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# Nanotechnologies in Cultural Heritage - Materials and Instruments for Diagnosis and Treatment

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## Abstract

This chapter aims to evaluate the nanomaterials that can be used to diagnostic, conservation and restoration of different artifacts and monuments and that can contribute to solving the problems which could appear during weathering processes of them. The nanotechnology, as a new and revolutionary area in science, can improve the traditional methods currently used for restoration and preservation in cultural heritage and can contribute to the creation of new highly specialized methods for diagnostic and treatment of different artifacts or even monuments. With a smaller size, a higher penetrability, viscosity, thermal and magnetic properties, in comparison with the traditional materials, the nanomaterials can contribute to solve the problems deriving from specific phenomena that could appear during the intervention and to identify the potential newly formed products in the treated materials. In this chapter, some aspects about the nanomaterials used for conservation and restoration of stone and paper artifacts are evidenced and discussed.

**Keywords:** nanomaterial, nanotechnology, cultural heritage, hydroxyapatite

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## 1. Introduction

The term “preservation” may have different meanings depending on the field in which it is applied [1]. The knowledge of the preservation of artworks on different artifacts is not limited to historical and semiotic analyses. Preservation nowadays requires an interdisciplinary team with a solid knowledge of materials science, chemistry, physics, microbiology, art history and nanotechnology in order to contribute and offer solutions to prevent the natural aging of some artifacts (paper documents, stone, paints, etc.) and to provide useful and basic

predictions about the degradation of the cultural patrimony and can come up with viable solutions [2, 3].

Generally speaking, the term “nano” defines an extremely small entity in the order of  $10^{-9}$  m [4].

The applications of nanotechnologies in the field of preservation of cultural heritage could include:

- Diagnosis of the damaged surfaces to obtain physicochemical and structural information on the materials that form the historic heritage and for identifying the surface damaging type: alveolarization, fractures and so on [5].
- New instruments and diagnostic methods, in order to make an informed decision on the materials to use during the further phases of restoration [6].
- Innovative methods for cleaning surfaces affected by polluting substances and black crusts [7].
- Treatment of surfaces (protection, waterproofing, self-cleaning) [8].
- New products for consolidation and protection of natural and artificial stones (compatible products) [9].
- Materials and innovative processes against raising of humidity and against sulfation for the conservation and/or restoration interventions on art manufactures of different nature [10].

The present chapter means to complete a survey on the use of nanotechnology for the preservation and restoration of the stone monuments and different damaged paper and stone artifacts. The scientific principles behind numerous nanomaterials on different types of common movable and fixed artistic substrates are discussed. Compared to traditional methods, these new tools have the benefit of considerably less impact on both the operators and the environment. Different types of nanoparticles currently used to produce conservation treatments with enhanced material properties are discussed.

### **1.1. Nanomaterials for restoration and conservation of cultural heritage**

Nanostructures represent a stage of matter between agglomerated molecules and structures and are typically characterized by a large surface area that affects their physicochemical properties. Innovative applications are of nanostructures and are based on two types of unique properties associated with nanostructures [11]:

1. New optical properties due to the generation of quantum effects.
2. Changes in reactivity and mechanical properties due to small physical dimensions and a large area of the specific surface. The advantages of small granule sizes in comparison with the agglomerated materials include: a low sintering temperature, super-elasticity, improved diffusion, improved dielectric and tribological properties.

One of the directions for the use of nanoparticles, nowadays, is the preservation of cultural heritage. The application of nanotechnologies to different artifacts has recently proved the huge potential of this science to apply in the field of preservation of universal cultural heritage [12, 13]. Solid nanodispersions, micelles, gels or microemulsions offer new viable solutions for the restoration and preservation of works of art. Some recently concerns are related to the synthesis and the application of nanoparticles of Ca and Mg or hydroxyapatite to paper and stone preservation [14]. In this chapter, the most used methods of nanoparticle synthesis and some of their recent applications for the preservation of artifacts are presented. The novelty of this area resides in a type of cultural heritage material (stone, paper) and starts with the main degradation paths and discussing protocols for the application of innovative nanomaterial-based tools for cleaning, consolidation or deacidification, which represent the majority of the case studies encountered in restoration and conservation procedures.

