

# Nanomaterials and nanotechnologies for the conservation of the materials of cultural heritage

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## ABSTRACT

The communication is aimed at the development of nanomaterials for the preservation and consolidation of the materials of cultural heritage objects, mainly the artifacts from limestone, sandstone, marl, etc. A cleaning agent was elaborated based on the joint action of micelles of non-ionic surfactants, 1-pentanol and acetates, which is able to effectively remove and solubilize layers of acrylates. A simple procedure was developed, which provides nanoparticles of calcium and magnesium hydroxides, whose size is as small as ca 10 nm, suitable for the consolidation of weathered stones with narrow pores. Based on the “bricks and mortar” approach, nanoparticle-modified gels of amorphous silicon dioxide were worked out, exhibiting only very small shrinkage due to syneresis and drying, which substantially limits their cracking and enhances their strength.

**Keywords:** Conservation of cultural heritage, cleaning; micellar solutions, inorganic nanoparticles, gels.

## 1 INTRODUCTION

Conservation science is one of the most complex topics in the materials science as it requires expertise ranging from the history of art and archaeology to the advanced analytical and physical chemistry. [1] However, the recent development has shown that the complex tasks of the conservation of the cultural heritage can be solved very effectively and as friendly as possible towards the treated artefacts and the environment using novel nanomaterials and nanotechnology procedures. [1]

The cleaning procedures enable to remove cautiously but effectively the dirt, corrosion products and remnants of earlier, sometimes unsuitable or already weathered, conservation measures. The consolidation nanomaterials ensure a highly stable conservation of the materials of heritage buildings degraded by the atmospheric action and biodegradation by the impregnation of the porous inorganic substrate with sols containing nanoparticles based on inorganic oxides and hydroxides. The nanostructured surface coatings minimize the retention of microflora and microfauna on the surfaces of both historic and modern monuments. Biocide agents based on metal nanostructures ensure a controlled release of the active component at an optimum concentration during a very long time. The

present communication is aimed at two aspects of the conservation of historic artifacts, namely at the micellar solutions suitable for the cleaning of the surfaces of historic materials and at stone consolidants with excellent mechanical stability.

## 2 CLEANING

Cleaning systems based on micellar solutions and microemulsions are very efficient in the removal of various polymeric deposits owing to their outstanding features. Micelles are able to solubilize polymers to achieve their complete removal from the surface and the porous structure of the artifact. Owing to their large surface area, the micelles have a great detergency capacity, which is usable for the interaction with the polymeric. As the micelles are dispersed in an aqueous system, the penetration of polymeric materials to be removed into the porous structure of cleaned artifact is maximally reduced.

We have chosen electrically neutral non-ionic copolymers as the most suitable surfactants, which have additional desirable properties. They are much less sensitive to the variation in the ionic strength of the solution than ionic ones. Last but not least the non-ionic surfactants are biodegradable and friendly to the environment.

Specific interactions with the polymer, which are needed for its efficient selling and separation from the surface, are provided by organic solvents dissolved in the aqueous medium in the presence of micelles. The whole process of the removal of the polymer deposits from the artifact surface is rather complex, involving at least three mechanisms operating synergistically: the swelling of the polymer, the peeling of the polymeric layer off the artifact surface and the solubilization in the organic media.

As a suitable test compound, we have chosen Paraloid B72, which is a random copolymer of methylacrylate and ethyl methacrylate. This polymer was often used for the consolidation of weather materials and its complete removal is important to render the surface suitable for new conservatory treatments.

We have developed very efficient cleaning agents containing aqueous micellar solutions of non-ionic Pluronic poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymers or diblock Brij 58P, with added 1-pentanol acting as a co-surfactant, which is solubilized inside the micellar core, and additional solvents, namely acetates, which help to degrade the deposit to be removed.

The acrylate deposit is peeled off the surface and completely solubilized in a non-aqueous layer floating on the water surface.

### 3 NANOPARTICLES OF CALCIUM AND MAGNESIUM HYDROXIDES

At the beginning of this century nanoparticles of calcium and magnesium hydroxides were shown efficient consolidants for the stabilization of weathered limestones and wall paintings. However, the preparation of suitable dispersions, whose particle size is suitable for the efficient penetration into the pore system of the material to be consolidated and which exhibit a narrow particle size distribution, is far from solved. Especially hard nut to crack is the preparation of dispersions of nanoparticles smaller than about 50 nm, which are indispensable for the consolidation of materials, whose pores are narrower than ca 1 micrometer.

