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# Hydroxide nanoparticles for cultural heritage: Consolidation and protection of wall paintings and carbonate materials

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ABSTRACT

Colloids and Material Science are nowadays providing innovative and effective technological solutions in a wide range of applicative fields. In the last decade, nanomaterials have been specifically designed to ensure the long-term restoration and preservation of movable and immovable artworks. The main tasks to address by conservation scientists concern the cleaning, the deacidification and the consolidation of different kinds of artistic substrates. The aim of the present contribution is to provide an up-to-date overview on the synthesis and preparation of colloidal systems tailored to the consolidation and protection of wall paintings, plasters and stones, highlighting the most recent improvements. Two case studies, widely representative of typical consolidation problems, are presented, i.e. the preservation of wall paintings belonging to a Mesoamerican archeological site and the consolidation of two Italian Renaissance buildings.



## 1. Introduction

Colloids and Interface Science has progressively played a leading role in a wide range of applicative fields, ranging from green chemistry, to aeronautics, construction industry, biomedicine etc., providing innovative and advanced tools for the development of improved technological solutions [1–5]. Nevertheless, whereas the progress in Materials Science has allowed the formulation of sophisticated nanostructured materials for different applications, the preservation of cultural heritage is still based on traditional methodologies and conventional products usually characterized by a lack of compatibility with the substrates that constitute the original work of art. Moreover, traditional treatments sometimes exhibit scarcely durable performances upon changes of environmental conditions caused by natural events or anthropic activities. As a matter of fact, the preservation of cultural heritage must aim to bestow both physical artifacts and intangible artworks for the benefit of the society, through a reasonably long time-span.

Colloids and materials science are providing effective tools for achieving several tasks related to the durable and compatible conservation of different artistic substrates, minimizing drawbacks and negative effects [6,7]. The main conservation targets addressed by research works in the field of colloids and interface science include cleaning, deacidification and consolidation of works of art.

Innovative tools such as micellar solutions, microemulsions, gels and responsive gels, specifically designed for the removal of detrimental coatings, i.e. natural and synthetic polymers traditionally applied by conservators in past interventions, have proven crucial for the selective cleaning of artworks and provide a major technological and cultural advancement to the traditional cleaning procedures [8–11].

A concerning issue in the field of conservation science is the preservation of the vast historical and documental heritage that is nowadays threatened by degradation reactions and sometimes inappropriate conservation strategies. It is worth noting that a recent survey on Western libraries has shown that almost two thirds of books and documents could undergo irreversible damages within 100 years, while one third is already in need of restoration [12]. Traditional paper conservation practice includes several aqueous treatments with basic solutions (i.e. using solutions with $pH \geqslant 9$) that imply drawbacks due to the exposure of oxidized cellulose to strong alkaline conditions. A significant improvement of the preservation of these substrates has been provided by the deacidification and the pH-control via non-aqueous dispersions of nanoparticles, mainly calcium and magnesium hydroxides, that ensure a long-lasting buffer against acid-catalyzed hydrolysis and oxidation reactions, which are the two main degradation pathways of cellulose-based materials, e.g. paper, wood and canvas [7,13–17].

Dispersions of alkaline-earth metal hydroxide nanoparticles are the best systems nowadays available for the consolidation and protection of immovable works of art, such as wall paintings, plaster and stone artifacts. Before the introduction of nanoparticles in

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the conservation field, synthetic organic materials were (and are still) widely applied by conservators for consolidation purposes, but their presence on artistic substrates was shown to be detrimental due to the different physico-chemical properties of polymers with respect to the materials constituting the original artworks. On the other hand, alkaline-earth hydroxides exhibit high compatibility with many artistic and architectonic substrates and thus represent a valid alternative to the organic coatings.

The nanosized structure of the applied crystalline phases, together with the dispersing medium, is a crucial factor for the efficacy of the consolidation: as a matter of fact the particle size influences their reactivity and penetration through porous matrices. Moreover, the particles polydispersity greatly affects their performance on substrates. For example, matrices to be consolidated often exhibit wide pores size distributions; in these cases the usage of suitable bimodal dispersions is advisable for the best consolidation.

It appears thus evident that the processes involved in the preparation of nanoparticles and their dispersion in carrier media, all play fundamental roles in determining the final effectiveness and applicability of these conservation tools. Synthetic pathways and peptization methods both are important to shape and finalize the particles down to the desired properties, so to meet the requirements of specific consolidation issues.

In the last 40 years, a fundamental contribution to the improvement of the synthetic strategies for the production of inorganic particles such as metal oxides and hydroxides, was provided by the work of several research groups [18–24]. In particular, the contribution of Egon Matijević to colloids and interface science has paved the way for the development of elegant, reliable and effective syntheses of stable colloidal systems with specific properties.