## 2. Artifacts conservation and restoration

### 2.1. Stone

#### 2.1.1. Influence of pollutants

The main types of atmospheric pollutants which could affect the stony monuments are shown in **Table 1**.

Usually, calcium carbonate can take three forms of polymorphs: calcite, aragonite and vaterite [15]. It is known that in the calcite variety (calcium carbonate variety detected by X-ray diffraction (XRD)) dissolution is affected by the presence of foreign substances  $Mg^{2+}$  (from  $MgSO_4 \cdot 7H_2O$ , called epsomite), which is considered one of the major cations in seawater and

Nr.crt.	Pollutant	Source	Effect on stone
1	Carbon dioxide and carbon monoxide	Internal combustion engines	Acid rain, soil pollution
2	Nitrogen and sulfur oxides	Combustion of fossil fuels by motor vehicles or thermoelectric power plants	Acid rain, soil pollution
3	Volatile organic compounds (hydrocarbons and hydrocarbon derivatives)	Combustion of fossil fuels, the evaporation of fuels, solvents used in various industrial processes	Acid rain, soil pollution
4	Suspended particulates—very small particles similar with gas may contain iron oxides, heavy metals (lead, cadmium, manganese, chromium), asbestos fibers or other pollutants	Combustion of fossil fuels, human activity	Acid rain, soil pollution

**Table 1.** Pollutant source and effects on stone.

groundwater. Also,  $\text{SO}_4^{2-}$  (from atmospheric pollution responsible for calcite conversion in gypsum) and  $\text{NO}_3$  (responsible for solubilizing the stone in the wall) are the most damaging pollutants or different artifacts [16]. Processes such as crystallization and salt dissolution contribute to new pores, which are responsible for an accelerated damaging process through the microcracks generated in the stone. The dissolution rate significantly increases in the presence of NaCl solutions, due to electrostatic reasons. Calcium carbonate ( $\text{CaCO}_3$ ) can be found in soils, rocks and sediments. Among the minerals, calcium carbonate is one of the most sensitive ones to weathering [17]. Due to rapid weather destruction, small amounts of  $\text{CaCO}_3$  can dominate the geochemical behavior of aquatic systems. Given the sensitivity of this rock, it is necessary to study the influence of climatic and environmental factors on this rock [18].

The pollutant effects on buildings and monuments degradation require a multidisciplinary approach using conventional and unconventional methods to achieve a good understanding of the mechanisms and consequences of such pollution [6]. It has been established that the hydraulic properties of stones and their traction resistance are the most important parameters that control the stone resistance to decomposition, and these parameters are widely used to estimate their durability.

The effects of the environment on some monuments (Basarabi-Murfatlar Churches) have been assessed through various analytical investigations: thermal analysis, XRD, EDXRF and ion chromatography. When the temperature is less than  $120^\circ\text{C}$ , a weight loss due to the absorbed water is recorded, especially in the absence of hydrated salts. In the temperature range  $200\text{--}600^\circ\text{C}$ , a loss of chemically bonded water is registered, but no other compounds subjected to weight loss. After  $600^\circ\text{C}$ ,  $\text{CO}_2$  loss is observed, due to the decomposition of carbonates, higher for the most degraded stones [19].

Stone surface alteration (determined by scanning electron microscopy (SEM) analysis coupled with diffused X-ray spectroscopy (SEM-EDX)) could be classified in several types:

- a. Surface damage caused by sulfur and calcium and by the calcite reaction with the sulfur oxides present in the medium.
- b. Alteration of the surface caused by deposits, when no chemical reactions occurred. These deposits are composed of dust from the anthropogenic particles. These degraded layers are mainly caused by the epigenetic formation of gypsum. In areas with high traffic, the sulfur oxide content is considerably higher [20]. There are two different mechanisms of destruction in the process of damaging the stones under the action of environmental conditions:
  - Chemical alteration of calcite and precipitation on gypsum that catches atmospheric particles on the surface.
  - Physical phenomenon of deposition of atmospheric particles on the surface.