Nanoparticles of calcium and magnesium hydroxides can be prepared by the precipitation from a solution of calcium or magnesium chloride using sodium hydroxide. It is essential to ensure the formation of a large number of nuclei at the very early stages of precipitation and to limit their growth and agglomeration. This process is difficult to control as the nucleation is endothermic while the growth of particles is exothermic. The solubility of calcium hydroxide decreases with increasing temperature. Consequently the precipitation reaction should be carried out at sufficiently high temperature to support the endothermic nucleation and to avoid the immediate dissolution of formed nuclei of calcium/magnesium hydroxide. Moreover, the dielectric constant of the medium should be high enough to guarantee the sufficient solubility of the ionic compounds.

We have tested two approaches to prepare calcium or magnesium hydroxide. First, ethylene glycol was used as the solvent, whose normal boiling point and relative dielectric constant equal 195 °C and 41.4, respectively. Ethylene glycol-based procedure was originally developed by Matijevic et al for the synthesis of nanoparticles of indium hydroxide. [2] Later on it was used by Dei et al for the precipitation of nanoparticles of calcium hydroxide ca 100 nm in size. [3] Alternatively, water, exhibiting normal boiling point and relative dielectric constant of 100 °C and 80, is another suitable reaction medium.

Using ethylene glycol, we have developed two procedures. In the first procedure 6M aqueous solution of sodium hydroxide was added to a 0.57 M solution of calcium chloride in ethylene glycol at 180 °C (molar ratio  $\text{CaCl}_2/\text{NaOH}$  of 1.4) at a flow rate of 7 mL/min. The obtained suspension was aged at the same temperature for 10 min. The formed primary nanoparticles of calcium hydroxide were joined into agglomerates several micrometers in size due to the action of ethylene glycol, whose two OH groups serve as bridges between the particles. Sodium chloride occluded in the agglomerates was removed by washing at 90 °C. Finally the agglomerates

were peptized in 2-propanol using ultrasound. This procedure provided particles of calcium hydroxide several hundreds nanometers in size.

Alternatively, a procedure originally developed for the preparation of nanoparticles of indium tin hydroxide was used. [4] In this method, calcium chloride dissolved in ethylene glycol was precipitated at 0 °C with sodium hydroxide also dissolved in ethylene glycol. Afterwards, the precipitated particles were autoclaved at 200 °C. The primarily formed micrometer-sized particles were successfully redispersed into 30 nm ones with only a very small proportion of larger ones. (Fig. 1)

It can be preliminarily concluded that the ethylene glycol-based procedures can under optimized condition provide the desired small particles less than ca 50 nm. However, the procedure requires rather demanding peptization, in which ethylene glycol is replaced with isopropanol. Due to its physico-chemical properties ethylene glycol is an excellent reaction medium with both high boiling point and dielectric constant. However, because of the presence of two OH groups it is strongly adsorbed on the surface of hydroxide particles and thus acts as a strong agglomeration agent. Therefore it is necessary to desorb it and replace with isopropanol, which prevents the particles from a direct contact and thus stabilizes the dispersion.

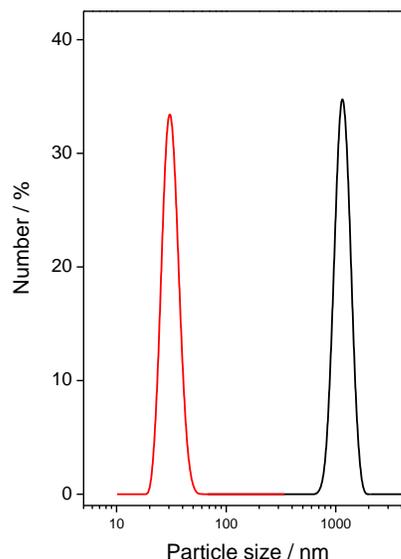


Figure 1: Particle size distribution for dispersions of calcium hydroxide prepared at 0 °C and autoclaved. Autoclaved (black), peptized (red)

Because of the inconvenience due to the necessity of the removal of ethylene glycol, water at 90 °C was used as a reaction medium. 0.5 or 6M aqueous solution of sodium hydroxide was added to a 0.57 M solution of calcium chloride at 90 °C (molar ratio  $\text{CaCl}_2/\text{NaOH}$  of 1.4) at a flow rate of 2.5 mL/min to practically instantaneous addition.

