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Inorganic Nanomaterials for Restoration of Cultural Heritage: Synthesis Approaches towards Nanoconsolidants for Stone and Wall Paintings

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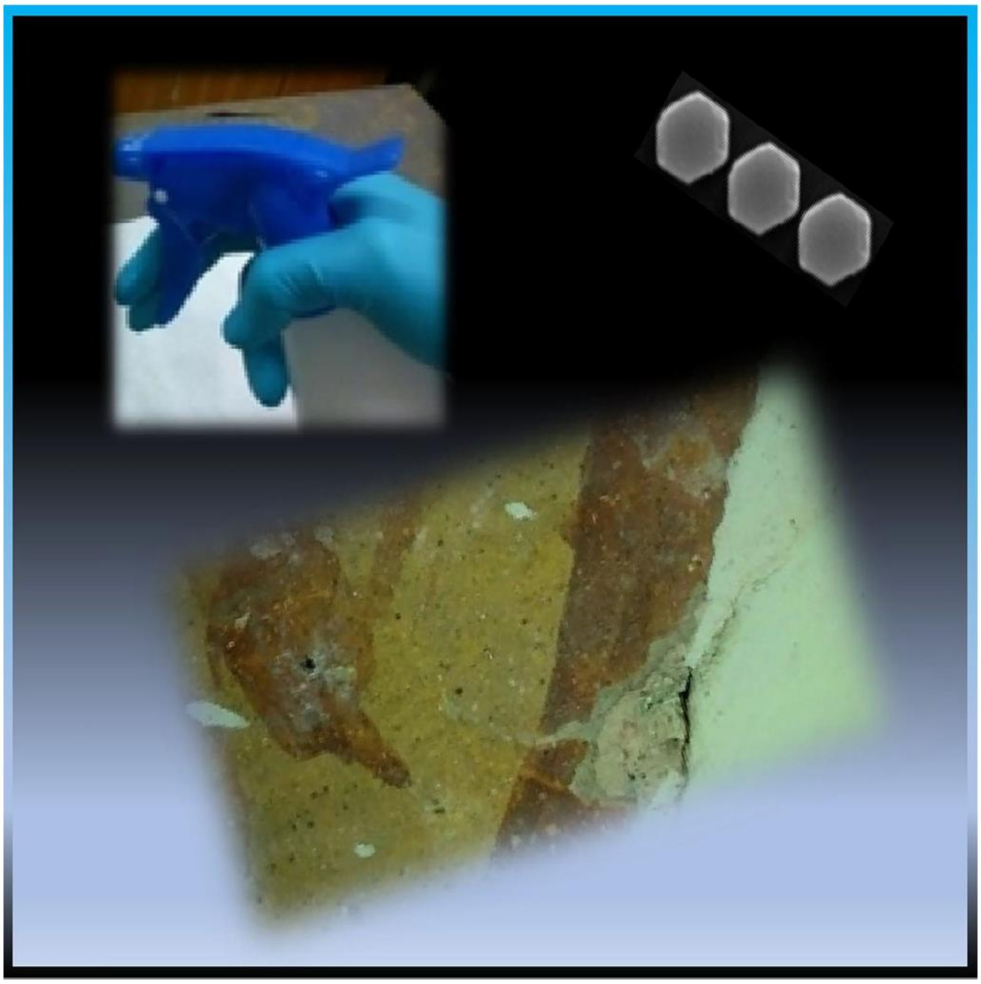

The synthesis of inorganic nanostructured materials for the consolidation of stone and wall paintings is reviewed. To begin, a description of the methods most commonly used to prepare nanoconsolidants is provided, particularly in the frame of colloid chemistry. Some concepts of the carbonation mechanism as well as the transport properties of some of these materials are addressed. An overview of the synthesis methods together with some of the application particularities of the distinct consolidants are presented thereafter. Furthermore, the requisites for efficient consolidants and some drawbacks of the nanoconsolidants are discussed.