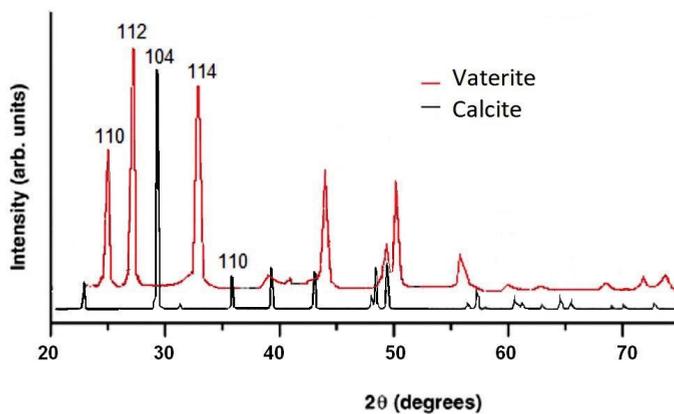
Kruhl and Nega [21] investigated the fragmented form of quartz particles and found that the size of the fragments decreases as temperature increases during suture formation, while Bernal et al. [22] concluded that the processes of degradation cause the fragmentation of the

surface size. Daniele and Taglieri [13] studied the morphology of quartz aggregates in granite and showed that the fragmented dimensions of the quartz aggregates are different depending on the type of granite. The sedimentary rocks are those originating:

- a. Sedimentation and cementation under natural pressure of particles of natural rocks eroded by wind, rain, sunbathing, conglomerate and sandstone.
- b. Precipitation from natural solutions—gypsum, limestone, dolomite and travertine; sedimentation and consolidation of residues of dead organisms (shells, shells)—diatomite, limestone and chalk. The limestone is derived from marine sediments and fossilized organic lakes (such as crinoids or brachiopods), consisting of calcium carbonate or calcite. Sandstones are the result of sedimentation of sand together with silica or calcium carbonate; the silica in the tiles may have the same adverse effect encountered at the granite. Both sedimentary rocks—limestone and sandstone—are easier to cut than granite, which has made them quite often used in the masonry of historical buildings [23, 24]. On the Romanian territory, there are many masonry made of siliceous sandstone or calcareous sandstone, the first being those with higher compressive strength. The mineralogical composition and crystal structure of the stone monuments before and after the conservation treatment can be determined by X-ray diffraction (XRD) [25, 26]. A sample of  $\text{CaCO}_3$  (**Figure 1**) has a series of diffraction peaks at  $2\theta$ : 29.5, 39.5, 47.6, 48.58, etc., corresponding to the calcite phase, which shows that in the water the precipitated calcium carbonate crystals were formed mainly of calcite.

In **Figure 2**, there are Fourier transform infrared (FTIR) peaks corresponding to the vaterite phase generated inside and outside of the damaged limestone surfaces.

Very clear bands could be observed in FTIR spectra, which show significant differences between not-treated and treated limestones, especially at the bands assigned to carbonate groups and to sulfate bands (**Figure 3**).



**Figure 1.** X-ray diffraction of calcite.

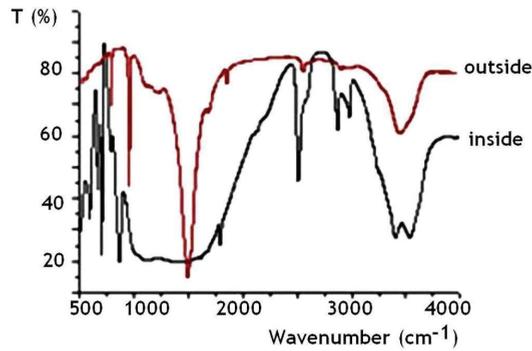


Figure 2. FTIR spectra of inside and outside treated limestone surface.

## 2.2. Causes of natural stone degradation

**The natural stone** is subjected to a slow and continuous process of deterioration (known as alteration— or degradation, or even “decay”), which is a phenomenon caused by physico-chemical causes other than mechanical actions: moisture; crystallization of salts in the mass of the material; deposition of pollutants on the surface of the rock, acting through chemical and/or biological processes; high temperature variations during day and night (strong heat cycles - temperature drop) or accidental fire action; and erosion due to strong winds (process without significant mechanical stress) [25–27].

**Moisture** is one of the main factors that attack stones through the capillary phenomenon, and limestone, dolomite and marble are most affected by this external factor [28]. During 10 years of exposure to a 100 cm column of atmospheric precipitation, calcareous rocks can reduce their thickness by 0.2 mm. Moisture can also affect the rocks that contain the tiny black, feldspar and tremolite. In the case of granite, the moisture from the pores can lead to the splitting of the stone into layers of 1–3 mm thick, through the expansion-contraction cycles (important to the reversible frost-thaw phenomena, because the freezing volume increases with 9%).