The obtained suspension was aged at the same temperature for 10 min. The suspension obtained was hot filtered and washed and finally peptized in isopropanol using ultrasound.

This procedure provided particles 500-1000 nm in size, which could be redispersed into 200-300 nm ones. Even if the process parameters of the preparation were varied we have not obtained particles smaller than ca 200 nm.

Therefore this procedure was further modified and optimized. In principle, two paths were followed. First the concentration of both reagents was substantially decreased. Second it was attempted to stabilize the primary particles and to prevent their agglomeration using non-ionic surface active agent, such as Triton X-100 block copolymer. Finally it was found that by the combined action of the low reagent concentration and polymer stabilization very small nanoparticles of calcium and magnesium hydroxides, or of their mixture, can be prepared.

The optimized preparation procedure was as follows. First 2 mL of Triton X-100 was dissolved in 200 mL of an aqueous 0.01 M solution of calcium chloride. Afterwards 200 mL of an aqueous solution of sodium hydroxide, whose concentration was between 0.017 and 0.025 M, was added to the mixture. The temperature of both reactant solution as well as the final mixture was carefully held 90 °C. The flow-rate of the hydroxide solution was 10 mL/min. The suspension obtained was aged at 90 °C for 10 min.

By this method, nanoparticles of calcium hydroxide were obtained, whose size is about 11-14 nm. The particle size does not depend much on the precipitation stoichiometry (Fig. 2).

The Triton-stabilized particles exhibit very good stability, which is important for their long shelf life. Further they are substantially resistant against the action of electrolytes including multivalent anions, which are generally strong coagulants. This is a very important property because the preliminary agglomeration on the artifact surface pores could make the sufficient penetration of the particles completely impossible. Because of the adsorption of non-ionic surfactant Triton X-100 on the particles' surface the zeta-potential is decreased from ca +35 mV to practically 0 mV, which suppresses the effect of anions on the stability of particles.

Finally we have also tested the possibility to increase the concentration of both reagents, i.e. calcium chloride and sodium hydroxide. We have found that that increasing the concentration of both reagents approximately 50 times does not much influence the particle size, actually the size of Triton-stabilized particles was practically the same, i.e. 14 nm. The possibility of increasing the concentration of reactants and thus decreasing the reactor volume is promising from the point of view of the scale-up.

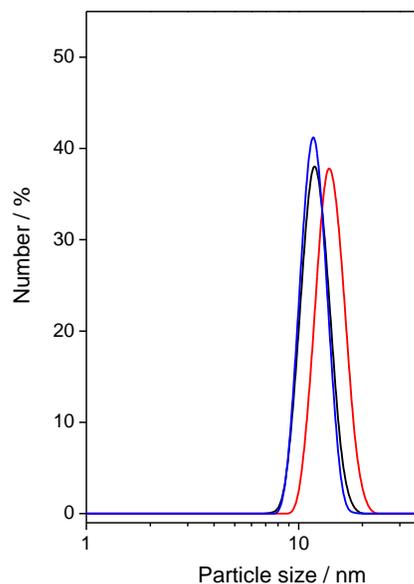


Figure 2: Particle size distribution for dispersions of calcium hydroxide prepared using low reagent concentration and Triton X-100 as stabilizer. NaOH/ Ca(OH)<sub>2</sub> = 1.7 (black), 2.0 (red), 2.77 (blue).