Several studies by Matijević et al. contributed to inspire our work on the synthesis of nanoparticles and preparation of dispersions specifically designed for the application to artworks. In particular, some papers have been published on the syntheses of metal oxide and hydroxide particles by precipitation from sol solutions, discussing the effect of temperature, pH, organic additives and the presence of co-ions [23,25–28]. Specifically, high temperature was shown to be crucial for the synthesis of very fine particles, as demonstrated in a study on nanosized indium hydroxide [29] where the role of peptization is stressed as an essential factor in order to prevent the aggregation of particles which otherwise might form microsized clusters. Since the stability of the nanoparticles dispersion is of paramount importance for their application onto valuable and artistic objects, this aspect has been given particular emphasis in the formulation of alkaline-earth metal hydroxides.

The aim of the present contribution is to provide an up-to-date overview on the synthesis and preparation of colloidal systems tailored to the consolidation and protection of wall paintings, plasters and stones. Considering the specificity of this topic, a brief introduction about the main conservation issues, the common restoration tools and their related chemical aspects, will be provided in the next section. Afterwards, the syntheses, dispersions and characterization of innovative calcium, magnesium, and barium hydroxide nanoparticles will be discussed, highlighting the most recent improvements. Finally, two case studies widely representative of typical consolidation problems will be presented, concerning the preservation of Mesoamerican wall paintings and the consolidation of Italian Renaissance buildings.

## 2. Hydroxide nanoparticles for consolidation: rationale, principles and practice

A typical wall painting, belonging to the classic tradition, consists of roughly three layers (see Fig. 1) whose main structural component is calcium carbonate, formed by the reaction of lime (calcium hydroxide) with atmospheric $CO_2$. Sand is added to lime as a filler, to prevent shrinkage and cracking upon drying and to increase the mechanical strength of the plaster. The inner layer, which is laid on the wall, is called *arriccio* and is the richest in sand. Moving towards the surface, the *intonaco* layer is found, consisting of a plaster that often contains an equal amount of lime and sand. The third and outer one is the paint layer, which is a thin film (50–500 μm thick) made by a mixture of pigments and calcium carbonate. In the so-called *buon fresco* technique, the pigments (dispersed in lime water) are directly applied on the wet *intonaco* layer, and upon carbonation are embedded into the crystalline carbonate network forming a smooth surface. Depending on the time between the laying of the outer lime layer and the application of pigments, several painting techniques can be defined.

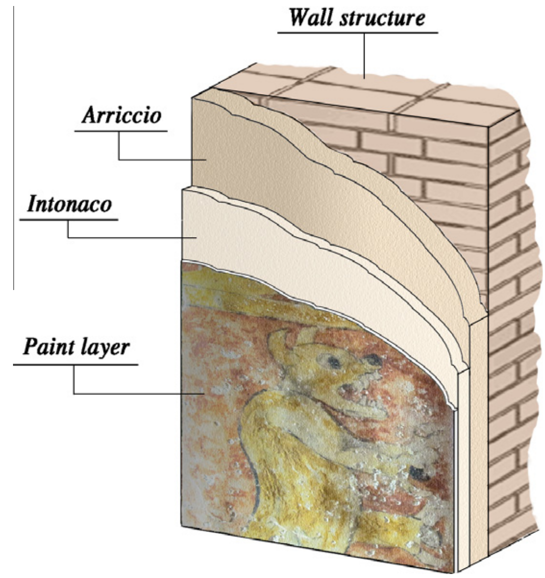


**Fig. 1.** Stratigraphy of a model fresco wall painting: the *arriccio* layer, which is the richest in sand; the *intonaco* layer, upon which the pigments are laid (paint layer).

The pigments can also be applied on the dried *intonaco* (*a secco* technique), by using organic binder such as egg, milk or vegetal extractives. It is worth noting that mixed *fresco* and *secco* techniques were widely used by artists.

Carbonates are also the main components of several stones, used for creating immovable artworks such as monumental and architectural objects.

Carbonate-based works of art are affected by a number of different degradation phenomena. Besides physical erosion, the main factors include chemical corrosion by acid rain containing sulfuric, nitric and carbonic acid, water freeze–thaw cycles due to the temperature and relative humidity variations and mechanical stresses from salt crystallization. In fact, salt solutions (either absorbed from the ground or formed on the artwork surface) can impregnate the porous matrix of the wall painting or stones, and migrate by capillarity. When the ions concentration exceeds saturation, crystallization of salts takes place inside the porous matrix of the artifact, usually leading to volume expansion and mechanical stresses that cause the flaking of the outer surface layer (see Fig. 2) [30–32]. A typical example is the formation of mono- or di-hydrate calcium sulfate upon the reaction of calcium carbonate with sulfuric acid.

Finally, degradation may occur due to the presence of bio-organisms, such as fungi, mold, lichens and bacteria [33,34], leading to the dissolution of rocks and mineral substrates through mechanical and chemical processes.

Based on the aforementioned considerations, it is evident that every consolidation intervention on wall paintings and stones