**Salt crystallization** is one of the main phenomena of the destruction of porous materials, which occurs by penetrating the material pores by the aqueous solution containing dissolved

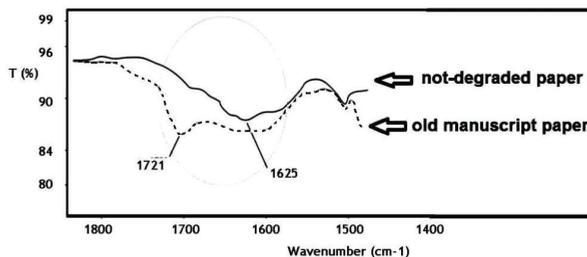


Figure 3. FTIR spectra of not-treated and treated limestones.

Nr.crt.	Factor	Source	Effect on stone
1	Moisture	Rain, freeze-thaw cycles, groundwater,	Construction, surface water mitigating through the shoulder, ditches or imbibing through in the paved surface of the pavement
2	Salt crystallization	Mirabilite (Na <sub>2</sub> SO <sub>4</sub> • 10H <sub>2</sub> O) and thenardite (Na <sub>2</sub> SO <sub>4</sub> )	Severe alveolar weathering, granular disintegration, efflorescences and subflorescences in buildings, monuments and quarry
3	Freeze-thaw cycles	Weather seasons	Severe alveolar weathering, granular disintegration, efflorescences and subflorescences in buildings, monuments and quarry
4	Black crusts - soiling on buildings. This aids the production of gypsum, which crystallizes on the surface	Exposition to moisture in the form of fog, mist or dew. Diesel engines are one of the most damaging particle sources	Ongoing decay mechanisms, such as salt weathering

**Table 2.** Causes of natural stone degradation.

pollutants, such as mineral salts, combustion gases, powdered plant residues and microorganisms, **Table 2**. The tensions in the surfaces that delineate the pores due to the salts crystallized here, known as “stone efflorescence,” represents a great danger for the durability of a historical structure. The most common salts in the efflorescence phenomenon of masonry are sulfates, carbonates and nitrates (sodium, magnesium, calcium, potassium), generated from the atmospheric pollutants (SO<sub>2</sub>, NO<sub>2</sub> and CO<sub>2</sub>), which are transformed in (HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>CO<sub>3</sub>) in contact with the mortars [24, 29].

**Freeze-thaw cycles.** If the mortar pores are filled with water, a pressure will be exerted on the pore walls of the mortar due to the increase in the volume (by 9%) of the frozen water. Thus, prolonged freeze-thaw cycles will progressively degrade mortars with moisture. The most sensitive to this phenomenon is lime mortars [30].

### 2.3. Type of inorganic nano-consolidants

The nanomaterials are adequate materials for the architectural heritage, due to their consolidation and protection capacity of damaged building materials. The nanoparticles are able of self-cleaning coatings for a preventive protection system for historical surfaces, preserving the original aspect of treated elements, decreasing the deposition of pollutants and soiling and reducing the onset of external degradation processes due to soiling phenomena. The nanoparticles must have the following attributes: thermal stability, biologically and chemically inertness, nontoxic, low cost, stable toward visible or near UV light, good adaptability to various environment and good adsorption in solar spectrum. In addition, these treatments can also have water repellent properties, which favor this self-cleaning action. On the other hand, the presence of soluble salts is recognized as an important decay agent of stone heritage.

Thus, in the last few years, the study of the application of nanoparticles as a desulfating agent for stone, mortars and wall paintings is being carried out [31].

The principle of the inorganic materials is to create an insoluble “paste” that fills the pores of the stone. There is a large area of such consolidants, as it is shown in **Table 3**.