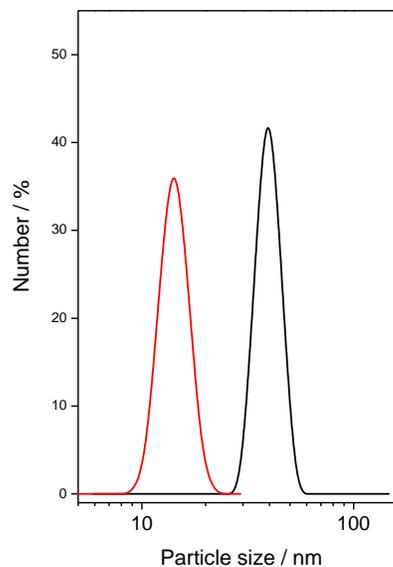


Figure 3: Particle size distribution for dispersions of calcium hydroxide prepared using higher reagent concentration and Triton X-100 as stabilizer. Without Triton stabilization (black), Triton stabilized (red).

## 4 PARTICLE-MODIFIED GELS

Silicon alkoxides, such as silicon ethoxide or its oligomers (so called ethyl silicates), are excellent consolidants for the weathered silicate materials. Their soft point is the cracking of formed gels due to the syneresis and residual drying stress leading to their decreased mechanical strength, and certain incompatibility of their physical properties with those of the stone. [5]

The shrinkage and cracking of the gel can be reduced by the formation of wide pores within the gels or by the modification with particles. Wide pores could be created by adding a template, such as polymers or latex particles, to the sol and removing it after the rigid mineral structure has been formed. By adding particles of oxides to the alkoxide sols composites are formed after the hydrolysis and polymerization, which exhibit microstructure of particulate systems and are distinct from the polymeric gels without particles.

Besides the decreased shrinkage of particle-modified gels, their physico-chemical properties, such as Young's modulus or the thermal expansion coefficient, are closer to those of the consolidated stone than properties of purely polymeric gels. The properties of the final composites, such as strength, porosity, thermal expansion or color, can be adjusted by the selection of particles according to the specific requirements. Finally there is the possibility of introducing another functionality specific for the particles.

We have aimed at two systems, namely on particle and particle-pore modified gels. Both approaches have provided materials with substantially improved mechanical properties.

We have recently developed a novel preparation strategy called "brick and mortar" based on the fusion of preformed nanocrystals with surfactant-templated sol-gel material, which acts as a structure-directing matrix and as a chemical glue. [6,7] The size of the particles incorporated should be smaller than about 10 to 20 nm. We have found that these technique is not only suitable for the preparation of thin layers for the application in solar cells, photocatalysis or sensors, but also enables to obtain consolidants with very suitable properties. First of all, the layers deposited by dip- or spray-coating or by brushing exhibit very good mechanical properties – their shrinkage due to drying is drastically reduced owing to the presence of nanoparticles. (Fig. 4) Owing to their properties, the polymers incorporated, such as triblock poly(ethylene oxide)-poly (propylene oxide) Pluronic copolymers, are easily removable by bio- or UV-light induced degradation. The physical properties of the porous particle-modified gels are much closer to those of the historical materials in comparison with purely polymeric non-porous gels.

Further if titanium dioxide nanoparticles were used, the composites exhibited photocatalytic activity. [7] Due to this additional ability the consolidants do not only restore the original stability of the weathered stone, but also enable to

reduce the deposition of dirt by its photocatalytic removal.

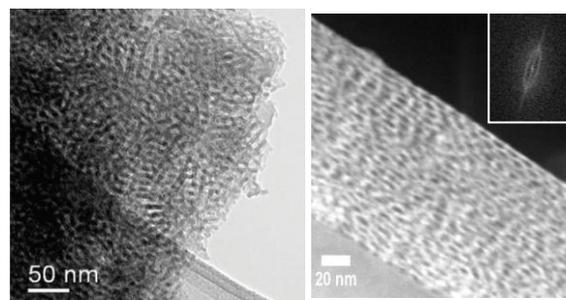


Figure 4: An example of porous layer of SiO<sub>2</sub> containing nanoparticles of TiO<sub>2</sub> prepared by the brick and mortar method. (right) top-view, (left) cross-section.

## 5 CONCLUSIONS

Methods and materials presented in this communication are based on the fast development in the field of nanomaterials and nanotechnologies, which is a prerequisite for new approaches in the consolidation of the objects of the world cultural heritage. It can be expected the developed materials will provide a higher effectiveness of cleaning and consolidation treatments in comparison with commercially available products. Owing to their variability, it will be possible to tailor the materials and procedures used for conservation treatments exactly according to the properties of treated objects.

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