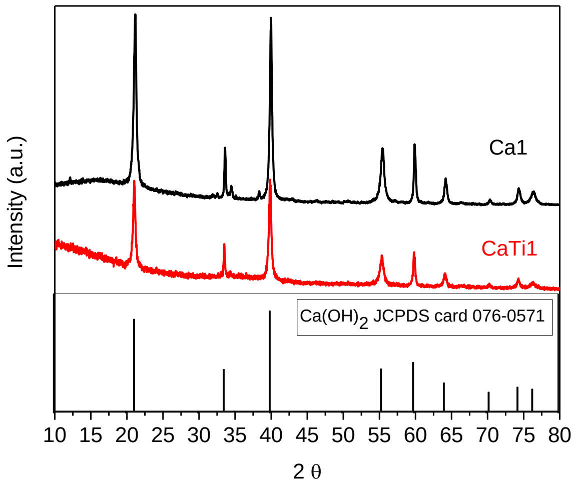

Fig. 2 - The XRD diffractogram of the tested nanosuspension of Ca1 and CaTi1 and their comparison with the $Ca(OH)_2$ library diffractogram

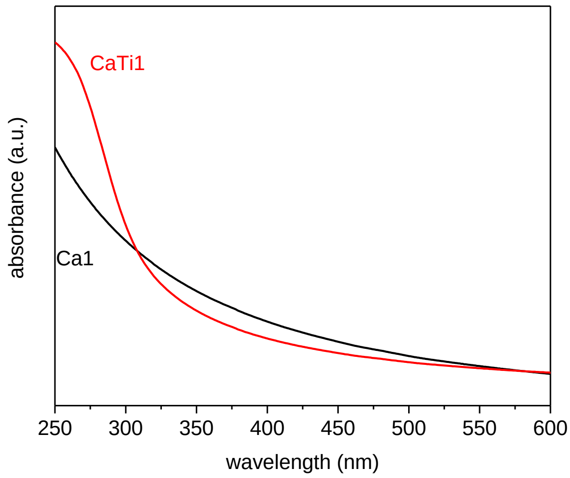

Fig. 3 - UV-Vis spectra of nanosuspensions Ca1 and CaTi1.

The important factor of $Ca(OH)_2$ nanosuspensions is the size of nanoparticles. The nanoparticle sizes were measured by dynamic light scattering method. DLS size distribution measurements were performed on the Zetasizer Nano ZS from Malvern. Obtained results are illustrated in Table 2. For the comparison of nanoparticle size, commercially available nanosuspension CaLoSiL® was used within this measurement as well. Based on the obtained values we can conclude, that both $Ca(OH)_2$ and $Ca(OH)_2/TiO_2$ nanodispersions prepared via hydrolysis of the alkoxides provides the systems with the nanoparticle size close to commercial CaLoSiL®.

Table 2 - Particle size measurements by DLS method.

sample	average Z-Ave (nm)	Peak1 (nm)	PDI
Ca1	298	275	0,269
CaTi1	249	241	0,231
CaLoSiL®	146	176	0,172

UV-Vis spectroscopy is important characterization technique for titanium species. Titanium dioxide exhibits absorption in UV region. This property is also crucial for the photocatalytic efficiency. With the application of UV-vis spectroscopy we can determine presence of Ti species represented by oligomeric titanium oxo clusters with tetracoordinated and hexacoordinated titanium atoms in mixed $Ca(OH)_2/TiO_2$ nanosuspensions. UV-Vis spectra measurements were performed on Perkin-Elmer Lambda 1050 with the Xe lamp and are displayed in Figure 3. Significant difference between $Ca(OH)_2$ (Ca1) and mixed $Ca(OH)_2/TiO_2$ (CaTi1) nanosuspension is observed in UV region where absorption of Ti species takes place. This absorption is represented by the steep increase of absorbance at ca. 330 nm.

CONCLUSION

From the results obtained, it is obvious that the use of prepared lime nanosuspension with TiO_2 dopant as a protective and self-cleaning layer of building materials exposed to weathering and UV radiation is promising. The present preparation of $Ca(OH)_2$ and $Ca(OH)_2/TiO_2$ nanosuspension by the hydrolysis of alkoxides yields results that are close to the commercial CaLoSiL® material. The advantage of the hydrolytic method is the purity of the resulting product and the relatively small particle size. The addition of titanium isopropoxide to the reaction mixture makes it possible to obtain $Ca(OH)_2$ nanoparticles with Ti species that will function as photocatalytically active centers. In our case, Ti species are amorphous in form of oligomeric titanium oxo clusters.

The issue of the preparation and application of a multifunctional suspension is still subject of laboratory testing. Identifying suitable manufacturing processes could lead to the practical use of nanosuspension in building and conservation practice.

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