Some inorganic materials, such as calcium hydroxide  $\text{Ca}(\text{OH})_2$ , magnesium hydroxide  $\text{Mg}(\text{OH})_2$ , barium hydroxide  $\text{Ba}(\text{OH})_2$ , strontium hydroxide  $\text{Sr}(\text{OH})_2$  and hydroxyapatite (HAp), have already been used as consolidants for different damaged carbonate stones [32]. Calcium hydroxide has been used as nanoparticles (130–300 nm), dispersed in alcohols, as nanosols (50–250 nm), as “pastelike” in ethanol and as calcium hydroxide microparticles (1–3 mm) [33]. But, due to their low porosity, high moisture content of the substrate, oversaturation of the material and quick evaporation of the solvent, calcium hydroxide is not an optimal

Nr.crt.	Consolidant	Effect
1	Alcalo-silicates	Deposition of silica in the limestone mass
2	Silico-fluoride	Silicone tiles can form a cemented crust on the outside, a layer of higher hardness. In general, these solutions are no longer recommended
3	Alkaline hydroxides	The consolidation effect is still low, requiring repeat treatment to make it more effective. The process remains relatively uneconomical
4	Strontium and barium hydroxides	These solutions seem to be more effective than calcium-based, but experts believe the problem of the durability of the treated stone, the application to historical structures
5	Inorganic builders (zinc stearate and aluminum stearate, aluminum sulfate, phosphoric acid, phosphate and hydrofluoric acid )	Superficial penetration into the pores of the stone. Danger of microorganism population
6	Alcosilanes (or alkoxyans). Increased mechanical strength has also been reported with approx. 20% of the silicon tiles treated, which is already performing	The best materials with a reinforcing function A deep penetration into the pores of silky tiles. The penetration of the alkoxyans in the stone occurs at a depth of 20–25 mm, which means much more than the inorganic builders
7	Acrylic polymers (methyl-methacrylate, methyl-acrylate, ethyl-methacrylate and butyl-methacrylate).	All of these builders have increased the resistance of the treated stone layer, but unfortunately they are unstable in color under the action of the already mentioned agents
8	Vinyl polymers (polyvinyl chloride, polyvinylchloride-chlorinate, polyvinyl acetate)	Polyvinyl acetate may cause a glossy-glassy appearance on the surface of the stone. On the other hand, if the polymers were insufficiently diluted in the solvent, layers were formed which could represent a screen for retaining the moisture and salts in the stone, that is, exactly the opposite of what was intended by applying the waterproofing treatment
9	The polyurethanes	Treatment is very effective, but warmth and light produce opposite effects

**Table 3.** Consolidants used for stone and their effects.

option for this monument [34]. This is the reason for finding other optimal materials. Also, a reduced penetration depth and a limited solubility of lime in water are causing chromatic alteration of stone surface [35, 36]. Except the metallic hydroxides above mentioned, for stone consolidation could be used hydroxyapatite (HAp) [37, 38]. It is a natural mineral form of calcium apatite having the formula  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$  and has the ability to readily accept in its structure numerous substitution ions for both  $\text{Ca}^{2+}$  and  $\text{PO}_4^{3-}$  ions, with the chemical composition altering and the morphological structure [39]. The  $\text{OH}^-$  ion may be replaced by fluoride, chloride or carbonate ions, producing fluorouracil or chlorapatite [40].

### 3. Paper

#### 3.1. Considerations on the methods of conserving the historical paper

Hydrolysis of acid-catalyzed cellulose is the main source of paper degradation. It is well known that the degradation process resides in the manufacture of low quality paper. At the beginning of the eighteenth century, papermaking technology changed and the paper began to be made of increasingly reactive materials (wood pulp) and acidic substances (rosin, used for sizing, chlorine for bleaching and so on). After a long period of exposure to environmental conditions (e.g., temperature, humidity, light), these substances accelerate chemical degradation of the paper. The global effect is the rapid decrease in the resistance to degradation of paper documents, especially on paper made since the eighteenth century [41–43]. There is a general consensus on the inevitable treatment of deacidification in paper preservation. Deacidification involves a complete neutralization of the paper and, in most cases, the introduction of an alkaline reservoir that opposes the acidity assault in the environment (e.g., pollution) [44]. In this context, many studies have been developed addressing acidity elimination processes [45]. The best methods of deacidification are based on nonaqueous solvents. Less polar fluids minimize the risk of ink solubility. Among these most important deacidification methods are the Wei T'o method and the Bookkeeper method [46].

Recently, a new method has been proposed based on alcohols dispersed in calcium hydroxide nanoparticles that give good results in deacidification of the paper. The above-mentioned studies have also been extended to the treatment of paper with magnesium hydroxide nanoparticles (brucellosis) because it has been shown that magnesium reduces the rate of oxidative degradation of the cellulose substrate due to exposure to light.