1. Introduction

The main challenge in materials science and nanotechnology is to tailor classical materials with controlled properties for specific uses. Most manufacturers are interested in the possibility of controlling particle size, particle shape, particle-size distribution, particle composition, and the degree of agglomeration. This can be achieved by paying special attention to the preparation methods that allow the synthesis of particles with uniform size distributions (in the range of 1–100 nm) and shapes (e.g., nanosized tubes, spheres, wires, rods, fibers, pyramids).

The self-assembly of nanoparticles (NPs) can be achieved by different approaches, either from bottom-up techniques (by assembling particles synthesized mostly in solution; the main chemical approaches are based on colloidal process) or from top-down techniques (different lithographic methods, grinding of bulk materials, thermal decomposition). The main difference between the two approaches is the starting materials from which the particles are obtained. In the bottom-up synthesis approach, the NPs are built atom by atom or molecule by molecule. In the top-down (or break-down) process, the starting materials are reduced from the bulk size to the nanoscale by using different forms of energy, such as mechanical, chemical, and thermal energy.

Several aspects must be considered in the consolidation of artwork mortars. The consolidant must have similar or, preferentially, the same chemical composition as the decayed substrate and must cover its mineralogical phases. Moreover, it is necessary to manifest good chemical and physical compatibility with the mortar. The physical and mechanical properties must be improved, whereas the esthetical appearance must not be altered. Good consolidants are characterized by good penetration from the surface to the interior.[1]

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1.1. Most common synthesis approaches to inorganic nanoparticles for consolidation of cultural heritage

A variety of methods for the synthesis of inorganic nanomaterials have been used, including co-precipitation, microemulsions, precipitation from solution, high-temperature decomposition of organic precursors, and sol–gel, among others.

A common synthesis route for inorganic NPs is precipitation from solution under controlled conditions with respect to thermodynamics and the principles of colloidal chemistry. A dispersion of narrow-sized particles (smaller than 1 μm) or a two-phase heterogeneous system consists of a dispersed phase and the dispersion medium, that is, a phase of one material in another form a colloid. The dispersed phase in a colloidal system is uniformly distributed in the dispersion medium that makes the colloid particle, and this colloid particle is formed by clusters of atoms and molecules and is undetectable by conventional optical microscopy. Colloidal particles are characterized by high area-to-volume ratios as a result of their small sizes, and this predetermines their specific properties and behavior. Sometimes, surface-active substances are added to a colloid to modify its properties. Inorganic colloids are usually prepared by precipitation reactions, which involve two steps: nucleation and growth of nuclei. To achieve monodispersity, the two steps must be separated and must not happen at the same time. The kinetics of these reactions for the synthesis of monodispersed colloidal particles were studied by LaMer, who investigated the formation of sulfur colloids from thiosulfate solutions.[2]

In 1968, Stöber and Fink applied a procedure based on LaMer's theory in different systems to prepare monodispersed silica colloids.[3] The basis of this method was the hydrolysis of a dilute solution of tetraethylorthosilicate (TEOS) in ethanol at a high pH value. They obtained uniform spheres of amorphous silica with sizes between 50 nm and 2 mm by changing the concentrations of the reactants. This method was improved later and has been modified and used by many other researchers. For example, Matijević improved and applied the Stöber strategy to many different materials (cubes, colloidal spheres, rods, and others).[4] A very common method for the synthesis of metal powders, alloys, and metal oxide NPs is the polyol method. Its mechanism is realized with respect of LaMer's theory and can be seen as a sol–gel process at high temperatures. The basis of this method is the reduction of metal precursors by high-boiling alcohols (polyols, such as glycerol, glycol, and ethylene glycol) to micron, submicron, and nanosized metal particles.[5] Besides acting as high-boiling solvents and reducing agents, polyols are seen as stabilizers to control particle growth. The reaction in solution occurs over four