Magnesium hydroxide nanoparticles,  $\text{Mg}(\text{OH})_2$  (brucite), can be obtained by hydrating Mg ( $\text{MgO}$ ), precipitating magnesium salts with an alkaline solution and electrolyzing an aqueous solution of a bounce magnesium.

$\text{Mg}(\text{OH})_2$  is usually accomplished by the first two methods [47]. When magnesium hydroxide powder is used as a precursor for the synthesis of magnesium oxide, the size of the hydroxide particles, the shape and degree of agglomeration of these are key parameters for many applications. An example is the sintering stage in the ceramic manufacturing process. Magnesium-based

alkaline compounds are of great importance in the preservation of cultural heritage. Such an area of interest is also the treatments for deacidification of acidic paper in order to preserve it. Both the Wei T'o and Bookkeeper methods are based on the use of magnesium compounds that generate  $Mg(OH)_2$  "in situ" after hydrolysis. Unfortunately, some studies have demonstrated a limited homogeneous distribution of alkaline reservoirs [48]. The purpose of the new studies was to synthesize magnesium nanoparticles following the procedure similar to that of calcium hydroxide, which yielded very good results. Unlike the Wei T'o and Bookkeeper methods, these nanoparticles once deposited on the paper immediately acquire the role of deacidifier or buffer. Synthetic pathways for  $Mg(OH)_2$  nanoparticles have an important role both theoretically and practically. Several papers have shown that the precipitation of metallic hydroxides in their salts is strongly affected by variation in synthesis parameters. These include high-temperature reactions, reagent concentration and aging time. In particular, it was demonstrated that temperatures above  $100^\circ C$  promote the formation of nanoparticles in nonaqueous media. Some studies also reported significant effects of organic solvents related to the shape and size of precipitated particles. The obtained particles were characterized for determination of their chemical nature by: FT-TR spectroscopy, specific surface area (SA) measurement of dry powder, X-ray diffraction (XRD) characterization and shape and size characterization by SEM and TEM electronic microscopy with scanning or electron transmission. Applying deacidification of nanoparticle paper is compared to Wei T'o [49].

In some cases, during the degradation process, it is possible to identify some odorous compounds such as vanillin or vanilic acid, well identified by gas chromatography, **Figure 4**.

### 3.1.1. Synthesis of nanoparticles of alkaline hydroxides

This process can be considerably stopped or slowed down by deacidification treatment. The excellent deacidification agents are  $Mg(OH)_2$  and  $Ca(OH)_2$  because they provide very good

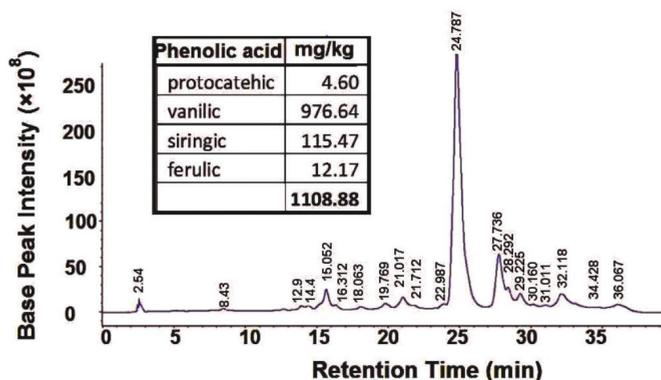


Figure 4. GC-MS chromatogram of the damaged paper.

physicochemical compatibility with the support, and after conversion into carbonates, they work as alkaline reservoirs without producing any undesirable side effect [50].

Nanoparticles dispersed in alcohols can be applied to the paper by spraying, impregnating or dipping [51]. This method produces in situ hydroxides and requires dispersants to stabilize the system. The solvents used are volatile, environmentally friendly and with low surface tension so that they act as carrier solids for solid particles and ensure the homogeneity and penetration of nanoparticles into the depth of cellulose fibers [52].

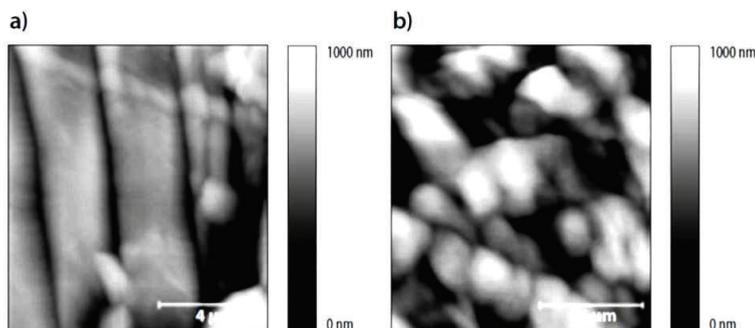
The synthesis of  $\text{Ca}(\text{OH})_2$  and  $\text{Mg}(\text{OH})_2$  nanoparticles was made in heterogeneous medium, and  $\text{CaO}$  and  $\text{MgO}$  reagents were used. The oxides in turn were obtained from the corresponding carbonates, which were initially milled and then milled to a size of  $100\ \mu\text{m}$ . Then, the carbonates were calcined at  $1000^\circ\text{C}$ . Both carbonates were of analytical purity.

The process consists of suspending in a mixture of isopropyl alcohol and water in each of the two stoichiometric proportions of the respective oxides according to the equations given above. The hydrolysis reaction was carried out at  $80^\circ\text{C}$  for about 30 min (using deionized water).

### 3.1.2. Treatment of paper document with suspension of alkaline hydroxide nanoparticles

The resulting particles were used to treat paper with HAp in isopropanol, and the historical paper was manually sprayed. The pulverized sheets were from a book printed in Romania, in Bucharest, from a private collection from the end of the nineteenth century. Untreated paper was taken as a reference. The paper was then treated with the nanoparticles of  $\text{Ca}(\text{OH})_2$  or  $\text{Mg}(\text{OH})_2$  and examined by scanning electron microscopy (SEM) [37, 38]. Initially untreated, unwritten, unprinted and uncolored paper was investigated by SEM and AFM, too, as a reference (**Figure 5**).

The cellular microarchitecture of cellulose was investigated by SEM. The micrographs obtained for this sample revealed a densely packed cellulose fiber network which, on a microscopic scale, inside the sheet of paper appears randomly oriented without having a majority



**Figure 5.** SEM images for not-damaged and damaged cellulose substrates.

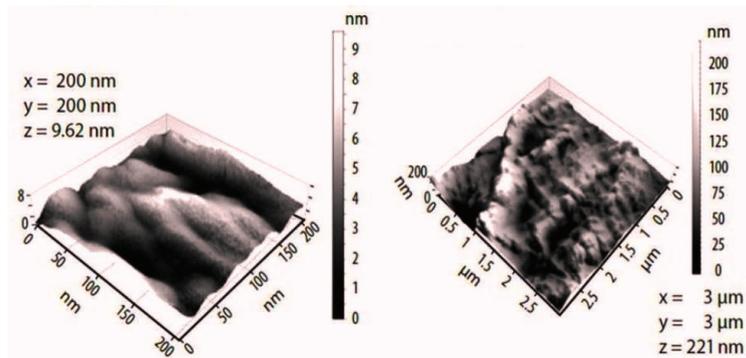
direction of microfiber orientation. The fibers are homogeneous and seem to come from plant fibers, perhaps cotton or linen. The size of the fibers is different, some of them are whole, others are broken. Some fibers have inlay that might be salt crystals. The presence of mineral crystals in paper can be considered as a consequence of how it is made (**Figure 6**). The presence of luminous areas on the image is a consequence of either the presence of a thicker part of the glue material or a rupture of the paper [53].

On a macroscopic examination of the sprayed sample of nanoparticles of  $\text{Mg}(\text{OH})_2$ , no negative influence on the optical parameters of the paper is observed. Some white deposits of  $\text{Mg}(\text{OH})_2$  were formed on the paper surface more pronounced in this case than in the case of  $\text{Ca}(\text{OH})_2$ , although both consolidants have the same concentration and volume applied to the same type of paper. Not all  $\text{Mg}(\text{OH})_2$  nanoparticles neutralize the acidity of the paper and the unreacted quantity will be carbonated over time in the presence of atmospheric  $\text{CO}_2$ .

### 3.1.3. Hydroxyapatite nanoparticles: synthesis and characterization

Hydroxyapatite (HAp) was obtained by the modified precipitation chemical method, and the synthesized substance was analyzed by spectral techniques: atomic force microscopy (AFM), scanning electron microscopy (SEM) (**Figure 7**) X-ray diffraction (XRD) and spectroscopy in Fourier transform infrared (FTIR).

As synthesis reagents were used, calcium nitrate tetrahydrate,  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , and dibasic ammonium phosphate,  $(\text{NH}_4)_2\text{HPO}_4$ , were previously dissolved each in deionized water. Then, the solution of  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  was added dropwise over the  $(\text{NH}_4)_2\text{HPO}_4$  solution, which was stirred vigorously at room temperature for about 1 h until a milky and somewhat gelatinous precipitate was obtained and further stirred for further 1 h to increase the reaction rate and homogenize the mixture [20]. The mixture was synthesized at  $100^\circ\text{C}$  for 24 h. Then, the precipitate was washed and filtered on a glass filter. After filtration, the compact and sticky cake was dried at  $80^\circ\text{C}$  in a furnace. The dried powder was then ground into a mortar and then calcined in an alumina crucible for 4 h [27].



**Figure 6.** AFM images of not-damaged and damaged cellulose substrates.

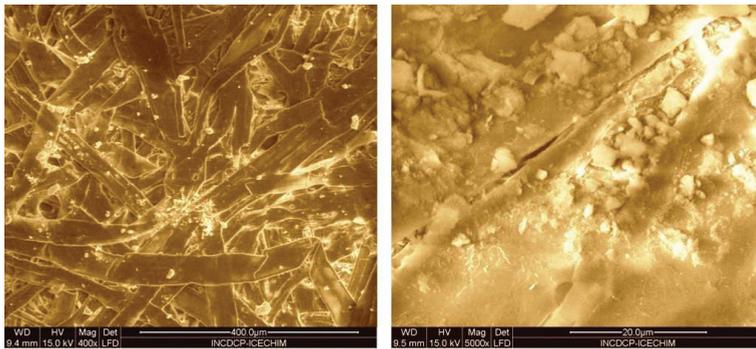


Figure 7. SEM images of not-treated and treated papers with Hap.

As a method of synthesis, a modified wet precipitation method has been chosen because this is more advantageous due to the ease with which it is achieved, the low working temperature, the relatively important percentage of the pure product and the synthesis equipment that is not expensive. It has been found that well-crystallized products with a low degree of sintering have been obtained, but relatively high calcination temperatures were required and the application of this long-term treatment, 4 h, was to obtain a finished product with the desired parameters [3]. Both X-ray diffraction and infrared spectroscopy showed the high degree of purity of the reaction products [54]. The study of SEM and AFM images was very consistent with the results obtained by other analysis techniques: thermal analysis [46]. It has been determined that the crystal size for HAp synthesized is 70–nm. It has also been concluded that a sintering temperature of the synthesis product above 850°C leads to the occurrence of a by-product reaction, namely tricalcium phosphate, and for its conversion into Hap, it is necessary to calcinate at 1200°C for 4 h.

#### 4. Conclusions

Nanomaterials bring huge enhancements of improvement endeavors for various applications, due to the extensive scale nanomaterials for auxiliary applications. The structure-handling property acquires an imperative segment in the cultural heritage. The present paper plans to do a review of the condition of workmanship on the use of some nanomaterials to the preservation and rebuilding of the stony and paper cultural artifacts. With a smaller size, a higher penetrability, viscosity, thermal and magnetic properties, in comparison with the traditional materials, the nanomaterials can contribute to solve the problems deriving from specific phenomena that could appear during the intervention and to identify the potential newly formed products in the treated materials. In this chapter, some aspects about the nanomaterials used for conservation and restoration of stone and paper artifacts are evidenced and discussed. Distinctive sorts of nanoparticles right now used to create preservation with upgraded material properties and novel functionalities have been discussed and exemplified in this chapter ( $\text{Ca}(\text{OH})_2$ ,  $\text{Mg}(\text{OH})_2$ ,  $\text{Ba}(\text{OH})_2$ ,  $\text{Sr}(\text{OH})_2$ , hydroxyapatite), both for their synthesis, characterization and specific applications for paper and stone surfaces.

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